Pathways to Electrochemical Solar-Hydrogen Technologies

Shane Ardo,[a*] David Fernandez Rivas,[b*] Miguel Modestino,[c*] Verena Schulze Greiving,[d*] Fatwa F. Abdi,[e] Esther Alarcon llado,[f] Vincent Artero,[g] Katherine Ayers,[h] Corsin Battaglia,[i] Jan-Philipp Becker,[j] Dmytro Bederak,[k] Alan Berger,[l] Francesco Buda,[m] Enrico Chinello,[n] Bernard Dam,[o] Valerio Di Palma,[p] Tomas Edvinsson,[q] Katsushi Fujii,[r] Han Gardeniers,[b] Hans Geerlings,[o] S. Mohammad H. Hashemi,[s] Sophia Haussener,[t] Frances Houle,[u] Jurriaan Huskens,[v] Brian D. James,[w] Kornelia Konrad,[d] Akihiko Kudo,[x] Pramod Patil Kunturu,[v] Detlef Lohse,[y] Bastian Mei,[z] Eric L. Miller,[aa] Gary F. Moore,[ab] Jiri Muller,[ac] Katherine L. Orchard,[ad] Timothy E. Rosser,[ad] Fadl Saadi,[ae] Jan-Willem Schüttauf,[af] Brian Seger,[ag] Stafford W. Sheehan,[ah] Wilson A. Smith,[o] Joshua Spurgeon,[ai] Maureen Tang,[aj] Roel van de Krol,[e] Peter C.K. Vesborg,[ag] and Pieter Westerik[b]

[a]University of California Irvine, Department of Chemistry, and Department of Chemical Engineering and Materials Science, Irvine, California, 92697, USA.

[b]University of Twente, MESA+ Institute for Nanotechnology, Mesoscale Chemical Systems Group, Enschede, The Netherlands.

[c]New York University, Department of Chemical and Biomolecular Engineering, Brooklyn, New York, 11201, USA.

[d]University of Twente, Science, Technology and Policy Studies Group, Enschede, The Netherlands.

[e]Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institute for Solar Fuels, Berlin, Germany.

[f]Amolf Institute, Center for Nanophotonics, Amsterdam, The Netherlands.

[g]Université Grenoble Alpes, Laboratoire de Chimie et Biologie des Métaux, CNRS, CEA, Grenoble, France.

[h]Proton OnSite, Wallingford, Connecticut 06492, USA.

[i]Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland.

[j]Forschungszentrum Jülich, IEK-5 Photovoltaik, Jülich, Germany.

[k]University of Groningen, Zernike Institute for Advanced Materials, Groningen, The Netherlands.

[l]Air Products and Chemicals, Inc., Allentown, Pennsylvania 18195-1501, USA.

[m]University of Leiden, Leiden Institute of Chemistry, Leiden, The Netherlands.

[n]École Polytechnique Fédérale de Lausanne (EPFL), Laboratory of Applied Photonics Devices (LAPD), Lausanne, Switzerland.

[o]Delft University of Technology, Materials for Energy Conversion and Storage (MECS), Department of Chemical Engineering, Van der Maasweg 9, 2629 HZ Delft, The Netherlands.

[p]Eindhoven University of Technology, Department of Applied Physics, Eindhoven, The Netherlands.

[q]Uppsala University, Department of Engineering Sciences - Solid State Physics, Uppsala, Sweden.

[r]University of Kitakyushu, Institute of Environmental Science and Technology, Wakamatsu-ku, Kitakyushu, Fukuoka, Japan.

[s]École Polytechnique Fédérale de Lausanne (EPFL), Optics Laboratory (LO), Lausanne, Switzerland.

[t]École Polytechnique Fédérale de Lausanne (EPFL), Laboratory of Renewable Energy Science and Engineering (LRESE), Lausanne, Switzerland.

[u]Joint Center for Artificial Photosynthesis and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA.

[v]University of Twente, MESA+ Institute for Nanotechnology, Molecular Nanofabrication Group, Enschede, The Netherlands.

[w]Strategic Analysis Inc., Arlington, Virginia 22203, USA.

[x]Tokyo University of Science, Faculty of Science, Department of Applied Chemistry, Tokyo 162-8601, Japan.

[y]University of Twente, MESA+ Institute for Nanotechnology, Physics of Fluids Group, Enschede, The Netherlands.

[z]University of Twente, MESA+ Institute for Nanotechnology, Photocatalytic Synthesis Group, Enschede, The Netherlands.

[aa]U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE), Fuel Cell Technologies Office, EE-3F, 1000 Independence Ave., SW, Washington, DC 20585, USA.

[ab]Arizona State University, School of Molecular Sciences, Biodesign Center for Applied Structural Discovery (CASD), Tempe, Arizona 85287-1604, USA.

[ac]Institutt for Energiteknikk, Kjeller, Norway.

[ad]University of Cambridge, Department of Chemistry, Cambridge, UK.

[ae]California Institute of Technology, Division of Engineering and Applied Sciences, Pasadena, California 91125, USA.

[af]Swiss Center for Electronics and Microtechnology (CSEM), PV Center, Neuchâtel, Switzerland.

[ag]Technical University of Denmark (DTU), Department of Physics, Lyngby, Denmark.

[ah]Catalytic Innovations, LLC, Adamsville, Rhode Island 02801, USA.

[ai]University of Louisville, Conn Center for Renewable Energy Research, Louisville, Kentucky 40292, USA.

[aj]Drexel University, Chemical and Biological Engineering, Philadelphia, Pennsylvania 19104, USA.

* corresponding authors: ardo@uci.edu, d.fernandezrivas@utwente.nl, modestino@nyu.edu, v.c.schulzegreiving@utwente.nl.

1. Introduction

Solar-powered technologies for the electrochemical production of hydrogen through water electrolysis are of significant immediate interest. These so-called “solar hydrogen” technologies are able to capture solar energy and efficiently store it as hydrogen for widespread use when demand is high, uniquely for stationary applications, as a mobile transportation fuel, and as a reductant for various chemical transformations. This application space complements others covered by alternative technologies that capture solar energy and generate electricity (e.g. photovoltaics) or heat (e.g. solar-thermal systems). Over the past decade, several large research programs around the globe have been implemented with the aim of accelerating the development of the science and technology of solar-hydrogen devices: The Swedish Consortium for Artificial Photosynthesis, NSF Center for Chemical Innovation in Solar Fuels, the Joint Center for Artificial Photosynthesis, The Korean Center for Artificial Photosynthesis, the Institute for Solar Fuels at the Helmholtz Center in Berlin, the Japan Technological Research Association of Artificial Photosynthetic Chemical Process, The VILLUM Center for the Science of Sustainable Fuels and Chemicals in Denmark, the Center for Multiscale Catalytic Energy Conversion and the Towards BioSolar Cells program in The Netherlands, the PEC House and Solar Hydrogen Integrated Nanoelectrolysis Project (SHINE) in Switzerland, the UK Solar Fuels Network, among others. These large-scale programs, in conjunction with the efforts of small teams of researchers worldwide, have contributed to a clearer understanding of the requirements and challenges of solar-hydrogen technologies,[1-10] placing us in an appropriate position to perform an informed assessment on the feasibility of their future deployment. On June 13–17, 2016, fifty-two participants from 10 countries and 32 different organizations with expertise in multiple areas of solar hydrogen gathered at the Lorentz Center in Leiden, The Netherlands (http://www.lorentzcenter.nl/). Participants represented leading research institutions, the industrial sector, social scientists evaluating the societal impact and perception of solar-hydrogen technologies, and delegates from several governments. Attendees with this breadth in expertise and experience in solar hydrogen and broad topic discussions made this workshop unique. Over the five days of the workshop multiple topics were discussed and debated, including the state-of-the-art and limitations of materials, device architectures, early-stage market opportunities, and a roadmap for the implementation of solar-hydrogen technologies into large-scale energy markets. Several coupled considerations were examined for successful implementation of solar-hydrogen devices: (1) technical constraints for the robust and stable long-term operation of the system, (2) economic viability and environmental sustainability, and (3) societal impacts and political drivers. The most important outcome from the workshop was a specific technology roadmap for solar hydrogen devices, which had not previously existed.

The minimum requirement for a practical solar-hydrogen system is that it uses sunlight to convert water to a hydrogen stream that contains oxygen at a concentration below the flammability limit.[11, 12] Here, we only consider devices and systems that generate H_2 via proton/electron-transfer redox reactions driven by gradients in electrochemical potential formed by non-thermal photovoltaic action resulting from sunlight absorption. While this includes processes such as solar photovoltaic plus electrolyzers, photoelectrochemistry, photocatalysis, and molecular approaches, we recognize that other processes are possible as well (e.g., using light to drive thermochemical hydrogen generation). For clarity and simplicity, we classify device architectures into two broad categories as described in Figure 1 and Table 1: photovoltaic-driven electrolysis (PV–Electrolysis) and photo-electrochemistry (PEC).[13-15]

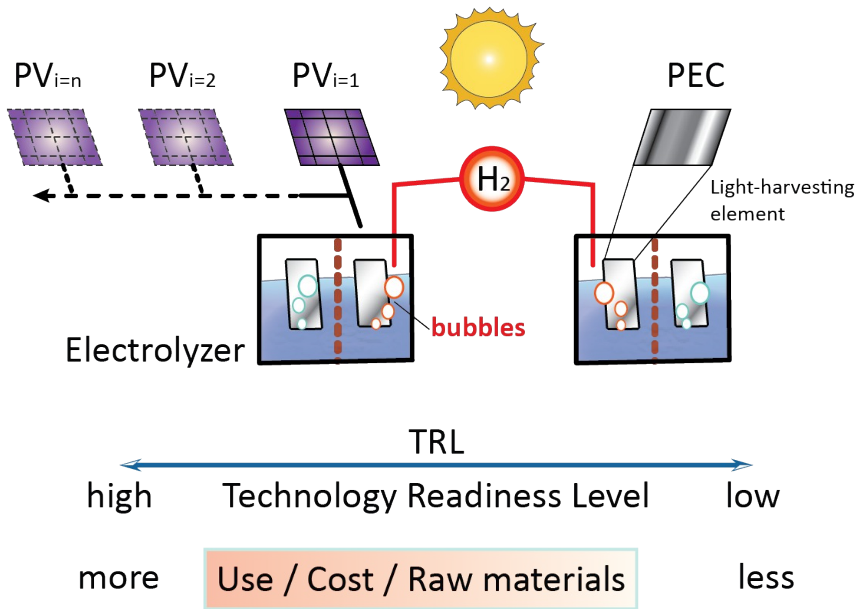

Figure 1. Scheme representing PEC and PV–Electrolysis device concepts, including current use, projected costs, amount of raw materials, and current relative level of technology readiness. For more details, see Table 1.

