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Scientific Assessment in support of the Materials Roadmap enabling Low Carbon Energy Technologies: Hydrogen and Fuel Cells

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STRATEGIC ENERGY TECHNOLOGY PLAN

Scientific Assessment
in support of the Materials Roadmap
enabling Low Carbon Energy Technologies

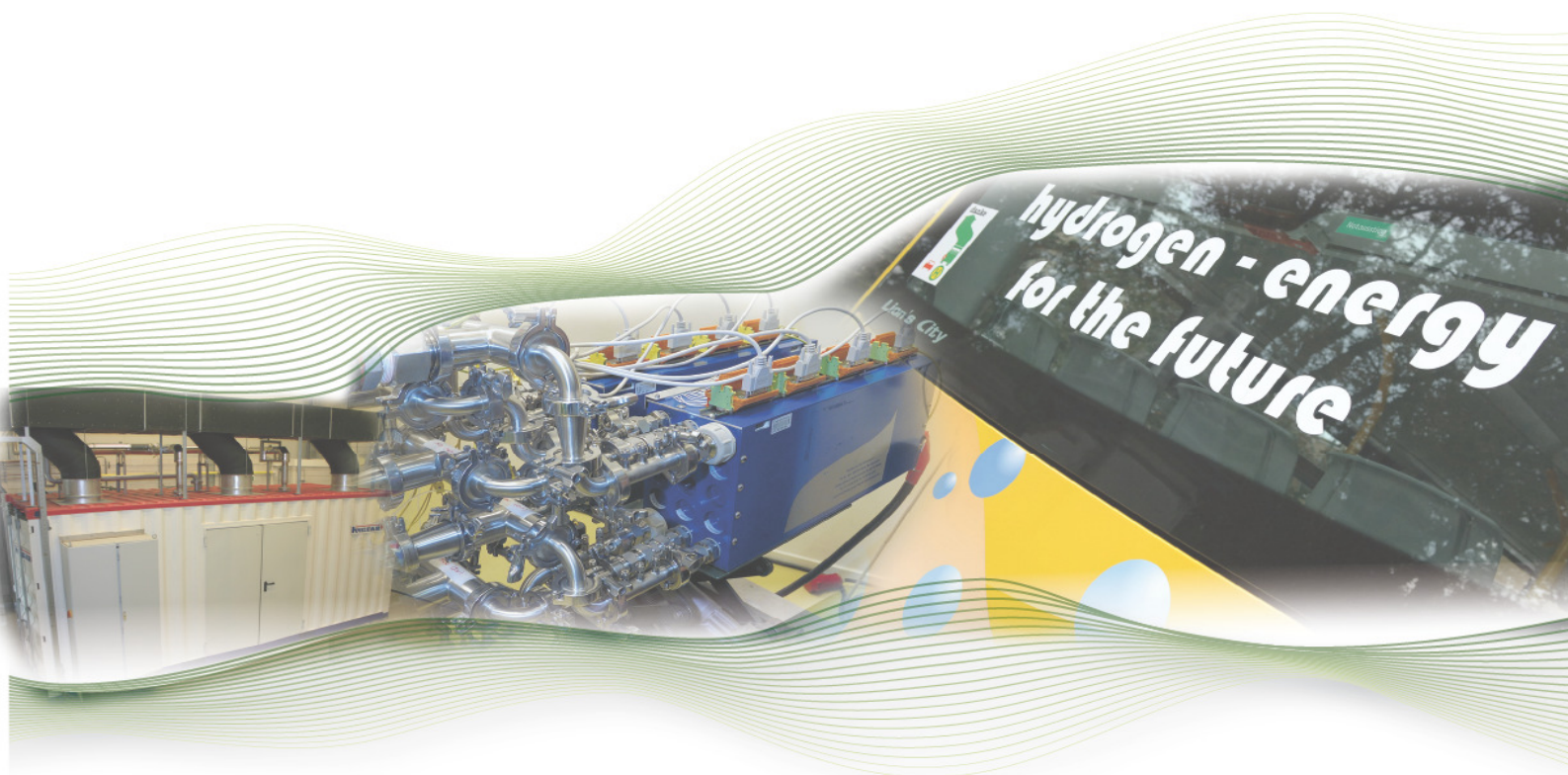
Hydrogen and Fuel Cells

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Preamble

This scientific assessment serves as the basis for a materials research roadmap for hydrogen and fuel cell technologies, itself an integral element of an overall "Materials Roadmap Enabling Low Carbon Technologies", a Commission Staff Working Document published in December 2011. The Materials Roadmap aims at contributing to strategic decisions on materials research funding at European and Member State levels and is aligned with the priorities of the Strategic Energy Technology Plan (SET-Plan). It is intended to serve as a guide for developing specific research and development activities in the field of materials for energy applications over the next 10 years.

This report provides an in-depth analysis of the state-of-the-art and future challenges for energy technology-related materials and the needs for research activities to support the development of hydrogen and fuel cell technology both for the 2020 and the 2050 market horizons.

It has been produced by independent and renowned European materials scientists and energy technology experts, drawn from academia, research institutes and industry, under the coordination the SET-Plan Information System (SETIS), which is managed by the Joint Research Centre (JRC) of the European Commission. The contents were presented and discussed at a dedicated hearing in which a wide pool of stakeholders participated, including representatives of the relevant technology platforms, industry associations and the Joint Programmes of the European Energy Research Association.

Aim and scope

The purpose of this technology chapter on Hydrogen and Fuel Cells (H₂&FC) technologies is to provide an overview of material issues in the field. Even though the Materials Roadmap is focussed on energy applications, it should be pointed out that H₂&FC technologies can potentially play a key role also in future transport applications. The chapter is covering the areas of fuel cells, hydrogen production processes and hydrogen storage technologies. There is a large variety of processes and materials which cannot be analyzed in detail within the limited format of this contribution. Some topics are deliberately considered less in this report: H₂ from fossil fuels, H₂ purification, H₂ from biological processes, large-scale-hydrogen storage and H₂ transport, but synergies with other technology fields have been identified. Materials specification targets at different time horizons have been defined by estimating the performances requirements of the different technologies for market introduction.

SECTION 1: TECHNOLOGY AND SYSTEM STATE OF THE ART AND CHALLENGES

1.1. Fuel cells

Fuel cells are classified primarily by electrolyte material because the electrolyte determines the specific chemical reactions, the fuel, the catalysts and the operating temperature. A comparison of main fuel cell technologies (Proton exchange membrane, phosphoric acid, molten carbonate and solid oxide), showing conventional materials and associated performances in state-of-art technology, is provided in Table 1.

	Alkaline FC	PEM FC	PAFC ¹	MCFC	SOFC
Main applications		automotive	stationary	stationary	stationary
Technology status	mature	mature	mature	mature	mature
Power range	10 – 100 kW	1 – 250 kW	50 kW – 1 MW	1 kW – 5 MW	1 kW – 3 MW
T range (°C)	+25 / +250	-20 / +100	+150 / +200	+600 / +700	+600 / +1,000
P range (bar)	1 – 5 bar	1 – 5 bar	1 – 5 bar	1 – 5 bar	1 – 5 bar
Fuel	H ₂	H ₂	H ₂	CH ₄ (NG, bio)	CH ₄ (NG, bio)
Oxidizer	air-O ₂	air-O ₂	air	Air	Air
Electrolyte / pH	30-45% aqueous KOH	perfluorosulfonic acid polymer	liquid H ₃ PO ₄	Li _{0.62} K _{0.38} CO ₃ Li _{0.5} Na _{0.5} CO ₃	Ytria-stabilized zirconia
Mobile species	OH ⁻	H ₃ O ⁺	H ₃ O ⁺	CO ₃ ²⁻	O ²⁻
Cathode catalyst	Ag, Pt	Pt	Pt	Li _x Ni _{1-x} O	LaSr manganite LaSr ferrites LaSr cobaltites
Cathode carrier	-	carbon	carbon paper	-	-
Cathode catalyst loading (mg/cm ²)	1.0-2.0	> 0.4	0.8-0.7	-	-
Anode catalyst	Raney Ni	Pt	Pt, Pt-Ru	Ni + 2 wt.% Cr	Ni-cermet Yr-stabilised ZrO ₂ + ceria
Anode carrier	-	carbon	carbon paper	-	-
Anode catalyst loading (mg/cm ²)	10-100	> 0.05	0.5-0.35	-	-
Separator	asbestos polyethylene polypropylene	PFSA polymer electrolyte	C, SiC	γ-LiAlO ₂	ceramic electrolyte
Bipolar plates	stainless steel	Carbon-based	metals, TiC, molded graphite	austenitic stainless steel	ferritic steel Cr96Fe alloy
Cell gasket	EPDM	silicone rubber EPDM fluoroelastomer	exfoliated graphite Viton, PTFE		glass, glass-ceramics
Containment	stainless steel	stainless steel	stainless steel	stainless steel	ferritic steel
Max. current density (A/cm ²)	0.5	1.5	0.2-0.3	-	-
Cell voltage with air as oxidizer (V)	0.5-0.6	0.6–0.7	0.5- 0.7	-	-
Max fuel-to-electricity efficiency (%)	60%	45–55 %	> 40 %	52-60 %	35-60 %
Max combined heat& power efficiency (%)	> 80% (low grade waste heat)	70–90% (low grade waste heat)	> 85 %	> 80 %	< 95 %
Durability (hours)	5,000 – 8,000	5,000-10,000	15,000-20,000	20,000-30,000	45,000

Table 1: state-of-art performances of main fuel cell technologies.

¹ S.R. Choudhary, Phosphoric acid fuel cell technology, In: S. Basu (Ed.), Recent trends in fuel cell science and technology, Springer 2007.

1.1.1. Alkaline Fuel Cells^{2,3,4,5,6}

AFCs operate well at room temperature, have a good cold start capability and provide extremely high power densities. In addition to that, this is a rather cheap technology. However, a major disadvantage is the CO₂ sensitivity of the alkaline electrolytes as non-conducting alkali carbonates are formed. As a consequence, the use of AFCs has been restricted to special applications, where no CO₂ is present (e.g. in space vehicles). Nevertheless, some commercialization efforts are underway. Key engineering components and key materials are: (i) *Electrolyte*: a static or flowing aqueous solution (30–45 wt.%) of potassium hydroxide (KOH) is normally used as an electrolyte. Asbestos has been used as cell separator. Its use is now prohibited; it could be replaced advantageously by alkali anion exchange polymer membranes (see section on alkaline water electrolysis) (ii) *Electrode/Catalyst Layer*: the oxygen reduction in alkaline environments as in AFC is more favorable than in acid environments, i.e., the voltage drop is lower or higher voltages are obtained at comparable current densities, leading to a higher efficiency of the system. Consequently, the use of smaller amounts of noble metal electrocatalysts and the use of non-noble metal catalysts is more favorable in an AFC than in any other system; Ni is used to oxidize hydrogen and silver/Pt to reduce oxygen; (iii) *Bipolar plates*: alkaline fuel cell stacks are mostly build in monopolar configuration of the cells. Some attempts have been made to develop bipolar design using stainless steel⁷. Conventional alkaline fuel cells are not prospective, but new concepts offer potential.

1.1.2. Proton Exchange Membrane Fuel Cells

Low temperature PEMFC are considered for automotive applications. Other applications are for back-up power units, micro Combined Heat and Power (mCHP) and small portable power supply units. Large scale stationary PEMFC are interesting when H₂ is available from industrial plants (e.g. chlorine industry). Key components of PEMFC are: (i) *Electrolyte*: state-of-the art electrolytes are based on perfluorosulfonic acid (PFSA) polymers such as Nafion⁸. While specific conductivities of about 100 mS/cm are reached in fully humidified membranes, the conductivity is several orders of magnitude smaller at dry conditions. As a consequence, PEMFC stacks usually require complex auxiliary components for the humidification of the reactants and limited operating temperature (80 °C). The Nafion-based membranes are costly primarily due to their complex fabrication process. Nafion can be produced by polymerisation of tetrafluoroethylene with appropriate amounts of the co-monomer in its sulfonyl fluoride form. After processing this melt-fabricable precursor into a membrane Nafion is obtained by hydrolyzing the SO₂F group with hot KOH followed by acid treatment⁹. Other commercially available PFSA membranes (Aciplex and Flemion¹⁰, Dow ionomer¹¹, Fumapem-F¹², Aquivion¹³) are characterized by slightly different structures of the side chain. Among non-fluorinated membranes, sulfonated polyarylene ether ether ketone (S-PEEK) has probably

² K. Kinoshita, Electrochemical oxygen technology, John Wiley & Sons, New York, 1992, Chapter 2, 19–112.

³ K. Kordesch, J. Gsellmann, B. Kraetschmer, Studies of the performance and life-limiting processes in alkaline fuel cell electrodes, Power Sources 1983, Vol. 9, 379.

⁴ K. Kordesch, Gibt es Möglichkeiten zur Herstellung und Verwendung von 'Low Cost–Low Tech' Zellen?, In: Brennstoffzellen: Stand der Technik Entwicklungslinien Marktchancen, H. Wendt and V. Plzak (Eds), VDI-Verlag, Duesseldorf 1990, 57-63.

⁵ K. Kordesch, The Choice of Low-Temperature Hydrogen Fuel Cells: Acidic or Alkaline?, In: Proceedings of the 4th World Hydrogen Energy Conference, California, USA, T. N. Veziroglu, W. D. V. Vorst, J. H. Kelley (Eds.), 13-17 June 1982, Vol. 3, 1139–1148.

⁶ F. T. Bacon, British Patent 1950, 667,298; DAS 1954, 1,025,025; British Patent 1955, 725,661.

⁷ E. Gülzow, M. Schulze, U. Gerke, Bipolar concept for alkaline fuel cells, J. Power Sources 2006, Vol. 156, 1-7.

⁸ DuPont Nafion PFSA membranes, DuPont product information 2005, www.dupont.com/fuelcells

⁹ Personal website of W. G. Grot, working on the development of Nafion at DuPont, <http://www.nafion.mysite.com/>.

¹⁰ M. Saito, N. Arimura, K. Hayamizu, T. Okada, Mechanisms of ion and water transport in perfluorosulfonated ionomer membranes for fuel cells, J. Phys. Chem. B. 2004, Vol. 108, 16064-16070.

¹¹ J. A. Kolde, B. Bahar, and M. S. Wilson, Proceedings of the 1st International Symposium on Proton Conducting Membrane Fuel Cells 1995, 193.

¹² <http://www.fumatech.com/EN/Onlineshop/fumapem-fuel-cells/>

¹³ <http://www.aquivion.com>

received the most attention¹⁴. Due to the absence of fluorine in the backbone, the acidity is weaker, its oxidative stability is less and phase separation is less pronounced when compared to PFSA polymers pores. Swelling of S-PEEK is a concern. With a too high sulfonation grade, the water uptake of S-PEEK becomes extreme, even far below 100° C¹⁵. This limits the sulfonic acid content and thus the proton conductivity. Reinforcements have been applied to control the swelling of S-PEEK. The main benefit of S-PEEK is its relative low cost. Sulfonated poly(arylene)ethersulfone (S-PES) has been proven not to be stable enough for usage in fuel cells¹⁶. (ii) *Electrode/Catalyst Layer*: The electrode can be divided into two sublayers: the so-called active or catalyst layer (CL) next to the membrane where the electrochemical reaction takes place, and the gas diffusion layer (GDL) for gas distribution and water management. In the CL the catalyst particles are dispersed on an electronically conducting carbon support that is connected to the GDL. Between and on the carbon support there is a proton conducting phase, usually recast Nafion, which is in contact with the catalyst. The advantage of using supported catalyst material is that it enables a high surface area of the catalyst. The penalty for this is that the active layer has a considerable thickness in the order of 5–15 µm. Currently only expensive Pt or Pt-alloy (Pt–Co, Pt–Ni, Pt–Fe, Pt–V, Pt–Mn and Pt–Cr) catalysts exhibit appropriate mass activities¹⁷. Therefore the CL significantly contributes to fuel cell cost. State-of-the-art cathode catalysts are Pt or Pt-alloy supported on carbon black materials with high Pt weight percentages, order of 20–60 wt%. Pt loadings in the order of 0.4 mg/cm² at the cathode and as low as 0.05 mg/cm² at the anode are commonly used¹⁸. Carbon blacks are prepared by thermal decomposition (acetylene blacks) or by partial oxidation of hydrocarbons (furnace blacks). Typical examples of furnace black are Vulcan, Ketjen black and Black Pearls. The different methods result in carbon blacks with different rates of graphite and amorphous carbons and with specific surface area in the order 10–2000 m²/g. The electrochemical stability of the Pt supported catalyst is a severe issue, especially at 90–100 °C. CL degradation is strongly affected by materials, manufacturing and fuel cell operating conditions. Voltage cycling increases the rate of electrocatalyst surface area loss while start-up/shut-down induces membrane degradation and carbon corrosion¹⁹. The GDL (200–400 µm thick) consists of macroporous, electronically conducting material and has an important function in the water management of the membrane electrode assembly (MEA). As under PEMFC operating conditions water is often produced in the liquid state, the GDL must allow the transport of liquid water in addition to water vapour without being flooded. On the other hand the GDL plays a role in keeping the membrane and active layers humidified when gas conditions are sub-saturated. In order to optimize the water management requirements a hydrophobic, microporous (pore sizes < 100 nm) carbon layer (MPL) with thickness 30–50 µm is often applied on the side facing the active layer; (iii) *Bipolar plates*: bipolar or flow plate materials must be resistant to acids, oxidation and hydrogen embrittlement in the fuel cell environment and make up for the major part of the weight (in the order of 80–90 wt.%) and volume of a fuel cell. So they are for a major part determining the power density of a PEM fuel cell stack. Presently several types of materials are being used in flow plates: Graphite, which exhibits high conductivity, is chemically stable, and can sustain high temperatures. However, it is brittle and lacks mechanical strength, and is also relatively permeable to hydrogen, which results in a minimal plate thickness of 5–6mm. Machining is the only suitable production technique, which is costly and

¹⁴ B. Bauer, D.J. Jones, J. Rozière, L. Tchicaya, G. Alberti, M. Casciola, L. Massinelli, A. Peraio, S. Besse, E. Rammuni, Electrochemical characterisation of sulfonated polyetherketone membranes, *J. New Mater. Electrochem. Syst.* 2000, Vol. 3, 93-98.

¹⁵ K. D. Kreuer, In: W. Vielstich, A. Lamm, and H. A. Gasteiger (Eds.), *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Vol. 3, John Wiley and Sons, Chichester, UK, 2003, Ch. 33.

¹⁶ A. E. Steck, C. Stone, In: O. Savadogo and P. R. Roberge (Eds.), *New materials for Fuel Cell and Modern Battery Systems: Proceedings of a Symposium*, Ecole Polytechnique, Montreal, PQ, Canada, 1997.

¹⁷ R. K. Ahluwalia, X. Wang, Direct hydrogen fuel cell systems for hybrid vehicles, *J. Power Sources* 2005, Vol. 139, 152-164.

¹⁸ H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs, *Appl. Catal. B–Environ.* 2005, Vol. 56, 9-35.

¹⁹ R. Borup, M. Inbody, J. Davey, D. Wood, F. Garzon, J. Tafoya, J. Xie, S. Pacheco, PEM Fuel Cell Durability, DOE Hydrogen Program FY 2004 Progress Report.

time consuming²⁰. The material is available from, among others, POCO Graphite (USA), and SGL Carbon (Germany). Several metallic alloys are envisaged as possible bipolar plate materials combining excellent gas impermeability and mechanical resistance. Stainless steels, aluminum, nickel, copper, titanium, bulk amorphous alloys and even carbon steels are investigated in the literature for this application. Most of the scientific reports focus on stainless steels due to a suitable conjunction of technical performance and ease of manufacturing at low cost²¹. It is not to be disregarded, though, that metallic bipolar plates undergo corrosive processes in the PEM fuel cell environment²². Hence, the growth of a less conductive oxide layer negatively affects the electrical conductivity of the plate. Furthermore, ions that are leached from the metallic surface may poison the catalyst layer in the membrane electrode assembly²³. Graphite-polymer composites with either thermoplastic or thermoset matrices are advantageous over metallic materials with regard to corrosion resistance and low weight. Additionally, they may be produced in an economical way, from compression, transfer or injection molding processes, depending on the number of units to be manufactured²⁴. There are several different types of commercially available graphite-polymer composite bipolar plates, e.g. polypropylene (PP), polyphenylene sulfide (PPS), polyvinylidene fluoride (PVDF) and phenolic resin²⁵. Nevertheless, they are more permeable to gases, and present lower bulk electrical conductivity and mechanical resistance than metallic plates. However, the mechanical strength for stationary applications is perfectly adequate and only envisaged as a problem if one considers the vibrations typical of vehicle applications when the fuel cells replace internal combustion engines²⁶. So, the uppermost handicap is the lack of electrical conductivity, which is critical independently of the final application of the device²⁷. The temperature of operation of conventional low temperature PEMFC has been extended over the last years by using proton-conducting polymers that can sustain higher operating temperature, leading to the concept of so-called high temperature PEMFCs. The development of materials such as Poly Benzimidazole (PBI), PBI blends or new High Temperature polymer electrolytes impregnated with phosphoric acid^{28,29} and appropriate electrocatalysts now allow the operation of PEMFCs at 130-200°C. In addition to higher kinetics, such cells can operate at ~180°C with a reformat gas containing up to 2% carbon monoxide (CO) whereas low temperature PEM fuel cells require high purity hydrogen fuel and cannot operate with even trace amounts of CO.

1.1.3. Phosphoric Acid Fuel Cells

Phosphoric acid fuel cells (PAFC) use concentrated ($\approx 100\%$) liquid phosphoric acid as the electrolyte (the acid is usually contained in a PTFE-bonded silicon carbide matrix) and porous carbon electrodes containing a platinum catalyst are used at both anode and cathode³⁰. Operating temperature

²⁰ www.poco.com/us/graphite/resinimpregnation.asp (2005).

