Elements of change in the evolution of solid-state hydrogen storage technology

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I, Simon Neil Dite, confirm that the work presented in this thesis is my own. Where information has derived from other sources, I confirm that this has been indicated in the thesis.

Abstract

The search for satisficing hydrogen storage materials (HSMs) is in an exploratory phase of development. This phase is associated with large uncertainties, and technological change that is difficult to anticipate. Nevertheless, it is a common (and necessary) practice to make claims about and form strategies around the perceived prospects of HSMs. Which of these diversely construed anticipations are reliable? This thesis aims to contribute a perspective, theoretically and empirically informed, that is valuable to an objective assessment of the prospects for materials-based hydrogen storage. Instead of offering a simplified narrative of future developments in hydrogen storage, the exploratory approach taken has addressed important aspects of a complex process. Three important evolutionary principles of technological change - variation, learning, and selection - have been represented.

Each chapter draws on a different set of concepts to address diverse questions. I study the extent of variation activity in research, and review prominent directions of search for fitter hydrogen storage materials. I ask about the relationship between progress, and expectations of progress embodied by the research community. I look at expert judgement as a source of bettering our understanding of hydrogen storage prospects. I also explore the possibility of anticipating a subset of the selection pressures, that will determine likely "survivors" among competing concepts.

Insights are gained that inform us on hydrogen storage prospects in various dimensions. For example, I argue that the dynamics of expectations is key to understanding the historic "trajectory of progress". An implication of expert foresight is that investments into a portfolio of research trajectories is compelling. A trend of convergence toward compressed hydrogen technology is evident, an option I show to be wholistically superior to solid-state concepts, assuming a variety of selection pressures. In all, the adopted perspective proves a useful framework for thinking about processes of technological change.

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1 Introduction

1.1 Context

1.1.1 Why hydrogen storage?

Hydrogen is nature's simplest atom, consisting, in its dominant isotope, of one proton and one electron. In the universe, hydrogen is the most abundant element (accounting for more than 88% of its mass [77]), while on Earth it ranks number ten [128]. It appears bound up with other compounds, such as hydrocarbons and minerals, but the most common source is water. Only traces of hydrogen can be found in a free state (e.g. in volcanic gases [128]), as it is very reactive and light (meaning it would escape Earth's gravity). Credit to be the first person to isolate hydrogen, and characterize its density, goes to Henry Cavendish, who did so in 1776 [130]. It has been found since that atomic hydrogen is a highly unstable species when in contact with other atoms, and forms compounds with all the known elements except the noble gases. In its desire to possess either a totally empty or a totally filled 1s electron shell, it exhibits three common oxidation states [77]: +1. 0, -1. Hydrogen invariably reacts to form a proton cation, or a hydride anion, thereby undergoing the largest relative change in the number of electrons surrounding the nucleus (±100%) of all the elements [77].

Hydrogen has a ubiquitous role in energy processes. Aside from it being the most basic fuel for solar energy production (i.e., nuclear reactions in the sun), it is one of the most important energy carriers on Earth. Nature depends on it (as in photosynthesis), as do our societal activities, expressed most poignantly by the pervasive use of hydrocarbons. The central question concerning its use as an energy carrier is simply, to what, if anything, should it be linked?

While hydrocarbons, especially in liquid form, offer an energy dense and practical form of energy, their use on a massive scale is unsustainable if based on natural resources, and it is excessively polluting. The use of hydrogen without carbon is therefore seen as a viable solution to these problems. Proponents of this idea, including Jules Verne, date back quite a while. In the 1920s, the British scientist J. B. S. Haldane proposed "great power stations where during windy weather the surplus power will be used for the electrolytic decomposition of water into oxygen and hydrogen [30]", for the hydrogen then to be used as a fuel. In 1970 John O'M Bockris coined the term "hydrogen economy", for which he envisaged "the use of hydrogen to transfer energy from large remote sources; combined with the massive use of hydrogen as a chemical in technology and for transportation and household energy; with the conversion of it to water as an essential part of the cyclical concept involved [30].” Energy from hydrogen would thus be sustainable and clean.

However, to obtain hydrogen in a free state means decoupling it from its source material - this requires energy, and hence, hydrogen would not be a “primary energy source” as we classify the hydrocarbons. Another drawback, due to its low volumetric density, is that the storage and transport of hydrogen is not efficient like it is with liquid hydrocarbons. Therefore, aside from compression and liquefaction, solutions are being investigated by which hydrogen is bound to a substrate material before it is released at the point of use. This approach offers the potential of increased volumetric and gravimetric energy densities as compared to physical containment methods. However, the problem of storage is broader in scope than merely a focus on energy density. And nature has not provided obvious solutions - materials that happen to match a specific set of stringent performance requirements we impose for different application contexts. Hence, since about the 1960s there has been a growing search effort, which has continually diversified, in order to find and design suitable hydrogen storage materials. As yet, there has been rather limited exploitation - or commercial use - of developed materials for energy storage purposes. In particular, the long sought-after “elixir” of hydrogen storage, a technology that would unlock the road to hydrogen powered transportation, has yet to be discovered.

That brings me to the motivation for this project. The big question that drives it is, what is the future for hydrogen storage technology in the context of providing key energy services? To be sure, this is a big question because a great deal of other questions depend on an answer to it. For instance, questions about visions of a hydrogen economy must entail some answer to it [21]. Questions on the innovation activities of innumerable companies need to address it, as must questions surrounding policies and funding of fundamental research, etc. Perceptions or expectations of the future of hydrogen storage technology (may they be based on a gut feeling or a sophisticated forecasting analysis) have a bearing on the strategies and activities of present day stakeholders. The aim of this PhD is to contribute a perspective on the evolution of this field of technology that aids in the construction of such forward looking assessments. A generic formulation of the research task is thus to study the prospects of hydrogen storage technology. Such a generic formulation leaves much scope for identifying precise aims however. Therefore, an initial challenge of this project was to select from a range of possible approaches and more closely define the research goals. Below I will provide a brief description of the roots of this thesis.

1.1.2 A background to this project

Studies relating to the analysis of technological prospects can be identified in several domains, and diverse techniques have been employed to suit specific purposes and premises (for a broad overview see, for example, [149]). During the course of this PhD I explored the potential of several such approaches.

Having begun the project with little theoretical knowledge about processes of technological change, it seemed reasonable to focus on a comparative analysis of the characteristics of different hydrogen storage technologies. With this in mind, an important choice on the type of information I would seek to compile was determined by whether the study had a normative or exploratory purpose. Normative style analyses seemed more accessible (at first), as they offered self-contained methodologies.

One type of normative study that I initially considered was to conduct a series of life-cycle assessments (LCAs). This type of analysis could in principle reveal the overall benefits of each technology with respect to criteria such as energy, pollutants, cost, etc. However, as my focus was on technology that was envisioned as part of much larger technical systems, and as these "super-systems" are still very much in a fluid phase of being designed and developed, there would be too many variables/unkowns to consider for such a normative assessment. As another example, in learning about the notion of "axiomatic design" [147], I considered a different kind of normative analysis during a later stage in the research. This school of design practice asserts that there are key principles (the axioms of design) that determine the "quality" of a design[1]. Once again, however, a challenge that confronted this analysis was the number of unknowns; in this case, detailed knowledge of the internal workings of prospective hydrogen storage systems.

One type of analysis - which has a core interpretation that is normative - that I ultimately adopted, first suggested itself while exploring the field of innovation management (e.g. [42]). In particular, the concept of "user needs" suggested a framework for appraising the usefulness of different hydrogen storage technologies. Initially, the notion of formal axioms of decision making were unbeknownst to me, which stalled the practical implementation of this approach. By discovering decision theory and techniques of multi-criteria analysis (see, for example, [46]), this approach later became viable - I employed it to explore the aspect of selection pressures in technological change. Another lesson offered by the innovation management literature was to question the appropriate unit/level of analysis. At what system level was I to study and compare hydrogen storage technologies? To resolve this question, I was drawn to understand more the process of technological change, and how to conceive of technology in this process. Hence, my focus was turning towards achieving a more exploratory (less normative) understanding of hydrogen storage prospects.

Broad frameworks for thinking about processes of technological change are afforded by (at least) two sociological concepts; the multi-level perspective, and the system of innovation perspective. Indeed, these approaches have frequently concentrated on the (emerging) field of hydrogen energy technology (e.g., see [69, 71, 148, 49, 10]). It is through this association that I became acquainted with these disciplines early on. It is certainly fair to classify them as holistic perspectives as they attempt to include in their theorizing all elements in the techno-, institutional-, econo-, and socio-spheres that are relevant to the process of technological change (note, these theories may be described as being of an "appreciative" nature (e.g., [61]) rather than formal). But while offering an impetus for considering contextual factors - and the relevance of a system's perspective - I could not decide how these approaches were applicable to the analysis of prospects for concrete technological concepts.

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[1] One such example is that all functional characteristics of a system should be independently modified by changes to the system's design parameters (known as the independence axiom) [147].

By encountering the field of evolutionary economics, I began to appreciate the existence of certain regularities in the development of technologies. Some of the (basic) ideas I came across in this domain were of interest to me as they provided for a degree of prospective thinking. Moreover, this was an entry point for asking more specific questions and for focusing the analysis (e.g., on what I could now delineate as different "phases" of technology development). Complementary to this, I became interested in the field of complexity science (good readings in this subject area are provided by [72, 86] for example). I found that this discipline could offer a different way of looking at a set of similar processes, so I became engaged in appropriating key concepts for a deeper understanding. In general, this approach helped me to better define technology - e.g., by a comparison with general properties of complex adaptive systems - and perform/interpret key analyses. Furthermore, I was in a better position to relate different branches of technology studies, and thereby identify where a potential synthesis was possible.

Within the general framework with which I began to view the evolution of technology, I sought to identify key analyses that would contribute toward a better understanding of hydrogen storage prospects. Again, this was an exploratory endeavor, with criteria such as data availability, technical requirements, and generality/depth of insight to be gained being key considerations. Examples of themes that drew my interest - not all of which came to fruition - include: the role of expectations in actor strategies and innovation processes; citation analyses of technological trajectories and scientific frontiers; elicitation of expert judgement; technometric analysis; modelling of patterns in basic research. The adopted analyses were aimed at providing partial perspectives on the processes of technological change in hydrogen storage. In sum, the research thrust became a question of how - indeed whether - this multi-disciplinary, complex adaptive system based perspective can improve our understanding of the prospects of hydrogen storage technology (solid-state versions in particular).

1.2 Research questions

The objective of this project is to contribute a perspective on the prospects of hydrogen storage development. In particular, my focus in this endeavour is on whether, and how, a multi-conceptual, complex adaptive system based perspective can improve our understanding of those prospects? I describe key concepts first, and then provide a contextual overview in chapter two. Further ideas and analyses about the evolution of technology are introduced and related/integrated in subsequent chapters. As the collective of these ideas does not originate from a coherent body of knowledge, I have decided to review the literature in this way, rather than providing a traditional, overarching literature review.

I attempt to relate, where possible, the theoretical concepts with key data elements to characterize and draw conclusions on specific patterns of change. I refer to "elements of change" in the title of this thesis, as the analysis is restricted to particular contexts in which evolutionary processes are unfolding. Hence, in this project, I do not and cannot account for a wide range of activity relevant to understanding hydrogen storage developmental prospects. Furthermore, the analysis is inherently tied to a fast moving target. Nevertheless, I suggest that the specific areas of my investigation concern pertinent questions. I centre my focus on processes in basic research and development, which is rather an untraditional place to study processes of technological change. The main research question I pursue comprises the following sub-themes:

What can other examples/models/abstractions of technological change tell us about regularities one might expect in hydrogen storage development? Conversely, what aspects of development are typically unpredictable? These are questions I begin to unpick in chapter two and three. In chapter three I focus in on the aspect of regularity in technological advancement. What can we say about it, particularly for early development phases, is addressed in this chapter and, through a different lens, in chapter six. To complement this assessment I also ask; what is the history of hydrogen storage development? In particular, what has been the relation between progress and the anticipation of progress? Finally, a motivating question of chapter four and eight are, how can we obtain a better sense of the comparative strengths and challenges of hydrogen storage variants?

How is this thesis structured? Chapter two provides first and foremost a context for interpreting the emergence of hydrogen storage technology. In the chapters that follow, I discuss, in more or less a sequential manner, the themes of variation, learning and progress, and selection, all of which are key operations of a complex adaptive system. Here are brief summaries of the content that is to follow:

Chapter Two: What are the opportunities that have been proposed for solid state hydrogen storage technology? Under what conditions might such opportunities arise?

Chapter Three: The exploratory phase of technological development is typically associated with substantial variation in the technical concepts being designed and promoted. How is this pattern reflected in the search for satisficing hydrogen storage materials? Furthermore, while such variation processes are associated with learning effects, what patterns of progress might one expect in the context of hydrogen storage development in basic research?

Chapter Four: In chapter three I alluded to a macro-picture of variation in hydrogen storage search. In this chapter I study more specifically what some of the more prominent variants in hydrogen storage are. I begin by sketching out a system view of hydrogen storage technology. This perspective emphasises the “niche” environment for hydrogen storage materials, and is thus indicative of the kind of “environmental changes” that can affect the fitness of material concepts embedded within the system. While general features of niche environments have already been conceived of in some areas of development, thus permitting the derivation of specific targets for hydrogen storage materials (which would ensure that the system targets are met as a whole), I ask: on what dimensions are variants of hydrogen storage materials being explored to find fitter alternatives for the proposed contexts? This discussion is mainly illustrative rather than pertaining to a specific design project.

Chapter Five: Having speculated on the subject of patterns of progress in chapter three, in chapter five I begin to explore this question more empirically. At its core, I present a "narrative" on the history of state-of-the-art hydrogen storage materials. I discuss my particular interpretation of "state-of-the-art" used for this context - in which a significant performance gap (to commercial viability) still needs to be overcome - and propose an historic sequence of materials that (more or less) match this definition. I draw general conclusions on the pattern of change in the state-of-the-art, suggesting that it has much to do with the nature of expectations of future possibilities.

Chapter Six: In chapter six I elaborate on the theme of technology related expectations that I introduced in chapter five. A key question is: what are the prospects for achieving more commercially viable performance levels with solid-state hydrogen storage concepts? I answer this question by attaching probabilities to events defined by specific levels of performance improvement in hydrogen storage. Of course, there are likely to be many objections to the particular probabilities I present, or the rationales on which they have been based. But indeed, opening a discussion would be a desired outcome. The inherent value the probabilities add lies not in offering a form of objectively reliable assessment of the future. Instead, they are taken to represent more precise measures (than informal expressions) of the subjective uncertainties of future progress. In particular, the probabilities are elicited through a special interview technique involving hydrogen storage expert assessments ("expert elicitation"). I contextualize the experts' uncertainties through a discussion of their expectations regarding specific aspects of the search process. For instance, how do external factors, or the strategies of search, affect the prospects?

Chapter Seven: Selection pressures operate on variant technical concepts throughout the lifecycle of a new technology. Though in different phases one may distinguish between different kinds of pressures of selection. Particularly in the early phases of technology development, the selection pressures are less consequential in terms of inadequate performance characteristics. In other words, there is scope for promoters ("enactors") of a particular variant to reinforce its attractiveness to selectors (e.g. funding allocation decision makers) by influencing their expectations for it (e.g. in terms of future performance potential, or in relation to changes in the market requirement etc.). Thus, in these phases at least, the competition among technologies is very much a strategic, socio-political process. At some point however, technologies must meet adequate cost/performance standards to be selected for serious commercial development. In many product development projects, such selection processes can be quite formalized. In chapter seven I therefore explore the character of selection pressures one might expect to be operating on hydrogen storage systems vying for application in automotive systems. I attempt to represent such pressures of selection by employing a multi-criteria analysis technique, combined with an online survey for eliciting key data from industry representatives. I note, the results of this chapter are not intended to be predictive. They provide, instead, an intuition for the kind of outcomes that might be expected under varying conditions of the selection criteria/performance characteristics.

Finally, I draw my conclusions from these analyses and perspectives in chapter 8.

1.3 Key conceptual perspectives

The fundamental epistemological position of this research is that technologies evolve. To characterize such an evolutionary process one requires a theoretical framework; something which tells you where to look. In other words, something that provides a guide to identifying what it is about technology that is changing, what the core drivers of this change are, and what some of the important factors involved in the process are? Such a perspective would enable me to abstract away key elements in the evolution of hydrogen storage technology. I lay out core theoretical ideas that have informed my perspective, and which I build on during the course of the thesis, in the following sections. First and fundamentally, what is technology - what is the unit of analysis?

1.3.1 What is technology?

1.3.1.1 Definitions

Many references to technology carry an implicit meaning of what it is. This can be confusing as it seems that multiple interpretations are in use. For instance, in neo-classical economics the notion of technology is really defined by a production function [61, 132]. The way one defines technology has important implications for the processes of change that the object of interest undergoes. The definition that I adopt in this thesis has been proposed by W. B. Arthur in [15] and I describe it below. Along with it, Arthur proposes two other definitions; I present these alternative forms to make clearer the distinction between the definition that is adopted here, and other common uses of the term technology.

The first and most basic definition is that a technology is a means to fulfil a human purpose. In other words, a technology is a purposed system. Identifying the purpose may sometimes be ambiguous, as it may be hazy and changing [15, p. 28]. In general, any purpose can be decomposed or broken down into a lower level (or more specific) description of functionalities (or needs) that satisfy that purpose. Of these, one may typically identify a set of main functions and a set of ancillary or subsidiary functions. For example, the purpose of a calculator may be described as; provide a practical means to make numerical calculations proficiently. This informal statement of a purpose could be decomposed into the main functional requirements (FRs) of making calculations quickly, accurately and easily. A subsidiary functionality may be for it to run on solar power. Using terminology from the practice of technology design [155], the purpose to be satisfied by a technology may equivalently be addressed as the most general level need of users of the technology. Or, from the designer's perspective, it is the top level problem that needs to be solved [147].

As defined, a technology may be material or it may be non-material. For example, a digital compression algorithm may be considered a technology [15, p. 28]. Arthur indicates that this definition subsumes things as technologies that are not traditionally thought of as such, for example, the monetary system [15, p. 54]. However, in so far as it is a means to satisfy some purpose, these things too can be thought of as technologies. In the case of money, it is a means to the purpose of exchange[2] [15, p. 55]. The focus in this study will be on physical devices; materials-based hydrogen storage technologies. Note, according to the adopted definition, hydrogen storage is not only defined as a technology at the level of a containment vessel; the hydrogen storage materials themselves are technologies. Each of them is designed to satisfy the purpose of absorbing (thereby compacting) and releasing hydrogen in a controlled manner. Admittedly, they are very elemental technologies. But as the definition contained no provision on the scale of the system (c.f. nanotechnologies), simply because these materials are largely the subject of basic research, does not invalidate their status as technologies.

The second definition of technology is a plural one; in this case technology is defined as an assemblage of components and practices. This definition covers technologies such as electronics or biotechnology [15, p. 28]. The third definition of technology refers to the entire collection of devices and engineering practices available to a culture [15, p. 28]. This is the definition typically referred to when one speaks of technology speeding up lives etc. [15, p. 28].

1.3.1.2 Principles of structure

Technologies are devices that harness some natural effect and transform it into an “output” which satisfies a human purpose. The general principle that describes how a particular need is connected to a base effect is identified with the “main assembly” of a technology [15, p. 33], or its operational principle [119]. Ensuring that the operational principle produces an output that meets many specific requirements (i.e. meets various elaborations on the main need), and that it works under a range of conditions, requires supporting components/assemblies. The combination of main assembly and supporting assembly, is claimed in [15, p. 33], to be a general feature of technology, coining it the “principle of assembly”.

Another general principle, which is implicit in the “principle of assembly”, is that technologies are combinations of components; they are put together from component parts or assemblies [15, 58]. But given that component parts perform some function - are based on some physical principle that contributes to the working of the whole - these too are means to a purpose (e.g. serving a technical need), and are therefore also technologies. Thus, not only are technologies combinations of parts, they are, at times, complex hierarchical structures composed of numerous layers of sub-technologies [15, 119]. In hydrogen storage technical devices, the hydrogen storage materials are very much at the bottom of the technical hierarchy (though one could argue that the material concept is based on a certain *combination* of elements too, each with a designated purpose in the hydrogen sorption process, e.g. catalysts reduce the activation energy). The materials operate deeply embedded

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[2] The principle of the monetary system is based on a behavioural phenomenon, namely, trust: “We trust a medium has value as long as we believe that others trust it has value and we believe this trust will continue in the future Arthur [15, p. 55].

in a “technical environment”. Hence, their prospects depend very much on the opportunities that emerge through the processes that shape the environment (or components) around them. This suggests that the analysis of evolutionary changes in hydrogen storage would benefit from an intrinsic perspective of technology. I emphasise the importance of this viewpoint in the next section.

1.3.2 Technological evolution and the need for an intrinsic perspective

According to John Doyne Farmer, our general understanding of technology is pre-Linneus. Unlike in the biological domain, in which, since the 18th century, a great deal of attention has gone into organizing organisms into groups, to better understand the underpinnings of such groups and to learn how they change over time, no similar effort seems to have been conducted for technologies. Far from creating a taxonomy of “technological species”, technologies have often been viewed as black-boxed, stand-alone entities in various academic investigations into technological change [15, 153].

An understanding of the intrinsic nature of technology is however important for understanding processes of technological evolution. Experiences in the field of evolutionary biology exemplify the relevance of linking macro-level observations with theories or concepts of the micro-level: In the early 1900s, before the “Modern Synthesis” on the principles of evolution, there was disagreement on the subject between the school of Darwinists and the school of Mendelians [117]. Until the discovery that most traits in organisms are determined by many (interacting) genes, each with several different alleles, there was no reconciling view, despite evidence of both, that allowed for both discrete variation (proposed by Mendel’s theory) and continuous seeming variation (asserted by Darwin’s theory) in an organism’s traits. It was later understood that the huge number of possible combinations of many different alleles can result in seemingly continuous variation of an organism’s traits [117, p. 82]. In more recent times, the conventional view of the evolutionary process has been profoundly challenged by new genetic discoveries. As is explained in [117, p. 87], “the idea that gradual change via natural selection is the major, if not the only force in shaping life is coming under increasing scepticism as new technologies have allowed the field of genetics to explode with unexpected discoveries, profoundly changing how people think about evolution.”

By analogy, the view of technology’s evolution is likely to be enriched (or even modified) by one’s understanding of the intrinsic aspects of technical change. An understanding of the inner nature of technology will suggest an internal logic to the way in which technologies progress [15]. The two main mechanisms responsible for technological evolution are summarized in the next section. These theoretical ideas give a fundamental perspective on the origins of hydrogen storage technology, and the ways in which it evolves.

1.3.3 Adaptive evolution vs. radical novelty

A fascination of biological evolution is that relatively simple principles are responsible for the emergence of great complexity and diversity. The prevailing view in biology has been that the driver of this process is one of incremental, cumulative adaptive change; a process which operates through gradual variation and selection (although, as noted in the preceding section, there is now some debate over the mechanisms of variation). Or, as the geneticist Steve Jones puts it, “genetics plus time” [90]. These basic ground rules of variation and selection have resulted in astounding complexity, and in the diverse set of species that make up the biosphere [94].

An analogous mechanism of incremental, cumulative adaptation - that works through variation and selection - can explain much of the change that occurs in the “techno-sphere”. Yet, it is not the sole mechanism of technological evolution. As noted in [15], one doesn’t obtain a turbo jet engine from incremental, cumulative changes to a piston engine. The former is based on a fundamentally different kind of base principle. Instead, there is another mechanism of variation, one which is responsible for creating new “species” of technology (assuming one permits a classification of technology based on operational principles, as proposed in [119]). We may identify this mechanism with the process of *invention* [15]. Thus, invention is the origination of a novel base principle[3].

While it has not been a tradition of literature on technological change to describe, in precise terms, the schema that define new technologies as inventive, they have nevertheless been identified as “radical novelties” [153, 83, 119]. But the process by which such novelties arise has either been viewed as a stochastic one [61], or as one of “individual genius” [153, 15], thereby creating an aura of mystic surrounding inventions. As described in [15], inventions are just novel combinations (or recombinations [58]) of existing components; “*To invent something is to find it in what previously exists* [15, p. 130].” In other words, inventions don’t arise from nothing, they are always combinations of existing technologies (or at least, the harnessing of a new base effect is made possible by existing technology) [15]. In this sense, Arthur characterizes the complex of technology as *autopoietic*; something which grows out of itself[4]. But while the concept of an invention is rather simple, how are these novel combinations actually conceived of?

An invention entails a novel combination of functionalities to some purpose. The combination is based on an idea, or principle, of some effect (or combination of effects) in action that will fulfil the needs of some purpose. An invention thus “arises from linking, conceptually and in physical form, the needs of some purpose with an exploitable effect (or set of effects) [15, p. 109].”The new principle by which to meet the need is necessarily appropriated from that which already exists (an invention does not come out of nothing) [15, p. 115]. Thus, a new overall principle may be the inspiration of combining previous functionalities (an example of high energy particle acceleration is given in[15, p. 113]), it may be suggested by theory, or it may be suggested by analogy of a principle based on a different base effect. The moments in which such creative insights actually come about

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[3] Under this definition, identifying an invention requires a judgement of the originality of the technology’s operational principle. Thus “we can say that Watt’s steam engine is an improvement of Newcomen’s. It provides for a new component - a separate condenser - but uses no new principle [15, p. 109].” While this definition is generally useful, it is acknowledged that it does not eliminate all ambiguities. It is not always clear-cut to what extent a base principle is novel [15, p. 109].

[4] One can appreciate that the scope of possibilities increases exponentially with the number of existing components.

is often associated with contingency and a "prepared mind". (Less frequently, they might also come about serendipitously; by *making discoveries by accident and sagacity, of things which they were not in quest of* [98, p. 1].) Ultimately, one may conclude that the generation of a novel principle rests on cognitive processes of creativity (more insight into such processes can be gleaned from [15] and [72] for example).

The creative insight of a new base principles concludes the first step in creating an invention. But this is merely a marker in the quite intensive process of finding a workable solution. A scope of possibilities opens up to realize, or instantiate, the invention [94]. Indeed, the early phases of technology development are characterised by quite radical explorations of variants to find better designs. Variations become more modest as the technology reaches an adequate level of performance and is thereafter characterised by incremental improvements (less radical exploration) [15, 94, 5, 61] - a process of adaptive change typical of a kind of Darwinian evolution. Finally, a common fact about technological improvement is that, after the "low-hanging fruits" of progress have been exploited, there tends to be a (more pronounced) period of diminishing returns. As more and more effort must be invested for rather marginal returns on progress, the technology gradually becomes less investable, and less likely to "survive" in the face of competition from new inventions.

In summary, this section has provided a basic perspective on the origins of a new technology, and the patterns of change one may expect to observe as it develops into the future. These are important insights for structuring an analysis on the prospects of hydrogen storage technology.

1.3.4 Technology as a complex adaptive system

In the foregone section I introduced the notion that technologies evolve (in part) through incremental adaptive change. Of course, and by contrast to biological evolution, the crafting of artefacts is guided by human intent and intelligence [94, p. 202]. But rather than describing technological evolution in terms of the actions of designers, I propose that a more intuitive perspective - one that emphasises the highly "organic" and configurable nature of technology [15] - is one that brackets out the actions of design (and takes them as a given), and treats technology as a complex adaptive system. I note that this perspective is not to be taken literally - technologies are not in fact autonomous beings - but rather serves as a useful framework for thinking.

As described in [72], complex adaptive systems have commonalities in the way they process information and how they operate. A passage in [72, p. 23], explaining the basic flow of information, serves as a template for understanding the adaptive behaviour of technology:

"*In studying any complex adaptive system, we follow what happens to the information. We examine how it reaches the system in the form of a stream of data. We notice how the complex adaptive system perceives regularities in the data stream, sorting them out from features treated as incidental or arbitrary and condensing them into a schema, which is* *subject to variation. We observe how each of the resulting schemata is then combined with additional information, of the same kind as the incidental information that was put aside in abstracting regularities from the data stream (as often happens, the additional special information comes from a later portion of the same data stream as the one from which the schemata was abstracted), to generate a result with applications to the real world: a description of an observed system, a prediction of events, or a prescription for behaviour of the complex adaptive system itself. Finally, we see how the description, prediction, or behaviour has consequences in the real world that feed back to exert "selection pressures" on the competition among the various schemata; some are demoted in a hierarchy or eliminated altogether, while one or more manage to survive and may be promoted.*"

To convey my perspective, it would perhaps help to express some of these features in the context of a technological system. The schemata being referred to may be conceived of as the operational principles of the technology (the abstract concept that identifies it). The data stream that the technology receives are the signals coming from interacting components. By signals I mean any kind of physical interaction. The regularity that the schemata extracts, in the context of technical designs, then refers to the subset of signals defining intended interactions - or at least, interactions that produce a desired effect. Unintended interactions may be thought of as the technical schemata extracting too much noise. Such interactions may be incidental, e.g. noise in electric circuits (digital converters extract the regularity that is desired), or they may simply be persistent but undesirable. Finally, selection pressures feed back on competing designs based on how well they perform - or satisfy the needs of end users. Mature designs will have undergone several generations of variation and selection, and one may appreciate that the schemata on which they are based are not merely instantiations of a particular idea, more than that, they encode past behaviour and effects.

Finally, a note about the word "complex" in the phrase complex adaptive system. As described in [72, p. 27], "complex" need not have a precise significance in this phrase, it is merely a conventional one. It derives from the belief that any such system possesses at least a minimum level of complexity, suitably defined. For the purposes of this study, I concentrate on the common operational characteristics of a complex adaptive system, rather than definitions of technology complexity, as strictly speaking the concept is used as a convenient metaphor.

2 A potential technological discontinuity

2.1 Introduction

The emergence of hydrogen technology is seen as an opportunity by some, and as a threat by others. The opportunities perceived for this technology relate not only to its commercial prospects; many see it as offering a (part) solution to broader challenges of society (e.g. in reducing greenhouse gas emissions). Meanwhile, the threat that is perceived is generally associated with a desire to maintain the current technical order (or *regime* [69]), and the practices and successes associated with it. Thus, the emergence of hydrogen technology has ignited a competition between new and old technical orders. This chapter places hydrogen storage technology within this context of change, and outlines several proposed opportunities for it. In doing so, I seek to identify high-level regularities in technological change that better describe this context. My main point of reference for this discussion is a concept developed in the field of evolutionary economics; the technology life-cycle model.

2.2 Technology life-cycles

2.2.1 Literature review

The progress of technology occurs through natural cycles. That is, periodically, a new kind of technology is adopted for solving particular problems/fulfilling a certain purpose. These cycles tend to follow a particular scheme. Figure 2.1 gives a graphic depiction of the main elements characterizing a technology's lifecycle. A new technology begins its journey following an event that we would most often call "invention". In the context of technical progress, an invention classes as a (technological) discontinuity; it doesn't fall smoothly in line with the technical developments that have preceded it. The event marks a definitive break in technology structure, and overall performance characteristics (though certain individual performance metrics may fall relatively smoothly in line). In the past, invention was usually treated as a chance event in the technology's cycle, or as the result of individual genius [11, 58]. But as described in section 1.3.3, there is nothing fundamentally mysterious about it.

In any case, it suffices to say that an invention ushers in a period of intense experimentation and variation in design. This period is characteristically one of high uncertainty. For a start, there is no reliable insight into the precise customer needs of the new technology

- critically, the customer is lacking experience in assessing his/her needs through the use of it [39]. This creates uncertainty regarding the important dimensions of merit by which to evaluate the new technology [153]. There is also considerable uncertainty inherent in the design process, and it is difficult to judge the attainable performance levels for different technical forms [156]. As a consequence, there is substantial design diversity and competition during the so-called "era of ferment" referred to in figure 2.1. On account of the degree of variation and experimentation, this period has also been characterized as the "fluid-phase" of technical development [5].

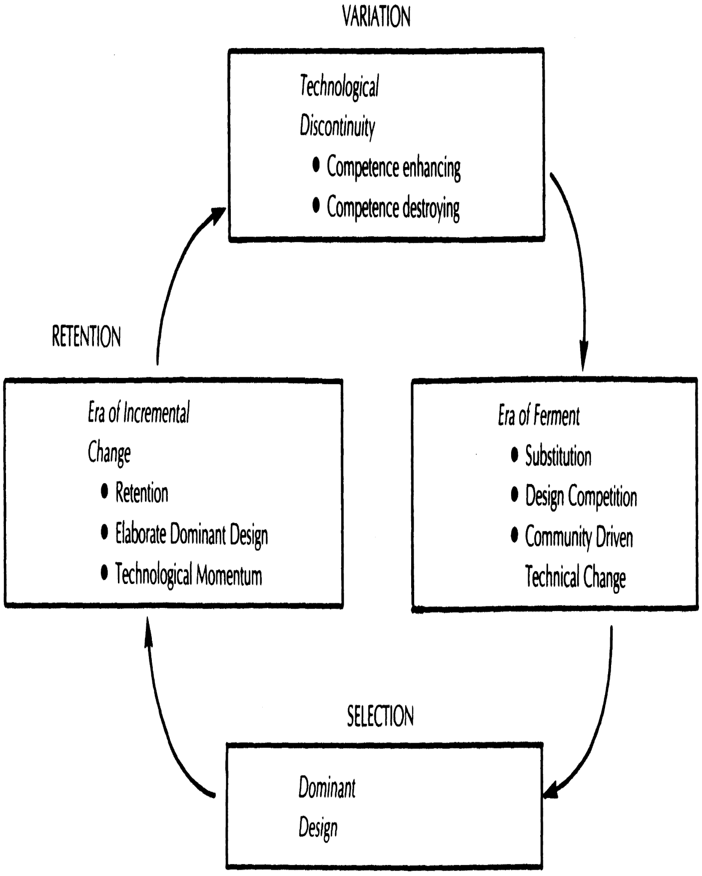

Figure 2.1: Technology cycle model. *Source:* [153]

The uncertainty associated with inventions is a key factor that explains why technological breakthroughs are most frequently driven by organizations outside the existing technical order (e.g. by universities, spin-outs, entrepreneurial firms) [153]. As W. Abernathy *et al.* [5] have explained it:

"In the initial fluid stage, market needs are ill-defined and can be stated only with broad uncertainty; and the relevant technologies are as yet little explored. So there are two sources of ambiguity about the relevance of any particular program of research and development - target uncertainty and technical uncertainty. Confronted with both types of uncertainty, the decision-maker has little incentive for major investments in formal research and development."

For several of the established corporations, larger research and development investments are only justified once uncertainty about markets and appropriate targets is reduced. Assuming that occurs, firms then have a more predictable agenda for technical development. But the era of ferment persists until the *technical* uncertainty is reduced at the industry level. While several differentiated, “unstable” designs are in competition, it is untenable for a technical regime [50] to develop around the new technology. Thus the era of ferment also characterizes the struggle of existing and new organizations to “absorb” the innovation. This barrier is typically overcome once a particular design starts to dominate (see figure 2.1). Only once a stable design - characterized by an invariant set of core components [119] - emerges, may certain kinds of benefits accrue. For instance, the production process no longer has to have the flexibility it needed during the experimental phase, and economies of scale may be achieved through focused optimizations [5]. Learning by repeated use becomes an important source of progress. Other potential benefits of technical convergence are described in [153]:

Technical clarity and convergence on a set of technical parameters permit firms to design standardized and interchangeable parts and to optimize organizational processes for volume and efficiency. Practitioner communities develop industry-wide procedures, traditions and problem solving modes that permit focused, incremental technical puzzle-solving. Dominant designs permit more stable and reliable relations with suppliers, vendors, and customers. If the product is part of a larger system, industry standards permit system-side compatibility and integration.

The transition of a new technology into the period of incremental change (see figure 2.1) is marked by the emergence of a dominant design. To achieve this status, the dominant design must not only succeed in competing for selection with variants within its own technology class [83]. It must also overcome a resistance to change exerted by the technical regime built around the old principle [11, 15]. The old technology presents a formidable opponent however, as it has the capacity to adapt and overcome limitations that have begun to challenge its reign. In this evolution, the mechanism for variation is the design process. In general, a new instance of a technology may be desired because a new level of performance is required; or a different physical environment may have to be designed for; or better performing parts and materials may have become available; or the market may have changed [15, p. 96]. The engine that drives variation - or design for better suited solutions - is fuelled by identifying new problems or needs. The process of finding a new solution involves a thorough redesign/rebalancing of the existing architecture. Broadly, there are two approaches to addressing a technology’s internal design problems: *internal replacement* and *structural deepening* [15].

The first case refers to situations in which developers can overcome limitations by replacing an impeded component - itself a subtechnology - by one that works better. “This might be one that uses a better design, a rethought solution, or one intellectually appropriated from a rival group. Another way is to use a different material, one that allows more strength per unit weight, say, or melts at a higher temperature...A great deal of development lies in searching over chemically similar materials for a more effective version of the phenomenon used. [15].” The improved component will require adjustments in other parts to accommodate it. Those parts may then themselves require adjustments in yet further parts, depending on the extent of the adjustment. This process of change bears resemblance to the dynamics of evolution in large ecologies described by the Bak-Sneppen model in [17]. In such an ecology, the process of change in the population of species is described by "punctuated equilibria", in which a change in the fitness of any one species may have an affect, anywhere from a minor influence, to a major impact that reshapes the entire ecology. The frequencies of events with different magnitudes of impact are described by a power law distribution (with minor events being the most frequent). This type of dynamic is in fact common to many complex systems with lots of interdependent parts [17]. We might imagine a technology as an ecology consisting of many species - subtechnologies. Each technology has a fitness[1], defined for example, by how well it fulfils its purpose (satisfies needs) without extracting/reacting to too much irregularity in its environment. A change in any given component (i.e. increasing the component's fitness) may create an "avalanche" of readjustments to other components in the technical system. Those avalanches may be small, implying minor adjustments, but may also extend to rethinking the technology's entire architecture. For instance, when the wooden framing of aircraft was replaced by metal framing in the 1920s and '30s, the whole of aircraft design itself had to be rethought [15].

The second pattern of change, referred to as "structural deepening", is the one largely responsible for the increasing complexity seen in maturing technological principles. By this approach, developers work around an obstacle by adding an assembly, or further system of parts, that takes care of it [15]. Here the component presenting an obstacle is not replaced by a different one. It is retained. But additional components and assemblies are added to it to work around its limitation. This process allows technology to greatly enhance its performance and widen the range of environment it can operate in. But as a costly and challenging process, it will require an economic driver. Apart from the pressures of rival technical designs, an important incentive for progress is given by the competition of new technological principles. These will at first struggle to compete on all dimensions of merit. After all, there is no reason why a new principle, fit for a specific purpose, should immediately fit the mould defined by a large set of intricately defined needs. But as time goes on, the performance of the new will become more competitive, and its primary performance gains over the old will no longer require difficult trade-offs. Meanwhile, the old technology becomes more and more complex as elaborations to maintain its supremacy are made in a process referred to in [15, p. 140] as "adaptive stretch". Eventually, the development process runs into fundamental limitations inherent to the old principle. A nice example is given in [15]:

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[1] The notion of fitness is a simplified concept, but may nevertheless be instructive. In terms of interpreting the measure of fitness, the biological analogue is useful: In stable environments, fitness is a characteristic that reflects how well an organism is able to exploit the regularities in its environment in order to find nutrients, stay safe, and reproduce. Those abilities will be selected for, thereby increasing the fitness of the organism in the long-run. This description may be applicable to a technology sold in a stable, non-competitive market, in which gradually the performance on some measure is increased. In complex, changeable ecological environments, a simple numerical measure of fitness, that reflects adaptiveness to prevailing selection pressures, is hard to define [72] (indeed, the expression "survival of the luckiest" may be as applicable as "survival of the fittest"). Inasmuch as fitness is meant to capture the differential propensity for reproductive success, fitness is a quantity related to population size. For technology, the analogue of population size is the number of adopters/adoptions.

> *"In the 1930a, high-speed high-altitude flight could have been achieved by the jet engine several years earlier than it was. But designers were not yet familiar with the gas-turbine principle. And so, when pressed to fly military aircraft at speeds that were most achievable in the thinner air at higher altitudes, they adapted and stretched the technology of the day, the aircraft piston engine. This forced piston engines against a limitation. Not only was oxygen scarce at high altitudes, but the ability to pump oxygen into the cylinder fast enough was itself limited by the rate at which oxygen could be combusted and processed within the four-stroke system. Superchargers and other system deepenings were added to pump in air faster at high pressure. The piston part of the piston-and-propeller principle was elaborated, and with great ingenuity. It was stretched. More difficult to stretch was the propeller. If it worked in the less resistant air of higher altitude, it would lose bite. If it were pressed to turn at higher revolutions, it would go supersonic. If it were enlarged to have a bigger radius, its tips would travel faster and again go supersonic. A fundamental limitation had been reached."*

Reaching the fundamental limits represents the mature phase of a technology's lifecycle. It also represents a real window of opportunity [69] for the new, simpler design to break-through. The character of this competition will be explored further in a later section. In summary, technological advance is driven by the combination of discontinuous variation, direct (social and political) action of organizations in selecting between rival technical regimes (artificial selection), as well as by incremental, competence-enhancing actions of many organizations learning by doing (retention) [153].

2.2.2 Positioning hydrogen storage technology

The use of hydrogen as an energy form is relatively novel. (I emphasize that its *use* is novel, rather than being a novel idea - already in 1874 Jules Verne had predicted in his novel "The Mysterious Island" that hydrogen would be a fuel of the future). In fact, with respect to traditional means of converting chemical potential energy, such as with gasoline and other fuels, the use of hydrogen by itself (taking the oxygen that it reacts with as a given) would represent something of a technological discontinuity. Indeed, hydrogen has very different fuel properties to gasoline. With a little stretch of the imagination one might say that hydrogen is a novel - a simpler - combination of parts for the purpose of energy storage, where the parts represent the atomic building blocks.

What about technology for the storage of hydrogen, is that based on a new principle? In different senses, hydrocarbons can be seen as both fuels and as stores for hydrogen (the carbon compacts the hydrogen) - very efficient ones at that. But they are single use storage concepts (perhaps, with synthetic production of hydrocarbons they would not be resource limited), and they entail the emission of waste products (CO2 etc.). The prospects for hydrogen therefore rely on different storage principles.

In a broad categorization of such storage principles, one would distinguish between the physical storage methods - compressed gaseous hydrogen, liquid hydrogen, and cryo-compressed hydrogen - and materials based hydrogen storage technology. Within each category there exist several more distinctions. This characteristic diversity of technical approaches suggests that hydrogen storage development (for services proximal to end-users) is currently positioned in the "era of ferment". In the case of the physical storage methods, development is focused mainly on the tank technology (e.g. materials (such as carbon fibre), layering, structure, vacuum insulation etc.), and on processing methods. The latter include methods for producing the vessel materials and constructing the vessel, as well as methods for compressing or liquefying the hydrogen. But all these innovations correspond to cumulative advancements of technologies that are already well-established. Materials-based hydrogen storage concepts on the other hand, introduce a fundamentally different approach. The base phenomenon being exploited in this case is an attractive interaction (or set of interactions) between hydrogen and some substrate material. The difference between the hydrocarbons, is that these approaches are designed for cycling (albeit some of the proposed materials require rather extensive regeneration processes to get the hydrogen back into the material), and the substrate materials are not involved in the energy conversion process.

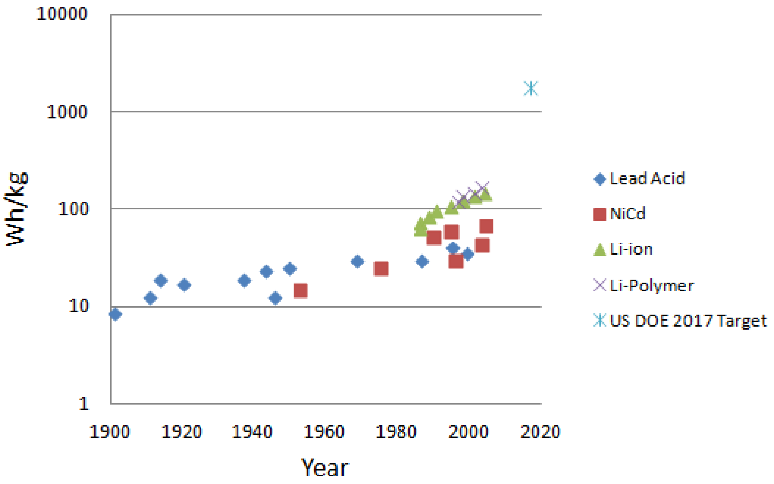

Figure 2.2: Historic progress in energy mass density in battery technology. Data for battery technology taken from [97]. The US DOE 2017 target provides a comparison for the proposed performance target of hydrogen storage technology.

As these concepts entail a novel base principle for the purpose of storing energy (hydrogen), one would be justified in classifying them as inventions (however, yet to be put to widespread use). A comparison of hydrogen storage technology with another traditional form of energy storage is made in figures 2.2 and 2.3. These graphs place the hydrogen storage concept (specifically, a proposed system target for the year 2017 set by the US Department of Energy[2]) in the context - in terms of energy density - of technological progress that has been achieved in battery chemistries. The discontinuity in performance with respect to batteries is exemplified (albeit that the 2017 targets might not be quite achieved).

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[2] I have chosen these target values as the comparison relates to commercial introductions of battery technology.

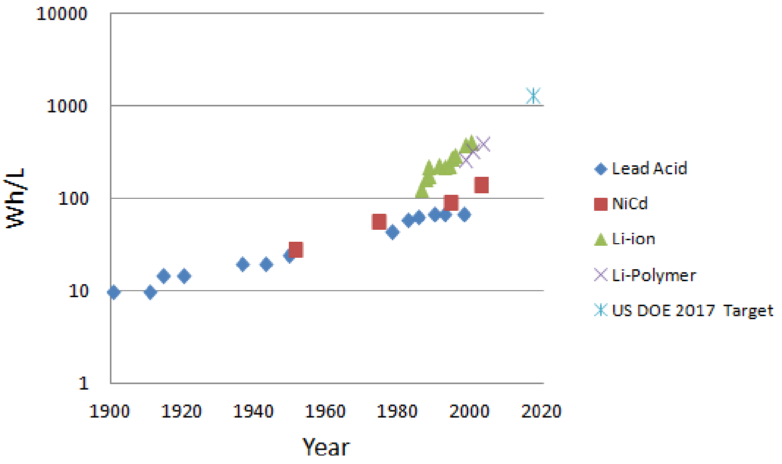

Figure 2.3: Historic progress in volumetric energy density in battery technology. Data for battery technology taken from [97]. The US DOE 2017 target provides a comparison for the proposed performance target of hydrogen storage technology.

Within materials-based hydrogen storage, many different approaches have been pursued, involving very different kinds of substrate materials, and different modes of interaction. One might argue that the major boundaries between various types of hydrogen-substrate interactions, for example, between chemisorption and physisorption mechanisms, also represent fundamentally different storage concepts. In any case, what is clear, is that there is a great diversity of approaches (several of which will be explored in more detail in a later chapter), which suggests, in part, inherent uncertainty about which technical pursuits will bear fruits. This is a typical characteristic of the era of ferment - technical uncertainty. Another uncertainty that rings true in the development process of hydrogen storage technology is the “target uncertainty” referred to in the previous section. I gauge this from 1) the lack of reliable targets for a range of proposed applications outside of auto-mobile ones, 2) a proliferation of targets for the automotive sector (although one set has been particularly dominant), and 3) a general lack of strict adherence to/interpretation of the automotive targets in hydrogen storage research (an impression I have gained from the litterature and from interviews with hydrogen storage experts. For example, a claim in [137] remarks that “one should keep in mind that most of the targets are not sharply defined, but should be more considered as guidelines”).

In the previous section I also referenced a claim in [5] which stated that, given a high degree of technical and target uncertainty, there would be little incentive for major corporations to be investing in fundamental research. In fact, the private sector has had a substantial share of involvement in hydrogen and fuel cell development. Many private companies have been involved in collaborations under the IPHE[3] and IEA HIA[4] programs (and other partnerships), but have also conducted their own commercially-sensitive research programs aimed at generating intellectual property and new products for market. Indeed, overall private spending on R&D is thought to dwarf spending by governments . An IEA report [1], published in 2004, reviewing national programs on hydrogen and fuel cells, estimated

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[3] International Partnership for Hydrogen and Fuel Cells in the Economy

[4] The International Energy Agency’s Hydrogen Implementation Agreement

an aggregate annual R&D budget of $1 billion from public funds, and roughly $3-4 billion invested by the private sector. (It is noted that these are speculative figures, especially as research budgets are usually not disclosed until a new product is ready for launch). A wide range of companies have considered it necessary to engage in hydrogen and fuel cell research activity, for example:

- Automotive manufacturers - all of the major companies
- Energy companies - including BP, Shell, Elf, Exxon Mobil, Chevron Texaco, Rio Tinto
- Fuel cell companies - including Ballard, United Technology Corporation Fuel Cells, Plug Power, ReliOn, Millenium Cells, Ceramic Fuel Cells etc.
- Other - covering hydrogen production, distribution, and storage technology companies

Some of the most noticeable commitments to hydrogen have been made by automotive manufacturers, and their engagement in R&D goes back 30-40 years for some. However, this commitment does not mean that they have no target or technical uncertainty. Evidence of this will be provided in the next chapter in the context of a discussion on the technical variation in hydrogen storage development. Taking this fact as a premise for now, it begs the question; why are auto-makers keen to invest in technologies whose prospects are so uncertain, and does this level of engagement with early phase technology not contradict the behaviour expected of corporations, as described in [5]? While there may be substantial uncertainty associated with particular technical variants, the investments in this area must be justified by a greater perceived risk of not investing. One could imagine, if one believes the marketing departments of many of these OEMs, that they have a great degree of confidence in the prospects of hydrogen in general. It would seem plausible that there are at least some OEMs that have this belief, and that are driving the agenda. For other OEMs (e.g. the late adopters in figure 3.4), it would then be a matter of reducing the risk associated with not investing in an area when their competitors are. An alternative explanation is given by the perceived risk of regulatory changes. In this scenario the investments are justified so as to avoid the potential of facing fines for not complying with a certain fleet-quota of emission free vehicles, which future regulations might stipulate.

Why is hydrogen technology seen as an opportune area to invest in? What problems might it address that cannot be solved at present? In terms of energy storage performance, hydrogen technology doesn't offer any advantage over current fossil fuel technologies, in fact, storage presents one of the major drawbacks. While hydrogen has an inherently high gravimetric energy density, seen in figure 2.4, it's very low energy content on a volumetric basis (figure 2.5) means that packing the hydrogen requires much more complicated technology than is the case for say a gasoline or diesel tank (typically made out of plastic). The prospects for hydrogen derive from different problems/limitations associated with the incumbent technology. One of the main problems seen with fossil fuels, one which originally spurred much of the early activity in hydrogen research (in the late 60s and 70s), is that its supply is not endless. Dwindling resources were expected to eventually make the price of fossil fuels prohibitive. Furthermore, the high degree of energy dependence on centralized oil production sites (many of which lie in politically unstable regions), raised concerns over energy security. While the finite supply of oil is a fundamental limit for fossil fuel technologies, just where that limit lies is a contentious matter. Certainly, early proponents of hydrogen energy were often overoptimistic in their forecasts. For instance, a Delphi study in the 1970s predicted that hydrogen would have a 10%/20% share of the private/public road transport market by the year 2000 (also 10% of the air transport market and 2% of the ship market) [157].

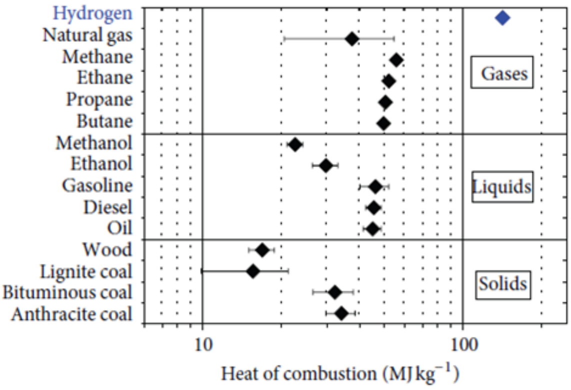

Figure 2.4: Heat of combustion on a gravimetric basis shown for various gaseous, liquid, and solid fuels under standard temperature and pressure conditions. Where ranges are given, this is because data was obtained from a multitude of sources. *Source:* [99]

Another limitation straining fossil fuel energy technologies arises from its polluting properties. This includes greenhouse gases (GHGs) and local air pollutants. As would be expected from the pattern of maturing technologies (described in the previous section), relevant technical components are being elaborated to address the encroaching limitations. This includes efficiency improvements of the internal combustion engine to address climate relevant issues, as well as things like catalytic converters to make regional air pollution less problematic. However, even with these improvements, fossil fuel technologies face fundamental limits[5] that don't reach up to the greener fuel properties of hydrogen (provided it is produced renewably). A key question on the prospects of hydrogen, relates therefore, to the extent to which these problems provide opportunities for technical change. I take up the theme of hydrogen storage opportunities in the next section.

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[5] The problem of greenhouse gases may be addressed by finding viable methods of synthetically producing hydrocarbon fuels.

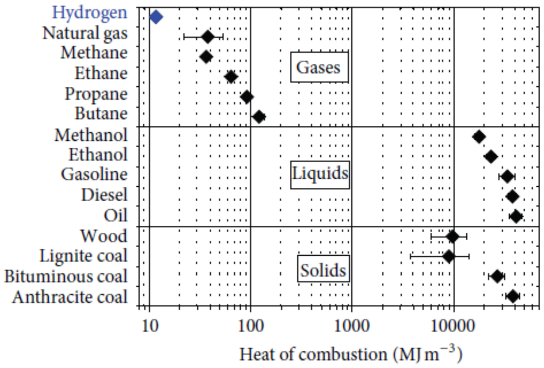

Figure 2.5: Heat of combustion on a volumetric basis shown for various gaseous, liquid, and solid fuels at STP. Where ranges are given, this is because data was obtained from a multitude of sources. *Source:* [99]

2.3 Opportunity niches for hydrogen storage

2.3.1 Basic concepts

In this section I present some basic ideas on thinking about a technology's opportunities. These concepts should provide an underlying logic to interpreting the prospects of technical change.

2.3.1.1 Needs

To call a technology into existence, the presence of a need is required, whether it is an expressed need or a latent one. It is the need which gives a technology its purpose, without which we would presumably just characterize it as an artificial phenomenon. At its core, a need is a perceived gap between some state of the world, and some desired state. It is helpful to think of needs as belonging to a particular domain, independent of the technology. It is the job of designers to create a mapping between the physical domain of the technology and the needs represented in the needs domain (or the customer domain [147]). This mapping is helped by formulating the typically informal and subjective quality of the customer's expressed needs [156], in terms of precise performance metrics, or product specifications.

As described in [15, p. 175], needs depend intricately and delicately on the state of society, and they elaborate as societies prosper. Human needs grow as technology builds out [15, p. 175] because it generates new perceived gaps (an example Arthur gives is that the technology of rockets creates the need for space exploration). Most obviously, the implementation of any given technology may immediately shift the need for a better performing alternative. Another source of need derives from the fact that technologies often cause problems (directly and indirectly). This results in the need for technical solutions (this at least seems to be true much more often than it results in the felt need for behavioural adaptations). A hydrogen power-train system for instance, could be viewed as a technical solution for the pollution problems created by conventional gasoline/diesel based systems in transportation technology. In this example, the solution involves a substituting technology, rather than one that builds on - or structurally enhances - the existing technological architecture, such as through the use of filters.

Finally, each innovation brings with it a set of ancillary needs. That is to mean, once the basic operational principle of a new technology has been established, there will be needs for sub-components that give support to and enhance the functions of the main system. Such components address needs for better, or more refined performance characteristics. W. B. Arthur refers to them as *technical needs* [15, p. 175], presumably as they become apparent by considering the internal structure of a technology and its requirements. This category of technical needs is responsible for a significant share of innovative activity in the economy. This follows from the recursive structure of technology, such that for each system level need being addressed, there are multiple sub-level needs that arise or are implicit, accumulating with the number of "layers" in the technology's hierarchy.

In sum, a need is a prerequisite for innovation to happen; it provides a non-zero probability for the adoption of a technology. Or, from the perspective of the technology, needs represent opportunities.

2.3.1.2 The technological niche

The opportunity to satisfy a need is realized by a technology filling a *niche*. The niche concept extends the idea of the *need* in that it draws attention to other elements important for the adoption of a technology. In ecology, an opportunity is realized - a niche exists - if an organism develops a schemata (or set of schemata) that allows it to stay safe, find nutrients, reproduce etc. The niche defines those elements of an organism's environment that are "built into" its schemata. The schemata are reflected in the characteristics and behaviours of an organism and the way in which regularities, which may pose benefits and threats, are extracted from its environment. Organisms thrive (are associated with a high fitness) when their schemata do a productive job of exploiting the regularities in their environment, i.e. avoiding threats, and making efficient use of resources. While it may not at first seem obvious, several parallels may be drawn to explain the case of a technology's niche.

An important aspect of the technological domain is its distinct form of selection pressures. While the "fitness" of a biological species could be assessed without knowing about the benefit its existence offers to say, parasitic organisms, an inherent and fundamental property of technology is that its fitness derives from its usefulness in providing a function. To illustrate the contrast, that would mean that the equivalent selection pressure operating in the biological domain would act to reduce the population of organisms at the top of the food chain. But while selection pressures may be different in form, the overall operation of evolutionary change in the technological domain is similar in principle.

In the case of technology, schemata represent the operational principles [119], or the technology's underlying concept. Meanwhile the niche, reflected in the technology's schemata, is composed of all elements that have some interaction with the technology of interest, whether intended or unintended. The intended interactions may be divided into inputs and outputs. To visualize them it is helpful to picture the technology as a chain, as described in [15, p. 110] (after all, technology may essentially be viewed as a combination of components); at one end of the chain is the need or purpose to be fulfilled, the output; at the other is the base effect (or set of effects), the input, that is harnessed to meet it. The links between the designated inputs and outputs represents the overall solution. The inputs may come from connecting technological components, or they may represent a human interface. Likewise, the outputs may be the requirements of further connecting components, or it may be an interface at the "opposite" boundary of the technology. The chain view is a rather tidy view of technical systems. For one, it hides from scene the prevalence of unintended interactions. By unintended interactions I am referring to behaviours that may impinge on the performance on certain metrics, or simply generate problems or negative perceptions. Undesirable vibrations or noise are two basic examples. Unintended interactions may be of a regular nature or may only occur during certain states of operation. One may use the analogy of good schemata usefully extracting regularity from its environment by identifying good concepts as ones that respond in a desirable way to a regular, expected input, but which don't respond excessively to undesirable interactions, or that are extremely sensitive to new, irregular conditions. One example may be runaway resonant oscillations in what is intended to be a rigid structure. Another may be the comparison between analogue and digital technology, and their dissimilar output given a noisy input signal.

2.3.2 The (recursive) niche structure of hydrogen storage opportunities

Hydrogen storage technologies form a distinct category of technology, one with the purpose of safely containing a given amount of hydrogen, and releasing it at a controlled rate when it is needed. Different concepts are known by which to implement this function, such as in a gaseous or liquid state, or bound up within a material. Logic would tell us that opportunities for these technologies arise whenever there is a supply of - and a need for hydrogen gas. Hydrogen is already used widely in laboratories and as a chemical agent in several industrial applications. Compressed hydrogen tanks have been the preferred method of storage for these uses. However, alternative concepts have started to be developed since opportunities are emerging in energy applications. Furthermore, these potentially impose very different performance requirements on the storage system. This section aims to provide an appreciation for how such opportunities could arise, and a brief overview of the requirements to be expected in different applications.

2.3.2.1 On the emergence of opportunity niches

Opportunities for hydrogen storage technology always rely on the possibilities for an appropriate niche structure to emerge. By this I mean methods for producing, (distributing,) and converting hydrogen into a useful energy form. Hydrogen storage is thus always a sub-solution to a bigger technical problem of providing energy services. This is an important point inasmuch as it means that the prospects for storage technology depend on the development and proficiency of appropriate niche technologies. Yet that is not all. Hydrogen is an energy *carrier*, and is therefore, as a concept, itself a sub-solution to bridging an energy gap. The properties of hydrogen cannot be exploited as the *base* effect in a complete energy chain as it is not an energy source - it does not occur in natural reservoirs in a free state but must first be extracted from one of a variety of naturally occurring substances in which it is bound up (e.g. methane, biomass, water, etc.). From this follows an important consideration that underlies all potential uses of hydrogen: the second law of thermodynamics. This dictates that there will be inevitable energy conversion losses through entropy, meaning that more energy is always expended than that which is available in the produced hydrogen. There must therefore be some extra benefit/rationale if one wishes to transfer energy via hydrogen.

The hydrogen component of the energy chain can link up with various forms of input - hydrogen may be produced via electrolysis, via chemical reactions, thermal water splitting, or in biological processes - and it can connect to energy services that require either heat (e.g. internal combustion engine), or electrical potential (with fuel cell technology) or both (e.g. in combined heat and power applications). Whether or not the hydrogen subsystem has a high “fitness”, depends on the type of energy source, and on the type and scale[6] of application being envisaged, as well as on its internal structure. In this discussion it is important to note that large scale energy transitions aren’t simply “manufactured” from the visions of a select group of “energy system designers”. They are not self-contained products as it were. As noted in [50, p. 100], “in the past, large-scale transitions of energy and transport infrastructures have usually occurred as an emergent result of interacting drivers and activities, rather than as the outcome of a managed transition.” The convergence towards an overall solution is an inherently political and social process [153]. As the selection pressures for various components of the energy chain will not be independent of their context, to appreciate the opportunities that might emerge for hydrogen (and therefore hydrogen storage technology), it is important to appreciate the possible pathways in which a transition could occur.

In the biological domain, to imagine the prospects of particular niches emerging in which the selection pressures are favourable for a given species of interest, one may have to imagine a branching process of alternative future histories. Each possible branch would represent a possible sequence of key events in the reshaping of the niche environment (some of which might not at all be conducive to the species of interest). These events might be treated as random mutations, or chance external influences (e.g. a meteor collision). Analogous “pathways” could be imagined for the case of energy transitions. However, rather than treating events marking technological changes as fundamentally random “mutations”, one could gain some insight from the knowledge that these changes, taking into account differing perspectives on the potential “fitness” of a given technology, are based on purposive or

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[6] Scale is an important issue as the weights attached to certain needs of “society” depend on it, such as concerns over pollution, security, and sustainability. It is a curiosity that the very success of fossil energy is in some sense responsible for creating an environment in which alternative energy concepts, including hydrogen, are becoming more attractive.

coordinated actions, and on strategic decisions informed by expectations of future market opportunities. This by no means implies that the dynamics of change are predictable. There exists a vast set of possible pathways. Many of the directions that are taken remain dependent on chance events. There is clearly also a lack of knowledge about all the multitude of factors that could influence the expectations of agents, and in addition, one would have to take into account fundamentally heterogeneous agent behaviours and the feedback loops involved in their strategic actions. Nevertheless, such an approach lends a structure for thinking about the kind of futures that could conceivably stimulate opportunities for hydrogen (and therefore for hydrogen storage technology). In fact, this kind of approach, involving technical "scenarios", has been comprehensively examined by McDowall *et al.* in [50] for studying hydrogen futures. Their work is based on an extensive series of workshops, interviews, and expert reviews. I will draw on their insights in the next section to discuss a small set of contrasting pathways that would enable the emergence of hydrogen opportunities.

2.3.2.2 Drivers of hydrogen in various transition pathways

McDowall *et al.* [50] explore four particular energy transition pathways that lead to hydrogen assuming a dominant role in energy services. Among showing the interdependence of selection pressures, they show the contrasting effects that might ensue with different actors being dominant in driving innovation in the energy sector.

The first transition pathway considered leads to a future energy system labelled as "electricity store". The essential features of this system are described in [50, p. 105] as:

"In this hydrogen future, hydrogen is not only the dominant road transport fuel, it also plays a vital role providing distributed energy storage to overcome the intermittency problems of renewable electricity generation. Hydrogen is produced locally in small-scale electrolysis units for forecourt refuelling and on-site storage, for use in domestic and commercial CHP units at times of peak electricity demand/limited supply."

Some of the key events in this pathway are the following:

- There is government action to support renewables and measures are taken at the regional and local level to facilitate distributed generation. This creates opportunity for entrepreneurial activity in renewable energy supply and micro-generation. Given the intermittent, and volatile nature of renewable energy supply, this development creates a need for, and hence opportunity for small scale energy storage applications in back-up power, premium power (due to power quality issues), and off-grid power, which are taken up by hydrogen fuel cell technology.
- Because carbons are taxed heavily, and because "society" is wary of nuclear and carbon sequestration schemes, there is an elevated selection pressure for renewables. As these become an increasingly important part of the supply mix, it creates a pressing need for back-up power solutions. Energy storage technology can solve this

problem, and also address the need for flexible demand-side management. Combined, these developments create selection pressures in favour of hydrogen. Meanwhile, smart metering and advances in grid technologies increase the potential fitness of hydrogen energy in this operating niche.

- By filling the growing niche market in providing back-up solutions, cost reductions in fuel cell technology are possible and other learning takes place. This opportunity has also enabled an increased coverage and potential supply of hydrogen fuel. This contextual development provides a burgeoning opportunity for hydrogen to be the fuel of choice for transport applications. Hydrogen becomes a dominant fuel for passenger vehicles if it can overcome competition with biofuels and hybrids.

The second transition pathway described in [50, p. 107] leads to a state described as "ubiquitous hydrogen". Again, the main elements of this system are outlined:

"In this hydrogen future, gaseous hydrogen is not only the dominant road transport fuel. Many buildings also use fuel cell CHP systems running on hydrogen. Distributed renewable generation predominates, reducing the need for long-distance transmission and distribution, and allowing hydrogen to compete directly with electricity as the main energy vector for the provision of domestic and commercial heat and power. Regional grids of hydrogen pipelines connect (predominantly local) hydrogen supplies with local needs."

The sequence of events that could lead to this kind of energy system might resemble the following:

- The important drivers of this pathway are the major corporations in the automotive industry. Given the sector's dependence on oil, amidst growing pollution and security concerns, the innovative actors in the sector see a shift to low carbon-system as desirable. Hence there are selection pressures working against the dominance of fossil fuelled automotive transport. Hydrogen technology is seen as a promising alternative. The selection pressures intensify from strategic competition among the major firms to be leaders in hydrogen technology. These positive expectations presumably make prospective fuel suppliers sense an opportunity, and joint ventures for an initial roll-out of hydrogen supply infrastructure form the basis for coordinated action.

- The selection environment for hydrogen cars is strengthened by certain policies, e.g. low-emission zones in cities, making the hydrogen car a more competitive prospect for consumers. The pioneering auto-makers use their lobbying powers to encourage further regulatory changes that support their activities. Additionally, reduced costs of hydrogen and fuel cell technology is possible through initial adoption of the technology in high-end markets, and through a continued investment in R&D.

- With increasing prospects for the hydrogen fuel cell vehicles market, major energy companies expect opportunities to arise from extending the hydrogen infrastructure, at first through distributed natural gas reforming and through trucked liquid hydrogen. Key events make a centralized, and fully integrated hydrogen grid (using natural gas pipelines) favourable in the future: Rising natural gas prices, health and safety regulation change to allow the use of alternative gas sources in the natural gas network, and advances in gas separation technology.

- Finally, success with hydrogen fuel cell technology in the transport sector creates opportunities in the wider energy system.

The third conceived future energy state is described as “centralized hydrogen for transport”, with the following events shaping its emergence:

- Initially, favourable selection pressures for hydrogen come largely from a strong government commitment (at both a national and regional/international level) to realizing its potential. The public sector and “national champion” industries work in partnership to build a hydrogen transport infrastructure. This drive stems from the threats of climate change and energy insecurity, and the search for solutions is *not* thought to be best left in the hands of the market.

- As more national governments decide to adopt this approach, it reinforces the selection pressures in favour of hydrogen, as strategic considerations among the leading, advanced and rapidly industrializing economies lead to action that supports the rapid development of hydrogen. Specific actions are taken through regulation, subsidies, and public procurement (e.g. by providing fleet vehicles). The use of near-term technologies is encouraged.

All in all, this pathway could be characterized as a “purposive transition”, and might lead to an energy system something like the following:

“In this hydrogen future, hydrogen has become the dominant transport fuel, and is produced centrally from a mixture of sources. Hydrogen is distributed as a gas by dedicated pipelines and as a liquid. In some applications, liquid hydrogen is the on-board storage mechanism, while in others, compressed gaseous hydrogen is used.”

The final transition pathway considered by McDowall *et al.* entails a synthetic liquid fuel as the fuel that is ultimately dominant in transport. The main ideas underlying this system:

“In this hydrogen future, renewably produced hydrogen is “packaged” in the form of a synthetic liquid hydrocarbon, such as methanol, to overcome the difficulties of hydrogen storage and distribution. The carbon for fuel synthesis comes from biomass and from the flue gases of carbon-intensive industries.”