Table 1. PV–Electrolysis *versus* PEC systems. Overview of general concepts, and comparison of unique characteristics, technological considerations, economic challenges and political factors for each device type.

	PV–Electrolysis systems		PEC systems
General concept	Over large areas, sunlight is used to convert water to a stream of hydrogen that contains an oxygen concentration below the flammability limit		
Terminology	*Components:* Light absorbers, Electrocatalysts, Ion-exchange membranes, Electrolytes, etc. *Devices:* PV, PEC, Light absorber in electrolyte with co-catalyst, etc.		
Unique aspects	Light absorption component (PV) physically separated macroscopically from water splitting (electrolysis) component		Light absorption and water splitting components are integrated in one region
Technological options	*Distributed* Hydrogen production is independent of energy generation (different sources, electricity grid)	*Centralized* Hydrogen production occurs at the site of energy generation; requires hydrogen transport	*Centralized* Design concept exclusively allows centralized operation
Technology readiness	Advanced stage		Early stage, and exploratory for: nano-/micro-structured, and particulate/molecular components
Maximum demonstrated Solar-to-Hydrogen	30% for > 48 h[16]		10% for > 40 h[17]

efficiency†		
Economic challenges	Competition with conventional sources of non-renewable energy (fossil fuel, nuclear), battery-backed renewable energy, and hydrogen generated by other means (methane reforming) in terms of cost, availability, and accessibility	
Socio-political factors	Investments are not always stable (e.g. elections, political agendas, influential special interest groups); events affect public and political perception, perceived relevance and public acceptance (e.g., oil spill, nuclear disaster, hydrogen explosion, decreasing energy prices, environmental benefits, societal push for renewable or more sustainable energy solutions)	

†Based on laboratory-scale device demonstrations capable of producing nearly pure H_2.

The first family comprises at least two devices where the light absorption component (PV) is physically separated from the water-splitting/electrolysis component (Electrolyzer). These types of devices are the most mature and benefit from modularity, allowing individual devices to be optimized for the integrated operation. However, this modularity also often necessitates use of two encapsulation and support structures. For the other category of PEC devices, the light absorption and water splitting components are co-located or assembled into a single component and the light absorber is directly influenced by the properties of the electrolyte potentially simplifying the device architecture. In this context, PEC devices include those based on photoelectrodes where two half reactions can be spatially separated by a membrane and particles suspended in an electrolyte where they cannot be separated.[13, 18] PEC devices are less mature, and therefore less technology readied, than PV–Electrolysis devices, yet we do not define a quantitative technology readiness level for either technology because of differing global metrics. In its place, we refer to “Low technology readiness” for technologies that are far from commercialization, and “High technology readiness” for technologies that are already commercialized or beyond the large prototype stage, and evaluated in their intended environment. A technology may be assigned a high technology readiness at the device or system level, while advanced components for improved performance may still be at a low technology readiness level.

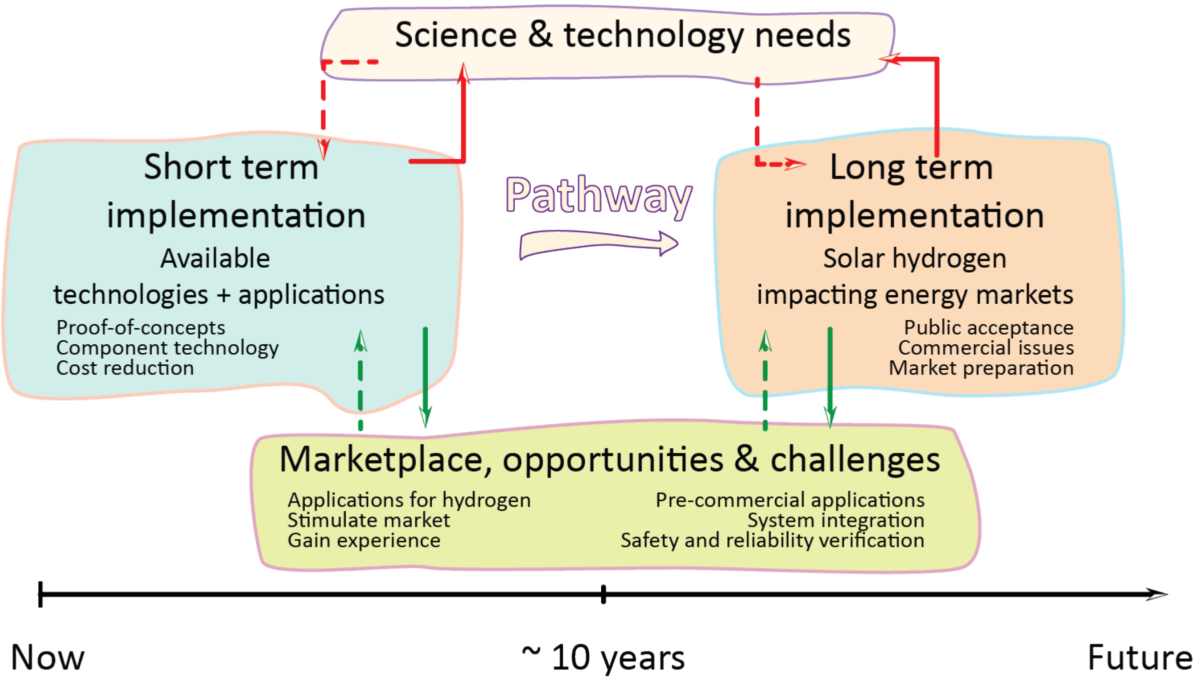

Figure 2. Schematic representation of a pathway and timeline for solar H_2 technologies and interrelated aspects discussed in this article.

In this perspective paper, we discuss potential pathways for solar-hydrogen technologies, as depicted in Figure 2. The first section describes general considerations for solar-hydrogen technologies, including technical approaches for device and system architectures, economic challenges, and societal and political impacts. The second section describes pathways for implementation of solar-hydrogen technologies, including specifically, markets for short-term implementation (≤ 10 years) of combined PV–Electrolysis devices and systems together with technological challenges and research opportunities. For long-term implementation, potential pathways for both combined PV–Electrolysis devices and systems, as well as PEC devices, are considered together with other important societal, economic, political drivers and technological requirements.

2. <u>General considerations</u>

2.1. Technical options

When evaluating the device categories (PV–Electrolysis or PEC), it is instructive to classify the design strategy. One classification is whether a technology is considered distributed or centralized. Within this article, *Distributed* approaches are defined as those that rely on the collection of sunlight by discrete solar-module installations followed by transport of energy to electrolyzer units at a different and possibly distant location. *Centralized* approaches are defined as solar installations that directly drive the water-splitting processes. Based on this technology classification, for a given hydrogen production goal, both *Centralized* and *Distributed* approaches could be implemented as either large-scale production facilities placed in one single location or as a collection of small-scale facilities dispersed geographically. PV–Electrolysis designs can be classified as either distributed or centralized while the inherent integrated nature of PEC designs necessitates that they are only centralized. Agnostic to the classification of the PEC or PV–Electrolysis designs is the requirement that they must operate with fluctuating energy inputs, because of the intermittency of solar irradiation. This challenge is significant and will also affect the implementation of centralized solar-hydrogen technologies. Section 3.1 presents a more detailed discussion on possible solutions for the PV–Electrolysis approach using alternative energy sources present in traditional electricity grids and the research opportunities that may provide solutions to overcome it in the short-term.

The distributed PV–Electrolysis design strategy can take advantage of electricity grids for the required electronic transport, and by doing so the electrolyzer can also utilize energy from various sources (e.g. from wind, fossil fuels), therefore avoiding fluctuations in its operation due to the intermittency of solar irradiation.[19] By having the option to transport charge instead of hydrogen over large distances, hydrogen transportation from centralized sunny locations to consumer centers is not necessary. Distributed approaches require implementation of power electronics to enable electricity transmission from PV installations to the electricity grid (e.g. DC–DC converters, AC–DC inverters) and subsequently to the electrolyzers.[20] Power electronics add to the cost of the system and decrease system efficiency, while transmitting electricity through the grid results in additional costs which are defined by the

19
20

electricity markets. A specific option for distributed approaches is the implementation of alternative electricity grids that are exclusively used for PV–Electrolysis (possibly operated under direct current, like those envisioned in Europe and China and only requiring DC–DC converters).[21, 22] If new infrastructure is needed for these DC grids, this approach requires a large upfront capital investment but saves operational expenses related with electricity grid transmission costs and management.

In contrast to the distributed PV–Electrolysis design strategy, an advantage of centralized PV–Electrolysis implementation is the ability to optimize the PV array operation for the electrolysis needs. This also enables the option to operate with minimal power conversion, which can result in cost reductions and efficiency improvements. Moreover, because larger sizes result in greater economic benefits, both the PV component and the electrolysis component can be implemented on very large scales; a similar situation can be seen for the centralized case. The main disadvantage of centralized solar-hydrogen facilities is the need to cover large land mass areas and then transport the generated fuel to its point of use. In the case of PEC approaches, by definition the light absorption and water splitting components operate at the same centralized location, and thus PEC has similar benefits and deficiencies as centralized PV–Electrolysis.