²¹ Y. Fu, M. Hou, G. Lin, J. Hou, Z. Shao, B. Yi, Coated 316L stainless steel with CrxN film as bipolar plate for PEMFC prepared by pulsed bias arc ion plating, *J. Power Sources* 2008, Vol. 176, 282-286.

²² A. Pozio, F. Zaza, A. Masci, R.F. Silva, Bipolar plate materials for PEMFCs: A conductivity and stability study, *J. Power Sources*, 2008, Vol. 179, 631-639.

²³ X. Cheng *et al.*, A review of PEM hydrogen fuel cell contamination: Impacts, mechanisms, and mitigation *J. Power Sources* 2007, Vol. 165, 739-756.

²⁴ A. Müller, P. Kauranen, A. von Ganski, B. Hell, Injection moulding of graphite composite bipolar plates, *J. Power Sources* 2006, Vol. 154, 467-471.

²⁵ L.-G. Xia, A.-J. Li, W.-Q. Wang, Q. Yin, H. Lin, Y.-B. Zhao, Effects of resin content and preparing conditions on the properties of polyphenylene sulfide resin/graphite composite for bipolar plate, *J. Power Sources* 2008, Vol. 178, 363-367.

²⁶ R. Blunk, M.H.A. Elhamid, D. Lisi, Y. Mikhail, Polymeric composite bipolar plates for vehicle applications, *J. Power Sources* 2006, Vol. 156, 151-157.

²⁷ S.I. Heo, K.S. Oh, J.C. Yun, S.H. Jung, Y.C. Yang, K.S. Han, Development of preform moulding technique using expanded graphite for proton exchange membrane fuel cell bipolar plates, *J. Power Sources* 2007, Vol. 171, 396-403.

²⁸ J.S. Wainright, J.T. Wang, D. Weng, R.F. Savinell, M.H. Litt, Acid-Doped Polybenzimidazoles : A New Polymer Electrolyte, *J. Electrochem. Soc.* 142, (1995) L121

²⁹ N. Gourdoupi *et al.*, Aromatic polyether copolymers and polymer blends and fuel cells comprising same, US patent 60/843,801

³⁰ A.J. Appleby, Fuel cells – Phosphoric Acid Fuel Cells, *Encyclopedia of Electrochemical Power Sources*, 2009, pp. 533-547

typically ranges between 150 and 220°C. This type of fuel cell is typically used for stationary power generation. Some PAFC have been used to power large vehicles such as city buses. In principle, high temperature fuel cells may have great advantages because hydrogen fuel can be utilized which still contains impurities such as CH₄, CO or SO₂ from the production process. Hence, much cheaper hydrogen can be used which makes the technique more attractive. In addition, the higher temperature level of 120 - 180°C allows the use of smaller heat management units and transfer of excess heat to the environment is less expensive. Also, the higher working temperature allows higher turnover frequencies at the catalytic centres which offer the design of smaller and cheaper devices. Current issues in the development are the lifetime of the membranes, the power densities and cold-start properties, e.g. in combination with other devices. Phosphoric acid fuel cells are already commercially available. UTC Power has developed systems (≈ 400 kW) that use natural gas as fuel for combined heat and power applications. In Europe, SERENERGY (DK) is an actor which already offers systems of several kW commercially.

1.1.4. Solid Oxide Fuel Cells

SOFC have been initially developed for operation temperature above 900 °C by using a ceramic oxide electrolyte. Dense ceramic electrolyte and porous ceramic and metal ceramic electrodes form a multilayer, all-solid-state system. Operation at lower temperatures (less than 600 °C) offers the advantage of using inexpensive metals as bipolar plates, a main component of a SOFC stack. Key materials for SOFC are: Ni-cermet as fuel electrode, yttria or scandia stabilised (substituted) zirconia as electrolyte and electronically conducting perovskites such as La-Sr-manganites, ferrite-cobaltite's as air electrode materials. An important structural element is the bipolar plate that interconnects the cells and controls the gas flows to fuel and air electrodes respectively. Depending on the operating temperature, stainless steels with high or low chromium content is used. To insure long-term operation, the interconnect (at least on the air side) is coated with an oxide (spinel or perovskite) to prevent oxidation and release of chromium oxide. The cells are sealed by using either glasses or glass ceramics. The fabrication processes related to materials can be considered applicable for all types of high temperature fuel cells. The ceramic powders are prepared from raw materials by either: (i) solid state reaction; (ii) combustion assisted processes (flame spraying); (iii) co-precipitation (yttria stabilised zirconia). Metal components are prepared by state of the art metallurgical routes. Forming and shaping of the ceramic layers/components involve screenprinting, tapecasting, and in some cases extrusion (MgAlO₄ support) or injection moulding³¹. The as prepared green layers, half cells and full cells are usually sintered in air. In case of metal supported cells, sintering takes place under inert or reducing atmospheres. The main challenges for solid oxide fuel cell technology are cost reduction and increased reliability and durability. SOFC technology is particularly considered for combined heat and power supply using micro-CHP systems but also for application in larger decentralised units for which operation times above 40,000 h are required (this is equivalent to degradation rates less than 0.5%/1000 hrs). Higher operation times have to be reached in micro-CHP applications through the reduction of parasite ohmic losses primarily originating from contact coatings, inter-diffusion processes at the cathode and electrolyte conductivity decay. The electric efficiency of a SOFC can be further increased by coupling the SOFC with a gas turbine (SOFC-GT). Electric power is thus generated by the SOFC (DC) and the gas turbine generator (AC) using the same fuel/air gas flow. Some detailed analysis have shown that electrical efficiencies close to 60% can be achieved at the 250 kW power range, and even 60% at the 1 MW power range using conventional gas turbines. By using more sophisticated gas turbines, electrical efficiencies of 70% or more are expected at the 2 to 3 MW power range.

1.1.5. Molten Carbonate Fuel Cells

MCFCs are efficient and environmentally friendly CHP and/or tri-generation systems fuelled by NG or biofuels. They can tightly respond to the load profiles of specific end users. The efforts in

³¹ D5.10 RRFCS Life cycle analysis

MCFC over the last 20 years have resulted in an improved stack technology and optimized systems. The main efforts in MCFC were on the development of improved stack and system designs and testing of full-scale demonstrator in the 50-1,000 kW range. Significant lifetimes (> 60,000 hours at the lab scale and 30,000 hours on-site) have been demonstrated³² but progress is still needed by improving system reliability and solving the major material issues like inter-diffusion processes in the electrodes, loss of electrolyte and corrosion of the bi-polar plates. Typical cell sizes are in the 0.75-1.0 m² range. Industrial manufacturing methods like tape casting are used for the cell matrix. Industrial metal forming and join process are applied for bipolar plates, frames and collector. Cost reductions in manufacturing, improvements of components are the main challenges to become competitive.

1.1.6. Direct Carbon Fuel Cells

An early report on a DCFC based on molten sodium hydroxide electrolyte operating at 400-500 °C was released in 1896³³. Since then, fuel cells using other fuels (in particular hydrogen) have received a larger attention, despite the fact that the energy released per unit volume for the direct oxidation of carbon with di-oxygen (23.95 kWh/l) substantially exceeds that of many other common fuels (5.9 kWh/l for methane, 2.6 kWh/l for hydrogen, 10.6 kWh/l for diesel³⁴). In addition to that, the DCFC offers different advantages such as (i) the use of a solid fuel with no specialised storage or handling requirements; (ii) limited NO_x and particulate emissions; (iii) a high conversion efficiency; (iv) the possibility to easily manage the sequestration of the CO₂ exhaust stream. Oxide-ion conducting Yttria- (YSC) or Scandia-(SSC) Stabilized Zirconia (YSZ) can be used as electrolyte, as in SOFC. Doped or un-doped (strontium) lanthanum manganate can be used as cathode electrocatalyst for the high temperature reduction of oxygen, as in SOFC technology. A large variety of materials (metals, ceramics, cermets) can be used as bipolar plates. Main criteria for selection are (i) high temperature corrosion resistance; (ii) long-term compatibility with electrode materials; (iii) high mechanical strength; (iv) a thermal expansion coefficient adapted to the solid electrolyte; (v) good electrical and thermal conductivity. Chromium based alloys can be used for that purpose³⁵. The main materials challenges in this type of fuel cell are chemical stability and obtaining high activity for the direct coal/carbon oxidation process which is currently about 50 mW/cm² for hybrid direct carbon fuel cells³⁶.

1.1.7. Unitized regenerative Fuel Cells

A unitized regenerative fuel cell is a device which can be used alternatively as a water electrolyser or a fuel cell. For material issues in low temperature URFC, see sections on PEM fuel cell and water electrolysis technologies. For those related to high temperature URFC, see sections on SOFC and water electrolysis technologies.

³² A. Moreno, St. McPhail, International status of Molten Carbonate Fuel Cell (MSCF) technology, IEA advanced fuel cells ENEA Roma, January 2008

³³ W.W Jacques, An improved electric battery, and method or process of converting the potential energy of carbon or carbonaceous materials into electrical energy, US Patent 1896, No 4788.

³⁴ S. Zecevic, E.M. Patton, P. Parhami, C-air fuel cell without a reforming process, Carbon, 2004, Vol. 42, 1983.

³⁵ W. Köck, H-P Martinz, H. Greiner, M. Janousek, Development and processing of metallic Cr based materials for SPFC parts, Proceedings of the 4th International Symposium on SOFC Technology, M. Dokiya et al. (Eds.), Electrochem. Soc. 1995, 841.

³⁶ C. Jiang, J.T.S. Irvine, Catalysis and oxidation of carbon in a hybrid direct carbon fuel cell, J. Power Sources 2011, Vol. 196, 7318-7322.

1.2. Hydrogen production

Main hydrogen production paths are listed in Figure 1. Additionally, hydrogen can be obtained as by-product from a number of industrial processes.

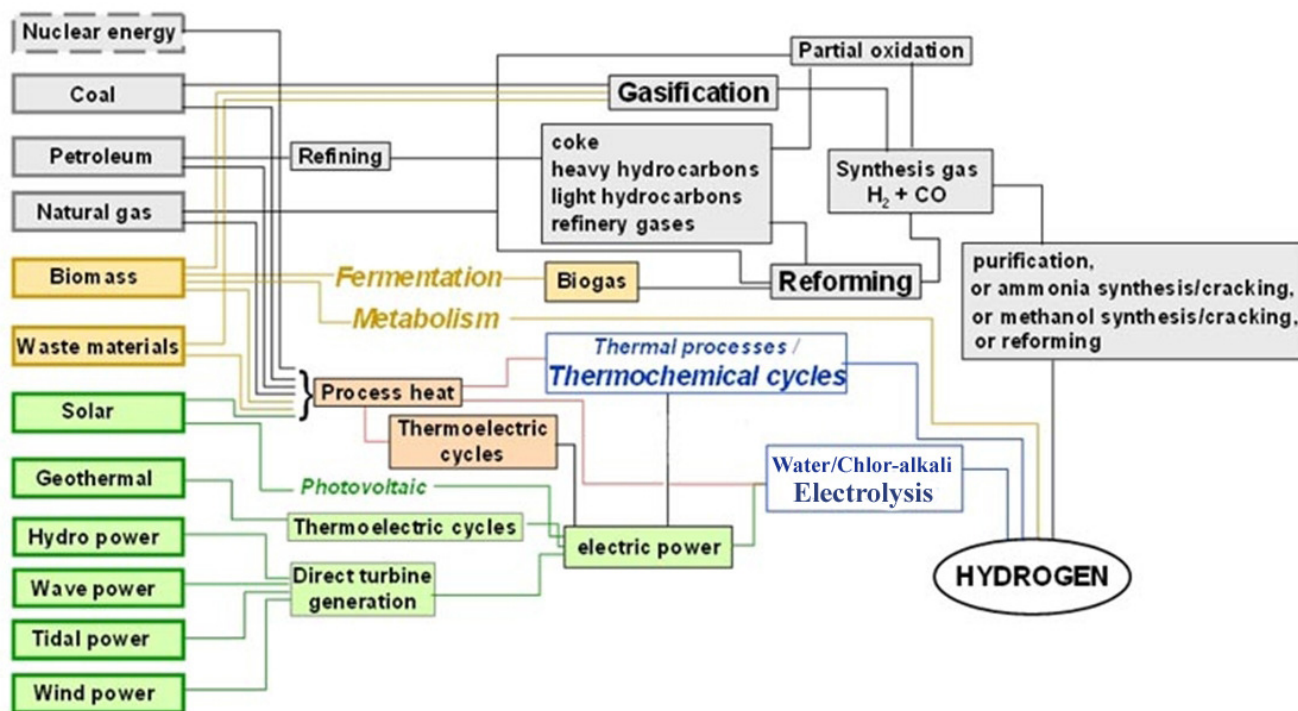


Figure 1: overview of H₂ production paths categorized by source & type of primary energy.

1.2.1. H₂ from fossil fuels

Cheapest hydrogen is obtained today from fossil fuels using mature technologies. Typically the cost of hydrogen using either coal or natural gas ranges from 7 to 15 €/GJ (compared to 25 €/GJ for electrolytic hydrogen). The coal gasification process converts coal by limited and controlled addition of oxygen and/or steam at high temperature (> 700 °C) into a fuel gas rich in hydrogen and carbon monoxide called synthesis gas or syngas. Compared to the traditional burning of coal, gasification appeared as a clean and efficient way to generate electric power due to its ability to turn coal into a fuel gas that can be cleaned of most of its pollutant-forming impurities and burned in a gas turbine. Coal gasification is currently used on industrial scales to generate electricity. Large projects have been launched in the 2000s in Australia, Canada and South Africa assessing proof-of-concept. The produced syngas can also be converted into pure hydrogen using an additional high temperature chemical stage: the water gas shift reaction (WGS). Main material issues concern metallic components in contact with hot syngas that undergo corrosion in sulphur environment, chloride-assisted stress-corrosion cracking or erosion due to particles³⁷. Start-up and shut down also generate acidic gas condensation. Steam methane reforming (SMR)³⁸, is the most common method used to produce commercial bulk hydrogen. This is a high temperature (700-1100 °C) process at 30-40 bar in presence of a metal-based catalyst. Natural gas (sulphur- and chlorine- free) is mixed with steam, heated by combustion of additional natural gas and is fed into the reformer where it reacts yielding carbon monoxide and hydrogen. The carbon monoxide (CO) can be transformed in the so called shift-reaction with additional steam over a catalyst into hydrogen and carbon dioxide (CO₂). Catalysts are made of 5-30% Ni deposited on aluminum oxide, aluminum-magnesium spinel or on silicon and magnesium oxides. Average service life of catalyst is 2 years. A possible side-application is offered by reformers integrated with or within

³⁷ W. J. Lochmann, Materials Problems in "Coal Gasification and Liquefaction", Metallurgical Transactions A 1978, Vol. 9, 175-181.

³⁸ Roads2HyCom Hydrogen web site

MCFC systems, fed by natural gas, used as cleaner technologies to supply H₂ to service stations for H₂ vehicles. CCS technologies are critical to avoid carbon emissions (see synergies in section 5).

1.2.2. H₂ from water electrolysis

Water electrolysis offers a convenient way to produce decarbonized hydrogen although the energy required by the process is about four times larger than the energy required for the production of hydrogen from natural gas. The total energy required for the water splitting reaction remains almost constant over an extended range of temperature (from room temperature up to 1000°C). However, the thermodynamics of the water splitting reaction is such that the electric consumption can be reduced by increasing the operating temperature and supplying the remaining amount of energy in the form of cheaper heat³⁹. From a technological viewpoint, different water electrolysis processes (operating at different temperatures and using different electrolytes) are available. A comparison of these processes, showing conventional materials and associated performances in state-of-art technology, is provided in Table 2. Both alkaline and PEM technologies have reach a level of technological maturity. Medium-temperature water electrolysis using proton-conducting ceramics as electrolyte and solid oxide water electrolysis using oxide-ion conducting ceramics are still the subject of extensive R&D programs.

	Alkaline ⁴⁰	PEM ⁴¹	Medium T	Solid Oxide ⁴²
Technology status	Mature technology		Lab-scale, R&D	
T range (°C)	ambient - 120 ⁴³	ambient - 90	250-600	800-1,000
Electrolyte / pH	25-30 wt.% (KOH) _{aq}	PFSA	polymer or Sr[Ce _x Zr _{1-x}] _{0.95} Yb _{0.05} O ₃ ⁴⁴ La _{0.6} Ba _{0.4} ScO _{2.8}	Y ₂ O ₃ -ZrO ₂ , Sc ₂ O ₃ - ZrO ₂ , MgO -ZrO ₂ , CaO-ZrO ₂
Mobile species	OH ⁻	H ₃ O ⁺	H ₃ O ⁺	O ²⁻
Cathode catalyst	nickel foam/ Ni-SS	platinum	Ni -YSZ or Ni- GDC Cermet with proton conducting electrolyte	Ni -YSZ or Ni- GDC Cermet
Cathode carrier	nickel foam/ Ni-SS Ni-Mo/ZrO ₂ -TiO ₂	carbon		
Anode catalyst	Ni ₂ CoO ₄ , La-Sr- CoO ₃ , Co ₃ O ₄	Ir/Ru oxide ⁴⁵	(La,Sr)MnO ₃ , (La,Sr)(Co,Fe)O ₃ ,	(La,Sr)MnO ₃ , (La,Sr)(Co,Fe)O ₃ ,
Anode carrier	-	-	-	Gd-doped Ceria
Separator	asbestos, PAM ⁴⁶ , ZrO ₂ -PPSF ⁴⁷ , NiO, Sb ₂ O ₅ -PS ⁴⁸	electrolyte membrane	electrolyte membrane	electrolyte membrane
Sealant	metallic	synthetic rubber or fluoroelastomer	glass and vitro- ceramics	glass and vitro- ceramics
Current distributor	Ni	titanium		ferritic SS (Crofer APU)

³⁹ P. Millet, In: 'Electrochemical Technologies for Energy Storage and Conversion', chapter 8, *Water electrolysis for hydrogen generation*, R-S. Liu, X. Sun, H. Liu, L. Zhang and J. Zhang Editors, Wiley-VCH (2011)

⁴⁰ D. Stolten, D. Krieg, Alkaline electrolysis: introduction and overview, In: *Hydrogen and fuel cells, fundamentals, technologies and applications*, Wiley-VCH, Weinheim, Germany, 2010.

⁴¹ Millet P, Durand R, Pineri M. New solid polymer electrolyte composites for water electrolysis, *J. Applied. Electrochem.* 1989, Vol. 19, 162-166.

⁴² M. Zahid, J. Schefold, A. Brisse, High-temperature water electrolysis using planar solid oxide fuel cell technology: a review, In: 'Hydrogen and fuel cells, fundamentals, technologies and applications, Wiley-VCH, Weinheim, Germany, 2010, 227-242.

⁴³ H. Vandenborre, R. Leysen, H. Nackaerts, D. Van der Eecken, Ph. Van Asbroeck, W. Smets, J. Piepers, Advanced alkaline water electrolysis using inorganic membrane electrolyte (I.M.E.) technology, *Int. J. Hydrogen Energy* 1985, Vol. 10, 11, 719-726.

⁴⁴ N. Sata, Proton conduction in mixed perovskite-type oxides, *Solid State Ionics* 1999, Vol. 125, 383-387

⁴⁵ A. Marshall, B. Børresen, G. Hagen, M. Tsyppkin, R. Tunold, Electrochemical characterisation of Ir_xSn_{1-x}O₂ powders as oxygen evolution electrocatalysts, *Electrochim. Acta* 2006, Vol. 51, 3161-3167.

⁴⁶ polysulfone-bonded polyantimonic acid

⁴⁷ ZrO₂ on polyphenylsulfone (PPSF)

⁴⁸ polysulfone impregnated with Sb₂O₅ polyoxide

Containment material	nickel plated steel	stainless steel	stainless steel	stainless steel
P range (bar)	1 – 200	1 – 350 (700)	1	1 - 5
Conventional current density (A/cm ²)	0.2 – 0.5	0 - 3	0 – 0.1	0 – 2
Efficiency (%) (at i A.cm ⁻² / U _{cell} V/ T°C)	60-80 0.2-0.5 / 2.0 / 80	80 ⁴⁹ 1.0 / 1.8 / 90	lab-scale tests	100 ⁵⁰ 3.6 / 1.48 / 950
Capacity (Nm ³ /hour)	1 – 500	1 - 230	1	1
Durability (hours)	100,000	10,000 – 50,000	500	500 – 2,000 ⁵¹
H ₂ O specification	liquid	$\rho > 10 \text{ M}\Omega\cdot\text{cm}$	steam	steam
Load cycling	medium	good	no data av.	no data av.
Stop/go cycling	weak	good	no data av.	weak

Table 2: comparison of main water electrolysis technologies.

a- Alkaline water electrolysis

Alkaline water electrolysis is already a mature technology. Current electrolysis modules have a capacity of approximately 60 kg/hour ($\approx 670 \text{ Nm}^3/\text{hour}$). The largest integrated electrolysis unit is located at Aswan (Egypt) with a capacity of ca. 3,000 kg/hour ($\approx 33,600 \text{ Nm}^3/\text{hour}$). From an economic viewpoint, its durability is considered as satisfactory for continuous operation. By design, current alkaline electrolysis cell can hardly operate at very low current density. This limits the flexibility of the electrolyser in load-following operation which will be necessary upon coupling to renewable energy sources. Most efficient diaphragms used to be made of asbestos which is now forbidden in most countries. They have been replaced by less hazardous materials (e.g. composite ceramic/polymer materials) but there is still room for improvement. Enhanced electro-catalysis is also an issue.

b- Proton Exchange Membrane water electrolysis

Current main materials manufacturing processes are: (i) *solid polymer electrolyte* (see PEMFC section); (ii) *electrocatalysts* are prepared from precursor noble metal salts. There is a wide variety of process used for plating catalytic layers, either on the porous current collectors or directly onto the polymer membrane. Carbon-supported catalysts used at the cathode for the HER (Hydrogen Evolution Reaction) are similar to those used in PEMFC. Iridium particles can be prepared from hexachloroiridic acid; Iridium oxide is prepared using the Adams-fusion method; (iii) *current collectors* are manufactured by sintering titanium metallic particles. This is an energy consuming and hence expensive process; (iv) *cell sealants* are made of fluoroelastomers (copolymers of hexafluoropropylene and vinylidene fluoride or terpolymers of tetrafluorethylene, vinylidene fluoride and hexafluoropropylene or perfluoromethylvinylether with additives). State-of-art PEM water electrolysis is already an efficient process. The challenge is to obtain similar efficiencies at higher current densities. PEM electrolyzers that can deliver several $\text{Nm}^3 \text{ H}_2/\text{hour}$ have also demonstrated their ability to operate in the 10,000-100,000 hours time range. In spite of this, non-energy costs remain elevated and PEM water electrolysis remains an expensive technology compared to the more conventional alkaline technology. This is mostly due to the use of noble metals as electrocatalysts (including expensive precursor salts) and expensive proton-conducting perfluorinated polymers. Cost reduction remains challenging although carbon-supported catalysts can be used at the cathode and iridium alloys with low iridium contents can be used at the anode. Alternative noble-metal-free catalysts (mostly used

⁴⁹ P. Millet, R. Ngameni, S.A. Grigoriev, N. Mbemba, F. Brisset, A. Ranjbari, C. Etiévant, PEM water electrolyzers: From electrocatalysis to stack development, *Int. J. Hydrogen Energy* 2010, Vol. 35, 5043–5052.