The following events would conceivably push an energy transition in that direction:

- One assumes that renewables and carbon capture technologies become major growth areas in the energy sector without government action. The artificial synthesis of liquid hydrocarbons becomes competitive when natural gas prices rise, and hydrogen is available for its production from renewable electrolysis, and carbon from either biomass or carbon capture schemes.

- A changing environment in the consumer electronics industry leads to changing user selection pressures; the need for more power on the go becomes the norm. This creates an opportunity in the portable power sector for fuel cells running directly on liquid hydrocarbons such as methanol. This opportunity arises largely as a result of market forces. Filling this niche coincides with a growing infrastructure for fuel cartridges. Liquid hydrocarbons achieve a comparatively high fitness for this application as there is a failure to develop more effective hydrogen storage techniques (other than in the form of a hydrocarbon).

- The growing infrastructure leads to opportunities in other markets, e.g. fuel cell scooters. Furthermore, there is a trend towards needs for more power in vehicles. This opens an opportunity for fuel cells in the transport sector as auxiliary power systems. Scale up and learning in fuel cell technology eventually lead to demand as a transport fuel, and the eventual dominance of synthetic liquid hydrocarbons.

The above examples all give a very high-level abstraction of the factors and behaviours involved in an energy transition (including making various explicit and implicit assumptions). If one were to devise a very detailed account of the energy transition, describing the rationale of every decision in terms of all the relevant factors, and accounting for all possible events that could have an influence (surely an impossible task), how many pathways would more or less subsume under one of the different scenarios outlined above? In other words, to what extent do the details matter? To answer this question it would be necessary to identify the appropriate level of "coarse-graining" [72] by which to describe socio-technical processes of technological change. For instance, a technological breakthrough could have game-changing effects on the entire energy system. What level of progress should be considered hugely influential, and what levels are more or less inconsequential in the grand description of things? It would seem that this is an important question to better understand the prospects for hydrogen storage opportunities emerging. Alas, I will continue without attempting to evaluate the promise of various applications. Instead, in the next section, I will give an outline of potential markets that have merely been proposed (in various literatures), and discuss some of the distinct needs associated with them.

2.3.2.3 Overview of potential hydrogen storage markets

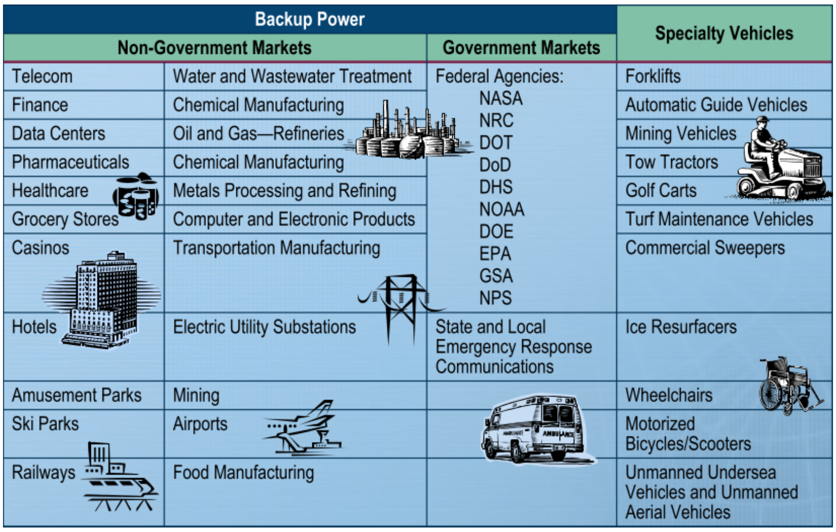
In the energy transition pathways described in the previous section, certain hydrogen storage applications would have been favourable, whereas others may have been impeded by specific transition processes. Here I give a quick summary of some of the proposed applications for hydrogen storage technology *irrespective* of the pathways they might be part of:

- Transport applications, including light-duty vehicles, heavy-duty vehicles, shipping, and trains. For these applications both fuel cells and (slightly modified) internal combustion engines (ICEs) are viable conversion technologies. As noted in [114], vehicles with ICEs running on hydrogen could provide low pollution vehicles that help stimulate a market for hydrogen, and provide a means for public familiarity with hydrogen as a fuel. Fuel cells would offer higher efficiencies and even lower emissions, though at present they are much more costly.

- Portable applications, including electronics and consumer goods (power levels approx. 1-250 W). These are widely seen as the most likely early fuel cell market [114].
- Stationary applications: This includes remote and off-grid power, as well as premium or backup power. Those that involve distributed production of hydrogen are particularly reliant on cheaper technical components.
- Auxiliary power units for vehicles - APUs would provide electricity in vehicles much more efficiently than current systems, and remain available when the engine is off, making them attractive to the military and long-haul trucks in particular [114].
- With increased penetration of intermittent, renewable energies (and assuming a system that is not entirely distributed), another important area for energy storage would be on the utility scale, for balancing out the grid. Such applications are potentially on the giga-watt scale. While this is currently practical only with pumped hydroelectric power, alternatives, including hydrogen, have been considered (hydroelectric stations are only viable in suitable geographic locations). Due to the scale of the storage systems required, and associated capital costs, these applications impose particularly stringent cost and efficiency requirements, likely making traditional techniques of hydrogen storage impractical (storage in underground caverns has been suggested).

These market descriptions represent broad categorizations. Within each we can expect to find many further distinctions, depending on the particular context (see figure 2.6). In fact, many such contexts will not yet have been thought of (or even exist). Each of the markets above will be filled by certain specially adapted technological designs. As one technological specialization becomes the basis from which further specializations are designed (branching), more and more market niches become accessible. This process is known as the differentiation of technology. Many more potential future opportunities for hydrogen storage might arise depending on other technological developments and changes in user behaviour. For example, in the 1970s and 80s, while hydrogen storage was an active area of research, few people will have predicted that portable applications (e.g. back-up charger for mobile phones) would one day be considered one of the early market opportunities.

At present, as in the past, one of the main areas of focus for hydrogen storage application is the transport sector, particularly, as a fuel for light-duty vehicles. Given that this represents the biggest market, and considering that the scale of its energy demand implies an opportunity to significantly address the energy crisis, it is not surprising that this area is a prime target for technological progress/breakthroughs. The significant pull of the market, compared with other mobile applications, is suggested by the data presented in figure 2.7, which shows the frequency of hydrogen fuel cell vehicle demonstration projects for different mobile applications. The data has been compiled from an online database, and although it is difficult to make inferences about absolute figures, I see no reason to presume that the distribution of this sample is not approximately representative.



Backup Power			Specialty Vehicles
Non-Government Markets		Government Markets	
Telecom	Water and Wastewater Treatment	Federal Agencies: NASA NRC DOT DoD DHS NOAA DOE EPA GSA NPS	Forklifts
Finance	Chemical Manufacturing		Automatic Guide Vehicles
Data Centers	Oil and Gas—Refineries		Mining Vehicles
Pharmaceuticals	Chemical Manufacturing		Tow Tractors
Healthcare	Metals Processing and Refining		Golf Carts
Grocery Stores	Computer and Electronic Products		Turf Maintenance Vehicles
Casinos	Transportation Manufacturing		Commercial Sweepers
Hotels	Electric Utility Substations	State and Local Emergency Response Communications	Ice Resurfacers
Amusement Parks	Mining		Wheelchairs
Ski Parks	Airports		Motorized Bicycles/Scooters
Railways	Food Manufacturing		Unmanned Undersea Vehicles and Unmanned Aerial Vehicles

Figure 2.6: An illustration of the many different potential contexts for backup power and specialty vehicle applications. *Source:* [108]

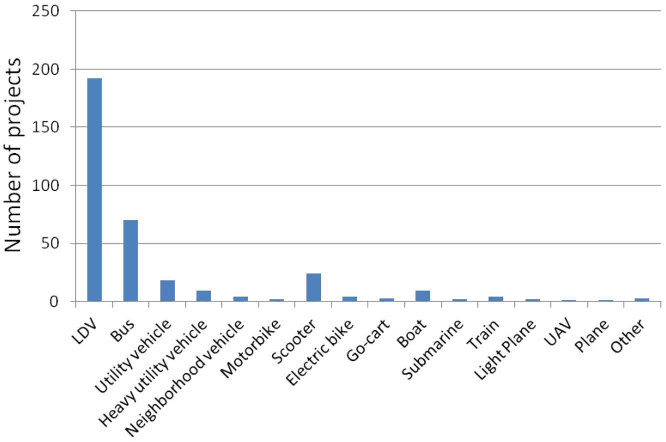


Figure 2.7: A distribution of the number of mobile application demonstration projects that have implemented hydrogen storage technology. The data was sourced from an online database [81]. It should be noted that, while this database is more comprehensive than most, it does not garuantee a representative distribution of mobile demonstration projects. Moreover, there is variation in the size of different projects that has not been accounted for, thus making a simple count an imperfect measure of the activity or “pull” of particular application domains. The categorizations are my own interpretation of the demonstrations listed in the database.

The same data set also contains information on which type of storage method (gaseous, liquid, or solid-state) was employed in the demonstration projects - an interesting but crude reflection of the opportunities perceived by innovators for different storage techniques. A cumulative running total of all methods is shown in figure 2.8, while a breakdown of the methods used is given in figure 2.9. It is somewhat curious to see a leveling off in the data entries in figure 2.8. It is claimed in [110] that the period of decline often overlaps with a rise in commercial project ventures. On the other hand, it could mean a (transient?) reduction of funding and interest etc., or it could also be an artefact of the particular data set. The data in figure 2.9 reflects quite well the common sense of the relative popularity for these storage methods, though one might have expected to see a keener interest developing for the 70 MPa variant of compressed hydrogen technology (CGH2). In particular for light duty vehicle applications, this currently appears to be the technology of choice. Perhaps this is explained by the fact that demonstration projects are often more concerned with proof of principle, for which the cheaper 35 MPa variant might suffice in many cases, rather than optimization.

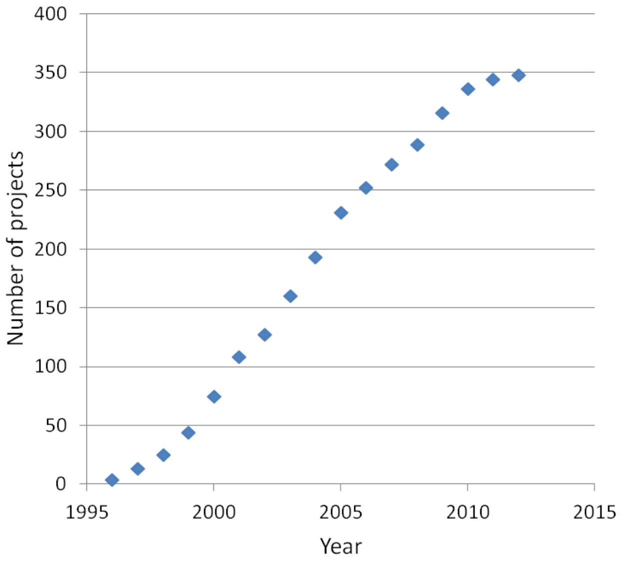


Figure 2.8: Cumulative total of mobile application demonstration projects that have implemented hydrogen storage technology. Data is from the online database [81].

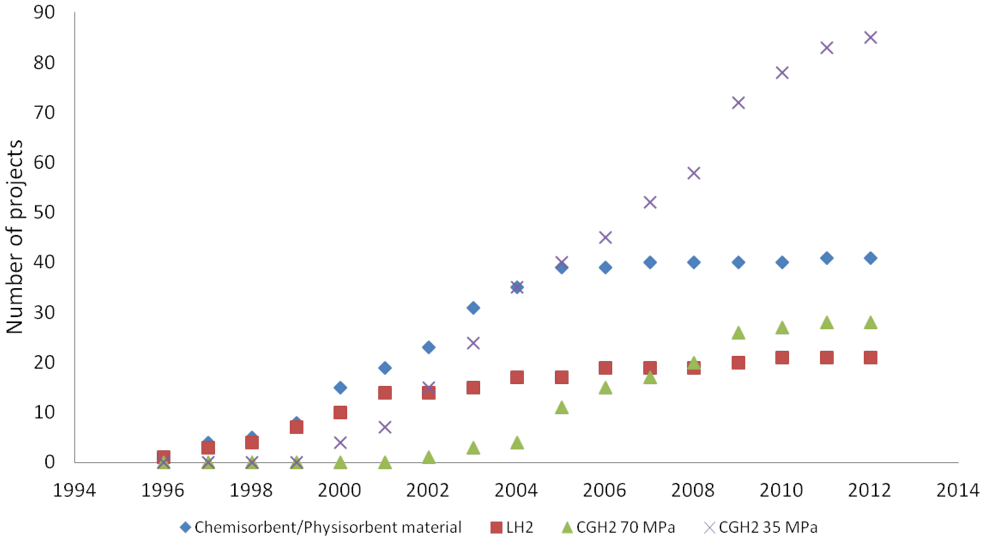


Figure 2.9: Number of mobile application demonstration projects using different methods of hydrogen storage. Data is from the online database [81].

2.3.2.4 Examples of product requirements

Several different market contexts have now been presented for which hydrogen has been declared a potentially useful energy form. Each application has different needs, and therefore requirements of its energy system. To realize these, varying sets of requirements will in turn be placed on the hydrogen storage sub-system. These requirements are the needs to be met by the storage sub-system. One may go further down the hierarchy and determine the requirements of sub-sub-systems. By continuing this process one would eventually reach a level at which it no longer makes sense to decompose the problem into sub-problems. This level would correspond to the fundamental parts of the technology, or, as described in [147], the "leaf" level. The specifications that are assigned to sub-systems are devised through a "flow-down" method [156]. This method may be quite complicated for complex technologies that consist of many levels, and numerous interacting components. A schematic of the general philosophy adopted by the hydrogen storage engineering centre of excellence (HSECoE) in the US in the development of hydrogen storage for fuel cell vehicles is shown in figure 2.10.

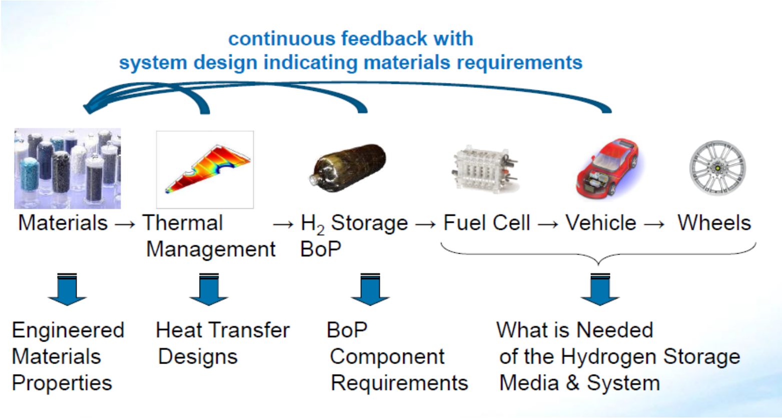


Figure 2.10: Illustration of the feedback process by which hydrogen storage material requirements are derived. *Source:* [13]

In the case of materials-based hydrogen storage technology, the desired properties of the material may be considered the leaf-level requirements. Requirements that are set at the material level would make it easier to set priorities and focus on problem areas, because it would be clear just how much improvement, if any, is required on each performance metric. On the other hand, having a fixed set of requirements implies that the design choices of the other components in the system are constrained (e.g. vessel, heat exchange system, BOP), as certain assumptions regarding their specifications would have been necessary to derive the material requirements. It could very well be that certain variations in the design would lead to overall better performance (an illustration of this problem is shown in figure 2.11). Most targets/requirements that are publicly available refer to the hydrogen storage system level, presumably to enable more exploration in design approaches. As there has generally been very little or no market experience with hydrogen storage systems (no feedback from user experience/behaviours with the product), one may assume that any targets which have been devised are associated with a fair amount of uncertainty.

The targets that have had by far the most influence on research activities have been those proposed by the US Department of Energy (DOE) in collaboration with the FreedomCAR and Fuel Partnership. An interesting background on the first edition of these targets is given in [91]:

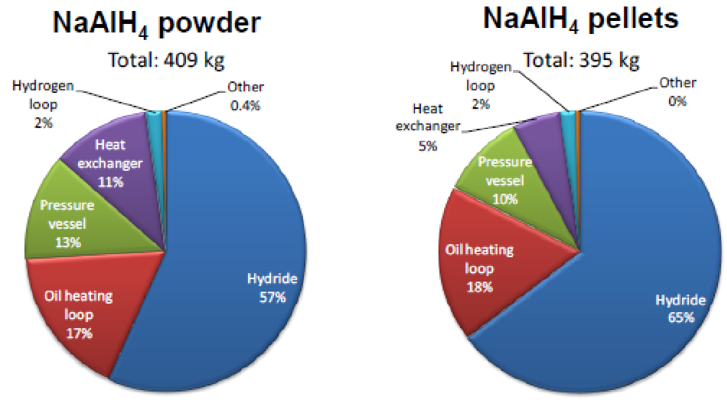


Figure 2.11: A comparison of two hydrogen storage system designs by component weight distributions. By varying the morphology of the base material (powder to pellet form), a significantly altered design is achieved in terms of the weight distribution of key components. *Source:* [13]

"The first formal goals are well represented by the United States Department of Energy (DOE) goals of 2003. This set of goals was based on the high business risk of introducing a new fuel source, a new power-plant - the fuel cell, and a new power delivery system in the form of power electrics and traction motors. In such an environment goals tend to be set high because of the high risk of meeting all goals at the same time. Initially, the long term goals (goals that would satisfy all sorts of customers over the full range of vehicle types currently sold) tended toward 10% storage by mass, liquid hydrogen density, fill times in 3-5 min, and costs comparable to gasoline vehicle systems. These were acknowledged as difficult goals to reach but they did generate a great diversification in the areas of hydrogen storage research. In time, areas of the globe that tend to favour smaller vehicles and shorter driving distances began to advocate less aggressive goals. As progress was made in the fuel cell and other subsystems, some of the demands were adjusted until today the DOE goals for 2015 are 5.5% by mass and 40 g/L, with 5 min fill times; roughly half the 2003 goals. None the less, meeting all the current targets of any government, or more importantly, the demands of customers, is still a formidable challenge."

A restricted version of the second edition of the DOE targets, from the year 2009, is presented in table 2.1. It may be of interest to draw a comparison to a similarly intended set of targets developed by an EU project; "StorHy". They are given in table 2.2. Details of the rationale behind the DOE targets, and a definition of all the metrics, can be found at [2].

Metric	*Unit*	*2017 Target*	*Ultimate*
Gravimetric capacity	wt.%	5.5	7.5
Volumetric capacity	kg H_2/L	0.04	0.07
Cycle life (1/4 tank to full)	Number of cycles	1500	1500
Minimum full flow rate	(g/s)/kW	0.02	0.02
Min/max delivery temperature	°C	-40/85	-40/85
Min delivery pressure from storage system; FC = fuel cell, ICE = internal combustion engine	bar (abs)	5 FC/35 ICE	3 FC/35 ICE
Max delivery pressure from storage system	bar (abs)	12 FC/100 ICE	12 FC/100 ICE
On-board efficiency	%	90	90
Well-to-powerplant efficiency	%	60	60
Fill time (5 kg H_2)	min	3.3	2.5
Fuel Purity	% H_2	99.97	99.97
Loss of usable hydrogen	(g/H)/kg H_2 stored	0.05	0.05
Storage system factory cost	$/kWh	TBD	TBD

Table 2.1: US DOE Hydrogen storage system targets devised in 2009. These targets were determined in order to satisfy the customer needs for a wide range of light-duty vehicles. *Source: [2]*

For a simple example of how storage system requirements may be derived, consider the following. An important vehicle requirement, for an average compact fuel cell car (~75 kW), is given as “range > 400 km (fuel economy = 3.6 L/100 km)”. Range performance is a function of several variables, one of them being the mass of the vehicle. Assuming the mass of the vehicle is constrained to some value, one must then budget the masses of individual subsystems. Assume that the mass of the storage system is budgeted to an upper bound of 100 kg. Obviously another important variable affecting range is the amount of fuel stored. Given a particular vehicle design, 4 kg of usable hydrogen is sufficient for a range of at least 400 km. Hence, in this example, one may specify that the storage system must have a gravimetric capacity of at least 4 mass%. Similarly, were one to constrain the volume to 150 L, this would impose a volumetric capacity of > 2.7 kg/100 L. The data for this example has in fact been taken from a different set of hydrogen storage system requirements, ones that were devised by DaimlerChrysler in 2006 for a 4 kg hydrogen store. The remaining targets from this set have been given in table 2.3.

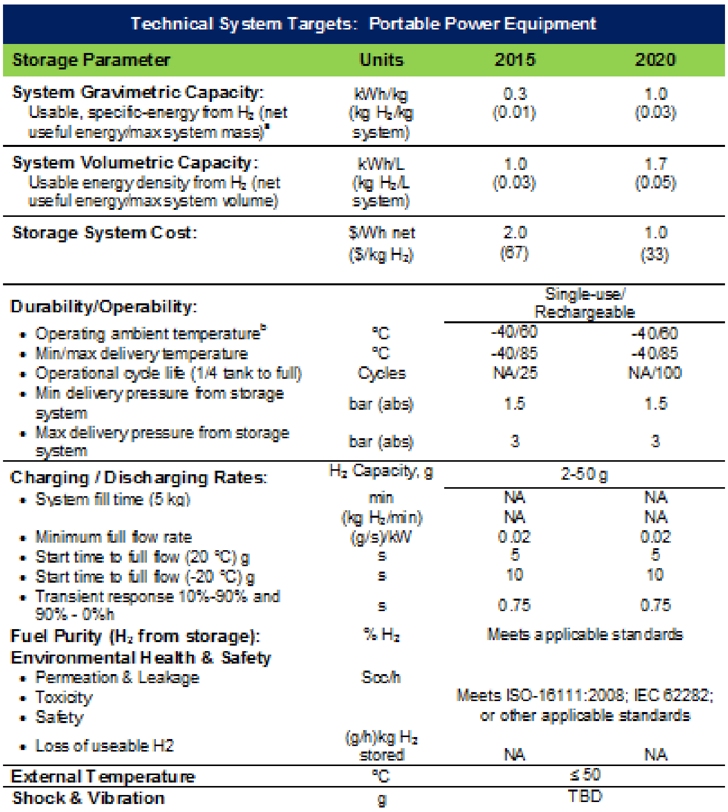
Metric	*Units*	*Target (2010)*
Gravimetric density	wt.%	6
Volumetric density	kg H2/L	0.045
Refuelling rate	kg H2/min	1.2
Max delivery rate	g H2/s	2.5
Delivery pressure (min)	bar	6
Cycle life	Cycles	?
Loss of usable H2	(g/hr)/kg H2	1
Cost	€/kWh	?

Table 2.2: Hydrogen storage system targets developed by the EU StorHy project. *Source:* [25]

Performance metric	*Targets*
Hydrogen supply pressure	0.6-1 MPa
Hydrogen supply rate	0 - 2 g/s (0 - 7.2 kg/h)
Full power response time	0.5 s
Shut off response time	<0.5 s
Cold start capability	like Diesel engine
Hydrogen leakage rate	bubble free for 3 minutes
Refuelling rate	1.2 kgH2/min (to 99% tank capacity)
Heat release or input during H2 discharging	tbd (depends on kind of system)
Temperature level for heat input	<80 °C
Loss of capacity during vehicle lifetime	<10%
"Passive" material temperature	-40 °C to +85 °C
H2 supply temperature	-25 °C to +70 °C
Hydrogen purity	tbd (see SAE J2719)

Table 2.3: DaimlerChrysler 2006 requirements for a hydrogen storage system in a 75 kW compact fuel cell car. [172]

Data on product requirements for portable and stationary applications do not seem to be widely available for the public. The information I have found is usually quite sparse or qualitative, nevertheless, some tentative data sets are available and useful. For comparative purposes, I therefore present some further examples of product requirements below. Table 2.4 shows a draft version of hydrogen storage requirements for portable power applications. These have been devised by the DOE Fuel Cell Technologies (FCT) Program in an effort to advance the development and deployment of fuel cells. In the portable power market (such as for batter chargers, consumer electronics, notebook computers, and emergency response mobile communications), it is thought that a high energy density alternative to existing technologies is required to fill the increasing gap between energy demand and energy supply.



Technical System Targets: Portable Power Equipment

Storage Parameter	Units	2015	2020
System Gravimetric Capacity: Usable, specific-energy from H_2 (net useful energy/max system mass)[a]	kWh/kg (kg H_2/kg system)	0.3 (0.01)	1.0 (0.03)
System Volumetric Capacity: Usable energy density from H_2 (net useful energy/max system volume)	kWh/L (kg H_2/L system)	1.0 (0.03)	1.7 (0.05)
Storage System Cost:	\$/Wh net (\$/kg H_2)	2.0 (67)	1.0 (33)
Durability/Operability:		Single-use/ Rechargeable	
- Operating ambient temperature[b]	°C	-40/60	-40/60
- Min/max delivery temperature	°C	-40/85	-40/85
- Operational cycle life (1/4 tank to full)	Cycles	NA/25	NA/100
- Min delivery pressure from storage system	bar (abs)	1.5	1.5
- Max delivery pressure from storage system	bar (abs)	3	3
Charging / Discharging Rates:	H_2 Capacity, g	2-50 g	
- System fill time (5 kg)	min	NA	NA
	(kg H_2/min)	NA	NA
- Minimum full flow rate	(g/s)/kW	0.02	0.02
- Start time to full flow (20 °C) g	s	5	5
- Start time to full flow (-20 °C) g	s	10	10
- Transient response 10%-90% and 90% - 0%h	s	0.75	0.75
Fuel Purity (H_2 from storage):	% H_2	Meets applicable standards	
Environmental Health & Safety			
- Permeation & Leakage	Scc/h	Meets ISO-16111:2008; IEC 62282; or other applicable standards	
- Toxicity			
- Safety			
- Loss of useable H2	(g/h)kg H_2 stored	NA	NA
External Temperature	°C	≤ 50	
Shock & Vibration	g	TBD	

Table 2.4: US DOE portable hydrogen storage system targets. These targets represent a preliminary set of targets (i.e. before further stakeholder feedback was requested by the DOE). Original notes explaining the targets: The targets are based on the lower heating value of hydrogen (i.e., 121 MJ/kg). Targets are for a complete system, including tank, material, valves, regulators, piping, mounting brackets, insulation, added cooling capacity, and/or other balance-of-plant components. All capacities are defined as usable capacities that could be delivered to the fuel cell. All targets must be met at the end of the expected service life. The proposed 2015 targets would enable a storage system (when coupled with a fuel cell) to be competitive with incumbent technologies for early market fuel cell applications and the 2020 targets would allow a system to equal or exceed the performance of incumbent technologies. *Source*: [135]

The information compiled in table 2.5 provides a crude, and largely qualitative comparison of differences in performance requirements for a variety of applications. An interesting point of comparison is the difference in mass densities desired. As one might expect, passenger cars impose the most stringent demands, though even 5 wt.% is considered mostly inadequate - an ultimate target of 7.5 wt.% is set by the DOE targets (table 2.1). Specialty vehicles by comparison, have a relatively low mass density requirement. Indeed, some applications require balancing loads (such as forklifts), and therefore might even benefit from lower mass densities. While one might not expect stationary applications to impose much of a weight restriction, one must consider that low mass densities imply that more material is necessary to achieve a certain fuel storage capacity. Particularly in stationary applications where large capacities might be necessary, this could impact significantly on cost.

Application	*Desired Attributes*
Stationary fuel storage (e.g. backup and remote power etc.)	> 2 wt.%, very low cost, efficient (e.g. uses waste heat)
Portable and mobile fuel storage (e.g. power and communication equipment, generators, etc.)	compact, > 2 wt.%, fast kinetics, high durability, uses air cooling or waste heat, low cost
Specialty and utility vehicles (e.g. forklifts, tow tractors, scooters, boats, submarines)	compact, low cost, uses waste heat, > 1 wt.%, fast kinetics, high durability
Passenger cars (internal combustion/fuel cell)	> 5 wt.%, uses waste heat, low cost, fast kinetics, durability during cycling, insensitive to contamination

Table 2.5: A comparison of important attributes for different hydrogen storage applications. *Source*: [96].

2.4 The challenge facing a new technological order

When radically new technologies enter the fray, the competition between old and new is often fierce; older technological orders seldom vanish quietly [11]. The overall performance of new technologies is often weak and costs are typically high [70] (production processes must be highly flexible, they are relatively labour intensive and erratic in work flow [39]). The new technology tends to dominate on a single (often a new) dimension of merit. This attribute relates to the main problem that challenges the old. But initially, new technologies typically also lag considerably behind the technical frontier on other critical dimensions of merit [153]. This pattern of innovation is reflected in the current climate of competition between fossil fuels and alternative fuels. Alternative energy carriers, such as hydrogen, clearly dominate on environmental criteria, but energy storage characteristics - such as energy density - fall short of the level set by the incumbent. If the new technology is to find opportunity for adoption by solving an existing "problem", it is claimed in [153], that it must either add an important functionality (or do away with an undesirable one) and do as well on existing metrics, or instead dominate on all the existing metrics. Perhaps this statement is not to be taken as an iron rule; technologies that add a new functionality may succeed even if performance on other metrics is lower, if the new functionality is weighted accordingly (a related concept in business theory, known as the "Innovator's Dilemna", speaks to this by emphasising the importance for established firms to anticipate future customer needs, to avoid failure at the hands of "disruptive innovations"). Otherwise, given the inherent technical challenges in terms of energy density, the outlook for hydrogen technology must be more pessimistic. In any case, the prospects of the new technology are difficult to estimate during the era of ferment, as neither dimensions of merit nor subsequent technical performance are clear [153].

As the new technology stakes a claim for future prosperity, the old technological order does not sit idly by. The response of the existing community of practitioners is often to increase the innovativeness and efficiency of the existing technical regime [153, 69]. A number of cases are reported in [153] which demonstrated sharp performance advances in the old technology in response to the new threat; mechanical typewriters, piston jets, spark gap radio transmission, gas lighting, and mechanical watches. As a result, technological discontinuities may not always come to dominate technologically. But the response of the old order often goes beyond an effort to improve performance.

Technological threats are met with resistance by technological momentum within the community of practitioners and within competing organizations, especially because any discontinuity is originally associated with substantial uncertainty, ambiguity, and implementation costs. The response of veteran firms and communities to external threats is often increased commitment to the status-quo [153].

This resistance goes back to interlinked competencies and relationships that have been built within established technological communities [153], and between suppliers, vendors and customers. Introducing a technological discontinuity might mean breaking or obviating many established relations and competencies. When the new technology is truly "competence-destroying" for many of the firms forming the incumbent technological order, it is thought that substitution processes take longer to be resolved [11]. Not surprisingly, firms confronted with the choice of abandoning existing know-how in the face of competence-destroying technical change will defend older technology more stubbornly, prolonging uncertainty about whether the new technology will become dominant [153].

Several of the preceding remarks are paralleled by innovation patterns observable in the "adaptive stretch" of the technological order (or regime) built around fossil fuels. For instance, the promise of cleaner, non-polluting fuels has triggered a response to develop carbon capture and sequestration (CCS) technologies - an elaboration of the existing system so as to confront technical limitations (see section 2.2). More generally, many efficiency measures are responses not only to environmental concerns, but to a large extent to the threat of competing energy services.

To surmize, this chapter has introduced the notion of the technology cycle model. I have used this concept to map out an intellectual landscape which focuses/structures my subsequent investigations. In the next chapter, I look more closely at high-level patterns evident in the exploratory phase.

3 Patterns of variation and technological evolution in the fluid phase of development

3.1 Introduction

The broader question that motivates this chapter is; are there high-level regularities of technological change, and if so, can we identify the “state” of hydrogen storage evolution? As described in the previous chapter (in the context of the technology cycle model), new technologies are generally quite weak in overall performance [15, 69]. This is not a surprising pattern. Indeed, rather than seeking to optimize individual parts, the early design process is heavily focused on merely obtaining a proof of principle [15]. Furthermore, to find a combination of parts that results in just the right levels of performance on a number of attributes, is also statistically unlikely when there are conflicting constraints [94]; there are many more ways to find combinations of parts that result in weaker performance profiles. (It is for this reason that studies on innovation processes have emphasized the need for “protective environments” as the technology is allowed to develop (e.g. as in the Strategic Niche Management (SNM) concept)[71, 69, 50, 70]). Thus, for a new base principle (a new technological “species”) to be successful, fitter variants need to be found. The focus of this chapter is on patterns in this search for fitter variants. I address two issues. One relates to the measure of diversity, while the other concerns performance improvement.

When the performance benchmark is low, significantly fitter variants are often searched for (and found) more frequently through radical exploration (as opposed to incremental adaptations) [94]. One aim of this chapter is to discuss the pattern of diversification in hydrogen storage search, beginning with a theoretical account, and following with empirical observations of technology prototyping and patenting activity data. These data support the view that development on this technology is largely within the so-called exploratory phase (as introduced in the previous chapter). A claim also supported in [19].

In the second part of this chapter I seek to gain insight into patterns of progress one might expect in hydrogen storage development. For this, I initially conduct a brief review of the literature on the subject of technological change. It is important to note that this literature pertains mostly to patterns of progress observed during the incremental phase of development. While there are schemes that can be used for “measuring” a technology’s readiness level (TRL) pre-commercial application [166], they are tools for orientation and categorization rather than seeking patterns of development (they are also not so useful in distinguishing a range of technologies that are in similar phases of development). I am unaware of other investigations into the patterns of progress during the exploratory phase. Hence, in drawing analogies and conclusions from the main body of literature, I speculate about issues and factors of progress in the hydrogen storage search process.

Finally, I anticipate a period of technical convergence - another stylized fact about innovation processes [142] - in a discussion on the emergence of dominant designs. The outcome of the dominance process is seen as a watershed moment in a technology's cycle [153], significant in determining the future course of a technology's trajectory. Such insight lends structure to making projections of hydrogen storage prospects.

3.2 Patterns of variation

3.2.1 Drivers

The process of technological variation is what makes "learning" possible, that is, technical adaptation which leads to better performance. Adaptive changes in technology are often divided into two phases [11, 5]. The era of ferment, or fluid phase, and the era of incremental change. Changes in the fluid phase are characteristically more experimental and radical, while, as the name suggests, the era of incremental change is marked by greater stability in the set of core components comprising the technology [119]. What is the reason for this change in emphasis?

When a new technology enters the incremental phase, it is usually because a workable design has been established which has proved successful amidst intense design competition [156, 11]. As it becomes adopted more broadly, more and more interdependencies are created with other technologies and practices. This reason alone would indicate that radical experimentation becomes less urgent or desirable.

A further theoretical explanation has been offered as well. To make this point it is necessary to formalize some basic notions: Any technical system must have some degree of interdependence among its components [24] (after all, any technology must have some interacting parts). For instance, a performance metric that is defined on the system level is generally a function of several performance metrics defined on a subsystem level. The architecture of these interdependencies is a key consideration in the design of a technology [143]. For example, a modular design approach is one that tries to avoid unnecessary interdependencies. Where there is an interdependence, it means that changing the state of one component will affect the "fitness" associated with another; it may have to be adjusted to restore its original functionality[115]. Elsewhere, these kinds of interdependencies are called "epistatic relations" [119] (a label that has connotations in Biology). By the degree of epistatic relations that is associated with a component, one may categorize a design change by whether it is incremental or radical. As may be imagined, an incremental design change is one that involves a component that has few such relations (a "peripheral" component), while a more radical change involves one with many - then referred to as a "core" design component [119]. It has been shown (in a study cited in [119]), using a technique called "fitness landscape modelling" (which has origins in studies of Evolutionary Biology), that changes to core components are less likely to lead to overall fitness improvements than changes to peripheral components (though when they do they typically have a bigger impact). Therefore, inasmuch as this theoretical model translates into actual design principles, one may argue that learning focuses on incremental change, once a core architecture has been established, due to the lower probability of an investment return.

By contrast to the incremental phase, the fluid phase of development is characterized by more radical experimentation and variation. There are a number of drivers of this. As mentioned in chapter 2, the era of ferment is characterized by both target and technical uncertainty. Under these conditions, the diversification of technical approaches is a natural consequence. Target uncertainty will mean that different producers are likely to interpret user needs differently, and therefore pursue a different design objective [39]. Even a single producer may want to diversify his/her portfolio to hedge against the uncertainty. Technical uncertainty means that designers do not know in advance which precise combination of components (design elements) will yield an adequate solution [58, 5]. As design problems are generally too complex to be formalized [156] (which would make the search for adequate solutions a lot easier), the best approach is to rely on intuition and to experiment (to the extent that cost/time constraints would permit). Another reason for fluid phase diversification is that firms will sometimes deliberately and strategically seek to differentiate themselves from rival variants [153]. The amount of diversity tends to go down in the era of incremental change because only a selection of the rival design concepts survive.

3.2.2 Experimentation and variation in hydrogen storage search

Being in the era of ferment, there is uncertainty and experimentation in hydrogen storage development. Some of this can be seen at the level of more mature product development activities, but in fact, most of the exploration is occurring at the level of basic research. In this section I aim to give a little insight into this experimentation and variation process.

3.2.2.1 Basic research

To appreciate the scale of the search agenda for hydrogen storage materials, it is informative to begin with an overview of the countries with hydrogen associations; on the basis that these organisations advocate a vision that involves hydrogen, such countries are not unlikely to have a stake in research and development. A complete list of these countries includes [139]: Argentina, Spain, France, Australia, Canada, China, Brazil, Europe, Japan, Italy, New Zealand, U.S.A., Mexico, Germany, UK. Many of these countries are also part of international associations for the promotion of hydrogen. Prominent ones include the IAHE (International Association for Hydrogen Energy), PATH (Partnership for Advancing the Transition to Hydrogen), IPHE (International Partnership for Hydrogen and Fuel Cells in the Economy), and the IEA HIA (International Energy Agency Hydrogen Implementation Agreement).

With such a large community of practitioners and researchers, as the number of hydrogen associations suggests, one can appreciate the rationale for coordinating search activities. Such was the motivation for setting up the IPHE, which was launched in 2003. Its role is to coordinate international hydrogen research and hydrogen technology development and deployment. The IEA (which was established in 1974) is also responsible for coordinating international initiatives. It does so through the administration of the Hydrogen Implementing Agreement. This agreement is intended to promote technical exchange between member countries and encourage task sharing [102]. At the outset of IEA's Hydrogen Programme it was decided that the potential of hydrogen required a long-term programme to be realized [102]. Indeed, the IEA has had hydrogen research programmes going on for 40 years now, making this an insightful projection.

In the domain of hydrogen storage research specifically, the IEA has also been an important coordinating body. Indeed, the IEA HIA Task 22 (2006-2012) was the largest international co-operative effort on hydrogen storage ever established. It composed 53 Experts from 18 countries and consisted of 49 sub-themes [82] (figure 3.1 depicts the size distribution - by number of research institutes per project - for a sample of 54 (more or less) prominent international hydrogen storage research projects). But there have been a great deal more projects (international and national). Indeed, I considered such "projects" to be an informative unit of analysis for characterizing the hydrogen storage research landscape, a reason for which I began to compile a database on national and international materials based hydrogen storage projects (using online searches).

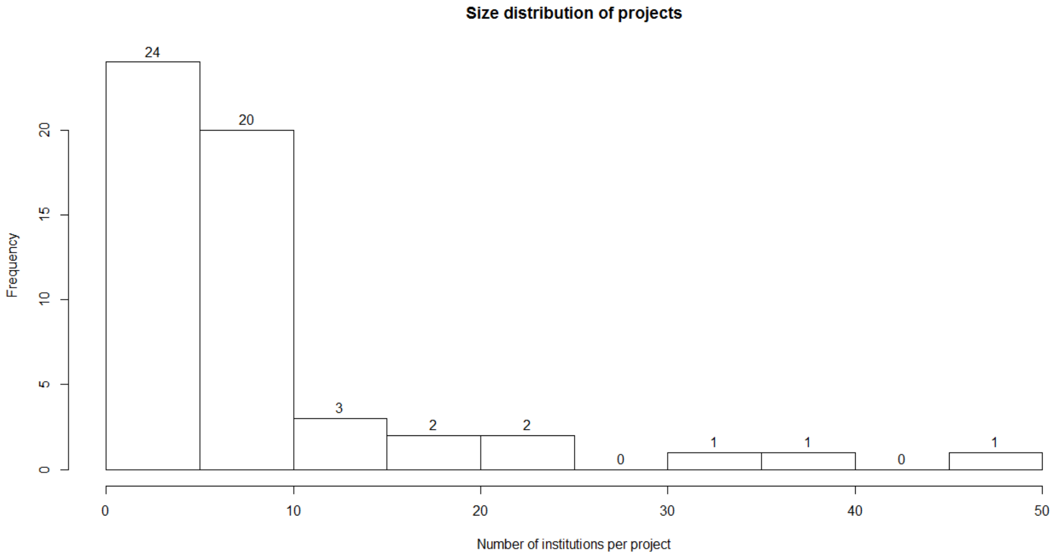


Figure 3.1: Size distribution (by number of research institutes per project) of a sample of international hydrogen storage research projects ($N = 54$) .

Project	*Key goals of search effort*
Hydrogen	One of the goals is to find the best possible hydrogen storage material for cheap on-board storage in reversible auto-mobiles.
HIA Task 17	Target 1: > 5wt.% at < 80°C, practical sorption rates.
Cosy	Focus is on fundamental research to improve hydrogen storage thermodynamic and kinetic properties of complex hydrides.
Fuchsia	Explore novel carbon and metallic materials giving hydrogen storage suitable for a light vehicle
New Alane	To develop catalysed systems based on aluminium hydride for hydrogen storage , where the main goal will be in getting a full advantage of the high overall storage capacity of AlH3 of 10 wt.% H by controlled doping in order to achieve hydrogen desorption with the desired rate below 100°C. To achieve control over the materials surface behaviour and microstructural state as related to hydrogen charge - discharge behaviours
FuncHy	FuncHy is aiming to achieve the requirements for a storage system for vehicle applications as proposed by the European Hydrogen Project StorHy
SSH2S	Some specific goals of the project include storage materials with capacities approx. 5 wt.% (for amides), and 7-11 wt.% (for mixed borohydrides). Aim is to develop a double materials concept. A particular challenge is the lack of reversibility in new developed materials. System storage density targets are for 4 wt.% and 4 kgH2/100L with hydrogen cycling close to room temperature and pressure.
Boron based	Develop and characterise high capacity boron-based metal hydrides with appropriate thermodynamics for hydrogen storage in vehicles. Study the effect of additives to improve kinetics and reversibility.
HIA Task 22	A. Develop a reversible or regenerative hydrogen storage medium fulfilling international targets for hydrogen storage. B. Develop the fundamental and engineering understanding of hydrogen storage by various hydrogen storage media that have the capability of meeting Target A.
HyCan	The main ambition of this project is to increase the energy density and the running time for current electrical energy sources by integrating a new and innovative hydrogen storage solution with a portable fuel cell. A 2 to 3 fold increase in weight and volume energy densities compared to batteries used today should be possible for equivalent production costs.
Bor4store	The most promising material(s), to be indicated by a rigorous downselection process, will be used for the development of a prototype laboratory H2 storage system that will be integrated and tested in connection with a 1 kW SOFC (representative for fuel cell applications e.g. for stationary power supply). Special attention will be given, practically for the first time, to significant cost reduction by pursuing cost efficient material synthesis and processing methods (target material price <50 EUR /kg) but also by investigating the level of tolerable impurities of the new materials (target system price 500 EUR /kg of stored H2).

Table 3.1: A sample of international hydrogen storage projects.

"Project" data provide for various useful measures such as funding, institutions (from which collaboration may be deduced), timeframes etc. But of most interest to the characterization of "search and experimentation" would be the project objectives, the materials of investigation, and the nature of the search strategies. Unfortunately, I did not anticipate well the magnitude of research projects, nor the lack of a consistent reporting on key data. It ultimately seemed impractical and fruitless to attempt to obtain a robust overview or consistent categorization of search efforts. The data presented in table 3.1 is merely a small sample of data I compiled on international hydrogen storage projects. These generally entail multi-partner, trans-national co-operation.

The data in table 3.1 indicates, to varying degrees, the type of research efforts involved, e.g. fundamental research, "exploration", search strategies to study the effects of doping, or system integration. It also indicates, even for such a small sample, a range of materials being explored; carbons, metallic hydrides, complex hydrides, alane, and boron containing metal hydrides. A marked feature running through almost all projects is that their objectives are design related - this feature applies more broadly. Hence, even at the level of basic research, there are clear objectives of exploring alternative designs for the sake of achieving technological improvements. All of the projects in table 3.1 started during the last decade, and indeed, from the availability of project data in general, it would appear that there was very much less activity prior to 2000. A typical timeframe on these projects is four years (timeframe is important inasmuch as it might place constraints on the type of activities to produce a certain level of required output). National projects in my database tend to go a bit longer.

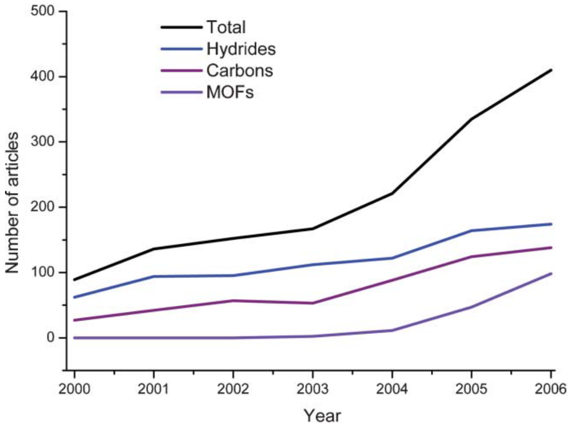


Figure 3.2: A comparison of research activity in different hydrogen storage search domains. *Source*: [158]

An alternative means for characterizing the hydrogen storage search activity is through bibliometric data analysis (e.g. number of publications, co-citation analysis, author-co-ocurrence analysis, etc.). One such account, provided in [158], and reproduced in figure 3.2, shows trends in the intensity of publication in different hydrogen storage search domains. In particular, it shows three areas of focus that subsume the vast majority of research attention: hydrides, carbons and metal-organic frameworks (MOFs). Not captured has been work in areas such as hydrogen clathrates, zeolites, or inorganic nanostructures [158].

While this graph relates to the amount of experimentation in general families of materials, it is important to note that there are many more quite distinct development trajectories within each. An illustration for the case of hydrides is given in figure 3.3. While this graph is based on numbers of entries to the online Sandia "Hydrogen Storage Materials Database" [3], which contains numerous repeat entries of certain materials, it paints an interesting picture of the variety of different materials that have been explored for hydrogen storage purposes, in terms of their hydrogen gravimetric capacities.

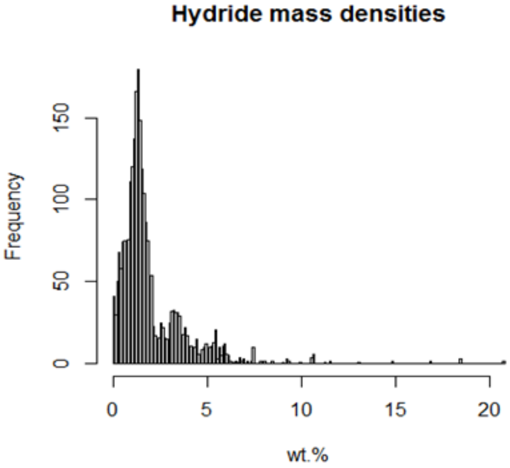


Figure 3.3: Histogram of hydrogen gravimetric capacities for hydride materials. The figure appears to exhibit a trimodal distribution, constituting, in order of increasing capacity, the families of interstitial hydrides, magnesium based hydrides (light weight metal hydrides), and complex hydrides. Note, the frequency values pertain to the number of entries made to a hydrogen storage materials database (which includes several repeat entries of certain types of materials). Data derived from:[3]

3.2.2.2 Applied R&D

While the extent of variation in basic research is such that one requires clever techniques for extracting the underlying structure of the many research fronts[1] (e.g. using co-citation analyses), the amount of variation reduces in going from basic to applied R&D/product development. Just as one expects market forces to apply selection pressures on commercial products - acting to converge the set of technical variants - so one would expect the distinct criteria of applied R&D projects to select only a subset of candidates emerging from basic research. (Precisely such a selection process is referred to in table 3.1 under the project title "Bor4store".) I present two examples which indicate that hydrogen storage development has been characterized by technical variation (and it would seem, a significant degree of target/technical uncertainty). Only recently has there been some convergence toward a design standard.

The first example is presented in figure 3.4 with data from [22].It shows sequences of prototype releases of hydrogen powered vehicles by a number of big automotive companies.

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[1] I attempted to characterize the research fronts using co-citation analysis of scientific papers. Unfortunately, I could not extract much meaning from the resulting network data; it appeared very cohesive on the whole, meaning that distinct subgroups were difficult to extract/identify.

Notice, the variation in technology that is displayed in this figure is based on the major components of the power-train; that is, storage system type, and conversion system. It can be seen (given the colour coding of different variants, simply a crude look at the colour variation would suggest it) that many different designs have been experimented with. It is also visible that there have been marked differences between the technology portfolios that some of the companies have pursued, as, for instance, a comparison between BMW and Daimler would suggest. Interestingly, there has been a striking increase in activity around 1998, and not long thereafter, it would appear that the fuel cell/compressed gaseous hydrogen combination starts to dominate - around this time the "Zero Emission Vehicle" ZEV mandate was introduced in California [170]. Metal hydrides meanwhile, were relatively popular until about 1999. In that last decade automotive companies have certainly moved away from solid-state storage options. To make this trend appear more convincing, I have contributed further data for the period 2008-2014. The data is summarised in table 3.2. It reveals that a solid-state storage method (a metal-organic framework) has been showcased by a major OEM only once in recent years (namely by Daimler).

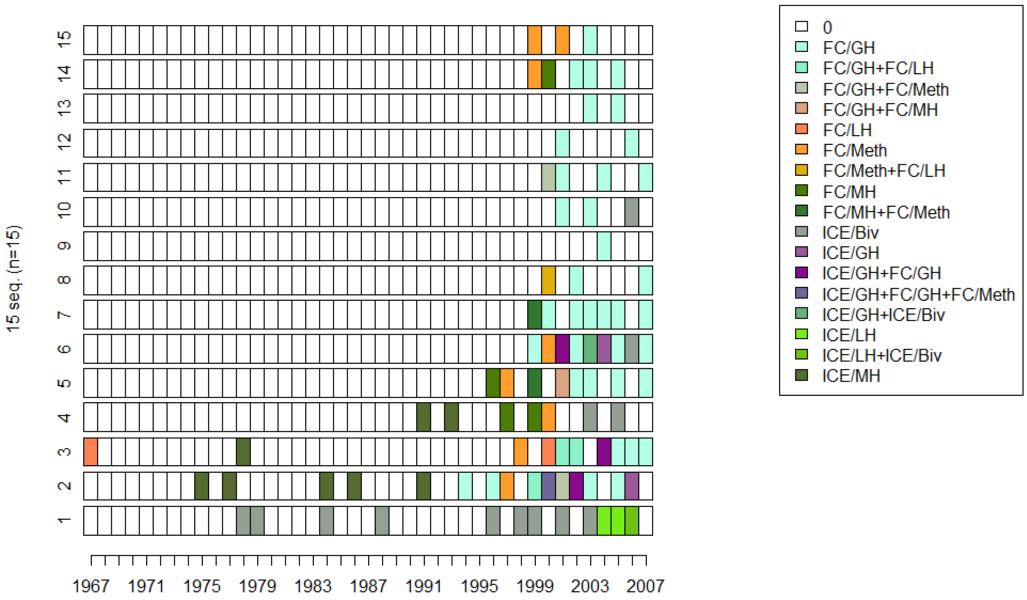

Figure 3.4: A partial history of hydrogen prototype vehicle demonstrations by major automobile OEMs. Original data: [22]. Key: FC = Fuel cell, ICE = Internal combustion engine, GH = Gaseous hydrogen storage, LH = Liquid hydrogen storage, MH = Metal hydride, Meth = Methanol reformation, Biv = Bivariate storage system based on gasoline and liquid hydrogen. The sequences are ordered as follows: 1) BMW, 2) Daimler, 3) GM/Opel, 4) Mazda, 5) Toyota, 6) Ford, 7) Honda, 8) VW, 9) Audi, 10) Fiat, 11) Hyundai, 12) Peugeot, 13) Suzuki, 14) Nissan, 15) Mitsubishi.

On the premise that the specific prototype technology pursued by a company can be seen as a proxy for its commitment to that particular technology for commercial prospects, one may wonder whether this period of technical convergence is indicative of a design that will emerge to be dominant in the commercial environment. To be sure, that would be a rather speculative claim, not least because the premise is not very sound; prototypes serve not

Year	*Sum of GH strategies*	*Sum of solid-state storage strategies*
2008	4	0
2009	6	0
2010	3	0
2011	1	1
2012	1	0
2013	2	0
2014	1	0

Table 3.2: Summary of hydrogen storage strategies pursued by major OEMs in recent years (GH = Compressed gaseous hydrogen). While there is additionally activity to implement hydrogen storage technology by companies outside of the set listed in figure 3.4, the data in this table refers only to these OEMs for consistency reasons. The source of data is the online database H2Mobility [81]. Thus, the data is merely indicative, and not to be viewed definitively.

only as test beds for experimentation with different technical designs, they serve also as marketing tools [22, 156]. That is, they demonstrate a firm's ability and desire to move technical development in a particular direction (e.g. low-emission vehicles). For such a purpose, the specific designs employed may be less relevant, and based more on convenience and reliability; technologies that are too experimental could jeopardize the marketing purpose [22]. As it happens, compressed gaseous hydrogen technology is currently the only practical and reliable of the options. On the other hand, the industry seems set to rely on compressed hydrogen storage for initial roll-outs of fleet vehicles (about 2016). Incidentally, this could have certain implications for the setting of industry standards. Indeed, such a roll-out could turn into a defining event that strongly influences/constrains the paths of future development, such that certain technical trajectories become "locked-out". In any event, it is a challenge to interpret the underlying process that has given rise to this dynamic of technology development, yet the evidence of technical variation has been illustrated.

As a final example of hydrogen storage technical variation, I present data on patenting activity - also within the automotive industry - in figure 3.5. While patents are taken as an indicator of the variety of technological options developed by firms, they give a different perspective on the variation processes. For instance, patents may be based on more experimental work than prototype testing. As claimed in [22], patents can be used to gauge the direction of innovation. Though as before, it is not a straightforward matter to infer the strategies of commercial exploitation based on measures of patenting activity. Not least of all, this would require a similar scope/incentive for patenting across all options. For example, as shown in figure 3.5, gaseous hydrogen receives rather few patents by automotive companies. But there are at least two convincing reasons for this: 1) automotive companies may not be big innovators of gaseous storage technology because they rely on/cooperate with gas suppliers who are have more experience in the technology, 2) up until the recent introduction of 700 bar compressed storage systems, gaseous storage was a fairly established and straightforward technology [22], perhaps permitting less scope for patented innovations. Nevertheless, the data in figure 3.5 displays an interesting pattern of variation inasmuch as it actually suggests an increasing trend of aggregate technical uncertainty (as determined by the measure of entropy; $H = -\sum p_i ln p_i$, where, in this case, p_i is the proportion of the total share patents, given by option i).

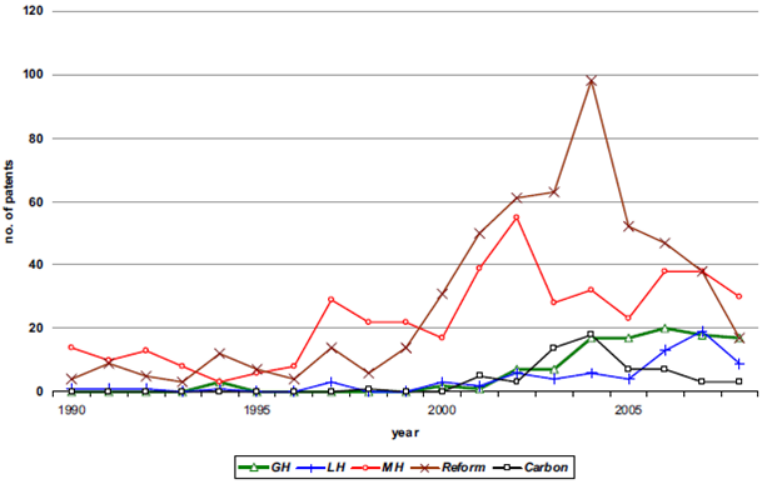

Figure 3.5: Hydrogen technology patenting trends in the automotive industry. This graph compiles information on four storage technologies (GH = Gaseous hydrogen, LH = Liquid hydrogen, MH = Metal hydride, and Carbon based hydrogen storage), and a reformation technology (Reform) whereby hydrogen is extracted by a reformation process of Methanol. Patent data were derived from the online European patent database; Esp@cenet, for 12 major automotive companies. *Source:* [19]

3.3 Technological progress

Learning exemplifies complex adaptive systems "at work" [72]. In a general sense, it entails the process of finding and selecting better schemata (i.e. either schemata for describing an observed system, prediction of events, or prescription for behaviour [72]). In the realm of technology, learning would thus imply the process by which schemata which represent technical designs (or operational principles) improve. This process entails design variation and selection. Variants offer different "interpretations", or extractions, of the "environment's" regularity. The fitter variants are adopted through the action of selection pressures (and go on to form the basis for further variation). Intriguingly, this process of improvement in technology has often been found to observe regular patterns. Describing these is the topic of the first part of this section.

The second part delves somewhat into the question of the underlying factors. Indeed, while certain patterns of technology improvement (typically called "learning curves") are well known, for instance, by economists and companies (who account for them in their budgeting of technology development [94]), there has been little in the way of scientific explanations. In this direction, I draw on (what I believe to be) key references, thereby introducing notions such as the search heuristic, and fitness landscapes. While insights gained here are most applicable to technical designs of some maturity, I speculate about key ideas, to open a discussion on the nature of progress in basic research.

3.3.1 Empirical "laws" of technological improvement

Technological progress (by some measure of performance) is often found to proceed with a high degree of regularity. So much so, that one can often describe it with a simple mathematical function [120]. This fact is surely one that explains the abundance of technological forecasting practices [116, 136], yet the underlying reasons for these trends are not altogether well understood. A number of hypotheses have been proposed in the literature by which to describe these common patterns of progress quantitatively. I present five such hypotheses, which have been analysed statistically in [120], below.

In the following equations a and c are parameters, y_t is a performance metric at time t - in the following it denotes cost (or some metric that is to be minimized), e_γ is the number of units produced prior to year t, and q_t is the number of units produced in year t.

$$Moore: \quad log(y_t) = c - at \tag{3.1}$$

$$Wright: \quad log(y_t) = c - a \times log(e_\gamma + q_t) \tag{3.2}$$

$$Goddard: \quad log(y_t) = c - a \times log(q_t) \tag{3.3}$$

$$Sinclear\, et\, al.: \quad log(y_t) = c - a_1 \times log(e_\gamma) - a_2 \times log(q_t) \tag{3.4}$$

$$Nordhaus: \quad log(y_t) = c - a_1 t - a_2 log(e_\gamma + q_t) \tag{3.5}$$

According to [53], Thomas Wright was the first person to propose a quantitative law of progress (equation 3.2). His "law" states that performance (in this case cost) improves as a power law in cumulative production (where $e_\gamma + q_t$ equals the total number of units produced up to time t). Moore's law, perhaps the most famous exposition, states that performance improves exponentially with time. Goddard's hypothesis relates the current performance with the current production capacity (q_t) only. Sinclear *et al.* proposed a model that separates out the factors of historic production and current production.

Finally, Nordhaus' hypothesis is a combination of Moore's law and Wright's law. It is interesting to note, as originally pointed out by D. Sahal [120], that Wright's law and Moore's law are potentially compatible. That is, under certain conditions of the trend in cumulative production, Moore's law and Wright's law are in fact equivalent [120]. If we let cumulative production simply be x, and express Moore's law as $y_t = Be^{-mt}$ (where B and m are parameters), and Wright's law as $y_t = Bx^{-w}$, then these two laws are equivalent if cumulative production increases exponentially with time, $x = e^{at}$, and $a = m/w$.

One motivation for the recent study [120] into the statistical performances of these hypotheses, is that these "laws" of progress have never been put to the test in a rigorous and comparative manner. The study set about doing so using a large compiled database on the historic performance characteristics of about 60 different technologies. Their data selection was based on data availability, rather than on specific criteria that might appeal to any of the proposed models. The quality of the models' performances was assessed through a statistical hindcasting technique and the construction of an error model [120]. Nordhaus's model came out the worst, while Moore's and Wright's model produced the most accurate forecasts [120]. As for the quality of these forecasts in general, it is noted that they do better than random guesses [53]. But there are some basic conditions to consider in deciding the applicability of the model. Firstly, one might not expect the hypothesis to be accurate when there is not a clear objective to improve the metric of interest. Indeed, one could argue that the hypotheses are in fact just special cases of a more general law that has to do with a composite measure of overall performance [53].

Another consideration, assuming the model is for the purpose of describing progress on a particular design concept (i.e., with a particular operational principle), is the phase of the technology's development. If the technology is in the maturing phase (see chapter 2), in which fundamental technological limits are being approached, one would expect diminishing returns to innovation effort [94]. By contrast, the commercialization phase is associated with a high learning rate and may exhibit inreasing returns to innovation effort for a period of time. In all, over the course of a technology's lifecycle, and given the case of a focused and consistent objective, one might then expect to see a pattern of progress that resembles an S-shaped curve with respect to time; an initial phase of exponential improvement followed by a period of diminishing returns. In the academic field of "technometrics", this S-shaped pattern of improvement has been specified as the logistic of progress [51].

But to what extent do these hypotheses reflect the underlying process of improvement? As noted in [53], while there has been considerable debate on the subject, there is still much to learn about the underlying reasons why technologies improve. For instance, Moore's law postulates that technological progress is inexorable; that is, it depends on time rather than controllable factors associated with research and development [120]. Goddard's hypothesis says, in the case of cost improvements, that it is solely the result of increases in economies of scale. These models don't explain the mechanics of progress. Wright's law may not seem to explain much either, however, cumulative production is often interpreted as a proxy for "level of effort", which, in turn, may be related to the notion of learning (i.e. knowledge accumulates the more that is produced [120]). In other words, cumulative output is not seen as the direct cause of improvement, but rather is simply an easily measurable quantity that is correlated to other variables such as accumulated knowledge [120]. The parameter a in equation 3.2 is called the “progress ratio” which is often defined as the ratio of cost after a doubling of cumulative production, to cost before a doubling of cumulative production. It has been suggested however [115], that a might characterize the ease with which learning can occur in a particular environment, for instance, by relating to the complexity of a technical design.

In any case, there is much scope for developing a more scientific understanding of the factors that drive technological improvement [53], and much effort in this direction has focused on the notion of search over design space.

3.3.2 Theories on the patterns of technological progress

3.3.2.1 Background

Literature on the question of the factors of progress have focused on processes of search through design space as a key determinant [53]. What is meant by these notions of search and design space? To put them into context, it is helpful to state some basic “facts” about the design process. A useful distillation of the quintessence of design may be found in [155]. Four key steps are identified:

- Design begins with a perception of a gap in the user experience. Without a gap, there is no motive for design. The gap may be perceived by users themselves or by observers.

- Define problem: In effect, problem definition is the creation by the designer of an explanation of why the user experiences a gap. This diagnosis can be thought of as an identification of user needs that are not being met in the current state and/or the recognition of criteria for a high-quality solution.

- Explore alternatives: Given a problem, designers almost always explore alternatives - this step is sometimes called search.

- Select plan: Exploration typically exposes more than one solution, so design requires some sort of evaluation and selection from alternatives. Some designers consider many alternatives simultaneously when selecting a plan.

This conception of design is so general that one may notice it applying to a whole range of contexts. For instance, it suggests that, given similar definitions of the problem (or objectives), the difference between design in basic research and design in more advanced product development comes down to the methods of exploration (these might for example depend on the tools of search, such as experimental equipment, theoretical ideas etc.). But why does design generally require exploration?

The answer is, depending on the "scale" of the technology (e.g. how many design parameters it is described by), that there is generally a vast scope of possibilities (of combining different components/design parameters), and little in the way of foretelling what the best design is. The notion of exploration is often perceived as a form of motion through design space. This is the space of possibilities defined by dimensions that represent the various design parameters defining the technology. Assuming a fixed number of discrete states per dimension, it is straightforward to appreciate that the number of potential sites to explore increases as an exponential function of the number of dimensions. With very simple designs one can explore every possibility and be guaranteed to find the optimal design. The challenge of doing so becomes increasingly harder as the number of dimensions increases, as a simple example exposes: assume a design space that comprises dimensions with five states per dimension. Assume further that it takes just one second to explore the "fitness" of a variant at a particular site. Then the time to search over the whole space ($5^N \times 1s$) would be 25 s and approximately 968 *years* for 2 dimensions and 15 dimensions respectively.

Faced with this uncertainty, designers tend to use search heuristics that reduce the complexity of the task, and they rely on knowledge (e.g. theoretical models) to direct the exploration [156]. Indeed, due to the difficulty of exploring new regions of the design space, as noted in [58], practitioners have long recognized the value of reuse and refinement. Altschuler (cited in [58]) recommends searching previous inventions for universal analogies and possible applications to new contexts.

The heuristics used in search might be thought of as being represented by kind of schemata of their own. These too are subject to variation and learning. In this context, theories about the underlying factors of technological improvement have seen learning processes as a key determinant; the search strategy is influenced by learning and enables targeted design alterations [53]. According to [53], this interpretation is supported by numerous examples in which economies of scale does not factor. But while it is quite conceivable that learning can be effective in solving particular (or familiar) design problems, it is hard to imagine how, and whether, it translates to new problems that crop up in the course of development [72, p. 268]. As noted in [58] in talking about *technological exhaustion* of search strategies, "*unfortunately for inventors, these benefits of familiarity do not last forever.*"

To make this point clearer, it is useful to illustrate a key difference between what is known as "local search" (or adaptive walks) in design space, and what (in the tradition of *fitness landscape modelling*) is understood by "long jumps". Local search, as the name suggests, is one in which neighbourhood sites of the current design configuration are searched. That is, only a few, or perhaps more accurately, only peripheral design parameters are changed gradually, to see what the consequences for performance are. By contrast, the "long jumps" involve changes to core components (c.f. section 3.2.1), or several design parameters at once. The reluctance of designers to test out core component changes (or explore regions of design space) can be gleaned from an example concerning the development of hydrogen storage technology (in particular, the use of solid fuels). As described in [4, p. 6680]:

“*Existing automotive components are of little use for solid fuels, as they are such a radical departure from the liquid hydrocarbon fuels of today. Based simply on the additional engineering requirements, auto-mobile manufacturers will be resistant to solid fuels that have to flow in a system. Likely methods involve auger or pneumatic transport systems, but these approaches can suffer from clogging problems. Another concern is the configuration of the reactor used to release hydrogen from a solid. It is likely to be a furnace-type device that is engineered to prevent blockages in the system.*”

In other words, by switching to a solid fuel (the fuel being a core component of the system), without making the required adjustments to other parts of the system, the performance would be drastically reduced. While I am not advocating the switch to solid fuels (this was just an example; solid fuels may not have any advantages even with further design alterations), a general feature of local search - i.e. search restricted to neighbourhoods in design space - is that it is likely to culminate at a local optima. In [132], D. Sahal explicates how the diminishing returns to scaling (i.e. cumulative adaptations of the current component set) was avoided in semiconductor technology. He states, for example, that if semiconductor inventors had restricted their usage to their original materials of aluminium and bipolar transistors, progress in the field would have halted long ago. However, because inventors began using new materials, such as copper interconnect and new combinations such as metal oxide semiconductors, semiconductor chips have continued to shrink and the trajectory has repeatedly avoided exhaustion.

In the next section I draw on theoretical ideas that relegate the search process to the manipulations of “*relatively blind watchmakers*” [94, p. 202] - i.e. the particular variations to find better variants are treated as being conducted at random. In this vein, I speculate about factors of progress more intrinsic to the technology. While this approach is speculative, it supports the hypothesis that, given certain conditions, power laws provide the appropriate description of how technologies improve.

3.3.2.2 Fitness landscapes and the diminishing scope for improvement

As described in [53], referring to the factors intrinsic to the technology in describing technological progress is known as “input decomposition” (as opposed to process decomposition - e.g. learning or economies of scale). Such factors may include the unit scale of the technology or the degrees of freedom of a device (defined as the number of modular parts that make up the whole [53]). Recent approaches have focused on the role of complexity in technology improvement [94, 115] (I refer to [53] for further references).