PV–Electrolysis devices have a higher technology readiness level than PEC devices.[23, 24] PV panels and electrolyzers are already established in the market and are continually optimized (as independent installations). PEC devices are still in the early stage of development and could enter the market in the medium-to-long-term (> 10 years) (Figure 2). In the medium-term, the technologies most likely to succeed are those that leverage semiconductor manufacturing techniques to fabricate planar photoelectrodes. In the long-term, advanced structural designs may be cost-effective where the PEC units are micro-/nano-structured, inexpensive flexible substrates are used, or particles or molecules are suspended or dissolved in liquid electrolytes. Complex PEC structures may ultimately enhance performance of solar-hydrogen devices, including light absorption, catalysis, and mass transport.[25, 26] Suspensions could benefit from economic advantages associated with low-cost plastic reactors that do not require electrical wiring or framing required to physically support heavy electrically conductive substrates.[27]

2.2. Economic challenges

In comparison to the technical options, the economic feasibility requirements are broader and depend on the ultimate application of the technology. Applications in the energy sector provide opportunity for the largest and most impactful implementations of solar-hydrogen technologies. The scale of these markets is massive (> 28,000 Terawatt-hours (TWh) per year in the US alone). In the energy share, solar-hydrogen technologies can be used for direct energy generation, as a fuel for transportation, or for temporary storage and ultimate electricity production. To date, hydrogen's direct contribution to energy markets is almost negligible, with hydrogen being almost exclusively produced from non-renewable energy sources, and small-scale uses of hydrogen that include demonstrations of grid-level energy storage, hydrogen fuel cell vehicles, and crude oil refining.[28, 29] The multiple orders-of-magnitude difference between the current scale of the energy markets and the hydrogen market represents a clear opportunity for solar-hydrogen technologies. For solar-hydrogen devices to be deployable at the energy-market scale, however, the conditions of cost competitiveness and availability must be satisfied; specifically, solar-hydrogen technologies must be scalable so that collectively they have the potential to supply a significant fraction of the future global hydrogen needs (likely hundreds of GW) at a competitive price point on a "per kWh" basis. In terms of the active components of the technology, the scalability requirement is related to the current and projected ease of accessibility and processability of the materials.[30, 31] While noble-metal catalysts that are currently implemented in state-of-the-art electrolyzers allow production of systems at a scale approaching GW/year, research on the development of improved utilization of precious metals and use of non-precious-metal electrocatalysts and low-cost light absorbers and ancillaries, such as transparent-conductive oxides and protective coatings, could enable production at larger scales.[32] This is a classic trade-off between cost and efficiency; the challenge is to optimize these aspects to improve the desired metric (\$/kWh or \$/kg H_2). This cost metric needs to account for not only the cost of the device and its balance-of-system costs, but also the costs associated with the operation and maintenance (O&M) of the technology. O&M costs may include, for example, energy costs associated with feeding water to reaction sites, cleaning of the system, gas collection, compression and transportation to distribution centers, each which are likely to cost more in integrated systems that operate at low current densities and therefore occupy large areas.

The bottom line for cost-competitiveness in the hydrogen market (where hydrogen is used not only for energy purposes, but also for chemical processing such as petroleum refining and ammonia and methanol production) is that solar hydrogen will need to compete ultimately with hydrogen from fossil fuels (i.e. usually produced from methane reforming and coal gasification routes, which tend to be situated in close proximity to points of utilization, such as ammonia production plants, thus reducing transportation costs). In the broader energy markets scale, the cost of energy produced via solar-hydrogen routes will need to compete with energy produced from other sources, e.g. fossil, nuclear, hydroelectric, wind. These non-solar energy sources define the baseline cost that determines the viability of solar-hydrogen technologies. At early stages of technological development, smaller-scale applications may benefit from use of solar hydrogen when the characteristics of the technology pose an advantage over other technologies. Below, a series of potentially viable market opportunities where solar hydrogen could be impactful in the short-term (i.e. within the next 10 years) are presented, and a critical assessment of the requirements for inclusion in large-scale energy markets in the long-term is made. For completeness, “cost” includes not only the monetary value of energy, but also any other value that society assigns to the externalities associated with different energy production mechanisms (e.g. CO_2 emissions, nuclear disasters, ecological damage).[33] In anticipation of the future global energy markets, the costs of externalities are incompletely internalized by either energy producers or energy consumers, and instead the monetary value of their impact is shared over many entities that may not have been involved in the energy-generation process or have not derived any benefit from the energy use. Although new successful applications of solar-hydrogen technologies will need to stand alone without heavily relying on regulation, advanced energy policies could incorporate the costs of externalities via various market mechanisms (e.g. carbon taxes, emission limits, incentives).[34] In practice, this could render polluting or risky technologies costlier on a monetary basis than safe renewable energy technologies, such as solar hydrogen.

2.3. Societal and political impacts

In addition to technical and economic challenges, other unknown or emerging societal and political events will influence the deployment of solar-hydrogen technologies. Building an adequate physical infrastructure (e.g., pipelines, fuel stations, two-way electricity grids) could favor the deployment of particular new technologies, including solar hydrogen. On the other hand, events such as oil spills, nuclear disasters, or hydrogen explosions can change public perception and the political agenda of specific governments, and therefore the funding scheme. The Fukushima nuclear accident in 2011, for example, received intense media coverage and led to demonstrations against nuclear power in Germany.[35] The growing public concern and resistance resulted in requests for more transparency and into a drastic change of the German national policy toward more renewable energy.[36, 37] The awareness and perception of risks and advantages of a new technology can thus influence the acceptance of the public for new technological or infrastructural changes which are crucial for its deployment. As social studies show, safety and price are the main concerns for public acceptance of hydrogen technologies.[38] However, the general attitude of people towards technology and the types of information they are given also greatly influences their opinion about hydrogen technology.[39, 40] In addition to public acceptance, political decisions can have an impact on technological development. In 1990 for example, the California Air Resources Board obliged major car manufacturers to bring zero emission vehicles to the market by 2003, which led to an increase in funding for research and development activities and pushed the development of new technologies in this field.[41] The political agenda in several countries support emerging technologies via funding schemes, e.g. in large programs on renewable energy. For example, Norway will ban the sale of fossil fuel cars by 2025.[42] Political and public attention around a particular topic thus help to mobilize research funding and relevant actors, while unfulfilled research promises can lead to a shift to other technological options. Hydrogen-based technologies for example have already seen major ups and downs in political and public attention in the past.[43, 44] Specific to solar-hydrogen technologies is that they must also compete with other research activities not only in the field of renewable energy but also with technologies that promise to reduce energy consumption or net CO_2 emissions. The scientific community will likely have more influence on the opinion of policy-makers if applied research goals are focused on realistic research targets that can be delivered in a timely fashion and that satisfy society's evolving expectations. Of course, realistic research targets are mostly based on pre-existing long-term fundamental research products.[45] Understanding how to continue to fund fundamental research, while yielding tangible deliverables that have social impact, constitutes a challenge for all stakeholders in the hydrogen technology sector.

3. Identifying pathways for implementation of solar-hydrogen technologies

A pathway for inclusion of solar-hydrogen technologies in energy markets likely requires successful incorporation in early-stage markets. In this section, we describe and critically assess short-term opportunities (≤ 10 years) for solar-hydrogen technologies and identify criteria for penetration of solar-hydrogen systems into large-scale energy markets in the long term, where it becomes critical for the technology to be socio-economically, politically, and technically beneficial.

3.1. Short-term implementation (10-year timeframe)

This subsection describes short-term markets and technological opportunities that could lead to favorable economic conditions for entry-scale implementation of solar-hydrogen technologies, specifically focusing on the more mature PV–Electrolysis devices.

3.1.1. Market opportunities

Although solar-hydrogen technologies use sunlight and water to generate hydrogen directly, under current market conditions they must compete with hydrogen generated from methane reforming or from grid-powered electrolysis. As long as fossil fuels remain as the predominant source of grid-level electricity, hydrogen produced by either of these non-solar routes has a substantial CO_2 footprint, and therefore, has clear environmental costs. Moreover, while hydrogen can be obtained inexpensively from methane reforming at large-scale plants, its use in the transportation sector could be hampered by the additional costs and added emissions from delivery to consumer locations. In addition, reformer-produced H_2 must have carbon species (e.g., CO, CO_2, CH_4), as well as trace sulfur in natural gas, removed from the reaction products at an additional cost.

While generating H_2 from a pure water feedstock does not require removal of carbonaceous reaction products, residual water must be removed in both cases. Given these product differentiators, application areas where solar-hydrogen technologies could potentially succeed in the near-term should aim at exploiting *a) environmental aspects of the production processes*, *b) generation of hydrogen close to the point of utilization*, and *c) purity of the produced hydrogen*. This would aid in the competitiveness of the technology in cost-inelastic markets that require high-purity hydrogen, production (decentralized) near the point of application, and with low environmental impacts that solar-based technologies can provide. Broadly speaking, plausible early-stage application fields can be divided in to seven distinct areas that are depicted in Figure 3: (i) grid-level energy storage, (ii) local or isolated permanent energy systems, (iii) transportation, (iv) as a precursor for the production of high-margin products, (v) the military industry, (vi) the space industry, and (vii) the agricultural sector.