⁵⁰ S.H. Jensen, P.H. Larsen, and M. Mogensen, Hydrogen and synthetic fuel production from renewable energy sources, *Int. J. Hydrogen Energy* 2007, Vol. 32, 3253-3257.

⁵¹ F. Lefebvre-Joud, M. Petitjean, J.-P. Ouweltjes, A. Brisse, J. Schefold, J. R. Bowen, S. D. Ebbesen, G. Ehora, C. Bernuy-Lopez and J.-U. Nielsen, High temperature steam electrolysis performance and durability in the RelHy project, *Proceed. 9th European Solid oxide Fuel Cell Forum*, 29 June – 2 July 2010, Lucerne, Switzerland.

at the cathode in place of platinum) have been reported with significant overall efficiencies (70 % at 1 A.cm⁻²)⁵², a route which still requires additional R&D efforts and could also have positive side-effects since the replacement of platinum would release the constraints on feed-water resistivity (Pt is highly sensitive to metal under-potential deposition). Concerning the solid polymer electrolyte, there is a need to develop polymeric proton conductors for operation at more elevated temperatures. Research in this field is driven by potential applications in the H₂/O₂ fuel cell technology for automotive applications. An operating temperature close to 150 °C would lead to more efficient fuel cells. It can be expected that the results of this research will also benefit to PEM water electrolysis. Pressure is also an important issue. Whereas only low pressure (1-50 bar) electrolyzers are available, some attempts have been made up to 150 bar and there are claims of operation up to 300 and 700 bar.

c- Water electrolysis using proton-conducting ceramics

There is an interest at performing water electrolysis at higher (800-1000 °C) temperatures using solid oxide water electrolysis: the amount of electricity required is lower and the kinetics of half-cell reactions is favoured. However, research in material science is facing very critical issues due to important corrosion effects and inability to sustain repeated thermal cycles. For these reasons, operation in the intermediate temperature range (400-600 °C) is now receiving larger attention. Some proton-conducting ceramics, in particular some simple or mixed perovskites present a high ionic conductivity when exposed to water vapour. They can potentially be used as thin (<100 µm) solid electrolyte for the manufacturing of water electrolysis cells⁵³.

d- Solid Oxide water electrolysis

Cell components are related to those used in SOFC. However, even though the Solid oxide cells can be operated in fuel cell or reversed electrolysis cell mode, the electrolysis operation poses additional challenges on the materials. As can be seen from Table 2, most significant challenges are found in material science (material dilatation, material stability and corrosion issues) due to the high operating temperature. The degradation rate of the ceramic cell under high steam content remains too high. It is accelerated by interconnect corrosion and cations release in the gases and in the electrodes. Gas purity has a large influence on the degradation rate; tightness is generally ensured by glass seals or vitro-ceramic seals that do not survive numerous thermal cycles. First tests made on five-cells units over 2,000 h at 800 °C and 0.3 A/cm² have revealed a degradation rate of cell voltage close to 15 % / 1000 h⁵⁴. Results obtained at CERAMATEC and Idaho National Laboratory⁵⁵ (INL) at limited current density also indicated a degradation rate close to 20 % / 1000 h at 800-900 °C. More recent tests performed within the EU FP7 RelHy project at 800 °C and 0.6 A/cm² allowed decreasing the degradation rate to less than 5 % / 1000 h⁵⁶. The nature of these degradations remains under investigations and only few experimental data are available on the subject⁵⁷. A compromise has to be found between performance and lifetime. Among various causes for performance degradation, the highly corrosive environment in the electrolyzer and mechanical and thermal constraints are responsible for most losses. An option would be to reduce the operating temperature down to the 700-800 °C range, to facilitate the usage of metallic components and to decrease degradation rates while keeping high electrochemical activity. At such temperatures, the ionic conductivity of yttrium

⁵² P. Millet, N. Mbemba, S.A. Grigoriev, V.N. Fateev, A. Aukauloo, C. Etiévant, Electrochemical performances of PEM water electrolysis cells and perspectives, *Int. J. Hydrogen Energy* 2011, Vol. 36, 4134-4142.

⁵³ N. Sata, H. Yugami, Y. Akiyama, H. Sone, N. Kitamura, T. Hattori, M. Ishigame, *Proton conduction in mixed perovskite-type oxides*, *Solid State Ionics*, 125, 1999, 383-387

⁵⁴ A. Brisse, J. Schefold, and M. Zahid, High temperature water electrolysis in solid oxide cells, *Int. J. Hydrogen Energy* 2008, Vol. 33, 5375-5382.

⁵⁵ S. Herring, J.E. O'Brien, C.M. Stoots, G.L. Hawkes, J.J. Hartvigsen, M. Shahnam, Progress in high temperature electrolysis for H₂ production using planar SOFC technology, *Int. J. Hydrogen Energy* 2007, Vol. 32, 440-450.

⁵⁶ J. Schefold, A. Brisse, M. Zahid, *Proceeding of the 217th ECS Meeting April 25-30, 2010, Vancouver, Canada.*

⁵⁷ S. Sohal Manohar, Degradation in Solid Oxide Cells During High Temperature Electrolysis, May 2009, Idaho National Laboratory, Idaho Falls, Idaho 83415, <http://www.inl.gov>, Prepared for the U.S. Department of Energy Office of Nuclear Energy Under DOE Idaho Operations Office Contract DE AC07-05ID14517.

stabilized ZrO₂ becomes insufficient. Scandia doped zirconium⁹⁴ and some nickelates (Ruddlesden – Popper compounds) have been proposed⁵⁸. An interesting extension is the co-electrolysis of water vapor and carbon dioxide that can be used to improve the efficiency of the process and to produce a syngas (H₂ + CO) which in turn can be used for the production of synthetic fuels⁵⁹.

1.2.3. H₂ from water and thermochemical cycles

Because of thermodynamic restrictions (the free enthalpy change of the water splitting reaction becomes negative only at very high temperature) acceptable yields in the direct thermal splitting of water can only be achieved at temperatures above 2000°C⁶⁰. Such high temperatures impose very challenging constraints on materials and reactor design. These temperatures can be decreased by considering thermochemical cycles which proceed in several steps alternatively reducing and oxidizing a suitable chemical compound such as a metal oxide with water vapor to form hydrogen and oxygen while recycling the chemical compound. The heat required by the thermochemical cycles could be produced by either nuclear or solar power plants. A large variety of cycles can be used to produce hydrogen from water and has been investigated⁶¹.

Cycle	No. of steps	Max. operation temp. (°C)	LHV efficiency (%)
First group (short term applications)			
Hybrid Sulphuric acid cycle (WH)	2	900	43
Sulphur-Iodine process (GA)	3	900	38
Ferrites	2	1100-1800	43
Second group (long term applications)			
Zn/ZnO	2	1800	45
CeO	2	2000	68
CuCl	4	530	39

Table 3: main thermochemical cycles for hydrogen production.

These promising processes for CO₂-free hydrogen production fall into two major categories, according to their level of maturity. The first group includes processes with industrial perspectives by 2020 and the second gathers those requiring additional developments for application beyond 2020 as illustrated in table 3 (R&D, demonstration). The major advantages of these cycles are their high efficiency and the possibility to couple them directly to concentrating solar installations (several hundred MW range). These processes require materials with optimized properties for each chemical step. Different materials (e.g. SiC or metals such as Ta, Zr, YSR, Hastelloys) that can sustain process conditions (high temperatures and corrosive environments) are under investigation.

1.2.4. H₂ from water and photo-electrochemical processes

Research in this field is more prospective but offers interesting perspectives. Although the concept of photo-electrochemical cells is frequently cited in the literature, the photo-electrochemical dissociation of water for the production of molecular hydrogen is not yet a mature technology. There are three different types of photo-cells: (i) n-type semiconductor photo-anode and metallic cathode; (ii) n-type semiconductor photo-anode and p-type semiconductor photo-cathode; (iii) p-type semiconductor photo-cathode and metallic anode. First kind prevails in experiments. Key engineering components of photo-cells are: (i) light transparent electron-conducting glasses; (ii) photo-electrodes;

⁵⁸ P. Stevens, J-M. Bassat, F. Mauvy, J-C. Grenier, C. Lalanne, Matériaux d'anode pour SOEC, French Patent EDF/CNRS WO 2006/008390.

⁵⁹ Z. Zhan, W. Kobsiriphat, J. R. Wilson, M. Pillai I. Kim, S. A. Barnett, Syngas Production By Coelectrolysis of CO₂/H₂O: The Basis for a Renewable Energy Cycle, Energy & Fuels 2009, Vol. 23, 3089-3096.

⁶⁰ M. Roeb, M. Neises, J-P. Säck, P. Rietbrock, N. Monnerie, J. Dersch, M. Schmitz, C. Sattler, Int. J. Hydrogen Energy 2009, Vol. 34, 4537-4545.

⁶¹ EU FP6 INNOHYP CA , IEA HIA Annex 25 and Gen IV collaboration on nuclear hydrogen production

(iii) electrolyte. The design of such cells has been reported in detail in the literature⁶². In 1979, Fujishima and Honda showed that a suspension of colloidal TiO₂ nanoparticles irradiated by sun-light could also be used to split water molecules into hydrogen and oxygen⁶³, although subsequent work showed that the use of TiO₂ requires the application of an external bias voltage⁶⁴. They also showed that oxide materials, which are highly corrosion-resistant, may be used as the photo-electrodes. The search for other oxide materials as candidates for photo-electrodes that do not require an external bias for water decomposition, has led to several oxide materials such as KTiO₃ and SrTiO₃, which however exhibit light energy conversions that are substantially lower than that of TiO₂⁶⁵. Then complex electrode structures have been developed to apply internal bias voltage, leading to an increase in energy conversion efficiency to more than 1 %⁶⁶. Further progresses have been obtained using two photo-electrodes⁶⁷. The light absorption of TiO₂ was then substantially increased by modification of its semiconducting and electrochemical properties through doping with alio-valent ions (producing solid-solutions with other oxides) as well as heterogeneous doping with nanoparticles of noble metals⁶⁸. Recent studies have shown the interest of dyes to increase light absorption (spectral sensitization⁶⁹). A lot of effort has already been made to develop and use synthetic inorganic dyes (transition metal complexes) and use them in photo-electrochemical devices to produce either electrical power ($\Delta G = 0$) or synthetic fuels ($\Delta G > 0$).

1.2.5. H₂ purification

The hydrogen purification process is intermediate step between hydrogen production and its utilization. The required purity of hydrogen strongly depends on application and technology used. It is a critical issue for several H₂&FC technologies (fuel cells and storage units) while for others is less stressed. On the other hand, nature and quantity of contaminants is depending on the technology used for hydrogen production. Thus, there are different purification techniques used depending on the actual boundary conditions:

- *Pressure Swing Adsorption (PSA)*: the feed gas passes through stationary adsorber layer (zeolite) at a maximum pressure of 40 bar and a temperature of 17-37 °C. All hydrogen pollutants (N₂, CO, CH₄, CO₂, H₂O, Ar, C₂-C₈, methanol, ammonia, hydrogen sulfide, organic sulfur compounds and many others) are trapped and purified H₂ is released.
- *Cryogenic process*: feed gas is cooled and main impurities are liquefied and eliminated using phase-separation techniques. In conventional technology, operating conditions are: a temperature of -173 to -153 °C and a maximum pressure of 60 bar. This is an expensive process not suited for the treatment of large quantities of H₂.
- *Filtration of molecular H₂*: porous or dense polymer or ceramic membranes are used as material.
- *Selective permeation of atomic hydrogen across metallic membranes*: palladium or palladium-alloys membranes are used as permeation material. This is a highly selective process which can be used to extract pure hydrogen from bio-fuels steam reformers feed a fuel cell but corrosion is an important issue.

⁶² T. Bak, J. Nowotny, M. Rekas, C.C. Sorrell, Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects Int. J. Hydrogen Energy 2002, Vol. 27, 991-1022.

⁶³ T. Inoue, A. Fujishima, S. Konishi, K. Honda, Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor poker, Nature, 1979, Vol. 277, 637-638.

⁶⁴ B.O. Seraphin. In: B.O. Seraphin, editor. Solar energy conversion. Berlin: Springer, 1979, 5–56.

⁶⁵ S. Chandra, Photoelectrochemical solar cells, New York: Gordon and Breach, 1985.

⁶⁶ E.R. Rochleau, E. Miller, A. Misra, High-efficiency photoelectrochemical hydrogen production using multijunction amorphous silicon photoelectrodes, Energy & Fuels 1998, Vol. 12, 3-10.

⁶⁷ A.J. Nozik, P-n photoelectrolysis cells, Appl. Phys. Lett. 1976, Vol. 29, 150-153.

⁶⁸ T. Bak, J. Nowotny, M. Rekas, C.C. Sorrell, Properties of TiO₂ as photoelectrode for hydrogen generation using solar energy, Ionics 2001, Vol. 7, 272-274.

⁶⁹ M. Grätzel, Perspectives for dye-sensitized nanocrystalline solar cells, Prog. Photovoltaics 2000, Vol. 8, 171-185.

1.3. Hydrogen storage

There are two main categories of H₂ storage processes: (i) physical storage (compressed gas, cryogenic); (ii) storage in solid materials (chemical storage, physisorption). In addition, there are a number of hydrogenated compounds (e.g. ammonia) which can act as hydrogen carrier. Quantitative characteristics of main H₂ storage technologies in state-of-art (2010) are compiled in Table 4.

Storage Technology	Volumetric density (kg H ₂ /m ³)	Gravimetric density (reversible) (wt %)	Operating pressure (bar)	Operating temperature (K)	Cost* (\$ / kg H ₂)
Compressed gas (H ₂) ⁷⁰	17 - 33	3 - 4.8 (system)	350 & 700	Ambient	400-700*
Cryogenic (H ₂) ⁷¹	35 - 40	6.5 - 14 (system)	1	20	200-270*
Cryo-compressed (H ₂)	30 - 42	4.7 - 5.5 (system)	350	20	400
High pressure - solid	40	2 (system)	350	243 - 298	
Sorbents (H ₂) ⁷²	20 - 30	5 - 7 (material)	80	77	
Metal hydrides (H) ⁷³	< 150	2 - 6.7 (material)	1 - 30	ambient - 553	>500
Complex hydrides (H) ⁷⁴	< 120	4.5 - 6.7 (material)	1 - 50	423 - 573	300-450*
Chemical hydrides (H) ⁷⁵	30	3 - 5 (system)	1	353 - 473	160-270**

* cost estimates based on 500,000 units production; ** regeneration and processing costs not included

Table 4: comparison of main hydrogen storage media.

Materials mainly used to improve the structure of the containment vessels are found in the first category. A huge variety of compounds working as active materials is found in the second category. The material's specification targets differ widely from one application to the other. Volumetric and gravimetric hydrogen densities of some selected hydrides compared with equivalent values describing alternative H₂ storage systems are plotted in figure 2⁷⁶. Mg₂FeH₆ shows the highest known volumetric hydrogen density of 150 kg/m³, which is more than twice that of liquid hydrogen. LiBH₄ exhibits the highest gravimetric hydrogen density of 18 mass%. Pressurized gas storage is shown for steel (tensile strength $\sigma_v=460$ MPa, density 6500 kg/m³) and a hypothetical composite material ($\sigma_v=1500$ MPa, density 3000 kg/m³).

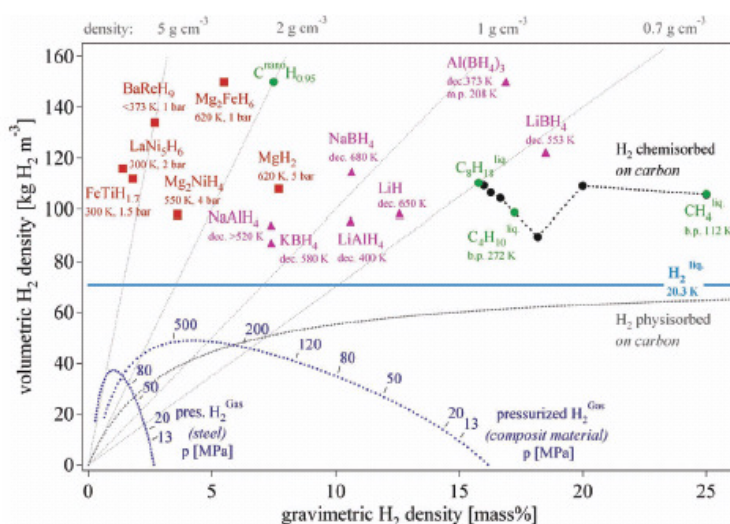


Figure 2: a plot of volumetric versus gravimetric H₂ densities for main H₂ storage paths.

⁷⁰ compressed H₂ in a lightweight composite reservoir

⁷¹ liquid H₂ tank (a few percent loss/day at ambient temperature)

⁷² High surface area carbons, MOFs

⁷³ reversible formation/dissolution of metal hydrides (H₂+intermetallic compounds); hysteresis but reversible; heat due to enthalpy of formation/dissolution of hydride phase

⁷⁴ e.g. alanates, borohydrides, amides / imides, etc. in a reversible manner

⁷⁵ off-board regeneration required

⁷⁶ A. Züttel, Materials for hydrogen storage, Materials Today 2003, Vol. 6, 24-33.

To date, compressed gas or cryogenic liquid tanks are used in demonstration vehicles. These tanks are heavier and bulkier than conventional fuel tanks. Although compressed gas and liquid storage are useful as temporary options on the short-term, they are not seen as the appropriate long-term solution to the storage challenge as they are expensive and fall far short of the demanding EC and US Department of Energy (DOE) targets (5.5 wt% and 40 g/l by the year 2010, and 7.5 wt% and 70 g/l as ultimate goals). Therefore, to ensure widespread use of hydrogen as a zero-carbon and safe fuel for fuel cells, advanced storage systems will be required, especially for automotive applications. On-board hydrogen storage for automotive applications remains a bottleneck process on the way to the hydrogen economy.

1.3.1. Physical storage a- Compressed H₂ Storage

From the material viewpoint, a compressed-H₂ (CH₂) storage unit is mainly a reservoir. Light composite cylinders which can sustain large pressures (up to 80 MPa) are available, offering the possibility to reach volumetric densities half that in its liquid form at the normal boiling point. A tank classification in four types is commonly used to illustrate the evolution of the technology and maximum allowable pressures.

Type	Structure	Material	Pressure (bar)
I	metal tank	aluminium	175
		steel	200
II	Metal tank + filament windings	aluminum/glass fiber	260
		steel/carbon fiber	300
		steel /aramide	300
III	Composite material fiber glass + metal liner	aluminium/glass	300
		aluminium/aramide	450
IV	Composite material fiber + polymer liner	carbon/polyeth.	800

Table 5: classification of compressed hydrogen storage tanks.

The tensile strength of common materials varies from 50 MPa (aluminium) to more than 1,100 MPa for some specific steels. Composite materials can further increase the limit (2,000 MPa) with lower densities⁷⁷. For initial launches, most car manufacturers are in favour of compressed hydrogen (CH₂) tanks due to their technical availability and the cost projections for the vehicle and the relevant infrastructure. All-composite (type IV) or metal lined composite (type III) tanks have been developed for automotive applications and significant progress has been achieved regarding their performance in demonstration fleets. Filling rates similar to conventional vehicles can be attained with pre-cooling of the hydrogen and communication during the fill. Cost is the greatest single barrier to large scale use of CH₂ tanks. Carbon fibre is well known as a cost driver for these tanks however assembly cost is also high at present, and there is also room for cost reduction in the binder⁷⁸. While CH₂ tanks are expensive at the current, extremely low, production volumes, the nature and amounts of raw materials needed allow us to consider that prices could be sustainable at high volumes. This aspect defines the most important research need – cost reduction. This can be pursued via novel methods of carbon fibre production, using fibres with a wider distribution of tensile strength, or by improved ways to assemble tanks to enhance throughput and reduce capital costs⁷⁸. Another valuable research area is enabling appropriate and effective codes and standards.

⁷⁷ F. Vollrath, D.P. Knight, Liquid crystalline spinning of spider silk, *Nature* 2001, Vol. 410, 541-548.