Design complexity is related to the degree of interdependence among the design parameters of the technology [24, 115](i.e. by changing one parameter - to improve a particular performance metric - it may render another design parameter’s function less adaptive (i.e. lead to worse performance)). Such interdependencies create conflicting constraints [94] when it comes to making improvements on one or the other performance metrics. This is because the technology’s parameters are finely in balance [15], tuned to the particular functions/operations each part is intended to perform.

In the early stages of design, such interdependencies may be less constraining. In other words, one may make improvements on one variable without negatively affecting others. As improvements are made however, further eking out progress tends to get more difficult. Figure 3.6 gives a visual metaphor of the concept of conflicting constraints.

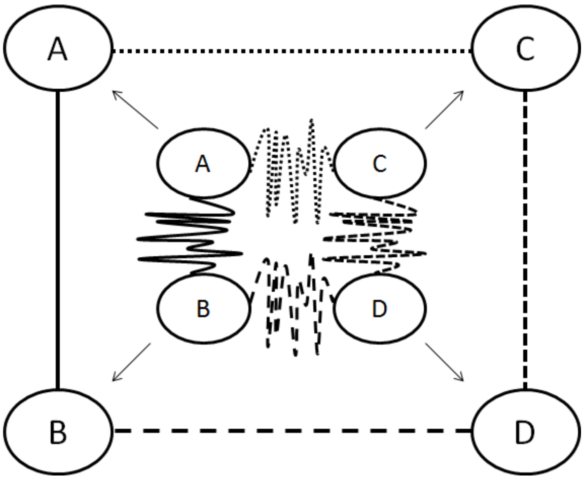

Figure 3.6: A visual representation of using up the “slack” to affect improvements on different, interdependent performance variables. Adapted from: [73, p. 15]

Quite recently, the notions of a space of design possibilities, complexity, and fitness, have been bound together in an exploratory model; the *NK*-model developed by Stuart Kauffman [94]. This model was the first of its kind to produce tunable fitness landscapes. The notion of a fitness landscape had been proposed some time earlier as a concept in biology [62], but this model offered a new approach to exploring its implications. Note, this model was originally developed for studies in biology, but is instructive for thinking about technology [59, 62], and I will use the terminology appropriate for talking about technical designs.

Simulations of Kauffman's *NK*-model are based on two parameters; N, the number of components (or design parameters) comprising the system, and K, a measure of the interdependence; the number of performance metrics affected by changing the state of any one design parameter [59]. As such, this model is actually quite restricted to particular types of architectures, namely ones in which each component's function is affected by the same number of components (design parameters) [62]. In the *NK*-model, the fitness values of a string, $W(s)$, are computed as the mean of the fitness values w_i associated with each parameter (or component) i [62]:

$$W(s) = \frac{1}{N} \cdot \sum_{i=1}^{N} w_i(s) \tag{3.6}$$

Due to *epistasis* (a term described in section 3.2.1), a fitness value w_i takes on a different value when design parameter i is changed, or when another design parameter is changed that affects the function of component i. Each time the state of an element is changed, the fitness value associated with this element is redrawn randomly from a uniform distribution between 0 and 1 [62]. By following this procedure, a fitness landscape may be constructed over the design space for various values of K. Depending on the value of K, the landscape varies from smooth and highly correlated (small values of K), to one that is more rugged and with shorter correlation lengths (higher values of K) [62, 94].

As described in [94] (and elsewhere), this fitness landscape model offers some intriguing ideas about the intrinsic factors of progress in technology. It is speculated in [94] that a common pattern of progress in technology may be explained as a natural consequence of the statistical features of the landscape. In particular, a power law pattern of progress is illustrated by considering adaptive walks (adaptive walks are changes in design parameters within the correlation length of the landscape - i.e. the fitness values of the new sites are fairly well predictable based on the fitness value of the current site) on rugged (say, K greater than 8 [94]) but correlated landscapes. The following two features are responsible. Firstly, given these rugged landscapes, the number of tries to find an improvement increases by a constant fraction after each improvement is found (the number of uphill possibilities diminishes the higher the fitness). Stated mathematically, if G is the number of trials to find an improved variant, and S is the number of expected improvements that result, then

$$G \propto e^{S} \tag{3.7}$$

(or $dG/dS \propto G$). Put another way, the rate of finding improvements slows exponentially. The particular rate of exponential slowing depends on K; the slowing is faster when the conflicting constraints are higher and the landscape is more rugged. The second feature concerns the question, how much improvement is achieved each time a fitter variant is found? It turns out that with each of the improvement steps, the improvement achieved is a constant fraction of the improvement achieved at the last step (i.e. denoting f for fitness, $\Delta f_{S+1} = \Delta f_S / a$, where a is some constant) [94, p. 205]. Thus the amount of improvement with each step also slows exponentially [94, p. 205]. The result of these two effects combined, according to [94, p. 205], is that there is a net diminishing rate of improvement described by a power law (e.g. in terms of cost c, $c \propto G^{-\varphi}$).

3.3.3 Progress in hydrogen storage research

3.3.3.1 Types of progress in basic research

Hydrogen storage research has now been on the agenda for over 40 years, and much has been claimed about the progress that has been achieved. In some reports it claims that much progress has been achieved, while other reports lament that it has been too slow. To be sure, such statements are sometimes misleading, as different kinds of progress may be referred to (particularly as a basic research enterprise) - progress in terms of finding better performing hydrogen storage variants may not always be the main metric of concern - as outlined in [55]:

Discovery. Science makes progress when it demonstrates the existence of previously unknown phenomena or relationships among phenomena, or when it discovers that widely shared understandings of phenomena are wrong or incomplete.

Analysis. Science makes progress when it develops concepts, typologies, frameworks of understanding, methods, techniques, or data that make it possible to uncover phenomena or test explanations of them.

Explanation. Science makes progress when it discovers regularities in the ways phenomena change over time or finds evidence that supports, rules out, or leads to qualifications of possible explanations of these regularities.

Integration. Science makes progress when it links theories or explanations across different domains or levels of organization.

Development. Science makes progress when it stimulates additional research in a field or discipline, including research critical of past conclusions, and when it stimulates research outside the original field, including interdisciplinary research and research on previously under-researched questions. It also develops when it attracts new people to work on an important research problem.

But nevertheless, many claims do in fact refer to a measure of progress that has been achieved in hydrogen storage performance. Such comments are interesting, not least, as they imply an expected rate of progress. The rationale for these expectations are, however, rarely explicated. This raises interesting questions as to what they might be based on. Furthermore, how much can be known in principle?

Bibliometric techniques offer a quantitative approach to studying scientific progress [66, 111], though discerning the nature of that progress is often contentious. One common measure of scientific output is the number of publications produced. By creating a citation index of materials based hydrogen storage research[2], using ISI Web of Knowledge, I have produced a time series of publication output in figure 3.7. Note, one should not try to infer from this graph the knowledge structure of a research domain. Trends of this measure should at best be viewed as "growth in scientific or technical information" [132]. In that vein, one might suggest that a significant proportion of the information in figure 3.7 refers to parameter-property relations that have been discovered for hydrogen storage materials (notice, information gains about specific relations does not imply theoretical knowledge has been gained). Considering the limited number of research areas within the solid-state

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[2] The search query for this citation data-set (on 16/06/14) included the following: Topic = Hydrogen storage, Publication type = Article and Review.

I included only the following research areas: Chemistry Materials science Energy fuels Electrochemistry Physics Metallurgy metallurgical engineering Spectroscopy Science technology other topics Engineering Crystallography Polymer science Thermodynamics Instruments instrumentation Mechanics

I then reduced the set by excluding the following Web of Science categories: Chemistry physical, Materials science multidisciplinary, Energy fuels, Electrochemistry, Physics mathematical, Chemistry multidisciplinary, Metallurgy metallurgical engineering, Nanoscience nanotechnology, Materials science ceramics, Physics applied, Engineering chemical, Engineering multidisciplinary, Physics condensed matter, Chemistry inorganic nuclear, Physics atomic molecular chemical, Chemistry applied, Crystallography, Environmental sciences, Polymer science, Chemistry analytical, Physics multidisciplinary, Materials science coatings films, Thermodynamics, Engineering environmental, Materials science composites.

hydrogen storage domain, this graph surely attests to much search on local variants of different material types.

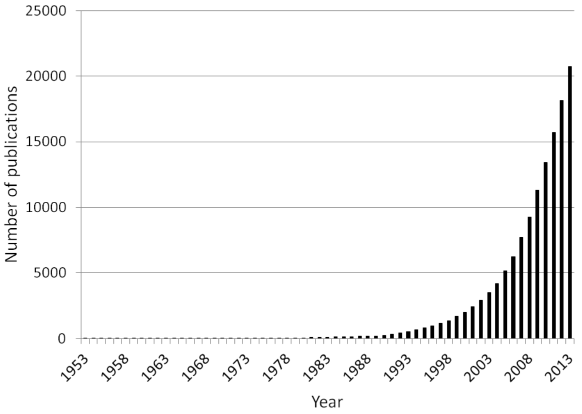

Figure 3.7: Trend in the total number of academic publications on different hydrogen storage themes. *Source*: ISI Web of Knowledge

Despite the fact that the data-set represented in figure 3.7 contains a small proportion of scientific papers that were not intended for this set, the trend shows a convincing increase in output. If one were to treat scientific publication output as a proxy that is in proportion to the number of improvement tries, then it would be interesting to compare the trend in this number, with the number of improvement steps that have actually been achieved. Has the increase in publications corresponded to an increase in the rate of finding improvements? Unfortunately, ascertaining the number of improvement steps seems inconceivable.

A related question concerns the effectivity of search (not necessarily in the sense of search heuristics in the context of design problems) - i.e. how much further activity tends to cumulate on a particular research output (represented by a publication). A popular bibliometric data unit used for this kind of analysis is the citation. Citations are the formal and explicit linkages between papers that have particular points in common [66]. For the purpose of studying key scientific developments and the like (e.g. for identifying “hot topics”), citations are often treated as representing the quality of an output. The nature of that quality is, however, left rather ambiguous. It has been described variously as “significance”, “impact”, “utility”, and “effectiveness”, but no one has succeeded in defining it in more tangible terms [66]. Although there a common theoretical objections to the interpretation of the citation counts of papers (e.g. citation rates could be inflated by self-citation, cited in refutation or as a negative example, a prestigious journal might draw more citations by providing more visibility, sloppy and even biased bibliographic practice (though if this can be seen as a random variable then it will get cancelled out) [66]), two propositions about citation measures are robust [66]:

1. it is a positive quality: it generally reflects credit on the scientific work involved
2. it plays a significant role in the formation of peer opinion.

If one permits the premise that citation rates measure the "impact" of a paper (e.g. one assumes that a higher citation rate indicates that more future work cumulates on the antecedent), then a frequency distribution of citation rates in a given research domain, could offer an interesting view of the reflectivity of search. In figure 3.8 have offered such a perspective on the domain of hydrogen storage research (using the same citation index as figure 3.7 was based on). Note, the graph shows only the trend for the top 200 cited papers in the citation index (categorized into bins of size 50 in the citation score). The graph shows that papers with a citation score of 1000 or more are few and far between. Less cited papers occur ever more frequently with an appreciable regularity. While this is not a probability distribution, and must be viewed as a static description of an evolving field (i.e. the citation scores change with time and more papers are added), the graph relates to an interpretation of how much influence any new investigation is likely to have on the directions of search.

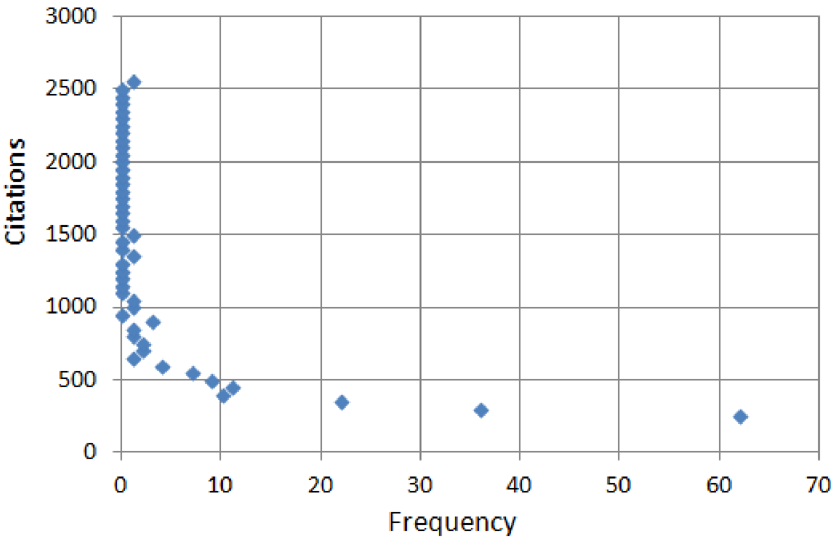

Figure 3.8: A frequency distribution of the top 200 cited research papers on hydrogen storage. Note, the citations have been categorized into bins of 50 (i.e. a citation score of 250 is mapped to the frequency of papers cited between 250 and 299 times). To reduce bias in the data I manually discarded papers in this set that were deemed to belong to a different subject matter.

To complement this graph, I have extracted the top 40 cited papers and summarized them in table 3.3. Note, this summary is based on "local citation scores" (LCSs)[3] , i.e. citations recieved from other papers within the citation index. In the table I denote a column that shows the percentages of LCSs with respect to global citations scores (GCS - citations received in the entire ISI citation index). Low percentages may imply that the paper is relevant more broadly than just within the citation index based on hydrogen storage research (i.e. they may represent 'exports' or 'imports' of important discoveries etc.). Also note, several documents in the table represent reviews. One may interpret them as being significant in terms of codifying a large body of work [111, 106].

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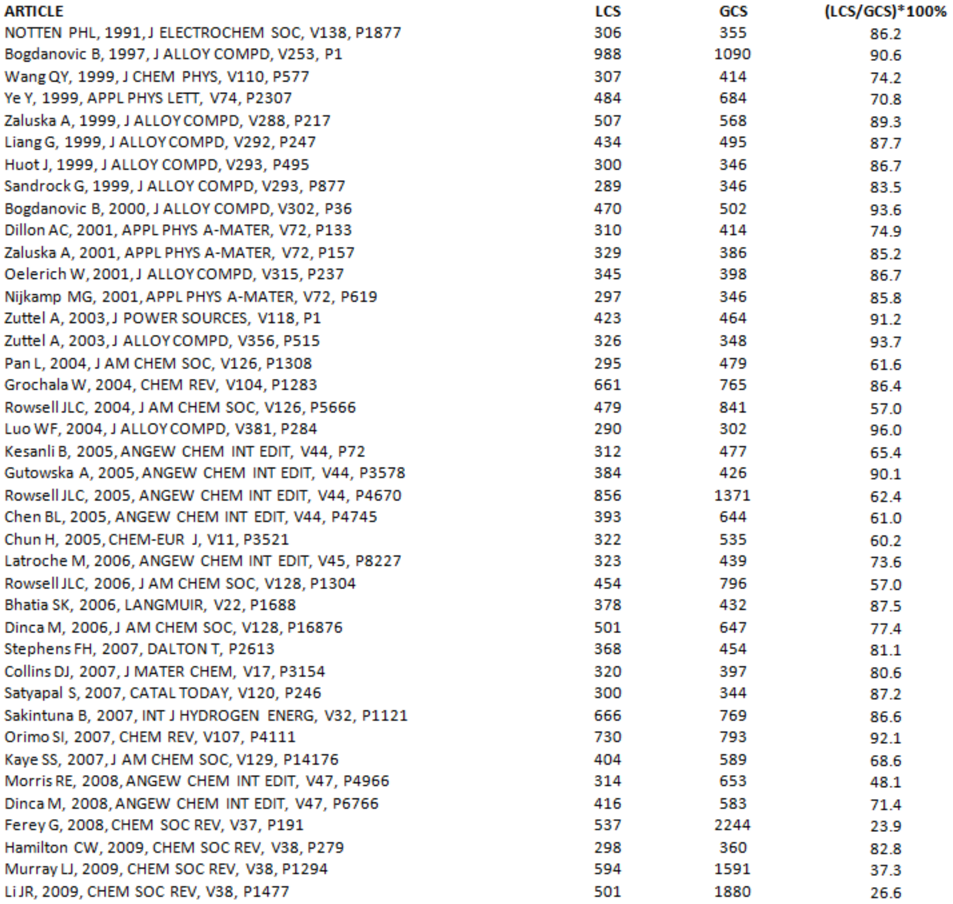
[3] The local citation scores of these papers where obtained using a program called HistCite (freely available online).

In terms of an overall pattern, one may observe that despite accumulative effects of citations to older documents, the balance of high citation scores does not seem to lie particularly in the past. Indeed, numerous later papers in table 3.3 show significant relevance (according to their LCS). As suggested in [106], this feature may indicate sensitivity to change with the passing of time within a research domain (e.g. old trajectories fizzle out when new important discoveries are made).



ARTICLE	LCS	GCS	(LCS/GCS)*100%
NOTTEN PHL, 1991, J ELECTROCHEM SOC, V138, P1877	306	355	86.2
Bogdanovic B, 1997, J ALLOY COMPD, V253, P1	988	1090	90.6
Wang QY, 1999, J CHEM PHYS, V110, P577	307	414	74.2
Ye Y, 1999, APPL PHYS LETT, V74, P2307	484	684	70.8
Zaluska A, 1999, J ALLOY COMPD, V288, P217	507	568	89.3
Liang G, 1999, J ALLOY COMPD, V292, P247	434	495	87.7
Huot J, 1999, J ALLOY COMPD, V293, P495	300	346	86.7
Sandrock G, 1999, J ALLOY COMPD, V293, P877	289	346	83.5
Bogdanovic B, 2000, J ALLOY COMPD, V302, P36	470	502	93.6
Dillon AC, 2001, APPL PHYS A-MATER, V72, P133	310	414	74.9
Zaluska A, 2001, APPL PHYS A-MATER, V72, P157	329	386	85.2
Oelerich W, 2001, J ALLOY COMPD, V315, P237	345	398	86.7
Nijkamp MG, 2001, APPL PHYS A-MATER, V72, P619	297	346	85.8
Zuttel A, 2003, J POWER SOURCES, V118, P1	423	464	91.2
Zuttel A, 2003, J ALLOY COMPD, V356, P515	326	348	93.7
Pan L, 2004, J AM CHEM SOC, V126, P1308	295	479	61.6
Grochala W, 2004, CHEM REV, V104, P1283	661	765	86.4
Rowsell JLC, 2004, J AM CHEM SOC, V126, P5666	479	841	57.0
Luo WF, 2004, J ALLOY COMPD, V381, P284	290	302	96.0
Kesanli B, 2005, ANGEW CHEM INT EDIT, V44, P72	312	477	65.4
Gutowska A, 2005, ANGEW CHEM INT EDIT, V44, P3578	384	426	90.1
Rowsell JLC, 2005, ANGEW CHEM INT EDIT, V44, P4670	856	1371	62.4
Chen BL, 2005, ANGEW CHEM INT EDIT, V44, P4745	393	644	61.0
Chun H, 2005, CHEM-EUR J, V11, P3521	322	535	60.2
Latroche M, 2006, ANGEW CHEM INT EDIT, V45, P8227	323	439	73.6
Rowsell JLC, 2006, J AM CHEM SOC, V128, P1304	454	796	57.0
Bhatia SK, 2006, LANGMUIR, V22, P1688	378	432	87.5
Dinca M, 2006, J AM CHEM SOC, V128, P16876	501	647	77.4
Stephens FH, 2007, DALTON T, P2613	368	454	81.1
Collins DJ, 2007, J MATER CHEM, V17, P3154	320	397	80.6
Satyapal S, 2007, CATAL TODAY, V120, P246	300	344	87.2
Sakintuna B, 2007, INT J HYDROGEN ENERG, V32, P1121	666	769	86.6
Orimo SI, 2007, CHEM REV, V107, P4111	730	793	92.1
Kaye SS, 2007, J AM CHEM SOC, V129, P14176	404	589	68.6
Morris RE, 2008, ANGEW CHEM INT EDIT, V47, P4966	314	653	48.1
Dinca M, 2008, ANGEW CHEM INT EDIT, V47, P6766	416	583	71.4
Ferey G, 2008, CHEM SOC REV, V37, P191	537	2244	23.9
Hamilton CW, 2009, CHEM SOC REV, V38, P279	298	360	82.8
Murray LJ, 2009, CHEM SOC REV, V38, P1294	594	1591	37.3
Li JR, 2009, CHEM SOC REV, V38, P1477	501	1880	26.6

Table 3.3: Top 40 scientific papers (by local citation score) on hydrogen storage.

3.3.3.2 Patterns of hydrogen storage improvement?

In this section I speculate on whether the discussion in section 3.3.2.2 may lend any insight into the pattern of progress one might expect in the search for fitter material variants.

As a first question, to what extent are the premises given that would permit a rugged fitness landscape representation of hydrogen storage material design variants? After all, there appears to be a considerable difference between the structures of conventional artefacts envisaged for such a representation, and the object of design in hydrogen storage research. Nevertheless, either design domain confronts a space of possibilities, and each is confronted with the challenge of conflicting constraints. Moreover, if one could describe the space of possibilities by a smooth (perhaps even single peaked) landscape, one might expect that a consistent heuristic for finding improvements would have already been identified. By contrast, the search for hydrogen storage materials can be characterized, to some degree, by a cyclic pattern of hype and disappointment (c.f. [20]). Such patterns would appear more related to fitness landscapes that are rugged to some degree (e.g. a simple of assumption of expectations going up whenever fitter variants are found, and going down when less fitter variants are found, produces a cyclic pattern of expectation levels, the period of which depends on the smoothness of the landscape). Finally, the fact that there is no simple objective function in hydrogen storage research (e.g. increasing capacity while completely neglecting other properties would not be considered progress), would seem to compound the challenge of conflicting constraints.

On account of these considerations, a rugged fitness landscape representation would seem appropriate. The issue could be resolved if one were to categorize each improvement try in the history of research, and each improvement step, and see the relation between tries and steps. Unfortunately, such a characterization is inconceivable. As a result, one must speculate about potential implications of this theory of progress. For instance, how high up the fitness scale are current state-of-the-art hydrogen storage materials in terms of their potential? How favourable are long-jump adaptations at the current state of development? The more further down the fitness scale, the more long-jumps will prove fruitful. As one gets higher, the scope possibilities diminishes and search tends to focus locally (however, they offer the only escape from local optima). As will be discussed more in chapter 5, the character of hydrogen storage research seems to be described by much local variation activity, punctuated by promising long-jumps.

The finding discussed in [94] that search on rugged landscapes exhibits an exponentially slowing rate of progress, may have implications for how progress in hydrogen storage is viewed. For instance, long periods of stagnation may be viewed as a natural consequence of the underlying landscape. On the other hand, Kauffman's NK-model paints an extreme view of search, in which variation activity is random (at least, with respect to the current location in design space). By contrast, one might expect that scientists do in fact obtain a sense of search directions that are promising, at least in the local neighbourhood (a claim supported in [60]). Ultimately, the progress that is achieved in hydrogen storage development (over long enough time-scales) might be describable in terms of a combination of different effects: 1) an exponential slow down in the rate of finding fitter variants (whereby more conflicting constraints result in a higher rate of slowing), 2) for local search, the amount of improvement achieved with each fitter variant slows down exponentially, and 3) learning of more adept search heuristics can counteract the above by finding fitter variants with increasing efficiency.

An interesting perspective on the proportion of tries that do not reveal *promising* variants in hydrogen storage research, is given in a US DOE Hydrogen Storage Center of Excellence progress report [125]:

"*Many scientifically interesting, but technologically inferior materials were set aside as a result of the Center's continuous decision tree driven down select process. Of the materials examined, 95% were down selected for further development as they were considered unable to meet all of the DOE technical targets simultaneously. The remaining 5% of these ma-*

terials or classes of materials that had the potential to meet all the targets are considered as candidates for continued research."

3.3.3.3 An example

Finally, I close this discussion with an interesting and, to some extent[4], comparable example of the search for superconductor materials, as exposited in [38]. This example shows certain reminiscent features of stagnation (potentially due to the exponentially growing number of tries required to find fitter variants), long-jumps, and learning in the search for locally adapted variants:

"*Superconductivity - in which the resistance of a material to electrical conduction becomes zero - has intrigued researchers since its discovery in 1911, but it took almost 50 years for a microscopic theory based on the interaction between electrons and the crystal lattice to explain how such a phenomenon could exist. For real materials, these calculations are so complex that the theory cannot guide the search for new superconductors. Phenomenological theories have shown that magnetic fields in superconductors form quantized flux vortices that behave as Faraday's lines of force. However, these theories do not predict the occurrence of new superconductors, which are found by a combination of luck, serendipity, and intuition...About 40 years ago, hundreds of compounds were tested for superconductivity, but MgB2 was missed - even though chemists had even unwittingly used this 39 K superconductor to make more complex superconductors with a critical temperature of less than 10 K. It may seem surprising that MgB2 was passed over given that it is a simple material readily available from chemical suppliers. The explanation likely lies in the over 8000 possible binary compounds of the 92 elements...Is MgB2 a one-off compound or the first of a new family of superconductors? In the past, an initial major increase in the critical temperature has usually been followed by announcements of one or two materials showing substantial further increases followed by several with smaller increments with increasingly unstable and difficult materials. It is too early to tell if this will be true of MgB2. Nevertheless, this material is unlikely to be the last surprise for scientists working on superconductors.*"

3.4 Dominance and the convergence of technical variety

In the fluid phase of development, with several variants of a new technology springing up, there is typically intense design competition [11]. Variants compete not only in terms of performance, but given the target uncertainty, and the fact that accurate notions of performance have yet to be defined, rival designs compete also on which dimensions of merit are considered important [153]. Even though it is largely still at the stage of basic research, both aspects of competition are evident in the course of hydrogen storage development - scientists must compete for funding. I refer to a study [21] that investigates the structure

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[4] An important difference may lie in the nature of the objective function. In the case of the superconductor, there was a rather focused objective to increase the critical temperature.

of competing claims made by proponents of different methods of hydrogen storage (e.g. metal hydride researchers) as a good example of this.

The competition continues as the technologies mature, until a specific "event" occurs (see figure 2.1) which dramatically changes the character of the prevailing selection pressures. It is the emergence of a design that begins to clearly dominate the rest. A dominant design is a single architecture that establishes dominance in a product class [153]. To make the delineation between rival designs more precise, so as not to assign dominance among variants within the same subclass (the focus should be placed on competing technological "species" so to speak), Murmann and Frenken have proposed [119] to make the definition of a dominant design rigorous. They propose to define a technology subclass by the set of "core" components that comprise a design (note, this principle may be applied at all levels of the technology's hierarchy). The literature on technological change treats the emergence of a dominant design as a watershed moment in the technology cycle; it is thought to entail a marked shift in the prospects of rival designs. As noted in [153]:

Once a dominant design emerges, future technological progress (until the next discontinuity) consists of incremental improvements elaborating the standard. Single designs emerge to dominate rival designs. These designs remain dominant until the next technological discontinuity.

Given the significance of establishing dominance, a lot of research has been attracted to the question, how does a dominant design emerge? And apart from very simple products, that are defined more or less by a single performance metric, dominance is often not explained by a "technological logic" [153]. That is, dominant designs cannot be reliably predicted on the basis of superior technological performance (though a certain minimum level of performance must clearly be given).

In general, the selection environment is fluid and is influenced by a great deal of socio-political persuasions. The importance that is attached to making one's design more favourable (selectable), means that technology "enactors" attempt to influence the selection environment [67, 21]. As said in [153], "during the era of ferment, organizations must develop not only technical competence, but also inter-organizational network skills to forge alliances in order to shape critical dimensions of merit and critical industry problems." Thus, when governed by socio-political influences, the outcome of the dominance process is difficult to predict. In some cases the market power of a dominant producer may swing enough weight behind a particular design to make it dominant [153]. An industry committee may establish a standard as in the case of computer communications protocols and operating systems [153]. A group of firms may form an alliance around a standard, or government regulation compels the adoption of standards, as in the case of television standards [153]. The domination of technically inferior options can in fact be triggered by minor chance events, which are followed by a process of increasing returns [15, 22]. Numerous kinds of selection pressures may characterize this process by which early success breeds success. For instance, customers may gain a preference for a particular technology because they have learned how to operate it and do not wish to re-learn. Imitation may be a powerful selection force in certain contexts as well, the influence of which over the intrinsic pay-off from the technology may be illustrated with the “replicator dynamics model”.

There are many more potential sources of a selection bias (in the extreme, the formation of industry standards). The more a technology gets adopted (particularly by designers), the more it is likely to be improved as well, and better performance will only act to yet further increase the chances of adoption. Hence, the process entails a positive feedback loop. When selection pressures act, in a self-reinforcing manner, to increase the preference for one particular technology disproportionately, one often speaks of “lock-in” [15, 50]. The idea that there is a certain resistance to pursuing alternative paths of technical development is sometimes referred to as “technological inertia”. An important reason why selection pressures may evolve in a direction that doesn't favour other forms of novelty is described in [153]:

Once a dominant design is selected a diverse community of practitioners develops increasingly interlinked competence and inertia. These emergent community and organizational processes work to resist subsequent competence-destroying technical changes. This resistance is substantial since roots of the inertia are spread throughout a wide and diverse network of practitioners, suppliers, customers and vendors. This resistance emerges out of the internal logic of the product as a hierarchical technical system, and from emergent processes within organizations and in the community of practitioners.

In summary, when adoption events are not independent, the process of technical change may be “path dependent”, with chance events having a potentially big impact on the outcome of competing technical schemata. A poignant example of the influence of a chance event may be extracted from a passage in [170], pointing to the competition between gasoline and electric vehicle concepts at the end of the 19th century:

When the executives of the Edison Illuminating Companies gathered for their annual convention in New York in 1896, the guest of honour at the closing banquet was the great man himself: Thomas Edison. The conversation at the head of the table got around to one of the big questions of the day, electric batteries and cars. A young man farther down the table, the chief engineer from the Detroit Edison Company - Henry Ford - had just built what he called a “quadricycle”. But it was powered by gasoline, not by a battery...Ford was shifted into the seat next to the hard-of-hearing Edison. In response to Edison's questions, Ford sketched out a design on the back of a menu. Edison was impressed that the electric vehicle carried its own fuel - what he called “hydrocarbon”. The problem with electric cars, said Edison, is that they “must keep near a power station” and the battery was, in any event, too heavy. Edison told Ford to stick with gasoline and the internal combustion engine. Edison struck his fist down on the table. “You have the thing”, he said to Ford.”Keep at it”

...Ford later said, “That bang on the table was worth worlds to me.” It was a blessing; for Ford revered Edison as “the greatest man in the world.” And now “the man who knew most about electricity in the world had said that for the purpose my gas motor was better,” said Ford.

These dominance processes are certainly relevant to an understanding of the prospects of competing hydrogen storage variants. If one gains an initial advantage, it could make the selection environment considerably less favourable for alternative concepts. Anticipating detailed effects on the prevailing selection pressures would be extremely challenging however.

3.5 Conclusions

In this chapter I have discussed three important issues in technological change: variation, learning, and the emergence of a dominant design. These are defining elements for characterizing the prospects of hydrogen storage materials. I argued that a substantial amount of activity is still in the exploratory phase - for example, in basic research, one may delineate between three broad domains which represent considerably different design approaches (there are several more niche investigations). For hydrogen storage materials to compete in such demanding markets as automotive applications, better variants need to be found. (In other application areas, such as specialty vehicles, auxiliary power units, or backup applications - indicated in chapter 2 - certain metal and chemical hydrides are more competitive). This requires further search, and hence, funding. Whether that can be maintained is likely to be a question of the level of progress that can be displayed [159]. But as I speculated in section 3.3, the rate of finding improvements may be a simple consequence of the statistical features of the fitness landscape defined by the design problem. To better inform expectations, and therefore, perhaps, requirements of the rates of progress, I would suggest a more in depth analysis of the learning rates to be expected of basic design problems encountered in areas such as hydrogen storage research.

Finally, the discussion on technical convergence and the emergence of a dominant design raises important questions. For instance, how does an initial roll out of hydrogen vehicles based on compressed hydrogen technology - as is planned for 2015 by some OEMs - change the selection pressures for up and coming technologies? It is easily conceivable that this roll-out would be accompanied by certain network externalities - such as infrastructural decisions, regulations for safety etc.. Such factors could make selection prospects much less favourable for various hydrogen storage concepts (at least any that could not offer significant performance gains). There is a specialized field of research on dominant design processes (see [11, 119] and references within) that could better inform assessments of potential outcomes given different patterns of technical convergence.

At the start of this chapter I posed the question as to whether we could characterize the “state” of hydrogen storage evolution. The concepts discussed in this chapter, which refer to key regularities in technological change, have suggested ways to look at this problem. In all, it appears that these ideas abstract well similar processes in hydrogen storage development. I may therefore conclude that some insight has indeed been gained with respect to the state of hydrogen storage development. A caveat to this conclusion is that we have not gained a depth of insight that would allow for detailed predictions.

In the next chapter I again employ the concept of search heuristics. But rather than looking at high-level patterns of technological change, I turn to analyse more intrinsic patterns (or trajectories) of technical development.

4 Variants in solid-state hydrogen storage technology

4.1 Introduction

In the last chapter I discussed patterns of “learning” and variation during the exploratory phase of technical development. These processes have their origins in the explorations through the space of different possible configurations of the design elements describing hydrogen storage materials. This chapter provides a low-level perspective on this search activity. In it, I endeavour to illustrate key technical challenges facing different storage concepts, and emphasise the importance of different points of view in assessing the fitness of a material.

I study more closely the “internal structures” of technology (c.f. section 1.3.2) being developed in the field of hydrogen storage. As such, this chapter represents somewhat of a departure in style compared with the preceding ones. My mode of analysis is to interrogate key design parameters and the functions associated with them. I do this on a storage subsystem level and at the material level. At first, I emphasize the hierarchical ’environments’ that embody candidate hydrogen storage materials, thereby hoping to offer more perspective on the type of external design choices, or niche factors, likely to affect the fitnesses of material concepts. Secondly, my discussion turns to the materials themselves. I provide a general characterization of three families of hydrogen storage materials (physisorbents, reversible complex hydrides, and chemical hydrides), and I discuss prominent search heuristics for each (c.f. chapter 3) - i.e., dimensions on which improvements are being sought. I note that while I don’t approach this topic as a chemist or as a materials scientist, my emphasis lies much more on technical details in this chapter as compared with the others.

4.2 Hydrogen storage system design

4.2.1 Storage system functions and performance

In the exploration of hydrogen storage system designs, the choice of material represents just one of the dimensions of variation in the design space. One may generalize and say that all system designs would benefit from improvements in the thermodynamic, uptake, and kinetic properties of hydrogen storage materials, though it is difficult to predict the best system design when there is no single material that dominates in all those performance areas. Thus, while a crude comparative evaluation of different storage materials is possible (e.g. for initial screening of candidates), the eventual selection pressures apply to the performances of the various *system* designs they comprise. For example, at present, the media in hydrogen storage system designs (i.e., the combination of hydrogen and the substrate material) contribute only about 50-60% of the system's mass. Moreover, this applies to the most aggressive designs[1] (i.e., minimal weight/volumes and highly integrated components) and under the most favourable operating scenarios [96, p. 386]. Hence, the *material's* gravimetric uptake capacity is not the ultimate arbiter of fitness.

What are the measures by which the functions of the storage system are assessed? By abstraction, a technology's function may be described in terms of an input condition and a state transition that it accomplishes. This "state-transition" is associated with some behaviour of interest, or an output condition. The input condition is the technology's predicate. The technology's outputs are associated with its main purpose, while the proficiency with which those outputs are achieved (indicated by basic parameters such as mass) relates to an elaboration of the needs attached to the main purpose. For example, the proficiency of a design may be low if its parameter states imply a negative influence on the performance of other functions within a technical system (e.g. one component's mass affects another component's function to provide acceleration - the proficiency is reduced if the mass exceeds a certain 'budget' it was assigned). All of these considerations feed into the evaluation of a design, whereby relevant target variables (i.e. performance metrics - measures associated with some need) are formulated explicitly.

For hydrogen storage systems, the input conditions may be identified as the operating conditions for charge and discharge of hydrogen. Appropriate design choices for these will be based on thermodynamic and kinetic properties of the materials involved, as well as consideration of available refuelling technology (e.g. 150 bar merchant hydrogen bottles are widely sold) [96]. Given these choices, several other system design considerations (i.e. choice of components and their parameters), which are based on the operating environment [96, p. 349], will be affected. The main purpose of the system is to "condense" and safely contain a certain quantity of hydrogen for a period of time, before releasing it according to some desirable specifications. The proficiency by which the storage system achieves its main function is captured by metrics such as:

- Uptake capacity (gravimetric and volumetric)
- Cycle life: Relates to the stability of the system's parameter states while implementing the functions.
- Efficiency: Ratio of usable hydrogen delivered to FC/ICE, to overall quantity of hydrogen required in the energy conversion process.

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[1] The actual weights and volumes of past and current hydrogen storage systems built and demonstrated under laboratory or field conditions have weighed more than the storage media by factors greater than two and sometimes as much as an order of magnitude. These increases reflect use of commercially available hardware components, efforts to minimize manufacturing and fabrication costs, and high safety factors to account for high pressure and temperature during testing [96, p. 386].

- Loss of usable hydrogen: Quantity of hydrogen ejected by system, either by some designed process (e.g. boil-off) or a design flaw associated with the containment vessel's material properties (e.g. permeation).

- Transient response: Performance measure of the time to implement all storage system sub-functions in achieving a specific hydrogen flow rate.

- Start time to full flow: The time to implement all sub-functions to achieve a full flow rate.

- Fill time: Time for recharging with hydrogen given certain operating conditions.

Some of the performance metrics that capture the desired specifications of the system's output include:

- Fuel purity: The purity state of released hydrogen gas from material and system.

- Minimum delivery temperature to FC (e.g. -40°C for automotive application)

- Maximum delivery temperature to FC: (e.g. 85°C for automotive application)

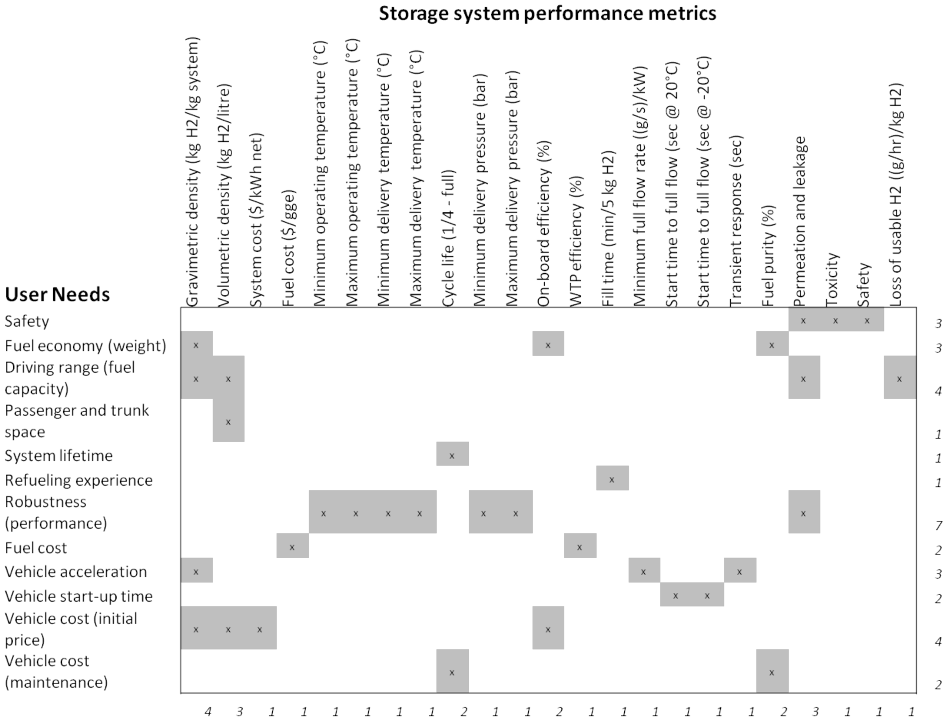
- Minimum delivery pressure: (e.g. 3 bar for automotive application)

  - As explained in [2]: This target acknowledges that the onboard hydrogen storage system is responsible for delivering hydrogen in a condition that the power-plant can use. Since there can be no flow without a pressure differential, a minimum supply pressure is required just to move the hydrogen from the bulk storage to the power-plant. If the hydrogen were merely available at the entrance to a fuel cell, for instance, any pumps necessary to push or draw that fuel through the stack would be considered part of the fuel storage system.

- Maximum delivery pressure: (e.g. 12 bar for automotive application)

  - As explained in [2]: This target ensures that the on-board hydrogen storage system should not be designed such that extraordinary measures for pressure regulation are required before fuel is supplied to the fuel cell system.

Figure 4.1 shows how various storage system performance metrics impact on different user needs. In this case the needs refer to users of passenger vehicles, though similar relations could be deduced for other applications.



Storage system performance metrics

User Needs	Gravimetric density (kg H2/kg system)	Volumetric density (kg H2/litre)	System cost ($/kWh net)	Fuel cost ($/gge)	Minimum operating temperature (°C)	Maximum operating temperature (°C)	Minimum delivery temperature (°C)	Maximum delivery temperature (°C)	Cycle life (1/4 - full)	Minimum delivery pressure (bar)	Maximum delivery pressure (bar)	On-board efficiency (%)	WTP efficiency (%)	Fill time (min/5 kg H2)	Minimum full flow rate ((g/s)/kW)	Start time to full flow (sec @ 20°C)	Start time to full flow (sec @ -20°C)	Transient response (sec)	Fuel purity (%)	Permeation and leakage	Toxicity	Safety	Loss of usable H2 ((g/hr)/kg H2)	
Safety																				x	x	x		3
Fuel economy (weight)	x											x							x					3
Driving range (fuel capacity)	x	x																		x			x	4
Passenger and trunk space		x																						1
System lifetime									x															1
Refueling experience														x										1
Robustness (performance)					x	x	x	x		x	x									x				7
Fuel cost				x									x											2
Vehicle acceleration	x														x			x						3
Vehicle start-up time																x	x							2
Vehicle cost (initial price)	x	x	x									x												4
Vehicle cost (maintenance)									x										x					2
	4	3	1	1	1	1	1	1	2	1	1	2	1	1	1	1	1	1	2	3	1	1	1	

Figure 4.1: Dependence of vehicle-level functions on storage system performance metrics. That is, this graphic indicates which user needs (corresponding to particular vehicle-level functions) are affected by the performance levels of various storage system performance metrics. The row numbers (sum of crosses in earch row) indicate the number of storage system metrics important for improving the corresponding function. Conversely, the column numbers (sum of crosses in each column) reflect the number of system level functions impacted by changes to particular storage system metrics. Adapted from: [146].

4.2.2 General assemblies in the system design

In this section I discuss major subsystems that are, in some form, common to all hydrogen storage designs. I outline some of the key parameters that influence performance on the functions of the respective subsystem.

4.2.2.1 High-aspect-ratio cylindrical pressure vessel

The storage vessel's main function is to contain a gas at high pressure - enabled by the phenomenon of tension in the vessel structure. Below I list some key parameters that impact performance on this component's main functions:

- Specific strength: This a structural parameter inherent to the material of the containing vessel, indicating its resistance to stress, and hence the various pressures at which the vessel may operate. The utilization of a pressure vessel is important in meeting both the DOE volumetric target as well as the charging target.

- Shape of vessel and thickness of walls: These are parameters that determine the pressure levels which may be safely operated at. Shape is important because it plays a role in the distribution of stress in the tank walls. Cylindrical shape is common as it, together with a spherical shape, create a uniform stress distribution [96, p. 353]. Hence, the wall thickness does not have to be so great, and hence the proficiency is improved with a lower mass parameter. However, an important consideration of vessel shape is the “effective volume occupied” to which the shape is linked. A cylindrical shape may be less proficient than a conformable vessel design which would use up less “useful volume”. Such designs are being worked on, but at present they would require higher mass due to higher wall thicknesses that would be required to ensure structural integrity for high pressures [96, p. 353] This is a potential area of innovation that would allow for improved performance on energy density.

- The parameter “vessel size” (or length of a cylindrical vessel) determines the rate of heat transfer for a given rate of hydrogen absorption/desorption, and a given enthalpy of ad-/absorption [96, p. 353]. While longer vessels are more desirable from weight and volume efficiency standpoints, the concept of multiple smaller units is proposed to improve performance on this sub-function of heat transferral. An adequate performance ensures that the material remains at a more or less constant temperature during absorption. An inadequate heat transfer rate may have implications for safety (e.g. if vessel were to heat up too much) and for slowing the rate of absorption (a temperature rise would slow down the absorption process - this self-regulating behaviour is in fact positive with regard to safety).

- Finally, the degree of modularity of the system may be varied. This could benefit the performance of a number of functions. As described in [96, p. 354], “modular system designs have been proposed whereby instead of having a single vessel containing hydrogen, the system consists of multiple smaller units, each containing a fraction of the overall quantity of desired hydrogen.” As mentioned before, smaller units may perform better on heat transfer. There would also be less risk posed to the whole system in the case of contamination. Furthermore, efficiency might be improved by controlling only to heat those units in which hydrogen is still present.

4.2.2.2 Heat exchange system

An internal or external heat exchange system is required in order to control the conditions for the sorption process. Part of this function is inherent to the hydrogen storage material, whose performance is expressed by its thermal conductivity, but extra components are generally required for adequate heat transfer. A most challenging design context for the heat exchange system is in automotive applications due to the short timeframe (2 - 10 minutes) in which a substantial amount of hydrogen must be transferred (about 6 kg). As explained in [96, p. 371], a common assumption for refuelling is that the cooling fluid, that is used for heat removal from the storage system, is supplied and circulated by the refuelling station. Thus, the only additional BOP components required for refuelling are the coolant lines that connect the heat exchanger to the refuelling interface. However, for those systems that require heat for H2 delivery to the conversion device, the heat exchange must take place while the system is in use. For these systems, heat of sufficient quality (temperature) must be generated and distributed to the H2 storage vessel on-board. With an internal heat exchanger, the heat transfer fluid is circulated through the hydrogen storage vessel through tubing. This tubing must withstand the internal fluid pressure along with the external hydrogen pressure. In addition, the tubing must be made of a hydrogen compatible material, limiting material choice [96, p. 369].

4.2.2.3 Safety system

The safety function is provided by components that prevent certain undesirable state transitions from occurring (for instance, in the event of unusual operating conditions). Since hydrogen gas is highly flammable, all storage systems need to be configured and constructed to minimize its leakage into any confined spaces [96, p. 385]. There are numerous other potential hazards associated with hydrogen storage systems: pressurized gas, pyrophoric or water-reactive material, and either high-temperature or cryogenic thermal hazards [96, p. 377]. The necessary performance that would have to be achieved by such safety systems is determined by codes and standards that govern the application in which it would be used.

4.2.2.4 Balance of plant

Balance of plant (BOP) components, which will be almost universal to all system designs, include: tubing, valves, pressure-regulators, pressure relief devices, and pressure transducers [96]. In addition, many advanced storage systems will require temperature sensors for operation and control. While a lot of attention in hydrogen storage development lies with the material concept or other major subsystems, improvements to BOP components may provide an important source of incremental progress. One example concerns components that are “wetted” by pressurized hydrogen; they will have the same compatibility requirements as the structural materials of the storage vessel [96]. Most BOP components used in H2 storage systems today are made of 316L stainless steel [96], but alternative materials may be found that meet or exceed the performance of stainless steel while lowering the cost.

4.3 Functional decompositions of storage system designs

4.3.1 Introduction

Several hydrogen storage concepts have been explored as commercial prospects. Figure 4.2 presents an overview of the main categories. From the point of view of a technology classification scheme, these categories would represent subclasses within an overarching class designated "energy storage via hydrogen". Specific concepts within each subclass are variants of a particular design principle. Even among a particular set of variants, there may be very different challenges to integrate the material into an overall system. For instance, candidate reversible hydrogen storage materials may vary in conditions required between 77 - 600 K, and 10s - 100s bar [96, p. 349]. In the following sections I discuss a number of components that provide critical functions for operation with different types of storage materials. The background information for these discussions is drawn largely from [96].

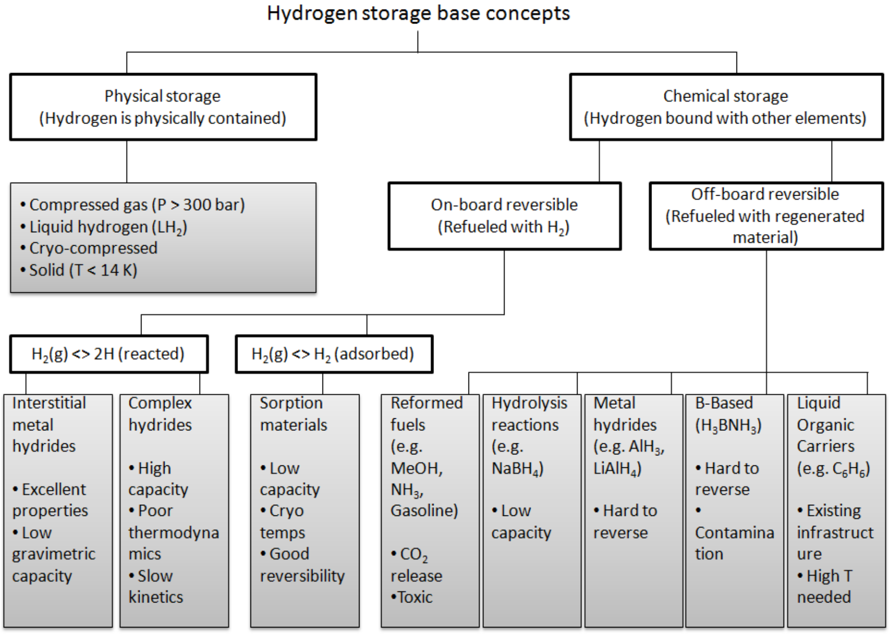


Figure 4.2: Overview of the main hydrogen storage technology categories. Adapted from: [96, p. 67]

4.3.2 Chemical hydride systems

Chemical hydrides differ from other hydrogen storage material concepts in that, after hydrogen release, the storage media must be removed from the system and regenerated at a separate off-board chemical processing facility [96]. They are too cumbersome to regenerate on-board. Two approaches have been considered for refuelling: 1) exchange the entire tank including the material, or 2) expel the spent material at refuelling station while filling with a new fuel.

Prototypical chemical hydrides that have been investigated include NaBH4 (sodium borohydride), AlH3 (alane), LiAlH4 (lithium aluminium hydride), and NH3BH3 (ammonia borane, and its derivatives) and liquid organic hydrogen carriers (LOHCs). Chemical hydrides can be either exothermic or endothermic discharge materials. For exothermic materials there needs to be heat exchanged during desorption. Endothermic media will require a continuous feed of heat to maintain the discharge reaction.

There are several material/fuel properties that need to be considered in the system design. For instance, the viscosity of the material (if indeed it is liquid phase) may have implications for the method of transporting the fuel around the system. This is one property that determines its “fitness” in the context of different types of system designs - which may or may not involve pumps for example. Other physico-chemical properties of the fuel that determine its fitness for various possible system configurations include [4, 6881]:

- Hydrogen energy density (i.e. volumetric and gravimetric capacity)
- Composition and phase
- Solvent and concentration
- Viscosity
- Surface tension
- Vapour pressure for solutions/chemicals
- Material compatibility issues (e.g. corrosion problems)
- Density
- Heat capacity
- For solids: packing density (bulk powder or pellets)

The volumetric performance of the material may be determined as a function of its gravimetric hydrogen uptake, its density, and, in the case of solids, its porosity. I have exemplified their relation (for a particular value of porosity) in figure 4.3.

Specific characteristics in relation to the hydrogen release reactions chemical hydride systems include:

- Kinetics
- Phase changes
- Catalyst morphology and amount
- Species and levels of gaseous by-products relative to hydrogen

An example of the implications associated with material properties such as those above, is given by considering the phase of the chemical hydride. The chemicals can either be liquid or solid, though solid materials may be combined with non-reactive liquids to form a slurry [96, p. 394]. In any case, it is preferred that the materials maintain their original form throughout the reaction to minimize BOP complexity [96, p. 394]. Liquids are most attractive since they are easily pumped and heat transfer is facilitated [96, p. 394]. Slurries are more easily transported (both onboard and offboard the system), but they have issues with separating over time. They can also be abrasive [96, p. 394]. Important requirements of the carrier liquid (i.e., restrictions on how the schemata respond to certain

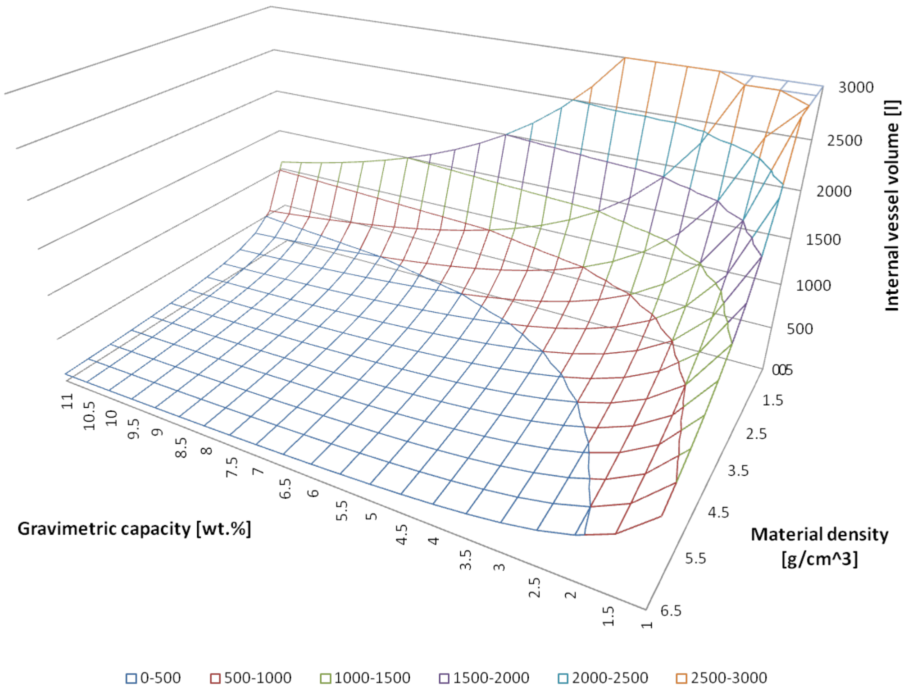


Figure 4.3: Internal vessel volume as a function of gravimetric capacity and material density. This graph is designed to show the importance of bed porosity, material density, and uptake capacity in determining the required internal vessel volume. The calculation is based on a simple model containing only four parameters. Parameters assumed for this model: porosity (volume material/volume based on packed bed) = 50%, usable hydrogen mass = 6 kg. Note, values exceeding 3000 have been cut off to scale the graph for better visualization. Note, the legend indicates colour codes for different bands of vessel volume.

conditions), are that it maintains chemical inactivity and a low vapour pressure at the chemical hydride's dehydrogenation temperature in the reactor.

A distinguishing component of the chemical hydride storage system is the hydride reactor. Many variants have been conceived of, of which a simple flow-through reactor is the simplest (i.e., with the fewest components) [4]. Figure 4.4 depicts variations of a typical chemical hydride system incorporating a flow-through reactor. Several other core components in these storage system designs are a bladder tank, a pump, a gas liquid separator, a heat exchanger, and a purifier. Their functions are detailed in [4]. Briefly, a bladder tank holds both fresh and spent fuel in a single volume separated via a movable diaphragm, thereby increasing the volumetric capacity of the system. The pump ensures the flow of the fuel. Both fresh and spent fuel need to flow in exothermic material based designs, where a portion of the spent fuel is recirculated to absorb excess heat generated in the reactor. The gas-liquid separator separates the evolved hydrogen from the liquid stream and returns the spent fuel to the bladder tank. High pressure hydrogen that is evolved from the reactor is stored in the gas-liquid separator for system transit operation. Finally, in the case of certain chemical hydrides, such as ammonia borane, a purifier would be employed to remove potential contaminants (such as diborane) and avoid poisoning of the fuel cell (if that is the conversion technology of choice).

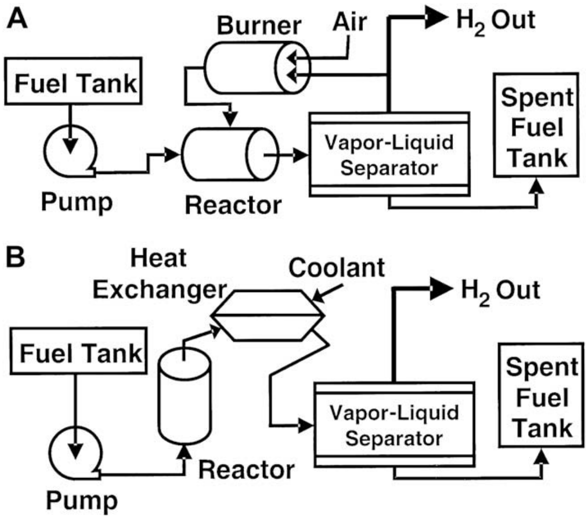


Figure 4.4: A comparison of two chemical hydride system designs. This diagram shows set-ups for two types of chemical hydride systems. In A) the design is for an endothermic chemical hydride that requires extra heating with the burner to release hydrogen in the reactor. In B) the design is for an exothermic chemical hydride. This diagram illustrates that different material properties can result in different system designs, and system performance. For example, the extra burner required in A is a penalty on weight and volume. *Source:* [4]

Chemical hydride storage systems have a particular challenge of finding technical sub-solutions that are not merely associated with the material. Some of the technical limitations that led to non-selection of a particular NaBH4 hydrolysis concept (in the context of passenger vehicle applications) by the US DOE in 2007 included the following [96, p. 82]: 1) unproven single-tank bladder system, 2) the requirement for large amounts of excess water on-board the vehicle, and 3) issues dealing with the precipitation of the NaBO2 product. So far, there remains to be an improved system configuration that involves the hydrolysis of NaBH4 for automotive applications. It should be noted that other applications, which require lower power levels ($\leq$ 10 kW, such as in portable applications), find certain system designs involving hydrolytic NaBH4 attractive [96, p. 82].

4.3.3 Complex metal hydride systems

The second type of storage system design I consider is based on complex metal hydrides (this class of materials is discussed more closely in section 4.4.3). From a system design point of view, similar concepts (i.e., with variations in component sizing) would function well with interstitial hydrides (see figure 4.2) [96, p. 392]. A prototypical complex hydride is sodium alanate (NaAlH4), and it is, at present, the most thoroughly investigated concept for engineering purposes[2]. However, this is due to its use as a learning test bed for

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[2] For example, in 2003, General Motors partnered with Sandia National Laboratories to develop an advanced hydrogen storage system based on sodium alanate [96].

materials with low thermal conductivities, kinetics that require catalysts, significant heat release during charging, and high reactivity [96]. Its commercial prospects for automotive applications are irrelevant as the capacity of NaAlH4 is considered too low.

Due to the thermodynamic sorption behaviours of complex hydrides, the storage tanks comprising such materials are typically pressure vessels. Free space within the storage tank not filled with media can be used to store compressed hydrogen gas which, in addition to maximizing gravimetric/volumetric capacity, may also serve as a buffer, supplying hydrogen under high-demand prior to the delivery of heat for dehydrogenation [96]. Most complex hydrides are not fit to operate at ambient conditions, hence a heat source must be integral to the storage system for such materials to be selected. Various heating sources, i.e. operating niches, may be imagined. In some cases, waste heat from the fuel cell might be sufficient to induce dehydrogenation of the storage material, though an adequate temperature gradient is required for this principle to be effective [165] (an ICE running at higher temperatures would enable a higher fitness for a broader range of materials that have high dehydrogenation temperatures). Other options include electrical resistive heating, and hydrogen combustion in a burner, or a catalytic hydrogen heater. The most efficient method is to react H2 and O2 in a catalytic heater. Heat is produced by the oxidation of hydrogen ($H_2 + \frac{1}{2}O_2 \rightarrow H_2O$) (producing 242 kJ of heat per mole of $\mathrm{H_2}$ (lower heating value) [96, p. 372]). Hydrogen for this process may be supplied by the storage system whereas oxygen may be taken from the surrounding air. However, a separate blower might be necessary [96, p. 372].

Another important system component concerns the heat exchange system. After all, hydrogenation of a substance like NaAlH4 requires the removal of heat on the order of 60 MJ [96]. Such a system will consist of tubing, fittings, valves etc. for the gases as well as heat transfer fluid. The heat transfer fluid represents one of the key design variables of the heat exchange system, in addition to parameters such as layout/geometry of the tubing. For many conventional metal hydrides, water can be used as the heat transfer medium since these materials are benign to potential water exposure from an inadvertent leak [96]. In the case of complex hydrides there would be a risk of water contact [96], such that prudent design is restricted to non-reacting heat transfer fluids. As described in the previous section, multiple hydrogen storage modules can benefit the exchange of heat between the storage vessel and the heat transfer fluid. While obvious areas to address the overall heat transfer function might be things like thermal conductivity of the hydrogen storage material, tubing layout, heat transfer fluid, less obvious components for innovation might include things like inlet manifolds which affect fluid flow patterns [96, p. 376].

4.3.4 Adsorbent systems

At present, for reasons that are elucidated in section 4.4.2, adsorbent hydrogen storage materials require low (cryogenic) temperature operating niches for their “fitness” in storing hydrogen to be appreciated. Moreover, their functions are performed best at elevated pressures. Such demanding niche requirements could in principle be supplied by liquid nitrogen cooled, insulated pressure vessels, for instance, a 200 bar Type III vessel enclosed in a multilayer vacuum-insulated jacket [96].

Although the heats of adsorption for physisorbent materials are much lower than for complex hydrides, the overall performance still depends on an effective heat exchange system. Without it, the material would heat up (significantly) during charging, thereby reducing the available capacity. One solution would be to pass chilled hydrogen gas (at 77 K) through the tank during charging. As it passes over the storage medium, the gas is heated and the media cooled. The exiting heated hydrogen gas would be returned to the fuelling station for either re-chilling or other uses [96]. Another possibility would be to use liquid nitrogen and to evaporate it as the medium is heated up, though the costs associated with cooling the substantial quantities of nitrogen required for the process might be unattractive [48].

As with the complex hydride system, the discharge process requires heat input into the tank (although the demands are far less severe, implying that the thermal energy from a PEM fuel cell would be sufficient). This could be achieved with an in-tank electrical resistance heater [96]. A difference to the complex hydride system is that the released hydrogen then needs to be further heated to ambient temperatures for use by a fuel cell. This would require a further heat exchange component. As explained in [96, p. 397], such a component is technically challenging since the outflowing gas is at cryogenic temperatures, and the ambient atmosphere with its moisture content will ice over conventional heat exchangers.

4.4 Design parameters for hydrogen storage material functions

4.4.1 Introduction

What are the main functions of a storage material? For metal hydrides and sorption materials they may be abstracted as follows:

- Transform a certain quantity of hydrogen in the gaseous state (at some specified temperature and pressure) into a more dense phase. In hydride materials this function is achieved by the phenomenon of absorption (involving the formation of relatively strong chemical bonds). In physisorbent materials it is the process of adsorption (based on weak van de Waal's interactions).
    - Certain design parameters will be desirable to ensure that this transformation process occurs at or above some minimum rate (the precise requirement being determined by the application). This function may cater to a human need (for instance due to lack of patience when refuelling a vehicle), or it may relate to a technical requirement, for instance, in the process of capturing excess energy from a variable power supply unit. Furthermore, a concept that performs hydrogen absorption at practical temperature and pressure conditions is more

    desirable. Hence, there is exploration for hydrogen storage material variants that have sorption properties more conducive to ambient operation.

- Release the condensed phase hydrogen - within some margin of required delivery conditions - into the gas phase. The reverse processes of absorption and adsorption are responsible for achieving this outcome.
    - Certain design parameters of the material may be explored, which impact on the state change of the substrate material during dehydrogenation. Such design parameters are explored to tune the material's reversibility. Desirable would be a process that entails minimal state changes, thereby ensuring reversibility over many cycles. Furthermore, this process should occur at or above some minimum rate depending on the application and requirements of the conversion device.

For the case of chemical hydrides, the process is not reversible, at least not within the confines of the system. This creates an additional technical need for the storage system to comprise an assembly, whose function it is to handle the "spent fuel". Alternative design parameters might be investigated to ensure that the spent fuel is easily handled, for instance, by controlling that the reaction pathway gives a liquid phase product.

In the following sections I review a variety of design parameters that represent, more or less, recent design explorations in solid-state hydrogen storage. These design parameters are descriptions of distinct physical characteristics of the material which, when varied, are found to have important effects on hydrogen sorption properties. It should be noted that what I present below is by no means a complete overview of activity in design space. Such would demand a great amount of detail, and would nonetheless be limited to a snapshot in time. My intention is to give an appreciation for the kind of design changes that are shaping the "genotypes" of the coming generations of hydrogen storage materials.

4.4.2 Physisorbent hydrogen storage materials

A wide range of porous materials have been discovered onto which hydrogen "physisorbs". "Traditional" materials include carbons and zeolites [151]. These have been the subject of investigation for many years. More recently, new kinds of materials have been discovered and/or attracted attention for hydrogen storage purposes. These include the families of metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), and microporous polymers [151].

Carbon materials interesting for hydrogen storage purposes include activated carbons, carbon nano-tubes and nanofibres and, more recently, microporous templated carbons [34, p. 21]. The following characteristics make such carbon materials interesting propositions for hydrogen storage applications [34, 54]:

- Low molar mass
- High porosity

- High specific surface area
- Chemical stability

Early reports claimed extremely high sorption capacities on carbon nano-tubes. Now it is widely accepted that these results were erroneous.

Zeolites and related compounds are crystalline microporous materials. They are in the strict sense of the definition alumosilicates, but nowadays other compositions, such as aluminophosphates, are also included in the definition [48]. The most important feature of zeolites which determines their selective properties for adsorbing certain substances, is the presence of micro- and/or mesopores within their structures. The configuration of these pores is an important parameter that governs the transport phenomena of guest species in zeolites [129]. A factor limiting the storage capacity of zeolites is the relatively high mass of the framework (containing Si, Al, O and heavy cations) [129].

The first report of a coordination polymer was in 1959 but it was not until 1989 that the structure of another similar material was reported. In 1997, the first report of gas adsorption on a MOF was published [151]. In particular, it was Omar Yaghi who pioneered the design and synthesis of MOFs in the mid to late 1990s. In 2003, Rosi et al. reported the first MOF-based hydrogen storage result [171]. MOF research, in general, became a rapidly expanding field since the late 1990s, with more than 2000 varieties having been reported worldwide [6]. MOFs may be synthesized from a wide range of ligands and metals or metal clusters, and thus have a wide range of compositions and structures [151]. An impressive feature of these materials, not least with regard to hydrogen storage, is their exceedingly high surface areas. While it is noted in [48] that the meaning of surface area, be it Langmuir or BET equivalent surface area, is questionable for materials with such small pores (they are primarily microporous structures), their values, which can exceed 5000 $m^2 g^{-1}$, are spectacular. A characteristic of MOFs is their ordered structured of pores and channels [129], which makes possible the observation of high resolution crystal structures [171].

Another category of material which has been studied for hydrogen storage purposes are the polymers of intrinsic microporosity (PIMs). How the interest in them originated is described in [36]: "*During the investigation of various gas permeabilities of PIM-1 and PIM-7, it was noted that their H2 solubility coefficients are greater than for any other polymer reported to date. This prompted a study of the low temperature (77 K) hydrogen adsorption properties of PIM-1 and the network polymers HATN-PIM and CTC-PIM...PIMs are rigid and contorted macromolecules, wholly composed of fused-ring components, which form microporous organic materials due to their inability to pack space efficiently.*" These materials have BET surface areas in the range of 440-1050 m^2/g [48]. Structural variations are enabled by a high diversity of synthesis techniques [48].

To conclude this short overview of physisorbent hydrogen storage materials, as mentioned in [34, p. 20], progress continues with the synthesis of new hybrid material classes, and new candidate materials are likely to emerge as the search, as well as the interest in these materials for a range of applications, continues.

4.4.2.1 General storage mechanism

Physisorbent materials induce a state of "stored" (or contained) hydrogen characterized by an enrichment of molecular hydrogen density close to the surface/pore walls of the material (adsorbent) [34, p. 8].This effect, which is called "physisorption", is dominated by weak intermolecular forces (van der Waals interactions) between the adsorbtive substance and the substrate. These interactions are characterized by the fact that they do not cause any significant change in the electronic orbital patterns of the relevant species [56]. Since the hydrogen molecule is the smallest molecule, with only two electrons, it is hard to polarize. Consequently, dispersion forces, created by temporarily induced dipoles, are relatively weak for this system [56]. The heat of adsorption for candidate hydrogen storage materials is in the range of about 4-10 kJ/mol H2 [54]. (One way of measuring it is to monitor the temperature rise in a sample with a known heat capacity [16, p. 411].) Such small energies can be absorbed as vibrations of the lattice and dissipated as thermal motion. Hence a molecule bouncing across the surface[3] will gradually lose its energy and finally adsorb to it in the process called accommodation [16, p. 411]. A positive aspect of small interaction energies involved in physisorption is that the adsorbed molecule and the adsorbent remain relatively unchanged during adsorption and desorption, thereby facilitating cycling [96, p. 213].