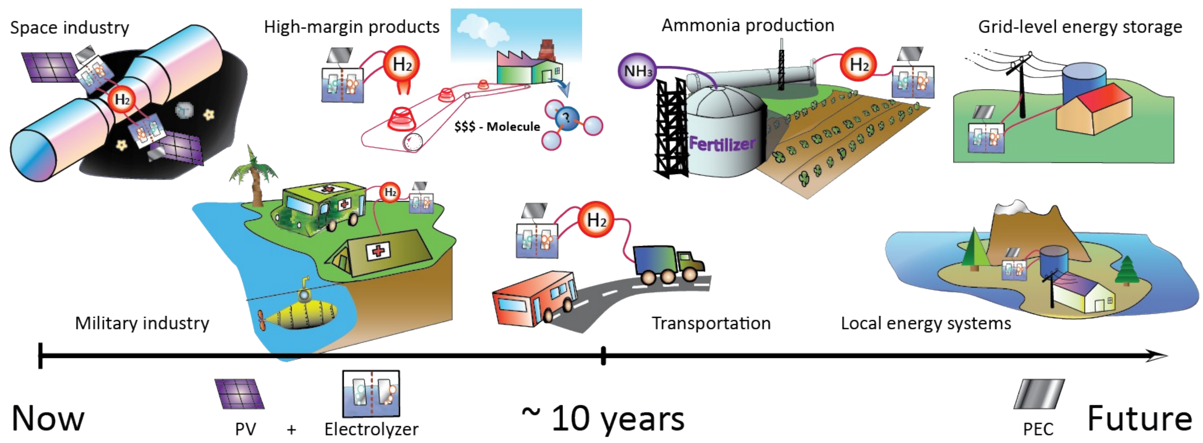

Figure 3. Short-term (10-year timeframe) application fields that are likely to provide the most promising utilization routes. The chronological ordering of these application fields is based on projected timelines for practical implementation.

i. Grid-level energy storage: While more challenging to break into, large markets are also of interest for solar-hydrogen technologies because even small impacts would result in large installations. Grid-level energy storage applications are advantageous because distributed solar-hydrogen technologies benefit from backing by the electricity grid. Therefore, challenges due to intermittency can be mitigated, at the expense of requiring some level of AC-DC and DC-AC conversion. For this proposed application field, both photovoltaic installations and electrolyzers that are coupled to a fuel cell or are regenerative (i.e. they serve the dual role of electrolyzer and fuel cell) would be connected to the electricity grid. The most cost-effective use strategy would be to generate hydrogen during periods of high solar insolation, when electricity prices are low due to a large supply of electricity generated from sunlight, and in certain locations with very high penetration of photovoltaics or other renewables, so low that the electricity is nearly free. The hydrogen would then be temporarily stored until solar insolation is poor and other sources of renewable electricity are scarce. The low supply of clean electricity would mean that electricity prices would be dictated by baseload power and would be high. Solar hydrogen could capitalize on these electricity prices by generating electricity through reacting hydrogen and oxygen (from the air) electrochemically in a fuel cell or by combustion in a turbine. Given the current relative high prices of electrolysis units and large energy losses incurred during both generation of hydrogen from water and recombination of hydrogen and oxygen, grid-level energy storage would be a difficult market to access and build a profitable business case.[46, 47] Under current market conditions, batteries are economically more viable for short-term energy storage due to their high round-trip efficiencies. Despite their own challenges, batteries would serve in the same role as hydrogen in grid-level energy storage, where, in general, most storage requirements are on the scale of days.[48-50] Additionally, gas peaker plants that operate on methane combustion are able to rapidly adapt to different electricity production levels, and can be used to smooth intermittent energy produced by solar or wind power installations both for short- and long-term energy storage needs.[51] In summary, the current alternatives (i.e. battery energy storage and natural gas fired power generation) tend to be more cost effective than solar-hydrogen technologies and therefore, it is unlikely that grid-level energy-storage solutions based on solar-hydrogen technologies will be economically viable in the short-term, although even small impacts represent large opportunities.

ii. Local or isolated permanent energy systems: Communities without grid access, including those on small islands, could benefit from localized, independent energy systems where the implementation of renewable energy sources may be advantageous. As such, solar-hydrogen technologies could play a key role in these energy solutions, especially when these communities or military bases receive high solar insolation. These implementations would also likely benefit from a local electricity microgrid that contains photovoltaics and energy-storage systems. As described above, battery economics favor short-term energy storage while electrolyzers coupled to use as a fuel cell compare favorably to batteries for larger periods of storage.[52] Unlike grid-level energy storage, which is backed by enormous baseload power that can adjust to seasonal variability, isolated permanent electrolysis units would serve the purpose of buffering long-term fluctuations in photovoltaic output (i.e. weeks to seasons). This time frame and scale are not practical for battery energy storage due to slow self-discharge that becomes significant over long timescales and unit size because battery mass scales proportionally with energy needs.[53] The distribution of batteries and hydrogen storage units would depend on seasonal fluctuations in local-specific resources. For example, desert locations would require fewer electrolysis units due to small seasonal fluctuations in solar insolation, while temperate regions would require larger and/or more electrolysis units due to more seasonal variability in the solar resource.

iii. Transportation: In the short-term, solar-hydrogen technologies can directly impact the transportation sector. Hydrogen can be mixed into natural gas pipelines to provide some of the available energy during combustion, even in internal combustion engines.[54] In addition, small fleets of hydrogen fuel-cell vehicles (HFCVs) recently entered the market, and they have been allocated in local communities with hydrogen fueling capabilities. Early adopters of HFCVs are predominantly environmentally conscious and technologically knowledgeable individuals with the appropriate economical means. Currently, the vast majority of hydrogen available for fueling is produced via CO_2-emitting methane reforming. This method is implemented because the cost of hydrogen production from a centralized methane reforming plant, while variable, is lower than via electrolysis methods. Also, large capital investments are required for compression, storage, and dispensing in hydrogen fueling stations which deters the additional investment required to produce renewable hydrogen locally. Nonetheless, given the low supply of hydrogen fuel, the price charged at hydrogen fueling stations must be significantly higher than the cost to produce and distribute hydrogen. A non-negligible subset of the population would be willing to pay a premium for hydrogen from clean sources, just as a subset of the population is willing to pay for a HFCV.

Public transportation represents a logical opportunity for implementation of HFCVs and use of solar-hydrogen technologies to generate hydrogen fuel. Already some example demonstration projects have been implemented in the US, Germany, Switzerland, Japan among others.[55-59] These projects are easier to implement than infrastructure changes required for personal HFCVs, because vehicles for public transportation have predetermined and limited routes, and require access to fueling stations in close proximity to their service route. Depots for public transportation vehicles can even be co-located with solar-hydrogen technologies so that the solar-hydrogen light absorbers can shade the vehicles from sunlight, thus keeping the vehicles cooler when not in use and ultimately saving on air conditioning needs. Furthermore, public transportation is often government regulated, and therefore a direct and rapid pathway to implementation may exist due to pressures from clean-energy policy. For similar reasons, long-distance shipping and transportation may benefit from HFCVs and solar-hydrogen technologies.

Nations in the process of developing their energy infrastructure represent opportunities for implementation of solar-hydrogen technologies, notably for HFCV car rentals in cities of the future. In these planned cities, it may make sense to locate fueling stations along the outer edge of each city, where there is more space available for large area photovoltaic installations and electrolyzers. In this scenario, people could use predominantly public transportation or battery-electric vehicles within the confines of the city, and rental cars for longer-distance travel to places outside the city, including for transportation to other cities. Car rental agencies would be located on the outer edge of the city and near the fueling stations. The ability to design a city with collocation of solar-hydrogen technologies (e.g. photovoltaic farms and electrolyzer plants), hydrogen fueling stations, and HFCV car rental agencies at the nexus of the city and open land, provides a unique opportunity for the design of synergistic infrastructure that optimizes the benefits of each technology. This is common practice in chemical plant design, where collocation of multiple plants that utilize equipment and use products from one plant in another process is often economical. Moreover, as in the case of personal HFCVs, consumers could drive this opportunity of synergistic infrastructures for solar-hydrogen technologies if tourism is a big market.

iv. High-margin products: Hydrogen is a chemical feedstock widely used in the electronics, food, pharmaceutical, cosmetics, lubricants, and chemical industries. For example, hydrogen is used to change the rheological and sensory properties of foods through hydrogenation of unsaturated fatty acids and many lipids. For many of these applications high purity hydrogen is required, with no trace of the typical contaminants found in hydrogen produced by methane reforming, which is a niche filled by solar hydrogen generated by electrolysis. Additionally, the cost of hydrogen in the final product is often negligible, in part due to the small volumes that are required, and small differences in the price of hydrogen do not affect the cost structure of these industries. Because purity is the dominant factor, these high-margin products are produced most economically via electrolysis. Moreover, implementing solar-hydrogen technologies in these industries will allow them to market their products to environmentally conscious consumers, especially for food and cosmetics. All of these characteristics of high-margin products make the short-term implementation of solar-hydrogen technologies potentially viable. Other high-margin chemicals include those produced on large scales in chemical plants, many of which can be made electrochemically, and several of which constitute rather large markets. If instead of electrolyzing water, solar-hydrogen generation could be coupled to another oxidation reaction, such as chloride oxidation to chlorine gas or perchlorate salts that would increase the economic incentive to produce solar hydrogen.[61]

v. Military industry: Military applications provide another specialized market entry point for solar-hydrogen technologies. Small-scale, easily deployable, portable, and robust microgrid energy systems are of interest to deployed troops in isolated locations. Larger installations could supply power for grid-independent bases, which are therefore less vulnerable to cybersecurity hacks or attacks on the electrical grid. Again, for remote and isolated applications, reliability, mass, and volume are often more important than the cost of the technology. In addition, remote generation of hydrogen is useful for powering fuel cells for aeromedical evacuations, which enable longer flight times compared to those powered by batteries. Similar to use for respiration during space exploration, the generation of medical grade oxygen from water splitting is also of importance for military hospital installations and any people who are involved in remote projects and expeditions.

vi. Space industry: Specialized applications in the space industry might also be a viable entry point for solar-hydrogen technologies. The cost of devices to generate hydrogen and oxygen are of minor importance, while the most important factors are reliability and the mass and volume of the systems, including feedstocks. For space applications, this is because enormous amounts of fuel are required to transport payloads and therefore the mass of the fuel, and oxidant for return missions, dominate the cost of space missions. Onboard generation of fuel (by reaction of H_2 with CO_2) and for prolonged and distant space missions (e.g. between Earth and Mars), generation of an oxidant (O_2) to release the energy stored in the fuel in space and create thrust, would result in a much lighter payload and therefore, a lower mission cost. For this reason, lightweight and flexible designs for on-demand energy production and storage are extremely beneficial strategies. Moreover, recycling water and electrolyzing it for direct onboard oxygen generation for respiration is a common approach used in space applications, and driving the process with sunlight affords a reliable, low-mass option for energy generation and storage. Lightweight solar panels consisting of thin films of III-V materials deposited on Kapton supports are already used in space applications, and lightweight designs for solar-hydrogen technologies have also recently been proposed.[16, 60] For these applications, it is even more critical that devices operate at the highest possible efficiency, and that is why the highest-performing photovoltaics are preferred over low-cost alternatives. In addition, the solar spectrum differs between space and earth, and terrestrial size constraints for deployed devices are often relaxed for implementations in space where vast regions are unoccupied, as long as the devices can be effectively bundled for delivery.

vii. Agriculture sector: More than half of the 50 million tons of hydrogen produced annually is used for the production of ammonia using the Haber-Bosch process, and more than half of the ammonia is used for the production of nitrogen-based fertilizers. Without these, we would not be able to grow enough food to sustain a population of 7 billion people. While the massive scale of the Haber-Bosch and fertilizer production processes make early-stage implementation of solar-hydrogen technologies unlikely, the sheer size of this market means that even small contributions from solar-hydrogen technologies will constitute substantial implementations that will further aid near-term deployment.