⁷⁸ S.W. Jorgensen, Hydrogen storage tanks for vehicles: Recent progress and current status, *Current Opinion in Solid State and Materials Science* 2011, Vol. 15(2), 39-43.

b- Liquid H₂ Storage

From the material viewpoint, a liquid-H₂ storage unit is mainly a reservoir. Aluminium or aluminium alloys (series 5000) and austenitic steels (AISI 316 L and 304 L) which retain good ductility at low temperature or PTFE (Teflon) and Kel-F are commonly used as tank component materials⁹⁵. Cylindrical tanks made of aluminium, which weighs 50 % less than standard steel designs and achieves a gravimetric storage density of 14.8 wt % (4.9 kWh/kg) and a volumetric density of 43 gH₂/l (1.43 kWh/l) have been developed. Moreover, flat mattress - like tank having storage density values of 6 wt% and 31 gH₂/l (2 kWh/kg, 1.03 kWh/l respectively) have also been developed. Although marked improvement in LH₂ storage has taken place in recent years, there is still some concern about maintaining low heat transfer into such a tank over the life of a vehicle that will experience a wide range of thermal and vibrational fatigue conditions. From an energy efficiency perspective, the energy consumed in hydrogen liquefaction is a problem that has reduced interest in liquid LH₂ systems – though there has been reconsideration of the so-called well to tank efficiency, which includes both production and delivery.

c- Cryo-compressed H₂ Storage

The cryo-compressed tank is an alternate design that greatly reduces the boil-off problem. It bases at combination of low temperature and pressure (cryo-compression). It not only reduce the losses of hydrogen caused by venting to cases of infrequent driving, but also improve the gravimetric and volumetric densities of hydrogen stored. Lawrence Livermore National Laboratory presented a cryo-compressed tank with system storage densities of 4.7 wt% and 30 gH₂/l (1.57 kWh/kg and 1 kWh/l). This method has been cited by the DOE as capable of reaching capacities of the order of 5.5 wt% and 42 g/l (1.83 kWh/kg and 1.4 kWh/l). While such tanks approach the levels of gravimetric and volumetric capacity required, the cost remains the main obstacle.

1.3.2. Storage in solid materials

From the material viewpoint, a solid-H₂ storage unit is a reservoir plus a hydrogenated compound. Tremendous efforts have been devoted to the R&D of materials that can hold sufficient H₂ in terms of gravimetric and volumetric densities, and, at the same time, possess suitable thermodynamic and kinetic properties. Over the last decade, the scope of candidate materials has expanded greatly, from traditional **metal hydrides** to **complex and chemical hydrides**, and from **activated carbon** to **metal-organic frameworks (MOFs)** and **porous polymers**, while the rapid progress in nanoscience in the past five years has opened groundbreaking directions. In solid-state storage, hydrogen is bonded by either physical (e.g. in carbon-based and framework materials), or chemical forces (e.g. in hydrides, borohydrides, amides and imides). In general terms, physisorption has the advantages of faster adsorption/desorption cycles, whereas chemisorption results in the absorption of larger amounts of gas but in some cases, it is not reversible and requires a high temperature to release the absorbed gas. It is now admitted that the most promising H₂ storage routes are based on solid materials that chemically bind or physically adsorb H₂ at volume densities greater than that of liquid H₂. The challenge is to find a storage material that satisfies three competing requirements: (i) high hydrogen density; (ii) storage reversibility at moderate temperature (80-100 °C); (iii) fast release/charge. An adequate thermal conductivity is also required to prevent decomposition by the heat released upon hydriding. In addition to these basic technical criteria, viable solid storage media must satisfy cost, lifetime, and safety requirements as well⁷⁹. A key factor in appraising the current and future states of solid hydrogen storage is **enthalpy**. High enthalpy increases the release temperature as well as the energy required to heat the tank to the release temperature (thus increasing the need for heavy and frequently expensive heat transfer systems). Achieving capacity and modest enthalpy simultaneously has to remain a primary research target. Another key is **kinetics**. Here there have been improvements too, but a more fundamental understanding is of high priority so that progress

⁷⁹ S. Satyapal, J. Petrovic, C. Read, G. Thomas, G. Ordaz, The U.S. Department of Energy's national hydrogen storage project: progress towards meeting hydrogen-powered vehicle requirements, Catalysis Today 2007, Vol. 120, 246-256.

can be made by design rather than empirically. **Safety** is another important issue and there are different scenarios which can be expected for the different storage options. In general solid storage systems offer lower risks when compared to high pressure (e.g. 700 bar) tanks. A final important goal is reduction of **cost**. Compressed gas tanks may be near the capacity they can achieve, but presently the short and long term costs of compressed hydrogen tanks set the standard that other storage systems must attain. This means that both the material used to store hydrogen, and the structural components of the tank must be durable and inexpensive. The use of more than trace amounts of expensive elements or those not easily found in the earth's crust must be avoided. With the logical focus on capacity in the early stages of research, costs have been less studied; however, as the field is maturing, it is increasingly evident that costs become critical to implementation. For all the above reasons, research on alternative storage systems should remain focused on storage materials. Most experiments are performed using high purity hydrogen but research is also ongoing to investigate the degree of impurity that can be tolerated by the various material types. Optimized materials for solid hydrogen storage can be based on the following: (i) Borohydrides⁸⁰; (ii) Amide/Imide systems⁸¹; (iii) Nanostructured and metastable hydrides⁸²; (iv) Composites with other hydrides based on the aforementioned storage materials⁸³; (v) Metal hydrides (AB₂, AB₅, Mg hydride, etc); (vi) Confinement of hydrogen storage materials in nanoporous scaffolds⁸⁴ such as MOFs⁸⁵; (vii) Porous hydrogen storage materials⁸⁶.

1.3.3. Large scale storage

Large scale H₂ storage is envisioned in natural geological sites (underground storage) such as salt domes, caverns or depleted oil/gas fields⁸⁷. The use of buried tanks is also an option.

1.3.4. H₂ transport

Hydrogen can be transported through pipelines⁸⁸. Industrial networks have been used for several decades in Benelux, Germany and the USA. The technology is proven and the transport costs are similar to those of natural gas. Alternatively, hydrogen can be co-transported in natural gas pipelines⁸⁹. Hydrogen can also be transported by trucks (in either compressed or liquid state).

⁸⁰ H. W. Li, S. Orimo, Y. Nakamori, K. Miwa, N. Ohba, S. Towata, A. Züttel, Materials designing of metal borohydrides: Viewpoints from thermodynamical stabilities, *Journal of Alloys and Compounds* 2007, Vol. 446–447, 315-318.

⁸¹ Y. Liu, K. Zhong, M. Gao, J. Wang, H. Pan, Q. Wang, Hydrogen storage in a LiNH₂-MgH₂ (1:1 system), *Chemistry of Materials* 2008, Vol. 20, 3521-3527.

⁸² R. A. Varin et al., *Nanomaterials for solid state hydrogen storage*, ISBN 978-0-387-77711-5, Springer Science & Business Media, LLC, 2009.

⁸³ J. J. Vajo, T.T. Salguero, A.F. Gross, S.L. Skeith, G.L. Olson, Thermodynamic destabilization and reaction kinetics in light metal hydride systems, *J. Alloys Compd.* 2007, Vol. 446, 409-414.

⁸⁴ S. Zhang et al., The synthesis and hydrogen storage properties of a MgH₂ incorporated carbon aerogel scaffold, *Nanotechnology* 2009, Vol. 20, 204027.

⁸⁵ *Metal-Organic Frameworks, design and application*, L.R. Mac Gillivray Ed., Wiley, 2010.

⁸⁶ K.L. Lim, H. Kazemian, Z. Yaakob, W.R.W. Daud, Solid-state materials and methods for hydrogen storage: A critical review, *Chem. Eng. Technol.* 2010, Vol. 33, 213-226.

⁸⁷ http://www.ika.rwth-aachen.de/r2h/index.php/Large_Hydrogen_Underground_Storage

⁸⁸ Air Product, DOE Hydrogen pipeline working group workshop, Augusta, Georgia, 2005.

⁸⁹ Naturalhy, preparing for the hydrogen economy by using the existing natural gas system as a catalyst, project contract SES6/CT/2004/502661, European Commission.

SECTION 2: MATERIAL SUPPLY STATUS AND CHALLENGES

Geopolitical issues regarding material scarcity and security of supply are considered in the 'Critical raw materials for the EU' report⁹⁰. Environmental and health risks of materials are due to their chemical composition (hazardous elements and compounds) and their microstructure (nano-sized materials). Associated regulations must be developed and implemented. IPR (Intellectual Property Rights) issues are important for commercialisation and should be considered, especially for 2050 technologies. However, IPR is unlikely to be an issue for technologies that should come to market in the 2020 time frame. For the polymers of PEM fuel cells (e.g. Nafion) no IPR issues are expected as many patents are already expired.

2.1. Fuel cells

2.1.1. Alkaline Fuel Cells

Due to inherent weaknesses of the technology (in particular for automotive applications), the deployment of AFC is not envisioned. Material issues are not considered.

2.1.2. PEM fuel cells

Most studies identify the catalysts and the membrane as the most expensive components of a complete fuel cell system. While the noble metal catalyst (mainly platinum) is expected to account for about 30-50 % of the cost of a 80 kW PEMFC system manufactured in 500,000 units a year⁹¹, the polymer membrane probably contributes to about 7 % to the cost of the stack⁹² and to about 4 % to that of the complete system. The net sale prices for classical PEMFC membranes in such systems have been calculated to be 2.5 to 5 €/kW of rated power of the fuel cell⁹³. Taking into account the fact that fuel cell membranes normally are less than 100 µm thick, the mass specific price is 100-500 €/kg. Even if in a later stage of development 15 million fuel cell vehicles are being sold each year, less than 30,000 tons of membrane will have to be produced annually worldwide. Recycling of polymers from fuel cells does not seem feasible (due to the expected relatively low amount and to the reduced quality of recycled polymer), but the production of sufficient polymer is not critical. PGM (Platinum Group Metal) recycling is established on the industrial mass scale. So recycling of PGM from Fuel Cells is not a technical issue but maybe a challenge with regard to re-collection of stacks from used cars. A highly efficient logistic chain is needed to collect the used stacks and recycle PGMs.

2.1.3. Phosphoric Acid Fuel Cells

Concerns regarding the use of Pt in PEMFC are also relevant for PAFCs (2.1.2.).

2.1.4. Solid Oxide Fuel Cells

The need of rare earth elements as alloying elements may cause a problem (production dominated by China). Rare-earth elements (La, Ce, Gd) and Scandium used in electrodes and electrolyte are of strategic importance. Ni is widely used but its processing requires some health protections (NiO). All other elements used in cell and interconnect have either a very high availability or are minor as compared to other applications dominating the consumption. The primary sources, supply chains and economics are well established.

The future supply of La is not considered to be critical for an annual SOFC power installation of up to 5 GW. Scandium is the 35th most abundant element in the Earth's crust. Scandium is rarely found at high concentration in minerals but abundant as constituent in other minerals and ores. The annual production is constant, at fluctuating high prizes due to the low demand in the very few

⁹⁰ http://ec.europa.eu/enterprise/policies/raw-materials/files/docs/report-b_en.pdf

⁹¹ J. Werhahn, PhD thesis, RWTH Aachen / Forschungszentrum Jülich 2008.

⁹² B.D. James and J.A. Kalinoski, paper presented at the DOE Hydrogen Program- 2008 Annual Merit Review, Project ID: FC7, 10.06.2008, Arlington, Virginia, USA, http://www.hydrogen.energy.gov/pdfs/review08/fc_7_james.pdf.

⁹³ M. Gebert, PhD thesis, RWTH Aachen / Forschungszentrum Jülich 2004.

commercial applications. Sc supply is not secured on the short term if demand is rising rapidly. For SOFC technologies, materials and supply chains are not considered a critical issue⁹⁴. Main materials used in SOFC stacks are metallic components (up to 90% in weight).

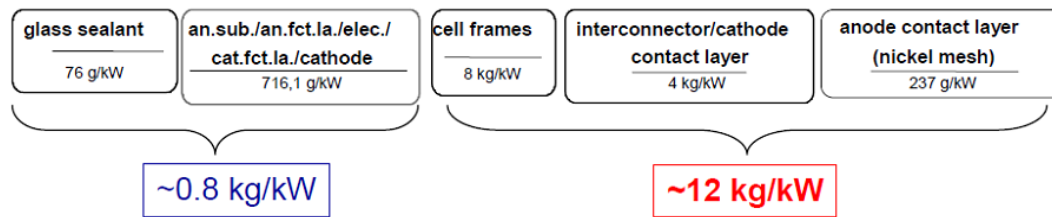


Figure 3: different components of SOFC stacks and their relative proportions.

According to figure 3, the SOFC stack can be considered as a 3 material composite system including metal-based materials, ceramic and glass. It can also be noticed that the amount of metal-based components is much higher (≈ 12 kg/kW) than glass and ceramic components (≈ 0.8 kg/kW) that is to say that metallic components represent around 94% of the stack weight.

2.1.5. Molten Carbonate Fuel Cells

The elements used in cell and interconnect have a very high availability or are minor as compared to other applications dominating the consumption like austenitic steels. The primary sources, supply chains and economics are well established. In the very long term the availability of Li in competition with battery applications could be of importance.

2.1.6. Direct Carbon Fuel Cells

(see sections on SOFC and MCFC technologies).

2.1.7. Unitized Regenerative Fuel Cells

Concerning the low temperature process (< 150 °C) using PEM technology, the situation is similar to that of PEM fuel cells and PEM water electrolyzers. Concerning the high temperature (> 600 °C) process using solid oxide technology, the situation is similar to that of SOFC and SOWE. An URFC can operate as a H_2/O_2 battery. Therefore, there is a need to store H_2 and O_2 . The most convenient way to do that is to pressurize the electrolyzer and store the gases in pressurized tanks. The higher the pressure, the higher the capacity of the battery will be. R&D on high pressure water electrolysis will also benefit to URFC technology.

⁹⁴ Real-SOFC deliverable 5.02

2.2. Hydrogen production

2.2.1. H₂ from fossil fuels

The main challenges for hydrogen production from fossil fuels will be: (i) to stay as cheap as possible even with the anticipated mid term rise of coal price and mainly natural gas price due to increasing scarcity; (ii) to keep the CO₂ emissions as low as possible. The challenge to lower the CO₂ emissions of such processes could be met if the ability to capture and store or recycle the CO₂ can be demonstrated in an economic way.

2.2.2. H₂ purification

No limitation is identified regarding resources or material scarcity for zeolites or ceramic membranes. Noble materials such as Pd used for membranes exhibit limited lifetime.

2.2.3. H₂ from Water electrolysis

a- Alkaline water electrolysis

No limitation is identified regarding resources or material scarcity.

b- PEM water electrolysis

State-of-art PEM water electrolysis is using platinum group metals (PGM) as electrocatalysts. This is a limitation to the large scale deployment of the technology and Europe relies strongly on foreign resources. The development of PEM water electrolysis is not a market-driven process. Private companies are active in the field but business is restricted to niche markets (meteorology, gas chromatography, etc.) or to the supply of prototypes for demonstration purposes. Electrolytic hydrogen from water cannot compete with hydrogen from methane in terms of energy costs. Regarding PGM catalysts and solid polymer electrolyte (SPE), PEM water electrolysis is in competition with PEM fuel cell technology. Also, growing automotive markets in emerging countries will require PGM for use in catalytic converters (car industry). *Economics*: (i) cost analysis of SPE products: fluorine is used in the SPE; SPE materials are manufactured and commercialized by US (DuPont de Nemours) and European (Solvay, Fumatech) firms. (ii) cost analysis of electrocatalysts: different PGM precursor salts are used. The cost of PGM can differ significantly from one salt to the other, depending on the chemistry used for the synthesis. There are US, EU and Japanese suppliers of raw materials. (iv) cost analysis of titanium components. Titanium is commonly available (50% of titanium demand comes from the aerospace industry). Ti-based porous current collectors remain expensive because of the energy consumption of the high temperature sintering process. They can be produced by European firms (e.g. GKN, Germany).

c- Solid Oxide Water Electrolysis

The same materials are used in Solid Oxide fuel cell or electrolysis technologies so the reader is referred to the SOFC section above.

2.2.4. H₂ from water and thermochemical cycles

The selection of the most promising thermo-chemical cycles has already taken into account the availability of the materials involved in the reactions. Problem for the supply of materials when deploying these technologies are not expected. Concerning structural materials for circuits and reactors, and chemical components, no problem is foreseen concerning material supply. However, the cost level of corrosion-resistant raw materials used in the process and the processing of materials such as SiC or “refractory“ metallic alloys is rather high. Regarding catalysts and membranes which are still under investigation, the selection will require taking into account scarcity issues.

2.2.5. H₂ from water and Photo-Electrochemical Cells (PEC)

At present, dye-sensitized photo-systems provide the only technically and economically credible alternative to solid-state (PN junctions) photovoltaic devices. The concept re-unifies the electrochemical stability of large band-gap semi-conducting photo-electrodes (TiO₂) with the efficiency of photovoltaic devices capable of harvesting sunlight energy in the visible range. The possibility of using the concept for the production of synthetic fuels such as hydrogen from water remains highly challenging but offers a huge potential which could also be extended to the photo-electrochemical reduction of CO₂. In terms of materials, the interest of these approaches is that very conventional and abundant materials could be used to develop cheap and easy to recycle compounds.

2.3. Hydrogen storage and transport

2.3.1. Physical storage

a- Compressed H₂ storage

Carbon fibres represent about 75% of the vessel material costs and about 50% of the whole storage system costs. The materials supply chain is secured. Reducing the mass of carbon fibres while keeping a high safety level, e.g. by implementing new safety approaches, may be an option to reduce the costs of CH₂ storage systems. It is needed to develop recycling concepts, material sorting and recycling technologies applicable to hydrogen vehicles. It will be necessary to improve the shredder approach to vehicle disposal and the material sorting technologies (capable of e.g. separating Al and Mg in their alloys), as well as to develop more robust recycling technologies (allowing e.g. recycling of carbon fibre separated from post-shredder streams)⁹⁵.

b- Liquid H₂ storage

Literature data on cost distribution of liquid hydrogen storage systems indicate that (i) assembly represents one third of the total costs, (ii) components stand for another third of the system costs, and finally (iii) tests, certification and sensors constitute the last third of the system costs. Today the manufacturing process of this technology consists to a large extent of manual working steps. The automation of the manufacturing process may lead to a considerable reduction of the assembly costs⁹⁵.

2.3.2. Storage in solid materials

Metallurgical techniques are commonly used to synthesize conventional hydride-forming intermetallics or alloys, whereas chemical reaction routes are used in the production of complex hydrides, chemical hydrides, and a sub-set of sorbent materials such as MOFs. The materials supply chain is secured as long as no rare-earth elements (which are of strategic importance) are used. Processing methods range from simple techniques such as heat treatment (to homogenize composition and microstructure) and cyclic evacuation/hydriding (activation), to more complex operations such as thin film deposition, sol-gel processing, and high energy mechanical ball milling (alloying). Scaffolding, a technique relatively new to the field of hydrogen storage, involves the deposition of a storage material within the (nano-sized) pores of a host scaffold material. High-throughput materials screening, a promising technique commonly used in the pharmaceutical industry, couples the steps of synthesis, processing, and characterization to accelerate the discovery of hydrogen storage materials⁹⁶. Investigation of new materials with long cyclic life is still required, and the safety properties of many systems have not been assessed (in particular the risk posed on health by nanostructured materials). Scalability is an issue of importance when candidate materials are investigated. The evaluation of different production routes (in terms of processing methods and raw materials) for Na-alanate or Mg-hydride, led to relatively simple processes enabling the synthesis of high quality products (fuelling times of the order of 10-20 min). The energy consumption during production was calculated to be 1-5 kWh/kg at an estimated cost of less than 10 €/kg. The main challenge is the decrease of cost of storage materials. Current prices for fine chemicals range from several hundred €/kg (room temperature hydrides) to up to several thousand €/kg (borohydrides, etc). Considering the target storage capacity of 6 wt.%, a cost of more 15,000 €/kg of stored H₂ is estimated using presently available fine chemicals. Market requirements call for *ca.* 20 €/kg or well below 500 €/kg of stored H₂. Besides the problem of storage material cost, the issue of availability should be considered, (in case of e.g. borohydrides the source of the boron, or with LaNi₅, the source of Lanthanum). The light alkaline and earth alkaline elements are available in large amounts. Lithium and Boron containing compounds are or might become difficult to access, and the catalysts might be the largest problem, in case rare earths are needed.

⁹⁵ FP6 Integrated Project STORHY Publishable Final Activity Report, 2008, www.storhy.net

⁹⁶ J. Yang, A. Sudik, C. Wolverton, D.J. Siegel, High capacity hydrogen storage materials: Attributes for automotive applications and techniques for materials discovery, Chem. Soc. Rev. 2010, Vol. 39, 656-675.

2.3.3. Large scale storage

In the case of natural cavities, properties of natural materials (porosity, permeability) are critical. H_2 can also stimulate sulfato-reducing bacterial activity or react with Pyrite (FeS_2), leading to the formation of H_2S . In the case of buried tanks (with either compressed or liquid H_2), material issues are similar to those of conventional tanks. However, corrosion issues due the different environment may differ.

2.3.4. H_2 transport

The influence of hydrogen on the different materials of a gas transportation and distribution network is diverse. According to the results of the NaturalHy project⁸⁵, steel materials can change their material properties in the presence of hydrogen if there is direct contact of hydrogen with clean metal surfaces. In this case, the fatigue properties and toughness of steels, used for the gas transportation pipelines, are influenced in a detrimental way. This material degradation results in higher crack growth rates and can lead to the initiation of new cracks. Consequently, the service life of pipelines can be decreased in comparison to service with natural gas. Polymer (polyethylene, polyvinyl chloride) are also used for the construction of distribution networks, in particular at the downstream end of the gas grids. Polymer pipes do not suffer from conventional corrosion even though they undergo degradation over their lifetime. However, they are less gas tight regarding the loss of gases through their pipe wall by permeation. Adding hydrogen to the natural gas leads to a change in gas losses through permeation, as the transport of hydrogen through the wall of polymer pipes is quicker than for natural gas.