Dynamic equilibrium between free hydrogen gas and the adsorbed hydrogen may be represented by the following equation [16, p. 412]

$$H_{2(g)} + A_{(surface)} \rightleftharpoons H_2A_{(surface)}. \tag{4.1}$$

The fractional coverage of the surface, abbreviated θ, which may be defined by (mass of adsorbed hydrogen/mass of hydrogen corresponding to complete monolayer coverage of the adsorbent), depends on the pressure of hydrogen and the temperature. The variation of θ with pressure at a given temperature is called the adsorption isotherm [16, p. 413]. According to the conventional classification of adsorption by IUPAC, isotherms can be of six general types (I - VI) [34]. Hydrogen adsorption by microporous materials corresponds to Type I, which is concave to the pressure axis and saturates at a finite limit (i.e. when θ approaches one). Moreover, Type I (Langmuir) adsorption isotherms indicate monolayer adsorption [54]. Indeed, as the boiling point of hydrogen is very low at 20.4 K (reflecting a low heat of condensation of 0.9 kJ/mol H2), only a monolayer of hydrogen can be expected to adsorb to the surface of the substrate at practical operating temperatures (far above the boiling point of liquid hydrogen) [54].

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[3] The collision flux on a region of the surface may be estimated from the kinetic theory of gases. To give a sense of magnitudes, for air at 1 atm and 25°C the collision flux is $3 \times 10^{27} m^2/s$. Given $1m^2$ of a metal surface, which consists of about 10^{19} atoms, this corresponds to each atom being struck about 10^8 times each second [16, p. 406].

4.4.2.2 Design parameters

Most design efforts on sorption materials have focused on increasing the gravimetric hydrogen storage capacity. Some concern has been directed at the low operating temperatures that would be required to run available physisorbent materials, and hence some effort has gone into addressing this issue also. Others believe cryogenic operation to be a viable option/niche for sorption material concepts, and are therefore not committed to improving performance on this dimension. Surprisingly little has been said about generally low performance in terms of material volumes required for adsorbing enough hydrogen for mobile applications (5-6 kg). I will simply remark that for systems defined by parameters which give a high number of adsorbed hydrogen atoms per substrate atom (mass density), the volumetric capacity is maximized by finding a physisorbent in which those parameter states are also defined by a high bulk density. Performance on other measures, such as kinetics and cyclability, are intrinsically good for the sorption material concepts.

In the search for good material parameters, even basic theoretical insight can be a useful guide. For instance, the gravimetric uptake capacity of an adsorbent is related to two important characteristics: the number of adsorption sites per unit mass of material, and the characteristic strength of the substrate-adsorbate interaction. Adsorption sites are given by surfaces or micropores [96, p. 216]. Hence, for a given mass of material, one may expect those physical characteristics to be important parameters in determining the uptake capacity. Binding energy, indicated by the enthalpy of adsorption [26], also plays a role in the hydrogen uptake capacity, however, its importance varies depending on pressure conditions at a given temperature. In particular, when pressures are low, then enthalpy of adsorption has an important influence by leading to tighter packing of molecules [158]. A higher density of hydrogen molecules in the adsorbed phase volume implies a greater excess adsorption. For any given material, it is the excess capacity which determines whether the material has an overall advantage over a free volume of gas at the same temperature and pressure. When pressures are higher, then it is the specific surface area which dominates the uptake capacity (the effect of higher interaction energies becomes less advantageous for a material's excess adsorption capacity over and above that of a material with a lower enthalpy of adsorption).

Parameters for uptake capacity At a given temperature and pressure, the excess gravimetric capacity scales with SSA (or specific micropore volume). It is claimed in [79, p. 216] that the relationship between excess hydrogen storage capacity and total specific micropore volume (and SSA) has been tested and validated for a variety of microporous adsorbents. It should however be noted that there have been controversial reports concerning the exact nature of the influence of micropore volume and surface area on the hydrogen uptake (see 4.4.2.2 for more details) [54]. For instance, one must consider that the distribution of pore size in a material is an important factor determining the uptake, and may be responsible for scatter in observed correlations. Below I give examples of some observed correlations.

The characterization of samples in terms of surface area is subject to controversy, especially for microporous materials (due to measurement techniques, e.g. the size of the probe molecules, temperature, etc., and the underlying theory of adsorption, e.g. layer formation (e.g. BET or Langmuir) or pore filling) [79, p. 127]. The technique of surface area determination based on the BET or Langmuir method assumes layer formation. It may be inappropriate to consider the arrangement of adsorbed hydrogen molecules resulting from pore filling in a strict sense of a "surface layer" [34]. Hence, in the presence of micropores, specific surface area (SSA) measurements based on these techniques include a component that measures an effective surface area [96, p. 216] given by the *micropore capacity* [34, p. 150/151]. Most candidate physisorbent hydrogen storage materials are microporous, that is, they exhibit Type I (or Langmuir) adsorption behaviour, and we might expect this component of their SSAs to dominate (e.g. as opposed to external surfaces) [34].

The first few examples pertain to carbon materials. Figure 4.5 gives a comparison of the dependencies between uptake and specific micropore volume and specific surface area. It can be seen that both parameters predict essentially the same quantity of uptake. A dependence specifically for SSA is discussed by Eberle *et al.* [48]. Calculated for -196 °C and the saturation pressure value of the Langmuir equation - that is, at pressures of several MPa [48] - the data shows that the excess gravimetric capacity scales with specific surface area (mostly as BET equivalent surface area) with a proportionality constant of 1.9×10^{-3}wt.% g m^{-2}. For lower pressures (0.1 MPa and -196 °C), the proportionality constant appears to be about 1.3×10^{-3}wt.% g m^{-2} [48].

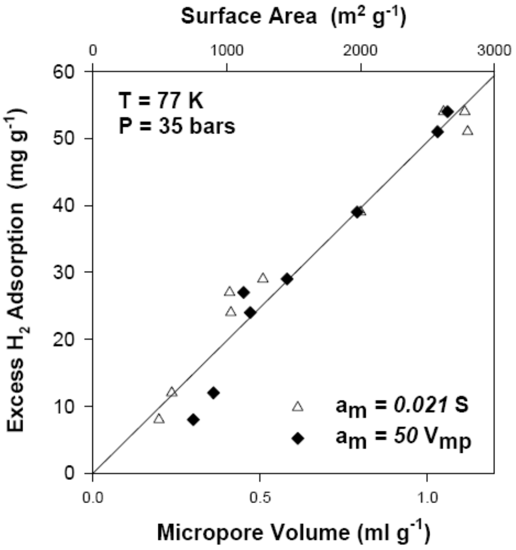

Figure 4.5: Excess gravimetric adsorption capacities for different carbon materials as a function of specific micropore volume and specific surface area. *Source:* [79, p. 215]

It is interesting to compare these proportionality constants to one obtained by considering a simplified theoretical model for adsorption on carbon materials proposed by Züttel *et al.* [173]. This model considers an idealized limit of adsorption on carbon materials by calculating the capacity of a perfect graphene sheet. Allowing for adsorption on both sides, and

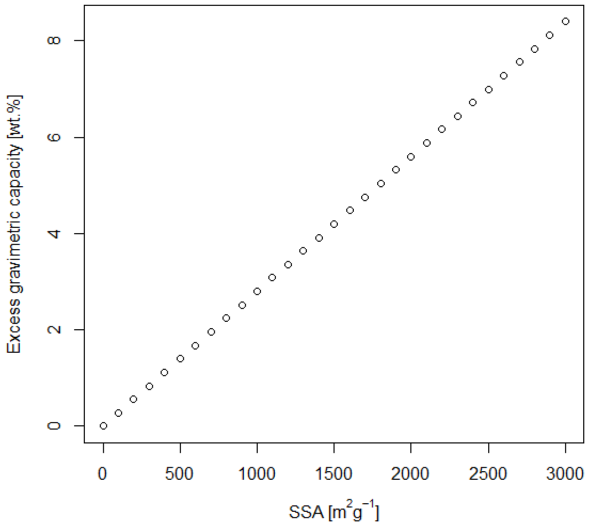

Figure 4.6: Theoretical model of hydrogen adsorption on carbons as proposed by Züttel *et al.* [173].

considering monolayer formation in a closed packed two-dimensional geometry, and with a density of liquid hydrogen, the calculation reveals a surface density of 2.28×10^{-3} wt.% g/m^2 (suggesting an ideal case, as confirmed by comparison to the other proportionality constants). We can plot uptake versus SSA, as shown in figure 4.6, by assuming that the same ratio of capacity over SSA holds for structures with smaller surface areas.

The extent of leverage on tuning the parameters SSA/micropore volume for uptake may be analysed by considering the limiting values that are achievable by different systems. The case for carbons has been discussed in [48]. With a value of 0.92 cm^3 g^{-1}, a system of graphene sheets separated by 0.7 nm is taken to represent the upper threshold for the micropore volume attainable in carbon materials [48]. The proportionality constant for a plot of *saturated* sorption capacities (based on Langmuir equation) versus micropore volume is roughly 7 wt.% cm^{-3} g^{-1} [48] (c.f. the value of 5 calculated in figure 4.5). Based on this relation, a limit of 6.44 wt.% excess adsorption may be estimated for uptake in carbon materials [48]. This value is confirmed by considering the limiting value for the surface area one may achieve with carbons, which is given by isolated graphene sheets. For adsorption on both sides, its SSA is estimated at 2630 m^2 g^{-1} [48], which, by inspection of figure 4.6, gives a limiting value of about 6.4 wt.%. Thus, target performance levels for automotive applications seem just beyond the reach of carbon systems [48].

Correlations between surface area and hydrogen uptake have also been studied for PIMs etc. (e.g. [36]). Figure 4.7 shows such a dependence. As can be seen, while the PIMs set a clear trend, the HCP falls slightly below it, though less so at the higher pressure condition. It is interesting that extrapolation of the data for saturation uptake suggests, other things being equal, that a PIM with a surface area of 2400 m^2/g would achieve 6 wt.% hydrogen uptake at 77 K [36], a value close to the limit for carbon materials. That being said, most PIMs have BET surface areas in the range of 440-1050 m^2/g [48], therefore a value of 2400

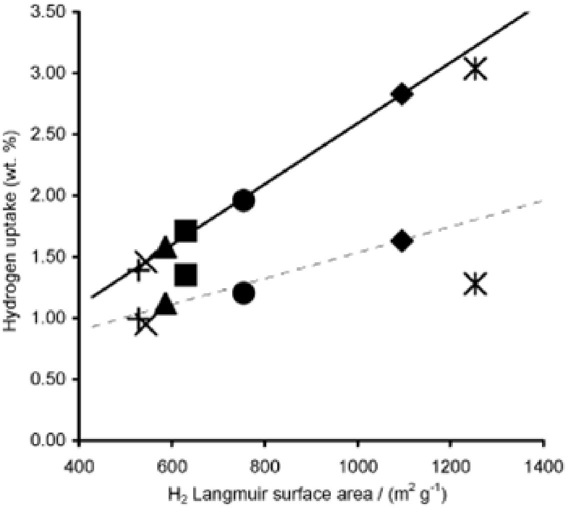

Figure 4.7: The dependence of excess hydrogen uptake on the Langmuir surface area at 1 bar and 77 K(dashed line) and 15 bar and 77 K(solid line) for PIMs: PIM-7 (+), PIM-1 (×), HATN-PIM (▲), CTC-PIM (■), Porph-PIM (●), Trip-PIM (◆), HCP (✶). *Source:* [36]

m^2/g would seem a challenge, though as noted in [36], a viable synthetic target.

Finally, an example of the same relation for MOF materials is given in figure 4.8. This graph shows that MOFs may reach impressive SSAs, and correspondingly, may achieve high adsorption capacities on a gravimetric basis.

Parameters associated with pore/channel structure have also been linked with uptake capacity. In one case, involving zeolite structures, the effect of pore width is in fact associated with an encapsulation mechanism as opposed to physisorption. In this process molecules are forced into normally inaccessible zeolitic cages at elevated temperature and pressure. Upon cooling to room temperature, hydrogen is trapped inside the pores and can be released by raising the temperature or applying force [129]. In a comparative study referenced in [129], a relationship is found between the amount of entrapped hydrogen and the ionic radius of the cation in zeolite A. In particular, the amount of stored hydrogen per gram of zeolite increases from $Na^+$to K^+, and then decreases radically from K^+ to Rb^+ and Cs^+. Increasing the cation size has the effect of reducing the effective pore width. It was proposed that encapsulation was most effective at a critical value of the pore width [129].

Studies on MOFs have for a long time been interested in the relationship between uptake and ligand structure. As far back as the first report of hydrogen uptake in MOFs the authors proposed that using larger aromatic ligands would increase the uptake capacity [171]. The idea is supported by theoretical studies [171]. A study referenced in [171] performed a systematic investigation on the influence on uptake capacity brought by the modulation of the organic ligands. The results showed no direct relationship between capacity and the chemical composition of the ligands. Instead, the authors suggested that the shape and size of channels instead of the ligand's chemical nature is responsible for the trend in uptake [171].

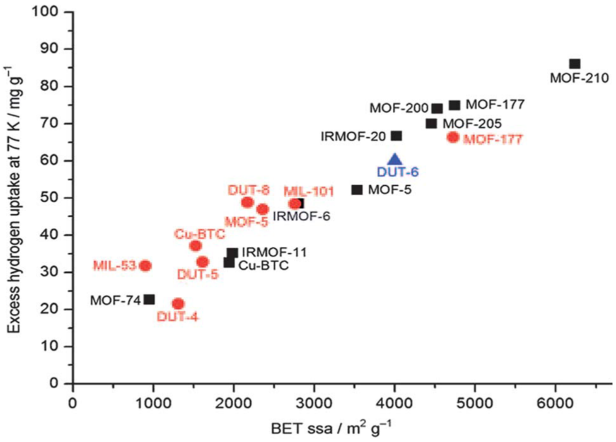

Figure 4.8: Excess hydrogen uptake at 77 K for selected high surface area MOFs. *Source:* [129]

Parameters for controlling the equilibrium adsorption difference between two pressure limits From an engineering perspective, the useful or practical capacity of an adsorbent is the difference in the adsorbed amount between two pressure limits, namely the maximum pressure at which the system may be maintained, and a lower pressure limit that is used for desorption. For instance, because of the requirements of proton exchange membrane fuel cells, hydrogen should be delivered with a minimum pressure of 3 bar [96, p. 219]. Say that the upper pressure limit is 100 bar, then for isothermal operation the capacity of an adsorbent is the difference in adsorbed quantity between 3 bar and 100 bar. This difference depends on the shape of the adsorption isotherm, which, in turn, is dependent on the characteristic enthalpy of adsorption. If the enthalpy change is too small, the amount adsorbed at the high pressure limit will not be sufficiently greater than the amount adsorbed at the lower pressure limit. On the other hand, the enthalpy change may be too high, such that the amount adsorbed at the low pressure limit is close to saturation capacity (i.e. the adsorption isotherm rises very steeply with pressure), and the difference between the pressure limits will not be substantial. The thermodynamics of the adsorbent must therefore be tuned such that there will be a large difference in hydrogen uptake in between the operating pressure limits. Assuming a constant enthalpy of adsorption (which is not realistic), the ideal value is estimated to lie between -15 and -20 kJ/mol H2 for the limits set at 3 and 100 bar [96].

This insight suggests a challenge for tuning the enthalpy of adsorption of different physisorbent hydrogen storage concepts. Below I give a limited exposition of design parameters that have an influence on binding energies (and hence on the shape of the adsorption isotherm).

- Pore size is a determinant of enthalpy of adsorption. Indeed, micropores (≤ 2 nm) contribute the most to total uptake as compared to pores of a larger size or flat surfaces due to their higher interaction energies, leading to a tighter packing of hydrogen molecules in the adsorbed phase volume (though this effect decreases with increasing pressure [54]). When pores are small enough the potentials from opposite walls overlap to an extent, resulting in higher adsorption energies (it should be noted that pores may have different shapes and they might be regular or irregular [79, p.

209]). Pore size distribution may be controlled by an appropriate processing technique. For example, in some amorphous carbons it is the use of an ordered zeolite template [84, p. 46]. In single-walled carbon nano-tubes (SWNTs), the surface interaction energy can be tuned by manipulating the radii of the tubes (one reason SWNTs have attracted attention for hydrogen storage is that they have a narrow pore size distribution). Incidentally, considering an alternative adsorption site, another parameter is important for the binding energy in SWNTs, namely the distance between nanotubes in a bundle [26]. At a certain distance, there is an overlap in the attractive part of the interaction potentials [26]. A “map” to guide the optimal configuration of parameters for uptake in SWNTs is presented in figure 4.9. It is noted that smaller distances between nanotubes would in principle lead to greater overlap. However, as is explained in [26], smaller distances reduce the specific surface available for adsorption, and therefore does not lead to greater uptake.

- It has been proposed that doping carbon nanostructures with certain metals (e.g. Titanium, Be, Sc, Cr, Pt, Pd) could lead to non-dissociative binding of hydrogen molecules [99]. Unsaturated metal binding sites have been proposed in MOFs, preferably formed by light metals (e.g. lithium or magnesium), that provide strong hydrogen adsorption sites [158].

- Theoretical work has predicted a benefit to introducing a spillover mechanism whereby metal sites act as catalysts in order to break H-H bonds so that the adsorbed species are hydrogen atoms rather than the molecule itself [99]. This method has yet to be proven effective experimentally, and may be impaired by the possibility of chemical bonds forming which would necessitate high temperatures for hydrogen release[99].

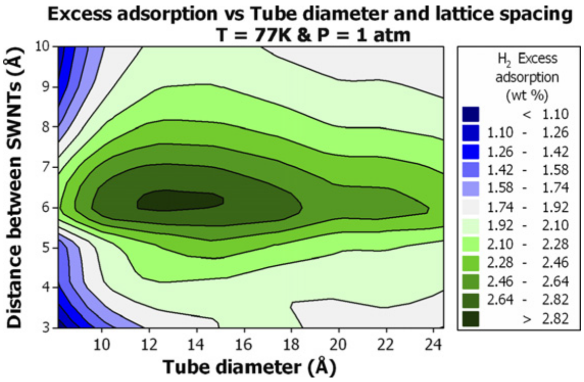

Figure 4.9: Contour plot of excess adsorbed hydrogen density as a function of SWNT diameter and spacing between tubes at 77 K and 1 atm (for a bundle of seven units). Values were obtained theoretically (using grand canonical Monte Carlo simulations). *Source:* [26]

Parameters for increasing uptake at ambient temperatures Physisorbent hydrogen storage materials have low interaction energies with hydrogen. This necessitates low temperatures to achieve reasonable quantities of adsorption. Design approaches that attempt to make sorption material schemata more appropriate for ambient operating environments have focused on parameters by which to increase the binding energy between hydrogen and the adsorbent, e.g. through chemical bonding. As an example, figure 4.10 shows a theoretical study with a dramatic enhancement of hydrogen uptake at 300 K on Li-doped MOFs. This example is a clear case in which theory may guide the search process.

As noted in [171], in addition to a number of cations, anions may also be helpful in hydrogen adsorption through enhanced binding. Theoretically, the "spillover" mechanism, for example by using certain heavy transition metals (such as Pt) on MOF structures, has also been proposed to lead to enhancement of uptake at higher temperatures (e.g. see [171]). It should be noted that when the MOF is doped, this reduces the available surface area [129].

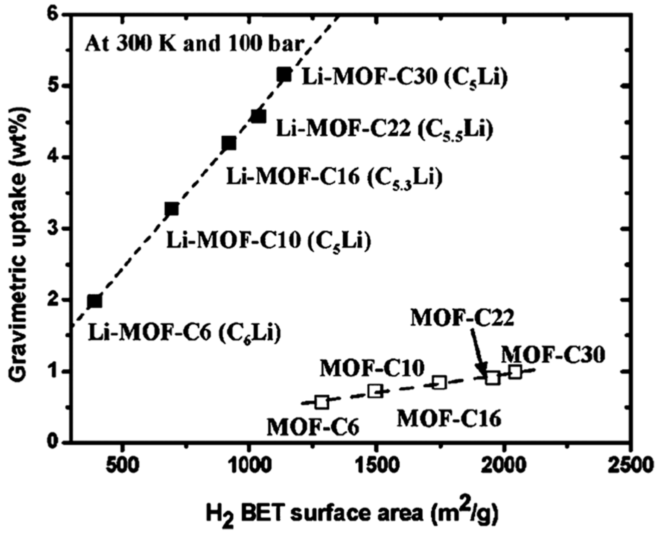

Figure 4.10: Optimum structures for Li-doped zinc carboxylate MOFs based on theoretical calculations. Theoretical calculations were used to predict optimum structures for Li-doped zinc carboxylate MOFs, and their hydrogen uptake respectively. The data shows a dramatic enhancement of hydrogen uptake at 300 K and 10 bar upon Li doping. Moreover, a correlation between SSA and uptake is maintained. This study suggests a potential for design parameters, such as Li-doping, that have the effect of increasing the binding energy with hydrogen, to increase uptake closer to ambient operating temperatures. *Source:* [129]

4.4.3 Onsite reversible hydrides

Onsite reversible hydrides is a category of materials that reversibly store hydrogen (i.e. release and reabsorb), yet form relatively strong chemical bonds in the process. The notion of reversibility is defined here, not in a strict thermodynamic sense, but rather it means that practicable changes in temperature and pressure conditions will reverse the process of dehydrogenation. "Onsite" is used as a generic term to identify hydrogen storage concepts which do not require that the storage material be reprocessed outside of the system in which it operates (referring to hydrogen fuel cell vehicles, the more specific term would be "onboard"). The set of potential hydrogen storage materials that comprise this category are mainly from one of three general types of hydrides [79, 34, 84, p. 188]:

- Interstitial metal hydrides: materials such as $LaNi_5H_x$ where hydrogen atoms are found in interstitial sites within the metal atom substructure

- Covalent metal hydrides: discrete compounds such as MgH_2 where the bonding between hydrogen and the metal is very covalent, localized and strong

- Covalent complex metal hydrides: compounds such as metal borohydrides, metal aluminium hydrides, metal amides, and mixtures thereof (multi-component hydride systems). Complex hydrides have the general chemical formula $A_xMe_yH_z$. They are salt-like materials in which hydrogen is covalently bound to central atoms (the crystal structures of these materials thus consisting of "complex anions" ionically bonded to cations [84, p. 117]). The bonding between hydrogen and the central atom (e.g. Al, B, and N) is highly covalent and strong [79, p. 188]. Compounds, where position A is preferentially occupied by elements of the first and second groups of the periodic table, and Me, occupied either by boron or aluminium (i.e. forming borohydrides and aluminium hydrides), are well known and have been intensively investigated [84, p. 117]. Complex hydrides may also be built by transition metal cations, as in Mg_2FeH_6, and are then referred to as complex transition metal hydrides.

In this section I focus on design approaches in complex metal hydride systems. This is because this domain represents the most active area of research among the reversible hydrides. While interstitial hydrides were in focus in the 1970s and 80s, complex hydrides (and lightweight covalent metal hydrides) became the focus of more recent efforts to improve on the one deficiency of the former, namely, gravimetric capacity [96, p. 134]. (I refer to several references, e.g.[84, 96, 133], for a more comprehensive coverage on various topics that I cut short). While chemists had known about complex hydrides for almost a century - they were used in organic syntheses - it was not until the mid-1990s that they were considered for hydrogen storage applications. Pioneering work of Bogdanovic and Schwickardi represented a sort of gateway event, one that lead to a flurry of activity in complex hydrides (and indeed to renewed interest in hydrogen storage in general). They showed that the addition of a catalyst could not only make the materials release hydrogen more rapidly, but it also made them reversible under moderate conditions [84, p. 117]. Many complex hydrides are commercially available today [84, p. 117], though considerable technical challenges still remain to make them more widely applicable, particularly for mobile applications.

4.4.3.1 General storage mechanism

Most hydride formation reactions are exothermic, and under suitable activation conditions, the formation reaction will be spontaneous. Hydrogen is covalently bound into the bulk of complex hydrides [34, p. 40]. Complex hydrides release molecular hydrogen by heating. In most cases the release and absorption of hydrogen occurs through bond-breaking decomposition and recombination reactions, sometimes through discrete intermediate phases. Many complex hydride systems, such as NaAlH4, involve multi-step chemical reactions that have multiple dissociation temperatures corresponding to different stable intermediate states [79, p. 188]. Due to the number of microscopic steps involved in de-/re-hydrogenation, the process of hydrogen sorption in hydrides is relatively more complex compared to molecular adsorption and desorption by sorption materials [34, p. 89]. A major goal is to understand these steps better to improve the performance of particular materials [84, p. 117]. Many research efforts centre on the thermodynamics and kinetics of dehydrogenation [129], as well as on-board reversibility [96, p. 135].

4.4.3.2 Design parameters

In general, there is room for improvement in complex metal hydride performance by acting on their thermodynamics and kinetics [158]. The following sections provide an overview of variations in design being explored to achieve those objectives.

Parameters for gravimetric uptake capacity To affect the gravimetric hydrogen capacity of the complex hydride system, one has, in general, two possibilities. Firstly, the use of improved catalyst systems, for which less catalyst is needed (hence, one achieves a smaller weight penalty given by the catalyst), already helps to some extent [137]. Secondly, to affect bigger changes, one can vary the constituent elements [137]. For instance, replacing Na (in NaAlH4) with the lighter Li (to get LiAlH4), or Al with the lighter boron (to give NaBH4). However, that really shifts the focus to other complex hydrides, which may have quite different properties. Instead, as explained in [137], one does not necessarily substitute one of the elements completely; mixed hydrides are also possible. Considering multi-component hydride systems, then changing the mixing ratios will also affect the capacity.

Parameters for tuning the conditions at which decomposition occurs Several definitions of capacity are in use in the literature [79]. The one of interest from an engineering perspective is the useful capacity, which is based on the practically reversible amount of hydrogen. For hydrides, this quantity is largely determined by the shape of its pressure-composition isotherm at a specified temperature (see figure 4.11; emphasizing hysteresis and that the plateaux are often not flat). The isotherm shape will determine the pressure range over which the majority of the reversible uptake will occur. The plateau pressure increases as a function of temperature. Obtaining a material with a high reversible capacity within the designated operating limits, means finding parameters that tune the conditions at which hydrogen is released (and how much of it), ideally, without incurring a significant penalty on other attributes.

The most important indicator of a material's practical capacity is its enthalpy of formation/decomposition. As noted in [96, p. 135], for a hydride material with an equilibrium pressure of 1 atm, a 10 kJ/mol H2 variation in ΔH results in about an 80 K change in the decomposition temperature. Below I list a number of approaches by which to tune (reduce) the reaction enthalpy, and that means reducing the decomposition temperature. Furthermore, reducing the activation energy is also important to reduce the hydrogen release temperature.

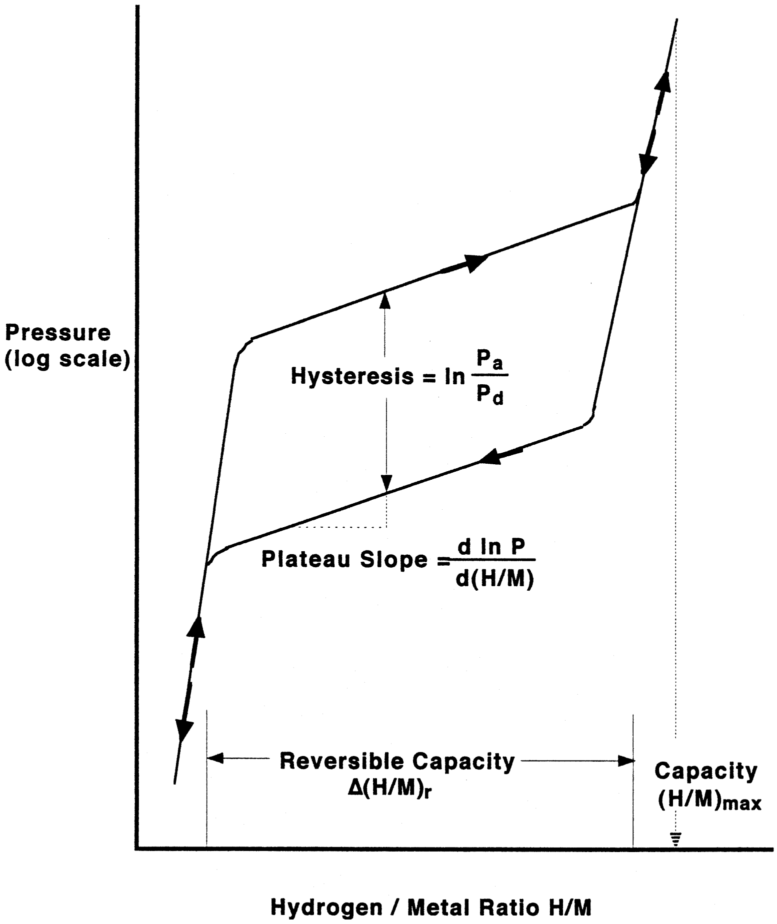

Figure 4.11: General form of a pressure-composition-isotherm (PCT plot) for hydriding metals. *Source*: [134]

The first example of a parameter for reducing the decomposition temperature concerns substitutional elements. The logic working behind this approach, at least for certain materials, is as follows. The bonding character and properties of complex hydrides consisting of alkaline metal and [BH4]$^{-1}$ or [AlH4]$^{-1}$ is related to the strength of ionic interaction between the metal cation and the anion. Hence, the decomposition temperatures of such complex hydrides are explained to a large degree by the difference in electronegativity between the cation and the boron and aluminium. Correlations between decomposition temperature and Pauling electronegativity of the cation are depicted in figure 4.12. Following such consideration, there have been proposals to destabilize the hydrides by using substitutional elements to suppress the charge transfer, e.g. as in $Li^+ \rightarrow [BH_4]^-$[164]. (Theoretical calculations have indicated that this tendency can be applied also to other borohydrides with alkaline-earth metals or some of the transition metals [112].)

As an example, Wang *et al.* [164] report on a study proposing an anion-doping approach for tuning the thermodynamics of LiBH4 and related complex hydrides. In this study, first-principles calculations suggested that doping LiBH4 with fluorine (F) may generate F^- (i.e. anion) - substituted hydride lattices in both the hydrogenated (LiBH4) and dehydrogenated (LiH) states. Apparently entailing a favourable thermodynamic modification. Moreover, it is stated that this improvement is obtained without a significant capacity penalty. Convincing experimental evidence is still required.

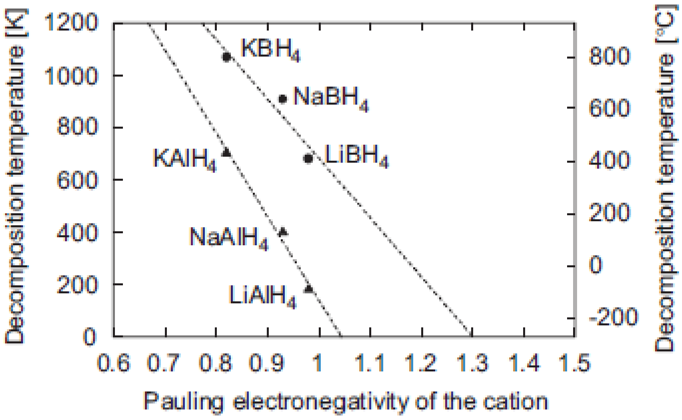

Figure 4.12: Relation between decomposition temperature and the Pauling electronegativity of metal cations in various complex hydrides. *Source:* [112]

Another possibility for affecting the thermodynamics is through dilution of an appropriate additive [31]. For instance, it is observed that titanium acts not only as a catalyst in alanate systems, but adds an enthalpic contribution in the sorption reaction [31]. By tuning its dilution one can change the plateau pressure of the system at a given temperature. Other additives are possible also, as described in [31]: "*Other additives which have the same effect could also be used for this purpose* [the means of adapting the hydrogen pressure achieved at a certain temperature], *as has been shown in the case of magnesium addition to LiBH4, which changed the free enthalpy by about 25 kJ/mol H2 due to formation of MgB2. However, this was at the expense of a strongly reduced storage capacity.*"

An enthalpic driving force may also be supplied through the addition of extra (e.g. hydride) components to the material storage system. Parameters for this approach exist for the types of constituent compounds and their mixing ratios. Altering the mixing ratios will result in different dehydrogenated states [84]. Destabilization, by adding a second, or sometimes a third component to a hydrogen storage material, occurs by opening up new reaction pathways with a different thermodynamics [48, 169]. One example is the addition of MgH2 to lithium borohydride:

$$2LiBH_4 + MgH_2 \rightleftharpoons 2LiH + MgB_2 + 4H_2 \tag{4.2}$$

In this example the additional enthalpic driving force occurs through the formation of MgB2. The result is a reduction of the decomposition enthalpy of the system of about 25 kJ per mol of H2 relative to pure LiBH4 [48]. Note, some such reaction schemes incur penalties in terms volatile reaction products, reversibility, and/or kinetics. Figure 4.13 shows the effects of adding reactive components on the decomposition temperatures for various systems.

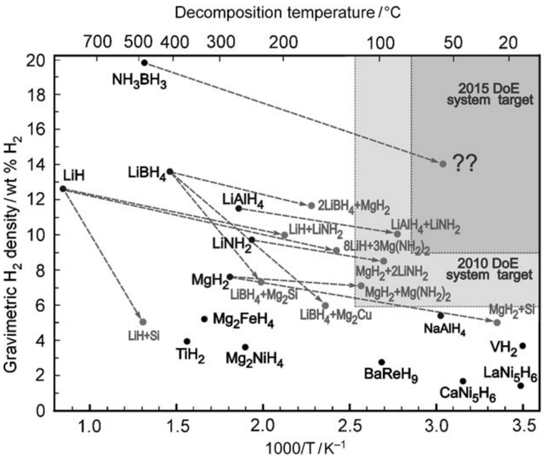

Figure 4.13: Effects of reactive components on the decomposition temperature of complex and metal hydrides. *Source*: [100]

A different approach using the LiBH4/xLiNH2 mixture is to produce a quarternary Li-B-N-H crystalline hydride through mechanical milling or heating [164]. One can parameterize the composition of this new hydride through the molar ratio (x) of the starting mixture. While these quarternary hydrides exhibit markedly decreased thermal stability compared to LiBH4, they are precluded from practical use (at least in vehicular applications) while they suffer from thermodynamic irreversibility as well as the problematic release of NH3 [164].

A final parameter I describe that seems promising for reducing decomposition temperatures is a nanostructuring approach (i.e. reducing the particle size of the material, and possibly its shape etc.). One example concerns nanoconfinement. This approach allows for tunable parameter states of the nanostructured material through different structure-directing agents, including nanoporous aerogel and acitvated carbon [164]. For example, nanoconfinement in porous carbon has shown reduced desorption temperatures for magnesium, lithium, and sodium borohydride compounds than their respective bulk compounds [112]. More specifically, it was shown that the pore size was the a processing parameter by which to reduce the desorption temperature; the smaller the pore, the more significant the reduction in desorption temperature [112]. Moreover, LiBH4 confined in 13 nm pores dehydrogenated up to 50 times faster than the non-confined material [112]. As reported in [164], yet another potential benefit of nanoconfinement is better cycling performance by inhibiting degradation of the host material during hydrogenation state transitions. Figure 4.14 gives an example of the thermal stability reducing nanoconfinement effect using an activated carbon structure-directing agent.

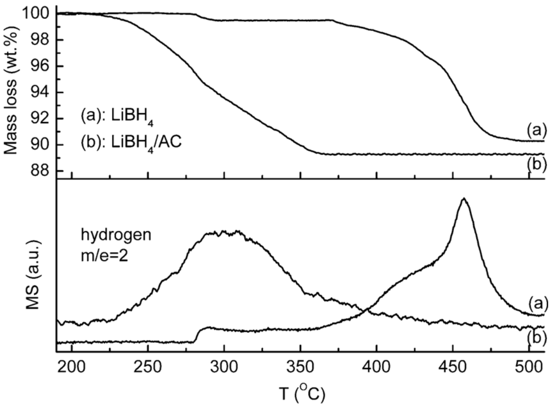

Figure 4.14: Nanoconfinement effect on thermal stability by reducing LiBH4 particle size in an AC nanocomposite. Thermogravimetric (TG)/mass spectroscopy (MS) results of the LiBH4/AC nanocomposite and pure LiBH4 are shown. Heating rate was 2 °C/min. *Source*: [164]

A different potential nanostructuring benefit, e.g. through ball milling (which reduces the particle size, and hence, increases the surface area, affecting the thermodynamics), is the reduction of activation energy. Other nanostructring methods have been experimented with also, e.g. hollow nanospheres of lithium imide (Li2NH) synthesized through a plasma metal reaction [129].

Safety: Parameters to change response to air and moisture contact With hydrogen release being an endothermic reaction, there must be a constant supply of heat to release hydrogen. Under normal circumstances, with operating temperatures not significantly above the desorption temperatures, the pressure build that would result from uncontrolled hydrogen release would pose no risk. However, if there was a temperature excursion, e.g. in a fire, there could well be a risk of substantial pressure build ups.

Safety concerns for hydride based storage systems is primarily related to issues of reactivity. For example, NaAlH4, especially when loaded with titanium, is a very reactive solid which can ignite with air or moisture [137]. One strategy that has been thought of to reduce this problem is to encapsulate the material in an inert high porosity solid. As explained in [137], this keeps the hydride in a distributed form such that local temperature excursions do not immediately lead to a runaway of the reaction.

Parameters for affecting the rate of sorption There are two main approaches to finding improved variants in terms of absorption/desorption kinetics. The first I will outline concerns the use of catalysts.

The significance of a simple parameter change, such as employing an appropriate catalyst, is exemplified by the case of sodium alanate. The undoped sodium alanate has very slow release rates, and rehydrogenation is not possible to any appreciable extent under moderate temperature and pressure conditions [31]. A catalyst can increase the reaction rates for both reactions, rendering the material reversible. This discovery by Bogdanovic *et al.* in

1997 had a significant impact and stimulated the search for better catalysts. Ones that have been studied include, titanium compounds (e.g. TiCl3), titanium nanoparticles (colloids), zirconium, iron, transition metal chloride-based materials, scandium, and cerium (note, they don't necessarily have similar effects on different hydride materials). But not just the type of catalyst is important, also the method of doping (controlling for its dispersion), precursors, and particle size can affect the results - hence, the number of possible states for this design parameter is large. Although many dopants have already been screened [137], considering the various possible explorations that exist, e.g. combinations of dopants is also little studied, it means that this search heuristic has not yet reached exhaustion. Furthermore, improved theoretical understanding of the catalytic effects of various dopants would likely support the search effort [137].

The second parameter for improving the kinetic properties of complex hydrides relies on the principle that reduced mass transport distances in a reaction speed it up. Hence, the general idea is to localize the H-exchange reactions of the hydride materials [164], thereby making the main parameter of interest the compartmentalization of the reaction. One way is size reduction to the nanoscale [158]. Another is nanoconfinement, as discussed above. For instance, as to be compared to the catalytic effect, facilitated desorption and absorption has been observed for the pure NaAlH4 when impregnated onto carbon nanofibres [31]. This has the effect of highly dispersing NaAlH4 and thus shortening the diffusion pathways [31]. An interesting example combines the enhancement effects of nanoconfinement and catalysis. It concerns the use of single walled carbon nanotubes incorporated with transition metal nanoparticles which were shown to markedly promote both dehydrogenation and rehydrogenation reactions in LiBH4 [164].

4.4.4 Offsite reversible hydrogen storage materials

The final general hydrogen storage category involves materials which cannot be regenerated onsite using hydrogen gas at "reasonable" pressures and temperatures [96, p. 80]. There are certain material subclasses in this category that I will not consider in this section. One of them involves reformation of hydrocarbons, since this approach necessitates release of the environmentally detrimental greenhouse gas CO2 during the creation of hydrogen. Moreover, the reformation process creates primarily gaseous by-products which are inconvenient to collect for reprocessing [96, p. 80] - thereby complicating the design concept. In contrast, compounds that I do consider comprise material classes that produce condensed phase products following hydrogen release [96, p. 80][79, p. 192]. Many of these materials release hydrogen in an overall exothermic set of reactions sequences (though organic hydrocarbon compounds are a notable exception), and the dehydrogenated products are too stable to rehydrogenate in a practical sense [79, p. 192]. In fact, they typically require considerably complex and energy-intensive processing, which would take place outside of the storage containers, to regenerate the original fuel.

Perhaps the most explored example of an off-board regenerable storage material is ammonia borane (AB, NH3BH3), a molecular solid [79, p. 192]. AB is an example of chemical hydrogen storage materials which are discrete molecular species based on covalent bonding [79, p. 192]. Other prominent examples are alane (AlH_3), and liquid organic hydrogen carriers (LOHCs). Another important approach involves the hydrolytic reaction of complex hydrides such as NaBH4 and LiAlH4.

The requirement for offsite regeneration processes essentially imposes problems on material cost and energy efficiency [164]. On the other hand, this same feature allows for an independent design of hydrogen release and hydride regeneration approaches [164]. The principle of hydrolytic chemical hydrides has proven its worth already in the 1940s during WWII when it was used for generating hydrogen for filling weather balloons [164]. It has also been used for feeding alkaline FC in manned NASA spacecraft [164]. Within the past decade, several organizations have built and tested laboratory prototypes of hydrogen storage/generation systems based on various hydrolysis reactions. A few companies, including Millenium Cell, Incorporated, Jadoo, and SiGNa Chemistry, have offered commercial portable systems for specialty or military applications [96, p. 82].

4.4.4.1 General storage concepts

Both hydrolytic and thermolytic (thermal decomposition) reaction concepts underpin the behaviour of various candidate offsite reversible hydrogen storage materials. One subcategory of the former includes so-called “liquid organic hydrogen carriers” (LOHCs). While, being liquids, they are easily transported and handled, making them an attractive option in a fuel infrastructure (as conventional fuels), they suffer drawbacks for the development of practical devices. These materials store hydrogen in covalent C-H bonds. They are liquid cyclic hydrocarbons that react reversibly with H2 gas at pressures of about 100 bar or lower, albeit at elevated temperatures of 500-600 K in the presence of suitable catalysts [96, p. 81]. At present, these catalysts do not perform efficiently enough. As they cannot satisfy the requirement of enabling dehydrogenation at lower temperatures, an alternative principle is needed to release the hydrogen. In this case, burning portions of the released hydrogen to maintain the reactor chambers at tempertures high enough to continue the dehydrogenation reaction [96, p. 81]. Examples of these liquid hydrogen carriers include benzene/cyclohexane (7.1 wt.%), toluene/methylcyclohexane (6.1 wt.%), and naphthalene/decalin (7.2 wt.%).

Other thermolytic candidates: Materials like AlH3 (alane) and LiAlH4 undergo catalzyed thermal decomposition in an endothermic reaction. On the other hand, materials like NH3BH3, amidoboranes, and numerous other B-N-H compounds (which store hydrogen in covalent N-H and B-H bonds), release hydrogen in an exothermic reaction [96, p. 84]. In both cases hydrogen release produces highly stable products (e.g. Al, BN, etc.) - this calls for sophisticated regeneration schemes. In general, hydrogen release from chemical hydrides proceeds in a stepwise manner, as discrete chemical intermediates are formed at each stage of dehydrogenation [79, p. 242]. The rapidity of the dehydrogenation reaction is highly dependent on the catalyst used. An example is given by the thermal decomposition of AB following three exothermic reactions:

$$xNH_3BH_3(s) \rightarrow [NH_2BH_2]_x + xH_2(g) \tag{4.3}$$

$$[NH_2BH_2]_x \rightarrow [NHBH]_x + xH_2(g) \tag{4.4}$$

$$[NHBH]_x \rightarrow BN + xH_2(g) \tag{4.5}$$

The first decomposition step can proceed rapidly upon melting of AB, and yields ca. 1 equiv. H2 and solid products consisting mostly of polyaminoborane (NH2BH2)x. While the first two equations outline the release steps, as is noted in [164], they oversimplify the actual decomposition process. Indeed, one of the problems with this system at present, is the release of volatile products (the mitigation of which will require a better understanding of decomposition pathways). The last reaction step, resulting in the product boron nitride (BN), requires temperatures in excess of 500°C, and would therefore not be of practical consideration in a storage design concept [164].

A second subcategory of irreversible hydrogen storage materials may be defined by the hydrolysis reaction scheme. The hydrolysis reaction, which involves reacting a component with either gaseous or liquid water (of sufficient purity), can be performed with some metals (e.g. Al), elemental hydrides (e.g. LiH, MgH2, CaH2), complex hydrides (e.g. LiAlH4, NaBH4, etc.), and boranes (e.g. NH3BH3 and NaB3H8) [96, p. 82]. Reactions in which both reactants contribute hydrogen are preferable for their higher yield, though hydrolysis of aluminium powders has been suggested for various systems (including submarines [96, p. 82]).

Many concepts based on these hydrolysis reactions combine the functions of storage, production, and delivery into a single system in which the reactants are kept separate until hydrogen is released [96, p. 82]. As with other materials discussed so far, adequate functioning of this system is controlled with suitable catalysts. The catalysed hydrolysis of sodium borohydride (NaBH4) is by far the most common candidate for hydrogen storage and generation based on the idealized reaction

$$NaBH_4(solution) + 2H_2O \rightarrow 4H_2(gas) + NaBO_2(aqueous) + \sim 300\,kJ \tag{4.6}$$

For a 30 wt.% NaBH4 solution, 6.7 wt.% hydrogen gas is available, neglecting the contributions from the catalysts, excess water to maintain the borate by-products in solution, and the containment and control components [96, p. 82]. Catalytic hydrogen generation (HG) from NaBH4 solution is a complicated process. The hydrolysis kinetics relies on a series of factors, including catalyst, concentrations of components, total amount of fuel solution, apparatus design, etc. [164].

4.4.4.2 Design parameters

Before proceding to discuss various material parameters of interest for the design of chemical hydride systems, it is worthwhile pointing to table 4.1. It contains a number of target levels that have been devised for chemical hydride materials in order to meet DOE system targets. It is interesting as a reference insofar as it offers precise measures by which to evaluate candidate materials, leaving less room for interpretation of what would satisfy system level targets. It must be said though, that these targets do not encompass what would be required/desired for *any* system design. Indeed, for them to have been derived, assumptions regarding the design parameters of other system components have to be made. In other words, a "niche environment" has been preconfigured.

Metric	*Units*	*Performance*	*Notes*
Gravimetric storage capacity	$\frac{g_{H2}}{(g_{H2}+g_{substrate})}$	> 9	Targets ensure that 2010 US DOE *system* targets are met
Hydrogen release temperature	°C	< 150	
Release rate	g/s	> 1.6	
Enthalpy of formation	kJ/mol H2	< 20	This is to ensure easier management of heat that is generated during refuelling
Volumetric capacity	$\frac{g_{H2}}{cm^3_{substrate}}$	> 0.0989	

Table 4.1: Performance levels targeted in the design of chemical hydride materials. Data: [44]

Material form In a chemical hydride system, where the material may have to be moved, the material will likely have to be divided [4, p. 6681]. A system employing a monolithic crystal is difficult to conceive [4, p. 6681]. Different form parameters being considered include: powder, closely-packed pellets, and single compressed pellets. The material form is an important parameter because it not only affects the ease with which the material may be moved, but it also determines performance in terms of volumetric density - the amount of void volume in a bed may make up a significant share of the total volume depending on the form (e.g. the void fraction of a powder bed is approximately 0.6).

Parameters for increased solubility For liquid solutions, there is a volumetric penalty to the capacity associated with the solvent volume, and a gravimetric penalty for the solvent mass [4, p. 6680]. The solubility of a material in a given solvent is therefore an important parameter (see figure 4.15). For instance, the limited solubility of AB in water is insufficient to meet the gravimetric density targets for transportation applications (~ 5 wt.% hydrogen capacity for a 26 wt.% solution at room temperature [164]). Alternative variants of hydrogen rich compounds that are more soluble in water than AB have thus been proposed [164].

For the final analysis, solubility and material capacity are not the only important parameters: the contribution of hydrogen from the solvent, such as from water in the hydrolysis reaction shown in equation 4.6, is a further consideration in order to maximize the capacity of the system.

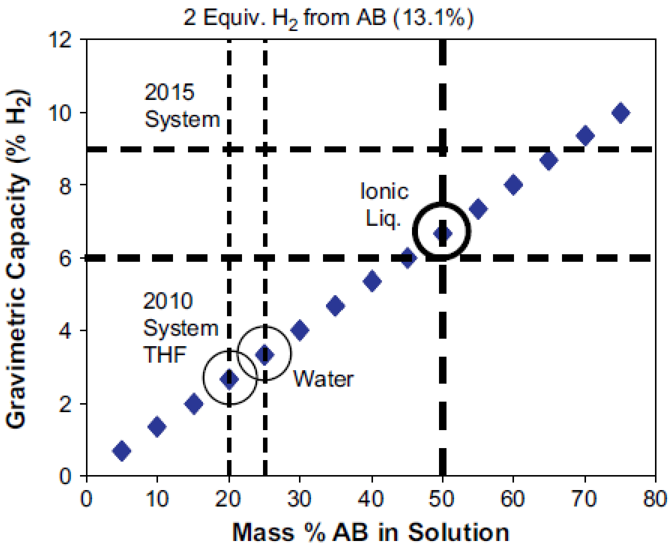

Figure 4.15: The relation of solubility of AB in different solvents (showing THF, Water, and an Ionic liquid) and the solution's gravimetric capacity (in terms of two equiv. hydrogen evolved from AB). DOE targets are given for reference. *Source:* [4]

Parameters for controlling the rate of hydrogen generation and extent of hydrogen release in hydrolysis reactions A control function implies that a certain state change (in this case rate change of concentration of hydrogen) may be both increased and decreased. A traditional (power) catalyst would be effective in increasing the rate of hydrogen generation (hydrolysis reactions at ambient temperature can be greatly accelerated using catalysts [164]), however, there would be no mechanism to control the rate. A recent solution involves supported catalysts: Various light-weight materials with relatively high surface area and satisfactory chemical stability have been used as catalyst support [164]. These provide the ability to easily separate the catalyst from the fuel solution, thus allowing for control of the reaction. Furthermore, this added functionality allows for re-usability of the catalyst. For the interested reader, various examples of catalyst support design parameters include: anionic exchange resin bead, honeycomb monolith, nichel foam, metal oxide pellet.

When it comes to the direct action of increasing the rate of hydrogen generation, catalyst type and morphology are important parameters. Favourable morphology characteristics are coarseness and a porous surface [164]. An illustration of the effect of morphology on the reaction rate in an aqeous NaBH4/NaOH solution is given in figure 4.16. Performance of the catalyst may be measured by its effect on either the hydrogen generation rate or apparent activation energy.

As seen in the AB system, the choice of catalyst is not only important for tuning the release rate, but may also impact on the extent of release, thereby positively affecting the gravimetric capacity of the system [164]. Different catalysts tested on the AB reaction include: Pt and Rh (among the noble TM species), Co, Ni, and Fe (among the non-noble TM species), and acid catalysts.

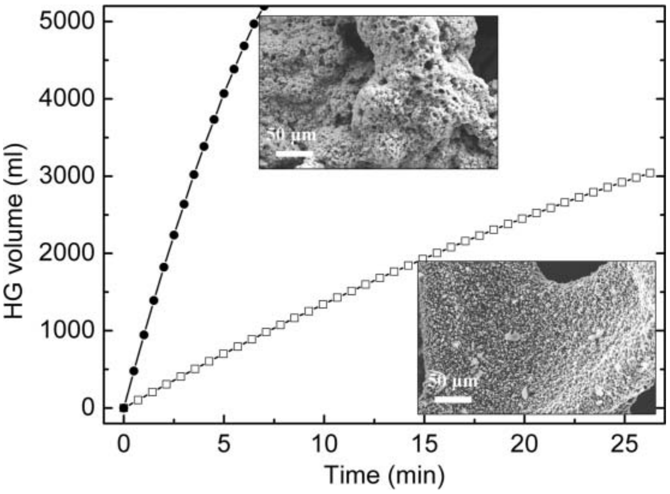

Figure 4.16: Effect of catalyst morphology on reaction rate: Hydrogen generation (HG) kinetics profiles of 20 wt.% NaBH4 + 10 wt.% NaOH solution at 30 °C in the presence of Co-B/Ni foam catalysts that were prepared by conventional (□) and modified ("EP") (●) methods, respectively. The insets show the SEM morphologies of the catalyst samples. *Source:* [164]

It is noted that the use of catalysts is more constrained in combination with solid chemical fuels. This is because the catalyst would have to be incorporated into the fuel formulation, leading to greater reaction rates at lower temperature and greater fuel instability in the storage tank [4, p. 6680].

Fuel stability For the NaBH4 system an alkaline stabilizer is added to ensure fuel stability [164]. Fuel stability is a requisite for safe storage of the fuel [164]. According to the literature, the NaOH stabilizer may affect the solubility of NaBH4 in water, and may also have an effect on the hydrogen generation kinetics [164]. This is an example of coupling: the stabilizer interferes with the function of the NaBH4 solution to provide a dense containment of hydrogen (energy), and with the parameters responsible for the kinetics of hydrogen release.

A different problem of stability is encountered in thermolosis of AB (indeed, aqueous solutions of AB are highly stable under an inert atmosphere). In a pure phase, AB melts at ca. 100°C and thereafter, in conjunction with hydrogen release, it foams considerably [44]. Certain additives (e.g. methylcellulose) may be added to the system to reduce the foaming [44].

Parameters affecting the release of volatile products Thermal decomposition of AB has the problem of producing volatile products, in particular borazine, which is poisonous for the fuel cell. A solution to it may be a method of confinement, the effect of which is to reduce the release of volatile products. Indeed, measurements show that confinement acts not to trap the borazine but to alter the decomposition pathway [164]. The effect of a specific parameter in reducing borazine formation, a mesoporous silica (SBA-15), is shown in figure 4.17. This graph also shows, through temperature programmed desorption mass spectroscopy (TPD-MS) measurements, that confinement reduces the onset temperature of decomposition by reducing the activation energies (from 184 kJ/mol in the bulk to 67 kJ/mol in the SBA-15 material [164]).

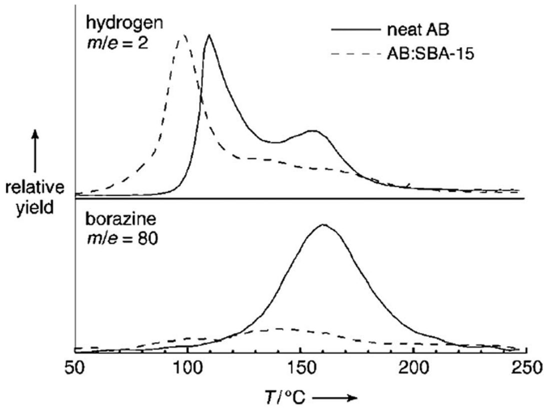

Figure 4.17: TPD-MS (1 K/min) measurements of AB nanoconfined in SBA-15 compared to neat AB. Observations show reduction in onset H2 decomposition temperature and reduction in borazine formation. *Source*: [129]

4.5 Discussion and conclusions

This chapter has outlined general assemblies and specific components that one may expect to find in different types of hydrogen storage system designs. Note, while I refer to *general* assemblies, they will exist in different variations that suit some materials better than others.

The discussion of the system context has emphasised the importance of various material properties (e.g. packing density, thermal conductivity etc.) that are often neglected in basic research. It is understandable that issues pertaining to scaled up materials - such as thermal conductivity - that are designed for practical operation are not always the focus of basic research (e.g. whose interests might lie more with understanding inherent kinetic mechanisms). There is presumably a belief that many such “problems” can be engineered out of the way, whereas various other material properties represent absolute constraints. On the other hand, due to interdependencies among the design parameters (c.f. chapter 3), “transfering” the solution to a particular problem might be associated with a conflicting constraint rather than eliminating the problem all together. I give an example below.

As described in [96], an important engineering model has been derived that relates material properties with parameters of a heat exchange system. Specifically, the model shows the relation between the following measures [96]:

- $\frac{\Delta m_{H_2}}{\Delta t}$, rate of hydrogen absorption by the material (one of its functional performance metrics),
- $\frac{1}{L^2}$, a key parameter that describes the heat exchange sub-system where L = characteristic length between heat transfer components,
- k, the material's thermal conductivity,

- M_{Hyd}, the mass of the hydride,
- ρ_{Hyd}, the density of the hydride,
- M_{H_2}, the molar mass of hydrogen,
- $\Delta H_{overall}$, the total enthalpy of absorption, and
- ΔT , the temperature difference allowable in the media to meet the absorption target.

The relation goes as [96]:

$$\left(\frac{1}{L^2}\right)\left(\frac{kM_{Hyd}\Delta T}{-\Delta H_{overall}\rho_{Hyd}}\right) = \frac{1}{mM_{H_2}}\frac{\Delta m_{H_2}}{\Delta t} \tag{4.7}$$

This relationship implies that the material's behaviour in transferring heat, defined in terms of its thermal conductivity, is an important consideration in choosing the parameter L of the heat exchange unit in order to achieve a target rate of absorption. In particular, for a given rate of absorption, increasing the media's thermal conductivity allows for more space between the heat transfer components. This in turn means less mass and cost. By extension, a material with better thermal conductivity would enable better performance on other system functions that depend on system mass (e.g. providing acceleration). By contrast, materials with poorer thermal conductivity may be employed if the heat exchange system has a tighter characteristic spacing, but this solution to the heat transfer function would entail a conflict with functions that depend on mass.

To be sure, detailed analyses into questions of design constraints are beyond the scope of this PhD. My aim was merely to illustrate the importance of a system's perspective in assessing the fitness of material concepts. Indeed, since radically different materials are likely to be used in very distinct "niche environments", comparing their fitnesses on a material basis is to some extent nonsensical (though rough comparisons can provide a good intuition for experienced designers). Fitnesses may be compared more sensibly for materials competing for the same niche. The implication is that the competition between radical variants depends not only on the material properties, but also on what kind of niche structures are more likely to emerge.

To conclude, the perspective presented has illustrated key challenges facing competing hydrogen storage concepts, but that this competition is not to be understood in terms of a simple analytical comparison. This perspective teaches us that the prospects of a material depend on the formation of numerous layers of enabling conditions. While the search for the "elixir" is not wrong, it is the system that counts. That said, there are fairly clear directions of improvement for the different families of hydrogen storage materials.

While this chapter entailed a small review of hydrogen storage search heuristics, the next chapter extends the focus - in a particular sense - by looking at an abstraction of the many lower level heuristics. The talk is of characterizing a history of hydrogen storage development. I construct this characterization by considering the anticipations/perspectives of researchers in the field. This task aims to address the relation between progress and the anticipation of progress.

5 On the history of state-of-the-art hydrogen storage materials

5.1 Introduction

The exploration phase of technical development is a very uncertain one, and there is typically a keen competition among the proponents of different strategies. Amidst the evolving profusion of future-oriented claims, it is pertinent to ask; what has been the connection between such anticipations and the pattern of progress that has in fact emerged?

The aim of this chapter is to describe an historical sequence of state-of-the-art (SOTA) hydrogen storage materials. I thereby hope to provide perspective on a general history of hydrogen storage research, and characterize the nature of progress. My methodology follows from an earlier attempt in which I experimented with an alternative notion of SOTA that I had discovered in the field of technometrics (e.g., see [40]). In this experimental study, I defined SOTA strictly in a performance sense. While there was an obvious lack of data quality (in part, due to a lack of consistent reporting of data), a rather convincing finding emerged. The general picture was that the rate of progress, in terms of the adopted formal definition of technological status, has been minimal if not negative. While representing an interesting talking point in itself, the finding also suggested to me that a strictly formal interpretation of SOTA - with respect to a set of performance characteristics - is an inappropriate concept for describing the nature of progress during the exploratory phase. Indeed, the technology does not yet have to perform, it is merely an idea in action. Hence, it seems plausible that the criteria by which a technology is judged are less standardized.

The approach that I eventually adopted was bourne out of the lessons from this earlier finding, and insights that are home to the sociology of expectations (see section 5.2). In it, I take SOTA to be a subjective concept (I define the concept of SOTA below). I construct the historic narrative from both quantitative data on key variables that characterize the performance of hydrogen storage materials, as well as a qualitative analysis of expectations related claims found in relevant papers in the hydrogen storage literature. While cautious of overstating what can be said from the data, I attempt to rationalize the sequence of changes in the SOTA. For instance, are changes prompted by new discoveries with remarkable properties, or are they perhaps preceded by modified selection pressures? Due to challenges in data collection, this study is based on a very limited sample size. Thus, it is hard to make a case for any underlying patterns that are detected. Nevertheless, the data is illustrative of some basic points, and in the least, it raises interesting questions with regard to development and progress in hydrogen storage research.

The remainder of this chapter is structured as follows: In section 5.2 I give a general introduction to the role of expectations in technological development. As the notion of "expectation" forms the basis of my interpretation of SOTA (discussed in section 5.3), this will provide a background to what is a key analytical perspective adopted in this study, as well as a reference for interpretation of the data. In section 5.4 I outline key considerations in the data collection, and in section 5.5 I present my results. Finally, I draw conclusions in section 5.6.

5.2 An introduction to the role of expectations in technological development

Expectations are fundamental to the process of technological development. New technologies take time to be realized/developed, and until such time, they serve no purpose, and they return no profits - they are merely ideas of a principle in action. The development process (which does not in itself benefit the developers) is premised on anticipatory behaviour (or expectations); that actions to achieve a particular design principle will yield a profitable product.

Expectations are associated with a degree of belief/uncertainty/probability. Moreover, one may conceive of a set of alternative expectations (or forecasting models/schemata) that compete in their predictions of which actions will lead to a particular outcome. Each schemata is given a rank (e.g. based on probability) and the one with the highest rank is the one currently adopted. The ranks may change, depending on either past performance on predictions, or other influences, e.g. an influential spokesperson, research results, findings in other technical fields, successful commercialization, and external trends and forces [160]. The fact that behaviour is very much connected to expectation, suggests that studying them would be helpful in understanding the social factors that drive technological change. Indeed, a "sociology of expectations" has developed to study their role in innovation. Below I summarize a number of relevant insights.

5.2.1 The promise-requirement cycle

In technological development, expectations are often made formal, e.g. through the construction of performance requirements that are specified as the objectives of development [159]. In social studies, it has been observed that taking this step is double-edged. On the one hand the formalization of targets helps to generate resources, and focuses and coordinates activities towards their realization. On the other hand, there is pressure to achieve the targets, for if they are not met, then this may lead to what are referred to as "negative expectations" in [159]. I interpret negative expectations as a lowering in the ranking of (or belief in) expectations that predicted a particular agenda (or plan of action) would lead to a desired outcome, thereby opening up opportunities to competing expectations (whose ranking will correspondingly increase). Expectations may be maintained (and elaborated upon) when a new technology is developed which satisfies all desiderata. According to [159], these elements form part of a cyclic process, called the promise-requirement cycle, shown in figure 5.1. In this depiction, the promise represents a highly-valued expectation and the niche represents a “protected space” for developmental work.

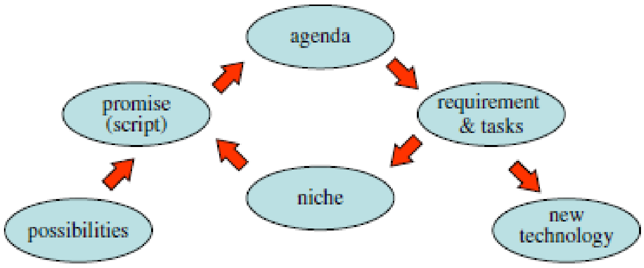

Figure 5.1: The promise-requirement cycle concept. *Source:* [159]

5.2.2 Self-fulfilling prophecies

The broadcasting or circulation of expectations (or claims about actions and consequences) is an important element in understanding how expectations become accepted propositions by individuals. As van Lente explains, voicing expectations may stimulate (or build interest among) other actors and coordinate their actions [159]. Coordination can be achieved when expectations are common reference points for actors in different communities or different levels of technology development [21]. It is interesting to note that this enables coordination of a community to emerge in a decentralized manner: by making expectations public, agents are signalling (broadcasting information on) their courses of action. This information is then processed by other agents who adjust their behaviours in order to align the desired outcomes (which may themselves by adjusted) of their actions. As noted in [160], particularly in the early stages of technology development, this dynamic plays a crucial part in defining roles and coordinating the dependencies within a network of actors (e.g. constructing mutually binding obligations). Often there is a strategic intention behind making expectations public, e.g. to entice new actors to “enrol” in a particular agenda. The fact that expectations may encourage action that works towards realising them has been seen as a dynamic of self-fulfilling prophecies [70]. The computer scientist Alan Kay coined the tech-world adage *“the best way to predict the future is to invent it”*[1]. The phenomenon of self-fulfilling prophecies suggests that a good way to invent the future is to predict it.

5.2.3 The credibility of expectations

Fundamentally, for research initiatives to be initiated (selected), it takes an environment of credible and optimistic expectations. Interestingly, as discussed in [67], optimism typically runs deep for researchers that are on the “inside” (often they even exhibit overconfidence [92], perhaps a necessary illusion for uncertain projects to go ahead). This contrasts with selectors of research programmes. They adopt more of an outside perspective in that they

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[1] Source: *http://en.wikiquote.org/wiki/Alan_Kay*

have the freedom to take a comparative view of different research agendas (insiders will be more committed to one particular agenda, i.e., in a sense they have already made their selection). While an inherent optimism will tend to drive the activity of researchers on the inside, for projects to be funded etc. in the first place, technological promises must be argued convincingly on the variables considered relevant to these outsiders (this issue is discussed more thoroughly in terms “framing” in [67], a useful theoretical background to which can be found in [154] and [92]). As argued in [67], such variables often pertain to broader questions, e.g. questions about the effects on society at large.

Expectations are mostly interlinked with further expectations, or they are hierarchically structured. Hence, the credibility of individual expectations is often dependent on the credibility of others. For example, one popular argument used to promote solid-state hydrogen storage research agendas is that physical containment solutions have no chance of meeting the long-term targets [21] (see section 2.3.2.4). This argument partly rests on the premise (or credibility of the expectation) that those targets are reliable guides. Seen more broadly, this expectation is contained within the expectation that hydrogen will play an important role in the future energy system.

5.2.4 Patterns of expectations

Studies have suggested that changes in innovation activities can be traced back to changing expectations [37]. Similarly, there are claims [70] that the stability of a technological trajectory is associated with shared and stable expectations, with changes in direction being preceded by a change in the content of expectations. This might suggest a rationale for measuring expectations to assess the near-term future of technological development. However, a limitation is imposed by the fact that the temporal dynamics of expectations are often more erratic than those of activities [37]. Nevertheless, such measures have been useful in showing that emerging technological fields often display characteristic expectation dynamics[2]. A typical pattern is that of alternating cycles of hype and disappointment [9, 69]. Another concerns changes in the nature of expectations over time: they go from being more general to becoming more specific, and from having a long-term focus to emphasising the short-term [9] (as might be expected).

5.2.5 Expectations and technology selection

S. Bakker *et al.* argue in [22] that during the exploration/development phase of technology, selection pressures (in terms of acting on performance and price properties) do not, for the most part, come from end-users; the technology is not yet well established and the market does not yet exist. It is true that often a considerable amount of judgement is required to assess whether a new product will satisfy the needs of the customer (indeed, even surveys of how customers expect to feel about a new product are often not a good predictor [57].

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[2] “Expecation dynamics” is apparently a technical term for patterns of expectations that are expressed about a technology over time [9].

The conditions or niche of the new product are often difficult to anticipate). In that sense one may appreciate that only when the market is very well understood, can one speak of the customer in effect exerting the selection pressure.

As the technology is also not well established early in its development, and its eventual performance is uncertain, it raises the question as to the importance of performance in pre-market selections. Clearly, at some point (around the time of launching the new product) a technology will have to be judged on its profit-making potential, and hence its price/performance characteristics. Before this time however, there is another important consideration that selectors (designers/developers) have to make, namely, they have to judge the technology's expected performance. Expected performance is not a single, measurable property of the technology (although things like 'length of time in development' are likely to be important factors). In fact, while objective properties are likely to inform such expectations, they are ultimately inherently subjective. Therefore, to better understand the selection pressures during the era of ferment, involving intense competition among alternative designs, it would be necessary to investigate the key factors that inform such judgements. In table 5.1, I reproduce an overview given in [22] of factors relevant to selection in different kinds of design competition (of particular relevance here is the third column). Clearly, in order to attempt an assessment of the near-term selection prospects of a technology, the information in this table is too vague, and it lacks an indication of the relative importance of different factors. However, in the context of judging changes in the state-of-the-art, it may be useful in suggesting where to look for possible reasons.