While the seven sectors mentioned above represent possible entry points for implementation of solar-hydrogen technologies, advances in the component technologies themselves could impact other industries involved in the electrochemical production of alternative commodity chemicals to hydrogen (e.g. chloralkali, zinc production, aluminum production)[61] or on electrochemical wastewater treatment.[62] These industries enjoy higher margins than the energy industry and already use electrochemical methods for large-scale production,[63] which could facilitate early-stage implementation of solar-hydrogen technologies.

3.1.2. Technological implementation

The technology readiness of solar-hydrogen technologies is low; the readiness of the specific subset of PEC solar-hydrogen technologies is even lower. Generally, for applications where cost is a significant market driver, the cost of the PV–Electrolysis device would be the most important factor. Because > 90% of the PV market consists of solar cells made from silicon (either mono-crystalline or multi-crystalline),[64] they are likely to be the most appropriate light absorbers to implement, although other commercially available light absorbers could compete with silicon based on the application. CdTe and CIGS photovoltaics represent a viable option which is likely to result in solar-hydrogen costs in a similar range to those achievable using silicon photovoltaics.[65] In most cases, PV modules based on III-V semiconductors are currently not economically viable for terrestrial applications, but are predominant in space applications where their efficiency and thin lightweight designs offset their capital cost. There are also active research programs aimed at lowering the cost of III-V solar cells and PEC devices while maintaining their conversion efficiency, thus enabling their use in conventional flat-plate and low-concentration applications.[66-68]

In terms of electrolysis technologies likely to be implemented in the short-term there are two prominent commercial options: alkaline electrolyzers and proton-exchange membrane (PEM) electrolyzers. Despite the fact that solid oxide electrolyzers are not discussed in this article, the conclusions and discussion also generally apply to this class of water-splitting devices.

Liquid electrolyte alkaline electrolyzers have been deployed commercially for more than 100 years.[69,70] Because of this, they have already been developed and implemented on larger scales than PEM electrolyzers, but they require additional attention and safety considerations due to the use of a strongly corrosive *liquid* alkaline electrolyte and the need for tightly balanced pressures of H_2 and O_2. Alkaline electrolyzers also tend to be less efficient than the acidic PEM electrolyzers at a given current density. This is due to the larger overpotential required for the alkaline-stable Ni-based electrocatalysts for hydrogen evolution and the larger ohmic losses caused by the lower conductivity of the electrolyte and the larger inter-electrode gap. Alkaline electrolyzers are also less amenable to changes in their operation conditions, because they usually implement porous separators between the electrodes with higher gas permeability and hence high crossover rates. Contrarily, PEM electrolyzers implement highly selective gas-separating ion-exchange membranes.

PEM electrolyzers are the state-of-the-art for most small-scale hydrogen generation applications. They implement ion-conducting polymer membranes as *solid* acid electrolytes that are selective for cations, allowing proton transport from the site of water oxidation to the site of hydrogen generation. Use of a solid electrolyte and liquid deionized water as a feedstock is much less of a safety concern than the corrosive liquid electrolytes needed in alkaline electrolyzers. Yet, because PEM electrocatalysts are in direct contact with the solid electrolyte membrane, which is acidic and corrosive, the only efficient catalyst materials that remain bound and stable are those based on noble metals (e.g. Pt and IrO_x are the state-of-the-art). While the terrestrial scarcity of noble metals could preclude the implementation of PEM electrolyzers on large TW scales, their implementation at early stages on GW scales is not expected to be limited by the availability of specific raw materials. In comparison to alkaline electrolyzers, PEM electrolyzers are in many ways more amenable to PV–Electrolysis devices. The use of state-of-the-art electrocatalysts in PEM electrolyzers allow for more efficient operation. Moreover, PEM electrolyzers operate more effectively under conditions of fluctuating power input, particularly when intermittent solar insolation drives electrolysis consistently outputting a pressurized hydrogen product (up to 30 bar).[71] While PEM electrolyzers do have significant technical advantages over alkaline electrolyzers, they still tend to be more costly (currently costing ~1.2 USD/W)[72] partly because of lower production volumes and limited system sizes, with the largest planned systems being on the order of several MW.[73, 74] As their production volumes increase, it is likely that their costs will continue to decrease due to economies of scale and technological advances.

3.1.3. Science and technology opportunities

There are significant challenges for the implementation of PV–Electrolysis devices, mainly arising from complications caused by the PV-driven intermittent use of electrolyzers. These challenges can at least in part be mitigated using today's electrolyzer technologies if electronic buffering mechanisms are in place to maintain operation above a threshold and therefore avoid large amounts of gas crossover and formation of explosive gas mixtures.[12] Buffering approaches include incorporation of an array of batteries or capacitors, or utilization of grid electricity, where available. An alternative to buffering is removal of the hydrogen and oxygen reaction products from the reaction chambers during periods of slow operation, for example, by flushing the system with water, or to implement other engineering approaches to avoid the formation of explosive gas mixtures.[75] Additionally, electrical circuits of photovoltaic arrays and AC-driven peripheral components (e.g. pumps, fans and control systems) could be re-designed to directly drive water electrolyzers without the need for power electronics (i.e. maximum power trackers or DC–DC converters).[16, 76] If electricity buffers, product removal, and power electronics could be avoided, a scenario that seems reasonable within the next decade, solar-hydrogen technologies will be simplified, therefore ensuring smooth operation and ultimately driving down their cost.

3.2. Long-term deployment in energy markets

The opportunities identified in the short term could help solar-hydrogen technologies enter energy markets and build the foundation for more widespread implementation in the long term. This subsection first describes societal and policy changes, as well as technological opportunities that could lead to favorable economic conditions for larger-scale implementation of solar-hydrogen technologies. Long-term pathways for both PV–Electrolysis and PEC devices are discussed.

3.2.1. Societal, economic, and policy changes and drivers

Environmental challenges associated with burning large quantities of fossil fuels to generate energy have triggered a strong interest in implementation of renewable-energy systems.[77, 78] As a testimony to this, the number of energy-conversion installations driven by sunlight or wind has experienced exponential growth over the past decade. In the case of solar energy, this growth is directly apparent from the enormous increase in the production capacity of photovoltaics, which has resulted in significant reductions in their cost.[79] On the production side, government incentives facilitated this market increase by providing strong investment that led to the rapid increase in production. An increase in demand was propelled by policy drivers that aimed to curtail use of non-renewable energy sources. For example, China, India, and even smaller size countries all have policies to promote renewable energy technologies. Further policy drivers such as controls on CO_2 emission as well as incentives for clean-energy technologies will help increase penetration of renewables into the energy markets and raise awareness for the need to realize accessible, reliable and affordable supply of energy. The Paris Climate Agreement helped set the stage for this development.[80] The Dutch government, for example, targets 40% renewable energy by 2030 and a > 80% reduction in CO_2 emissions by 2050.[81] Societal aspects can also trigger the large-scale adoption of clean energy technologies. Changes to the environment, violent and more frequent natural disasters, and local pollution can favor the adoption of clean technologies on the basis of world energy and global transportation scenarios created by the World Energy Council.[82] Additionally, investment in education and in accessible and accurate information regarding environmental effects of various energy sources can help shape society's perceptions of the energy markets. Ultimately, these changes in public perception can decisively lead to the enactment of long-lasting clean energy policies. [83, 84]

Changes in energy markets can also favor clean technologies. Market failures in the gas and oil sector (e.g. drop in demand, decrease in production, curtailments) can lead to spikes in energy prices, therefore indirectly improving the economic viability of alternative renewable-energy sources. Additionally, market and ecological factors could lead to the collapse of large-scale fossil fuel suppliers, therefore necessitating the development and broad deployment of clean-energy technologies.[85, 86] To date, the growth of the photovoltaic sector has been facilitated by the ability to integrate solar-energy-conversion devices into our current electricity transmission and distribution infrastructure. A larger penetration of photovoltaics into the energy markets will result in changes in the operation of the electricity grid. Energy storage mechanisms will have to be implemented to bridge the time gap between production periods and consumer demands. Under conditions of direct storage and use, an electricity grid may not even be required. This will further motivate the decoupling of photovoltaic installations from the grid, favoring options like centralized solar-hydrogen facilities for the production of transportation fuels and for long-term energy storage needs. Similarly, as outdated and unreliable grid structures continue to age, new energy-efficient systems such as microgrids emerge, which are in general more compatible with renewable technologies over traditional large-scale power plants.[87, 88] Moreover, as government incentives for PV phase out, soft costs must continue to decrease to keep PV competitive with fossil sources of electricity.

3.2.2. Science and technology opportunities

In the long-term, solar hydrogen generated by both PV–Electrolysis and PEC routes could play a significant role in the energy market. The socio-economic and policy drivers mentioned above would facilitate the use of solar-hydrogen technologies as a competitive energy-storage option. At the same time, significant scientific and technological barriers need to be overcome in order for the technologies to succeed in a highly competitive market. Despite some demonstrations of functioning devices, the long-term stable operation of efficient and cost-effective devices has not yet been proven for PEC routes. Possible technology development pathways are presented below for the two families of devices that, if successful, could lead to viable solar-hydrogen systems.