SECTION 3: ON-GOING RESEARCH AND ACTORS IN THE FIELD OF MATERIAL RESEARCH FOR ENERGY TECHNOLOGY APPLICATIONS AND CHALLENGES

R&D on H₂&FC technologies is actively supported through many national (e.g. US DOE, Japan, Germany, French ANR, etc.) and international (e.g. Fuel Cell and Hydrogen Joint Undertaking, FCHJU; FP6 and FP7 of the European Commission) research programmes.

3.1. Fuel cells

3.1.1. AFC

Due to inherent weaknesses, AFC are not considered for application in the automotive industry and there are few if any R&D programs for such applications.

3.1.2. PEMFC

a- PFSA membrane in PEMFC

On-going research focuses on cost-effective materials that could operate at high (100-200 °C) temperatures (better catalyst tolerance to CO and cooling strategy for fuel cell). Proton conductivity should be high and significantly less dependent on humidification. Membrane research is actually focusing on enabling classical PFSA membranes for higher temperature application. Among these approaches are (i) the use of shorter side groups to strengthen the inter-chain attractions of neighbouring macromolecules and thus to allow higher density of sulfonic acid groups at sufficient mechanical properties; Solvay Solexis is developing Aquivion ion ionomers, also known as short side-chain (SSC) ionomers (originally developed by Dow Chemicals Company and then abandoned⁹⁷); (ii) the incorporation of water-retaining additives such as nano-scale oxides or (iii) the fabrication of composite membranes in which proton-conducting inorganic materials such as heteropolyacids or layered zirconium phosphates can actively contribute to the overall conductivity at high temperatures⁹⁸. During the last twenty years, extensive research has been devoted to the development of alternative non perfluorinated membranes. However, these materials suffer from a lack of chemical and mechanical stability in addition to lower conducting properties. Sulfonated PEEK membranes are commercialized by Fumatech GmbH in Germany. Partially fluorinated and crosslinked material are now under evaluation.

b- Platinum catalyst in PEMFC

Currently Pt or Pt-alloy catalysts supported on carbon are commercially available from different suppliers (E-TEK, Tanaka Kikinokoku International, Umicore and Johnson Matthey). In general, two major approaches are underway to address issues of low ORR activity, high cost, and insufficient stability: (i) Exploring non-noble metal catalysts that cost much less but still demonstrate the necessary performance under PEMFC conditions; (ii) Reducing Pt loading in PEMFC catalyst layers while maintaining high performance. Among non-noble metal catalysts two major approaches have gained momentum. The first of which is to replace the Pt with another less expensive precious metal, such as ruthenium or palladium⁹⁹. The second is to use non-precious metal catalysts (NPMC). Bashyam and Zelenay examined the cobalt–polypyrrole–carbon (Co–PPY–C) composite. Some studies are focused on heat-treated Fe and Co–N/C catalysts¹⁰⁰ or on materials such as Cu, Pd/Co,

⁹⁷ V. Arcella et al., Membrane electrode assemblies based on perfluorosulfonic ionomers for an evolving fuel cell technology, *Desalination* 2006, Vol. 199, 6-8.

⁹⁸ B. Smitha, S. Sridhar, A.A. Khan, Solid polymer electrolyte membranes for fuel cell applications – a review, *J. Membrane Sci.* 2005, Vol. 259, 10-26.

⁹⁹ N.A.Vante, H. Tributsch, Energy conversion catalysis using semiconducting transition metal cluster compounds, *Nature* 1986, Vol. 323, 431-432.

¹⁰⁰ C.W.B. Bezerra et al., A review of Fe–N/C and Co–N/C catalysts for the oxygen reduction reaction, *Electrochim. Acta* 2008, Vol. 53, 4937-51.

$\text{Mo}_{4.2}\text{Ru}_{1.8}\text{Se}_8$, WC + Ta and $\text{LaMnO}_{3+\delta}$ ¹⁰¹. Early NPMCs exhibit much lower performance than Pt¹⁰², but an OCV of 1.04 V and a volumetric ORR activity of 165 A/cm³ which meets the DOE 2010 target has been obtained with a cyanamide–Fe–C catalyst. A rapid improvement of performances (around 30 times from 2008 to 2010) has been obtained with several other NPMCs such as PANI-Fe/EDA–Co–C. Electronically conductive stable ceramics are a new promising class of materials under investigation and development as electrocatalyst and support material for Pt and Pt-alloy catalysts. The Pt loading is an important factor in the electrode development. The DOE target is 0.3 and 0.2 mg/cm² for 2010 and 2015, respectively, and most recently the 3M Company achieved 0.15 mg/cm² with a PtCoMn alloy¹⁰³. Improving the Pt utilization is another way for reducing the Pt loading and CL cost. To improve the CO tolerance of PEM fuel cells, the use of binary Pt–Ru catalysts and an oxygen bleeding technique were proposed in the 1980s and 1990s¹⁰⁴ and various materials for CO tolerant catalysts (Zeolite support, Pt–Mo, Sulfided catalysts, etc) are under research¹⁰⁵.

c- Bipolar plates in PEMFC

Graphite composite: Despite the well-established commercial products available for the manufacturing of PEM fuel cells, there is a constant search for better composites with maximized electrical conductivity. The pathway to tailor such advanced materials is to incorporate other carbon based conductive fillers in the polymer matrix. These are carbon black, multi-walled and single-walled carbon nanotubes (MWCNT and SWCNT), carbon fibers, expanded graphite and combinations thereof¹⁰⁶. *Non-coated metals:* Various types of metals and alloys are currently under testing and evaluation to develop bipolar plates that possess the combined merits of graphite and metals: high corrosion resistance and low surface contact resistance, high mechanical strength, no permeability to reactant gases and no brittleness. Candidates such as stainless steel, aluminum, titanium and nickel have been tested and used as bipolar plates¹⁰⁷. Exposed to an operating environment similar to that of a fuel cell with a pH of 2–3 at temperatures around 80 °C, they are prone to corrosion or dissolution¹⁰⁸. *Coated metals:* Metallic bipolar plates can be coated with protective coating layers to avoid corrosion. Coatings should be conductive and adhere to the base metal without exposing the substrate to corrosive media. Two types of coatings (carbon-based and metal-based) have been investigated¹⁰⁹. Carbon-based coatings include graphite, conductive polymer, diamond-like carbon, and organic self-assembled monolayers. Noble metals, metal nitrides and metal carbides are some of the metal-based coatings.

3.1.3. Phosphoric Acid Fuel Cells

There are no significant activities on PAFC development in Europe to date. Phosphoric acid is, however, used in other fuel cell types (e.g. added to a PBI polybenzimidazole membrane for high

¹⁰¹ B. Wang, Recent development of non-platinum catalysts for oxygen reduction reaction, J. Power Sources 2005, Vol. 152, 1–15.

¹⁰² P. Zelenay, Advanced cathode catalysts, In: 2010 Hydrogen program annual merit review and peer evaluation meeting, Washington, DC, 2010.

¹⁰³ M.K. Debe, Advanced cathode catalysts and supports for PEM fuel cells, In: 2010 Hydrogen program annual merit review and peer evaluation meeting, Washington, DC, 2010.

¹⁰⁴ S. Gottesfeld, J. Pafford J, A new approach to the problem of carbon monoxide poisoning in fuel cells operating at low temperatures, J. Electrochem. Soc. 1988, Vol. 135, 2651-2652.

¹⁰⁵ K.S. Dhathathreyan, N. Rajalakshmi, Polymer electrolyte membrane fuel cell, Anamaya Publishers, 2006.

¹⁰⁶ C. Du, P. Ming, M. Hou, J. Fu, Q. Shen, D. Liang, Y. Fu, X. Luo, Z. Shao, B. Yi, Preparation and properties of thin epoxy/compressed expanded graphite composite bipolar plates for proton exchange membrane fuel cells, J. Power Sources 2010, Vol. 195, 794-800.

¹⁰⁷ A.J. Appleby, E.B. Yeager EB, Solid polymer electrolyte fuel cells (SPEFCs), Energy 1986, Vol. 11, 137-152.

¹⁰⁸ S. Geiger, M.A.J. Copper, Fuel cell small stationary market survey, Fuel Cell Today 2003.

¹⁰⁹ Hydrogen, fuel cells & infrastructure technologies program multiyear research, development and demonstration plan. In: EERE (Energy efficiency & renewable energy), 2007, 24.

temperature PEMFC cells). Recently, so-called “solid acids” have attracted interest as proton conductors at temperatures above 200 °C¹¹⁰.

3.1.4. Solid Oxide Fuel Cells

R&D activities on materials for SOFC technology take place on both fundamental and applied levels. **Basic R&D.** *Electrolytes:* (i) Apatite based materials, (ii) Thin film development and corresponding performance; *Anode:* (i) Nano scale investigations (“Impurity segregation”); (ii) Electrochemical kinetics; (iii) Model electrode studies: patterned electrodes; (iv) Ni-free ceramic anodes (Sr-titanate based materials). *Cathodes:* (i) Alternative cathode materials: Nickelates (Ln₂NiO₄), SOFC600: Pr₂NiO₄, 0.130 Ω.cm composite with ceria; (ii) Electrochemical processes, oxygen exchange kinetics; (iii) Nano scale investigations (“Impurity segregation”). *Materials for cells and stacks:* basic R&D on metal-ceramic composite materials is on-going. Thermo-mechanics, materials stability in presence of biogas related impurities is also investigated as well as the impact of real environment (humidity, trace elements from air) on materials stability and performance). New materials and concepts for operation at 600-700 °C, and sealing materials are also investigated and need to be integrated faster into component development and cell production. **Applied R&D.** *Electrolytes:* (i) Development in EU is focused on fluorite based electrolytes: yttria-scandia stabilized zirconia, with other modifications to increase conductivity at around 600 °C; (ii) barrier layer development in ASC with cobalites and ferrites cathodes, durability and cell performance. *Anode:* (i) tolerance and durability to realistic fuels and operation conditions (Sulphur, C:H:O ratios, redox cycling), fuel flexibility; (ii) internal reforming; (iii) Poisoning mechanisms; (iv) Degradation mechanisms, accelerated testing; (v) Development of new cell concepts: metal supported cells, upscaling of production, durability; (vi) Full ceramic cells: integration of ceramic anode materials into large scale SOFC cells; (vii) Enhancement of electrocatalytic activity (infiltration of electro catalyst into porous backbones¹¹¹). *Cathodes:* (i) Increase durability, development of low temperature cathode materials and integration into cells; (ii) Degradation mechanisms, accelerated testing; (iii) Enhancement of electrocatalytic activity (infiltration of electro catalyst into porous backbones). *Interconnect:* (i) corrosion resistance: tailoring of composition; (ii) protective coatings to prevent corrosion. *Sealings:* (i) tailoring glass and glass ceramic compositions to match thermo mechanical requirements (load cycling); (ii) Cell level related to materials; (iii) Accelerated testing routines; (iv) Thermomechanical properties of components and cells; (v) Advanced diagnostics; (vi) Thin film SOFCs (micro SOFC) technique and prototype development. There are well defined programmes in EU, and at Member state level: (i) EU: FCH JU, Marie Curie, member states have national R&D programmes: DK national SOFC Roadmap¹¹²; (ii) PCSOFC (proton-conducting solid oxide fuel cells)¹¹³: Only lightly covered with two on going project in the FP7 join NMP-Energy programs EFFIPRO on efficient and robust fuel cell with novel ceramic proton conducting electrolyte and IDEAL CELL on a new concept of cell mixing proton conducting anode side and anion conducting cathode. Main european industrial developers of SOFC components and systems of pilot size are CeramTec, H.C.Starck, Kerafol, Ikerlan, CFCL EU/AUS, Ceres Power, Sofcpower, Hexis & Haldor Topsoe. There are several research institutes & universities involved in SOFC research: CEA, DLR, FZ Juelich, IKTS, Inasmet, Risø, VTT; Imperial College, Univ. St Andrews, CNRS (Bordeaux, Paris, Grenoble). The R&D activities in EU, US, Korea, China, and Japan are basically addressing the same aspects.

¹¹⁰ S.M. Haile, C.R.I. Chisholm, K. Sasaki, D.A. Boysen, T. Uda, Solid acid proton conductors: From laboratory curiosities to fuel cell electrolytes, Faraday Disc. 2007, Vol. 134, 17-39.

¹¹¹ J. Laurencin, R. Laucournet, J. Mougin, High-temperature fuel cell with internal reforming of hydrocarbons, From Fr. demand 2010, FR 2945378 A1 20101112.

¹¹² Danish SOFC Strategy: <http://www.hydrogennet.dk/log/DInew/library/NationalSOFCStrategi20102020.pdf>

¹¹³ F. Lefebvre-Joud, G. Gauthier, J. Mougin, Current status of proton-conducting solid oxide fuel cells development, J. Appl. Electrochem. 2009, Vol. 39, 535-543.

3.1.5. Molten Carbonate Fuel Cells

Durability and cost reductions are the key issues in MCFC development. Further R&D is needed to understand the causes of microstructural changes in the electrolyte support material that lead to early stack failure and to limit these changes. Development of more robust cathode materials is needed to increase stack lifetime to 10 years. Cost reductions can be expected if production quantities are increasing and more automated manufacturing steps can be introduced. The standardization of stack elements could be an important step. A 30 to 50 % increase in lifetime is required for the complete system. The two most important life-limiting factors being: (i) Nickel oxide dissolution from the cathode and its deposition as nickel metal in the electrolyte matrix; (ii) Electrolyte loss from the matrix, resulting in the intermixing and leaking of fuel and oxidant. CFC Solutions (Germany) is a power plant installer but activities are planned to stop by the end of 2010. Ansaldo is developing pressurized MCFC and demonstrated several units up to of 500 kW range. On-going R&D is on : (i) development of highly reproducible and cost effective synthesis processes for submicronic alpha-LiAlO₂ powder; (ii) validation of operability with a larger fuel variety; (iii) definition of material and component suitable for specific fuels and in particular for NO_x abatement; (iv) improved understanding of reaction mechanism and simulation of performance by accelerated testing; degradation mechanism and failure modelling; (v) identification and set up materials and processes to coat by proper nanomaterials the electrode is a way suitable to increase power density. Few universities and research centers are still active in MCFC: ENEA, Rome, Universities of Perugia, Siena and Genoa, Otto-von-Guericke University, Magdeburg, ENSCP of Paris, Royal Institute of Technology, Stockholm. Fuel Cell Energy (FCE, US) is a world leader in the development and manufacturing of MCFC for electric power generation with products ranging from 300 kW to 2.4 MW.

3.1.6. Direct Carbon Fuel Cells

Activities are still on lab scale. Recent advances on H₂/O₂ Carbonate Fuel Cell (MCFC)¹¹⁴ have led to improved concepts of DCFC¹¹⁵. There are some groups working on this technology (USA, UK, China, Australia). From a technical viewpoint, the main challenge is that most efficient fuel cell concepts are using zero-gap cells and solid electrolyte. Gaseous or liquid fuels can be easily supplied to the anode but solid fuel offers very little interaction with the solid electrode/ electrolyte interface. Usually, the problem is circumvented by using high-temperature liquid electrolyte concepts. Alternatively, a slurry of liquid electrolyte and solid electrode can be used to avoid the problem of solid-solid contacts¹¹⁶. The use of a solid oxide electrolyte as separator and a molten carbonate electrolyte on the anode side or the use of a liquid metal/oxide redox shuttle¹¹⁷ offer new perspectives for the technology.

3.1.7. Unitized regenerative Fuel Cells

At low temperature (PEM technology), technological developments are using “reversible” hydrogen and oxygen electrodes. The concept presents significant drawbacks, mainly a problem of material stability at the anode during water electrolysis which leads to rapid loss of performances (the corrosion of carbon as catalyst carrier, GDL and bipolar plate). More reproducible performances are obtained using redox electrodes (the anode in WE mode is used as anode for H₂ oxidation in FC mode and the cathode in WE mode is used as O₂ reduction cathode in FC mode)¹¹⁸. There is no specific R&D activity for the improvement of membrane electrolytes of solid oxide URFC technology which

¹¹⁴ J. Larminie and A.Dicks, Fuel Cell Systems Explained, Wiley and Sons 2000.

¹¹⁵ J.L. Cooper, US Patent Number: US 2003/0017380 A1.

¹¹⁶ K. Pointon, B. Lakeman, J. Irvine, J. Bradley, S. Jain, The development of a carbon-air semi fuel cell, J. Power Sources 2006, Vol. 162, 750-756.

¹¹⁷ T.T Tao, W. Bai, S. Rackey, G. Wang, International Patent WO 03/001617 A2.

¹¹⁸ S. A. Grigoriev, P. Millet, K.A. Dzhus, H. Middleton, T.O. Saetre, V.N. Fateev, Design and characterization of bi-functional electrocatalytic layers for application in PEM unitized regenerative fuel cells, Int. J. Hydrogen Energy 2010, Vol. 35, 5070-5076.

benefits from the progresses made in the corresponding fuel cell and electrolysis fields which are using same electrolyte, same catalysts in terms of materials and are facing similar challenges in terms of performances. Proton Energy Co. (USA) is active in the field and develops systems. Similar approaches are ongoing on the high temperature electrochemical systems. The particular advantage of a SOFC operated in electrolysis mode is the potential to produce not only hydrogen but also syn-gas, a pre-product to synthetic fuel production, or even methane¹¹⁹.

¹¹⁹ S.H Jensen, M. Mogensen, S. Ebbesen et al., Risø National Lab, various publications.

3.2. Hydrogen production

3.2.1. H₂ from fossil fuels

Some main R&D initiatives related to the production of H₂ from fossil fuels are (i) the Clean Energy Partnership in Germany and (ii) the “Hydrogen and Clean Coal Fuels Program” funded by the DOE in the USA. R&D issues concern the improvement of existing technologies (mainly regarding CO₂ capture) but also new concepts for the production of H₂ from coal are under development worldwide. These new concepts are based on (i) steam gasification (ii) hydro gasification of coal with CO₂ capture/separation (iii) underground coal gasification¹²⁰, (iv) membrane reactors directly used for the production of H₂ from coal, (v) molten bath processes originally used for metal smelting processes and adapted to the production of H₂ and (vi) plasma melting gasification processes.

3.2.2. H₂ purification

On going research concerns mainly the lifetime and the efficiency of separation membranes. This is the focus of the DEMOYS project (FP7-Energy program) that addresses dense membranes for efficient oxygen and hydrogen separation.

3.2.3. H₂ from water electrolysis

a- Alkaline water electrolysis

A list of the main suppliers of alkaline water electrolyzers with the main characteristics of some of their products is provided in Table 6.

Manufacturer	Country	Capacity range Nm ³ /h	Pressure Bar g	Consumed energy kWh/Nm ³ (ΔH efficiency)
Hydrogenics	US/EU	Various ranges from unity to few tens and few hundreds	10 - 25	≈ 4 (≈ 80 %)
Teledyne	USA	Various ranges from unity to few tens and few hundreds	4 - 16	~ 6 (~60 %)
Hydrogen Technologies SA	Norway	Various ranges from unity to few tens and few hundreds	0.02 - 12	~ 4 (~80 %)
IHT	CH	few hundreds	30	~ 4 (~80 %)
Accagen	CH	few hundreds	10 - 200	from 4 to 6 (80 to 60 %)
Idroenergy	Italy	from unity to few tens	2 - 4	from 5 to 6 (~70 – 60 %)

Table 6: Main manufacturers of alkaline electrolyser and system characteristics.

Industrial alkaline water electrolysis is a mature technology. Several MW industrial electrolyzers can be used for the large scale production of hydrogen. From the process viewpoint, some improvements are still possible. In the open literature, attempts made to identify alternative electrocatalysts such as transition metal macrocycles¹²¹ and to develop alternative diaphragms¹²² have been reported. Major research efforts concern advanced diaphragms with adapted electrodes/catalysts and intermittent operation for the coupling with renewable electricity sources. Challenges concern lifetime of systems and maintenance costs. An option of interest would be to use hydroxyl-ion conducting fluoro-polymers that would allow the use of inexpensive catalysts (see section on alkaline water electrolysis).

¹²⁰ HUGE, Research Fund for coal and steel on H₂ oriented coal gasification for Europe.

¹²¹ D.L.Pile and D.H.Doughty, Sandia National Laboratory, report on DOE contract DE-AC04-94AL85000 (2005).

¹²² J. Divisek, J. Murgén, Diaphragms for alkaline water electrolysis and method for production of the same as well as utilization thereof, United States Patent 1983, 4,394,244.

b- PEM water electrolysis

Current activities in basic research: (i) research on noble-metal free catalysts (also applied research); PGM are used for benchmarking electrochemical performances; (ii) research on alternative SPE is mostly driven by the needs of fuel cell industry; (ii) reduction of platinum loadings at the anode by developing stable catalysts carriers or alloying ruthenium with iridium and an inert oxide (tin, titanium, etc.). In applied research: (i) reduction of platinum loadings at the cathode using carbon carriers and/or specific printing methods such as screen printing. (ii) surface treatment of titanium bipolar plates and current collectors to reduce contact resistance (Pt coatings are expensive, nitrides, carbides, etc.). Main challenges for PEM water electrolysis are to identify and synthesize alternative materials with performances similar to those used in state of art technology. Another challenge is to upscale efficiency and durability performances obtained at the lab-scale and to develop and optimize large systems (industrial electrolyzers are limited to a low capacity range $< 10 \text{ Nm}^3 \text{ H}_2/\text{hour}$). They still cannot compete with alkaline technology because of prohibitive non-energy costs. R&D in this field but also on hydrogen as an energy carrier is actively supported at EU level (FCH-JU: GenHyPEM, NextPEL), at national levels (ex. French Agence Nationale de la Recherche) and more locally in Universities. In Europe, several SMEs have appeared recently: Héliion/Aréva, CETH in France, Fumatech in Germany. Similar efforts are made in other developed countries (US, Japan) and most emerging countries. A list of some international suppliers and companies active in this field is provided in Table 7.