Phase	Successive dominant designs in the market	Dominant design in new product class in the market	Pre-market emergence of dominant design
Selection criteria and mechanisms	Superior performance and price	Superior performance	Promising breakthroughs in performance
	Compatibility with existing dominant design	First to market or initial (niche) market leader	Regulation
	Regulation	Network externalities	Organizational support
		Strategic manoeuvring	Strategic manoeuvring
		Standardization and regulation	Demonstration of technical feasibility in a prototype

Table 5.1: An overview of selection mechanisms according to dominant design theories. *Source:* [22]

5.3 Interpretation of "state-of-the-art"

The term "state-of-the-art" (SOTA) is a familiar one in public discourse on technology, though it generally lacks precision [75]. In general, it is associated with some distinguished state of a technology. One interpretation, giving a formal, quantitative measure of SOTA, is presented in [75]. To give some context, the paper reports on research conducted by The Futures Group designed to explore conventions for describing the technological SOTA of essentially any technology. One of the proposals put forward is represented by equation 5.1. The following terms are included: n is the number of parameters - or measures of performance - included in the analysis, P_n is the instantaneous value of the n^{th} parameter, P'_n is a reference value of the n'th parameter, and K_n is the weight - that is, the relative importance - of the n'th parameter[3]. If $P_n \leq P'_n$ and the values of K_n sum to 1, then the value of the state-of-the-art index will also lie between 0 and 1. Hence, the current state-of-the-art of a technology - the technology with the highest index value - may be reported in terms of its proximity to some reference[4]. Note, the equation represents one of two forms: a multiplicative version (the one presented), and a linear weighted sum. The multiplicative version applies to cases in which *one* parameter must be present to some degree, or the state-of-the-art is zero (an example given is that of an antibiotic being able to kill selected micro-organisms - this, after all, is its main function or purpose) [75].

$$SOTA = \frac{P_1}{P'_1}\left[K_2\frac{P_2}{P'_2} + K_3\frac{P_3}{P'_3}\ldots + K_n\frac{P_n}{P'_n}\right], \tag{5.1}$$

The interpretation of SOTA represented by equation 5.1 is quite intuitive as it measures the excellence of a technology in achieving its objectives. Therefore, would this be an appropriate measure to employ in this study? I believe, that during the exploratory phase of technological development, its interpretation for representing the SOTA is problematic. For one, the niche environment for each hydrogen storage concept is likely to vary, and is not even well defined in most cases. Performance should rightly be defined with respect to achieving the objectives implied by a specific niche, therefore, it would seem inappropriate to use the same reference values of the parameters for different concepts. Secondly, we might expect that the SOTA value would monotonically increase with time. However, during the exploration phase, it may be that an "inferior" design is adopted instead of a currently better performing alternative, because it is believed to hold out more potential.

These caveats suggest that this interpretation of SOTA may be inapplicable to the invention process. While running the risk of stretching its usual interpretation, I propose to use the concept of SOTA differently in this study. The interpretation I propose associates the status of a technological concept (in this case classes of hydrogen storage materials) with the relative degree to which an avenue of exploration is expected to be fruitful. This

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[3] The weights for each proposed parameter are assumed to be unity, are assigned judgementally, or are estimated statistically [75].

[4] "Reference values for each parameter must be provided: these reference values can be the ultimate limits that the parameters might achieve, given some kind of physical boundary, or the value of the parameter at some previous or future time.Where the value of the parameters at some prior or future time is used, the state of the art is, in effect, indexed to that time." - [75]

"degree of expectation", in turn, is interpreted as follows: I assume a set of agents (researchers/designers) who are involved in the development of hydrogen storage materials. Each agent has an ordered set of expectations about the potential associated with various avenues of exploration represented by key material concepts. The ordering/ranking is determined by the probability, or degree of belief, that the agent attaches to each expectation.

These rankings are subject to change, for instance, as described in section 5.2, due to research results or to changing expectations of requirements etc.. The state-of-the-art in a technological domain is given by the concept with the highest global rank - that is, the highest aggregate score when considering all agents' expectations in the research community. According to this interpretation, the history of SOTA hydrogen storage materials may be viewed as a history of the most highly anticipated storage concepts within the research community. To be sure, there may be a range of disparate views on an individual level. Moreover, global expectations may even be associated with low degrees of belief, as long as they are high relative to expectations referring to other *available* concepts. Given the initial fluidity and uncertainty of notions such as performance or the niche, basing the interpretation of SOTA on the perceptions of technology developers (enactors), well positioned to judge the quality of an infant technology, seems to be appropriate.

In order to reveal the pattern of performance in SOTA hydrogen storage materials using this interpretation, the next step is to figure out how to identify those materials in the first place. While the above description is how I *formally* interpret the state-of-the-art, its practical identification is a different matter. Unfortunately, it relies on much speculation. I outline my approach in the next section.

5.4 Data collection

This study was based on the following data collection steps: (1) identify an initial list of SOTA materials, (2) refine the list based on supplementary data and judgement, (3) identify claims that either give support to, or reasons for changes in, SOTA status, and (4) identify representative variants of the reduced list of SOTA materials and compile performance data on key variables.

Based on the interpretation of SOTA put forth in the previous section, the main challenge was to identify the materials to which the highest aggregate expectation scores were attached during a specific time period. Because I am relying on expectations that are codified in written claims, a substantial degree of interpretation was involved. I tried to evaluate claims based on the context in which they were made, and by comparing them to other claims. I speculated about the proportion of researchers that might share similar expectations based on a variety of, potentially flawed, cues. The cues I was looking for are ones that suggest a material was broadly popular, and was considered to have promising advantages over competing designs. For example, an important cue was the frequency with which a material was mentioned in review papers (or simply claims that were made of popularity). Or whether a material was mentioned in connection with offering a promising solution to a pressing problem that was felt. Claims that focus retrospectively on limiting drawbacks are sometimes uninformative, because they argue with the benefit of hindsight, and do not necessarily reflect the perspectives that were prevalent at the time. Ultimately, I made a judgement about the state-of-the-art for a given time period. Because I gather much of the information from review style papers, it is quite possible that there is a time lag in some of the SOTA selections I have made.

The final selection seems founded on quite uncertain terms. For example, it is likely that many claims arise out of a degree of bias (e.g. overconfidence [92]), which is difficult to identify. However, there is perhaps some defense for my selection given by other compilations of important materials in the history of hydrogen storage. This corroborative evidence is presented in section 5.5.3. While I try to draw conclusions from the final SOTA selection, I note that the sample is small, and that some observations may be based on noise.

In order to gather performance data, it was first necessary to identify suitable variants that represented the SOTA. SOTA claims were often relatively vague by referring to material subclasses (see section 4.3) rather than specific examples, thus I had to choose particular variants (e.g. choice between an experiment performed with a catalyst or without) and ensure that data was available. This choice was an important step given that performance can vary significantly between variants. The variables that were chosen to represent performance were *reversible gravimetric capacity, reversible volumetric capacity, operability* (or *enthalpy of absorption*), and *sorption rate.* Initially, I intended to collect quantitative data on all four performance variables. It was soon realized however, that sorption rate couldn't be reliably compared quantitatively.

Sorption rate may be defined as the rate of change of concentration for reactants and products in the hydrogen sorption process (absorption or desorption). The rate of the chemical reaction depends on several factors. Factors that may be controlled for different kinds of reactions (i.e. that are not intrinsic to the material) include reactant concentration, the physical state of the reactants (rates scale with surface area), temperature etc. [79, p. 119]. It turns out that heat transfer and thermal effects dominate rates for nearly all reactions in hydrogen storage measurements. The temperature of sorption/desorption is the most influential variable in hydrogen storage kinetics for both chemisorbing and physisorbing materials [79, p. 124]. Now to ensure a fair comparison of sorption performance across different materials, one ideally requires similar experimental conditions. Therefore, other variables aside, one requires at least similar thermodynamic perturbations from equilibrium for the duration of the sorption measurement. Unfortunately, the ability to control temperature is fairly limited in systems with poor heat transfer and fast kinetics [79, p. 124]. The heat generated or taken up during hydrogen-substrate interactions can cause local temperature excursions that profoundly affect rates. But heat transfer is not the only challenge. In general, it is concluded that comparisons between measurements with different experimental equipment, different experimental conditions, different sample shapes, sizes, morphology and composition are difficult if not impossible [79, p. 142]. Yet even if it was possible in principle, there would be no available data based on matching experimental set-ups for precisely the selection of materials I have made.

An alternative mode of comparing kinetic performance was to consider a material's intrinsic kinetic character. A number of different intrinsic properties of a storage material may control kinetics including surface interactions, transport phenomena, hydrogen-substrate storage mechanisms and phase change [79, p. 123]. The kinetics in metal hydrides can be modelled by the relation $\frac{dC}{dt} = K(T)F(C,P)$, where K(T) is the temperature-dependent rate constant, and F(C,P) is a function dependent on the hydrogen concentration in the material C and gas pressure P [79, p. 135]. Certain parameters of the function F could be used as a proxy for performance comparisons with other metal hydrides. However, it is not easy to perform measurements to accurately determine the potential intrinsic rate-controlling mechanism [79, p. 124], and, for a wide range of hydrogen storage materials, there exist few reliable models of their intrinsic kinetics [34].

As a consequence of the above considerations, I decided to restrict myself to a qualitative assessment of sorption performance. For this evaluation it was helpful to consider, where available, measured sorption rates (by convention typically up to 90 or 95% capacity), and claims that go some way in adjudicating between varying experimental conditions.

5.5 Results and discussion

5.5.1 Contextual developments

The principle of solid hydrogen storage was discovered in 1866, when hydrogen was observed to absorb in palladium [29]. Early applications of the principle of solid hydrogen storage began over half a century ago with materials such as LiH and CaH2 (saline hydrides), which were used as portable means of storing hydrogen for inflating meteorological balloons [78]. The hydrogen was released by reacting the hydride with water, thereby rendering the material irreversible in any practical manner. In 1958 Libowitz discovered the reversible hydride ZrNiH3 [134]. This signposted search efforts to a new class of material for hydrogen storage; intermetallic hydrides, compounds which store hydrogen in interstitial sites. ZrNiH3 itself was thought to be impractical, in part for having a high desorption temperature of about 300°C at 1 atm hydrogen pressure [134].

The class of intermetallic hydrides may be divided into subclasses represented by the generic chemical formulas A2B, AB, AB2, and AB5, in which "A" represents an element that strongly absorbs hydrogen (e.g. Mg, Ti, La), and "B" denotes an element that does not (usually lighter transition metals (e.g. V, Cr, Fe, Co, Ni, Cu, Mn)) [29]. Other classes exist (see [134]), but these have not been the subject of investigation for hydrogen storage. Observations of intermetallic compounds such as LaNi5 and TiFe in the late 1960s (LaNi5 was discovered at the Phillips Research Laboratory [65] while TiFe was discovered at the Brookhaven National Laboratory (BNL) [131]) stimulated extensive investigations on metal hydrides [29], which continued throughout the 70s and early 80s when the BNL conducted an extensive screening program to determine the behaviour of various metals and alloys with hydrogen [138].

Practical AB2 hydrides were identified in the 1970s by groups led by Shaltiel, Gamo, Buschow, Wallace, Reilly, Burnasheva, and others [134]. These groups continued into the 1980s and were joined by efforts led by Kierstead, Bernauer, among others [134]. By the mid-70s an AB hydride, TiFeH2, had been demonstrated as an energy store on an engineering scale and was considered one of the most attractive metal-hydrogen systems for such use [85]. The LaNi5 hydride was also a popular research focus in the 70s, however, the high cost of lanthanum proved a significant drawback [65]. MmNi5 (where Mm is a mischmetal) was developed to mitigate the cost of pure La (toward the end of the 70s)[35]. The tuning of metallic hydride properties (thermodynamics etc.) was largely being approached through alloying, and towards the end of the 70s, alloy hydrides based on compositions such as Ti-Cr-Mn were technologically quite advanced [35]. Although considered otherwise attractive, another class of material, complex hydrides - such as Mg(AlH4)2 [85] or LiAlH4 [131] -, were not generally thought to be viable during the 70s as they did not satisfy the requirement of reversibility [85].

At the time, metal hydrides were considered for both stationary and for mobile applications. In particular, hydrogen was being discussed as a non-polluting fuel [107]. In places, hydrogen was even perceived as a short to medium-term prospect for providing city transport [35]. Its potential in this domain, where special emphasis would be placed on environmentally harmless operation, was justified on the basis that (1) hydrogen could be produced centrally from coal or natural gas at a favourable price, (2) hydrogen engines have particularly favourable exhaust composition, and (3) hydrogen can be stored much easier than electrical energy [35]. At least in Germany, such prospects were the main reason for initiating many fields of hydrogen technology research [27]. In the early phases of hydride storage system development, there was wide optimistic sentiment about the programme's potential. While acknowledging insurmountable deficits to gasoline tanks in terms of energy density, a claim in [131] indicates that hydrides were seen to have the potential of providing a fuel storage system that was "price and convenience competitive". This initial optimism might be understood (at least in part) by the nature of prevailing expectations. Firstly, some search heuristics were tuned to the longer-term:

"If there was a need for a hydrogen storage system to be commercial by 1980, then without doubt the physical storage methods could be engineered into useful vehicles by that date. However, hydrides represent more promising storage methods that have longer term potential [131]."

Secondly, there was uncertainty over goals, and hence scope for basing opportunities on more convincing search heuristics:

"There is at present insufficient experience with hydrogen systems and the gasoline price and supply situation is too unstable, to permit a reasonable estimate of what fuel storage weight and volume handicap is acceptable for a hydrogen system [131]."

One of the main problems that was pursued was to find a metal or alloy that would (ideally) form a hydride with a hydrogen dissociation pressure of about 1 atm at ambient temperatures [131].

Daimler-Benz had already begun testing hydride storage tanks in the early 1970s [27, 52] (Billings Energy Corporation also produced demonstration vehicles based on hydrides in the 70s/80s [161]). The experience with such prototype systems gradually brought into focus the limitation of metal hydride concepts. In relation to the total weight of the storage unit, the hydrogen which could be stored would only amount to about 1 wt.% (hydride capacity 1.8 wt.%) [27], thus severely limiting the travel radius. Alloy hydrides were developed which had very many favourable engineering properties (near-ambient operation (0 - 100 °C, 1 - 10 atm), reasonable thermal conductivity, good kinetic performance, high volumetric density, and good cyclability), however, they were often claimed to be expensive [43], and a growing concern over the limitation of low mass densities eventually led the head of vehicle development at Daimler to conclude that they were too heavy for vehicular use [43, 80]. The 80s thus saw a general decline in the expectations that were attached to metal hydrides.

It should be mentioned that this period also saw high expectations for the concept of liquid hydrogen storage (LH2), as a view expressed in [127] would indicate: “No on-board hydrogen storage option can compete with cryogenic storage.” BMW was a prominent player invested in LH2 technology in co-operation with partners in the cryogenics and gases industry [43]. Indeed, while the rationale for developing hydrides was largely based on overcoming some of the challenges associated with LH2 (such as high cost, low efficiency), realizing that no significant improvements had been achieved on metal hydrides (in a 10-15 year timeframe; expectations for hydrides were not met), many researchers suggested paying more attention to LH2 and addressing the issue of boil-off [43]. Compressed hydrogen technology (CH2) was inferior to LH2 in terms of energy density (and hence in delivering range in automotive applications), though some considered it to be a promising avenue for technological progress [43].

Meanwhile, materials-based hydrogen storage research was diversifying, with options such as glass microspheres, organic liquid hydrides, or cryoadsorption on activated carbons being considered [121]. These options were generally thought less attractive, in part, due to worse performance [161]. For instance, physisorbent materials, for which, during the 80s, activated carbons were the main promise, suffered from low capacities [121]. To address this issue, search was focused on the parameters of surface area and chemical modification of surface properties [121]. Another reason why expectations may have been lower for such materials is due to a lack of attention [121] - quite conceivably, the level of expectation is related to the amount of activity in a search area. Hence, for such “outside” candidates to move more into the spotlight, it required some significant discovery to draw attention. Indeed, in the early 90s such a discovery would occur; although they later proved to be erroneous experimental measurements, the 90s saw reporting of remarkable storage capacities (about 50 wt.%) in carbon nanostructures. In generating a small hype, these misguided discoveries certainly drew attention to the field of carbon based hydrogen storage (for a brief period possibly even considered state-of-the-art among some) [45].

Following the metal hydrides, the next general area of focus in hydrogen storage research was likely to be a domain that addressed the low mass density problem. Light weight metal hydrides would fit this bill, but this area required viable heuristics, that would make predominantly high temperature hydrides more workable (e.g. reduced enthalpies of absorption, overcoming kinetic barriers), to raise the expectation for this category of material. A promising heuristic was given by mechanical alloying techniques, whose growing popularity is presumably linked to the emerging popularity of Mg-based hydrides during the 80s and 90s. As noted in [88]:

"Mechanical alloying is a promising new way to fabricate hydrogen storage materials consisting of unusual pairs of metals. Mechanical alloying can be used more easily for fabricating Mg2Ni, other Mg-Ni and intermetallic systems than melting and sintering techniques. Systems such as Mg-Fe, Mg-Co, Mg-Nb and Mg-Ti, that cannot be prepared by conventional techniques, can be fabricated by mechanical alloying."

In addition to varying the thermodynamics of Mg-based hydrides through mechanical alloying, it's kinetics could be improved by affecting the compound's microstructure. A particularly prominent focus was the Mg-Ni system which was investigated intensely for nearly three decades [134]. Mg2Ni is a material that was discovered in the late 1960s by Reilly and Wiswall. Actually, Mg2NiH4 is not a metallic hydride but a transition metal complex [134]. It was considered attractive for its hydrogen capacity and cost properties [134], and its kinetics are improved relative to MgH2. On the other hand, the desorption temperature was still considered too high for most applications [134]. Numerous variants of the Mg-Ni system have been investigated, e.g. in different compositions.

In the early 90s, optimism in hydrogen storage research was relatively low. Yet the field received a boost in the middle of the 90s, when lots of interest developed around the study of non-transition metal based complex hydrides. While the potential use of these complex hydrides for hydrogen storage had been previously considered, they were primarily developed for use as convenient and efficient chemical reducing reagents [84, p. 128]. The thermodynamics of most compounds (requiring fairly high desorption temperatures), and high kinetic barriers were among the limiting factors for their use as reversible hydrogen stores. Another disadvantage of complex aluminium hydrides is that many members of this family cannot be rehydrogenated under reasonable physical conditions. As noted in [56], "until recently, the development of a high-capacity, lightweight metal hydride that could be used to reversibly store hydrogen under ambient conditions, seemed all but unattainable." That was until a pioneering discovery of Bogdanovic and Schwickardi in 1996 which showed that, by the addition of catalysts, the complex hydride NaAlH4 could be made to reversibly release and absorb approximately 4 wt.% hydrogen under more moderate conditions [56]. Furthermore, the kinetics are accelerated by the catalyst. NaAlH4 is one of the most studied materials and has served as a useful surrogate for investigating the engineering properties of complex hydrides [96]. Yet, while for a time it was considered state-of-the-art, its capacity is too low, and its thermodynamics remained unfavourable (at least for a low temperature fuel cell; $<$ 100°C) for it to be taken forward as a serious contender.

Typical complex hydrides are composed of light metal cations (mainly including alkali or alkaline earth metals Li, Na, Mg, Ca, etc.) and hydrogen-containing anion complex in which hydrogen atoms are covalently bonded to central atoms, such as B, Al, or N. Among them, the metal-N-H-based combination systems have attracted considerable attention since Chen *et al.* reported in 2002 that lithium nitride (Li3N) had a theoretical hydrogen capacity of about 11.4 wt.% [104, 103]. As early as 1910, the reaction between Li3N and hydrogen had been observed [84, p. 159], but only recently, since the investigation of its reversible hydrogen uptake properties, has it gained significant attention for hydrogen storage purposes [103]. The hydrogenation process occurs in two steps [103]:

$$Li_3N + H_2 \longleftrightarrow Li_2NH + LiH \ \Delta H = -116\, kJ/mol \tag{5.2}$$

$$Li_2NH + H_2 \longleftrightarrow LiNH_2 + LiH \ \Delta H = -45\, kJ/mol \tag{5.3}$$

This system has an attractive theoretical hydrogen capacity, but it requires temperatures in excess of 320°C to achieve complete desorption [103]; too high for onboard applications. The level of expectation attached to this kind of system thus depended on a viable strategy for lowering the operating temperature (not to mention improvements in kinetics). Such was given by efforts of thermodynamic destabilization, an approach by which alternative hydride composites result in lower reaction enthalpies[104]. Hence, a wide range of other amide-hydride systems were studied, including Mg(NH2)2 and MgH2; LiNH2 and MgH2; Mg(NH2)2 and NaH; Ca(NH2)2 and CaH2; LiNH2 and LiBH4; and LiNH2 and LiALH4 [103]. As described in [104], "excitingly enough, the Li-Mg-N-H combination system composed of Mg(NH2)2 and LiH exhibits moderate operating temperatures, good reversibility, and a relatively high hydrogen capacity of 5.6 wt.%." By similar arguments, composite hydride systems - with reduced reaction enthalpies (also called "reactive hydride composites") - based on other complex hydrides (e.g. the MgH2/borohydride composite discovered independently by Vajo *et al.* and Barkhordian *et al.* in 2004 [84, p. 159]) were being viewed as very promising candidates for hydrogen storage [84, p. 159].

5.5.2 A sequence of state-of-the-art hydrogen storage materials

In this section I report a sequence of SOTA hydrogen storage materials, and provide an overview of data on various performance measures. Table 5.2 gives details on the selected materials and the associated time frames of SOTA status, while table 5.3 gives references for the performance data. Figure 5.2 shows the trend in gravimetric capacity and enthalpy of formation associated with a particular sequence of SOTA materials, while figure 5.3 shows the trend in gravimetric capacity for an alternative sequence (i.e. by choosing different materials for selected time periods). As can be seen, in either sequence there seems to be a general increase in gravimetric capacity. The reduction in capacity observed for the last SOTA material is somewhat surprising seeing as it was eventually acknowledged that NaAlH4 had insufficient capacity. But figure 5.2 also indicates a concomitant improvement (reduction) in absorption enthalpy. It is tempting to argue that the shift in expectation is not directly connected to the potential of the Mg(NH2)2:LiH system (at least not for mobile applications), but with the search heuristic that it represents (this perspective will be explored more in the next section).

Class	*Material*	*Approx. time interval*	*Key ref.*
Interstitial hydride	FeTiH2 (Mg-5 wt.%Ni)H2	1975-1979	[131, 85]
Interstitial hydride TM complex hydride	Ti-V-Mn FeTiH2 Mg2NiH4	1980-1984	[28] [35]
TM complex hydride	Mg2NiH4	1985-1989	[144][127]
TM complex hydride	Mg2NiH4	1990-1994	
Magnesium based-composite (Mg+Mg2Ni)	Mg75Ni25 (nanocrystalline)	1995-1999	[80]
Non-TM complex hydride	NaAlH4	2000-2004	[78, 41, 84]
Non-TM complex hydride Li-Mg-N-H hydride composite	NaAlH4 Mg(NH2)2:LiH	2005-2009	[56] [56, 104, 169]

Table 5.2: Table of SOTA hydrogen storage materials. TM = transition metal.

Material	*References*
TiFe	[134]
Ti0.98Zr0.02Cr0.05V0.43Fe0.09Mn1.5H1.95	[27, 134, 65]
(Mg-5 wt.%Ni)H2	[144]
Mg2NiH4	[134]
Mg75Ni25 (nanocrystalline)*	[105]
Na3AlH6 <> 3NaH + Al + 1.5H2**	[84]
Mg(NH2)2:LiH (1.1:2 ratio)	[162]

Table 5.3: Chosen references for the performance data of SOTA hydrogen storage materials. Note, some performance data are not taken from a time at which I have indicated SOTA status. *Material exhibits two plateaus; one due to absorption on Mg2Ni phase, second due to absorption on Mg. I use the higher value of absorption enthalpy representing the hydrogenation of Mg. **Second decomposition step was chosen for the enthalpy of decomposition value as it is higher than that of the first.

Meanwhile, figure 5.4 shows the trend in the volumetric capacity of SOTA materials. Quite convincingly, a comparison with figure 5.2 would suggest that volumetric capacity has been

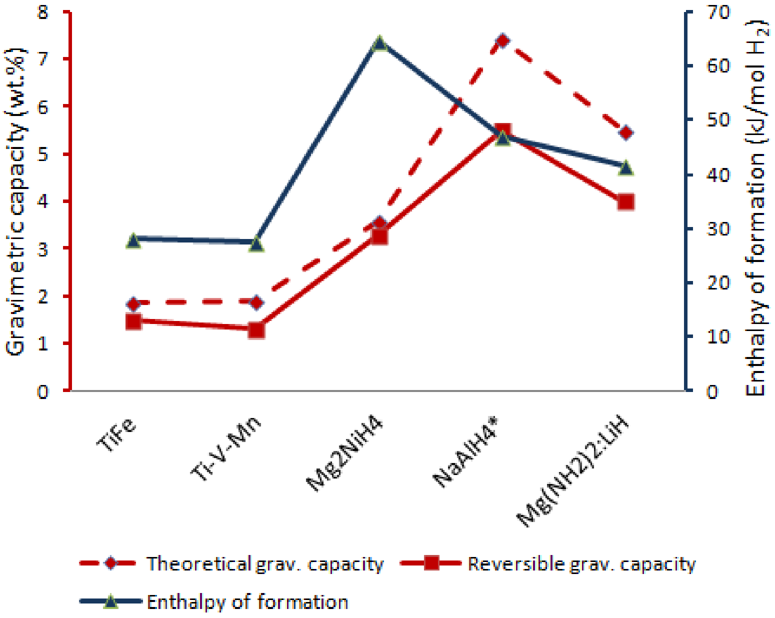


Figure 5.2: Changes of performance in gravimetric capacity and enthalpy of formation in the sequence of SOTA hydrogen storage materials.

traded off in favour of higher gravimetric capacities. It is probably fair to generalize this interpretation of the emphasis in search heuristic across a wide spectrum of hydrogen storage research (such as work involving metal organic frameworks). Given that the DOE 2017 target for volumetric capacity is 40 g/L (70 g/L for the ultimate target, see table 2.1), and assuming a reduction of the system's capacity of about 50%, then the material would be required to have a volumetric capacity of at least 80 g/L. Thus, the trend in SOTA materials raises a question as to why volumetric capacity has appeared a less important search strategy for progress in hydrogen storage.

Figure 5.5 is a van't Hoff plot of the SOTA materials. The main region of interest for near ambient operation is indicated by the shaded area. One may see that the mission to find better materials has taken the search effort outside of the target area, though the most recent SOTA material is once again approaching it. This search "strategy" once again raises a question.

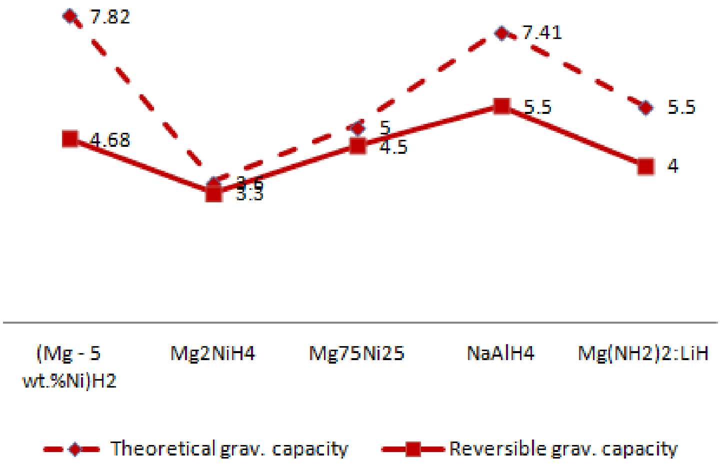


Figure 5.3: Changes of performance in gravimetric capacity for an alternative sequence of SOTA hydrogen storage materials.

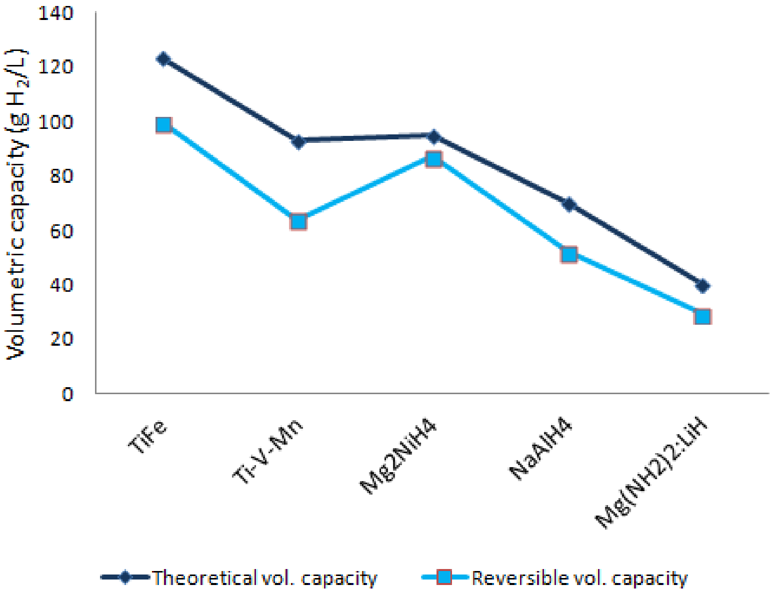


Figure 5.4: Changes of performance in volumetric capacity for SOTA hydrogen storage materials.

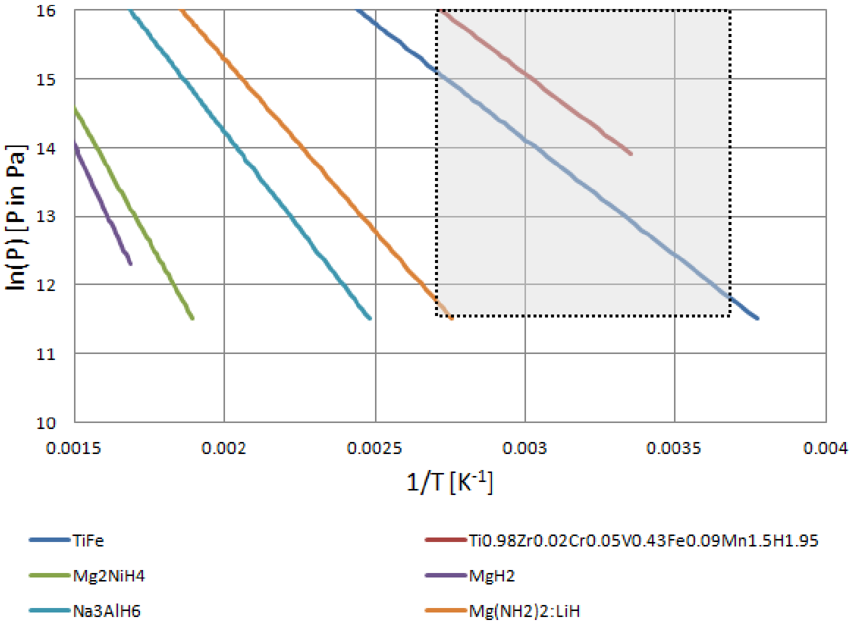
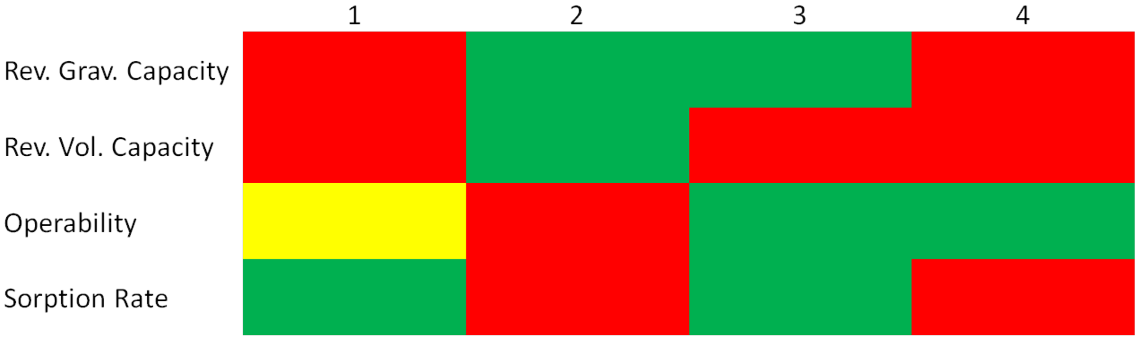


Figure 5.5: van't Hoff plot of SOTA hydrogen storage materials. The main region of interest for (mobile) storage applications is indicated by the shaded area, which marks the temperature range from ambient to 100°C (373 K) and the pressure range from 1 atm (0.1 MPa) to 100 atm (10 MPa). Data were calculated from low pressure equilibrium plateau conditions, and enthalpies of formation given in [134, 163, 105, 84].

Finally, figure 5.6 gives an illustration, albeit a crude one, of the trade-offs that were implicit with each change in the SOTA. While it would be bold to draw any strong conclusions from this representation, inasmuch as the data is reliable, it admits at least an hypothesis about the importance of the "current" level of performance. After all, while the crudeness of the data (and the fact we are not considering differences in importance) may be deceiving, there seems to be no clear pattern of progress. Such an hypothesis will be explored in section 5.5.4. Before that, it is worth questioning the reliability of the data. This is done in the next section.



	1	2	3	4
Rev. Grav. Capacity	🟥	🟩	🟩	🟥
Rev. Vol. Capacity	🟥	🟩	🟥	🟥
Operability	🟨	🟥	🟩	🟩
Sorption Rate	🟩	🟥	🟩	🟥

Figure 5.6: A selection of design trade-offs in the history of SOTA hydrogen storage materials. Even as a very basic and crude representation, this chart illustrates well the design trade-offs that accompany changes in the state-of-the-art among four important performance variables. Green = improvement, Red = decrease in performance, Yellow = no change. The ordinate axis represents the sequence of changes in the state-of-the-art. 1 represents the first change in SOTA to a Ti-V-Mn system (w.r.t. TiFeH2), 2 represents the second change w.r.t. Ti-V-Mn, 3 w.r.t. Mg2NiH4, and 4 the change from NaAlH4 to the Mg(NH2)2:LiH system.

5.5.3 Corroborative evidence

In the last decade, due to the proliferation of research trajectories, I would argue that it has become a more contentious matter to pick a SOTA material, a fact which may undermine some of the objectives of this study. Other materials, which have not been listed in the SOTA sequence, have received significant attention also. Some noteworthy examples include:

- Physisorbents: MOFs [63, 109, 171] (e.g. MOF-5, MOF-177, MOF-210 tested in a Daimler fuel cell vehicle a few year ago[5]), AX-21 and carbon nanotubes [45].
- Chemical hydrides: NaBH4, ammonia borane (AB) [95, 145], alane (AlH3) [76]

To give some defense to the SOTA selection I have made, I have sought corroborative evidence. Figure 5.7 presents a perspective on the trajectory of progress achieved in the reversible gravimetric capacity of hydrogen storage materials [56]. Even though the criteria for the selection of these materials is not made explicit, there is an encouraging degree of correspondence (at the least in terms of material types) with the SOTA sequence founding the basis of this study. Complementary to this is a compiled list of materials in table 5.4. This list refers to a selection of “state-of-the-art” hydrogen storage materials, as per the perspective of the author [165]. Here too there is a general overlap in the type of materials that are considered particularly important historically, and in some cases there is exact agreement.

Finally, it is interesting to draw a comparison to solid-state hydrogen storage materials that have been employed in automotive prototype demonstrations. I have compiled such

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[5] Information on this is difficult to find, but see for example: http://www.hydrogen.energy.gov/pdfs/review11/st049_yaghi_2011_p.pdf

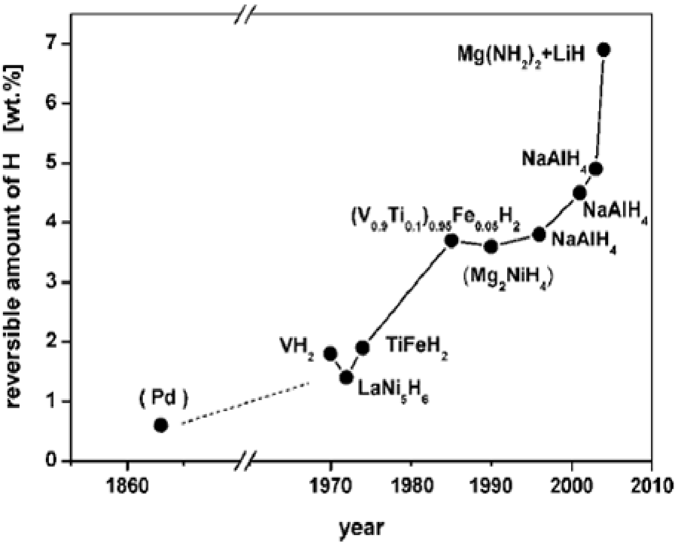

Figure 5.7: Historic progress in reversible gravimetric hydrogen storage capacity as represented by low- and medium-temperature hydrides. *Source:* [56]

Substance	*Max gravimetric capacity [wt.%]*	*Enthalpy of hydrogenation [kJ/mol H2]*
LiBH4 + 1/2MgH2	11.46	41
LiNH2 + LiH	6.47	45
Na2LiAlH6	3.49	56
Mg(NH2)2 + 2LiH	5.54	44
1/3Na3AlH6 + 2/3Al	1.85	47
NaAlH4	3.7	37
LaNi5H6	1.38	30
Ti0.98Zr0.02V0.43Fe0.1Cr0.05Mn1.5H3	1.8	22-29
TiMn1.5V0.45Fe0.1H3	1.5	28

Table 5.4: List of hydrogen storage materials compiled in [165] referred to as “state-of-the-art”.

a list in table 5.5[6]. Most noticeable is a general trend from metal hydrides to complex hydrides (for which the concept of hydrolytic sodium borohydride[7] is clearly dominant), though metal hydrides remain important throughout. The most recent demonstration involves a physisorbent, which is also the only entry of its kind in the list. Apart from a general shift towards new concepts, and away from interstitial metal hydrides, there is not much that convinces of a similarity existing with the SOTA sequence. However, one must bear in mind that the selection criteria are likely to be quite different for practical demonstration projects. For one, the material must have a minimum technical maturity to be integrated within a working system; a limitation which is not imposed on the selection of a research agenda for example. There will also be a time lag between discovery of a new, promising material, which may quickly raise expectations, and the point at which it is ready for system integration. In conclusion, while it might be reasonable to presume that a higher share of SOTA-type materials would be selected for demonstration projects, there may be many variables other than SOTA status which affect the selection process at a given moment in time. Nevertheless, it suggests to take the SOTA sequence with a pinch of salt.

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[6] While we may certainly not expect this list to be exhaustive, it may be presumed to capture a broad base of actual demonstrations during different time periods.

[7] Hydrolytic sodium borohydride is also sometimes referred to as a chemical hydride.

Time	*Name of concept car*	*Storage concept*	*Variant*	*Ref.*
2011	Daimler F125! F-CELL pug-in Hybrid	MOF	MOF-210*	[64]
2004	Ovonic/Quantum H2 Prius (MH)	Metal hydride	Ti-Zr-Cr-V-Mn-Fe-Al alloy	US Patent No. 20060266219
2003	Pac-CAR 1	Complex hydride?	Mid-temperature hydride	[126]
	H2 Prius	Metal hydride	Ti-Zr-Cr-V-Mn-Fe-Al alloy	[81]
2002	H2O Firefighter	Complex hydride	Sodium Borohydride Hydrolysis	[81]
2001	Natrium	Complex hydride	Sodium Borohydride Hydrolysis	[81]
	New Jersey Genesis	Complex hydride	Sodium Borohydride Hydrolysis	[81]
2000	FCHV-3	Metal hydride	Ti-Cr-V alloy	[81]
	X-terra FCV	?	?	[81]
	Ford Crown Victoria H2	Complex hydride	Sodium Borohydride Hydrolysis	[81]
	Ford Explorer H2	Complex hydride	Sodium Borohydride Hydrolysis	[81]
	Precept	Complex hydride	?	[81]
1999	Demio FCEV: small passenger car	Metal hydride	Alloy hydride**	[14]
	FCHV-MH	Metal hydride	Alloy hydride**	[33]
1997	FCX-V1	Metal hydride	?	[81]
	FCEV: small passenger car	Metal hydride	?	[81]
1996	RAV4 EV	Metal hydride	?	[81]
1993	HR-X 2	Metal hydride	?	[81]
1991	HR-X	Metal hydride	?	[81]
	LaserCel 1	Metal hydride	?	[81]
1984	Delivery Car TN 310	Metal hydride	Ti-V-Mn alloy	[33]
	Passenger Car 280 TE	Metal hydride	Ti-V-Mn alloy	[33]
1978	H2-4 Chevy	Metal hydride	?	[81]
1977	H2 Cadillac Seville	Metal hydride	?	[81]
	H2 Postal Jeep	Metal hydride	?	[81]
1933	Hydrogen	Chemical hydride	Ammonia reformation	[81]

Table 5.5: List of solid-state hydrogen storage materials used in auto-mobile prototypes. *Speculation based on the high specific surface area of the material reported in connection with the prototype. **Speculation based on the low gravimetric capacity that was reported for this storage system.

5.5.4 Patterns of change in the state-of-the-art

In this section I speculate about a possible interpretation of the quantitative and qualitative findings presented in the previous sections.

5.5.4.1 A general hypothesis

The results presented in the previous section illustrate at least two key features about the nature of progress in hydrogen storage research. Firstly, progress entails a substantial degree of trade-off in the performance characteristics of hydrogen storage materials. This is not a surprising finding. Secondly, progress has been largely defined by fundamental changes in the materials. This may seem like an obvious point, but it implies that progress in the state-of-the-art has, to a significant extent, not been a cumulative process. In other words, it is not the case that the most significant improvements have derived from changes to a particular storage concept. Perhaps it is the lack of a cumulative learning process that explains why one wouldn't even expect to see a pattern of performance improvement as it exists for many commercial technology ventures (e.g. following Wright's law). Instead, a pattern of progress resembling the search for superconductors (discussed in chapter 3) is possibly more expected; slow periods of marginal advancement, punctuated by attention-grabbing discoveries. To be sure, this doesn't restrict the possibility that search heuristics develop cumulatively; search strategies that worked on one system, e.g. ball milling, catalysis, and theoretical models, may well be adopted for experimentation on other systems.

But if not by a pattern of cumulative progress, how is the history of SOTA hydrogen storage materials explained? I would speculate, based on the available evidence, that the notion of progress has really been defined by transitions from one set of search heuristics - associated with some material -, to another set of search heuristics - associated with another material. The latter is always endued with a higher degree of belief (or confidence) with respect to the former. In other words, SOTA status is really connected to the level of expectation associated with the particular problem set that a material represents. For instance, confidence may be high following the discovery of a new material or a new effect, simply because of the perceived scope of possibilities to solve a new set of problems. Alternatively, considering that expectations may subdue after long periods of fruitless search, a transition in the SOTA could also occur, largely by virtue of another search strategy's failing. In the history that I have depicted in the preceding section, one might suggest a trend in which the new SOTA is particularly valued in terms of search heuristics that lost their credibility in connection with the old SOTA. I will try to backup these ideas of the history of SOTA hydrogen storage materials with examples below.

5.5.4.2 Examples

Competing problem sets During the late 1960s and early 70s, metal (interstitial) hydrides were being considered for both stationary and mobile applications [85]. In particular, these materials were being pitted against conventional hydrogen storage techniques (liquid and compressed), and were valued for offering high volumetric storage densities and inherent safety features (among other things) [107]. However, in comparisons to gasoline powered vehicles, it was conceded that they could not replace the incumbent technology without compromising an automobile's weight, cost, or complexity [131]. Moreover, while low temperature hydrides, such as $FeTiH_2$, were considered to have favourable engineering properties (by 1976, $FeTiH_2$ (discovered at Brookhaven National Laboratory (BNL) some years prior [131, 134]) had been demonstrated as an energy storage medium on an engineering scale and was considered the most attractive metal-hydrogen system for such use [85]), early experience demonstration projects etc. created an intensifying need for higher capacity hydrides.

Initially, there must have been some optimism for finding suitable variants within the family of interstitial hydrides. On the other hand, there is also evidence of propositions to search within other classes of hydrides; "*Nearly satisfactory alloy hydrides have been developed. Hopefully, better metallic hydrides will be developed, but there are inherent limitations to their use (weight, volume, contamination sensitivity, high temperature for desorption, etc.) and hence, there is considerable reason to look at other classes of hydrides* [131]." However, the potential for complex hydrides such as $LiAlH_4$, as was proposed in the same study, was not generally considered viable due to challenges of rehydrogenating the material; one might say that the problem set was (in general) perceived with lower expectation than the problems that confronted research on the interstitial metal hydrides. Another comparison might be drawn with high temperature metal hydrides, such as MgH_2 or Mg2NiH4. These materials have higher gravimetric capacities than the interstitial hydrides, and were also considered interesting. However, they presented the challenge of low sorption rates and impractically high desorption temperatures [35]. I would not like to suggest that there was a sudden and definitive shift in expectation from one type of material to the other, but in time, the higher temperature hydrides gained in relative popularity - perhaps catalysed by some measures of progress on these systems. However, one might suspect part of the reason to be that it wasn't until the urgency for higher capacities increased, and the realization that interstitial metal hydrides could not offer the solution, that the problems associated with higher temperature hydrides became a more promising problem set to address.

Interestingly, while the problem of high temperature operation is now commonly associated with the available waste heat of the polymer electrolyte membrane (PEM) fuel cell (FC), at the time, the technical challenge was related to the requirement of having to use engine waste heat rather than the heat content of the cooling water [35]. To be sure, the waste heat from an internal combustion engine (approximately 1000°C) allows for a much greater scope of materials than would the heat content of waste heat from a PEM fuel cell ($<$ 100°C). However, there would still be a problem of start-up; while the exhaust gas was not hot enough, the idea described in [35] was to supply hydrogen with a low-T hydride, and through an auxiliary heater. It goes on to say: "*owing to the relatively low values for the storage unit weight and additional fuel consumption, the auxiliary-heated high temperature storage unit could be particularly suitable for use in passenger cars. The first storage unit prototype in the world with high temperature hydrides and auxiliary heating is currently* *being produced by Daimler-Benz, and will then be tested in a vehicle.*"

A final example is the discovery of reversibility in sodium alanate (NaAlH4). Before this time, NaAlH4 was considered a promising candidate but for the key disadvantage that unfavourable kinetics limited its reversibility (furthermore, the dehydrogenation temperature was considered too high, and the kinetics too slow for any application) [84, p. 128]. The "breakthrough" came with the discovery of Bogdanovic and Schwickardi that doping sodium alanate with a catalyst not only improves the kinetics of dehydrogenation, but also makes the reaction reversible [84, p. 128]. As the hydrogen content of NaAlH4 was considered to be sufficiently high to make it a promising material for solid hydrogen storage [84, p. 128] (by today's requirements it is considered too low), this discovery considerably reduced its overall problem set.

Note, by the time sodium alanate was viewed as a real prospect, the preferred choice of conversion technology was a fuel cell. Such niche developments can have important implications for the perceived challenge of the problem set. In particular, the interpreted performance of the NaAlH4 system (for mobile applications) depends on the fuel cell operating conditions [84, p. 137]. For low-temperature fuel cells (approximately 100°C), the decomposition temperature for the second decomposition step of NaAlH4 is too high. Thus, the development of high-temperature PEM fuel cells, with operating temperatures up to 200°C [84, p. 137], would open up new potential for NaAlH4; "*at working temperatures of 150°C for the NaAlH4 tank and 200°C for the fuel cell, a temperature difference of 50°C is available as a driving force for the heat transfer from the fuel cell to the tank*[84, p. 137]."

Fruitless search and diminishing expectations A poignant example of expectations that diminished over time for a particular search heuristic, is the case of metal hydrides. To be sure, research on these materials has proved fruitful for a variety of other purposes. But low temperature metal hydrides suffer from particularly low gravimetric capacities (around the 2 wt.% mark), and in terms of overcoming this limitation and developing these materials into viable candidates for automotive applications, this search direction could not sustain its initial promise. I have dug out a few historic claims that restate this viewpoint.

- "*There are many gaps to be filled and particular areas of R&D to follow within the framework of AB5, AB2, AB, A2B and V solid solution alloys, to be sure. However, it must be argued that we are reaching a point of diminishing returns involving limits to the inherent thermodynamics and metallurgy of these conventional families of hydriding alloys. We need to explore new and different approaches…The development of reversible metal hydrides has had a long, interesting and successful history. There are numerous alloys and intermetallic compounds that have properties of real commercial interest and value for applications. However, those hydrides that will readily release their hydrogen at room temperature have reversible gravimetric* H_2*densities no more than about 2 wt.%. This is not sufficient for fuel cell vehicles, perhaps the most active new area of hydrogen application…Greater promise for the future lies in* *catalysed hydride complexes. In the non-metal area, carbon has offered some renewed potential* [134]."

- "*Metallic hydride storage has been investigated in the past without considerably improving the low mass ratio. A big step advancing the technology does not seem to be in view* [52]."
- "*Serious efforts to increase the storage capacity of low temperature metal hydrides have been made. However, the development of low temperature metal hydride materials for hydrogen storage applications has been almost stagnant for more than 10 years* [80]."

It seems reasonable to suggest that diminishing expectations for a particular system makes a transition in SOTA more probable. For instance, Mg2NiH4, the material which I have categorized as the subsequent SOTA in table 5.2, did not enter the scene as a remarkable new discovery. Rather, it had already been considered for some time, but the diminished expectations for low temperature metal hydrides - in terms of achieving higher gravimetric capacities - gave a relative advantage to the less practical light weight metal hydrides, which had higher H_2mass densities to show for. Incidentally, the decline in expectation for the Mg-Ni system followed a similar trend of research that bore no fruits. As described in [134]:

- "*Mg2Ni is not very amenable to modification of pressure-composition-temperature (PCT) properties by ternary and higher-order substitutions. Numerous attempts to significantly decrease desorption temperatures have not been particularly successful. There have been several successful attempts to increase absorption and desorption kinetics by surface treated or nanocrystalline and amorphous versions of Mg2Ni-related alloys (sometimes including catalysts), but the basic hydride thermodynamics have not been improved much.*"

New search heuristics and the promise of variation My modest reading into the history of hydrogen storage development suggests another generality; firstly, discoveries of new materials, which then became associated with new search heuristics (or, at least, traditional search heuristics applied to a new context), tended to have been met with a lot of optimism. Secondly, discoveries of new effects, which themselves lead to new search heuristics, have also lent optimism to research on certain materials. Often these discoveries then prompted basic heuristics of search to address focal problems (either associated with the new material, or associated with the particular effect that had been discovered); variation of key parameters thought to be responsible for a particular change in property. Note, such heuristics may or may not be underpinned by theoretical insight. I am not suggesting that it always followed a basic trial and error approach (though it was often guided by intuition rather than theory).

Clearly, these discoveries must have signalled some measure of improvement to be viewed optimistically - e.g. higher capacities, improved thermodynamics etc.. Indeed, the history of SOTA (see in particular figure 5.6) hydrogen storage materials does not contradict this logic. However, from an outside perspective, one struggles to interpret the sequence of discoveries in terms of a coherent pattern of overall progress. That leads me to speculate whether one reason for the optimism was not simply the scope of possibilities that was yet to be explored. In other words, the prospects for affecting (positive) change through a large number of potential design approaches, supplied confidence. The fact that those opportunities were yet to be explored, meant that there had been little negative feedback on the expectation of finding a suitable variant. Of course, in some instances particular heuristics were successful. With the following paragraphs I describe pertinent search heuristics in the history of hydrogen storage R&D, and expectational claims that were associated with them.

Hight temperature metal hydride alloys were investigated because they have higher gravimetric capacities than the low temperature hydrides. Their problem, however, tended to be poor kinetics, and, as their name suggests, high desorption temperatures. Optimism was instilled in the search for suitable variants by a relatively recent and promising heuristic; nanostructuring (e.g. mechanical alloying or high energy ball milling [80]). Because the sorption kinetics of Mg-based alloys is diffusion limited, nanocrystallinity was considered promising [80, 88, 144]. Indeed, this approach found some success; nanocrystalline Mg-based alloys were produced that exhibited very fast kinetics - according to [80], at a temperature of 300°C and under 1.2 MPa hydrogen pressure, almost the theoretical capacity of Mg75Ni25 can be absorbed in only a minute. Hence, the effect of nanostructuring lent optimism to the search for a suitable light metal hydride type material. I glean this optimism from various claims, such as the following quote in [80]: "*Metal hydride tanks based on a new generation of fast kinetics nanocrystalline light weight hydride alloys have a good chance to compete with cryotanks as well as pressure tanks for powering combustion engines, because waste heat can be used for desorption.*"

But the initial optimism for this material was not sustained indefinitely. For example, improved kinetics were accompanied by cycling problems; grain growth was observed - as a function of temperature - of the Mg2Ni phase (which varied for different compositions of the *Mg - x wt.%Mg2Ni* composite) [105]. Perhaps more significantly, the attempt, within this family of materials, to reduce the high Mg-H binding energy by alloying techniques, and thereby decrease the operating temperature, showed no record of success [80]. In mixtures that do reduce the working temperature below 200°C, the hydrogen storage capacity drops down dramatically [80].

The case of the complex hydride, sodium alanate (NaAlH4), is another example of the optimism that got instilled in a research agenda by the discovery of a particular effect; certain catalysts can significantly increase the kinetics of NaAlH4, and also make rehydrogenation practical [84, p. 128]. Furthermore, the initial discovery was followed by a pattern of searching for variants among the catalysts (the promise of variation). As stated in [84, p. 128]: "*At first, compounds such as titanium butoxide were under consideration, but the catalyst precursor preferred nowadays is TiCl3 which is added already during synthesis of NaAlH4 by ball milling. Besides Ti, many different metals, such as Zr, Fe, or V, have* *been tested as possible catalysts. However, TiCl3 is still one of the best catalysts in terms of accelerated dissociation and rehydrogenation. Excellent performance was observed for Ti nanoparticles.*" Moreover, a pattern of variation also followed in the investigations into complex hydrides that were now considered potential candidates.

In addition to catalysis, nanostructuring was also found to be a promising heuristic for the complex hydrides [56]. In particular, it lent optimism to the prospects that nanoscales can have on certain physical and chemical properties (e.g. kinetics and thermodynamics). Furthermore, as described in [56], some of the associated phenomena, such as surface interactions, material transport, defects, vacancies, phase transitions, grain boundary phenomena, and the formation of new and metastable phases, were thought to play an important role in achieving high cycling stability.

Finally, in a more recent example, the case of thermodynamically destabilized multi-component hydrides. The agenda for work on this system really began with the discovery by Chen *et al.* of the reversible absorption and desorption of hydrogen via the formation of lithium imide (Li2NH) [168]:

$$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2 \tag{5.4}$$

This reaction has a promising theoretical gravimetric capacity of 6.5 wt.%, but the enthalpy of reaction is 66 kJ/mol H2, a value which is too high for near-ambient operation [168], and the kinetics are limiting. Therefore, efforts focused on overcoming the thermodynamic and kinetic barriers associated with the LiNH2/LiH system. As described in [168], a particularly successful approach was suggested by Luo and Xiong *et al.* who lowered the hydrogen desorption temperature by substitution of LiH with MgH2 in equation 5.4. This substitution results in an effective decrease in the hydrogen desorption temperature from 280°C to 80°C at 1 bar hydrogen atmosphere (according to [168]) via the following reaction:

$$2LiNH_2 + MgH_2 \Rightarrow Li_2Mg(NH)_2 + 2H_2 \tag{5.5}$$

(The rationale behind this approach is that substitution with a more electronegative element (such as Mg) weakens the ionic interaction between the cation and the anion ($[NH_2]^-$), thereby destabilizing the compound [103]). At 5.5 wt.% the theoretical capacity is somewhat reduced [168], but the improvement in thermodynamics made this type of heuristic a promising one. As claimed in [56], reactions of this type open up a new field in the development of hydrogen storage materials. One example is the LiH:Mg(NH2)2 composite, with a prominent search strategy on this system being the variation of mixing ratios [84, p. 162]. Varying this parameter has the effect of varying the dehydrogenated states [84, p. 162], and it is found that the hydrogen storage capacity depends strongly on the stoichiometries [104]. Other heuristics to improve the hydrogen storage properties include adding catalysts, reducing particle size, and understanding the reaction mechanisms [104].

But once again, this example has illustrated a pattern of discovery (and of possibility), a rise in expectation, and the promise of variation. A rather definitive claim that underscores the optimism that was perceived for this type of system is given in [103]: "N*otwithstanding the issues which currently bedevil their use, lithium nitride and carbon nanotubes appear to have the most potential for a breakthrough which may lead to viability in terms of hydrogen storage: discovery of a suitable dopant, which can change the thermodynamics of lithium nitride sufficiently to lower the absorption and desorption temperatures by 50-100°C would bring this system within reach of the US DOE criteria.*" One of the issues that hinders their use, besides rather low gravimetric densities , is the release of small amounts of ammonia (NH3) during the reaction - even very small amounts of this impurity would be damaging for the fuel cell. Moreover, the kinetics of the system becomes worse after a few cycles [84, p. 182]. The issue of ammonia release and that of poor kinetics may be related.

5.5.5 The need for credible expectations

In the preceding section I claimed that one reason why research trajectories (or particular search heuristics) tend to fizzle out is because expectations diminish among the researchers. But another reason, which is no less important, is that expectations among the "selectors" of research programs loose confidence. These may be funding agencies, investors, etc. This pressure of selection means that researchers have less freedom of action. In order to secure funding/support, they must create positive expectations - convince their funders of the credibility of their agenda - and maintain them. If the promise-requirement cycle, as depicted in figure 5.1, is broken, due to failure in meeting expectations, then the prospects of a particular agenda diminish. Therefore, an important question on the prospects of hydrogen storage developments is: how are those expectations constructed and maintained, and what might be the implications associated with the pattern of progress discussed in the previous sections?

The objectives of proponents of a technology are clear: convince others, in particular selectors, of the credibility of their agenda. In other words, they need to tell credible expectations [23]. Expectations are inherently associated with a goal. Setting targets formally however, is a crucial element in defining the confidence that enactors and selectors have in a particular agenda [23]. But while amitious targets might raise expectations, there is a danger of inflating them. If ever they were inflated, "*a lot of repair work is required*" [23]. The less specific the targets are, the less accountable are the enactors, and so setting unspecific ones is a common goal of enactors [23]. Yet, such a strategy can only work for so long; at some point, a project's success will be judged on tangible output.

It is generally the case that expectations for one technological option are pitted against the expectations of competing options. After all, innovation is associated with technical diversity and limited resources. Hence, according to [21, 23], expectations of one option are often strongly related to expectations of competing options. Selectors have a number of available options they can choose from, and it is up to the enactors to convince them that the other options are not as promising. In terms of performance, this essentially implies projecting a steeper learning curve for one's own option. The credibility of those projections will in part depend on the history of credibility, or of recent progress in performance. These elements, in the construction of expectations, have been indicated visually in figure 5.8. Finally, expectations may also be contended on the grounds of the actual selection criteria (or target measures). Enactors will tend to emphasize those performance measures that are most favourable to their solution and less so for their competitors.

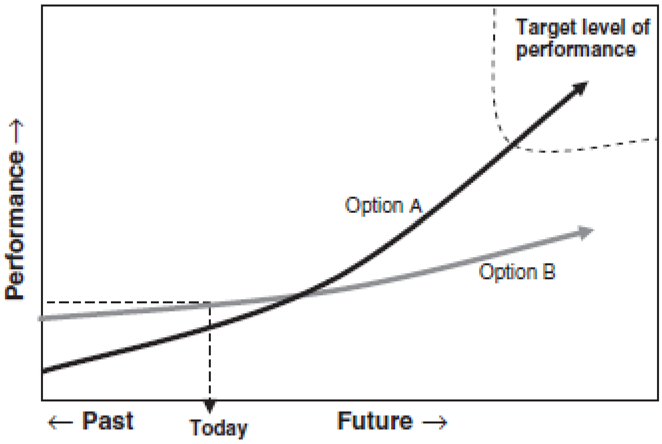

Figure 5.8: Elements in the construction of credible expectations. *Source*: [23]

A case study [23] of expectations at the US DOE's Hydrogen Program, has revealed basic insight into the perspective of an important selector of hydrogen technology. First and foremost, the DOE expects technologies to move stepwise from basic research toward commercialization. In this context, it was found that any option that continues to make progress seems to be assured of continued support. Options that show stagnation are scrutinized more closely. In case progress for a technological option seems questionable (i.e. the proponents of it have lost credibility); a go/no-go decision is made. An example of a no-go decision for onboard reformation of hydrocarbons, and the underlying views for it, is interpreted in [23]:

"*Even though progress was made in terms of proofs of principle and working prototypes, the targets for start-up times and start-up energy were not met. Furthermore, there was no reason to assume that these targets could be met in the future: no pathway to increase the performance was identified. Perhaps even more important was the fact that similar emissions reductions could also be achieved with gasoline hybrid vehicles: there was no longer need for such complex solutions. The car industry involved in the Hydrogen Program also indicated that it no longer took interest in on-board fuel processing.*"

Another example given pertains to a higher level in the US selection hierarchy. It pertains not to the requirement of securing funding for sub-programs, but for funding of the hydrogen program as a whole. (Famously, when energy secretary Steven Chu first entered office, he expressed very low expectations for the prospects of hydrogen energy. His view was heavily informed by the lack of progress that had been achieved, particularly in storage technology.) This particular example is derived from the meeting notes of a "Hydrogen Technical Advisory Committee" (HTAC) meeting. One of its objectives was to devise a strategy for securing funding. As described in [23], with increasing pressure from the selectors, it was decided that hydrogen needed to be reconstructed as a short term option. As a result, the enactors started to stress that hydrogen is not only an option with great potential for the long term, but also something that is very much happening today, such as in early niche markets for fork lifts, or in test programs with fleets of hydrogen vehicles [23].

Assuming that this kind of interplay between enactors and selectors applies more broadly, what would be the implications for the development process in basic hydrogen storage research? From an outside perspective, how would selectors evaluate the nature of progress in hydrogen storage (e.g. as presented above)? More to the point, in stipulating requirements/targets for future output, what kind of expectations would selectors apply to the pattern of progress? Or is it the case that selectors simply form an expectation of the reliability of the enactor's expectation (remeniscient of the concept of "erwartungserwartungen" proposed by Niklas Luhman), thereby putting a premium on an infallible track record?

If the selector has an inherent expectation of the pattern of progress, what is it based on and is it reasonable? This is a key question because if it is unreasonable, then the enactors will have a tough time maintaining credibility, despite perhaps having a strong belief in the prospects of a technology. Do unreasonable expectations have an effect on the nature of work, e.g. more experimental rather than theory driven (which perhaps would entail a longer pathway to success)? If it is the case that the selectors form expectations of the enactor's expectation, then one would argue that constructing realistic expectations is key, and that may involve communicating the levels of uncertainty. A search heuristic that has a low probability of success may still be based on a credible expectation, despite not delivering the goals/progress that was intended for it. I believe that the expression of credible uncertainties is in fact a relevant issue, and I explore it more closely in the next chapter in which I characterize the uncertainties in achieving particular hydrogen storage goals, by eliciting probabilities from experts.

5.6 Summary and conclusions

In this chapter I set out to study the existence of regularities in the trajectory that hydrogen storage research has taken. A sequence of state-of-the-art hydrogen storage materials has been presented. No consistent pattern of performance change is apparent. Rather, "progress" is associated with a considerable degree of trade-off. I caution, however, that describing this pattern on the basis of such limited data (which in turn was gathered on rather speculative grounds) may entail a significant degree of "overfitting". To what extent is a new SOTA material (or variant) identifiable with a performance improvement? Unfortunately, aside from requiring a larger data set, a robust answer to this question would require a standardized and consistent interpretation of progress (presumably including more performance properties). Given varying directions of improvement with each new SOTA, it would seem overall progress has been marginal however.

By combining the pattern of performance change with expectational claims related to SOTA materials, I have formulated a general hypothesis that explains the historical sequence. In particular, there appears a pattern by which an increased level of expectation is associated with a SOTA change. I speculate about the nature of raised expectations. For instance, they tend to be associated with the perception of an increased scope in possibilities. As such, changes in SOTA - I would generalize - tend to be preceded by significant discoveries, e.g. new materials/search heuristics, increasing the perceived potential of progress. They need not, however, represent significant advancements in overall performance.

The final discussion point relates to some (possibly critical) implications of the highlighted pattern of progress. A material's prospects depends not only on the sustained expectation of its enactors. It depends, moreover, on the expectations of selectors. Enactors engage in "expectation work" [23] to, at the least, maintain the credibility of their agendas (proposed search heuristics). As suggested by figure 5.8, selectors' expectations are thought to be informed by historic progress, among other things. Furthermore, selectors, by definition, have more freedom of action (choice), and need not be as concerned about what can be achieved as compared to what should be achieved. Nevertheless, to the extent that selectors buy into expectations of what can be achieved, I suggest that the construction of realistic ones should be the goal. This is especially true if, as I speculate, one may conceive of selectors' expectations as expectations of the validity of the expectations promoted by enactors.

The methodology adopted in this chapter is subject to important biases. There is the possibility of personal bias that I introduce in the "decoding" of claims that I perceive as relating to expectations, and there are biases inherent to the "encoded" claims themselves. For instance, the competition for resources to fund projects is likely to effect inflated claims by proponents of competing strategies (a lengthy discussion on this topic can be found in [21]). As already discussed, there are also issues to do with a lack of data quality. For all of these reasons the results have to be interpreted tentatively. Indeed, the findings have been formulated as a hypothesis, one which is at the least consistent with the data used for analysis. Assuming it is valid, it tells us that technological progress during this early phase has been defined in terms of shifting enthusiams rather than a trajectory of performance gains. It also presents an underlying mechanism for the well known phenomenon of hype cycles. In any event, this study has set a challenge to validate or reject its findings.

May we conclude that the methodology has proven itself as an effective tool? Clearly, improvements to sampling and the "decoding" of expectations would be desirable. It is quite conceivable that I have at times thought I was measuring an expectation, when in fact, the statement merely reflected a strategic purpose (or something else). The implication is that a repeat experiment may not produce an exact replica of the findings. On the other hand, such encodings represent a valuable - if somewhat treacherous - data source, with the potential to uncover high-level explanations of the trajectory of research (that are somewhat robust to variations in the details of analysis). Alternatively, and perhaps more reliably, this purpose could also be served by way of a survey of researchers in the field.

Finally, in this chapter I have presented a first look at the study of expectations in understanding technological prospects. In chapter 6 I will explore a new facet of this study. I will pursue an original model of analysis by applying a technique that - as I will argue - allows us to quantify technology related expectations by their strength of belief.

6 Technological advancement: Expectations and probabilities of progress in hydrogen storage materials

6.1 Introduction

In the last chapter I looked at a particular kind of history of hydrogen storage materials, namely, one told from the perspective of a form of community expectation of commercial prospects. In this chapter, in which I report on a case study involving hydrogen storage experts, I delve more deeply into the nature of their individual expectations. The purpose of this more refined study of expectations is given by the hope that the experts' views can enrich our understanding and comparative assessment of technological prospects in the field of hydrogen storage. Concretely, this study seeks to analyse the experts' beliefs on the issue of progress in the performance of hydrogen storage materials. Qualitative insights into their views on this subject matter are gained from face-to-face interviews. In addition, this study aimed to elicit formal representations of the experts' uncertainties with regard to the attainment of certain levels of improvement in hydrogen storage properties. This included the elicitation of joint probabilities and conditional probability distributions.

The core methodology that was appropriated for the purpose of this study arose circumstantially. As a tool that promises to return plain numeric results, it had an intrinsic appeal to be used to measure the prospects of progress in hydrogen storage. However, I understood that the application of this methodology is justified only in certain circumstances. Moreover, on closer assessment of the approach, I learned that a more intricate interpretation of the elicited probabilities would be required. Indeed, while the approach promises to reveal the best available guesses on specific uncertain propositions, the elicited probabilities in this study are not to be viewed as formal predictions. At least not from a frequentist's perspective of probability theory. After all, the frequentist's epistemological position on the meaning of probabilities is that they are based on the relative frequencies of outcomes, given a very large number of repeatable "experiments" (events) [141]. There is hardly a suitable sample set from which to extract the probabilities of technical progress resulting from fundamental research on hydrogen storage materials. A more natural interpretation of the experts' probabilities is given by the Bayesian axiom of probability theory. In this view, the expressed probabilities reflect degrees of belief, or confidence, held by the experts regarding certain propositions - in this case, a proposition related to the advancement of hydrogen storage performance. As a matter of fact, this interpretation was attractive for an unsuspected reason; the methodology could now be viewed as a tool for quantifying expectations of technological change.