3.3. Pathways for PV–Electrolysis

To a large extent, PV–Electrolysis advances can be commercialized by independently optimizing each of the constituent components,[10] i.e. the PV module, the cell stack materials, and the electrolyzer design. However, the ultimate goal of a practical system coupling the two components must be kept in mind while performing this independent optimization. Although at a first glance this statement might seem obvious and non-constraining, there is a significant number of peripheral components (mainly power electronics) that are incorporated into PV installations and electrolysis units to couple their operation with the electrical grid. These components account for a non-trivial fraction of the overall capital costs of the equipment, and furthermore poor integration will result in efficiency decreases on the order of at least 10%, with ~5% losses on each of the two AC/DC conversion steps, and even larger losses at low power output. While under some circumstances PV–Electrolysis will operate in conjunction with the grid to maximize the utilization of the electrolyzer unit, lean alternatives with fewer peripheral components and a more integrated operation will likely be preferred as the technology progresses and electrolyzers become more capable of operating with fluctuating loads. This integrated PV–Electrolysis approach would not require that power electronics be incorporated in current electrolyzers systems, as PV arrays may be designed to directly power electrolyzers units with the appropriate DC characteristics. The reduced balance-of-system costs of integrated PV–Electrolysis devices and the higher efficiencies achievable due to short transmission distances could favor their implementation in the long term, assuming that no new durability challenges emerge during intermittent or fluctuating operation.[5, 7, 8] In the short term the value proposition of on-site or wastewater-derived solar-hydrogen generation can be realized in niche markets. Those gains would need to compensate for the economic losses from the low utilization of the electrolyzer units if powered exclusively with solar energy.

In the photovoltaic space, it is likely that silicon will continue to be the most promising technology in the short to medium term (< 30 years). Laboratory-based examples of silicon PVs directly coupled to electrolyzers have demonstrated efficiencies for hydrogen production in excess of 14%.[76] Following a pathway of reasonable improvements, silicon PVs could be implemented in solar-hydrogen devices to attain efficiencies of up to 18%. These advances involve improvements in surface passivation of Si, introduction of back contacting techniques in the cell fabrication, and small improvements in the quality of the crystalline silicon solar cells. Achieving even higher efficiencies using single silicon PVs would be difficult. On the cost side, only small reductions are expected from silicon manufacturing, as the prices have already decreased significantly (currently at < USD 0.5/W) and gains from economies of scale will saturate. Alternative materials for PVs including cadmium telluride, copper indium gallium selenide (CIGS), hybrid organic–inorganic halide perovskites, III-V semiconductors, or tandem architectures could be disruptive to the PV space.[16, 89] However, currently they are significantly disadvantaged with respect to Si PVs.[65, 90] There are many factors that limit the practicality of each alternative PV material, such as stability, toxicity, efficiency, durability, but ultimately each of these technologies suffers from the same limiting factor for large-scale viability: economic competitiveness. Advances that improve PV scalability, cost, stability, and performance for these materials classes will be needed before they have a significant impact on solar-hydrogen devices. Lastly, inexpensive optical concentration or light management schemes and heat and mass transfer optimizations that enhance efficiency and materials utilization of PV–Electrolysis over PV or electrolyzers alone, could improve the viability of PV–Electrolysis.

Although the contribution of the electrolyzer to the projected costs of a PV–Electrolysis system is minor, an improved efficiency of this component means that less PV cells are needed to produce the same amount of hydrogen, so that the hydrogen can become significantly cheaper. While the PV industry has grown aggressively in the recent past, and current yearly installation levels approach a 85 GW capacity,[91] the electrolyzer industry lags behind in terms of installations by more than two orders-of-magnitude. The production scale of the electrolysis industry will need to approach levels comparable to the PV sector, and as this happens, significant cost gains for both technologies are expected. Porous transport layers and bipolar plates are important from cost, stability, and efficiency perspectives. Their optimization enables higher current densities and lower catalyst loadings. Active component improvements in performance and stability (catalysts layers and membranes) are also needed. In particular, as the scale of production increases, it will be important to develop earth-abundant electrocatalysts with comparable performance to the noble-metal electrocatalysts used in current PEM electrolyzers. In addition to standard cation-exchange-membrane-based electrolyzers, membrane-free systems have seen significant advances due to their tolerance for impurities in water feedstock and potentially lower upfront capital costs.[92-95] Moreover, the development of anion-exchange membranes can enable implementation of alkaline polymer–electrolyte–membrane electrolyzers that use high-performing and earth-abundant Ni-based catalysts.[96, 97] These membranes must exhibit long-term stability and avoid excessive gas crossover even at lower sunlight-driven rates.

In addition to economies of scale, cost reductions in electrolyzers may arise from lowering the capital cost requirements of the system (currently at ~1/3 of the total cost), or by reducing costs associated with the electricity feedstock required for their operation. Solar-to-hydrogen efficiency improvements will directly affect electricity feedstock expenses, as less electricity will be needed for a given rate of solar-hydrogen production. Important sources of efficiency improvements in current PEM electrolyzers may come from reduction of ionic resistances in membranes, improvement in electrocatalyst activity, and mitigation of mass transport limitations in catalyst and porous transport layers.[98] If the efficiency improvements lead to larger operating current densities, electrolyzer units could be designed with smaller footprints for a given production level, thus reducing their capital costs. Additionally, the feedstock costs could be reduced if the electrical grid is circumvented in a direct PV–Electrolysis configuration. In this configuration, the costs associated with electricity transmission and distribution through the grid would be eliminated. Opportunities exist for defining application-specific guidelines for membranes used for direct PV–Electrolysis. Research and development of membranes for direct PV–Electrolysis configurations include identifying those with lower gas permeability and optimal ion-transport and mechanical properties, information on the molecular and morphological characteristics of membranes during mass transport processes, and ion-conducting membranes that can operate under intermittent electrolysis conditions. These fundamental science developments can lead to advances in the long term that ultimately may brighten the economic prospects of PV–Electrolysis technologies.

3.4. Pathways for PEC

Even if all the advancements in component performance and cost of coupled PV–Electrolysis systems are achieved, the nature of their design will require significant cost reduction of the auxiliary components in order for them to be cost-competitive with other hydrogen production pathways. This is similar to the case of current PV plants where the cost of the PV does not dominate system cost. Such cost reductions might not even be possible given the inherent system architecture of coupled PV–Electrolysis systems. For this reason, PEC systems could provide an opportunity for this necessary cost reduction, given that their design can be completely different than PV–Electrolysis systems and therefore could lead to disruptive and significant cost reduction. Opening up the design space to a broader set of architectures can only have a positive impact on the potential to identify a cost-optimal option. One example is systems based on photocatalyst particles.[4, 99, 100] However, to date, large-scale deployment of PEC-based solar-hydrogen technologies appears to be disadvantaged with respect to PV–Electrolysis approaches. PEC devices are significantly less developed, and their efficiencies are generally worse than for coupled PV–Electrolysis devices.[101] Moreover, they suffer from poor stability due to the requirement of light absorbing materials to be in contact or close proximity with often caustic electrolytes. Despite great efforts to develop protection strategies, this challenge remains largely unsolved and precludes deployment of PEC technologies.[101] One important development challenge is the scale: for PEC devices to reach the same rate of H_2 output as PV–Electrolysis technologies the projected electrochemically active H_2 production area would have to be at least ~50 times larger.[5, 14] These large electrochemical areas would lead to significant challenges in product handling due to the low current density at the photoelectrode surface, but could result in higher operating efficiencies and less stringent catalytic requirements. Enabling large-scale efficient PEC devices requires advances in materials durability and the ability to control at the atomic-level reproducible material engineering across macroscopic areas.[102] From a topological viewpoint, PEC devices are a subset of PV–Electrolysis devices where the electrocatalytic components are collocated with the light absorbers, and in fact can then be the same material. However, viable implementation pathways for PEC architectures will require the discovery of a PEC system that can perform solar water-splitting at a cost per kg of H_2 that is equal to or lower than available PV–Electrolysis systems, and as a consequence, PEC devices cannot be based on components that could also be used to fabricate a PV–Electrolysis device with equivalent or higher economic benefits. If this goal is not achieved, long-term solar-hydrogen technologies will tend toward PV–Electrolysis architectures. In a PV–Electrolysis configuration, each of the device components (e.g. light-absorber and water-splitting units) can be independently engineered so that the overall device is optimized, often with the aid of power electronics. Furthermore, there are significant fundamental advantages of decoupling the light-absorption and water-splitting functions in solar-hydrogen devices, which arise from increased flexibility in device design, optimization, and operation. For example, in a PEC configuration, the light absorbers will require innovative electrode designs to minimize shading due to optical absorption and scattering by the catalysts and to facilitate gas evolution and mitigate occlusion of electrocatalytic sites, for example, due to evolved bubbles that can block mass transfer and light incidence.[103]

It has been argued that economic benefits for PEC devices arise from the component integration aspects of light absorbers with electrolysis technologies, no peripheral electronics, the possibility of achieving higher efficiencies when the reactions take place at semiconductor–liquid junctions due to fewer ohmic losses, and the ease of forming a high-quality junction.[101] While the first two potential advantages have not been demonstrated, there are several additional advances that could facilitate realizing them. Understanding at a fundamental level the interfacial interactions between light absorbers, electrocatalysts, and electrolytes might lead to improved solar-to-hydrogen efficiencies and better stability. Also, continuing to use chemical engineering principles to develop design rules and demonstrations of integrated devices and solar-hydrogen production plants would provide realistic prospects on the economic and environmental viability of PEC approaches.[8, 26, 104-112] Furthermore, developing engineering solutions for the mass-production of promising PEC materials will be needed to achieve large-scale hydrogen production.[113] Specifically, to the case of so-called photocatalyst particle-based PEC devices, selective catalysis approaches will need to be developed to preferentially drive the water-splitting reaction,[114, 115] while avoiding undesirable recombination reactions of the products.[100, 116] In addition, avoiding the formation of explosive hydrogen streams will require development of new separation materials and engineering schemes, including flow-cell designs that introduce improved mechanisms of gas separation and collection,[104, 117] especially over large areas.