Manufacturer	Country of origin	Capacity range Nm^3/h	Pressure Bar g	Consumed energy kWh/Nm^3 (ΔH efficiency) ¹²³
Hydrogen Technologies AS	Norway	0-20	1-16	no data available
Proton Energy Systems	USA	0-6	1-15	-
		0-50	1-15	-
		0-230	1-30	4.2 (84%)
Hydrogenics	Canada	0-2	1-8	4.9 (72)
Héliion/AREVA	France	0-10	1-50	no data available
CETH2	France	0-5	1-16	5.0 (70 %)
		0-20	1-16	5.2 (65 %)
ITM-Power	UK	0-5	1-200	6.25–7.14 (57-50%)

Table 7: Some manufacturers of PEM water electrolyzers and system characteristics.

c- Solid Oxide water electrolysis

The process is not mature. Some SOFC components, stack and system producers are involved in research programs (Aréva, TOFC, Haldor Topsoe, HTc-SOFCPower, Ceramatec). The major research actors in the field are: (i) Idaho National Laboratory (INL), MIT, Argonne National Laboratory in USA; (ii) Risoe DTU, CEA, EIFER in Europe. On going research addresses essentially degradation mechanisms (at $1 \text{ A}/\text{cm}^2$), temperature decrease (from $800 \text{ }^\circ\text{C}$ to $600 \text{ }^\circ\text{C}$) using both anion or proton-conducting materials, operation under pressure and co-electrolysis of water and CO_2 for the production of syngas.

3.2.4. H_2 from water and thermochemical cycles

All the research teams involved in the development of thermochemical cycles are now focusing on innovative material solutions for higher corrosion resistance and durability. SiC components have been developed for different applications (heat transfer, inertia against chemical reactions and solar

¹²³ The theoretical energy consumption to produce hydrogen from water at 298K is $39.6 \text{ kWh}/\text{kgH}_2$ (ΔH° or HHV value) or $34.7 \text{ kWh}/\text{kgH}_2$ (ΔG° or LHV value) equivalent to 3.54 and $3.10 \text{ kWh}/\text{Nm}^3\text{H}_2$ respectively.

collectors) by the Research Center of the Japanese Atomic Energy Agency (JAEA), by the Company General Atomic in the USA and by the European consortium of the FP7 project HYCYCLES. In parallel some projects are focused on the scale-up of thermochemical cycles with a solar heat sources (Europe: FP6 HYDROSOL 2, FCH JU HYDROSOL 3G, Swiss Federal Office of Energy PSI Project on Solarthermal ZnO decomposition; US: SANDIA CR5)^{124,125}.

3.2.5. H₂ from water and PEC cells

Very significant M\$/year projects have been launched during the last years in the USA and Japan to investigate the potential of the field^{126,127}. Less-significant projects have been launched in the EU (FP6 Solar-H, FP7 Solar-H2). Research in photo-electrochemistry requires a multi-disciplinary approach as many different fields of basic science including material science, photo-physics and chemistry are relevant. Some critical material challenges are: (i) adjustment of the band-gap energy of semi-conductors to the visible spectrum; (ii) identification of corrosion-resistant semiconductors that could be used in photo-electrochemical cells; (iii) development of efficient and stable synthetic inorganic dyes that could harvest energy from visible light; (iv) development of catalytic modules (bio-inspired approaches); (v) interconnection of photo-sensible molecules to electro-active functions.

¹²⁴ M. Roeb, J.P. Säck, P. Rietbrock, C. Prah, H. Schreiber, M. Neises, L. de Oliveira, M. Ebert, W. Reinalter, M. Meyer-Grünefeld, C. Sattler, A. Lopez, A. Vidal, A. Elsberg, P. Stobbe, D. Jones, A. Steele, A. Lorentzou, C. Pagkoura, A. Zygogianni, C. Agrafiotis, A.G. Konstandopoulos, Test operation of a 100 kW pilot plant for solar hydrogen production from water on a solar tower, *Solar Energy* 2011, Vol. 85, 634-644.

¹²⁵ R.B. Diver R.B., N.P. Siegel, T.A. Moss, J.E. Miller, L. Evans, R.E. Hogan, M.D. Allendorf, J.N. Stuecker, D.L. James, Innovative Solar Thermochemical Water Splitting. Sandia Report_2008, Albuquerque, NM, Sandia National Laboratories.

¹²⁶ Global Climate & Energy (GCEP) Project, Stanford University, 2009.

¹²⁷ Helios Project, Lawrence Berkeley National Laboratory.

3.3. Hydrogen storage and transport

Main international R&D programs are: (i) Hydrogen & Fuel Cells Joint Undertaking (European Commission – Industry); (ii) US DOE Hydrogen Storage Programme¹²⁸; (iii) NEDO ‘HYDRO-STAR project’, Japan; (iv) The German NOW program and other European National Programs (in France, UK, Spain, Italy, etc.); (v) International Cooperation Activities (IPHE, IEA HIA-Task 22); (vi) the Natural Sciences and Engineering Research Council of Canada; (vii) the Commonwealth Scientific and Industrial Research Organization, Australia. Major actors in European industry (car manufacturers, gas suppliers, material producers) and academia have participated in the FP6 & FP7 hydrogen storage projects funded by the EC for the development of materials and tank systems (e.g. STORHY, NESSHY Integrated Projects; HYCONES, NANOHY, FLYHY, SSH2S Collaborative Projects; HYTRAIN, COSY Research Training Networks). Such actors include organizations from France (CEA, CNRS), Germany (MPI, KIT, HZG), UK (Univ. Manchester, Birmingham), Italy (Univ. Milano, Padova, Rome, Torino, CNR), the Netherlands (Univ. Amsterdam, Nijmegen, Utrecht), Denmark (DTU Lyngby, Risoe, Univ. Aarhus), Sweden (Univ. Stockholm), Norway (Univ. Oslo, IFE), Spain (Univ. Barcelona) and several others (the list is by no means meant to be exhaustive). The European activities are among the leading ones worldwide and several base patents are held by European groups.

3.3.1. Physical storage

a- Compressed H₂ Storage

For 700 bar compressed hydrogen storage, the FP6 IP STORHY has made significant contributions. DOE-funded projects focusing on weight reduction, sensor integration, cold fuelling, thermal modelling and cost aspects have also led to significant improvements. Best value reported for a small-sized tank (28 l inner volume \approx 1.1 kg H₂ at 700 bar) is 2.49 wt.% (0.83 kWh/kg) for the system, using commercial grade carbon fibers. Quantum claims that its ‘full-scale’ storage tank of 160 l inner volume (\approx 6.3 kg H₂ at 700 bar) has high potential of meeting the goal of 4.5 wt.% (1.5 kWh/kg), whereas the current volumetric density of their 700 bar system is 24.3 g/l (0.8 kWh/l). The TUFFSHELL® tank by Lincoln Composites currently exhibits the best performance for a 700 bar (type IV) cylinder: with roughly 1.3 kg H₂ stored, the ‘pure’ filled tank reaches a gravimetric storage density of 4.83 wt.% (1.61 kWh/kg). Baltico GmbH (Germany) presented a novel design for high pressure storage vessels, which reaches storage density values of 6.2 wt.% (2.06 kWh/kg) and 31 g/l (1.02 kWh/l)⁹⁵.

b- Liquid H₂ Storage

Liquid H₂ can be stored in open cryogenic tanks at 21.2 K and atmospheric pressure. In a closed tank, the pressure would reach unacceptable levels. Main challenges are: (i) the efficiency of the liquefaction process - the theoretical energy required for the liquefaction process is 3.2 kWh/kg, but real processes may require as much as 15 kWh/kg; (ii) the thermal insulation of the storage vessel used to reduce boil-off effects which requires the development of specific materials. The H₂ boil-off rate is a function of the tank size, 0.4 %/day for 50 m³ tanks, 0.2 % for 100 m³ tanks and 0.06 % for 20,000 m³ tanks (using double-walled vacuum-insulated spherical dewars). Liquid H₂ is not an efficient storage medium, at least for the storage of small volumes.

c- Hybrid methods for H₂ Storage

Europe has a relatively weak position in hybrid H₂ storage combining solid storage with high pressure technology, a combination with good prospects. Tanks based on this technology mix are already close to realisation elsewhere.

¹²⁸ http://www.eere.energy.gov/hydrogenandfuelcells/storage/hydrogen_storage_testing.html

3.3.2. Storage in solid materials

a- Metal hydrides

There is a large variety of alloys and intermetallic compounds which form hydrides of practical interest. The most interesting feature of a metallic hydride is the high volumetric density of hydrogen stored. A value of 115 g/l is obtained for the reference material LaNi₅. However, most metal hydrides suffer from low (< 6 wt.%) gravimetric densities. Hydrides' enthalpy of formation is another critical parameter; typical values (bracketed by those of HoH₂ (+ 226 kJ/mol) and FeH_{0.5} (+ 20 kJ/mol)) are usually rather high and heat effects during absorption/desorption cycles require specific management.

b- Complex hydrides

Such compounds contain transition metal – hydrogen complexes in their structure and usually offer very high volumetric densities. A maximum value of 150 g/l is reported for Mg₂FeH₆ and Al(BH₄)₃. The gravimetric density is also larger than those found in metal hydrides (e.g. 5.5 wt.% for Mg₂FeH₆ and Mg₃MnH₇). The thermal dissociation of these compounds requires high temperatures (> 200 °C) and is not fully reversible. A number of European groups have been active in this field, in a number of national and European projects. (IP StorHy, IP NESSH_y, RTD NANOHy, FlyHy, SSH2S). The European activities are among the leading activities worldwide. Several base patents are held by European groups.

c- Chemical hydrides

The most studied hydrolytic system to date is NaBH₄. However, in practice hydrogen production by hydrolysis is non-reversible and off-board regeneration is required, a fact that renders such systems potentially useful for niche applications but limits their large scale applicability in transportation¹²⁹. Some organic liquid systems based on the hydrogenation and dehydrogenation of cyclic hydrocarbons (e.g. naphthalene/decalin with 7.2 wt% capacity) have also been proposed. Again the target application is not on-board vehicle hydrogen storage but rather their use as a buffer in renewable energy systems or as a hydrogen carrier for dehydrogenation at hydrogen filling stations¹³⁰. Carbazoles are further organic materials investigated for their hydrogen storage properties as they exhibit capacities in the range 4-6.2 wt% but their high decomposition temperature and high melting point are considered as important disadvantages. Likewise, materials related to ammonia borane are being actively investigated as candidate hydrogen storage systems^{131,132}.

d- Physisorption

Carbon nanostructures (graphitic nanofibers, multi-wall or single-wall carbon nanotubes¹³³, etc.) are attractive candidates for H₂ storage applications because of large surface areas (1,000 to 3,000 m²/g), micro-porosity, low mass and good adsorption ability. However, H₂ uptakes are limited to 1-3 wt%¹³⁴. At low temperatures (liquid nitrogen temperature, 77 K) and under pressure (20 bar), gravimetric densities close to 5 wt.% have been obtained using very large surface area carbons (3,000 m²/g)¹³⁵. Weak chemisorption of H₂ on carbonaceous materials at close to ambient temperature is used

¹²⁹ F. Schüth, B. Bogdanović, M. Felderhoff, Light metal hydrides and complex hydrides for hydrogen storage, Chem. Commun. 2004, Vol. 21, 2249-2258.

¹³⁰ Y. Okada, E. Sasaki, E. Watanabe, S. Hyodo, H. Nishijima, Development of dehydrogenation catalyst for hydrogen generation in organic chemical hydride method Int. J. Hydrogen Energy 2006, Vol. 31, 1348-1356.

¹³¹ C. W. Hamilton, R.T. Baker, A. Staubitz, I. Manners, B-N compounds for chemical hydrogen storage, Chem. Soc. Rev. 2009, Vol. 38, 279-293.

¹³² T. B. Marder, Will we soon be fueling our automobiles with ammonia-borane?, Angew. Chem. Int. Ed. 2007, Vol. 46, 8116-8118.

¹³³ S. Iijima, Helical microtubules of graphitic carbon, Nature 1991, Vol. 354, 56-58.

¹³⁴ H. Kajiura, S. Tsutsui, K. Kadono, M. Kakuta, M. Ata, Y. Murakami, Hydrogen storage capacity of commercially available carbon materials at room temperature, Appl. Phys. Lett. 2003, Vol. 82, 1105.

¹³⁵ R. Chahine, T.K. Bose, Low-pressure adsorption storage of hydrogen, Int. J. Hydrogen Energy 1994, Vol. 19, 161-164.

to overcome the energy of the hydrogen bond and to facilitate the formation of covalent C-H bonds. Uptakes of more than 2-3 wt% have been reported taking advantage of the so-called spillover effect in that respect. Metal Organic Frameworks (a new class of extremely porous structure) have also been studied for their H₂ storage properties. Materials of large surface area (more than 3,000 m²/g) and storage capacities of more than 8 wt.% have been reported at 50 bar and 77 K¹³⁶. Pore volume and surface area can be adjusted by changing the organic linkers and the metal.

3.3.3. Large scale storage

The main industrial players for large hydrogen storage systems are actually the major international companies that are supplying industrial gases, namely Praxair, Air Products, BOC, Linde, or Air Liquide. The research and development projects are mainly focused on reducing cost and hydrogen leaks. Safety can also be an issue.

3.3.4. H₂ transport

Large-scale and long distance transport of hydrogen is already a mature technology.

¹³⁶ G. Férey, M. Latroche, C. Serre, F. Millange, T. Loiseau, A. Percheron-Guégan, Hydrogen adsorption in the nanoporous metal-benzenedicarboxylate M(OH)(O₂C-C₆H₄-CO₂) (M = Al³⁺, Cr³⁺), MIL-53, Chem. Commun. 2003, Vol. 24, 2976-2977.

3.4. Innovative concepts, innovative materials, emerging technologies

In addition to the conventional (more mature) technologies described in the previous sections, some emerging technologies and associated innovative materials are more specifically considered here.

3.4.1. Innovative polymer electrolyte cells

- basic research on innovative concepts of ionic-conductors : ultra-thin membranes, ultra-high conductivity, enhanced chemical and thermal stability.
- development of non-PGM catalysts for low temperature acidic applications; target cost reduction by a factor of 10-15 and catalytic activity as close as possible to those of PGM catalysts.

3.4.2. Innovative SOFC

Most of the innovative SOFC materials developments are not yet mature to be transferred into system applications. See more details in section 3.1.4.

3.4.3. Innovative water electrolysis

Some innovative concepts of water electrolysis are also under investigation in various research groups: (i) *low or medium temperature electrolysis of liquid water using a liquid acid electrolyte*: In France, a company is investigating such concept which is the reverse of a phosphoric acid fuel cells¹³⁷; (ii) *medium temperature electrolysis of water vapor using a proton-conducting ceramic*. The concept of solid oxide water electrolysis faces very challenging problems related to the thermal stability of the materials. An option would be to reduce the operating temperature down to the 400-600 °C range (so-called medium temperature range). Although there are many good non-organic solid proton-conductors¹³⁸, most of them are unstable at temperatures above 300 °C and decompose to liberate water. Some perovskite-type oxides are proton conductors at elevated (400-1000 °C) temperatures¹³⁹. In particular, some perovskites (simples or mixtes) present an encouraging ionic conductivity when exposed to water vapour (10^{-3} - 10^{-1} S/cm). They can potentially be used as thin (< 100 μm) solid electrolyte for the manufacturing of water electrolysis cells. For example, $\text{Sr}[\text{Ce}_x\text{Zr}_{1-x}]_{0.95}\text{Yb}_{0.05}\text{O}_3$ which shows a maximum of conductivity for $x = 0.8$ ¹⁴⁰ can be used in solid-oxide electrochemical applications. Another example is given by $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{2.8}$; (iii) *water electrolysis using ionic crystals as electrolyte*: ionic crystals are studied for application in electrochemical devices because they can offer an interesting ionic conductivity over an extended temperature range.

3.4.4. Advanced materials for H₂ storage and H₂ carriers

- Innovative hydrogenated materials with enhanced gravimetric capacity and improved hydrogen storage reversibility
- New materials for physical containment (high tensile strength materials for light weight pressure vessels for enhanced gravimetric capacity).
- Several potential liquid hydrogen carriers such as ammonia and methanol (obtained from carbon dioxide and hydrogen) are increasingly studied for their potential application as a hydrogen source for mobile and automotive end-uses.

¹³⁷ <http://www.ceramhyd.com>

¹³⁸ S. Sandra, Proton conductors in superionic solids and solid electrolytes, In: S. Chandra et al. (eds), Academic Press 1989, 185-226.

¹³⁹ H. Iwahara, Proton Conductors, Solids, membranes and gels, materials and devices, In: P. Colomban Ed., chapter 8, Cambridge University Press 1992, 122-137.

¹⁴⁰ N. Sata, H. Yugami, Y. Akiyama, H. Sone, N. Kitamura, T. Hattori, M. Ishigame, Proton conduction in mixed perovskite-type oxides, Solid State Ionics 1999, Vol. 125, 383-387.

SECTION 4: MATERIAL'S SPECIFICATION TARGETS FOR MARKET IMPLEMENTATION IN 2020/2030 AND IN 2050

Materials specification targets at different time horizons presented in this report are defined by estimating the performances requirements for market introduction of the different technologies.

4.1. Fuel cells

4.1.1. AFC

Conventional AFC technology is a viable technology only for applications which are not discussed here.

4.1.2. PEMFC

a- Targets for PEMFC electrolyte (automotive perspective)

Characteristic	2010 Status	2020-30 Target	ultimate goal
PEMFC stack (operating conditions)			
Peak stack temperature (°C)	90	120	150
Operating pressure (atm)	2	1.5	1.2
PEMFC electrolyte			
Hydrogen crossover (mA/cm ²)	> 2	< 0.5	0.1
Operating temperature range (°C)	-20 to 90	-30 to 120	-40 to 150
Proton conductivity (S/cm) at -20 °C	0.01	0.05	0.1
+ 20 °C	0.07	0.1	0.15
+ 90 °C	0.1	0.2	0.3
+ 120 °C		0.1	0.2
+ 150 °C			0.1
Cost (€/m ²)	200	100	10
Durability with cycling (h)	2,000	5,000	5,000
PEMFC catalyst			
Pt total content (g/kW)	0.5	<0.1	<0.02
Pt total loading (mg/cm ²)	0.4	<0.1	<0.05
cost (€/kW)	26	6	3
Mass activity, A/mgPt at 900 mV (iR free)	0.14	0.4	0.6
specific activity, μA/mgPt at 900 mV (iR free)	500	900	1500
Durability with cycling (hours)	2,000	5,000	5,000
ECSA loss (%)	< 30	< 10	< 5
PEMFC bipolar plates			
H ₂ permeation flux (Ncm ³ /s/cm ²)	1 - 2x10 ⁻⁶	< 1x10 ⁻⁷	< 1x10 ⁻⁷

Table 8: PEMFC specifications (automotive perspective).

b- Targets for PEMFC (mCHP applications 1 – 5 kW)

Property	State of art	Target 2020-2030
Fuel	NG	NG, Biomass Fuel
DC efficiency	32 %	40-50%
CHP efficiency Gas (LHV)	85%	90%
Power Modulation (%)	50-100	30-100
Load cycles	n.a.	80,000
StartUp time	n.a.	1 h
StartUp /Shut down cycles	n.a.	1000
Durability (h)	10,000	50,000
Costs (€/kW)	< 4000	< 1000

Table 9: PEMFC specifications (mCHP perspective).

4.1.3. Phosphoric Acid Fuel Cells

Catalysts issues are similar to those of PEMFC: reduction of PGM contents, need for alternative low cost catalysts.

4.1.4. Solid Oxide Fuel Cells

Primary requirements for SOFC are improvement of lifetime, robustness and pilot scale production in order to produce reliable components with low failure rates. Target figures (for cells & stacks in m-CHP and 500 kW CHP, 1MW SOFC-GT) are listed in Table 10.

Property	State of art	Target 2020-2030	Ultimate goal
Operating temperature (°C)	800-950	600 - 700	550-700
Operating pressure (bar)	1	1 - 4	1 - 4
Fuel	NG	NG, Biomass Fuel	NG, Biomass Fuel
Area specific resistance (Ωcm^2)	0.3 - 0.6	0.2 - 0.3	0.1 - 0.3
DC efficiency (%) POx ref.	35%	40-50%	direct -internal
SR 2:1 ref.	50%	65%	90%
CHP efficiency Gas (LHV)	85-90%	90-95% ¹⁴¹	>95%
Load cycles	1,000	80,000	best practice
StartUp time (h)	5-12	1-6	best practice
StartUp /Shut down cycles	<10	100	best practice
Cell voltage degradation (at 1 A/cm ²)	> 0.5 %/1000hrs	< 0.5 %/1000hrs	0.2 %/1000hrs
Durability (h)	15,000	50,000	75,000
Sulphur tolerance (ppm)	< 10	< 10	n.a.
Costs (€/kW)	< 4000	1000 5000 (for mCHP)	90% materials cost

Table 10: SOFC specifications.

4.1.5. Molten Carbonate Fuel Cells

Main requirements for 2020 are: (i) increase power output of the MCFC stack from 120 mW/cm² to 150 mW/cm²; (ii) extend service life from five to ten years; (iii) reduce manufacturing costs to less than 2500 (€/kW) by redesign and volume production¹⁴²; (iv) development of new cell materials to reduce compressive loads and use most corrosion-resistant materials. If the 2020 target figures can be reached, implementation of improvements will follow the common product cycle with continuous optimization loops.

4.1.6. Direct Carbon Fuel Cells

State-of-art performances reported in the open literature were obtained at the lab-scale using surface area of a few cm². Maximum current densities less than 50 mA/cm² have been measured at 800 °C. Coking effects are expected to appear as for the high temperature oxidation of hydrocarbons¹³⁶. The concept is that of an emerging technology and discussion on market implementation in 2020/2030 seems premature.