While the primary goal of this chapter is to enrich our understanding of hydrogen storage prospects through analysing expert expectations (e.g., by formally ranking different concepts according to their perceived prospects), one may argue that formally representing subjective probabilities can be useful for other reasons. One of them, is that a more precise awareness of the uncertainties of others enables better communication of challenging issues. Secondly, the process of thinking deliberately about uncertainties can shed light on the origins of the uncertainty one is confronted with (e.g. known unknowns, unknown unknowns etc.), and therefore, may help to manage risks. Thirdly, I would hold that the act of expressing uncertainty encourages a reflection on performance in predicting, and thereby will tend to improve understanding - not least about whether the environment is regular enough to allow for reasonable predictions -, through feedback.

6.2 Expert elicitation background theory: The nature of judgements under uncertainty

The expert elicitation technique has been employed in a wide range of contexts [124]. For instance, expert assessments of uncertainties may be sought in risk assessments (e.g. in nuclear system designs [124]), in Bayesian model building, in business forecasts etc. An application of elicitation that relates closely this study is on the prospects of technological progress in lithium battery technology [18]. I have come across little more with a similar focus in my humble reading of the literature. Yet, there are no particular reasons why this method should not find a use in the context of technology and progress. In this section, in which I discuss the background theory to expert elicitations, I hope to back up this claim.

6.2.1 Subjective probability

The main purpose of an expert elicitation is to ask experts about the probabilities they would assign to particular events. Given that we are interested in their subjective views, it implies that we attach a particular meaning to the notion of "probability". Indeed, the methodology is based on a Bayesian philosophy of probability, which says that probabilities reflect an individual's degree of uncertainty about a given proposition. In the extreme, this philosophy holds the view that probability is inherently subjective. Probabilities are not objective properties of the world at all (except perhaps in the quantum world). This view clashes with two other interpretations; the classical theory of probability and the long-term relative frequency (LTRF) view. In the classical view, probabilities are based on fractions of equally likely outcomes. This view appeals to an underlying form of symmetry to account for the probabilities of events, though it is difficult to apply in anything but the simplest situations (e.g. toss of a coin, roll of a die etc.) - it lacks a general definition of what "equally likely outcomes" are. The second view holds that probabilities are the long-term relative frequencies that things settle down to given a very large (strictly speaking an infinite) number of repeat experiments.

This case study seeks to assign probabilities to events that refer to progress (over a specified time period) in the performance of hydrogen storage materials. There is hardly a repeatable experiment that could reveal an "objective" probability for this type of event. Even if, in principle, the underlying process could be modelled on the history of achievements in similar areas of science, the number of conditions that are different would make it unreasonable to apply a frequentist's interpretation of probability to the event - the "experiment" is not one of a set of repetitions. So in order to describe the probability of this chance event, we are left with a subjective interpretation of the uncertainty. Such a probability judgement will inevitably be dependent on the subject's experience and knowledge. Not only might the expert construct a judgement of the odds based on regularities in his experience (though only partial information with regard to the conditions of the new event), his feeling of likelihood will likely also depend on the considered application of his knowledge to a new domain/condition.

While the subjective approach to probability is sometimes dismissed in science for its very lack of objectivity, there is nothing particularly unusual about the process of making such judgements. One might say that subjective probability judgements are based on using available knowledge to make guesses about what will be observed in a future experiment. This, in fact, is a fundamental part of doing science (for instance, confidence goes up for a theory, the more times it is validated by experiment). A key feature of the expert elicitation, is that the subject is asked to give a *formal* representation of the "confidence" he has in his guesses.

So the Bayesian view of probability accepts that judgements are subjective, and are therefore based on what is known. But how does what we know inform our judgements of probability? On what basis might experts update their beliefs? How is the available information combined to construct a judgement? In the next section I try to address these questions by looking at the nature (or psychology) of probability judgements.

6.2.2 The nature of probability judgements

In a recent book, "Thinking, fast and slow" [92], the prominent psychologist Daniel Kahneman introduces the layperson to two systems[1] of thought. One is slow and is defined by an investment in attention and effort (system two). The other is fast and seemingly effortless (system one). Rational thinking is usually attributed to the former, while the latter is normally called intuition. For example, being asked "what is17×89?", doesn't usually bring anything to mind very quickly. To solve it, one has to engage in an effortful process of calculation. By contrast, if one were asked, what is $2+2$, an answer immediately comes to

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[1] The distinction between two "systems" is used pedagogically, rather than referring to a matter of fact in psychology.

mind. It is effortless, and more than that, the answer is simply delivered, without the subject being aware how it got there. This point marks a way of distinguishing the two modes of thought; in the more effortful mode, the subject is aware of the information processing strategy he/she employs (in the above example, application of the rules of arithmetic), while in the intuitive mode, the subject is unaware of it.

To understand probability judgements (at least in the context of an expert elicitation), is to understand better the nature of intuitive thought. After all, when the expert is asked about his uncertainty regarding some proposition, he/she does not set about building a statistical model. They are more likely to respond with an intuitive judgement. In psychology, they refer to the information processing strategies underlying those judgements as “heuristics” [124]. One of the first waves of insight into the workings of some of those heuristics was achieved in the 1970s and 80s with pioneering work of Daniel Kahneman and Amos Tversky on the so called “heuristics and biases” programme [124, 101]. The discovery of certain predictable biases of human judgement was key; the fact there were systematic errors in judgement in effect opened a window onto the nature of certain heuristics that people tend to use under conditions of uncertainty. Three prominent ones are known as the “representativeness”, “availability”, and “anchoring and adjustment” heuristics [101]. The most popular biases which were shown to arise from the use of these were the conjunction fallacy, the base rate neglect, and miscalibration [101]. Elaborate explanations of these can be found in [124] or [92].

The research programme, and the congruent focus on biases, had an important effect on the general perception of the quality of human judgement under uncertainty, namely, that it was error-prone and statistically flawed. But there is an important issue that puts the poor performance that was achieved in laboratory style experiments into perspective. It is the fact that performance was often tested through rather unconventional type questions. In other words, the subjects did not very often have much experience in answering those kinds of questions. By relying on their intuition, the subjects did something quite usual in unfamiliar situations; they substituted the real question for a simpler one they could answer intuitively. A passage in [92, p. 150] describes this:

“People who are asked to assess probability are not stumped, because they do not try to judge probability as statisticians and philosophers use the word. A question about probability or likelihood activates a mental shotgun, evoking answers to easier questions (such as similarity or representativeness)... System 1 generates an impression of similarity without intending to do so.”

A characteristic of system two, meanwhile, explains why so many wrong answers were given to questions that were relatively simple. As described in [92], system two has a tendency to be “lazy” (or energy efficient). And while its function is to “monitor” what system one is doing (e.g. by checking answers to problems), it will frequently let proposed solutions (delivered by system one) go through if they feel about right. So, one might argue that the heuristics and biases programme really focused on types of heuristics that are employed under conditions of unfamiliarity. In the least, the generalizability of the conclusions from this line of research has been questioned [124].

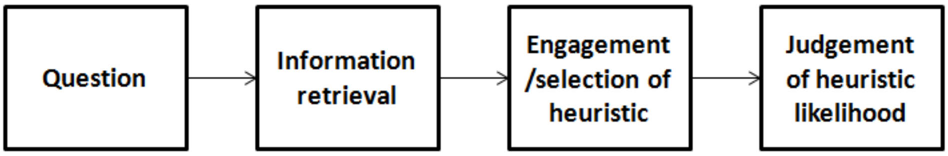

Figure 6.1: Elements of probability judgements.

Based on a modest reading of the literature on probability judgements, it is my understanding that there are four determinants of their quality. I have depicted these (perhaps naively) in figure 6.1. To begin with, the question that is asked is important. This provides not only the cue as to the type of answer that is sought, but the way in which the question is phrased may have an effect too [124]. The reason is that it may contain other cues that shape the way memory is searched for information (the second element in figure 6.1). As explained in [124, p. 36], memory is not simply based on items of information that are accumulated one by one in in a kind of 'storage bin'. Rather, memory search is a constructive process [124] that works by association [92]. In other words, "different thoughts and feelings will tend to activate (or bring to consciousness) other thoughts and feelings with which they have been associated [124, p. 36]." The importance of the question, and of memory search - and hence, also of experience, mood, etc., - is linked to the dependence of the heuristics on the information that is "retrieved".

Third in the chain is the heuristic itself (or information-processing method), which is clearly an important factor in probability judgements. First, there is presumably a set of heuristics that *could* be relevant to a particular question - yet they are unequal in their validity -, and it may be subtle cues that determine which one is evoked. Second, the "quality" of any one heuristic is largely dependent on experience (or training) in a given domain. When and where we can rely better on the quality of heuristics is the subject of the next section when I talk about "expertise".

Finally, how does the heuristic allow us to make judgements about numbers on the probability scale? It seems[2] to me that there are two ways. In the first case, the probability judgement is "learned" as the direct output of an initial condition. For example, most people know intuitively that the probability of heads in a coin flip is 0.5 (presuming it is a fair coin). Though many people won't know this from actual experience of flipping a coin over and over again (I admit, many people will have tried this). Instead, the response of 0.5 could simply be learned as the "correct" answer to the cues that the question "what is the probability of heads in a coin flip?" provides. In any case, the answer comes to mind largely unawares, as in the question; "what is $2 + 2$?"

In the second case, probabilities are judged according to some more innate feeling of likelihood or propensity[3]. This process makes use of an ability to translate from one scale onto another. This ability is called *intensity matching* [92] and is by no means specific to probability judgements. But how do those feelings of likelihood or propensity arise? While I am speculating here a little bit, it is probably safe to say that the frequency, with which a

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[2] I am speculating somewhat on this point.

[3] I use these words instead of probability as then there is no requirement for those feelings to be coherent within a framework of probability theory.

particular heuristic suggests an outcome that is confirmed by experience, is related to the confidence we have in the judgement associated with that heuristic. And that feeling of confidence or likelihood is then translated onto the probability scale. It should be noted, that many judgements will be based on sets of heuristics (e.g. $a \to b$, $b \to c$, etc.). In that case, the feeling of confidence is related to the "coherence" of the overall set or story that it produces [92]. By this second account of probability judgements, the often observed phenomenon of *overconfidence* [124] may be explained by either incorrect tallying, or to misattribution of the initial conditions, or causal chain of events that led to a particular outcome. As described in [92, p. 218]:

> "*The illusion that we understand the past fosters overconfidence in our ability to predict the future... The often-used image of the 'march of history' implies order and direction... We think that we should be able to explain the past by focusing on either large social movements and cultural and technological developments or the intentions and abilities of a few great men. The idea that large historical events are determined by luck is profoundly shocking, although it is demonstrably true.*"

During the enlightenment, around the time of the emergence of probability theorists, the view was held by many logicians and philosophers that human judgement and probability were two sides of the same coin [167]. More recently, particularly in the 1970s and 80s, much more doubt was cast over the quality of human judgement. Even more recently, the question has started to shift away from *whether*, to where and when human judgement under uncertainty is reliable. That is the topic of the next section.

6.2.3 Conditions for expertise

"Expertise" in subjective prediction has been tested across a number of disciplines. An important study by Philip Tetlock [150], which illustrates very poor performance by self-proclaimed expert political pundits [141, 124] (the experts performed worse than they would have if they had simply assigned equal probabilities to each of the outcomes posed in the questions about political forecasts they were set [124]), raised serious questions about intuitive prediction skills. On the other hand, there are many examples in which the performance of subjects was good [124]. Consequently, arguments over the quality of professional judgement, per se, are of little value. Instead, and more to the point, Tetlock's study raises questions about how to identify "true" expertise.

An important principle that is illustrated by Tetlock's study, is that the confidence that people have in their intuition is not a reliable guide to their validity [93]. One reason suggested for this is that the person who acquires more knowledge develops an enhanced illusion of his/her skill and becomes overconfident [124]. Overconfidence is tested by comparing the frequency with which sets of events occur which have been assigned particular probabilities by the subject - through this comparison one may test for "calibration" of the subject. If events with assigned probabilities between 0.5 and 1 systematically occur less frequently than predicted, then that is an indication of overconfidence (equally, if events with assigned probabilities between 0 and 0.5 systematically occur more frequently than predicted). Related to overconfidence, is the finding that non-specialists often outperform "semi-specialists" because they give too much weight to low validity cues. This has been termed the "less is more" effect [124]. Therefore, if confidence, or status (e.g. as a professional), is an unreliable guide, what are the conditions under which intuitive prediction skill might be expected?

A line of study which, by contrast to the "heuristics and biases" programme, has focused on the successes of expert intuition, is called the Naturalistic Decision Making (NDM) approach. It grew out of early research on master chess players [93]:

"DeGroot showed that chess grand masters were generally able to identify the most promising moves rapidly, while mediocre chess player often did not even consider the best moves. Chase and Simon (1973) described the performance of chess experts as a form of perceptual skill in which complex patterns are recognized. They estimated that chess masters acquire a repertoire of 50000 to 100000 immediately recognizable patterns, and that this repertoire enables them to identify a good move without having to calculate all possible contingencies."

Such studies pointed to key conditions that needed to be met in order for a subject to acquire intuitive skill in dealing with uncertainty in a particular task. Two basic conditions are [93]:

- An environment that is sufficiently regular to be predictable
- An opportunity to learn these regularities through prolonged practice

When both conditions are met, intuitions are likely to be skilled. Acknowledging that expertise in a domain is not typically a single skill, but a collection of skills, helps appreciate the required conditions for becoming an expert [92].

May we expect intuitive expert skill in predicting the ways of progress in hydrogen storage development? With enough years of experience in the field, there would be no reason to expect that the second condition given above would be an obstacle. After all, there are high stakes in learning about the conditions for technical progress (in addition, there is a natural, intuitive propensity to try and identify patterns, even when these may only be spurious [141]). But is the nature of scientific discovery perhaps too irregular to expect a high degree of prediction skill? While it would be too speculative to guess at the information processing heuristics employed by the experts in this study, it is interesting to think about whether there are opportunities for productive learning in principle.

I would argue that there are at least two components of uncertainty. To describe the first it helps to conceive of a fitness landscape [58] that maps from every point in design space to a fitness value. Fitness values represent aggregate measures of individual performance characteristics. Higher points on the fitness landscape represent better performance (in other conventions the intuition is reversed in that lower points represent higher fitness). Meanwhile, the coordinates in design space represent variations on a given hydrogen storage concept, with axes denoting different structural parameters. A basic intuition (whether reliable or not) of the probability of achieving a certain level of performance, or fitness, requires some notion of the landscape. For example, how many sites in a region of design space are of a particular height (fitness)? There is an interesting study that suggests that scientists can in fact provide a sort of map of the design space that guides search (on average) towards more effective solutions [60]. One might expect that the acquisition of this kind of intuition would depend largely on the degree of correlation of the fitness landscape [119]. In one that is very correlated (e.g. a single peak), a simple heuristic may be relatively easily tuned to the consequences of moving in a particular direction in design space, for instance uphill or downhill. In a complex and rugged landscape, heuristics are likely much more uncertain in their outcome.

A second component of uncertainty in predicting scientific discovery concerns the nature of the search activity. In other words, what is the pattern by which sites in design space are searched? I am much less able to comment on this aspect of predictability. I would speculate however, that any form of intuitive prediction skill would have to rely on relating scientific output to coarse patterns of search behaviour. Of course, even then there would be the uncertainty of which patterns of search unfold, which presumably follows a complex, nonlinear dynamic. To eliminate from the equation this source of uncertainty, the expert may condition his/her judgement of progress in hydrogen storage on certain characteristics of the search process.

6.2.4 Avoiding bias

In statistics, a bias means a systematic deviation from the correct answer (e.g. incorrectly calibrated scales). In probability elicitation, a bias is associated with systematic errors of reasoning (which may lead to systematic deviations from the correct answers). They are thus associated with particular heuristics. For example, the representativeness heuristic is associated with base rate neglect. Some biases are associated with heuristics that seem little related to the expert's sought-after knowledge. For instance, there is a documented tendency for people to divide up their judgements evenly across an interval [124]. Another example is "priming" [92], through which the "anchor and adjustment" heuristic leads to adjustments of judgements based on completely uninformative cues (e.g. the time). The expert is not consciously aware of priming effects etc. I am not clear whether these types of biases are restricted to cases where the expert has considerable epistemic uncertainty, or whether they might also apply even when the expert is highly trained in a prediction domain.

In any case, having knowledge of potential biases helps to design the elicitation so as to reduce them, and thereby maximize the component of relevant expert knowledge in the elicitation. As an example, take the strategy to counteract the "availability heuristic". Hereby the subject assesses a probability to a question by translating his/her feeling of cognitive ease (by applying "intensity matching", as described above) for recalling pieces of information relevant to the question (i.e. making the information "available") [92]. As there may be many factors that affect the recollection of relevant evidence in an intuitive judgement (c.f. associative memory search), such as mood, this heuristic is not very reliable in providing a true reflection of the subject's knowledge and experiences. The relevance of this heuristic may be reduced however, by asking the expert to actively reflect on evidence prior to forming a judgement [124]. Making more information available may also reduce the tendency for overconfidence. For example, one method is to ask the expert to imagine a future history in which the event of interest did not occur. The intention here is to draw away from the tendency to focus on optimistic scenarios. This strategy was one among several used in this study to minimize the potential for bias.

6.3 Elicitation design

One aim of this study was to collect quantitative data on the probabilities of progress in the performance of hydrogen storage materials. In particular, I sought to encapsulate the expert's knowledge in the form of two types of probabilities; joint probabilities and conditional probability distributions. The variables that constitute the events that were judged are given in section 6.4.2. The elicitation of probabilities was achieved through one on one, face-to-face interviews. The interview was structured primarily for this purpose. However, to build up to the relevant questions, it was necessary to ask preliminary, non-numeric type questions. The strategy was to have the expert deliberate on a topic prior to making probabilistic judgements about it. This would hopefully minimize the potential for bias (discussed in the previous section). Through these questions, the experts offered a wealth of insight that would be interesting for analysis in its own right. Hence, this study has a qualitative component to it as well. In the following sub-sections, I discuss the main issues concerned in the elicitation design.

6.3.1 The SHELF Protocol

The general scheme - or protocol - that the interview followed is known as the Sheffield Elicitation Framework (SHELF) [124]. SHELF is essentially a compendium of best practice notes. It draws on several case studies and insights into the psychology of probability judgements, in order to suggest appropriate methods of probability elicitation. With the aim of eliciting credible probability judgements, I studied the SHELF guidance documents closely, and drew extensively on [124] - a leading textbook in this field on which SHELF is largely based. Deviations from the suggested protocol were thoroughly thought through. Ultimately though, one must acknowledge that "measuring" a subject's uncertainties is by no means an exact science. I will discuss the main elements of SHELF that were considered for the elicitation process.

- The elicitation was conducted through individual, as opposed to group, interviews. According to SHELF, group interviews are preferable so as to enable debate during the elicitation. In this study, the elicitation events are not identical across experts. Firstly, they make judgements based on their own views about the most promising (and least, yet still viable) hydrogen storage material. Secondly, they occasionally adopt different definitions. There is also a third reason why their probability judgements are conditioned slightly differently (see below). Due to these discrepancies, a group elicitation would be less productive than it might otherwise have been. Furthermore, group interviews are more difficult to facilitate.

- Before the interviews took place, each expert was supplied with briefing notes and background material, including information on the nature of the interview and the type of variables to be assessed. No issues/concerns were raised prior to the interviews.

- The interview was projected to last between one and two hours. At the beginning of an elicitation, it has been suggested [124] to conduct some preliminary training questions to familiarize the expert with the procedure and with probability judgements. Basic experiments have shown that training may improve - calibrate - a subject's accuracy for subsequent questions [124], and therefore SHELF proposes to apply initial training as a method of obtaining better results in expert elicitations. However, one might contest the deduction that training improves accuracy in expert elicitation contexts; it isn't obvious that practice, feedback and increased accuracy on questions of the training domain should transfer to questions of the expert domain[4] [101]. Due to time restrictions, and as I was not thoroughly convinced of the value added by "training the expert", I refrained from this proposition, and instead, settled for a brief introduction to the nature and pitfalls of probability judgements.

- The first part of the interview entails a discussion about the performance variables being assessed. The first aim was to agree on their definitions. I wanted to ensure that each expert felt intuitively comfortable with the chosen definitions. The first set of probabilities to be judged are joint probabilities. These are based on setting particular target levels, which were also agreed upon in this part of the interview. The reason for not holding the expert to fixed targets is that they don't operate on a "one size fits all" basis when it comes to deciding challenging yet realistic limits of improvement for different hydrogen storage materials. Finally, the expert decided on one or two of the most challenging of the selected variables on which to give judgements for conditional probability distributions.

- In the conditioning phase of the interview, SHELF recommends reviewing relevant evidence. I decided to ask the experts a number of questions on the history of development in hydrogen storage. This included a general history, a history of specific materials, and an imagined future history, to reflect in detail on the type of challenges confronting future progress. On the one hand, I was trying to discern if the expert recalled any forms of regularity in terms of scientific progress. On the other hand, given the nature of probability judgements, one aim of this approach was simply to make more information "available", not least in the expert's mind. In particular, asking the expert to think about scenarios in which the target event was not achieved (in the case of the joint probability assessments), was a strategy to avoid overconfidence.

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[4] There is an argument to be made that training calibrates the probability scale with the subject's feeling of uncertainty.

- The second part of the interview was on the actual elicitation of probabilities. In total, six variables had been prepared for the elicitation, yet only four of those would be judged in any given exercise, depending on whether the material in question was of the onboard reversible, or irreversible type. A complete description of the uncertainty regarding future performance on all four variables, would be a multivariate probability distribution. Such could be constructed relatively easily if all the variables were independent. If X_1 is variable 1, X_2 is variable 2, and so forth, the probability of any joint event $(X_1 \geq x_1) \cap (X_2 \geq x_2) \cap (X_3 \geq x_3) \cap (X_4 \geq x_4)$, is simply $p(X_1 \geq x_1, X_2 \geq x_2, X_3 \geq x_3, X_4 \geq x_4) = p(X_1 \geq x_1)p(X_2 \geq x_2)p(X_3 \geq x_3)p(X_4 \geq x_4)$. In that case, a multivariate probability distribution can be established by eliciting four cases of univariate probability distributions. However, if the variables are dependent, then much more demanding (perhaps non-intuitive) elicitation techniques would be required. There is scarce evidence on the efficacy of this type of elicitation technique [124], and hence, little with which to back up the credibility of the associated judgements. As this study involves variables which I expected would not be seen as independent, I sought an alternative for maximally representing the expert's uncertainty. Using target values that are particularly meaningful, I chose to adopt a joint probability format for one of the assessment tasks. Additionally, I chose to elicit univariate conditional probability distributions on select variables that the expert considered most challenging. While eliciting joint probabilities requires a fairly straightforward question, the elicitation of univariate probability distributions entails a choice of techniques and they are more involved. I adopted the quartile method described in SHELF, in which experts are asked about a plausible range, and their median, upper and lower quartiles. These are used to fit a parametric distribution real-time (using a selection of distributions functions provided in a designated software package in R (suggested for use with SHELF)), after which the experts would have an opportunity for assessing/revising their data-points.

- A final important consideration for elicitation technique regards methods of aggregating a "pool" of expert probability judgements (e.g. simply averaging them). Aggregation usually provides more accurate probabilities than the best individual predictions (c.f. diversity prediction theorem), and is hence a valuable tool. However, aggregation would not be applicable to this study, as the experts are judging different target events.

6.3.2 Expert selection

As an innovative approach to predicting technical advance in basic research, it was appropriate to limit the expert set to a comparatively small number, between 5 and 10. I approached experts that have a broad base of knowledge about hydrogen storage research, and a substantial amount of experience. These attributes were favourable in terms of selecting an expert skilled, not only in the theoretical descriptions of hydrogen storage concepts, but also in the regularities (or lack thereof) of research progress. Out of 9 invitations, 7 experts were able to participate. They are listed in table 6.1, in which I have

Name	*Label*	*Institution*	*Estimated years of experience*
Walker, Gavin	GW	University of Nottingham	7
Züttel, Andreas	AZ	Empa	15
Mays, Tim	TM	University of Bath	12
Book, David	DB	University of Birmingham	17
Harris, Rex	RH	University of Birmingham	15
Hirscher, Michael	MH	Max-Planck-Institut für Metallforschung	11
Anderson, Paul	AP	University of Birmingham	9

Table 6.1: List of experts interviewed. Note, the data for "estimated years of experience" (in 2012) were based on the expert's first publication in the field of hydrogen storage (as per an author search on the Scopus database).

also provided an estimation of their experience based on the year of first publications in the domain of hydrogen storage (year of study 2012).

6.4 The target events

6.4.1 Expectations of promising storage concepts

Near the beginning of the interview, the experts were asked to name two material subclasses - representing (relatively) distinct domains of research activity - which would provide the basis for their probability judgements. One of them should be considered the most promising in terms of achieving future state-of-the-art (SOTA) status for automotive applications. The other, to give an idea of the range in their uncertainties, should be considered the least promising - yet not be an unrealistic option for attaining future SOTA status. The reason for choosing this format is that there are many candidates for hydrogen storage, and I wanted to capture the prospects of the field broadly. Moreover, as remarked by one of the experts, people are looking at a broad class of materials because there is no obvious consensus of the current state-of-the-art. The material selections made by the experts are listed in table 6.2. I should note that, while this approach allows us to define an event and attach probabilities to it, there is the possibility that the future state-of-the-art emerges from a discovery we have yet to conceive of. A similar argument is expressed by one of the experts, thereby drawing a comparison to the search for superconducting materials:

If you look at the rate of progress since this all started [hydrogen storage research]*, and that goes back to the 50s, one would be pessimistic. But all you need is one significant breakthrough and you are there; you are home and dry. Will it be a design breakthrough or will it be serendipity, my guess it will be serendipity....If you did this exercise* [expert elicitation] *would you ever have predicted any of the sort of major developments, like the* *high temperature ITC superconductors? With the same exercise would you have predicted or come up with a high probability of them being oxides, basically looking very much like insulating materials?*

In the remainder of this section I highlight some of the salient views that appear to generate the expectations concerning the prospects of future SOTA materials. I present these views (primarily) in the form paraphrased statements; some of them may thus appear to be more definitive in their conviction than the expert originally suggested. I emphasize, however, that these statements are *expectations*; I merely choose this format for brevity by extracting the kernel of the expectation. The expectations, pertaining to the various storage concepts, have been expressed by both supporters and sceptics of a particular system.

Expert	*Most promising family of materials*	*Less promising family of materials*
GW	Complex hydride (transition metal based)	Multi-component system (LiBH4/MgH2)
AZ	Synthetic octane	Liquid complex hydride (LiBH4)
TM	Variant of NaBH4	MOF
DB	Multi-component system (LiBH4/MgH2)	Hydrolysis (e.g. NaBH4)
RH	MOF	High pressure metal hydride system
MH	MOF (like MOF-177)	Multi-component system (LiBH4/MgH2)
PA	Multi-component system (including an amide)	MOF

Table 6.2: Expert views on promising hydrogen storage concepts for mobile applications.

6.4.1.1 Compressed hydrogen

- Compressed hydrogen - maybe 700 bar -, while giving you the weight capacity, the charging times and so on, will not give you a comfortable working pressure. You would say you have to come up with an alternative for long-term viability - you cannot imagine all the cars in 2025 having 700 bar pressure tanks. Furthermore, you have to expend about 15% of the energy pressurizing the hydrogen - you can't just take it straight from an electrolyzer (you might get tens of bars from an electrolyzer) for instance and stick it into the system. This energy penalty makes the whole system much less efficient.

- Car companies have opted for high pressure tanks because there has been no real progress in solid-state hydrogen storage. There may be a compromise in having a lower pressure involving a metal hydride or a metal storage system as part of a high pressure tank which doesn't require the very large pressures, so say 350 bar rather than 700 bar.

6.4.1.2 Metal-organic frameworks

- Porous materials are never going to hit the volumetric capacity target.
- Porous materials will not be more practical than compressed gas; they will be too voluminous. Moreover, compressed gas technology is simpler and cheaper.
- We are not quite there yet, but knowledge of the right kind of structure (concerning shapes and sizes of pores) to design MOFs, could enable significant development.
- MOFs, or other high-surface area materials, may depend on being filled with liquid hydrogen to achieve adequate rates and capacity efficiencies. Therefore, these materials may be dependent on having a liquid hydrogen network, and I wonder about whether it would ever make sense to invest in that type of distribution network.
- To achieve the volumetric capacity requirements in MOFs you will need to do some clever things. Advances in cryogenics will help the prospects of MOFs by enabling cheaper cooling, better recharging and capacity.
- I am unsure about whether the cryo-compressed technology that has been developed at BMW will succeed in the field. But if cryo-compressed refuelling is offered at the gas station, then that will help the cause of physisorbents as you can also use the cold gas. MOFs may be quite competitive with the cryo-compressed technology. Compared to compressed or cryo-compressed there might be a volumetric reduction with the physisorbents, but not a dramatic one.
- Two viable options for hydrogen distribution: 1) Pipeline network; this would be possible in a very dense area, 2) in trucks for long distances. If the distribution is liquid, or if it is stored in liquid form at the gas station, that would be an advantage for physisorbents. It may be advantageous to store liquid hydrogen at gas stations because compressed hydrogen at, say, 200 bar, takes up a much larger volume, and you cannot have it all at 700 bar. Moreover, there is almost no boil-off in liquid form because the surface volume ratio is so small.
- The maximum limit of specific surface area has almost already been reached in MOFs. Improvement is a question of having this in a more compact form along with better heat conduction properties. This will be the focus of work (at least for this special application) on these framework structures.
- The value of MOFs will be as a higher temperature version of cryogenics, which perhaps uses less energy.

6.4.1.3 Complex hydrides/Reactive hydride composites

- The problem for multi-component systems is going to be the charging rates. You are always going to have this competition between the stability of the hydride and the need to be able to cycle in and out quickly and be able to this under moderate temperatures and pressures.

- Confinement of the composites (to improve the kinetics), e.g. within porous materials, looks like a very nice idea conceptually, but it is difficult to achieve. Moreover, confinement of the material reduces the volumetric density significantly.

- We already know of all the compounds that allow us to store the most hydrogen.

- Liquids (complex hydrides) was something that was very little investigated in the past but that would have a lot of advantages for the application. Its not very nice for research because they have no structure so its difficult to investigate. But they will play a more important role in the future.

- The exploration of complexes which exist between lithium and nitrogen (and elements such as Mg or Al) will play an important role in the future. We will not go to elements that are significantly heavier than nitrogen. That will not lead to an interesting storage density, and they will become expensive and very limited if we were to go to heavier elements.

- If solid-state storage materials are going to be used in the near-future, say by 2020 (maybe earlier), the ones that will start to be used are the chemisorption materials. But there are all sorts of issues attached to that, not just performance issues; for example, what would happen if you pierce a cylinder tank with very fine powder? There is a race between porous materials and chemisorbent storage concepts. They are positioning themselves with respect to each other. There could be step changes with one or the other, and either one could win in the race to be taken up commercially.

- The chemisorption materials will probably get there sooner. The chemisorbent category is more likely to represent the 2025 SOTA material, although it bothers me to say that because I'm a porous material researcher. There might, however, be some transformative developments in the area of porous materials that will lead them to be sort of partners in crime by 2025.

- NaBH4 is a classic material that appears to have the right kind of inherent storage performance, though there needs to be further modifications, either chemical or physical. Chemical modifications intrinsic to the material might include changing the stoichiometry, or maybe introducing new elements into the structure, or catalytic modification, which would lead to the material being a little bit more unstable so it releases its hydrogen at lower temperatures. Physical modification by very fine milling also presents an opportunity; the smaller the particle size, the easier it is for the hydrogen to come out (crudely speaking). These opportunities suggest to me that materials like NaBH4 will be successful, though its not my area.

- The best material is maybe the MgH2/LiBH4 composite; it is a complex hydride but it has some reversibility and is getting near some of the targets.

- It is almost impossible to find an easy system; many get so complicated to reach a lower desorption temperature and higher mass density that it may not be practical because it decomposes or it has cyclability problems.

- A lower gravimetric capacity than 11 wt.% is not a game-breaker; the difference between a material that has got 5 wt.% and one with 10 wt.% is roughly the weight of an adult male passenger.
- A mixture like LiBH4/MgH2 - not necessarily the same elements -, is most likely to reduce the operating temperature.

6.4.1.4 Synthetic hydrocarbons

- We will reduce the CO2 and use it to form hydrocarbons and use these as the hydrogen carrier. This has by far the greatest energy density and is the easiest to store.
- Since I think in future we will have a positive development to higher energy density, to more comfort, not a step back to the horse, I think the only way is to try to synthesize the hydrocarbons with hydrogen and store it this way. Complex hydrides, MOFs etc., all of that is possible if we accept a significant reduction of driving range, of comfort etc. Then of course, this would be feasible. But I don't think this is what we want to have in future; we want to have more not less. Technological development is based on progress not on stepping back. Of course you can do this calculation, you could have this kind of storage with a very efficient fuel cell, that would allow to live with half of the energy density to get the same amount of energy out of the system, but still to reach half of the energy density of fossil fuels is already a real big challenge and probably not possible based on what we know today.
- Hydrocarbons are the most interesting ones, but also the most difficult to realize because we have to collect the CO2, and since CO2 is a gas at all conditions we have in the atmosphere, it doesn't allow us to collect it easily.

6.4.2 Event variables and definitions

Below is a list of the variables that were considered in the expert elicitation. Note, they pertain to a material, not system, level. They were used for joint probability estimations, and for conditional probability elicitation. Table 6.3 indicates the adopted definitions by different experts, depending on which they were most comfortable assessing.

- Mass density: mass fraction of the reversible quantity of stored hydrogen - available under feasible operating conditions (defined by expert), and at the end of the operating life of the storage material. Two alternative definitions are provided, with the variables in the equations in table 6.3 defined as follows:
  - m_{Rev}: reversible mass of ad-/absorbed hydrogen
  - $m_{Tot_{H2}}$: total mass of ad-/absorbed hydrogen (i.e. including a component of hydrogen that is not available under the specified operating conditions)

  - m_{sample}: mass of substrate material

- Volumetric capacity: volumetric density of the reversible quantity of stored hydrogen. Different definitions were applied for the storing volume, depending on the expert's preference. The alternatives are defined by the following variables:
  - V_{bed}: bed phase material volume, i.e. volume of host material plus void spaces in between particulate matter
  - $V_{sample+H2}$: skeletal volume of sample material after ad-/absorption of hydrogen
  - $V_{sample-H2}$: skeletal volume of sample material before ad-/absorption of hydrogen
- Charging time: time required for ad-/absorption of the reversible quantity of hydrogen. It is assumed that charging rates pertain to isothermal charging conditions (i.e. perfect heat transfer)
- Cycle life: number of cycles achievable under feasible operating conditions
- Regeneration efficiency: the maximum energy efficiency of regenerating irreversible hydrogen storage materials. The variables defining this quantity are:
  - e_{H2}: usable hydrogen energy content (LHV), where "usable hydrogen" is a measure of the capacity extractable from the material under feasible operating conditions (defined by the expert).
  - r: energy required to regenerate the hydrogen storing material

6.4.3 Statistical dependencies of storage properties

In this section I report on an interview question that was intended to establish perceived statistical dependencies among hydrogen storage properties. The primary purpose of doing so is to condition the conditional probability judgements. Specifically, in the elicitation of the univariate probability distributions - each based on a single hydrogen storage property -, the experts were asked to condition their judgements on the event that any dependent hydrogen storage properties would meet high target levels that were decided for them (see section 6.4.4). The notion of subjectively "perceived" dependencies is emphasised here, as the experts' views need not necessarily be based on established causal relations. In addition to this "structuring" procedure, the responses to the question offer insight into challenges of the search process for improved hydrogen storage materials (e.g. suggesting correlations of the fitness landscape).

The main perceived dependencies have been summarized in table 6.4. As can be seen, most variables are seen to be independent of each other (though this independence is not always stated with much conviction). The main dependencies that are perceived involve kinds of

Material-level hydrogen storage properties	*Experts*	*Measure of property*
Mass density (wt.%)	GW, RH, DB, PA, MH, AZ	$\frac{m_{Rev}}{(m_{Tot_{H_2}}+m_{sample})}$
	TM	$\frac{m_{Rev}}{m_{sample}}$
Volumetric capacity (g/L)	GW, AZ	$\frac{m_{Rev}}{V_{bed}}$
	RH, DB, PA, MH	$\frac{m_{Rev}}{V_{sample+H2}}$
	TM	$\frac{m_{Rev}}{V_{sample-H2}}$
Charging time (min)	All	$\int_0^{m_{Rev}} \frac{1}{rate} dm_{H_2}$
Cycle life	All	number of charge/discharge cycles
Regeneration efficiency	AZ	$\frac{e_{H2}}{(r+e_{H2})}$

Table 6.3: Table of event variables and their definitions.

	Mass density	*Volumetric capacity*	*Charging rate*	*Cycle life*
Mass density	nd	(TM, DB)	(GW, MH, PA)	nd
Volumetric capacity	nd	nd	nd	nd
Charging rate	nd	nd	nd	nd
Cycle life	nd	nd	nd	nd

Table 6.4: Perceived statistical dependencies among hydrogen storage properties. Notes: "nd" = no perceived dependence.

trade-offs between mass density and volumetric capacity or kinetics. In what follows, I present quotes which state the dependencies that experts perceive in their own words.

For complex hydrides (and reactive hydride complexes):

- *I think volumetric capacity sits on its own, and is pretty much independent of the rest. The problem always seems to be that in trying to go to a high mass density material, that is affecting either the temperature or the kinetics (the charging or discharging). So with the ones that we've got here, charging time and mass density seem to be linked.*

- *I guess there is a general dependence between weight and volumetric density. Its not always predictive...I mean essentially if you know what elements are in there, without knowing the structure of the material, you can come up with good predictions knowing one. So there is some dependence it would seem, that would be fair.*

- *For complex hydrides mass and volumetric capacity is not so directly linked. I think* *they are more independent, in the sense of, if you improve one, you get a penalty on the other.*

- *All the systems with high mass density usually have a high heat of absorption, and this of course gives you a problem in charging.*
- *The relationship comes through the materials classes themselves in the sense that if I tell you - its just an empirical observation at the moment - that if we do very well on variable A, those materials are pretty bad on variable B, but there is no scientific direct link between those its just that's the way it appears to be. Because of these dependencies it may define the type of material I might be thinking about, if say it had to have a certain performance level on one of the variables. But I don't see that there is a direct relationship between any of those that it must fundamentally be the case that if this one improves this one doesn't. But for example, I think that we may need to sacrifice mass density in order to get charging time.*

For MOFs:

- *For MOFs, I think that the mass density and the volumetric capacity are somehow linked in this. At least the first publications to improve the packing density by compaction to achieve a higher volumetric capacity have shown that you can go to a certain limit but then you loose on the gravimetric storage density, because you reduce the internal surface area or something. And those two are quite linked, if you gain an advantage in one you have a penalty in the other one, and this is a little bit a problem.*

One of the experts identifies dependencies very generally, i.e., across all material types:

- *Mass density and volumetric capacity are very closely linked. As one goes up, so does the other. It may not be linear, but the relationship is probably easy to establish. So if you have a high gravimetric capacity you are likely to have a high volumetric capacity. It is not as linear as that... When it comes to kinetics, that is almost in many cases disconnected. You can have materials with very high capacity but its almost impossible to get it out or get it in on the chemisorption side. On the physisorption side you don't have such a problem with kinetics actually, is actually quite easy to get hydrogen in and out. To my mind it is not actually a given that getting hydrogen in and out quickly will mean it will last a long time. You might be able to get it out quickly, but you might be able to do it once. So some of these aspects are completely decoupled from each other. There may be very interesting links, but its probably very specific to a particular material system.*

Finally, one of the experts points out a dependence associated with the chemical regeneration of materials:

- *Its not a physical dependence, but in general the higher the energy density, the more difficult it is to synthesize it in an efficient way.*

6.4.4 Joint probability performance targets

6.4.4.1 Overview

In the elicitation, I sought probability judgements on the prospects for achieving jointly (hence, joint probabilities), a set of four performance targets by the year 2025. Two target levels were set, high and low, both of which are shown in table 6.5. These target levels serve to define the event of interest more precisely (e.g. rather than specifying a probability for, say, "future SOTA status"). Moreover, the probabilities were conditioned on certain basic assumption about research activity. Specifically, each expert was asked to assume that the level of research would continue at the present level at least, and that there would be a general focus on problem areas identified by the expert. Ideally, setting these conditions means that we can identify the experts' probabilities with technical uncertainties, rather than, say, political uncertainties associated with funding decisions and the like.

The high target levels shown in table 6.5 were designed to be perceived as challenging by each expert, yet not unrealistic. Each expert had input into setting the target levels if the proposed ones (that I had determined) did not satisfy this criterion. Hence, there is some variation in the target levels being judged. In addition to being challenging, the high targets are intended to be informative for assessing prospects for automotive applications. With suitable adjustments (e.g. to account for the additional system components), these targets can be compared to the US DOE targets in table 2.1. Table 6.5 also shows low target values; these were considered considerably less challenging and are intended to give a range on the probability assessments - they were not necessarily considered viable for automotive applications. As it was a fairly challenging process to set the target levels, particularly the high ones, one should acknowledge a margin of uncertainty in them. Hence, one should also interpret the probability judgements as pertaining "more or less" (rather than precisely) to the proposed target levels. In fact, to provide a better appreciation of how the experts felt about the target levels, and what their expectations regarding commercial requirements are, I have summarized their views in the next section.

Before proceeding, I note that due to varying targets levels, there is a caveat to drawing direct comparisons among the elicited probability judgements. Moreover, as discussed in the previous section, there is some variation in the adopted definitions for the attributes "mass density" and "volumetric capacity". This means that equivalent numeric target levels would in fact correspond to different levels if the performance metrics were transformed into the same definition. I will try to make comparisons easier by indicating the conversions (for the original definitions see table 6.3).

In the case of mass density: let $\varphi = \frac{m_{rev}}{m_{sample}}$, $\sigma = \frac{m_{rev}}{(m_{Tot_{H2}} + m_{sample})}$, and $m_{Tot_{H2}} = m_{rev} + x$, where x is an unknown quantity. Then,

$$\varphi = \frac{1}{(\frac{1}{\sigma} - \frac{(m_{rev}+x)}{m_{rev}})} \tag{6.1}$$

If almost all of the absorbed hydrogen is reversibly stored (i.e. theoretical capacity = reversible capacity), then $x \approx 0$, and φ reduces to:

$$\varphi = \frac{\sigma}{(1-\sigma)} \tag{6.2}$$

In the case of volumetric capacity, we can say the following: $V_{bed} = \mu V_{sample+H2}$, where μ indicates the porosity of the packed bed. A reasonable assumption for the porosity is 200%, making $V_{bed} \approx 2V_{sample+H2}$. Meanwhile, we may set the other relation as $V_{sample+H2} = yV_{sample-H2}$, where y is an unknown factor. In the case of hydrides, y may be approximated to one, whereas the expansion of porous materials, such as MOFs, during hydrogen absorption, may be more significant. In any case, if we let $\tau_{bed} = \frac{m_{rev}}{V_{bed}}$, $\tau_{sample+H2} = \frac{m_{rev}}{V_{sample+H2}}$, and $\tau_{sample-H2} = \frac{m_{rev}}{V_{sample-H2}}$, then their relations are:

$$\tau_{bed} = \tau_{sample+H2}/\mu = \tau_{sample-H2}/\mu y \tag{6.3}$$

For example, the volumetric target level set by GW, which refers to the bed volume occupied by the material, is equivalent to a material volumetric capacity of at least 120 g/L, if one achieves a bed porosity of no more than 133% (and assuming y is negligible). To compare the gravimetric capacity targets, consider the level set by TM - 11 wt.%. According to his chosen definition, this target translates into a somewhat more relaxed target of 9.91 wt.% in the units chosen by the other experts.

Exp.	*Feasible operating conditions (T/P)*	*Mass density [wt.%] (high/low)*	*Volumetric capacity [g/L] (high/low)*	*Charging time [min] (high/low)*	*Cycle life [cycle number] (high/low)*
GW	$\sim$ 200°C/100 bar	11/6	90/60	3.3/10	1000/200
AZ	?	11/7	60/40	?	1000/200
TM	77 - 300 K/< 350 bar	11/7	120/90	3.3/6	1000/200
DB	?	11/6	120/100	3.3/6	1500/100
RH	$\gtrsim$ 77 K/<100 bar	11/7	120/90	3.3/6	1000/200
MH	$\gtrsim$ 77 K/<100 bar	11/7	90/60	3.3/6	1000/200
PA	$\sim$ 200°C/< 100 bar	11/7	120/90 (non-MOF assessment) 60/40 (MOF assessment)	3.3/6	1000/200

Table 6.5: High and low performance targets considered in the probability assessments by each expert.

6.4.4.2 Justifications for target levels

Operating conditions Not surprisingly, whether an expert considers a particular storage concept to be promising is very much connected to his expectations about the feasibility of future operating conditions. For instance, high expectations for complex hydride materials was seen to be associated with the expectation of the future introduction of high temperature PEM fuel cells:

- *The move will be to high temperature PEMFCs. With low temperature PEMFCs you are really stuck with things that operate below 100°C. With high temperature PEMFCs you are maybe looking at materials that can operate at up to 200°C, opening up a broader spectrum of materials.*

Interestingly, this outlook, on the prospects of allowing for higher desorption temperatures, was also held by some experts most in favour of MOFs:

- *I think even if one had a new fuel cell which allowed a little bit higher temperature like 150°C - to get it* [hydrogen] *out I think is not the problem, I think this can be done.*

- *I don't know if we have such a hard and fast figure in terms of upper temperature limit. If it was to go above 300°C I think it's a non-starter because that would require materials and energy investment that almost outweigh the benefit you gain by storing the hydrogen in the first place.*

By contrast, one expert felt much less confident about the prospects for the implementation of high-temperature PEMFCs:

- *If it is a fuel cell* [as opposed to a combustion engine where temperatures of around 1000°C are available] *then the available heat for desorption may be much less. Moreover, a high temperature fuel cell in mobile applications is not realistic. If you ask the DOE then they say it has to desorb below 80°C or something like that in order that the PEM fuel cell produces sufficient heat (there is always a temperature drop in order to transport the heat)...If we could operate the fuel cell at maybe 160°C, then we could use the heat to desorb, but this is all very speculative. Based on thermodynamics 160°C would be kind of ideal, but on the other hand, it would take significantly more time to heat up, and in winter we are going to be maybe 200°C away from that point. So even allowing for higher temperatures there are going to be significant drawbacks.*

Another distinct property of complex hydrides is their relatively high absorption enthalpy. This creates particular challenges of heat transfer during refuelling. In addition to expectations of more lenient desorption temperatures in the future, one expert therefore emphasized the benefit of allowing for greater scope in refuelling conditions:

- *There is a difference between what might be required operating and what might be possible for the few minutes when you are rehydriding. It is possible that you could go to a higher temperature for the few minutes that you are recharging, than the* *temperature at which you might want to operate. Anything that you can recharge quickly enough below 200°C is very good indeed. If it gets closer to 300°C, it gets much less desirable very quickly.*

In the discussion of low temperature limits, there were similar inclinations for more lenience among proponents of physisorbent materials, though perhaps stated with less conviction:

- *Cryogenic conditions would be feasible in the future.*
- *I look at how far away we are from ambient conditions (which is 1 bar and 300 K - in round figures). Any technology that goes below 77 K is infeasible. 77 K is routine - the technology is not difficult - but it makes life a lot easier if you don't have to expend energy in getting to those temperatures and maintaining them.*
- *My view may of course be biased by physisorption. I think that temperatures around 100 K (100 K or 77 K its not so much difference, 77 K is just because everybody uses liquid nitrogen) might be feasible in the future.*

One expert sees an opportunity for physisorbents to benefit from a possible introduction of liquid hydrogen refuelling technology, which, in his view, is in many ways a more suitable method of storing hydrogen at refuelling stations (higher density, and low rates of boil-off given a high volume to surface area ratio):

- *There is an argument to be made for cold filling compared to high compression filling. From a talk at WHEC* [World Hydrogen Energy Conference] *it seems that there is a liquid hydrogen pump from Linde which can achieve very quick filling. By contrast, with a 700 bar compressed tank you cannot compress immediately when the car arrives; you have to have a buffer where you already have over 700 bar. That could lead to a problem if five cars come in a row; the buffer might empty and the last car would have to wait considerably longer. By fuelling with liquid hydrogen you would not need to wait for a buffer to be filled. This technology, if it were to be accepted, would be beneficial for physisorption systems.*

A view opposing these expectations for the prospects of liquid hydrogen is expressed by a proponent of hydride materials, saying "*cryogenic temperatures would be too costly - 30% of your stored energy is used to actually liquefy hydrogen.*"

As for assessing pressure limits, there is quite a discrepancy among some of the expectations. One expert notes quite generally that it is desirable to stay below 500 atm on the basis that it gets quite expensive above this value (due to the cost of compressors etc.). Another expert acknowledges that pressure requirements are of more technical relevance for physisorbent systems, noting that chemisorption is much more a thermolytic process. Physisorbents are certainly expected to be used with higher pressures, and this expert expects that 350 bar would be "*perfectly reasonable; the energy and materials investment in 350 bar is marginal compared to 700 bar.*" Higher pressures are not considered feasible for reasons of energy intensity, safety, and cost, but also in anticipation of the regulatory environment. Interestingly, a different expert expects "tens of bars" to probably be adequate for the adsorption systems. "*If you don't want to spend a lot of money on the containment systems, you should be talking about tens of bar.*" Finally, another expert claims that 50 to 100 atm is about the limit beyond which it wouldn't make much sense, reasoning that with higher pressures you lose the advantage of being able to construct your vessel from lighter materials and with much lower cost. Lower pressures (about 50 atm) could also enable the design of more conformable vessels - greatly benefiting volumetric efficiency.

Capacity targets The capacity targets were probably the most challenging to determine. Particularly, as the experts were asked to choose two types of materials as the basis for their probability judgements, setting targets that were not unrealistic for either was difficult. As seen in table 6.5, one expert was keen to set a reduced volumetric target for the case of assessing a MOF type material. Perhaps one of the shortcomings of this study, was not to be more fastidious about whether the target levels were truly appropriate for both material types. On the other hand, it was really the aim to investigate the range in prospects for achieving the same outcome. In any case, to give an appreciation of the expert's sentiments in determining the capacity targets, I present some relevant quotations below.

To start with, it is interesting to restate the view of one of the experts, which puts into context his expectations of the requirements for any type of future energy store (irrespective of whether it is technically in reach):

- *Seeing it in a global context, what we need in the future is something that replaces the fossil fuels, and that means we need an energy carrier or storage system that allows us to similar amounts of energy as we do today. I don't think that we are going to step back in future and live with lets say half of the energy density. I think in future we still want to have at least the same, if not more. On that basis, competing with fossil fuels requires that we achieve a mass density that is certainly above 11 wt.%; it would have to be close to 30 wt.% (if one takes into account the relatively higher efficiency of a fuel cell system, it is still significantly higher than 11 wt.%).*

Reflecting on the technical feasibility, and hence on setting gravimetric targets for hydrogen storage concepts, he states: "*in terms of the technical feasibility, we know that, on a material basis, we will not exceed 20 wt.% unless we bind hydrogen to carbon. And most materials which have a high mass density will not deliver all the hydrogen. Therefore, 11 wt.% is really the maximum of what is physically possible. 7 wt.% is not a bad number.*" Referring to the volumetric capacity targets - note, in his assessment it is defined on the basis of the bed volume -, he states; "*no material will ever deliver 120 g/L, considering that you cannot deliver all the hydrogen from the material. 90 g/L is certainly closer to reality. But this looks unlikely if you look at where we are today. 60 g/L is still very ambitious, but theoretically possible.*"

Some of the other poignant responses were:

- GW: *The ones I am grappling with at the moment are mass density and volumetric capacity. I think you could get a completely dense phase material that has a volumetric* *capacity of 90, but for the bed material it is very difficult to achieve.* (Again, this expert's assessment was defined on a bed volume basis, as shown in table 6.3)

- PA: *The high target for mass density is considered very demanding, the low target is quite demanding. The volumetric capacity target is achievable relatively straightforwardly.*
- MH: *90 is a very high volumetric capacity for porous materials. At 77 K, "7 or even 12 wt.% is not a problem, but the volume is maybe only 30 or 40* [g/L] *to be honest.*"
- DB: *If it is relating to what is desirable and challenging, then the target of 11 wt.% looks fine. In terms of solving the problem, maybe lower than 11 wt.% would be sufficient.*

Charging rates The charging rate targets were also considered to be quite challenging by some. Yet, there seemed to be little debate about whether there was scope for reducing them - perhaps reflecting an acknowledgement of their importance. While, according to the definition I set forth in table 6.3, charging rate was to be considered in terms of inherent kinetic limitations, that is, assuming perfect isothermal charging conditions (which is surely unrealistic in a practical device), some of the experts drew attention to potential limitations of physisorbent systems given technical challenges of heat transfer. As expressed by one expert, MH; "*the charging time target is challenging. To achieve it it may be required that you connect the system to an additional hose of cooling water or something.*" Referring to the otherwise favourable sorption kinetics of physisorbents, another expert remarked: "*charging time is certainly no problem, you could hit the high target.*"

In reference to the hydride materials, one expert gave a rather pessimistic outlook on the prospects for achieving the high target charging rates with hydrogen storage materials. On asking about whether the target for charging time should be reduced (in terms of difficulty), he said: *"It depends if you consider carbon as a material for storing hydrogen* [as in synthetic hydrocarbons]. *Without carbon I don't think that we will ever achieve that, with carbon yes.*" A different expert (PA) similarly proclaimed doubts, yet to a lesser extent, about achieving the charging rate target:

"*Charging time is where all the problems are from my perspective. Most of the types of materials that I am familiar with, they take 30 mins to recharge and these are the good ones. So this is a really difficult target. Under mild conditions, the kinetics of reaction are a tough problem. Normally solid state reactions tend to occur at very high temperatures, so getting something that works around 100, 150, 200, this is very, very demanding and challenging...I'm quite happy to go through and give my probabilities based on the targets that are set, its just whenever there are questions related to charging time, then inevitably I might score that quite low because I think its a real issue.*"

Cycle life Setting the target for cycle life required the least time in general. On the one hand, this may be because it was considered less demanding, on the other, because there was a relative lack of insight into how materials tended to perform in cyclability tests (primarily due to a lack of available data). Expectations expressed in this context - some of which pertain to expectations of commercial requirements rather than technical prospects -, were as follows:

- *1000 refills is probably a reasonable number.*
- *Cycle life, I think is not as demanding.*
- *Cycle life, now I don't know about that, but if you're not absorbing into the material...(when it goes in, you get a huge volume expansion) that upsets everything, introduces defects etc. and that can give you cycle problems. With a MOF, it will be sensitive to impurities, but other than that cycle life should be pretty good.*
- *Cycle life has hardly ever been tested; it has always just been put out there. The target is based on requirements of a normal car's operation, and what we come up with has to meet that.*

6.4.5 Conditional probability variables

In addition to joint probability assessments, this study also sought to represent uncertainties in form of conditional probability distributions. These distributions would be based on key hydrogen storage properties that the experts felt were among the most challenging to improve for a particular material. Capturing the uncertainty the expert perceives over a range of possible outcomes reveals much more insight, than single probability assessments would, into the level of the challenge for research. I have broadly characterized these univariate distributions as conditional probability distributions, for the reason that many of the chosen variables were considered to be statistically dependent on some of the other hydrogen storage properties, as reviewed in section 6.4.3. Even though the experts could not necessarily specify the precise nature of the dependence, I asked them to condition their judgements on the event that the high targets for these other variables would be achieved.

While probability distributions are much more informative, they are also harder to obtain, and they entail a significant degree of assumption [124]. For instance, to make the elicitation practical, it is common to assume that the expert's uncertainty can be represented by a parametric distribution. While one presumes a considerable amount of structure on the probabilities by using parametric distributions (generally considered a reasonable assumption[5] [124]), it has the benefit of enabling a more undemanding elicitation technique. In this study I used the "quartile method" as described in the SHELF protocol. As the name suggests, it entails the elicitation of the quartiles of a probability distribution, thereby revealing plausible ranges for a variable, its median value, and upper (third) and lower (second) quartiles. This procedure was carried out in an R software package running a particular function ("shelf2.R") developed by the University of Sheffield for the

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[5] In the context of this study, it is at least reasonable to expect a finite-variance distribution.

very purpose of elicitation. The elicited probabilities were fitted with a distribution during the elicitation. The software package allowed the choice of 6 distributions to produce an appropriate fit with the data. They were the Normal, Student-t, Scaled Beta, Log Normal, Log Student-t, and Gamma functions. At the end of fitting a distribution the expert was given feedback on some of the implicit percentiles of the distribution. For instance, one could ask the expert whether he thought it reasonable that there was a 10% probability that the performance value achieved would be less than x or greater than y.. The expert was also asked to comment on the general shape of the distribution.

6.5 Results

6.5.1 Views on the history of hydrogen storage development

6.5.1.1 Patterns of progress

Experts were asked to reflect on general patterns of development and progress in hydrogen storage research. A general consensus seems to emerge from their responses, one which I will try to summarize:

Progress in terms of knowledge gains about "performance-material parameter" relations is plentiful - although specific theoretical insight is claimed to be seriously lacking in many areas. Progress in terms of overall performance enhancements is viewed somewhat more discouragingly. For instance, one expert claims that in terms of getting closer towards the targets, there has been progress, but at a much slower rate than people felt it was going to "at any given time along that timeline." People tended to be overly optimistic in their expectations of what they could achieve. Another expert says that progress has been marginal.

What insights did the experts have in terms of the patterns of discovery? One expert refers to MOF materials, claiming that there has been a steady increase achieved in gravimetric storage capacity. Another, who tends to work on new materials/systems, relates to the fact that improvements don't tend to drift upwards nicely; "*they tend to occur in jumps and whatever else.*" Similarly, another expert observes: "*I think there has been lots of predictable development punctuated by some unexpected new materials appearing like sodium alanate, the borohydrides, lithium nitride - which kind of almost appeared from nowhere. And then works on the composite type material, have been based on known materials as it were.*" By contrast, one expert notes that there have not been many unexpected elements in hydrogen storage discoveries: *"In the last 20 years or so, there have been no discoveries that have been completely unexpected or random.*" In other words, by this account, most discoveries have resulted from search heuristics which, presumably many people, quite confidently must have believed would result in the goals they were trying to achieve. Another expert seems to confirm this perspective, at least as it concerns the discovery of metal organic frameworks; "*I think sometimes time maybe ready for something new. Like the MOFs;*

all these framework structures have been coordination polymers for quite a long time but I think then a few people really succeeded in making these frameworks stable even though the solvent was removed, and making porous frameworks really. I don't know, its not totally serendipity, there are some developments of polymer chemistry, and all this together, and then at a certain stage somehow its almost ripe to develop this. There is of course one or two key figures that maybe make it a few years faster. I think some of these things may have developed maybe two or three years later if not one really clever guy was the first one."

An example of what these experts presumably would have perceived as quite an unexpected discovery is that of high-temperature superconductors. But while there may not have been a similar type of surprising discovery in hydrogen storage research, at least not one of the same magnitude, one might draw assurance from the very example of the search for high temperature superconductors. As one expert identifies, historical precedence, of having made little headway, is not necessarily a decent guide to future prospects. It may well be that the pursuit of search heuristics associated with low levels of expectation are the very strategies that result in discovering a new mechanism or a new source of material. "*Up until about the 1980s there was bugger all change* [in the transition temperature of superconductors]*, it was all clustered. And you thought, well that's it, never going to change, and then bam, up it goes with a huge jump in the transition temperature - from 30 K to 120, 130 K. Now again everybody is waiting if we can get it up to room temperature of course.*"

6.5.1.2 Characteristics of the search process

In this section I attempt to abstract away key characteristics that describe the general search process in the history of hydrogen storage development.

The unfolding of search trajectories I would propose, based on expert responses, a general description that can account for many historic patterns of hydrogen storage research. This description entails the following three elements: 1) a significant discovery is made, e.g. of a material that solves a particular problem that seemed unsolvable with a previous material (this attracts a lot of attention), 2) a 'primitive' search heuristic is pursued (e.g. simple variation of a constituent element), and 3) a more reasoned (less random) search heuristics gradually come into play. Additionally, after a while, many search heuristics experience a reduction in the expectations that are associated with them. In this case, a shift in the trajectory of search may occur even without a significant discovery that draws away the attention.

One example is the discovery of reactive hydride composite systems (a combination of a complex hydride (e.g. LiBH4) and a metal hydride (such as MgH2)). The discovery entailed the realization of improvements in the thermodynamics of the system compared to the complex hydride on its own. This prompted search for variations - different types of composites -, leading to the realization of a "*whole family of quite a large number of possible combinations.*" But while this heuristic was promising in addressing problems of thermodynamics, it did nothing to address the kinetic limitations. Hence, the trajectory of search shifted to solving this problem, requiring deeper insight into the factors of kinetics. As noted by one of the experts in the study: "*what people are doing now is trying to get around the problems of the microstructure material. Confinement is one area - it doesn't look like it is going to solve it but...*"

One expert argues that, historically, there was more of a rationale associated with the direction of search (producing incremental but definite progress). More recently, since the "*explosion of interest*" in hydrogen storage research, it has appeared much more random. He continues; "*I think we are only starting now, in the last few years, to start looking a bit more at trying to understand what the bottlenecks are and why its not working and why we can't get it to work and putting a bit more direction into it.*" The prevalence of these more 'primitive' approaches to search, e.g. through more or less random variation, is in fact explained by one of the experts: "*My understanding of the chemical storage is that the understanding is not there in terms of why does a particular combination of alloys produce the effect that it does, why does a particular catalyst work for one system and not for another; very difficult and challenging questions that can only be answered at the molecular level ultimately. And in the old way, metallurgy was a bit bucket chemistry, you just lobbed a bit of stuff in and see what happened. There is an element of that...I suspect its permutation chemistry, you just try a lot of combinations and find out which one works, and then try to understand it.*" Moreover, he explains why theory is weak in particular areas, and hence, why a lot search activity is reliant on intuition and guessing. One of the problems lies with accurately modelling hydrogen, either, as in the case of physisorbents, with van der Waal's interactions, or, as with hydrides, with proper chemical bonding; hydrogen, with only one electron, is supposedly notoriously difficult to do that with.

Dominant search goals Hydrogen storage development seems to be typified by particular search strategies which gain dominance for a period of time. In other words, the search is focused on solving a particular problem in that time. In the succession of such periods, research seemingly follows a trajectory of "one problem at a time". As one of the experts explains, talking about developments in hydride materials, there has been a lot of fixation on gravimetric capacity, ignoring other important criteria. So while weight percent has been increasing, other properties, such as kinetics, were just appalling.

A similar account holds for development on MOFs. For a long time, the goal that drove framework development was to achieve higher specific surface areas. This is because physisorption is a surface effect; the more surface you offer the more molecules you can pack on the surface. By doing so however, researchers never considered the volumetric point of view. "*Of course, this is really the problem that by achieving this* [high surfaces per mass], *you usually make a more porous material and therefore on a volumetric side you have a less dense material.*" Looking forward, one of the experts anticipates that compromises will have to be made between capacity, kinetics, and stability. "*This is a robust application so it has got to be a robust material.*" But in fundamental research these trade-offs are not considered enough. And so he also anticipates that *people will go on and look for increased* *capacity, but they probably won't look for cycle life and that sort of thing. I guess when they have got something interesting and really exploitable, I guess they may then spend some time on that.*"

But while progress is often characterised by a focus on one problem at a time, this is not necessarily so. Whether by intention or by a lucky discovery, as the following quote shows, some search strategies have the potential to solve more than one problem at once:

"I think these materials have been under-represented a bit because people have been concerned about ammonia release from something containing nitrogen like an amide, there has also been some important improvements to systems that have been made to reduce ammonia release, or, in fact, remove it all-together in certain cases. For people who work in fuel cells, ammonia is kind of a deal-breaker, so the fact that we can cut that out is a significant step forward that will make people to start to take these materials more seriously...There are two or three different ways shown to do that. The one I'm thinking of happened over the last 2 or 3 years, pieces of research that say, if you add this to your system, it will improve your kinetics and it will stop that. There seems to be a link between those actually; if you can improve your kinetics, the ammonia release reduces. I believe there are actually two competing mechanisms, and if you can make one of them go faster, then you avoid this pathway that goes through ammonia gas.

Search biases In a crude way, one may remark that hydrogen storage development has been characterized by inflated expectations, and a general sense of overconfidence. For example, talking about developments in metal hydride materials, one expert recalls that expectations were initially high for search heuristics that were associated with the achievement of high targets, despite giving any real consideration to the material options that were there, and what their potential might be. *So people were expecting to have a whole range of materials at sort of up to 10 wt.%, and that's been extremely difficult to get materials that do have 10 wt.%. They were still expecting to achieve such high goals with relatively simple systems like metal hydrides - you are not going to be able to do that without incurring other significant problems. So, alane is probably the only one that is going to get you high enough, but its then got to be an off-board regeneration.* As another example, the expert talks of the initial optimism following the investigation of certain complex hydrides. This eventually gave way somewhat to pessimism, following the realization that the release of impurities (such as NH3, which also affects ammonia borane) could mess things up.

In all, the remarks offered by the experts - along with background material (such as that presented in the previous chapter) - lead me to suggest a few possible reasons for the overconfidence that has often been displayed: 1) an initial focus on the potential benefits of a search strategy, rather than on potential drawbacks (an issue related to the *framing effect*), 2) a large scope of combinatorial possibilities may give rise to high expectations associated with more primitive search heuristics of simple variation (trial and error), and 3) initial success of a search heuristic (that is not actually founded on any underlying regularity) may give rise to high expectations. A famous example of the third point is the erroneous discovery of extremely high storage capacities in carbon materials. This led to a flurry of activity in the area. Another example, described by one of the experts, is the spillover effect: "*times have changed also; in former times people would publish something when they were really sure, and now you want to be the first and then there are these mistakes and a long fight about what is true and not, and there are many of these stories, like the spillover effect; I don't believe in it. No one was able to reproduce it, and now we are at a state where this effect has been shown but it is so small that it is technologically totally irrelevant.*"

Decreasing expectations for a search heuristic Finally, while research in a particular area might come to a stop due to the realization of fundamental limitations, it often tends to fizzle out - the expectations of particular search heuristics gradually decrease. Talking about work on MOFs, one expert explains: *At least a lot of people at the beginning were claiming they could increase the heat of adsorption, and I think all those attempts, more or less - not failed - but I think this high goal, that we could maybe do it at room temperature, in this respect they* [didn't meet expectations] .

6.5.2 Conditions for success

6.5.2.1 Context

During the elicitation I asked several questions about hydrogen storage development, such as, "what are the challenges of commercial success?", "what is going to be the likely research focus going forwards?", or, "imagining the year 2025 has arrived and the targets for hydrogen storage development have been achieved, what is the history of development?". This section is formed largely from the responses that were given to these questions. In figure 6.2 I have depicted a form of information processing network. This is a network that indicates the relations that are perceived among the states of different variables[89]. It has the semblance of an "influence diagram", but strictly speaking, there is a difference. An influence diagram attempts to depict actual causal relations, whereas with the information processing network I am merely trying to capture important variables and their "perceived" relations, which, one might assume, ultimately affect expectations on the prospects of hydrogen storage materials succeeding.

I must note, figure 6.2 has not been based on a single expert's views. Instead, it is an assemblage of the different responses. As I did not specifically ask about *all* of the important variables, I think that figure 6.2 is probably a more complete representation of factors that each expert is likely to consider. In the remainder of this section I give specific instances - or states - of the variables and relations depicted in the diagram, that were considered conducive to success.