4. Conclusions and perspectives

This article presented a broad perspective on pathways for the implementation of solar-hydrogen technologies. Several niche market opportunities were identified for solar hydrogen implementation on the short-term (≤ 10 years). In this time frame, it is anticipated that PV–Electrolysis systems will be the only approach that could be implemented for such applications and still be economical. In the long term, solar-hydrogen technologies could be deployed more broadly in the energy markets. For that to happen, hydrogen produced via solar routes might need to be competitive against other energy carriers, such as fossil fuels. This is a daunting challenge, as the cost of energy from fossil sources has been historically low, even though extremely volatile, and it suggests that hydrogen production costs today would need to sum to less than \$2/kg hydrogen.[118] Despite the scale of the challenge, solar-hydrogen technologies provide a promising path to clean alternative fuels, and if externalities from fossil fuel utilization were internalized, the prospects for hydrogen fuel implementation would be greatly enhanced. Implementing PV–Electrolysis units manufactured using currently available commercial devices would lead to costs of hydrogen that exceed this value by at least a factor of three.[7] Therefore, achieving that cost target with PV–electrolysis devices would require significant technology advances, cost reductions, and possibly also political/policy measures, such as a CO_2 tax. Currently, one high-impact research focus is to advance electrolysis that is directly driven by PV installations. Under this mode of operation, electrolyzers will need to accommodate the natural intermittency of solar irradiation, in a stable way over lifetimes comparable to current PV technologies. This approach would result in significant capital cost reductions due to elimination of power electronics required in existing systems, and would increase overall efficiency; at the expense of a reduced capacity factor of the electrolyzer. Important long-term goals include the ability to operate PV–Electrolysis devices using inexpensive and efficient electrocatalysts. This will require the development of new catalytic materials that are stable under acidic electrolytes or anion-exchange membranes with significantly improved stability. PEC routes present even more significant challenges but have a significantly more disruptive potential. For a PEC system to be implemented, it would have to perform at least equally as well as available PV–Electrolysis alternative systems on economic grounds. Additionally, if the components used for the fabrication of such a PEC device could be utilized in a PV–Electrolysis arrangement, the integrated PEC architecture would need to be economically preferable to an alternative PV–Electrolysis arrangement and also show advantages in terms of sustainability even while it is less flexible in design, optimization, and operation. Understanding fundamental science aspects and developing reactor engineering design guidelines can help to achieve these goals.

Even if the scientific community achieves all of the advances in PV–Electrolysis or PEC devices outlined in this report, it is uncertain whether solar-hydrogen technologies will be competitive in large-scale energy markets in the long term. This will depend on a variety of factors that include, but are not limited to, system efficiencies, materials cost, balance-of-system costs, lifetime, externalities, social acceptance, and price of energy or hydrogen from alternative sources. The possible impact of some of these factors have been described in more detail in recent DOE reports.[119] Economic policy mechanisms to account for the environmental effects of CO_2 emissions can help facilitate this prospect. As a worldwide community, we should emphasize the development of CO_2-free, sustainable energy technologies at comparable cost than today's CO_2-heavy alternatives. While scientific curiosity should never be hindered by economic considerations, cost can and should be considered at a stage when more applied research programs or policy decisions need to be designed. There has been tremendous progress in the fundamental understanding of solar-hydrogen systems in the past decades and the interdisciplinary knowledge accumulated can be implemented in new electrochemical processes, wastewater treatment, or applications for which the purity or sustainability of the hydrogen is more important than the price, with greater prospects for profitability, sustainability, and societal impact. The creativity of the scientific community and its ability to pivot into new promising application areas will have a decisive effect on the future societal and environmental impacts of solar-hydrogen technologies.

5. <u>Acknowledgments</u>

The authors thank the Lorentz Center for hosting this workshop and all attendees of the workshop for their invaluable input, vision for solar and/or hydrogen technologies, and candid discussions. We are also grateful to other participants who voluntarily are not co-authors on this manuscript: Peter Achterberg, Sjoerd Bakker, Paulien Herder, Lai-Hung Lai, Eric McFarland, Christophe Moser, Rianne Post, and Martijn Van den Berge. The views and opinions expressed in this article are those of the authors and do not necessarily reflect the position of any of their funding agencies. SA thanks the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Incubator Program under Award No. DE-EE0006963 for support. DFR acknowledges support by The Netherlands Centre for Multiscale Catalytic Energy Conversion (MCEC), an NWO Gravitation programme funded by the Ministry of Education, Culture and Science of the government of The Netherlands. Part of the material on photoelectrochemical systems presented in the workshop is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993, which provides support for FH. VA thanks the European Commission's Seventh Framework Program (FP7/2007-2013) under grant agreement n° 306398 (FP7-IDEAS-ERS, Project PhotocatH2ode) and Labex Program (ArCANE, ANR-11-LABX-0003-01). TR acknowledges the UK Solar Fuels Network for his travel bursary. The contributions of DFR and HG were carried out within the research programme of BioSolar Cells, co-financed by the Dutch Ministry of Economic Affairs. PW and HG acknowledge the support by the Foundation for Fundamental Research on Matter (FOM, Project No. 13CO12-1), which is part of the Netherlands Organization for Scientific Research (NWO). SG is funded through research grant number 9455 from the VILLUM FONDEN. The views and opinions of the author(s) expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or

usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

6. References

1. N. S. Lewis and D. G. Nocera, *Proceedings of the National Academy of Sciences*, 2006, **103**, 15729-15735.
2. N. S. Lewis, *Science*, 2016, **351**, aad1920.
3. D. G. Nocera, *Accounts of Chemical Research*, 2017, **50**, 616-619.
4. B. A. Pinaud, J. D. Benck, L. C. Seitz, A. J. Forman, Z. Chen, T. G. Deutsch, B. D. James, K. N. Baum, G. N. Baum, S. Ardo, H. Wang, E. Miller and T. F. Jaramillo, *Energy & Environmental Science*, 2013, **6**, 1983-2002.
5. C. A. Rodriguez, M. A. Modestino, D. Psaltis and C. Moser, *Energy & Environmental Science*, 2014, **7**, 3828-3835.
6. P. Zhai, S. Haussener, J. Ager, R. Sathre, K. Walczak, J. Greenblatt and T. McKone, *Energy & Environmental Science*, 2013, **6**, 2380-2389.
7. M. R. Shaner, H. A. Atwater, N. S. Lewis and E. W. McFarland, *Energy & Environmental Science*, 2016, **9**, 2354-2371.
8. M. Dumortier, S. Tembhurne and S. Haussener, *Energy & Environmental Science*, 2015, **8**, 3614-3628.
9. A. Facchini, *Nature Energy*, 2017, **2**, 17129.
10. S. W. Sheehan, E. R. Cave, K. P. Kuhl, N. Flanders, A. L. Smeigh and D. T. Co, *Chem*, 2017, **3**, 3-7.
11. V. Schröder, B. Emonts, H. Janßen and H. P. Schulze, *Chemical Engineering & Technology*, 2004, **27**, 847-851.
12. S. A. Grigoriev, V. I. Porembskiy, S. V. Korobtsev, V. N. Fateev, F. Auprêtre and P. Millet, *International Journal of Hydrogen Energy*, 2011, **36**, 2721-2728.
13. A. C. Nielander, M. R. Shaner, K. M. Papadantonakis, S. A. Francis and N. S. Lewis, *Energy & Environmental Science*, 2015, **8**, 16-25.
14. T. J. Jacobsson, V. Fjallstrom, M. Edoff and T. Edvinsson, *Energy & Environmental Science*, 2014, **7**, 2056-2070.
15. M. A. Modestino and S. Haussener, *Annual Review of Chemical and Biomolecular Engineering*, 2015, **6**, 13-34.
16. J. Jia, L. C. Seitz, J. D. Benck, Y. Huo, Y. Chen, J. W. D. Ng, T. Bilir, J. S. Harris and T. F. Jaramillo, *Nature Communications*, 2016, **7**, 13237.
17. E. Verlage, S. Hu, R. Liu, R. J. R. Jones, K. Sun, C. Xiang, N. S. Lewis and H. A. Atwater, *Energy & Environmental Science*, 2015, **8**, 3166-3172.
18. J. R. McKone, N. S. Lewis and H. B. Gray, *Chemistry of Materials*, 2013, **26**, 407-414.
19. J. M. Vindel and J. Polo, *Atmospheric Research*, 2014, **143**, 313-327.
20. N. G. Kulkarni and V. B. Virulkar, *Energy and Power Engineering*, 2016, **8**, 17.
21. China powers ahead with a new direct-current infrastructure, https://www.economist.com/blogs/graphicdetail/2017/01/daily-chart-14, (accessed 12/20/2017).
22. C. Macilwain, *Nature*, 2010, **468**, 624-625.
23. *US DRIVE, Hydrogen Production Technical Team Roadmap*, U.S. Department of Energy, 2013.
24. *Fuel Cell Technologies Office. Multi-year Research, Development, and Demonstration Plan*, U.S. Department of Energy. Energy, Efficiency and Renewable Energy Office, 2012.
25. K. Walczak, Y. Chen, C. Karp, J. W. Beeman, M. Shaner, J. Spurgeon, I. D. Sharp, X. Amashukeli, W. West, J. Jin, N. S. Lewis and C. Xiang, *ChemSusChem*, 2015, **8**, 544-551.
26. M. A. Modestino, S. M. H. Hashemi and S. Haussener, *Energy & Environmental Science*, 2016, **9**, 1533-1551.