4.1.7. Unitized Regenerative Fuel Cells

Material issues are those of individual (PEM, solid oxide) fuel cells and electrolyzers.

¹⁴¹ A. Atkinson , S Barnett, R.J. Gorte, J.T.S. Irvine , A.J. McEvoy, M. Mogensen, S. Singhal , J. Vohs, Advanced anodes for high-temperature fuel cells, Nature Materials 2004, Vol. 3, 17-27.

¹⁴² <http://www.nrel.gov/docs/fy10osti/49072.pdf>

4.2. Hydrogen production

4.2.1. H₂ from fossil fuels

(not considered here).

4.2.2. H₂ from Water electrolysis

a- Alkaline water electrolysis

Alkaline water electrolysis is already a mature technology but there are still needs for advanced diaphragm materials with limited gas cross over and for more efficient catalysts.

Property	State of art	Target 2020-2030	Ultimate goal
Operating current density (A/cm ²)	0.2–0.5	0.1–1	0–2
Operating temperature (°C)	ambient – 120	Ambient - 150	ambient - >150
Operating pressure (bars)	1-200	1-350	1-700
Durability (h)	10 ⁵	> 10 ⁵	> 10 ⁵
Cyclability	Poor	improved	high
Production capacity of electrolysis units	Up to 50 kg/hour (≈ 500 Nm ³ /hour)	> 100 kg/hour (≈ 1000 Nm ³ /hour)	> 1000 kg/hour (≈ 10 000 Nm ³ /hour)
Non-energy cost (€/kg H ₂)	5	2	1

Table 11: Alkaline water electrolysis specifications.

b- PEM water electrolysis

A tentative roadmap for the improvement PEM electrolyzers is provided in Table 12.

Property	State of art	Target 2020-2030	Ultimate goal
Operating current density (A/cm ²)	0 – 1	0 – 2	0 – 5
Operating temperature (°C)	50-80	80-120	100-150
Operating pressure (bar)	1-50	1-350	1-700
Enthalpic efficiency with PGM catalysts	80% at 1 A/cm ²	80% at 2 A/cm ²	80% at 4 A/cm ²
Enthalpic efficiency with non-PGM catal.	30-40% at 1 A/cm ²	60% at 1 A/cm ²	60% at 1 A/cm ²
SPE Voltage drop (mV at 1 A/cm ²)	150	100	67
SPE ionic conductivity (S/cm at 80°C)	0.17	0.20	0.30
SPE gas permeability to H ₂ (cm ² /s.Pa) (80°C, full humidity)	10 ⁻¹¹	10 ⁻⁹	10 ⁻⁹
Cathodic PGM (Pt) content (mg/cm ²)	1.0-0.5	0.5-0.05	< 0.05
Anodic PGM (Ir, Ru) contents (mg/cm ²)	1.0-2.0	0.5-0.1	< 0.1
Durability (h)	10 ⁴	10 ⁴ – 5.10 ⁴	> 10 ⁵
Production capacity of electrolysis units	1 kg/hour (≈ 10 Nm ³ /hour)	> 10 kg/hour (≈ 100 Nm ³ /hour)	> 100 kg/hour (≈ 1000 Nm ³ /hour)
Energy (kWh/kg H ₂ at 80°C, 1 A.cm ⁻²)	56	< 50	48
Non-energy cost (€/kg H ₂)	5	2	1

Table 12: PEM water electrolysis specifications.

c- Solid Oxide Water Electrolysis

Property	State of art	Target 2020-2030	Ultimate goal
Operating temperature (°C)	800-950	700-800	600-700
Operating pressure (bars)	1-5	1-30	1-100
Operating current density (A/cm ²)	0-0.5	0-1	0-2
Area Specific Resistance (Ω.cm ²)	0.3-0.6	0.2-0.3	
Enthalpic efficiency	100% at 0.5 A/cm ²	100% at 1 A/cm ²	100% at 2 A/cm ²
Cell voltage degradation (at 1 A/cm ²)	> 10 %/1000hrs	< 1 %/1000hrs	< 0.1 %/1000hrs
Durability (h)	10 ³	10 ⁴	10 ⁵
Electrical modulation	Unknown	0-100	0-100
Load cycles	Unknown	10,000	> 10,000
StartUp time (hours)	12	1-6	< 1-6
Shut down time	Few hours	Few minutes	Few minutes
StartUp /Shut down cycles	< 10	100	1000
Production capacity	<1 kg/hour (≈ 10 Nm ³ /hour)	10 kg/hour (≈ 100 Nm ³ /hour)	100 kg/hour (≈ 1000 Nm ³ /hour)
Non-energy cost (€/kg H ₂)	5	2	1

Table 13: Solid Oxide water electrolysis specifications.

4.2.3. H₂ from water and thermochemical cycles

To date, thermochemical cycles have been evaluated mostly at the laboratory scale. Only few demonstrations have been made at the prototype scale. There is still a need to establish the ability of the different materials to sustain a significant number of thermal cycles. Corrosion and cost issues have to be solved¹⁴³.

4.2.4. H₂ from water and PEC cells

Property	State of art	Target 2020-2030	Ultimate goal
Operating current density (mA/cm ²)	0 - 5	0 - 10	0 - 50
Operating temperature (°C)	room	room - 80	room - 80
Operating pressure (bar)	1	1	1
Photo-anode material	TiO ₂ , KTiO ₃ , SrTiO ₃ , SnO ₂ , WO ₃		
Electrolyte	NaOH, H ₂ SO ₄	polymer	polymer
Cathode material	Pt	non-PGM	non-PGM
Photo-cathode material	ZnO		
Energy efficiency (light source)	0.4 % ¹⁴⁴ (sunlight) 1.6 % ¹⁴⁵ (sunlight) 18.3% ¹⁴⁶ (50W halogen lamp) 4.46% ¹⁴⁷ (dye-Zr-SrTiO ₃)	5 % (sunlight) 5-10% (dye)	10-15 % (sunlight) 10-15% (dye)
Durability (h)	few	10 ³	10 ⁴
Production capacity	10 Nmilli-liter/hour	10 Nliter/hour	10 Nliter/hour

Table 14: PEC cell specifications.

¹⁴³ D. Graf, N. Monnerie, M. Roeb, M. Schmitz, C. Sattler, Economic comparison of solar hydrogen generation by means of thermochemical cycles and electrolysis, Int. J. Hydrogen Energy 2008, Vol. 33, 4511-4519.

¹⁴⁴ A. Fujishima, K. Kohayakawa, K. Honda, Hydrogen production under sunlight with an electrochemical photocell, J. Electrochem. Soc. 1975, Vol. 122, 1487-1489.

¹⁴⁵ J. Akikusa, S.U.M. Khan, Photoresponse and AC impedance characterization of n-TiO₂ films during hydrogen and oxygen evolution reactions in an electrochemical cell, Int. J. Hydrogen Energy 1997, Vol. 22, 875-882.

¹⁴⁶ S. Licht, B. Wang, S. Mukerji, T. Soga, M. Umeno, H. Tributsch, Efficient solar water splitting, exemplified by RuO₂-catalyzed AlGaAs/Si photoelectrolysis, J. Phys. Chem. B 2000, Vol. 104, 8920-8924.

¹⁴⁷ M.Y. El Zayat, A.O. Saed, M.S. El-Dessouki, Photoelectrochemical properties of dye sensitized Zr-doped SrTiO₃ electrodes, Int. J. Hydrogen Energy 1998, Vol. 23, 259-266.

It is currently not possible to predict the price of hydrogen produced from water using solar energy. Former studies¹⁴⁸ indicate that efficiencies in the range 10–15 % may be economical. Therefore, solar conversion efficiency¹⁴⁹ remains the critical issue on the mid- to long-term. Some technical and material specifications related to photo-electrochemical hydrogen are listed in table 14. To date, there are insufficient data to allow a meaningful discussion on the durability of photo-electrodes and PEC units. Also, little is known of the costs of PEC units because their development has been limited to the laboratory scale.

4.2.5. H₂ purification

Hydrogen purity levels are critical for a number of H₂&FC applications, in particular for fuel cells and for hydrogen storage applications^{150, 151}. From the material viewpoint, specifications are directly related to the operating conditions of the process. Main KPIs are (i) purity levels; (ii) kinetics; (iii) durability; (iv) cost issues.

¹⁴⁸ D. Morgan, F. Sissine, Congressional Research Service, Report for Congress, The Committee for the National Institute for the Environment, Washington, DC 20006-1401, 28 April 1995.

¹⁴⁹ B. Parkinson, On the efficiency and stability of photoelectrochemical devices, *Acc. Chem. Res.* 1984, Vol. 17, 431-437.

¹⁵⁰ J. Ohi, Hydrogen Fuel Purity Guidelines and Specifications Workshop, NREL ISO/TC 197 Hydrogen Technologies, 2004.

¹⁵¹ S. Watanabe, Influence of Impurities in Hydrogen on Fuel Cell Performance, Japan Automobile Research Institute, 2004.

4.3. Hydrogen storage and transport

Specifications are provided by type of application.

4.3.1. Automotive industry specifications and targets

Taking a hydrogen powered 75 kW_{el} fuel cell car as reference, the amount of hydrogen that has to be stored on-board for a range of at least 400 km is about 4 kg. The targets for the storage of 4 kg of hydrogen are (i) a total weight of the system of about 100 kg and (ii) a total volume of about 150 l, corresponding to a gravimetric density of 4 wt% (1.33 kWh/kg) and a volumetric density of 27 g/l. None of the current hydrogen storage technologies meets the combined gravimetric, volumetric, and system cost targets (figure 4). The industry prepares to enter the H₂ market using compressed hydrogen tanks to compete successfully with standard gasoline-fuelled vehicles. The on-board heat management during charging/discharging of the hydrogen tank is an additional critical point if a hydride material is chosen as storage medium (a reaction enthalpy in the 15-30 kJ per mol H₂ range is required). The refuelling rate of the hydrogen storage system should be 1.2 kg of hydrogen per minute. Including the time for connecting and disconnecting the distribution elements, this results in a refuelling time of about 4 minutes for a 4 kg hydrogen storage system. A heat exchange during refuelling is possible. It is also possible to exchange the content of the tank if waste products are produced or even to exchange the tank itself¹⁵².

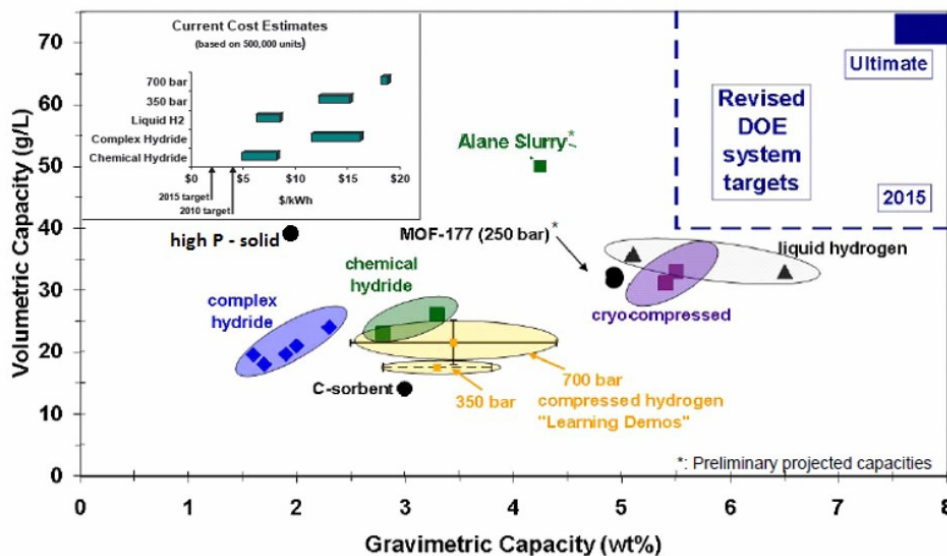


Figure 4: H₂ volumetric vs. gravimetric density targets. Insert: cost targets.

Figure 5 (from the DoE 2010 Annual Merit Review) summarizes targets for 2015 and beyond along with the current performance of numerous materials / systems (porous sorbents in blue, metal hydrides in red, chemical hydrides in orange).

¹⁵² US DOE Office of Energy Efficiency and Renewable Energy and the FreedomCAR and Fuel Partnership. Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles, September 2009. Available at https://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage_explanation.pdf

SECTION 5: SYNERGIES WITH OTHER TECHNOLOGIES

Materials with similar properties but used in different technologies are listed in this section.

5.1. Fuel cells

5.1.1. AFC

Alkaline water electrolysis and brine electrolysis are using similar materials (catalysts, electrolyte, diaphragm) with similar properties.

5.1.2. PEMFC

Polymer electrolyte (**Nafion**) membranes are also used in (i) chlor-alkali production; (ii) gas drying or humidification; (iii) superacid catalysis for the production of fine chemicals; (iv) water electrolysis, electrolytic regeneration of spent chromium plating solutions, sensors. The **platinum group metals** are used in a large variety of industries: (i) autocatalysis (platinum, palladium and rhodium); (ii) industrial use (i.e. platinum-based in the nitric acid, in the glass and petroleum industry, palladium in hydro-cracking). **Carbon** products find application in areas including industry - steel and aluminum production, glass making, aerospace industry, nuclear power, and electronics. **Graphite** products are used in applications such as brake linings, foundries, lubricants, and batteries. About two thirds of all **titanium** metal produced is used in aircraft engines and frames. The petrochemical and chemical industry uses titanium in heat exchangers and reactors. The automotive industry uses titanium in the body frame and components as connecting rods, valves, and suspension springs. There are synergies between membrane electrode assemblies and batteries manufacturing concerning coating processes.

5.1.3. Phosphoric Acid Fuel Cells

Cell separators have similarities with valve-regulated lead-acid batteries.

5.1.4. Solid Oxide Fuel Cells

High-temperature fuel cell technology (SOFC, MCFC, PCFC, DCFC) has synergies with high temperature electrolysis and fuel processing (cell materials and catalysts, respectively). SOFC materials with good oxygen ion, proton or mixed conductivity can also be used in solid state high temperature membranes used in sensor, gas separation, carbon containing fuel processing and CO₂ concentrators.

5.1.5. Molten carbonate Fuel Cells

The design of MCFC systems can be adapted for CCS (Carbon Capture and Storage) applications. On the materials side, there are hardly any synergy levels visible. However, the forming and assembly of metal sheets into bipolar plates are common to manufacturing processes used in other FC technologies.

5.1.6. Direct Carbon Fuel Cells

There are synergies in terms of process and materials with H₂/O₂ SOFC and MCFC technologies.

5.1.7. Unitized regenerative Fuel Cells

There are synergies between URFC and H₂/O₂ fuel cells or water electrolysis (for both PEM and Solid Oxide technologies) in terms of electrolyte, catalysts and cell components.

5.2. Hydrogen production

5.2.1. H₂ from fossil fuels

Coal gasification and biomass gasification share common issues related to metallic component resistance to corrosion in the presence of syngas containing impurities such as sulphur or chloride. Corrosion-erosion of metallic components is also an issue. CCS technologies are critical for the production of “green” H₂ from fossil fuels. These technologies are complementary.

5.2.2. H₂ from Water electrolysis

a- Alkaline water electrolysis

(see alkaline fuel cell 5.1.1.).

b- PEM water electrolysis

There are several similarities between PEM water electrolysis and PEM H₂/O₂ fuel cells, both in terms of principles and materials. PEM technology can also be used in sister-technologies such as hydrogen purification, hydrogen electrochemical compression and unitized regenerative fuel cells. These different technologies require similar materials with similar properties (ionic conductivity, chemical, mechanical and thermal stability, electro-activity, etc.).

c- Solid Oxide Water Electrolysis

There are close links between ceramic oxide water electrolysis technologies and fuel cell technologies. In particular, material stability is the main requirement for durability and robustness.

5.2.3. H₂ from water and thermochemical cycles

Since thermochemical cycles use heat as main energy source, some synergies can be expected with heat management technologies in miscellaneous industrial fields including nuclear power plants (heat exchanger and energy efficiency) or solar heat sources. Other synergies can be expected with thermo-chemical processes used for the treatment of biomass.

5.2.4. H₂ from water and PEC cells

There are close similarities and materials between photo-electrochemical devices capable of producing electric power ($\Delta G = 0$) and those capable of producing photo-synthetic fuels ($\Delta G > 0$). There are also synergies with water electrolysis technology.

5.2.5. H₂ purification

Low cost and high efficiency separation membranes are required for hydrogen purification after gasification or gas reforming processes. Similar requirements exist for CO₂ capture after all combustion processes. Other H₂ production technologies may require other processes for purification. This depends also on end user hydrogen quality specifications.

5.3. Hydrogen storage and transport

Compressed H₂ storage requires hydrogen compression technologies. H₂ can be compressed using standard piston-type mechanical compressors. Metal hydrides can also be used to obtain compression ratios larger than 20:1 and final output pressures larger than 1000 bar¹⁵³. Direct pressurized water electrolysis is also an option. PEM electrolyzers used for O₂ generation for underwater applications are known to have a large potential up to 700 bar. Cross-permeation effects across the polymer can reduce the efficiency. Thicker and PTFE-reinforced membranes can be used to increase the delivery pressure but the energy consumption increases with the thickness of the membrane. Alternatively, hydrogen electrochemical compressors using a H₂ fuel cell anode and a H₂ water electrolysis cathode can also be used¹⁵⁴. Metal hydrides are also found in other technologies¹⁵⁵, with applications over a wide temperature range, from a few Kelvin up to 500-600 K. The ZrNi-H₂(g) system has been used for hydrogen isotope storage, separation technology¹⁵⁶ or in closed-cycle hydride cryo-coolers¹⁵⁷. They are also used in hydrogen batteries, heat pumps, gas compressors and refrigerators. Important potential synergy exists between CH₂ storage and solid state hydrogen storage. Combining these two techniques may considerably increase the storage density of a H₂ tank, as was demonstrated recently by a Japanese car manufacturer. Thus, 5 kg H₂ could be stored at high pressure (up to 350 bar H₂) in a system with a mass of 220 kg and a volume of only 95 l. Compared to the performances of a 700 bar H₂ tank (125 kg, 220 l volume), this is a great achievement. There is still room for improvement, especially in the combination of new hydrides in a pressurized tank system. Europe could make significant contributions because there is a profound expertise in the materials development and system design amongst European groups. Another important synergy is found in the development of materials. Recent H₂ storage materials from the family of complex hydrides are based on the so-called conversion principle which means that chemical reactions take place in the solid when H₂ is absorbed or desorbed. The material undergoes a considerable change in its chemical composition during this process and new phases are formed or consumed during cycling. This is different from the storage mechanism of classical metal hydrides where the H atoms are intercalated and bound at interstitial sites of a remaining host metal lattice. A similar paradigm change from intercalation to conversion is currently observed also in the battery development. There, the conversion principle seems the only option at the moment to achieve storage capacities which are considerably beyond those of current Li ion batteries. Interestingly, the scientific principles, the challenges and the barriers are very similar in both cases and the gain of knowledge in one field may be successfully transferred e.g. from H₂ storage materials to battery materials or vice versa. Synergy exists also between the construction of H₂ storage systems and the development of high temperature PEMFC which work at temperatures up to 180 °C. Thus, the off-gas of the fuel cell can be utilized to desorb the hydrogen from, e.g. a complex hydride.

5.3.3. Large scale storage

Large scale storage of hydrogen can be envisioned using natural geological sites. The management of such natural tanks require specific technologies (and associated materials issues) which are similar to those required for the large-scale CO₂ sequestration. Synergies are also expected with the underground storage of radioactive wastes.

¹⁵³ E.L. Huston, Proceed. 5th WHEC, July 15-20 1984, Vol. 3, Toronto, Canada.

¹⁵⁴ S.A. Grigoriev, I.G. Shtatniy, P. Millet, V.I. Porembsky, V.N. Fateev, Description and characterization of an electrochemical hydrogen compressor/concentrator based on solid polymer electrolyte technology, Int. J. Hydrogen Energy 2011, Vol. 36, 4148-4155.

¹⁵⁵ P. Dantzer, in H. Wipf (ed.), Progress in Metal Hydride Technology, Topic in Applied Physics, Hydrogen in Metals (III), Springer-Verlag, 1995.

¹⁵⁶ K. Watanabe, K. Tanaka, M. Matsuyama, K. Hasegawa, ZrNi alloys as candidate getter materials for tritium processing, Fusion Engin. and Design 1991, Vol. 18, 27-32.

¹⁵⁷ R.C. Bowman, P.B. Karlmann and S. Bard, Brilliant Eyes Ten-Kelvin Sorption Cryocooler Experiment (BETSCE), Final Report, JPL Publication 97-14, 1997.

5.3.4. H₂ transport

There are synergies with long-distance transport of natural gas. Some material issues (such as corrosion resistance of pipes, threshold H₂ concentration) have been investigated in some EC projects.

SECTION 6: NEEDS AND RECOMMENDATION OF ACTIVITIES ADDRESSING 2020 AND 2050 MARKET IMPLEMENTATION

The specification targets for “2020 and 2050 market implementation” detailed in section 4 of this document cannot be achieved with state-of-art materials. Significant breakthroughs are required in both basic and applied research (analysis and modelling of material properties, new material developments). To reach the objective of market implementation, several generations of materials (and preparation processes) presenting improved properties and stability with lower fabrication costs should be developed and optimized. A continuous effort on basic research is necessary all along the market implementation process. The order in which the recommendations are given does not reflect any raking of priority.

6.1. Fuel cells

6.1.1. AFC

It is recommended to develop new concepts in order to avoid carbonate poisoning (e.g. use of novel polymers or increase temperature of operation). Also anion exchange polymer membrane development for AFC and related MEA development should be supported. Performances should be evaluated against those of PEM technology. Target costs (850 Euro/kW 2015, 600 Euro/kW 2020 excluding inverter and related control equipment) are also critical.