6.5.2.2 External factors

As part of the external factors, things like economic climate and climate change were mentioned. For instance, there was concern that the current economic climate would

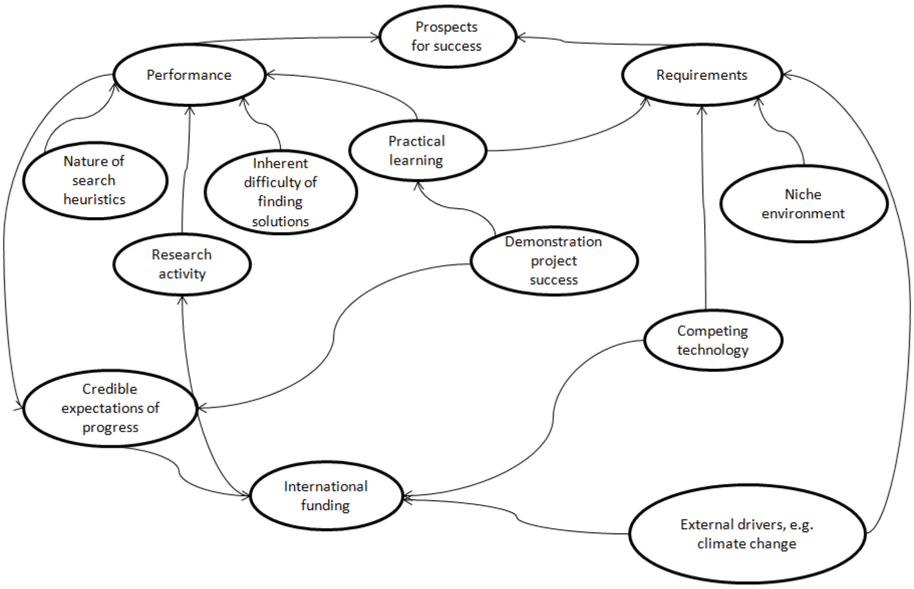


Figure 6.2: Information processing network of important influences on the judgements of hydrogen storage prospects.

not guarantee a high level of continuing support for hydrogen storage research. Expressing concern over local funding conditions one expert noted that the *"UK is quite under-invested and vulnerable in terms of rolling this* [hydrogen technology] *up the commercial chain. I think the Americans, the Japanese, the Koreans, are much further along the road than we are".* Another expert noted that climate change, through increasing concerns about carbon emissions and the introduction of a carbon tax, would influence the requirements of hydrogen storage technology by making higher costs more tolerable; "*Climate change etc. are part of the equation; they will determine what technology is acceptable".*

Another external factor that was mentioned frequently was outside technology. On the one hand, there is the factor of direct competition. For instance, as viewed by one expert, "*if we are able to produce the synthetic hydrocarbons then complex hydrides will not play any role.*" On the other hand, certain competing technologies, such as batteries, may also benefit the prospects of hydrogen storage; "*I don't see a straightforward dependence there. Improvements in hydrogen fuel cell vehicles will always need batteries, and the vehicles that we are talking about will always be some kind of hybrid. So there is going to be a balance between the batteries and the fuel cells. So improved performance could mean certain models of car could be all battery. The question is what will that do for the impetus for investing in hydrogen infrastructure. But on the other hand, improving batteries could also make things technologically easier or more viable for the hybrid fuel cell vehicles.*"

Finally, as the prospects of hydrogen storage technology will very likely depend its niche environment (and hence the requirements imposed on it), there is reason to speculate on the potential impact of other innovative technologies. For instance, high temperature PEM fuel cells would increase the fitness of many complex hydride system designs that operate above 100°C. Conversely, innovations in cryogenics or superconducting technology may be beneficial for physisorbent system designs, as remarked by one of the experts: "*Also you have to keep in mind that there might be other technologies being developed by 2025 which* *themselves need cryogenics. Maybe there will be more use of the high T superconductors at that time for motors for instance. So it is very difficult to know how things are going to go, but if by then there is a parallel development of cryogenics to power the electric motors which drive the system - and that certainly can be done with superconductors now - then using the refrigeration to store the hydrogen as well is not really a big issue any more.*"

6.5.2.3 Maintaining credibility

In addition to external factors, several experts expressed views about maintaining credibility to achieve the ultimate goals of the hydrogen storage agenda. Doing so was seen as key to ensuring further funding and support. For example, a few comments relate to the success of demonstration projects, and how that can affect the sustained interest in hydrogen storage technology:

What is going to be key is that the early hydrogen market starts to develop. Because there are going to be commercial vehicles by 2014/2015, and if they aren't starting to make an impact by 2025, then I think that means that hydrogen research for transport is going to be dead. So I think that it requires that there is starting to be some buy-in in the developing market for hydrogen vehicles. And if that doesn't happen, then the research will dry up very quickly. Potentially there could be no hydrogen research for vehicle applications in 2025, depending on that early market. What I feel is going to be the case is that with the early markets starting to develop, then that is going to bring in more research activity in the area because it is going to be more of a certainty that there is going to be a market for the materials that are being developed.

As another expert states: "*Factors that would affect my judgements on the prospects of the materials we are considering; it would be international funding would be one. Another big one would be, what is happening with the role out of hydrogen vehicle prototypes. That is a big thing. 2015, 2016 there are supposed to be hundreds of fillings stations built in Japan, Korea and Germany and thousands of vehicles hitting the road..*" Moreover, the expert considers the more complex implications of the level of success that initial fleets - comprising compressed hydrogen storage technology - achieve. While a degree of success would give incentive for further development on materials-based hydrogen storage, 'too much' success could weaken the proposition. These dependencies may be extracted from figure 6.2; a significant amount of "demonstration project success" would entail practical learning and performance levels that satisfy initial expectations - thereby creating/maintaining credibility for the technology. In turn, that would mark down expectations for other storage concepts (as the goals would now be higher), which would negatively affect their funding prospects. Another likely effect of demonstration activity (also shown in figure 6.2) is learning more about the necessary requirements of hydrogen storage systems (and therefore of hydrogen storage materials). As noted by the same expert: "*it is going to be identifying more clearly what some of the barriers are, and what some of the more realistic targets are for what's required. Because with the targets that are being thrown about at the moment, there are potentially ways in which we engineer around some of those.*"

More generally, and parallel to the need for demonstration success, is the pressure to produce any form of convincing research output (e.g. practical outcomes). Because an incessant focus on basic research and discovery might go for long periods without much to show for it, there is a risk of failing to secure further funding - e.g. as I attempted to depict in figure 6.2, a lack of performance improvements may have an effect on reducing selectors' expectations and ultimately funding. Unfortunately however, as evidence presented in chapter 3 indicates, high-risk projects are more likely to deliver significant advances. Both points were picked up by one of the experts: "*The only danger is, because there is no progress, then the amount of work and effort put into this area diminishes because it is difficult to get funding. And then it becomes self-fulfilling in a sense, because if there isn't the effort, then you won't get the possibilities of coming up with a viable system.*"

6.5.2.4 Nature of search

The approach that is taken to searching for better materials is obviously a factor in the kind of progress one expects to achieve. On a crude level, one may distinguish between research that is more oriented toward understanding the theoretical basis of hydrogen storage - and the properties that result -, and research that is following more of a trial and error approach (which nonetheless may lead to learning), with the mere objective of finding better materials. Either approach has its strengths in identifying opportunities. The importance of theoretical insight is illustrated by considering a case of the search for semiconductor materials; in an example described in [60], progress was impeded for a long time because a change of merely one particle in 10 million of a semiconductor dopant changes the conductivity by a factor of 10 thousand. Thus, scientific understanding can be seen to provide a sort of "map" of local areas in the fitness landscape [60]. On the other hand, these problems can rarely be formalized entirely; the design space is simply too large. Thus, by following a purely theoretical approach, one might miss opportunities further afield (in addition to being slowed down in the search process).

The issue about the focus of search was also addressed by the experts in this study. To start with, it appears, from what one of the experts said, that the way search is conducted is influenced by the underlying motivation: "*often it is driven by curiosity at the academic level; its just an interesting and difficult area and you just wonder what is happening. It may be completely decoupled from aspects of energy supply or security. More and more though, almost all of these talks you will ever see about hydrogen will normally be preceded by something about climate change and security of supply. In the past that may not have been the case, certainly not climate change, which wasn't high on the agenda. Before security was an issue it may have been simply, well how does hydrogen interact with the material, let's have a look. Now I think that the motivation is clearly environmental and security of supply issues.*"

There also appears to be some disagreement on the required focus of search efforts for making progress. While one expert sees a shift in balance towards more coordinated/directed search activity as desirable (e.g. adding that more cooperation with automotive companies for practical development is needed), another sees the lack of theoretical understanding as detrimental; "*I think hydrogen storage materials is an area where there still needs to be funding for fundamental research because we don't understand well enough how hydrogen interacts with solids and what those processes are. There is an absolute pile of work on hydrogen storage materials and there is an absolute dearth of mechanistic information about how hydrogen reacts with the materials and how it is desorbed, and there is an incredible amount to be learned there and learning that is likely to point us in new promising directions. There is danger that the closer we get to the target, a lot of the money goes into things further down the line and the we end up losing focus on understanding the fundamentals of this. Why is it important in this case, well its important because I don't think we yet have the material that is going to solve the problem, so we do need to make new materials discovery in this area and not just try and engineer the problem away.*"

While echoing similar concerns about missing opportunities, the other expert sees the balance of focus somewhat differently, saying "*we have to be very careful here because around the corner could be the one breakthrough discovery that you need. If you put everything onto tram lines and say right, this is what we need to do, then you are going to kill the one chance there is to have a breakthrough. On the other hand, I would urge there to be close liaison and working with practical demonstrators, because it may be that a lot of what is now available can be exploited. If we go on looking for the elixir, the thing that will answer all the problems, I think we might be missing an opportunity to develop something which is already there.*

In addition to commenting on the general focus of search, experts also gave examples of specific strategies. As one example, an expert suggests that theoretical insight may give rise to focused search heuristics by which to improve the kinetic properties of complex hydrides; "*for me the key thing is for atoms to diffuse through the material at relatively low temperatures. So we think that looking, and this is something that has been neglected so far almost completely, at how quickly atoms can actually diffuse through the solids. Our current work has been based on the fact that there are ways of measuring the mobility of H atoms and ions in solids. So that is something that I think will be researched quite a lot in years to come, because it relates to charging time.*" Talking about MOFs, and the need to focus more on improving thermal conductivities, another expert says: "*I think in the past, the focus was mainly to achieve higher gravimetric density and higher surface area and other aspects were not so much considered. I think it is similar if one goes to the complex hydrides or even these mixtures* [reactive hydride composites]*, people are happy to find mixtures that give higher release or something, but they don't think so much about how you can get rid of the heat if you have several kilograms of it.*" Going further, he suggests that research activity will be going a little bit away from pure development of new materials, and focusing more on problems of scaling up the material to a more technological scale. That includes investigating methods of compacting MOFs, and ensuring adequate heat conduction. For these purposes, he suggests funding needs to go in this direction.

6.5.2.5 Inherent challenges of search

Finally, in addition to the nature of the search process, a condition for achieving success in finding better materials relates to the inherent challenges (physical or chemical) nature poses for finding solutions. It would be interesting to obtain an estimate of something like the parameter a seen in chapter 3, which is thought to characterize the ease of learning in a particular design environment. Alas, as one expert puts it: "*it is difficult to say where we can get stuck. This is not specific to this field, this is a general problem. Magnetism is the same. If you look at the history of magnetism, every 25 years there was a big step up in the ferromagnets (a big step up in the magnetization) and then, yeah, sometimes it just doesn't happen.*"

6.5.3 Subjective probabilities of progress

In this part of the results section I present the quantitative results of this study. I report on the probabilities that the experts provided on the prospects of discovering/designing a material by 2025 (of the kind specified by each expert in section 6.4.1) possessing a minimum of certain hydrogen sorption characteristics. At first, I present the joint probabilities of achieving a set of high and low performance targets. After that, I present and discuss the conditional probability distributions that were elicited for a selection of variables that were considered particularly challenging to make improvements on. The primary goal of this section is to contribute probability data that might be of interest to decision makers, researchers, etc.

6.5.3.1 Joint probabilities of achieving performance targets

Figure 6.3 contains all of the information about the elicited joint probabilities. While some of the judgements refer to somewhat different targets - the targets mainly differ in terms of volumetric capacity - comparisons between experts are nevertheless informative; all the targets were set to levels considered viable for automotive applications. In other words, one may crudely interpret these probabilities as representing the level of expectation that materials will be developed to a standard favourable for commercial success. In terms of this crude interpretation, one may rank the storage concepts by probability of commercial viability, which I have done in table 6.6. I must remark, however, that some targets are probably - to some extent - unrepresentative. In particular, due to mistakes I made during the elicitation, there are two target levels I would like to draw attention to. The first one is the high volumetric capacity target (120 g/L) judged by TM in the case of the MOF assessment; I am unsure as to whether the expert was aware of the high level this target was set at during the probability judgement. In the second instance, I note that the volumetric capacity target, set for GW, is perhaps higher than was considered necessary for automotive application. In an instance where a less consequential error had been made, this was addressed through a follow up question. These more fundamental errors could not be corrected simply without introducing other uncertainties. On account of these caveats, the ranking in table 6.6 is to be taken very cautiously.

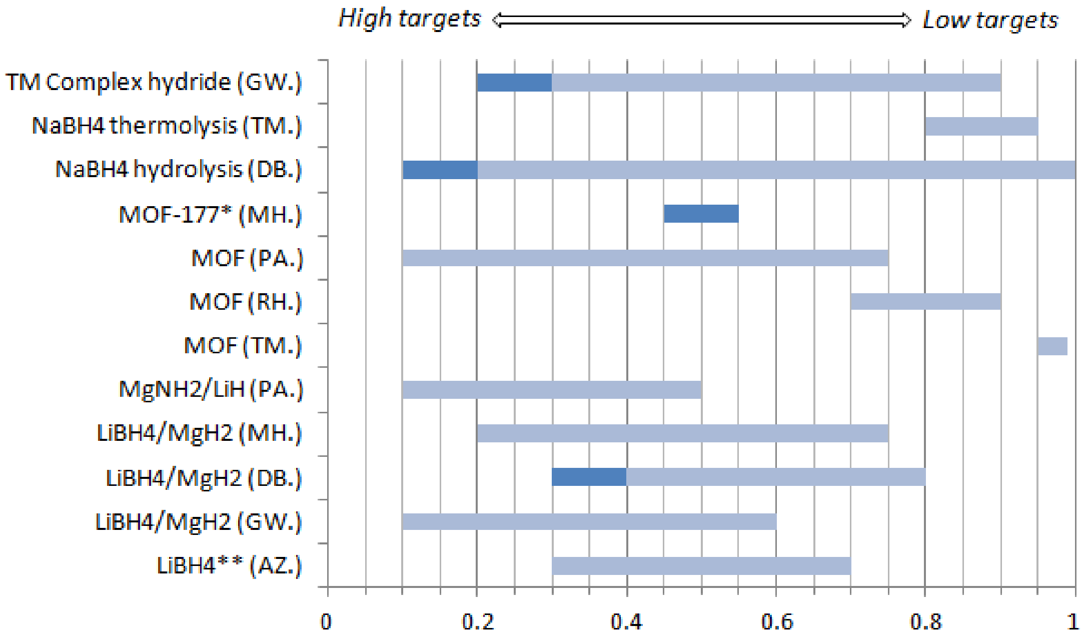


Figure 6.3: Comparison of expert judgements of joint probabilities for the achievement of hydrogen storage targets (set respectively for each expert). The left hand side of the bars indicate the probabilities judged for achieving the set of high targets, while the right hand side of the bars refer to probabilities for the set of low performance targets. The darker shaded areas represent uncertainty ranges that were occasionally specified for the high target probability judgements. *Did not feel comfortable quantifying a probability for the high targets (presumably they were set too high), therefore this uncertainty range corresponds to achievement of the low targets. **In liquid form.

Focusing on the high target probabilities shown in figure 6.3, one may notice that there is a predominance of low probability judgements; four attach a value of 0.1, and all but three are set at 0.3 or below (considering the more pessimistic value where an uncertainty range has been specified). A few probability judgements stand out. One of them pertains to the reference material “MOF”. The probability attached to this type of material achieving the high targets is 0.95, which is very confident indeed (especially as it was considered the less promising option (see section 6.4.1)). Achievement of the low targets is considered almost a certainty for this material (indeed, a higher probability was given to it than to the NaBH4 variant). A salient feature of the judgements is, in general, the relatively big difference between the probabilities for the high and low targets. Clearly, the experts thought the high targets were much more challenging. Exceptions are the judgements made by TM and RH. One might wonder what it is that determines the significance of the difference. Does it relate to the fact that there are less search heuristics the expert can think of that achieve the goal in the high target case, or do the prospects of the material simply depend on a search heuristic that the expert has more or less confidence in?

Ranking	*Reference material*
1	MOF (TM)
2	NaBH4 (TM)
3	MOF (RH)
4	LiBH4 (AZ)
5	LiBH4/MgH2 (DB)
6	LiBH4/MgH2 (MH)
6	TM based complex hydride (GW)
7	LiBH4/MgH2 (GW)
7	MgNH2/LiH (PA)
7	MOF (PA)
7	NaBH4 (DB)

Table 6.6: Ranking according to probabilities of achieving respective high targets (using the more optimistic probability value where applicable).

Taking an outside perspective (e.g. as described in [67]) of progress in hydrogen storage, a pertinent question to ask is; how many distinct events are being judged and are they independent? Given that, in terms of information flows and funding decisions etc., hydrogen storage research appears to be quite a coherent/interconnected academic discipline, could one argue that the event of one material achieving the high targets is independent of another? If one could, then it is easy to see that the number of distinct materials (or domains of research activity) considered viable prospects for the high 2025 targets, is significant in terms of the probability that at least one material will actually achieve it. On that basis, one must wonder how many more material types would have been selected, if more experts had been interviewed? As an example, we may focus on two distinct events - domains of research activity - represented in figure 6.3, say, MOF type materials, and reactive hydride composites. One may take either material, and attach a probability to the event that it achieves, in meeting the high targets, a commercially relevant performance. To estimate this probability for the MOFs, in a rather crude approach, one may use a simple average of the high target MOF probabilities (see figure 6.3); that gives a probability of 0.58. An average for the reactive hydride composites gives 0.175. The calculation that at least one of these events occurs, goes as follows;

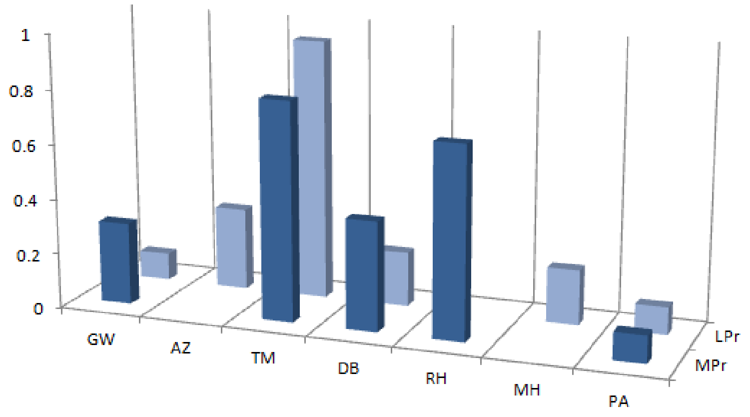
$$P(no\,event\,occurs) = P(MOFs\,fail) \times P(RHCs\,fail) \tag{6.4}$$

$$\Rightarrow (1 - 0.58) \times (1 - 0.175) = 0.3465$$

$$P(at\,least\,one\,event\,occurs) = 1 - P(no\,event\,occurs) = 0.6535 \tag{6.5}$$

This probability can only increase by considering more viable material types. From an outside perspective then, the probabilities given in figure 6.3, suggest quite strongly (if one assumes the events to be independent), that the hydrogen storage agenda has a fairly good chance of producing a material that will hit targets relevant for automotive applications. Of course, a key underlying assumption for drawing this conclusion is that the events are indeed independent. It must be noted that this is not a terribly strong assumption. For instance, one possible argument against it is that the funding levels for one project is not independent of funding for another, or in fact, that the number of researchers drawn to a project is also dependent on the opportunities offered by other approaches.

A final observation of the probability data presented in figure 6.3 is the difference in probability between the most and least promising material. I have made this comparison easier to make in figure 6.4. It is interesting to note, in the cases where data is available, that there tends to be little difference in these probabilities. In fact, in the case of TM, the material considered less promising (clearly not in purely technical terms) achieves a higher probability.



	GW	AZ	TM	DB	RH	MH	PA
MPr	0.3		0.8	0.4	0.7		0.1
LPr	0.1	0.3	0.95	0.2		0.2	0.1

Figure 6.4: A comparison of the probabilities assigned to the most (MPr) and least (LPr) promising materials for the achievement of the respective hydrogen targets.

6.5.3.2 Conditional probability distributions of selected variables

Charging time Charging time was one of the particular challenges associated with the hydride materials. The conditional probability distributions for two types of materials are shown in figures 6.5 and 6.6. A striking difference between the two is their respective plausible ranges; the first figure, representing a complex transition metal type hydride, exhibits one of 14 minutes, while the second, referring to an amide based multi-component system, has a range a factor of four greater (57 minutes). In the second case there are clearly very low probabilities apportioned to the possibility that charging time will reach its high target as displayed in table 6.5. In fact, considering the somewhat approximate distribution fit in figure 6.6, one might attach a probability of about 6% to the prospect of achieving a charging time in line with the target. This low probability, which presents a small discrepancy with the joint probability estimate shown in figure 6.3 , is a reminder that the target values on which the joint probability judgements are based, are to be taken approximately. More interestingly, the distribution of this material indicates that the most likely outcome is around 20 mins - certainly quite a distance away from the DOE targets. One of the ways people are attempting to improve the kinetics of multi-component hydrides, as one expert notes, is to find ways of confining the reactions (e.g. forming new microstructures). The distribution for the complex transition metal based hydride looks a great deal more promising, even suggesting the possibility of recharging the material, at least at isothermal conditions, in one minute. For this system, a moderate charging time of about 6 minutes is the most likely outcome.

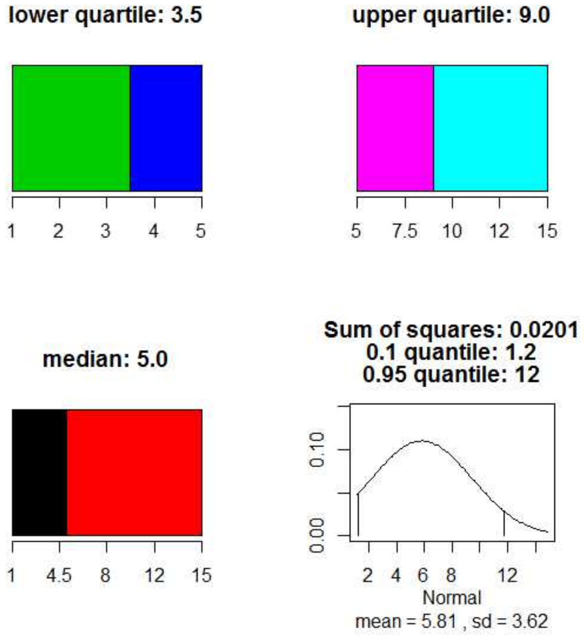


Figure 6.5: Probability distribution over the potential outcomes of the charging time of a complex transition metal type hydride (as judged by GW). Notes: The charging times displayed on the x-axis are in units of minutes. The three boxes were used as visual aids during the elicitation of three key percentiles; the lower quartile, median, and the upper quartile. The colours carry no significance other than to aid the visual assessment.

Finally, for these materials, one should note that in more practical situations, it is not alone the inherent kinetics that presents a challenge. As one expert explains; "*the refuelling time is a problem because of the heat evolution. So I think I have more doubts that these hydrides can be used in a mobile application because of the charging I think.*"

Gravimetric capacity To put things into perspective, one of the experts feels that 11 wt.% is a very ambitious target. In fact, he feels that it is really the maximum of what would be "*physically possible.*" He substantiates this view with the claim that we will certainly not exceed 20 wt.% in the material (unless we bind hydrogen to carbon), and most materials which have close to such a high mass density don't deliver all the hydrogen under reasonable conditions. The following probability distributions for gravimetric capacity, shown in figures 6.7, 6.8, and 6.9, appear somewhat more optimistic. Each has a median

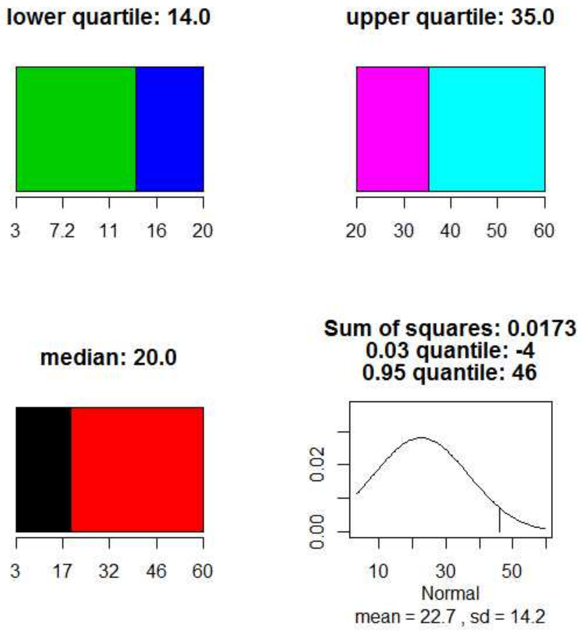


Figure 6.6: Probability distribution over the potential outcomes of the charging time of a multi-component amide containing material (as judged by PA). Notes: The charging times displayed on the x-axis are in units of minutes.

value of 8 or 9 wt.% (taking into account the definitions used for DB and GW). The distribution for TM (figure 6.9) exhibits the largest range (accounting for the conversion in the definition for capacity according to equation 6.2) of about 12 wt.%. That of DB and GW is 9 wt.% and 8 wt.% respectively. In fact, the distributions for DB and GW are quite similar (despite being fitted by different parametric distributions) in terms of shape, and both put the upper limit at 14 wt.%[6]. Both distributions refer to hydride type materials. In the first case, multi-component hydride systems, and in the second, complex transition metal hydride type materials. While the former is associated with various high capacity materials, such as LiBH4 (with a theoretical capacity of 18.4 wt.%), it is somewhat surprising to see such high potential perceived for the latter. After all, most of the known materials of this kind, while generally exhibiting very high volumetric capacities (e.g. Mg2FeH6 even reaches 150 g/L), have relatively low gravimetric capacities [84, p. 148] (MgFeH6 is up there with 5.5 wt.%). But although these materials have not received that much attention, partly for the reason of relatively low capacities and high desorption temperatures, as noted in [34, p. 44], it seems likely that there are many more, as yet undiscovered, multinary complex hydride compounds, and continued work into this area may yet prove fruitful.

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[6] Note, one should not interpret the fitted distributions too precisely. For instance, the fact that the fitted distribution in figure 6.7 indicates a 5% probability of exceeding even 14 wt.%, does not necessarily reflect the expert's view. The experts were asked to specify an upper bound which would be extremely unlikely to be exceeded. On occasion, the fit of the distribution might slightly distort this picture.

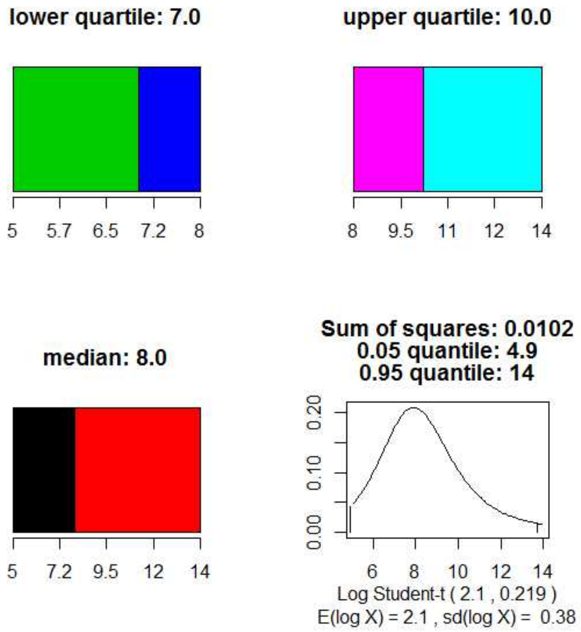

Figure 6.7: Probability distribution over the potential outcomes of the gravimetric capacity for a multi-component hydride system (as judged by DB). Notes: The capacity values displayed on the x-axis are measures of weight percent as per the definition used by DB.

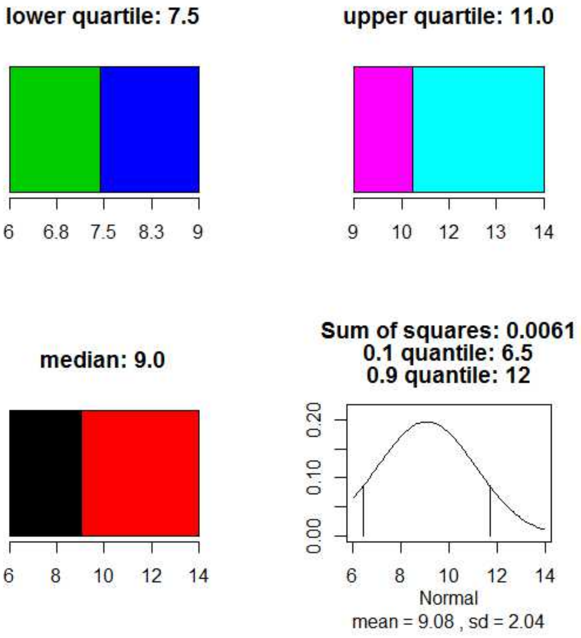

Figure 6.8: Probability distribution over the potential outcomes of the gravimetric capacity for a complex transition metal type hydride (as judged by GW). Notes: The capacity values displayed on the x-axis are measures of weight percent as per the definition used by GW.

Figure 6.9, representing a MOF type material, illustrates an interesting comparison to the hydrides. While TM has the highest uncertainty, as reflected by the range of his probability distribution, that is largely due to seeing scope for even higher capacities than the hydrides

- up to 16.7 wt.% (again, making the conversion in the definition he applied). Evidently, MOFs can achieve very high gravimetric capacities even now, but as depicted in table 6.4, there is a trade-off type dependence with these materials between gravimetric capacity and volumetric capacity (greater specific surface areas tend to come with more volume). One might wonder whether the upper range in gravimetric capacity is truly conditioned on the event that the volumetric capacity reaches its respective high target (which for TM was set at an extremely high target for MOFs[7] - 120 g/L) - an assumption which was required for this judgement task. If it is, then figure 6.9 is truly a surprising result. More likely, this target value was simply overlooked in the judgement tasks, reflecting an error on my part for not providing adequate feedback.

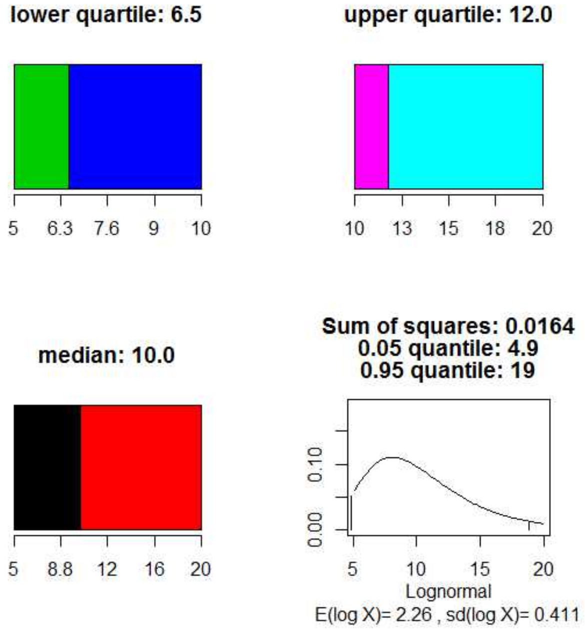

Figure 6.9: Probability distribution over the potential outcomes of the gravimetric capacity for a MOF type material (as judged by TM). Notes: The capacity values displayed on the x-axis are measures of weight percent as per the specific definition used by TM.

Volumetric capacity Finally, figure 6.10 shows the conditional probability distribution for the variable "volumetric capacity". This distribution pertains to the technical prospects of metal-organic frameworks, as judged by MH. Immediately, the shape of the distribution is striking with respect to the previous ones. It attests to the fact that the expert perceives little chance of achieving volumetric capacities that are significantly above contemporary accomplishments. Indeed, owing to the particular shape of this distribution, the most likely value is approximately equal to the lower bound. According to the particular fit, there is about a 10% probability of achieving 60 or higher, with the upper bound set at 65 g/L. Comparing this outlook to the demands of the DOE - requiring, for the ultimate target, 70 g/L on a *system* level (table 2.1) -, certainly raises questions over the commercial viability of adsorbent systems for automotive applications; even if the upper bound were achieved,

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[7] Even considering single crystal densities

it would require very efficient compaction methods (such that there is not a significant volumetric penalty at the level of the bed phase), and balance of plant components, such that this type of system would not be out further than a factor of three. But as was indicated in a preceding section, part of the expectation for this type of system derives from the prospect of conformable vessel designs (thus reducing the required capacity level).

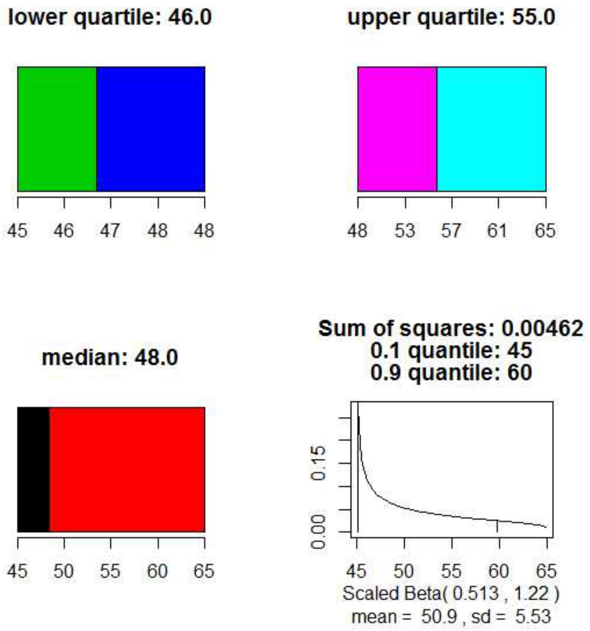

Figure 6.10: Probability distribution over the potential outcomes of the volumetric capacity for a MOF type material (as judged by MH). Notes: The capacity values displayed on the x-axis are in units of g/L as per the definition used by MH.

6.6 Discussion

Probabilities on the prospects of advancement in hydrogen storage materials were elicited. These probabilities are given the meaning of subjective degrees of belief. Moreover, I interpret them as representing measures of technology related expectations. In turn, the expectations may be seen as relating to views on the pattern of discovery and progress in hydrogen storage materials search. How much relevant experience and knowledge they ultimately draw on is difficult to say. For instance, the probabilities may strictly pertain to the confidence that specific search heuristics will uncover a variant of the required fitness. They might draw on a more general experience of patterns of progress (e.g. employing a form of “reference class forecasting”). The main sources of judgement error in this study are presumably overconfidence (simply because it is a prevalent trait [92, 124]), and the inherent lack of predictability associated with the task context.

In terms of expectations of promising materials, the extensive interviews revealed that they are very much linked to expectations of the material’s future niche. Hence, an expectation that cryogenic operating temperatures would be infeasible in the future, would likely rule out any high expectations for physisorbent material concepts. Interestingly, cost did not seem to play as big a role by comparison. Different choices of material concepts that were considered viable candidates, also implies that the current level of performance is not decisive in determining the level of expectation. As one expert noted: "*Just to put things into perspective, I acknowledge that some of the things I categorize as least promising score very well on variables such as volumetric capacity or mass density, perhaps better than some of the materials I am regarding as more promising. The reason for that is that with these other categories it is very difficult to meet, I don't think they will meet those targets.*" Hence, material specific expectations are really related to the promise of search heuristics for the respective materials (as suggested in chapter 5). Incidentally, these insights into the construction of expectations in basic research inform us on some of the selection pressures present in this early phase of development. Finally, it is telling that there is some variation in the target levels that were decided upon, and discrepancies among expectations that were given to justify them; it suggests there is still a general uncertainty about future requirements, indicating a lack of (convincing) convergence toward technical standards.

In principle, the elicited probabilities could be of interest for several reasons. For instance, if one attaches a high reliability to the assessments, they could assist in portfolio allocation decisions. A basic procedure might be 1) assess which target set is considered necessary/desirable, 2) compare probabilities for all options that satisfy those targets, 3) apply the probabilities to a portfolio allocation decision rule, e.g. as in [140]. From an outside perspective, a complete set of probabilities for all viable candidates would be of interest, as that would give some indication of the probability that at least one storage concept achieves the relevant target levels. However, one must be cautious in treating the prospects of different materials as independent events.

A further benefit of probability elicitation may derive from the communication of such formal measures of uncertainty; it may reduce the possibility of inflated expectations because an individual is more accountable to their predictions. Periodic measurements of technological advancement probabilities could also serve as an interesting measure of progress. By being updated periodically, the trend in probabilities would reflect the learning process and, for example, indicate domains where knowledge (e.g. of a region in design space) is lacking due to high or increasing uncertainties. The conditional probability distributions elicited in this study would be most informative for this purpose (e.g., a series of measurements of the entropy of uncertainty).

6.7 Conclusions

There are important (potential) sources of judgement error that must be considered in this study. Firstly, as was discussed, there exists an inherent lack of predictability within this task context. How much, is challenging to say, perhaps a calibration study could shed light on this. It is presumably the most difficult source of judgement error to nullify.

Secondly, there are the biases of judgement. One that has been found in many contexts (e.g., see [152]), and is unlikely to be completely dismissible in this one - despite special interview techniques - is the overconfidence bias. Other sources of judgement bias may be dependent on systemic/contextual factors. While the study sought to condition the uncertainties for the search process more or less equally, it would perhaps be naiive to think that various factors such as research culture, funding, etc., did not play a role the experts' judgement processes. One way to control somewhat for such a "noisy" influence on the desired judgements would be to scale up the study. In other words, the goal would be to have a sufficient number of experts with diverse perspectives judging the prospects of the same material. Important variables to consider, that would describe these perspectives, would be geographic location (e.g. EU, USA, Japan, Korea), funding outlook, theoretical vs. experimental focus, and the type of research institute. This approach would permit us to compare different perspectives more directly than was possible in the current study. Perhaps more interestingly, it would enable us to provide an aggregate perspective on the prospects of a particular material. Such an aggregate could take the form of a simple average of the probability judgements, or it could involve more complicated weighting schemes. Viewing this study as an excercise in foresight, an aggregate perspective is interesting inasmuch as it promises to be more accurate (see [124], c.f. the "diversity prediction theorem").

While acknowledging the potential scope for more refined and robust insight, this study was nevertheless able to produce interesting output. An appreciation was gained for the nature of expectations underpinning the search process. Contrasting expectations depend not only on the inherent technical prospects that are perceived, but also on contrasting views about the most likely enabling conditions - that is, target niches - that are to emerge.

In terms of the quantitative results, this study indicated that individual material variants tend to be associated with rather low expectations for achieving the set of high performance targets. On the other hand, the diversity of "promising" materials that apparently exists implies that a less partial perspective may anticipate technical breakthroughs with a reasonable degree of optimism. The conditional probability distributions documented in an original way our ignorance over the outcomes that are thought to be attainable on challenging metrics. The distributions that were elicited tended to be quite broad, indicating a considerable scope for learning (learning, in this context, can be viewed as a reduction in uncertainty). By tracking the learning process, for example, through a measure such as entropy, it might be interesting to investigate what kind of search strategies prove to be more effective. Of course, such studies would rest on the assumption that the expert elicitation technique is reliable in representing the expert's true uncertainties. In the least, this study has given no indication that this view should be discouraged.

During the interviews I discovered that most experts do not actively tend to think probabilistically about the prospects of their research projects. It is interesting to ask whether more probabilistic deliberation could influence the way in which expectations are formed and communicated, and if so, to what effect.

The end of this chapter marks a closure on the theme of learning and progress in hydrogen storage technology. In the next chapter I shift my focus to another core element of technological evolution: selection. Given the relatively immature status of most hydrogen storage concetps that are of interest to this project, the pressures of selection that I seek to study apply during an early period of the technology life-cycle. Were one to know all of the selection pressures with infinite detail, then one could, at the least, predict which technologies - in their current form - will not succeed. Much more modest knowledge of the prevailing selection conditions would allow one to anticipate - crudely - promising directions of development. Working with yet more uncertainty about the actual selection pressures, the next chapter is more exploratory in nature. The objective is to examine a methodology that would serve the purpose of better anticipation.

7 An exploratory analysis of selection pressures operating on hydrogen storage system concepts for automotive applications

7.1 Introduction

Whether in the biosphere or the technosphere, selection forces play a central role in the becoming of new species. This theme was thus considered an appealing focus for a study on technological prospects. How such selection pressures (particularly in the fluid phase) might be studied productively, and thus contribute to better anticipations of technical development, is one question this chapter seeks to address.

The ultimate selection environment that technologies face is most commonly the market. To get there, the concepts must "survive" several rounds of earlier selection phases however (for example, in funding allocation decisions). In these earlier phases of selection, the notion of performance is more fluid [21, 32], and indeed, there is deliberate strategic action to influence the prevailing selection pressures. As described in [67], actors play "socio-cognitive games" in trying to affect technology assessments in their favour. As technologies get closer to market, the selection pressures of the market increasingly have more influence. Indeed, it is common for firms to employ formal selection procedures to aid the "concept selection" phase of their product's development [156]. The criteria that will be dominant in these selection rounds are closely tied to the firm's assessments of market needs (additionally, evaluation criteria will be based on competitor offerings, cost, and manufacturing issues) [156].

The objective of this study is to explore such selection pressures that exist in the automotive sector (or at least, a close approximation to them), and use them for a comparative analysis of a select number of hydrogen storage system designs. One key question would be for example, how much do varying performance levels matter across different selection pressures.

The approach to studying selection pressures emerged from an appraisal of various methods by which to assess the status of a technology with regard to its comparative performance excellence. In other words, the original motivation for this chapter lay in a simple comparative assessment. Such would have had a normative interpretation. However, I elaborated this approach on discovering selection/winnowing down methodologies commonly used in industry practice. There are two key data sources that underlie this analysis; 1) data on the performance of hydrogen storage systems, and 2) value data that form the basis of the selection models. The former was collected through literature searches, while the latter was obtained through an online survey. The survey is structured according to a multi-criteria decision technique. I justify its use and provide a background discussion on it in the first two sections. I then outline key choices made for my particular analytical approach (methods section), and finally present results and conclusions.

7.2 Multi-criteria analysis: A model for representing selection pressures

7.2.1 Selection context

For technologies to be successful, they must do a good job at "predicting" their selection environment, i.e. predicting which levels of performance will lead to adoption (leaving aside influences of selection that don't directly relate to a technology's performance/cost characteristics). Ultimately, their rate of adoption is determined by market selection forces (or by forces in non-commercial applications). But even to reach this stage, there is often tough competition among design variants to be selected for further development by a design team. In the early phases of design exploration, the competition is typically between design variants of different subclasses, and hence, winnowing down this set is known as the "concept selection" phase of the design process [156]. It should be noted that although concept selection is a convergent process, it is frequently iterative and may not produce a dominant concept immediately [156]. A large set of concepts is initially winnowed down to a smaller set, but these concepts may subsequently be combined and improved to temporarily enlarge the set of concepts under consideration [156].

Concept selection is often performed in two stages. Screening is a quick, approximate evaluation aimed at producing a few viable alternatives [156]. The US DOE's Hydrogen Storage Engineering Centre of Excellence (HSECoE) down selection process is a suitable example of this. "Concept scoring" is a more careful analysis of the narrowed-down set, in order to choose a single concept most likely to lead to success [156]. Note, this method is applied at the level of the overall product concept (at the beginning of the development process), but also at subsystem levels (later in the development process) [156]. At the product level, the system is relatively easily evaluated in terms of its attributes (chosen to reflect how well the needs of customers are met). At the subsystem level, an evaluation of a concept would have to take into account the effects that different performance levels on its attributes would have on the overall performance of the system. To do so, one would have to make assumptions regarding the design variables of other system components where there is an interdependence in meeting the needs of the product as a whole. While these evaluations are typically not exact (there is no mathematical formalization of the entire system), one may expect that experienced designers have a feel for changes in fitness associated with changing certain parameters. The designer's judgements are ultimately exerting the pressure on subsystems to adapt favourably. The complex mental effort faced by designers is described in [24, p. 34]:

> *To imagine a better new design, the designer must know the relationships between structural elements, which are dictated by the laws of physics and logic. The designer must also know which functions he or she intends for the artefact to fulfil, and how these functions constrain the artefact's structure...The designer must have mental concepts of value and of value changes. The designer's concept of value may be primitive (it works or it doesn't) or refined (market prices, option values), but some concept of value must be in the designer's head, to provide a guide for action (the new design is worth trying or isn't)...The designer must first associate changes in the structure of the artefact (the design parameters) with changes in its functions. Then the predicted changes in function must be projected onto a change in "value"...Although the concepts of structure, function, and value must be present in designer's minds, the relationships between these concepts need not be framed with precision. The notions may be very fuzzy, perceived as intuitions and hunches, not articulated or voiced.*

At present, compressed gaseous hydrogen (CGH2) is the dominant choice for automotive OEMs. As seen in figure 3.4, convergence toward CGH2 hydrogen storage technology has been the trend of late in prototype demonstrations. Going forward, several OEMs have projected rolling out initial fleets in the coming years based on 700 bar CGH2. However, aside from innovations in the conformability of tanks (with significant potential to improve volumetric capacity) etc., the performance potential of these systems is fairly restricted, and not utterly convincing with respect to the performance levels customers are used to. Therefore, one would expect a substantial competitive drive for automotive OEMs (and/or their suppliers) to eke out improvements with alternative storage subsystems, albeit that these would entail a fundamental redesign (see section 4). The aim of this chapter is to gain an appreciation for the kind of selection pressures that various storage system designs will be up against in vying for adoption in design projects. In the next section I discuss a possible approach for exploring the nature of these selection pressures.

7.2.2 Requirements of a selection model

In practice, concept selection may follow a variety of methods. Some of them are [156]:

- External decision: Concepts are turned over to the customer, client, or some other external entity for selection.
- Product champion: An influential member of the product development team chooses a concept based on personal preference.
- Intuition: The concept is chosen by its feel. Explicit criteria or trade-offs are not used.

- Multi-voting

- Pros and cons: The team lists the strengths and weaknesses of each concept and makes a choice based upon group opinion.

- Decision matrices: The team rates each concept against pre-specified selection criteria, which may be weighted.

Structured selection methods are favourable in terms of effectiveness, but are more time-consuming/costly. Decision matrices are used when increased resolution is required to better differentiate among competing concepts [156]. The concepts are rated on the individual criteria, and weights are derived to reflect the relative importance of the selection criteria. Concept scores are determined by the weighted sum of the ratings [156]. As described in [156], several different schemes can be used to weight the criteria, such as assigning an importance value from 1 to 5, or allocating 100 percentage points among them, or assigning weights subjectively by team consensus.

In light of these points, there are a few basic requirements for representing the selection pressures one may expect to be operating on hydrogen storage design concepts. Firstly, one requires a list of the relevant criteria on which to assess hydrogen storage concepts, Secondly, one requires ratings/judgements about different levels of performance on those criteria, and thirdly, importance weights are necessary for combining the ratings into overall scores. These elements are all common to methods of multi-criteria analysis (MCA). It therefore seems reasonable to apply such a technique, in combination with judgements of active “designers” of hydrogen storage systems, to build a tool for simulating the implications of “selection rules” in the automotive industry. This might, for instance, provide insight into key design parameters. Before providing details of my methodology, I give a background discussion of multi-criteria analysis in the next section.

Finally, I note that the selection model I apply in this study is exploratory in nature. It is not intended to give predictions of which storage concepts will be selected; there are too many unknowns for this type of claim, not least arising from my methodology. Even if I could attest to the representativeness of the model that was used, these methods are not, in practice, iron selection rules. As explained in [156], “the final selection is not simply a question of choosing the concept that achieves the highest ranking after the first pass through process. Rather, the team should explore this initial evaluation by conducting sensitivity analysis...Based on this selection process, the team may decide to select the top two or more concepts. These concepts may be further developed, prototyped, and tested to elicit customer feedback. The team may also create two or more scoring matrices with different weightings to yield the concept ranking for various market segments with different customer preferences.”

7.3 Background: Multi-criteria analysis

7.3.1 Terminology

I begin this overview by defining some basic terms used in multi-criteria analysis [74]:

Objective: An objective is an indication of the preferred direction of movement. Thus, when stating objectives, terms like "minimize" or "maximize" are used.

Attribute: An attribute is used to measure a performance in relation to an objective. E.g. it is the variable we would like to minimize or maximize.

Value: Values are numerical scores that are derived to represent the attractiveness of an attribute's performance to a decision maker.

Utility: Where the decision involves uncertainty, utility scores are derived instead of value scores, which take account of the risk as well as the value.

Weight: Weights are determined for each attribute of a decision problem to reflect how important the attribute is to the decision maker.

7.3.2 Axioms of decision making

Decision analytic techniques are not designed to give the final word on how to choose, but rather, act as a guide for the intuition. Probably the most thought-provoking issues revolve around *rationalizing* a subjective decision. However, if one accepts certain axioms, decision analytic methods can assist by pointing in the direction of choice that would be "rational" within the framework of logic built upon those axioms. The generally accepted propositions of decision-making are [74]:

1. Decidability: The decision-maker is able to decide on a preference between two options that perform differently on a given attribute.

2. Transitivity: If A is preferred over B, and B is preferred over C, then A must be preferred over C.

3. Summation: If A is preferred over B, and B is preferred over C, then the strength of preference of A over C must be greater than the strength of preference of A over B.

4. Solvability: This assumption applies to the *bisection method* of obtaining a value function. It assumes that there are no 'gaps' in values in between two other stated values.

5. Finite upper and lower bounds for value: It is assumed that the 'best' and 'worst' options are not assigned values that are either plus or minus infinity.

7.3.3 Overview of the analysis

Multi-criteria analysis (MCA) is really a family of techniques [46], each with the aim of giving support in decision problems. A common philosophy among these approaches is that they decompose a decision problem to focus attention on one aspect at a time. What distinguishes them is the type of judgements they require, and how the data is combined to produce an overall assessment. The technique I use in this study is called the Simple Multi-attribute Rating Technique (SMART), put forward in 1971 [74]. An attractive feature of this method is that it requires simple responses of the decision maker [74]. This approach has been widely adopted, also because the analysis is relatively simple. In the following overview of MCA, I will use this approach as a template, drawing on [74] as a main reference.

It is necessary to consider the following steps in MCA [74]:

1. Identify the decision maker(s)
    - In this study, the decision makers are designers/developers who have the responsibility of winnowing down a selection of hydrogen storage concepts that are being promoted for use in automotive vehicles.
2. Identify the alternative courses of action
    - These are the alternative methods of hydrogen storage.
3. Identify the attributes which are relevant to the decision problem
    - An overview of attributes is given in section 7.4.2.
4. Assign values to measure the performance of the alternatives on each attribute
5. Determine a weight for each attribute
6. For each alternative, take a weighted average of the values assigned to that alternative
7. Make a provisional decision
8. Perform sensitivity analysis

In step 4, the aim is to map performance in the original units of the chosen attributes onto a “value scale”. The value scale is an interval scale in which intervals represent the strength of preference of one option over another. For example, A has a value 20, B = 40, and C = 60. We cannot say that the preference for B is two times A and that C is three times A. But we can say that the strength of preference of C over A is twice that of B over A. Broadly, there are two approaches to eliciting a decision maker’s values. Firstly, there is simply to ask for them directly (hence the “direct value elicitation method”). This approach requires that the decision maker is intuitively competent at assessing his/her values. A second method is to elicit value functions, i.e. functions that map attribute performance to the value scale. It is sometimes easier to derive a value function than eliciting values directly [74]. There are several methods to elicit value functions but one of the most widely applied is the *bisection method*. "Bisection" because the decision maker is asked to evaluate midpoints, such that an increase from one end of the scale to the midpoint is valued the same as an increase from the midpoint to the other end of the scale. At the end of the process, five data points are elicited - performances corresponding to values of 100, 75, 50, 25, and 0. With these data points one may estimate a plot for the value function, which then enables us to assign value scores to any option whose performance lies within the function's range.

One may question at this point, what are logical choices for the worst (where value = 0) and best (value = 100) performance levels for a given attribute? A logical choice for the worst performance would either be the lowest performing candidate, or, a level of performance below which an option would not even be considered for a decision problem. These cut-off performance levels are also referred to as "benchmark requirements" [46]. Likewise, in the case of the upper limit, the highest performing candidate one would expect to find for a particular attribute would represent a logical choice. One should also consider that certain attributes have performance levels above which the decision maker no longer accrues any significant value (the value function on that attribute flattens out). It is important to note that the value scales that have been derived for different attributes may not necessarily be equivalent. That is, one unit increase in a preference score of attribute a, may not equal the same unit increase for attribute b. In other words, the value scales have not all (necessarily) been calibrated in the same way to the true underlying preference scale (see figure 7.1). This issue is an artefact of how the range limits were set.

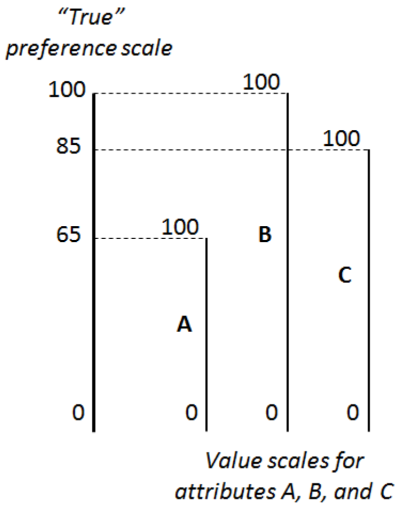

Figure 7.1: The potential in-equivalence of value scales judged for different attributes.

To arrive at an overall decision (or ranking of options), the decision maker needs to combine the values for the different attributes in order to gain a view of the overall benefits which each option has to offer. An intuitively appealing way of achieving this is to attach weights to each of the attributes which reflect their importance to the decision maker [74]. However, there is a "problem" if that intuition leads to a view that treats those weights in some absolute sense. The aim of deriving weights, part of step 5, is to equate the units of preference, so that the values for different attributes may be compared and combined. This means that the weights should take into account any perceived differences in the ranges between the least preferred and most preferred preferences scores (as example, see difference in ranges in figure 7.1). A popular approach to asking the decision maker to consider those differences is through the *swing weighting* method [74, 46]. At first, the decision-maker is asked to rank order the attributes by considering which of them he/she would most preferably swing from its worst performance level to its best. The most important attribute is automatically given a score of 100. The other swing weights are derived by asking the decision maker to compare a change (or swing) from the least-preferred value on each of the other attributes to a similar change in the most important attribute (e.g. if a swing in the second most important attribute is 80% of the value of changing the most important attribute (from its least preferred level to its most preferred level), one would assign a score of 80 to the weight of the second attribute). By convention, the weights are normalized following this procedure.

Step 6 entails an aggregation of the elicited data. The most widely used approach for this is the additive model [46]. This simply involves adding an option's weighted values scores together to obtain an overall score, but it assumes the condition of "mutual preference independence" among the given attributes. That is, by assuming that the benefits of individual attributes add up to an overall value, one assumes the problem is decomposable and compensatory (i.e. lower performance on one attribute may be compensated by higher performance on another). Mutual preference independence (or, preference independence among all the attributes considered), can be assessed by asking the decision maker to consider whether he/she is able to judge a difference in value on one attribute, without knowing the performance of other attributes[1].

Step 7: Given overall rating scores, one may now establish a formal ranking of the candidates and arrive at a provisional decision. The decision is "provisional" because the analysis is only intended as a guide for intuition, and one may require further sensitivity analysis (step 8). Furthermore, it is at this point where cost is typically brought into the equation. The trade-off decision between cost and benefit may be supported with a plot of benefits versus costs (with the costs axis inverted). This graph makes explicit the *efficient frontier*; options beneath it are dominated, while non-dominated options lie on the frontier. As described in [74], the choice between options on the efficient frontier depends on the relative weight the decision maker attaches to costs and benefits.

7.4 Method

In this study I employed the SMART method (as described in the previous section) to construct the selection models. In the following sections I justify this choice and review

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[1] Whether two attributes are preferentially independent says nothing about whether or not they are causally/statistically independent.

other key steps that were involved in deriving the selection models. The second requirement for this analysis were hydrogen storage system performance data (required as the input for the selection models). At the time of this study there were few available data sources of this type. I make references in the main to publicly available US DOE hydrogen storage reports for the required data.

7.4.1 Choice of technique

There are two main advantages of the SMART method that are relevant to this particular study:

1. Most decision analysis is carried out by a facilitator in face-to-face meetings with the decision maker(s). The facilitator has an important task in guiding the judgements of the decision maker. By contrast, I opted to elicit the decision maker's judgements through an online (Google form) survey. Since there would be no opportunity for discussion and feedback, there was a premium on ensuring that the required responses would be easily understood, and (reasonably) accurate without feedback. The SMART method fits this requirement.

2. The second consideration is one of practical relevance. In order to function as a prototypical model of selection pressures, the technique is required to reflect reasonably well the type of decision analysis that is carried out in practice. The SMART approach is similar in philosophy to the concept scoring method described in the previous section.

An important consideration, within the SMART approach, was the method of value elicitation. Rather than eliciting values to specific performance levels that would only apply to a restricted set of hydrogen storage candidates, I considered it important to elicit value functions. These could then be used to interpolate values for any hydrogen storage system whose performance lies within the range of the function.

How similar are the judgements that are required in SMART compared to the concept scoring method discussed in section 7.2.2? In both cases the judgements that are exercised are performance ratings/values and weights. The structure imposed on those judgements may differ (e.g. weights may be given on a scale of 1-5 or 1-100), as may the mode of translating a performance onto a value/rating scale. It is difficult for me to say how sensitive the overall (relative) scoring of concepts is, not to variations in the response parameters, but to the structure of judgements.

It is also pointed out in [156] that concept scoring will sometimes rely on a weighted sum of the ratings to compute overall scores. As discussed in the background section, strictly speaking, in multi-criteria analysis, this procedure assumes the condition of "mutual preference independence" among the considered attributes. I attempt to test for this in the survey, but it is often reasonable (approximately) to assume that the condition is satisfied whenever the performance levels of interest lie above the specified cut-off levels (or benchmark requirements) [46, p. 117]. I structured the survey so as to ensure that this was the case.

All in all, there are various sources of uncertainty regarding the true "representativeness" of SMART as a selection model. Not least, there was speculation about which performance metrics (attributes) to include in the analysis - I present my choice of these in the next section[2]. Nevertheless, given broad similarities, I think it is reasonable to adopt the SMART method as an exploratory tool.

7.4.2 Storage system attributes

This section contains a list of the attributes (and their definitions) that were assessed in the online SMART survey. For the attributes 1-12 the respondent was asked to provide his/her assessment of benchmark performance levels. For performance metrics 6-12 these were the only judgements required. It was assumed that there was no particular emphasis on maximizing or minimizing these attributes. Rather, achieving a minimum level of performance would be seen as adequate. This assumption meant that the survey was considerably less demanding, as only attributes 1-5 would have to be assessed in terms of value functions and relative importance. Judgements about cost (attribute 13) were asked for following the questions on the performance metrics.

1. **Storage system mass density**, in units of wt.%, refers to the gravimetric density of recoverable hydrogen available towards the end of the required operating life of the storage system. It is a measure based on the net recoverable hydrogen mass divided by the total storage system mass which includes the maximum hydrogen charge, including unusable energy (for reactive systems that gain mass during discharge, the maximum mass of this process is assumed), storage materials, any required insulation or shielding, electronic controllers, sensors, compressors, pumps, filters, safety features, vessel, interfaces with refuelling infrastructure etc.

2. **Storage system volumetric capacity**, in units of (grams H2)/(Litre system), refers to the volumetric density of recoverable hydrogen available towards the end of the required operating life of the storage system. The system volume is considered to be an effective box volume comprised by the tank and all of the necessary balance of plant components as described above.

3. **System fill time**, measured in minutes, refers to the time taken for the storage system to be completely refuelled.

4. **Cycle life** is defined as the number of cycles that can be achieved (as a mean value) by the storage system.

5. **Storage system efficiency** (in %) is defined as the ratio of the total amount of energy delivered to the power-plant (considering the lower heating value of hydrogen) over the total energy contained in the tank for a given tank rating (e.g. 5.6 kg H2).

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[2] It may be expected that several other attributes, e.g. ease of manufacturer, would also enter the analysis.

6. **Maximum operating pressure** of the storage system, in units of bars, is a measure of the pressure at which hydrogen is contained.
7. **Minimum supply pressure** of the storage system, in units of bars, is a measure relating to the minimum acceptable delivery pressure of hydrogen to the power-plant.
8. **Maximum desorption temperature** of the storage system, in units of Kelvin, is defined as the maximum acceptable temperature at which hydrogen is desorbed from a material-based storage system.
9. **Minimum operating temperature** of the storage system, in units of Kelvin, is defined as the minimum temperature at which hydrogen is contained.
10. **Flow rate**: rate of flow of hydrogen delivered by the storage system, measured in units of grams/second.
11. **Transient response** is defined as the time taken in which to change between 10% flow of hydrogen and 90% flow, or 90% flow and no flow.
12. **Hydrogen loss** by the storage system is measured in (grams/hour)/kg H2 stored.
13. **Storage system cost**, measured in 2012 USD/kWh, refers to the manufacturing cost of a hydrogen storage system.

7.4.3 Survey details

To implement SMART, somewhat unconventionally, an online survey was set up with Google forms. This approach was chosen to minimize costs and time invested, and to have the potential of a broader reach. The drawback of a survey is less opportunity for feedback or clarifying questions during the elicitation. The response rate was 10% out of roughly 70 invitations. While this survey was quite demanding for the respondent (it would take at least 30 mins), the number of responses was somewhat lower than was hoped for. Furthermore, some of the responses were incomplete, reducing the set of analysable surveys to only four. On reflection, this type of analysis is thought not to be best suited to an online survey format. Despite considerable efforts, the survey could not be made simpler. Hence, provided there are no limiting resource constraints, I would advise that the more conventional interview format is better suited.

What is the significance of sample size in this context? This type of analysis measures the ranking that is likely to result from various selection conditions. Were one to treat "rank" as a random variable, then given a large enough sample of selection conditions, one could estimate probability distributions of the rank for different hydrogen storage concepts. Moreover, it would give greater insight into the ways in which different selection rules compare. As it stands, a small sample is useful for exploratory purposes and provides for more in-depth analysis. For instance, by conceiving of the selection models as functions that map from performance onto a fitness landscape, they may be used to study the paths of most efficient ascent.

Invitations were sent to about 70 respondents. This study sought the judgements of hydrogen storage designers/developers. Hence, invitations were sent to people who had the requisite technical expertise, and who serve, at least as a proxy, as representative "selectors" of hydrogen storage systems (i.e. they may not have had the official responsibility of selecting concepts, but their judgements were considered valuable nonetheless). Invitations were sent primarily to major automotive OEMs, but also to start-ups, and some were university employed. The survey received responses from each category, though further details are kept anonymous.

ID	*Timeframe*
5	2015-2020
6	2022
7	2016
8	2020

Table 7.1: Timeframe over which the survey responses are considered to be relevant.

In addition to judgements on benchmark performance, value functions, and weights, a number of other issues had to be addressed. Firstly, what is the timeframe over which the exercised judgements were thought to be relevant by the respondents? I list their answers in table 7.1. Secondly, I attempted to assess the condition of preference independence discussed in the background section. From their answers it seems that the question was perhaps not well understood. This is not unlikely given it was a challenge to formulate a relatively unfamiliar concept concisely in a survey. Lacking insight on this question is not considered significant however, as it does not appear to be a relevant issue in the concept scoring methods (see above). Finally, given a fair degree of uncertainty involved in the online elicitation of values etc., it seemed appropriate to ask the respondents about the confidence they had in their judgements. Their responses are given in table 7.2.

ID	*Confidence level*
5	8
6	6
7	4
8	7

Table 7.2: Degree of confidence in the survey responses on a scale of 1- 9.

7.4.4 Derivation of value functions and importance weights

Value functions were derived by applying the bisection method (described in the background section) to elicit five data points. These correspond to values of 0, 25, 50, 75, and 100. Based on these data points I estimated a value function. Given a margin of uncertainty in the data, I thought that deriving the best fit was unnecessary and would probably entail over-fitting. Therefore, I simply exercised judgement, requiring that the value function varied smoothly and that there were no (obvious) points of inflection. Commonly one would expect linear, concave, or convex value functions (depending on the objective) [74]. On occasion I had less than five data points at my disposal for deriving a value function, either because the respondent had skipped a question, or because I assumed them to be outliers. These data points are shown in table 7.3. A summary of the derived value functions is shown in table 7.4. It shows a prevalence of nonlinear value functions, and some disagreement about curvatures.

ID	*Attribute*	*Coordinate (performance, value)*
5	Mass density	(5.2, 25)
		(NA, 25)
5	Volumetric capacity	(NA, 50)
		(NA, 75)
6	Cycle life	(500, 50)

Table 7.3: Table of data points that were not considered in the derivation of the value functions, either because values were not given, or they were assumed to be outliers. This enabled a smoother representation of the value function.

The weights were elicited by applying the swing weighting method (see background section). A summary of these is shown in the results section in table 7.6.

ID	*Attribute*	*Functional form*	*Sign of gradient function*
5	Mass density	linear	0
6		logarithmic	-
7		linear	0
8		polynomial order 2	+
5	Volumetric capacity	linear	0
6		polynomial order 2	-
7		linear	0
8		polynomial order 2	+
5	Fill time	polynomial order 2	+
6		polynomial order 2	+
7		polynomial order 2	+
8		polynomial order 2	+
5	Cycle life	NA	NA
6		linear	0
7		logarithmic	-
8		NA	NA
5	Efficiency	linear	0
6		polynomial order 2	-
7		polynomial order 2	+
8		polynomial order 2	+

Table 7.4: Summary table of derived value functions.

7.5 Results and analysis

7.5.1 Benchmark requirements

Table 7.5 lists the survey responses of what were considered benchmark performance requirements for hydrogen storage systems to be integrated in auto-mobile application devices. It should be noted that these have a slightly different meaning to the DOE targets given in table 2.1. The DOE targets suggest “reasonable” goals of performance, in order for the hydrogen fuel system to be competitive with the gasoline incumbent. The notion of “reasonable” is thereby left somewhat ambiguous. By contrast, benchmark requirements are intended to elicit specific performance levels, namely, the minimum which would be required for an option to be considered commercially. Hence, inasmuch as the values given in table 7.5 are an accurate reflection of the decision-maker's viewpoints, they serve as a useful basis for screening proposed design concepts.

Performance metric	*ID5*	*ID6*	*ID7*	*ID8*
Mass density (wt.%)	4.8	5	3	5
Volumetric capacity (g/L)	23-45	50	30	30
Fill time (min)	3-5	3	5	4
Cycle life (cycles)	10 years	500	50	10000
Efficiency (%)	95	90	80	99
Max operating pressure (bar)	700	5	10	500
Min supply pressure (bar)	2	2	1	10
Max desorption temperature (°C)	60-70	250	200	87
Min operating temperature (°C)	-196.15	-193.15*	-10	-243.15
Flow rate ((g/s)/kW)	0.02**	0.0167**	0.08988***	0.03**
Transient response (s)	NA	5	NA	0.75
Hydrogen loss ((g/h)/kg H2)	0****	0*	0.01*	0.2

Table 7.5: Table of performance values stated as benchmark requirements in the survey. Notes: * no units stated, ** values were computed based on assumption of a 100 kW power plant, *** original value given was 1 L/s: the indicated value is computed assuming a 100 kW power plant, and assuming 1 L of hydrogen refers to quantity at STP, ****based on response: "virtually zero"

A general look at the values in table 7.5 reveals, quite interestingly, a rather varied set of requirements. There appear to be few metrics on which there is close agreement. Moreover, there are certain metrics for which there is a huge range in the required benchmark performance levels. "Cycle life" and "Max operating pressure" are two cases in point. On the whole, it appears that ID7 has requirements that are relatively less stringent (apart from certain operating requirements), while ID8 seems to have several very demanding ones (e.g. cycle life, efficiency, min supply pressure).

On account of the high variation in the operating requirements, one might speculate about the varying kinds of storage system niche environments that have been envisaged in the performance assessments. For instance, the difference between higher and lower "max desorption temperatures" might be suggestive of whether a high temperature PEM fuel cell has been envisaged or a low temperature one. For a low temperature fuel cell the max desorption temperature would have to be significantly below 100°C in order to utilize the fuel cell's waste heat. The "min operating temperature" requirement is presumably suggestive of whether cryogenic systems are considered viable or not. In the case of ID7, such a system would seem to be precluded. The metric "max operating pressure" is presumably related to a few considerations; what kind of a refuelling infrastructure is envisaged, what kind of storage material, if any, is in mind, what kind of vessel and balance of plant system is desired etc. While the responses of ID5 and ID8 would in principle permit a wide range of storage materials (though one would unlikely wish to operate at 700 bar, even in the case of physisorbent materials), the responses of ID6 and ID7 would preclude all but those targeted by the US DOE 2017 requirements (in the case of ID6 it would be an even smaller set of potential candidates). Indeed, 5 bar is set as the *minimum* delivery pressure target in table 2.1. One might read the low figures of ID6 and ID7 as suggesting a dislike for extensive balance of plant equipment for pressure regulation. On the other hand, one must admit the possibility that the survey question has been misinterpreted, thereby placing an unnecessarily stringent limit on the max pressure limit of the storage system. The minimum supply pressure requirements are all rather relaxed (except those of ID8) as compared to the DOE targets.

It is interesting to compare the benchmark requirements for capacity with those of other target sets. With the DOE stating a 2017 target of 5.5 wt.% and an ultimate target of 7.5 wt.%, and the StorHy target set at 6 wt.% (table 2.2), most of the values in table 7.5 show a fairly close correspondence (accounting for a degree of leniency). ID7 requires at minimum 3 wt.%, a value which would even put systems like NaAlH4 into close contention - assuming a factor of 2 in the reduction of *system* capacity. A similar comparison holds for the volumetric capacity values (c.f. DOE targets: 40 g/L (2017), 70 g/L (Ultimate), StorHy target: 45 g/L). The requirements of ID6 would likely preclude any physisorbent materials in this case (requiring close to 100 g/L on a material basis).

In conclusion, the varied set of benchmark requirements stipulated in a sample of only four, might reflect that we are not yet close to converging on a dominant standard. In other words, substantially different power-train system designs are still being explored, resulting in a varied set of minimum requirements for the hydrogen storage subsystem. A further possibility is that the perceived goals (user needs) are different. In any event, on the basis of these assessments, there would seem to be potential for quite a varied candidate list of hydrogen storage materials, provided they are not eliminated in previous selection rounds. As a final word, one must be cautious not to overestimate the reliability of the assessments, given the challenging context in which they were elicited.

7.5.2 Value functions and importance weights

The following figures (7.2 to 7.6) display the value functions that were elicited for the five hydrogen storage system attributes: hydrogen storage gravimetric capacity, volumetric capacity, fill time, cycle life, and efficiency. In addition, table 7.6 gives the importance weights that were elicited in the SMART survey.

On the whole, these value functions exhibit a fair degree of variety. Not only do the function domains differ quite substantially in cases, also the functional forms show striking differences on occasion. Where there is good agreement is between ID7 and ID8 in figure 7.2, between ID5, 7 and 8 in figure 7.3, and at least functionally, between all four in

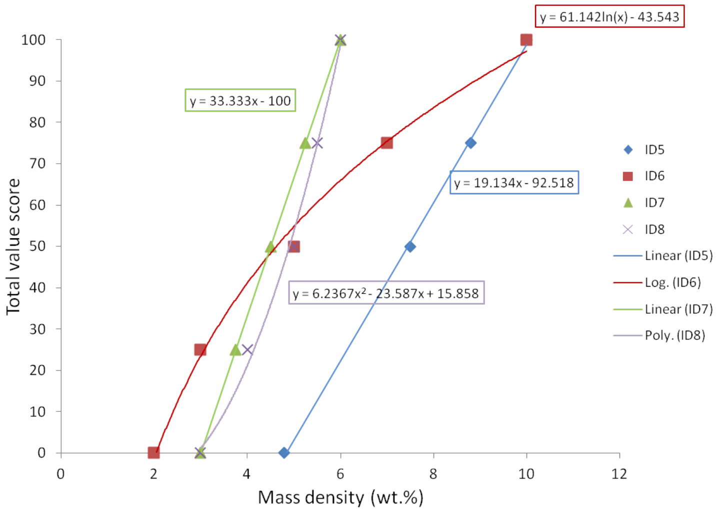


Figure 7.2: Mass density value functions. That is, a plot that maps performance onto a range of subjectively judged values.

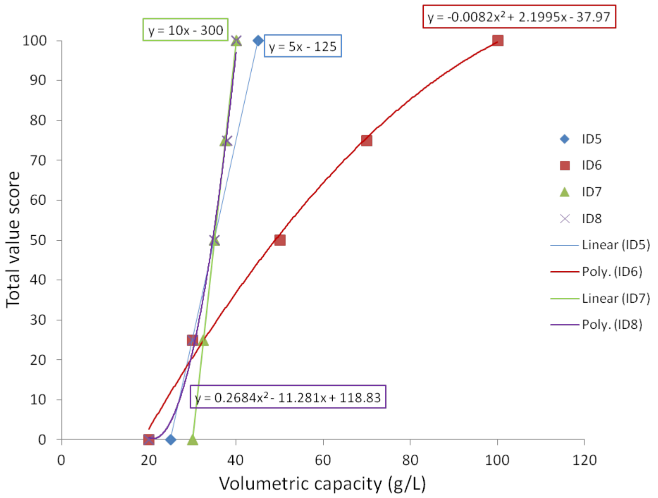


Figure 7.3: Volumetric capacity value functions.

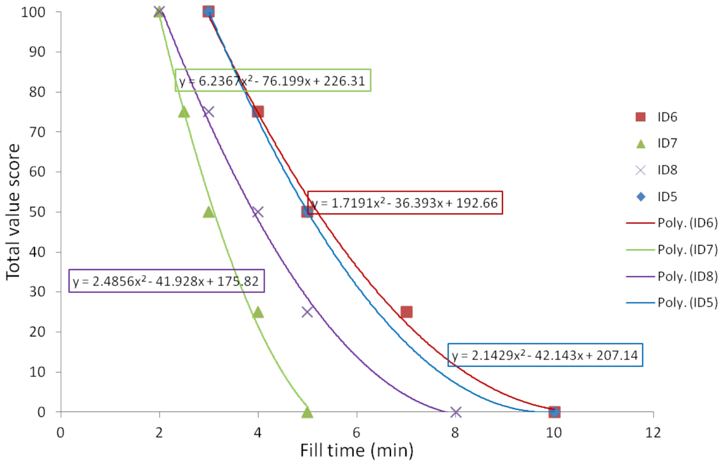


Figure 7.4: Fill time value functions.

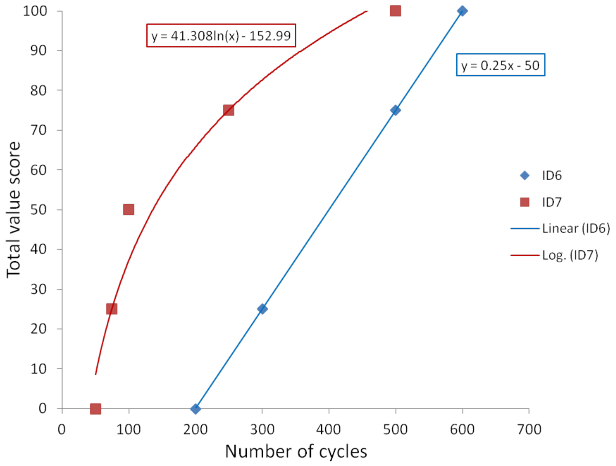


Figure 7.5: Cycle life value functions.

figure 7.4. Relatively little convergence is given for the metrics “mass density”, “cycle life”, and “efficiency”. A rather striking value function is that of ID6 for the attribute “volumetric capacity” (figure 7.3). The point at which the other respondents seemed to gain the maximum benefit - at about 45 g/L, either because they would not expect any better performing options in the near-future (noting that the 2017 DOE target is 40 g/L), or because they would not value improvements above 45 g/L (this would seem less likely) - amounts to little over 40 points in the value score of ID6. The maximum benefit for ID6 lies at about 100 g/L. This value might assume some remarkable material discovery in the future (with a volumetric capacity that would likely have to be close to 200 g/L), or it may not make any assumption at all in terms of materials. It could also assume that vessels will be designed to be conformable, in which case, the net effect of a larger tank, would be to have a higher density with respect to “useful” volume occupied. This interpretation would however presume that the respondent assumed a modified definition of the metric - i.e. in terms of “useful volume occupied” (see section 7.4.2). By contrast, one could also argue that the relatively low maximum values for ID5, 7, and 8, relate to an assumption of tank conformability, thereby reducing the required volumetric density with respect to “overall” volume.

In any case, while one assumes these value functions to be reliable reflections of the respondents’ preference evaluations, the divergences between them raise interesting questions. Most fundamentally, to what extent are the differences explained by technical uncertainty (i.e. uncertainty about the technical system in which hydrogen storage devices would be embedded, or of technological progress), target uncertainty (i.e. uncertainty about the precise needs of the market to which certain performance characteristics relate), or simply by the difficulty associated with the survey task?

Finally, table 7.6 exhibits the elicited importance weights. It is together with these data points and the value functions that overall preferences may be derived. While one might be tempted to interpret these weights in some absolute sense, for instance by saying that person A considers attribute 1 more important than person B, one should bear in mind that they were derived to reflect the ranges in performance given for the value functions. As

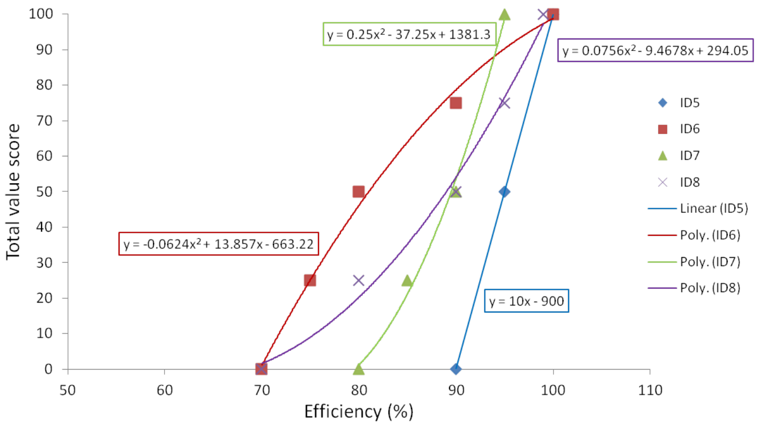


Figure 7.6: Efficiency value functions.

these are quite varied, direct between-respondent comparisons are made somewhat trickier.

ID		Mass density	Volumetric capacity	Fill time	Cycle life	Efficiency
5	Ranking	1	1	1	2	2
	Weight	0.26	0.26	0.26	0.1	0.1
6	Ranking	1	2	3	5	4
	Weight	0.25	0.25	0.2	0.13	0.18
7	Ranking	1	2	5	4	3
	Weight	0.3	0.3	0.12	0.13	0.15
8	Ranking	4	3	5	1	2
	Weight	0.12	0.19	0.01	0.35	0.33

Table 7.6: Elicited weights of the relative importance of different attributes. Note, certain weights were not provided by the respondent. In such cases I deduced a reasonable value based on the rankings that were provided for the attributes. In particular, the missing weights were: ID5 - cycle life, efficiency; ID8 - mass density, volumetric capacity, fill time, efficiency.

7.5.3 Comparative analysis of hydrogen storage performance by applying the selection models

The aim of this section is to build an intuition for the effects of different selection pressures acting on contemporary hydrogen storage technology. The focus of this analysis is not to give definitive predictions of selection outcomes, or indeed statements regarding the value of a technological option. Rather, it is to explore the pattern in which a set of hydrogen storage options might be reduced (i.e. technological convergence in the automotive sector), assuming reasonable characterizations of the selection pressures. I offer comparative insights into hydrogen storage systems and the selection models in the first two parts of this section.

An additional use of the models is as a tool for mapping out favourable directions of improvement (given the selection environment defined by the model). This potential use is discussed in the final part of this section.

7.5.3.1 Hydrogen storage system performance data

Before presenting the output of the selection model analysis, I provide an overview of the performance data for five types of hydrogen storage system. Three of them, materials-based, were selected, primarily, for data availability. While there exist several studies on the performance of solid state hydrogen storage systems, few of them report comprehensive enough data sets for the purpose of this study. As can be seen in table 7.7 - a compilation of data on the performance of various storage systems -, even among the selected ones, certain assumptions have been made whereby data from different sources (and therefore, potentially from varying system designs) have been combined. Also shown in table 7.7, is data for two physical storage methods - compressed and cryo-compressed. These systems were chosen to provide a benchmark for comparison with the solid-state options.

	Type IV, 700 bar CH2		Gen-3, 272 bar CcH2		NaAlH4 system		AX-21 system		Ammonia borane system	
Performance metric	*Perf.*	*Ref*	*Perf.*	*Ref*	*Perf.*	*Ref*	*Perf.*	*Ref*	*Perf.*	*Ref*
Gravimetric capacity (wt.%)	5.2	[7]	5.5	[122]	1.18	[12]	2.95	[12]	3.25	[12]
Volumetric capacity (kg H2/L)	0.026	[7]	0.042	[122]	0.012	[12]	0.01	[12]	0.021	[12]
Fill time for 5 kg (min)	3.3	A	3.3*	[122]	10.5	[12]	4.2	[12]	15	[12]
Fuel purity (% H2)	100	A	100	[122]	100	[12]	100	[12]	85	[12]
Cycle life (1/4 tank to full)	5500	[7]	5500*	[122]	100	[12]	1000	[12]	1000	[12]
Factory cost in $/kWh (2005 USD)	19	[7]	12	[122]	11	[122]	NA		NA	
Loss usable hydrogen ([g/h]/kg H2)	0	A	1.6	[122]	0.1	[12]	NA		2.2	[12]
Onboard efficiency (%)	83	[123]	NA		75	[12]	90	[12]	97	[12]
WTP efficiency (%)	NA		41.1	[122]	46	[8]	40	[8]	37	[8]
Operating range (low °C/high °C)	-40/60	A	-40/60	A	-30/50	[12]	-30/50	[12]	-30/50	[12]

Table 7.7: Compilation of hydrogen storage system performance data. For comparison, I have included data on two physical storage systems in addition to three solid-state devices: 700 bar compressed hydrogen (CH2) in a type IV tank, and a generation three 272 bar cryo-compressed hydrogen (CcH2) system. Certain performance measures have been omitted as they were not seen to pose a technical challenge for the systems under consideration. These include “transient response” and “minimum full flow rate”. Notes: A = assumption; NA = Not available. *Conservative estimate based on a given performance range.

To make comparisons of the data in table 7.7 easier, I have constructed spider diagrams for each storage system (figures 7.7 to 7.11). In order to plot the performance measures on the same scale, one has to normalize the data. The procedure is different for attributes with a maximizing objective than it is for attributes with a minimizing objective. Normalizing the former simply involved the following equation,

$$score = (p - w)/(b - w)$$

where p is the performance of the system under consideration, and w and b represent suitable reference values, in this case, the worst and best performers respectively. By contrast, normalizing of the latter was calculated as

$$score = (p - w)/(t - w),$$

where the additional variable t, was chosen as the US DOE 2017 target. Attributes in this analysis with a minimizing objective include “fill time”, “loss of hydrogen”, and “factory cost” (for which an old target of 4 \$/kWh is used).

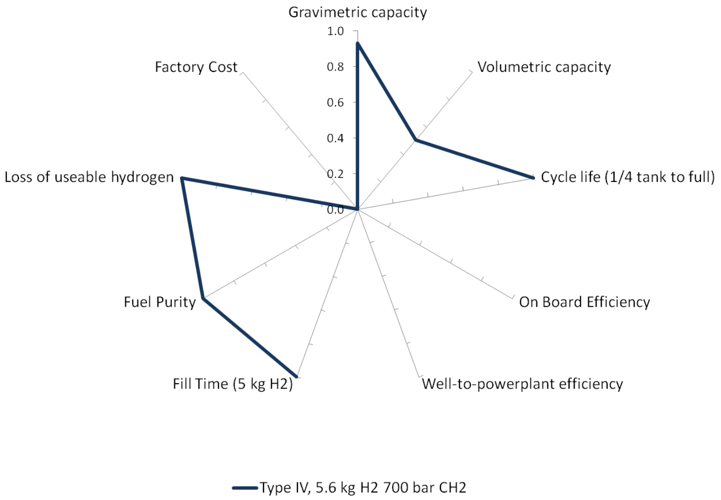


Figure 7.7: Spider diagram depicting the performance of a compressed hydrogen storage system.

As depicted in the spider diagrams, there are several pronounced differences in the performance of the storage systems. To be sure, these performance profiles represent approximate snapshots of current developments in storage system design. There is much scope for progress in many of the systems. For instance, the AB system depicted in figure 7.11, requires temperatures on the order of 250°C to deliver the hydrogen from the material at a sufficient rate. Achieving those temperatures in turn requires extra heat exchangers, which obviously impacts on the system performance. Better catalysts for the AB system could hold out much promise, not merely for the kinetic properties of the material, but also, for example, in terms of weight on the system level. One should also be aware that data reliability is questionable at times. For instance, the 97% on-board efficiency of the AB system seems too high, considering the design entails combustion of some of the hydrogen for heat management purposes [96]. It has not been possible for me to find an explanation for this figure, therefore, it would be prudent to take into account a level of uncertainty associated with it. Incidentally, the well-to-powerplant (WTP) efficiency of the AB system is certainly a drawback at present (due to challenges in the reconstitution of the material). Therefore, leaving aside the on-board efficiency for a moment, the potential of this kind of system relies heavily on technology that can efficiently (and cheaply) regenerate the material.

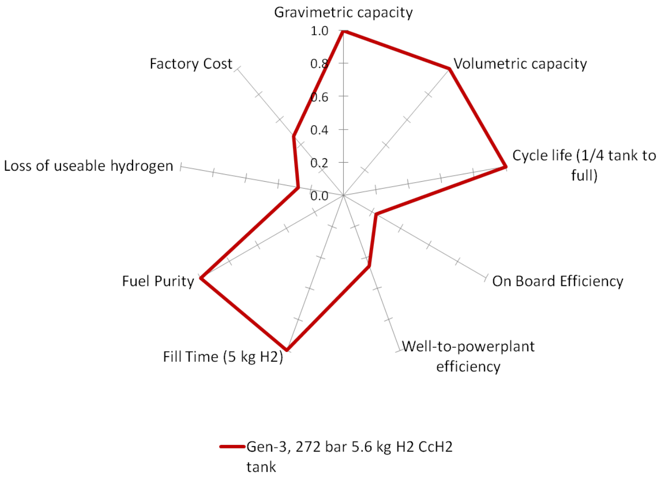


Figure 7.8: Spider diagram depicting the performance of a cryo-compressed hydrogen storage system. Note, on-board efficiency is assumed to be 80%. Unfortunately, no reference could be found that supplied a reasonable estimate on this measure. I speculated on this number for the sake of analysis.

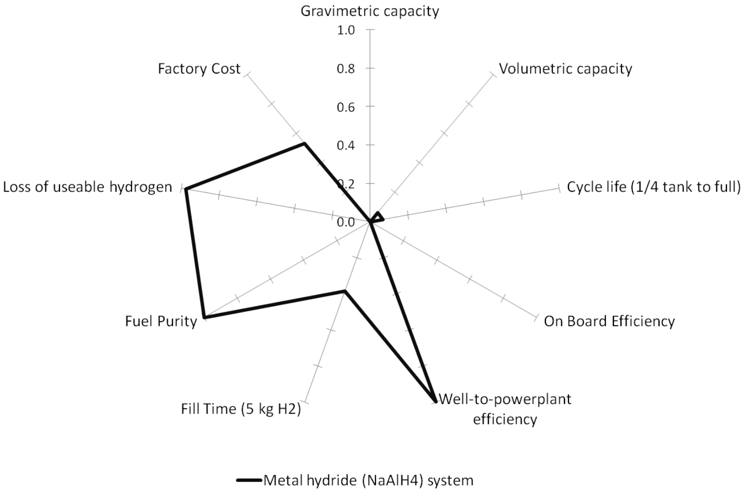


Figure 7.9: Spider diagram depicting the performance of a metal hydride storage system.

Perhaps somewhat counter-intuitive is the low capacity values achieved in the NaAlH4 system (figure 7.9). After all, one of the main motivations of solid-state hydrogen storage research is to overcome the capacity limitations of the physical storage methods. However, the latter are more advanced on a system level at this stage - in fact, they are in line with the 2017 DOE targets. Material drawbacks such as high heat transfer requirements and desorption temperatures, have a compounding effect on the system performance of sodium

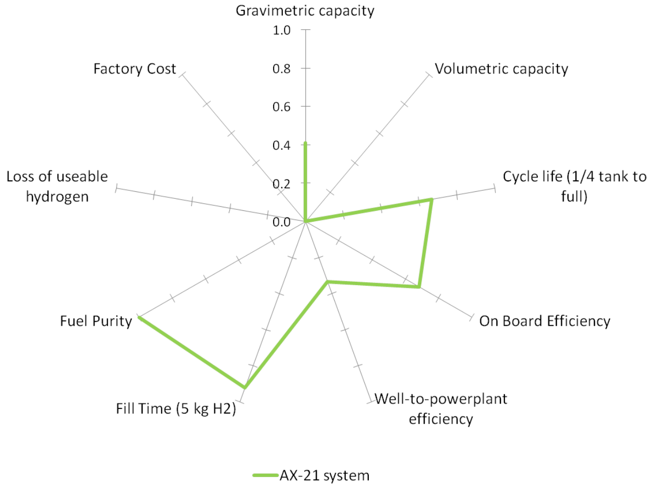


Figure 7.10: Spider chart depicting the performance of an adsorbent hydrogen storage system.

alanate. One should also bear in mind that performance data pertaining to this type of system stem from early design explorations; this, and similar systems, will not have been trimmed to optimal performance by using state-of-the-art components etc.

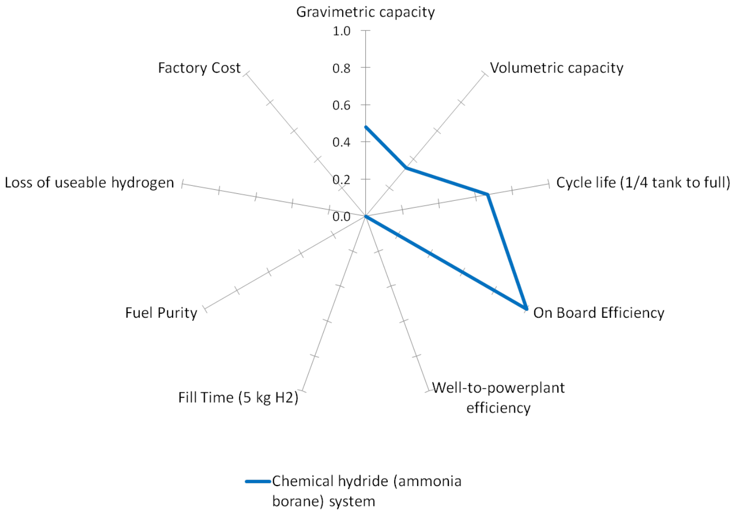
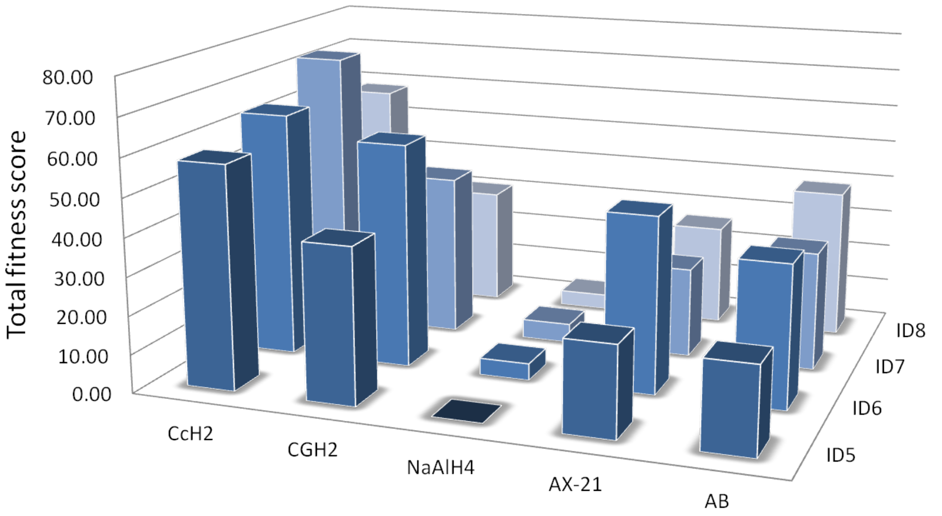


Figure 7.11: Spider chart depicting the performance of a chemical hydride storage system



	CcH2	CGH2	NaAlH4	AX-21	AB
■ ID5	58.14	40.62	0.00	23.53	22.56
■ ID6	63.96	58.60	4.38	45.91	37.10
■ ID7	73.34	42.33	5.03	23.52	30.95
■ ID8	58.43	30.85	4.02	26.38	38.98

Figure 7.12: Comparison of storage system performance (in terms of "total fitness") as computed based on the selection models of ID5, 6, 7, and 8.

7.5.3.2 Selection model analysis

The results of applying the selection models to the storage systems - characterized by five performance variables; mass density, volumetric capacity, fill time, cycle life, and efficiency (see section 7.4.2) - are shown in figure 7.12. In particular, it shows the aggregate performance, or "fitness", of the storage systems, with respect to each selection model. It appears that, despite considerable variation in the selection models, there is broad agreement in the aggregate results. The particular rankings that result are summarized in table 7.8. Quite clearly, the physical storage methods have an advantage, and the NaAlH4 system performs the worst in each scenario. Differentiating between the AX-21 and the AB system is a more contentious matter. To aid in the assessment of the types of scenarios that would be conducive to selection of a particular storage method - given the current state of play -, I have presented in table 7.9 the most favourable selection models by system type.

Ranking	*ID5*	*ID6*	*ID7*	*ID8*
1	CcH2	CcH2	CcH2	CcH2
2	CGH2	CGH2	CGH2	AB
3	AX-21	AX-21	AB	CGH2
4	AB	AB	AX-21	AX-21
5	NaAlH4	NaAlH4	NaAlH4	NaAlH4

Table 7.8: Storage system ranking according to selection models.

Ranking	*CcH2*	*CGH2*	*NaAlH4*	*AX-21*	*AB*
1	ID7	ID6	ID7	ID6	ID8
2	ID6	ID7	ID6	ID8	ID6
3	ID8	ID5	ID8	ID5	ID7
4	ID5	ID8	ID5	ID7	ID5

Table 7.9: Ranking of most favourable selection models for each storage system.

To explore the contribution that the performance differences had on the selection model results, I constructed an artificial selection model. That is, one based on the simple assumption of *linear* value functions between the limits of best and worst performance across all of the storage options (i.e. best = 100, worst = 0, and all the other values are scaled accordingly). In this construction, each performance measure lies somewhere in the value function domain - this is not always the case in the above selection models, a fact which compresses discrepancies with performance measures that lie outside of the domain. I varied the importance weights attached to each attribute randomly in 1000 trials. The results are depicted in a boxplot in figure 7.13. Ranking of the mean "fitness" agrees perfectly with the models of ID5 and ID6. Comparing the ranges between the 5th and 95th percentiles (marked by the edges of the solid boxes) suggests that this ranking is robust to variations in this model's weight parameters. Hence, it seems likely that, given the levels of discrepancy in performance, small variations in the selection models above would not significantly change the overall picture. Incidentally, figure 7.13 provides some justification for an earlier finding that most automotive OEMs have converged on CGH2 technology rather than solid-state concepts. While bearing in mind an earlier discussion that said that technical domination is not the sole criterion for technology adoption, figure 7.13, as well as table 7.9, concurrently raise the question as to why CcH2 is not the most popular choice? One reason might be that CGH2 technology is more compatible with existing infrastructure. The technical domination (and outlook) of CcH2 over CGH2 is perhaps not so great so as to justify a different infrastructure strategy.

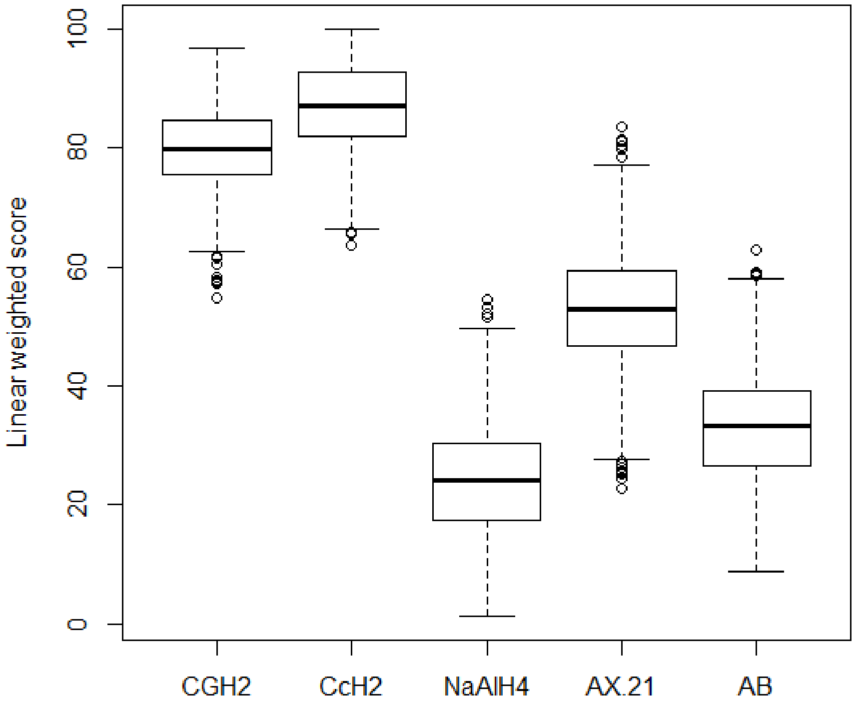


Figure 7.13: Boxplot comparing the overall performances of different hydrogen storage systems. The solid boxes show the range of data between the 5th and 95th percentiles - the solid lines indicating the means (data points outside of the range of the dashed line are treated as outliers). The data are based on a sensitivity analysis (1000 random trials) of attribute weights that were used in the calculation of linear weighted scores of overall performance (fitness) using the attribute performance data given above. This model assumes linear value functions between the limits of best and worst performance of the storage options.

The spider charts above give a useful overview of technical gaps in hydrogen storage performance. But it is not immediately clear what meaning to attach to those gaps (other than, perhaps, to interpret them in terms of technical challenge/viability). The selection models that have been derived for this study may contribute to this assessment by providing a decomposition of “fitness value deficits”. In figures 7.14 to 7.17 I have presented such an analysis; they show a breakdown, for each storage system, of the maximal fitness increases that may be gained by improving each attribute from its current performance level. Note, the graphs may be somewhat misleading if consideration isn’t taken of the following: Several performance measures lie outside of the value function domain - i.e. in some sense those performance levels are undefined. The figures 7.14 to 7.17 depict the maximum gain in fitness that is achievable. If a performance lies below the zero value mark however, one should take into account that this gap must first be bridged before any value-making improvements ensue. I have summarized the performance measures that lie outside of the value function domains - in the direction of decreasing value -, in table 7.10.

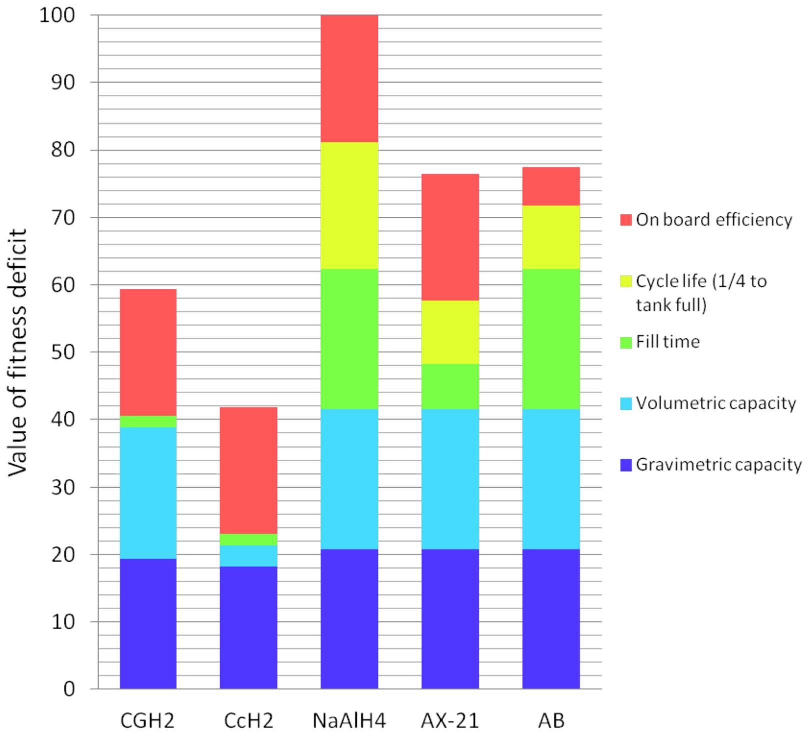


Figure 7.14: Fitness deficits among competing hydrogen storage systems according to selection model ID5. An overview of improvement potentials - in order to reach a maximum fitness score - associated with different storage systems given their current levels of performance.

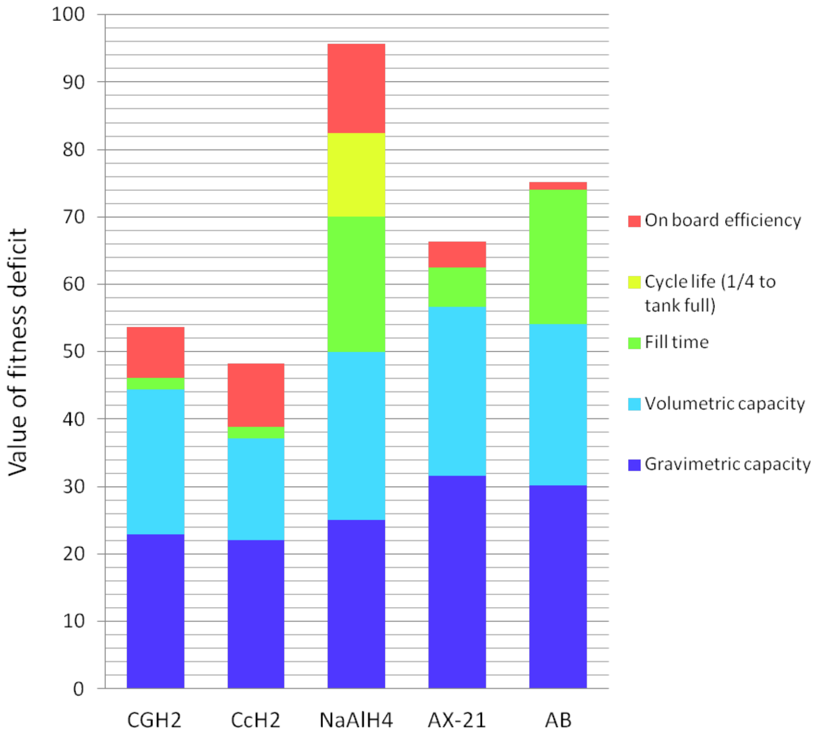


Figure 7.15: Fitness deficits among competing hydrogen storage systems according to selection model ID6. An overview of improvement potentials - in order to reach a maximum fitness score - associated with different storage systems given their current levels of performance.

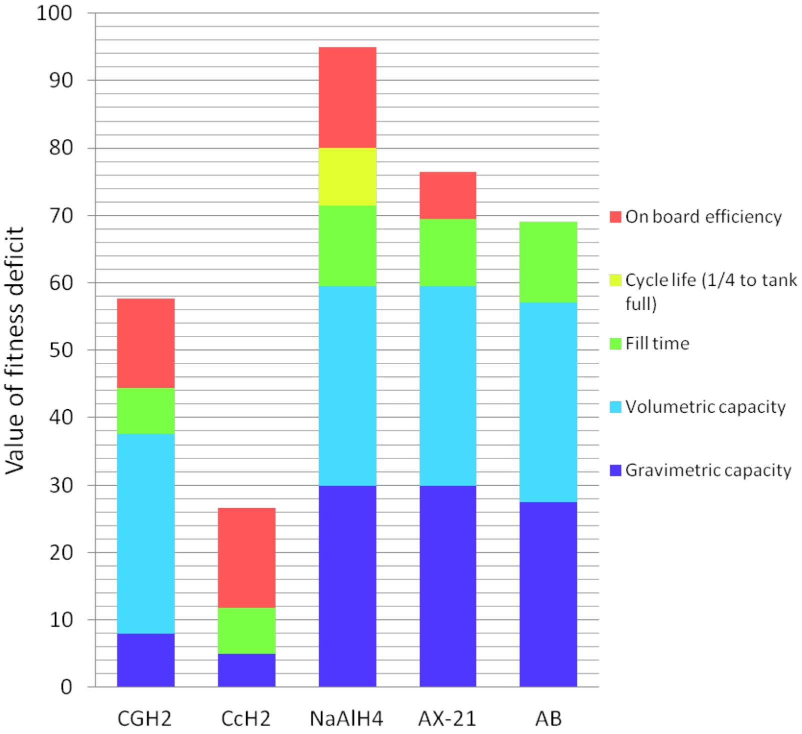


Figure 7.16: Fitness deficits among competing hydrogen storage systems according to selection model ID7. An overview of improvement potentials - in order to reach a maximum fitness score - associated with different storage systems given their current levels of performance.

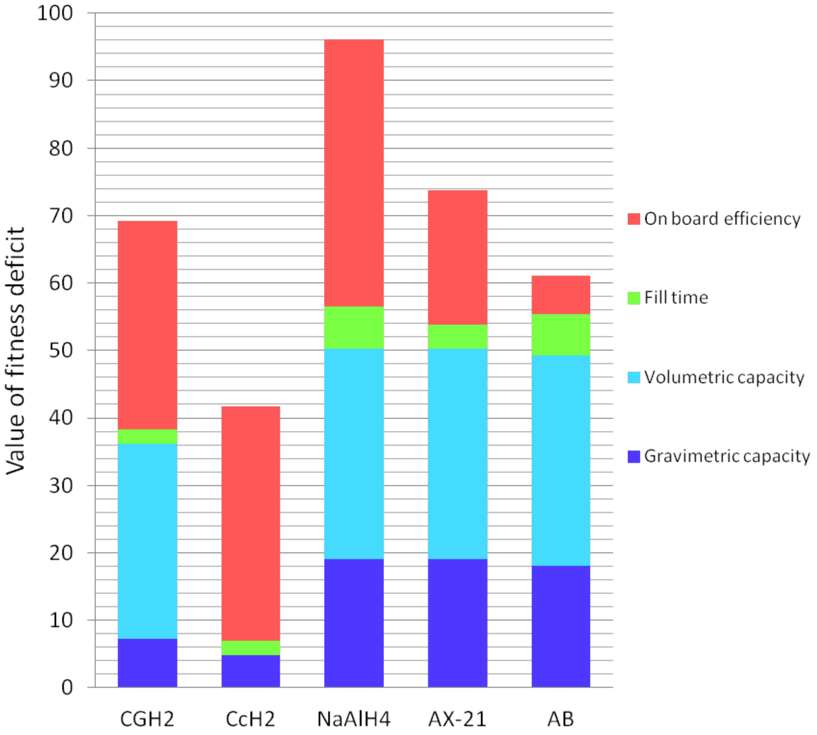


Figure 7.17: Fitness deficits among competing hydrogen storage systems according to selection model ID8. An overview of improvement potentials - in order to reach a maximum fitness score - associated with different storage systems given their current levels of performance.

System	*Mass density*	*Vol. capacity*	*Fill time*	*Cycle life*	*Efficiency*
CGH2				8	5
CcH2				8	5
NaAlH4	5, 6, 7, 8	5, 6, 8	5, 6, 7, 8	5, 6, 8	5, 7
AX-21	5, 7, 8	5, 6, 8		8	5
AB	5	5	5, 6, 7, 8	8	

Table 7.10: Performance measures lying outside of value function domains in direction of decreasing value. The numbers in the cells identify the survey respondent (or selection model variant) to which this applies.

7.5.3.3 Mapping routes of adaptation

The selection models derived for this study are based on value *functions*. Thus, there is no restriction on employing the models to analyse other storage options. In this section, I point to a more general use of the models, which, I believe, is quite interesting. Namely, one can use them to analyse aggregate performance levels (i.e. fitness values) over entire regions in performance space. Hence, one would have the potential to map out the path of most efficient “ascent” in fitness. That is, if one assumes a unit of “innovation effort” (e.g. as described in [51]), given the selection models, one would, in principle, be able to identify the set of points - coordinates in performance space (bounded by the value function domain limits) -, that represent maximal gains in fitness per unit of innovation effort. For this computation, one would additionally require an assessment of the “distance” in performance space in which one could travel, per unit innovation effort, in varying directions. Practically, there are of course infinitely many directions. But one could find satisficing solutions by estimating the distances for a reduced set.

A special case is given when the same potential distance is available in any direction of improvement. That is, when there is no reason to presume that there are any particular combinations of metrics that are easier to improve, per unit of innovation effort, than others. When that is the case, it is relatively easy to calculate the path of most efficient ascent; it is equivalently the path of steepest ascent.

Assuming, as in this study, one has five performance variables, x_1, x_2,...,x_5, five associated value functions, v_1, v_2,..., v_5, (as can be reviewed in section 7.5.2) and five importance weights w_1, w_2,..., w_5. Then the function for fitness, F, according to the additive model of the SMART approach, is simply the linear weighted sum; $F = \sum_{i=1}^{5} w_i v_i(x_i)$. If we express F in terms of normalized performance measures, then we can usefully conceive of a unit distance in (normalized) performance space, as a definitive measure of fractional progress in any direction. By computing the gradient of F, $\nabla \cdot F$, one obtains a vector whose direction points in that of maximum fitness increase, and whose magnitude is the change in fitness per unit distance in normalized performance space. Performing this calculation iteratively, one may identify the set of points that lie on the path of steepest ascent. Note, that path depends on the starting point.

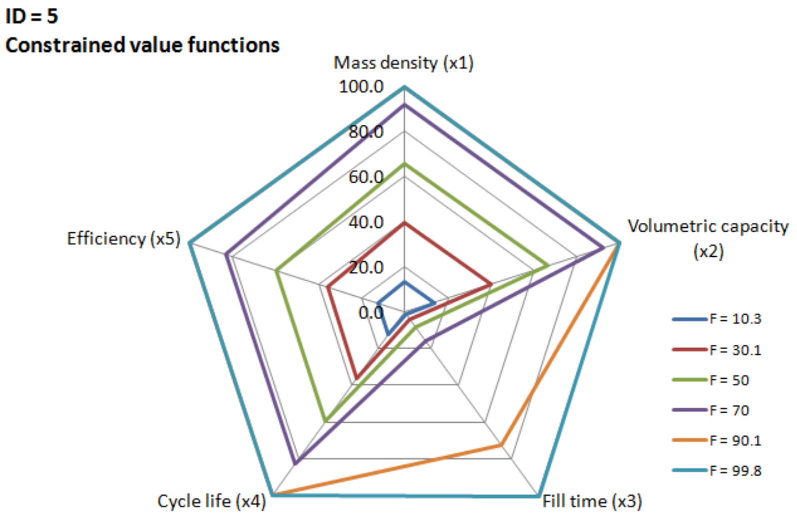


Figure 7.18: Selection model ID5: Performance evolution along the path of steepest ascent. Each line represents how the performance profile changes with a certain increase in the total fitness score F. The intervals that were chosen - to give a thorough impression of the performance evolution along the path of steepest ascent - are roughly 10, 30, 50, 70, 90, and 100. These scores, as shown in the legend, are not always exact due to the way in which the performance intervals were calculated.

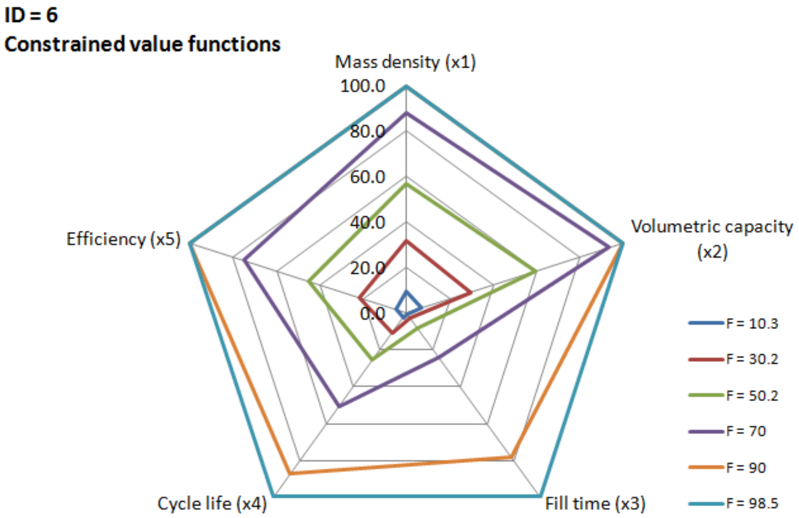


Figure 7.19: Selection model ID6: Performance evolution along path of steepest ascent.

To illustrate the approach I have performed these computations for the selection models derived in this study. In figures 7.18 to 7.21 I have plotted outputs for the four selection models. I consider a point close to zero in fitness as the starting coordinate for each path. Since the fitness function is defined by five dimensions, one's ability to make a plot of the path of steepest ascent is restricted. I have thought to use spider diagrams to depict the performance evolution along intervals on this path. I note that, in the calculations, which were performed in an Excel model, I have had to manually constrain improvements in particular directions, once maxima of the value functions were reached (F is essentially treated as undefined outside of the value function's domain).

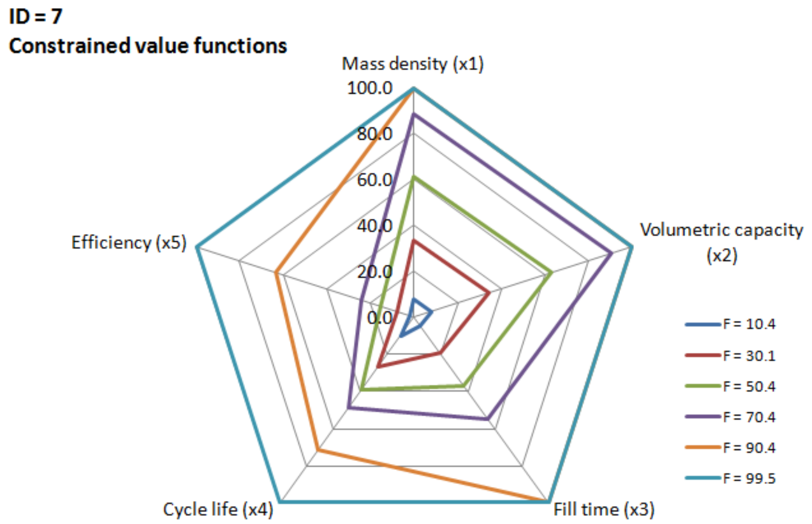


Figure 7.20: Selection model ID7: Performance evolution along path of steepest ascent.

Figures 7.18 to 7.21 illustrate quite effectively how the performance attributes are valued relative to each other. “Fill time” is consistently among the least important contributors to fitness in the early stages of ascent - this is most noticeably so in model ID8. There is also fair agreement on the importance of capacity. Apart from in ID8, volumetric and gravimetric capacity are generally the first measures to max out. In ID8, efficiency, and especially cycle life, are important early contributors to fitness. I conclude, that this kind of an approach, which is premised on the reliability of the underlying selection model, provides a useful guide to the planning of performance improvements. However, I emphasise that the above example is restricted to the assumption that every direction of performance improvement is equally challenging. Based on this, and other limiting assumptions, one could even argue that these kinds of plots map out an expected course of evolution in the phenotypes of the hydrogen storage “species”[3].

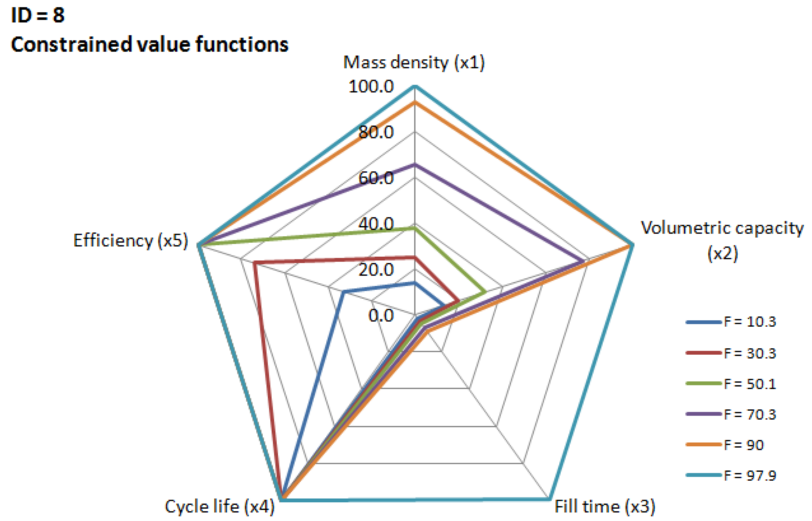


Figure 7.21: Selection model ID8: Performance evolution along path of steepest ascent.

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[3] Assuming designs with higher fitness are more likely to be selected.

7.6 Discussion

An exploratory analysis was performed to study the relations between the fitness values of hydrogen storage systems, and various selection pressures relating to automobile applications. A multi-criteria decision analysis technique was employed for the purpose of mimicking the selection rules. Such a tool enables us to consolidate the performance levels on numerous attributes into an an aggregate measure of "benefit" or fitness. In particular, this study used the SMART technique combined with an online survey elicitation format to derive the value data. The respondents to the survey were representatives of OEMs, start-ups and academia.

Leaving aside for the moment concern over data reliability, we observe that the analysis has presented rather striking differences in various aspects of the selection models. For instance, there are rather large differences in value function domains and shape. One may speculate over these discrepancies. Are they related to target uncertainty? Or do they perhaps reflect different assumptions regarding the powertrain's technical configuration? Are such differences a general feature, and if so, what would that imply? One might then expect a high diversity of technical variants to persist until the selection pressures change, provided there is not a large difference in the storage system performance profiles.

Of course, we may only begin to ask such question given the limited sample size of this study. Besides sample size, the findings ultimately rest on the quality of data input. It must be remarked that the analysis was based on various assumptions (e.g., of performance levels) and data which could not be validated by other sources. Moreover, the online elicitation format creates further uncertainties (e.g., there was no opportunity for feedback). As a consequence, the results should not be viewed as offering definitive statements on the benefits that various hydrogen storage methods offer. Indeed, the ranges in performance for the selected storage systems are sometimes larger than the value function domains; this leads to scale compression, making discrepancies in performance that exist either side of the domain "value-less". Nevertheless, there were large enough differences in the performance levels of the hydrogen storage systems for a robust ranking to emerge (in which the physical storage methods dominated).

By taking cost into account, the decision between these storage options can be represented as in figure 7.22. Indicated is an efficient frontier; a frontier defined by options that are non-dominated [74] (i.e. options for which there are no alternatives that perform better on both metrics). To choose between options that lie on the efficient frontier it requires trading off benefits with costs. With the options given in the diagram, the sensible choice seems to be the cryo-compressed storage option (CcH2). While the other option on the frontier, the sodium alanate system, is cheaper, its low fitness makes it hardly worth considering. Thus, this approach has taught us that solid-state systems are currently significant "underdogs". In a business context, research projects involving such underdogs are likely viewed as high risk projects (in terms of technical prospects). It therefore requires institutions (e.g., universities) in which many failures are tolerated, in order for such systems to be further developed.

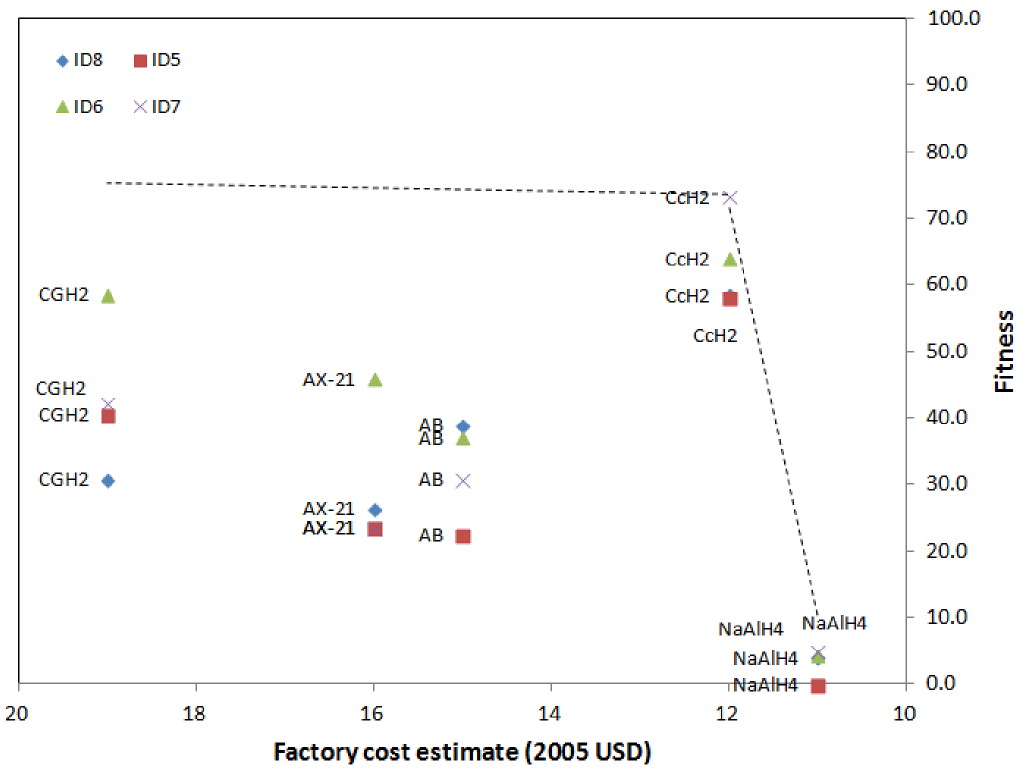

Figure 7.22: Plot of fitness against costs based on the different hydrogen storage options and selection models presented in this chapter. The "efficient frontier" (a frontier of non-dominated options) is indicated by the dashed line. Cost data estimates are based on: [7, 122, 12]. These data pertain to storage systems designed for storing roughly 5-6 kg H2. They may not share common design goals in other respects. Notes: Estimate for AX-21 is based on the cost value indicated for a MOF-177 prototype system [7]; The estimate for the AB system is not supported by any sources.

7.7 Conclusions

Whether or not the overall methodology that was adopted in this study is a cogent/useful approach remains undetermined. While I would still argue that the underlying scheme on which the approach was based - namely, a multi-criteria analysis that reflects common industry practices [156] - provides a reasonable representation of actual selection pressures, the mode in which I collected data for the analysis has clear weaknesses. Due to the number of uncertain variables in this study - and therefore, no simple way of performing a comprehensive sensitivity analysis - there is a strong argument to collect data via face-to-face interviews (resources permitting) rather than an online survey.

A desired benefits of a survey approach, namely a potentially larger sample, was not achieved. The demanding nature of the survey was certainly a limiting factor in this. The small sample size was an impediment to the usefulness of this particular approach. As a consequence, generalizations can only be made highly speculatively. Nonetheless, the findings at least gave an impetus for considering striking features, such as the variability of the responses (even within such a small sample). In this analysis it turned out that the variability of selection models played only a small role in the rankings that emerged. Hence, this type of study is most informative when the performance levels are more evenly matched across different technical variants. In such cases it would be significant to understand the underlying reasons for variability in the selection models. For instance, as was speculated, were they to reflect different assumptions for technical niche configurations, then the focus shifts to understanding how particular niche structures emerge.

While I caution not to view the results as a definitive guide, I also exhibited a potentially useful way of using MCA data to assess technical fitness deficits. Such a perspective can be useful in prioritizing metrics for improvement. Indeed, with the data that has been provided, there is no restriction on using the selection models for other types of storage systems. Finally, I conclude also that the technique can be used as an interesting - if somewhat academic - tool for investigating paths of progress. This idea was illustrated with an example of the “steepest path of ascent” (a special case of the most efficient path), as defined by a selection model’s parameters and a particular starting position. Finally, whether the approach taken in this study was successful in representing selection pressures operating on technical variants, must be determined through validating the results somehow.

8 Summary and conclusions

There have been numerous studies on understanding large scale processes of change toward hydrogen energy (e.g., [10, 87, 47, 114, 113, 50, 37]). Relatively few studies have thus far explored the perspective of hydrogen storage technology specifically (e.g., [19, 21, 118]). The broad and diverse field of technology future oriented analysis presents a rather uncoordinated body of knowledge, which suggests a degree of uncertainty, but also freedom in selecting a method of study. In this study I chose to adopt a complex adaptive system based perspective of technological change. Furthermore, with the philosophy that a single model is generally insufficient to account for a complex process, I have pursued a pragmatic, multi-disciplinary approach[1]. This strategy was pursued with the goal of better understanding the prospects for solid-state hydrogen storage technology.

Several insights that have been gained into the patterns of change in technology allow me to conclude that our understanding of the prospects for solid-state hydrogen storage technology has been improved in at least some dimensions. As a prolusion to reviewing these, it is important to appreciate the limitations for understanding prospects in this task context. There appears to be a strong restriction on conceiving of any model that allows for predictions of the technosphere's evolution to a high degree of resolution. (Indeed, an argument is made by Stuart Kauffman that such a model is unattainable by matter of principle even). Hence, any attempt at foresight must be understood as a statement made under a large set of assumed conditions. Moreover, it implies a limit on the level of detail at which an analysis can operate. Observations of regularities in technological change are usually made at various levels of abstraction. Considering these limitations, we may now ask, in what dimensions has our understanding of hydrogen storage prospects improved?

In chapter two I provided a contextual overview, a perspective which placed the hydrogen storage species in a context of technology lifecycles. In addition to providing a structure for thinking about evolutionary processes, this perspective brought into focus the competitive challenges that face a technological discontinuity like hydrogen storage. On the scale of energy system transitions (e.g., as would be the case for the substitution of the fossil fuel driven transportation system), such competitive challenges are immensely magnified. We saw that there are no iron rules that determine which of several possible outcomes (given a coarse-grained view) occurs, but that technical domination on at least one important dimension of merit is a vital requisite for the substitutional technology. (Other important contextual factors can be found in literature that focusses on these transition processes,

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[1] This approach would fit the description of a "fox-like" strategy, a label conceived by Philip Tetlock [150] to distinguish from a "hedgehog-like" strategy, which is characteristic of overconfidence by relying on a single model to draw conclusions on a complex, multi-faceted process.

e.g., [68]). This model contributes to the research objective - at least in one respect - by offering a qualitative appreciation for the contextual factors that influence the prospects of a new technology. Notwithstanding the competitive challenges, I referred to various transition scenarios that could conceivably create opportunities for hydrogen energy. Such practice is informative for defining the prospects in the first place. Amidst emphasizing the significant role of uncertain/unkown contextual variables, I should also note that I claimed that hydrogen storage technology has potential is less impervious environments than, say, the automotive industry, that is, where the details don't matter as much; I outlined various proposed applications in chapter two.

By focusing on the competitive intensity within the emerging technical order in chapter three - by characterizing aspects of the variation process in hydrogen storage development - I found that solid-state hydrogen storage technology is not, at present, a dominant prospect. An indication for this was the degree of technical convergence toward CGH2 in the automotive industry. I speculated further that the trend in convergence towards CGH2 could have important effects on the prevailing selection pressures (e.g., through network externalities), thereby changing (likely reducing) the prospects of emerging variants. This lesson was drawn from the notion of path dependent processes and potentially game-changing effects of small, chance events through feedback loops. These concepts provide a "mechanistic" explanation of the often observed pattern that initially dominant technical variants succeed to be locked-in. Hence, an improved understanding of the prospects of different variants requires a look at important variables involved in the occurrence of positive externalities/feedback processes. It must be said, however, that this would reduce only the epistemic component of uncertainty with regard to domination processes.

Following the discussion on variation processes, I reviewed concepts on the subject of technological progress (chapter 3). I discussed that many theories on the patterns of technological improvement have focused on the process of search over design space as a key determinant. I used such concepts as an invitation to speculate on the pattern of progress in hydrogen storage research. While this was a very speculative endeavour, the idea that progress in finding fitter variants might be largely subject to statistical features, defined by the topography of a fitness landscape of the material design, was intriguing. In any event, concepts of complexity science seem to provide a promising avenue for research on technological evolution.

Following a characterization on an aggregate perspective of variation and progress in chapter 3, chapter 4 was about identifying specific heuristics of finding fitter variants. I reviewed popular domains of inquiry into hydrogen storage materials, highlighting key design parameters being explored in the design space. This analysis provides a primitive form of anticipating the features of new generations of hydrogen storage variants. It also has the potential - as was exemplified - of exposing conflicting design constraints. Examples of this were also illustrated on a higher system level. Knowledge of these is informative as they point to key design trade-offs or functions for which new operational principles are required. A more in depth analysis of the underlying materials science - which was beyond the scope of this PhD - would have been able to provide a more informed sense of why certain search heuristics are considered promising.

Chapter four also emphasized the perspective of the niche environment. This concept led to the conclusion that - unless the material happens to have a lot of “credit” in the eyes of the designers - the prospects for competing material concepts will largely be determined by which system design configurations are likely to prove more popular (e.g., whether cryogenic devices will be adopted or not). Hence, the niche concept appears to be a useful thinking tool in studies of technological evolution.

In chapter five I asked about the connection of progress and the anticipation of progress in basic research activities. I approached this question by investigating patterns of change in the history of SOTA hydrogen storage materials research. In particular, I suggested that, rather than being identifiable in terms of a consistent pattern of performance improvements, progress has been defined by shifting enthusiams - transitions in the most promising search heuristics. I also proposed a scheme that provides a rationale for the particular changes in the state-of-the-art that occurred. A case in point; the pattern of change in the state-of-the-art suggested that attention-grabbing discoveries are often related to gateway events that open up a wide scope of possibilities. The initial optimism associated with a concept is likely related to the very scope of perceived possibilities, while expectations diminish over time when particular search heuristics bear no fruits - i.e., provide no reason to maintain confidence in the search heuristic.

Given the lack of an obvious and coherent pattern of progress in hydrogen storage, I deliberated on the issue of maintaining expectation credibility in the light of potential scrutiny from technology selectors. Finally, the sequence of state-of-the-art hydrogen storage materials shown in chapter five, does not, for the most part, reflect a cumulative pattern of progress. Instead, applying the terminology from chapter three, variants that were perceived as improvements over the old state-of-the-art, were typically found through long-jumps in design space. This suggests that the funding of research is currently founded on the expectation that “radical” exploration is a relatively unrisky strategy. The less frequently such projects produce findings of comparable value to more established research trajectories, one might conjecture that this will lead to a change in strategy, one in which more cumulative development is considered a promising heuristic. I concluded that while the method adopted in this chapter lacked robustness, it offered ideas that advance a discussion on the nature of progress in basic research. The insights gained provide a foothold for understanding better the pattern of anticipation in basic research.

Interestingly, the most recent state-of-the-art that was described in chapter five, is “local” to a material concept that was selected by many hydrogen storage experts as the most promising to reach technically demanding targets by the year 2025. This assessment of expert views on the prospects of hydrogen storage materials was the subject of chapter six. It revealed insight into the construction of expectations with regard to promising storage concepts. In particular, I emphasized the importance of expectations regarding the future niche of hydrogen storage materials (e.g., which technical components would be used in conjunction with the storage material). Such insight, which was an unintended finding benefitted by the in depth expert interviews, contributes by providing a rationale for analysing the validity/veracity of expressed expectations.

Chapter six also provided an original contribution to quantifying the prospect of hydrogen storage. Namely, probabilities were presented that expressed a set of experts' uncertainties regarding certain propositions of technological advancement. Two kinds of probabilities were discussed; joint probabilities - for the simultaneous achievement of a set of performance targets -, and conditional probability distributions - which revealed uncertainties pertaining to a particular storage property expressed over a range of plausible outcomes. While accounting for the potential of certain biases of judgements, and assuming statistical independence among distinct research trajectories, an aggregate view of the probabilities permitted a fair degree of optimism with regard to at least one storage option achieving commercially relevant target levels. These conclusions were, however, subject to one's assessment of the approach's reliability. Unfortunately, this is a feature that cannot be directly measured, but may be inferred from calibration studies. A larger and more diversely selected sample of experts would likely lead to more accuracy when results are interpreted in the aggregate. To conclude, inasmuch as expert opinion on this subject matter is valued as improving the general perception on the status and outlook of research, then the expert elicitation technique sets a benchmark in how to elicit those opinions.

If a variant of the kind targeted in chapter six were found - i.e., representing a material that would dominate on most, if not all, measures of interest, then one might anticipate that technical determinism would ensure this option achieves dominance. The subject of chapter seven was one in which no single option dominated on all metrics. In particular, a multi-criteria analysis technique was employed to identify the fittest variants and their respective fitness deficits. This exploratory approach was motivated by the prospect of realistically mimicking the selection pressures operating on storage concepts vying for auto-mobile applications.

The study concluded that the cogency of the methodology - in which selection models were constructed on the basis of survey data returned by hydrogen storage system designers - was limited by data quality and sample size, but that interesting insights could be made nevertheless. For instance, it was observed that the experimental selection pressures all gave similar results; they favour physical storage methods over materials-based options. In particular, the cryo-compressed storage method performs the best, while the sodium alanate storage system has huge deficits on almost every metric (according to the particular selection models being experimented with).

This general approach to studying selection pressures presumably becomes more informative when the storage options perform more comparably, that is, when the focus of assessment is on small margins of performance differences. On the other hand, to add value in such situations, the data and the selection models would need to be validated. In the least, assuming this approach has abstracted away some relevant aspects of the selection process, it provides a lens that focuses attention on stand-out variables. For example, figures 7.14 to 7.17 showed that the materials based storage methods have all got significant 'fitness deficits', in terms of capacity (gravimetric and volumetric), across all selection models. Indeed, the volumetric capacity deficits are often more profound. Finally, this chapter also presented a more general application of the experimental selection models. It was shown that they could be used to map out routes of favourable directions of performance improvement. The conclusions that are tentatively drawn from this chapter aim to contribute to an objective approach to identifying a subset of fitter variants.

Was the approach as a whole successful? There is no “best practice” for studying the prospects of a technology. Particularly when considering technology in its early phases of development, there is little prescription for definitive modes of analysis. Various approaches are possible, and new tools and insights (e.g., in complexity science) broaden the scope of possibilities. My attempts to understand some of the complexities of technological evolution payed dividend by providing a sense of the limitations to foresight. The choice to take a somewhat open, multi-perspective approach is consistent with the philosophy that the best approach to understand a complex process is by way of a fox-like strategy [150], one that draws on several models to describe different aspects of the process. That being said, several analyses that I performed leave scope for deeper/more reliable insights to be gained. Prime examples are the expert elicitation and the multi-criteria analysis. A better choice may have been to trade some of the focus here.

The rather more experimental attempt to reconstruct patterns of search through the notion of SOTA (as defined - ideallistically - by an aggregate community level expectation), proved to be more rewarding than I had anticipated. However, I acknowledge that my conclusions were close to the edge of outrunning what the data says. To investigate these conclusions with more rigour would likely require the eye of an historian of science.

The concept of a complex adaptive system provided a particularly useful analytical lens. Not only did it structure the thinking around evolutionary processes in technology - to my mind suggesting a deep and concrete principle, it in fact also lent itself to thinking about the competition of expectations, and the heuristics of probability judgements.

The overall selection of analyses and perspectives appears to have been sound/reasonable inasmuch as there seemed to be useful intersections and ideas that supported one another. This success - if one may call it that - must be attributed to somewhat of a trial and error approach however. That is, a significant number of potential analyses were ultimately rejected or did not come to fruition. Moreover, the depth of insight that was to be gained from individual studies was not always well foreseen. Finally, this approach requires the synthesis of several separate analyses. It is not the case that this PhD builds incrementally and singularly on an established body of knowledge.

Were there lessons for improving the approach that I took? An important skill that I acquired as a result of many failed analyses, is a better ability at identifying the applicability/relevance of a particular approach. Key aspects that I learned to look for were: what is the definition/conception of technology that is used? What is the model's perspective, e.g., is it a systems view (and what are the elements comprising the system)? How coarse-grained is the perspective? What are the conditions under which a regularity is observed? Then there are the more obvious issues of data availability, skills and other resources required, etc.. All in all, consideration of these issues should lead to a better assessment of the potential lessons an analysis has to offer.

Might a different approach altogether have been advisable? The approach I adopted has provided some structure for thinking about hydrogen storage prospects. More was not expected. There was nothing intrinsic to the methodology that suggested to me that a qualitatively different approach might have been more productive in addressing the research question at the level of analysis that I was interested in. Instead, there are several areas of analysis that might be explored to complement the perspective I have begun to sketch out. For instance, a better understanding of the mechanisms of dominance - for which there exists a designated branch in the literature - might be useful when applied to the context of hydrogen storage innovation. Studying the concepts of search heuristics, discoveries and technological trajectories that ensue was intriguing, and is an area where I believe deep insights might be gained. A question in this realm, with bearings on understanding hydrogen storage prospects, might be: what are the factors that affect changes in risk-taking in the search process? Finally, a related question that arises directly from the use of one of the techniques applied in this study is: how does the technical uncertainty among experts for making progress evolve concomittant to the nature of progress that is achieved?

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