6.1.2. PEMFC

Till 2015-2020 it is necessary to facilitate the growth of early markets for fuel cells used in portable, stationary, and specialty-vehicle applications to overcome a number of barriers for market penetration, including the lack of operating performance data, the need for applicable codes and standards, and the need for user acceptance. The development of niche-market applications for hydrogen fuel cells has been identified as the quickest way to achieve early market penetration. Promising near-term opportunities have been identified in fuel cells to provide power to forklifts and backup power for telecommunications. Taxi, post and sweeper vehicles are being recently demonstrated in Europe as ideal solutions in urban areas to reach customer acceptance providing an efficient, clean and reliable service to the community. It is therefore recommended that specific funding is provided for market transition to accelerate the deployment of fuel cells in early market applications, to collect valuable data on the status of the technologies in real-world operation and information that will be used to validate the benefits of the technologies and potential needs for further R&D. Significant R&D progress is needed to enhance the durability of the current system in order to make PEM fuel cell technology a robust and reliable power source. The most necessary breakthrough to bring down the cost and making it competitive and affordable is expected to be the scale up of manufacturing capabilities for stationary and mobile units. Performance needs to be progressively improved by R&D on innovative polymer membrane material able to operate in a broad range of operating conditions (especially with regard to humidity and temperature).

Recommendation 1: develop high proton-conductivity polymer at low water content (0.1 S/cm at 150 °C, 20 % RH);

Recommendation 2: develop polymer electrolyte for operation up to 100-150 °C;

Recommendation 3: overcome carbon corrosion and Pt dissolution in FC catalyst (targeting 50,000 hours operation for stationary);

Recommendation 4: catalyst with reduced precious metal content ($< 0.05 \text{ mg.cm}^2$) ; non-PGM based catalysts and alternative (non-carbonaceous) carriers for Pt alloy catalysts;

Recommendation 5: development of corrosion stable and mechanically stable gas distribution layers as well as low cost bipolar plates with improved durability under temperature and current density cycling.

Recommendation 6: development of specific technologies for mass production;

Recommendation 7: stack demonstration in prototypes to gain technological insight and customer acceptance;

Recommendation	2011 - 2013	2014 - 2015	2016-2017	> 2018
1	Basic Research new concepts/	Applied Research	Pilot	
2	Basic Research new concepts/	Applied Research	Pilot	
3	Applied Research	Pilot	Demo	
4	Basic Research new concepts/	Applied Research	Applied Research (MEA development)	Pilot followed by Demo
4 (non PGM and alternative supports)	Applied Research (more mature concepts)	Applied Research incl. MEA development	Pilot	Demo
5	Applied Research	Pilot	Demo	
6			Demo	
7	Applied Research	Pilot	Demo	

Table 15: PEMFC recommendations and timelines.

6.1.3. Phosphoric Acid Fuel Cells

(not considered in this report)

6.1.4. Solid Oxide Fuel Cells

Lifetime requirements impose a need for accelerated testing procedures based on a sound understanding of materials and cell durability. The functionality of materials and components has to be characterized under realistic field application conditions. The impact of the variable environment, humidity, fuel composition (qualities of natural gas, biogas) and trace elements in air on degradation of materials and components has to be studied in long-time exposures.

Recommendation 1: investigation of main causes of degradation in SOFC cells and stacks; development of innovative solutions and materials to reach > 40,000 h lifetimes;

Recommendation 2: manufacturing and long-time testing of novel cell/stack/module concepts; obtain significant cost-reductions and increased lifetime at state-of-art performance level (e.g. full ceramic cell, Ni < 2 %, metal supported cells);

Recommendation 3: continue demonstration of mCHP systems with improved stack lifetimes to reach 20,000 units installed at EU level by 2020;

Recommendation 4: up-scaling of components, development of appropriate manufacturing techniques; demonstration of large-scale CHP (blocks or full systems) and SOFC-GT units.

		2012	2013	2014	2015	2016	2017	2018	2019
Recommendation 1	App.R&D	X	X	X	X				
Recommendation 2	Pilot act.			X	X	X			
Recommendation 3	Demo	X	X	X					
Recommendation 4	Demo			X	X	X	X		

Table 16: SOFC recommendations and timelines.

6.1.5. Molten Carbonate Fuel Cells

Considerable extension of the cell lifetime has to be achieved in the next 10 years in order to exploit the potential of MCFC for large-scale power systems.

Recommendation 1: encourage joint efforts of the few worldwide developers to reduce the cost of cell components;

Recommendation 2: investigation of the degradation mechanism in cell and stacks during unusual transient operating modes;

Recommendation 3: development of materials and process solutions to increase lifetime towards 60,000 hours.

6.1.6. Direct Carbon Fuel Cells

Basic research is needed to bring the cell performance close to its theoretical potential, especially as regards to electrode activity for direct carbon oxidation. Applied R&D up to a proof-of-concept state is needed to identify most optimal concepts and designs as well as engineering problems to be solved. This technology has a clear synergy with SOFC and MCFCs since the development lines are related to either one of these technologies or are considered a mixture of both. A need for demonstration, in particular at system level, can be expected from 2020 onwards, after first concepts have been demonstrated.

6.1.7. Unitized regenerative Fuel Cells (URFC)

The development of efficient low temperature URFC base for example on polymer electrolyte technology remains a challenging task due to the poor reversibility of the water-oxygen redox system. There is a need to improve the performances in both fuel cell and water electrolysis modes and to maintain these performances during a much larger number of operating cycle. Performances of URFC operating in fuel cell modes can be evaluated by comparison with those of conventional PEMFC and performances of URFC operating in WE mode can be evaluated by comparisons with those of conventional PEM water electrolyzers. Most R&D efforts made separately in H₂/O₂ fuel cell and water electrolysis technologies (improvements of materials) will also have a positive effect on URFC technology on the same timeline. But there is also a need to improve the URFC technology itself (preparation of specific MEAs for reversible operation, reduce cost and increase durability of cell sub-components) and to develop larger systems. The development of high temperature URFC appear to be less challenging (prototypes are currently tested) but some specific cell components are also required.

6.2. Hydrogen production

6.2.1. H₂ from fossil fuels

(see technology chapter on fossil fuels energy sector).

6.2.2. H₂ purification

Hydrogen purity is critical for several H₂&FC technologies (fuel cells using PGM catalysts and H₂ storage materials). Impurities on the upstream side of the membrane can be categorized into two-classes: those producing reversible and those producing irreversible surface damages. Concentration levels of impurities are related to degradation losses, maintenance operations and recycling processes. Purity requirements on the downstream side can differ significantly from one impurity to the other, and from one application to the other. Cost is also an issue.

Recommendation 1: investigation of manufacturing processes for ultra-thin (submicron thick) metallic membranes and support to reduce cost and improve permeation kinetics;

Recommendation 2: optimization of advanced, cost-effective ceramic and highly durable polymeric and metallic membranes with long life-time for CO₂ over H₂ separation, hydrogen purification by permeation, separation of (inhibitory or intermediary) products from biomass processes.

6.2.3. H₂ from Water electrolysis

a- Alkaline water electrolysis

Even if alkaline electrolysis is already a mature process, large scale water electrolysis still requires a substantial scale-up in the size of electrolyzers. Massive hydrogen production by water electrolysis has already attracted attention as a mean for power-grid regulation using off-peak nuclear electricity (peak shaving)¹⁵⁸. In the near future, there will be a need for larger water electrolyzers for the massive production of hydrogen from off-shore wind-farms. The efficiency of commercially available alkaline electrolyzers is usually close to 80 % (HHV) at 0.5 A/cm². Similar efficiencies at higher current densities are still achievable and could bring significant cost reductions. Improvements that would allow this technology to sustain large load variations would have a significant impact on hydrogen production from intermittent renewable energy sources. Operation at low power loads usually reduces gas purity because of gas permeation effects through the diaphragm. Also, protective polarization currents are usually used to prevent electrode corrosion. Advanced alkaline water electrolysis materials and concepts are required to overcome these limitations. The concept of Hydroxyl Exchange Membrane (HEM) water electrolysis (a hybrid process using a hydroxyl-ion conducting polymer electrolyte and combining the advantages of PEM and alkaline technologies) is more prospective and should be investigated thoroughly.

Recommendation 1: development of advanced cell materials for alkaline water electrolysis;

Recommendation 2 : development of advanced concepts for coupling with transient power loads;

Recommendation 3: investigation of HEM technology (development of hydroxyl-ion conducting polymers of adequate chemical and thermal stability).

Recommendation	2011 – 2013	2014 - 2015	2016 – 2020	> 2020
1-3	Basic research / new concepts		Applied research	Pilot

Table 17: alkaline water electrolysis recommendations and timelines.

¹⁵⁸ Solid polymer electrolyte water electrolysis technology development for large-scale hydrogen production. US Department of Energy 1981 [DOE/ET/26 202–1].

b- PEM water electrolysis

PEM water electrolysis offers a high potential of improvement. Whereas state-of-art PEM electrolyzers are operating at 0.8-1.0 A/cm² at 80°C (75% LHV efficiency), it seems possible to operate at higher current densities (of several A/cm²) to reduce non-energy costs. To maintain similar efficiencies, it will be necessary to operate at higher temperature (100-150 °C). In terms of materials, new polymers and new catalytic compositions that could sustain such temperatures are needed (synergies with FC technology). Concerning the anodic catalyst, there is a need to develop electronic carriers of large surface area stable under O₂ evolution and catalytic composition that could stabilize ruthenium. R&D on non-noble catalysts should be pursued to reduce non-energy costs. There is a need to replace bulk Ti bipolar plates and expensive porous current collectors. Durability and mean time before failure issues are also a challenge, as well as diagnostic, monitoring and maintenance. Finally, R&D on high pressure electrolysis is still required. Whereas only low pressure (1-50 bar) electrolyzers are available, some attempts have been made up to 150 bar and there are claims of operation up to 300 and 700 bar. Such systems are needed in refueling stations for the direct and safe storage of pressurized hydrogen for automotive applications. Polymers with low gas solubility and gas cross-permeation monitoring processes are required. In the near future, there is a need for larger water electrolyzers for the massive production of hydrogen from off-shore wind-farms. Durability with stable electrochemical performances and minimized maintenance operations should be extended to the upper range of the 10,000-100,000 hours time interval.

Recommendation 1: development of electron-conducting catalyst-carriers for the OER (Oxygen Evolution Reaction) to reduce PGM contents (< 0.1 mg/cm²);

Recommendation 2: development of polymer electrolyte for operation at higher (100-150°C) temperature;

Recommendation 3: development polymer electrolyte for operation at elevated (> 100 bar) pressure;

Recommendation 4: development of non-PGM catalysts for the HER and the OER and evaluation of performances against conventional PGM catalysts;

Recommendation 5: cost reduction of non-MEA cell components (current distributors, cell spacers and bipolar plates) to match EU cost targets of electrolytic hydrogen;

Recommendation 6: extend operation durability (towards 50,000 hours) of large (>100 Nm³ H₂/h) electrolyzers;

Recommendation 7: develop automated manufacturing processes for high performance MEAs.

Recommendation	2011	2012	2013	2014	2015	2016	2017	2018	2019
1	Basic research		Applied Research			Pilot			
2	Basic research			Applied Research		Pilot			
3	Basic research		Applied Research		Pilot				
4	Basic research			Applied Research		Pilot			
5		Applied Research				Pilot			
6-7	Pilot			Demo					

Table 18: PEM water electrolysis recommendations and timelines.

c- Solid Oxide Water Electrolysis

In order to improve the technology, significant efforts are needed on cell and stack reliability and durability, at relevant performance level ($i \sim 1$ A/cm²), with adapted flexibility (in terms of load variation, start up and shut down frequency and in term of steam mixtures with CO₂). To reach such performances, a better understanding of degradation processes is required, the adaptation of the microstructure of current SOFC materials and even new materials are needed. Another option would be to reduce operating temperature. However, operation in the 550-650°C temperature range (which is close to the range of operation of proton-conducting ceramic materials) requires the development of advanced ceramic materials and new sealants. The development of efficient oxide ion conducting materials operating at such low temperatures is a challenge for material science.

Recommendation 1: improve material and stack component durability (towards 75,000 h);
Recommendation 2: improve material durability upon thermal and load cycles;
Recommendation 3: decrease sensitivity to steam impurity and cell scale up;
Recommendation 4: development of oxide-ion conducting materials operating at lower temperature (550-650°C).

6.2.4. H₂ from water and thermochemical cycles

Recommendation 1: demonstration Sulphur-Iodine process at pilot scale;
Recommendation 2: improve performances of hybrid sulphuric acid cycle;
Recommendation 3: pilot demonstration¹⁵⁹ and further material development for Ferrites cycles;
Recommendation 4: pilot demonstration for CuCl, Zn/ZnO and CeO cycles.

6.2.5. H₂ from water and PEC cells

Photo-electrodes fall into two groups of materials¹⁶⁰. The first group includes ionic compounds, such as oxide materials. Although, at present, these exhibit low energy conversions (< 0.6 %), their corrosion-resistance is high. Stable performance over extended periods of time is a prerequisite for practical applications. For example, PECs using SrTiO₃ are the only cells that do not require any bias (their electromotive force is above that required for water decomposition) but its energy conversion efficiency is low (< 0.1 %) due to its relatively large band gap (3.4 eV)¹⁶¹. New materials are needed. The second group includes valence semiconductors, such as GaAs. Although these materials exhibit high energy conversions (up to 18 %), they are readily subject to corrosion in aqueous environments. Dye sensitization is very promising in processing photo-electrodes that exhibit an increased energy conversion¹⁶² but sensitizers that exhibit a stable performance in aqueous solutions are still required. Therefore, it is recommended to launch specific R&D programs on photo-hydrogen processes. Cross-activities in the fields of dye-sensitized photovoltaics and photo-hydrogen production should be encouraged.

Recommendation 1: develop semi-conducting materials for absorption of visible light stable in aqueous electrolytes;

Recommendation 2: develop stable dyes with improved turn-over and larger absorption band to harvest visible light;

Recommendation 3: demonstrate the possibility to direct photo-dissociation of water without external bias in a photo-electrochemical cell and improve energy efficiency (towards 10 %).

	2011	2012	2013	2014	2015	2016	2017	2018	2019
Recommendation 1	Basic research					Applied research			
Recommendation 2	Basic research					Applied research			
Recommendation 3	Applied research								

Table 19: photo-electrochemical water dissociation: recommendations and timelines.

¹⁵⁹ A 2^x100 kW is in operation. A 1 MW is in preparation by the FCH JTI project HYDROSOL 3D.

¹⁶⁰ T. Bak, J. Nowotny, M. Rekas, C.C. Sorrell, Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects, Int. J. Hydrogen Energy 2002, Vol. 27, 991-1022.

¹⁶¹ H.O. Finklea, In: H.O. Finklea, editor. Semiconductor electrodes. Elsevier Amsterdam 1988, 1-145.

¹⁶² W.-P. Tai, Photoelectrochemical properties of SnO₂/TiO₂ coupled electrode sensitized by a mercurochrome dye, Mater. Lett. 2001, Vol. 51, 451-454.

6.3. Hydrogen storage and transport

Currently no hydrogen storage technology can be taken out of the race. All technologies, however, still need further evolution to reach large-scale commercialization.

6.3.1. Physical storage

a- Compressed Gas Storage

Progress is still necessary, particularly in view of the long-term goals (e.g. 7.5 wt% or 120 €/kg).

Recommendation 1: reduce costs: develop new and innovative materials, investigate use of low cost fibres, develop vessel concepts and manufacturing processes; develop techniques that recover compression energy during vehicle operation; develop activities on the regulatory level to introduce approval criteria and testing procedures for impact resistance of high pressure storage containments against crash loads; a fundamental understanding of failure mechanisms of high pressure vessels is required to define new safety regulations and standards towards more flexibility for further improvement of gravimetric and volumetric energy densities;

Recommendation 2: develop recycling concepts, material sorting and recycling technologies applicable to hydrogen vehicles;

Recommendation 3: improve system reliability (pressure vessel & components); develop approaches to improve conformability of storage systems.

b- Liquid and cryo-compressed H₂ Storage

Recommendation 1: specific challenges (such as boil-off and permeation) need to be tackled in future R&D activities. Also, there is need to develop more efficient liquefaction processes, to improve long term reliability and stability of the system, and to advance filling solutions to minimize the H₂ return-gas during filling;

Recommendation 2: reduce cost and improve capacity of cryo-compressed storage tanks.

6.3.2. Storage in solid materials

a- Metal hydrides

There is still a need to identify new materials with higher volumetric capacities, real reversibility, adequate kinetics and thermodynamics, and larger gravimetric capacities (using for e.g. magnesium-alloy hydrides).

Recommendation 1: enhance gravimetric capacities of low temperature hydrides; reduce temperature of operation of high temperature hydrides; address heat management issues in a holistic, integrated manner;

Recommendation 2: investigate hybrid concepts combining high pressure (up to 350 bar) and solid storage tanks;

Recommendation 3: develop novel, energy efficient, compact and cost effective hydrogen storage solutions at low pressures in the areas of hydrogen production from renewables, grid independent energy supply systems, etc.

b- Complex hydrides

Recommendation 1: Develop novel materials combining both theoretical and experimental approaches; improve reversibility, thermodynamics, kinetics aspects; destabilization of high temperature hydrides by thermodynamic tailoring and/or nanostructuring seems to be a promising route but needs much more research efforts;

Recommendation 2: integrate solid hydrogen storage systems with high temperature PEMFCs, SOFCs; address heat management issues in a holistic integrated manner;

Recommendation 3: conduct cross-cutting research in materials testing, reactivity and safety to guide material selection and risk mitigation strategies.

c- Chemical hydrides

Recommendation 1: Develop cost efficient off-board regeneration methods;

Recommendation 2: investigate the applicability of liquid organic carriers with emphasis on refuelling and infrastructure aspects (addressing regeneration energy and cost issues).

d- Physisorption

Recommendation 1: state-of-art sorbents possess sufficient gravimetric capacities and reversibility with good kinetics; however, they require cryogenic temperatures; there is a need to develop new materials capable of operation at ambient temperature while retaining main properties of existing materials and to investigate and understand weak chemisorption effects (e.g. doping);

Recommendation 2: upscale novel nano-structured materials; design of new structures with the aid of modelling approaches;

6.3.3. Large scale storage

Recommendation : support R&D programs on large capacity tanks and geological H₂ storage; possibly link to those on large scale CO₂ sequestration.

6.3.4. H₂ transport

Recommendation : R&D programs on H₂ transport could be linked to those on transport of natural gas.

Table of acronyms

AFC	Alkaline Fuel Cell	ORR	Oxygen Reduction Reaction
APU	Auxiliary Power Unit	PAFC	Phosphoric Acid Fuel Cell
CCS	Carbon Capture and Storage	PAM	Poly AntiMonic acid
CH ₂	Compressed Hydrogen	PBI	Poly BenzImidazole
mCHP	micro- Combined Heat and Power	PCSOFC	Proton-Conducting Solid Oxide Fuel Cells
CH ₂	Compressed Hydrogen	PEC	Photo-Electrochemical Cell
CL	Catalyst Layer	PEM	Proton-Exchange Membrane
DCFC	Direct Carbon Fuel Cell	PEMFC	Proton Exchange Membrane Fuel Cell
DMFC	Direct Methanol Fuel Cell		
DOE	Department of Energy	PFSA	Per Fluoro Sulfonic Acid
EC	European Commission	PGM	Platinum Group Metal
EPDM	Ethylene Propylene- Diene-Monomer	PP	Poly Propylene
		PPS	Poly Phenylene Sulfide
EU	European Union	PPSF	Poly Phenyl Sulfone
FC	Fuel Cell	PS	Poly Sulfone
FCH JU	Fuel Cell and Hydrogen Joint Undertaking	PSA	Pressure Swing Adsorption
		PTFE	Poly Tetra Fluor Ethylene
FP6/FP7	Sixths / Sevenths Framework Program	PVDF	Poly Vinylidene Fluoride
		R&D	Research and Development
GDL	Gas Diffusion Layer	SMR	Steam Methane Reforming
H ₂ &FC	Hydrogen and Fuel Cell	S-PEEK	Sulfonated polyarylene ether ether ketone
HEM	Hydroxyl Exchange Membrane		
HER	Hydrogen Evolution Reaction	S-PES	Sulfonated Poly Ether Sulfone
HOR	Hydrogen Oxidation Reaction	SETIS	Strategic Energy Technology plan Information System
HT	High Temperature		
IPR	Intellectual Property Rights	SME	Small and Medium Enterprises
JRC	Joint Research Center	SO	Solid Oxide
KPI	Key Performance Indicator	SOWE	Solid Oxide Water Electrolysis
LH ₂	Liquid Hydrogen	SOFC	Solid Oxide Fuel Cell
LHV	Lower Heating Value	SOFC-GT	Solid Oxide Fuel Cell-Gas Turbine
MEA	Membrane Electrode Assembly		
MCFC	Molten Carbonate Fuel Cell	SPE	Solid Polymer Electrolyte
MOF	Metal-Organic Framework	SSC	Short Side Chain
MPL	Micro Porous Layer	SWCNT	Single-Walled Carbon Nano-Tubes
MWCNT	Multi-Walled Carbon Nano-Tubes		
		URFC	Unitized Regenerative Fuel Cells
NG	Natural Gas		
NPMC	Non-Precious Metal Catalysts	WE	Water Electrolysis
OCV	Open-Circuit Voltage	WGS	Water Gas Shift
OER	Oxygen Evolution Reaction		

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Abstract

A group of experts from European research organisations and industry have assessed the state of the art and future needs for materials' R&D for hydrogen and fuel cell technologies. The work was performed as input to the European Commission's roadmapping exercise on materials for the European Strategic Energy Technology Plan. The report summarises the results, including key targets identified for medium term (2020/2030) and long term (2050) timescales.

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