27. M. Wang, Y. Yang, J. Shen, J. Jiang and L. Sun, *Sustainable Energy & Fuels*, 2017, **1**, 1641-1663.
28. M. Götz, J. Lefebvre, F. Mörs, A. McDaniel Koch, F. Graf, S. Bajohr, R. Reimert and T. Kolb, *Renewable Energy*, 2016, **85**, 1371-1390.
29. R. Chaubey, S. Sahu, O. O. James and S. Maity, *Renewable and Sustainable Energy Reviews*, 2013, **23**, 443-462.
30. P. C. K. Vesborg and T. F. Jaramillo, *RSC Advances*, 2012, **2**, 7933-7947.
31. E. Kemppainen, A. Bodin, B. Sebok, T. Pedersen, B. Seger, B. Mei, D. Bae, P. C. K. Vesborg, J. Halme, O. Hansen, P. D. Lund and I. Chorkendorff, *Energy & Environmental Science*, 2015, **8**, 2991-2999.
32. E. W. McFarland, *Energy & Environmental Science*, 2014, **7**, 846-854.
33. T. E. McKone, W. W. Nazaroff, P. Berck, M. Auffhammer, T. Lipman, M. S. Torn, E. Masanet, A. Lobscheid, N. Santero, U. Mishra, A. Barrett, M. Bomberg, K. Fingerman, C. Scown, B. Strogen and A. Horvath, *Environ. Sci. Technol.*, 2011, **45**, 1751-1756.
34. C. Seidel, *The International Journal of Life Cycle Assessment*, 2016, **21**, 337-348.
35. N. Goebel, Hundreds of thousands protest against nuclear energy across Germany, http://www.dw.com/en/hundreds-of-thousands-protest-against-nuclear-energy-across-germany/a-14945340, (accessed 07/14/2017).
36. B. B. F. Wittneben, *Environmental Science & Policy*, 2012, **15**, 1-3.
37. L. Grossi, S. Heim and M. Waterson, *A vision of the European energy future? The impact of the German response to the Fukushima earthquake*, 2014.
38. S. J. Cherryman, S. King, F. R. Hawkes, R. Dinsdale and D. L. Hawkes, *Public Understanding of Science*, 2008, **17**, 397-410.
39. P. Achterberg, *Public Understanding of Science*, 2014, **23**, 445-453.
40. M. Ricci, G. Newsholme, P. Bellaby and R. Flynn, *International Journal of Energy Sector Management*, 2007, **1**, 34-50.
41. California Environmental Protection Agency, Air Resources Board. Zero, https://www.arb.ca.gov/msprog/zevprog/zevregs/zevregs.htm, (accessed 07/14/2017).
42. J. Staufenberg, Norway to 'completely ban petrol powered cars by 2025', http://www.independent.co.uk/environment/climate-change/norway-to-ban-the-sale-of-all-fossil-fuel-based-cars-by-2025-and-replace-with-electric-vehicles-a7065616.html, (accessed 12/20/2017).
43. S. Bakker, H. van Lente and R. Engels, *Technology Analysis & Strategic Management*, 2012, **24**, 421-434.
44. N. Melton, J. Axsen and D. Sperling, *Nature Energy*, 2016, **1**, 16013.
45. M. Ahmadpoor and B. F. Jones, *Science*, 2017, **357**, 583-587.
46. B. Pivovar, H2 at scale: Deeply decarbonizing our Energy System, https://www.hydrogen.energy.gov/pdfs/htac_apr16_10_pivovar.pdf, (accessed 07/14/2017).
47. DOE-EERE, H2@Scale Program, https://energy.gov/eere/fuelcells/h2-scale, (accessed 07/14/2017).
48. M. A. Pellow, C. J. M. Emmott, C. J. Barnhart and S. M. Benson, *Energy & Environmental Science*, 2015, **8**, 1938-1952.
49. T. Nguyen and R. F. Savinell, *The Electrochemical Society Interface*, 2010, **19**, 54-56.
50. J. O. G. Posada, A. J. R. Rennie, S. P. Villar, V. L. Martins, J. Marinaccio, A. Barnes, C. F. Glover, D. A. Worsley and P. J. Hall, *Renewable and Sustainable Energy Reviews*, 2017, **68**, 1174-1182.
51. E. Verdolini, F. Vona and D. Popp, *National Bureau of Economic Research, Working Paper 22454*.
52. J. Newman, P. G. Hoertz, C. A. Bonino and J. A. Trainham, *Journal of The Electrochemical Society*, 2012, **159**, A1722-A1729.

53. M. Beaudin, H. Zareipour, A. Schellenberglabe and W. Rosehart, *Energy for Sustainable Development*, 2010, **14**, 302-314.
54. In a national first, UCI injects renewable hydrogen into campus power supply, https://news.uci.edu/2016/12/06/in-a-national-first-uci-injects-renewable-hydrogen-into-campus-power-supply/, (accessed 11/13/2017).
55. A. Sgobbi, W. Nijs, R. De Miglio, A. Chiodi, M. Gargiulo and C. Thiel, *International Journal of Hydrogen Energy*, 2016, **41**, 19-35.
56. E. Baldassari, Greening the commute: AC Transit to nearly double hydrogen fuel cell fleet, http://www.eastbaytimes.com/2017/02/14/greening-the-commute-ac-transit-to-nearly-double-hydrogen-fuel-cell-fleet/, (accessed 12/20/2017).
57. L. Eudy and K. Chandler, *American Fuel Cell Bus Project: First Analysis Report*, U.S. Department of Transportation, Federal Transit Administration, 2013.
58. Clean Hydrogen In European Cities Project, http://chic-project.eu/, (accessed 07/17/2017).
59. R. Harding and K. Inagaki, Japan gambles on Toyota's hydrogen powered car, https://www.ft.com/content/328df346-10cb-11e7-a88c-50ba212dce4d?mhq5j=e1, (accessed 02/15/2018).
60. Addressing the Mars ISRU Challenge: Production of Oxygen and Fuel from CO2 using Sunlight, http://kiss.caltech.edu/workshops/isru/isru.html, (accessed 07/17/2017).
61. B. Mei, G. Mul and B. Seger, *Advanced Sustainable Systems*, 2017, **1**, 1600035.
62. C. Chen, A. J. Bloomfield and S. W. Sheehan, *Industrial & Engineering Chemistry Research*, 2017, **56**, 3560-3567.
63. D. Pletcher and F. C. Walsh, *Industrial electrochemistry*, Springer Science & Business Media, 2012.
64. I. Fraunhofer, Photovoltaic Report, https://www.ise.fraunhofer.de/content/dam/ise/de/documents/publications/studies/Photovoltaics-Report.pdf).
65. C. Battaglia, A. Cuevas and S. De Wolf, *Energy & Environmental Science*, 2016, **9**, 1552-1576.
66. A. Zakutayev, Opportunities in Novel Thin Films Inorganic PV Materials, https://www.nrel.gov/pv/assets/pdfs/20161018-sunup-zakutayev-thin-film.pdf, (accessed 11/13/2017).
67. EFRC, Center for Next Generation of Materials Design: An Energy Frontier Research Center, https://www.nrel.gov/pv/assets/pdfs/20161018-sunup-zakutayev-thin-film.pdf, (accessed 11/13/2017).
68. A. L. Greenaway, J. W. Boucher, S. Z. Oener, C. J. Funch and S. W. Boettcher, *ACS Energy Letters*, 2017, **2**, 2270-2282.
69. N. Guillet and P. Millet, in *Hydrogen Production*, Wiley-VCH Verlag GmbH & Co. KGaA, 2015, DOI: 10.1002/9783527676507.ch4, pp. 117-166.
70. D. M. F. Santos, C. A. C. Sequeira and J. L. Figueiredo, *Química Nova*, 2013, **36**, 1176-1193.
71. K. E. Ayers, E. B. Anderson, C. Capuano, B. Carter, L. Dalton, G. Hanlon, J. Manco and M. Niedzwiecki, *ECS Transactions*, 2010, **33**, 3-15.
72. W. Colella, B. D. James, J. Moton, G. Saur and T. Ramsden, Techno-economic Analysis of PEM Electrolysis for Hydrogen Production, https://energy.gov/sites/prod/files/2014/08/f18/fcto_2014_electrolytic_h2_wkshp_colella1.pdf, (accessed 11/13/2017).
73. A. Wilson, J. Marcinkoski and D. Papaeorgopoulos, Fuel Cell System Cost, https://www.hydrogen.energy.gov/pdfs/16020_fuel_cell_system_cost_2016.pdf, (accessed 11/13/2017).

74. M. Kopp, D. Coleman, C. Stiller, K. Scheffer, J. Aichinger and B. Scheppat, *International Journal of Hydrogen Energy*, 2017, **42**, 13311-13320.
75. F. V, S. A. Grigoriev, P. Millet, S. V. Korobtsev, V. I. Porembskiy, M. Pepic, C. Etievant and C. Puyenchet, Hydrogen Safety Aspects Related to High Pressure PEM Water Electrolysis, https://www.hydrogen.energy.gov/pdfs/safety_biblio/ichs2007/2.1.73.pdf, (accessed 11/11/2017).
76. J.-W. Schüttauf, M. A. Modestino, E. Chinello, D. Lambelet, A. Delfino, D. Dominé, A. Faes, M. Despeisse, J. Bailat, D. Psaltis, C. Moser and C. Ballif, *Journal of The Electrochemical Society*, 2016, **163**, F1177-F1181.
77. T. A. Faunce, W. Lubitz, A. W. Rutherford, D. MacFarlane, G. F. Moore, P. Yang, D. G. Nocera, T. A. Moore, D. H. Gregory, S. Fukuzumi, K. B. Yoon, F. A. Armstrong, M. R. Wasielewski and S. Styring, *Energy & Environmental Science*, 2013, **6**, 695-698.
78. T. Faunce, S. Styring, M. R. Wasielewski, G. W. Brudvig, A. W. Rutherford, J. Messinger, A. F. Lee, C. L. Hill, H. deGroot, M. Fontecave, D. R. MacFarlane, B. Hankamer, D. G. Nocera, D. M. Tiede, H. Dau, W. Hillier, L. Wang and R. Amal, *Energy & Environmental Science*, 2013, **6**, 1074-1076.
79. N. M. Haegel, R. Margolis, T. Buonassisi, D. Feldman, A. Froitzheim, R. Garabedian, M. Green, S. Glunz, H.-M. Henning, B. Holder, I. Kaizuka, B. Kroposki, K. Matsubara, S. Niki, K. Sakurai, R. A. Schindler, W. Tumas, E. R. Weber, G. Wilson, M. Woodhouse and S. Kurtz, *Science*, 2017, **356**, 141-143.
80. G. P. Peters, R. M. Andrew, J. G. Canadell, S. Fuss, R. B. Jackson, J. I. Korsbakken, C. Le Quéré and N. Nakicenovic, *Nature Climate Change*, 2017.
81. A. Hof, C. Brink, A. M. Beltran and M. d. Elzen, *Greenhouse gas emission reduction targets for 2030. Conditions for an EU target of 40%.* PBL Netherlands Environmental Assessment Agency, 2012.
82. WEC, Global Transport Scenarios 20150, https://www.worldenergy.org/wp-content/uploads/2012/09/wec_transport_scenarios_2050.pdf, (accessed 11/13/2017).
83. M. M. E. Moula, J. Maula, M. Hamdy, T. Fang, N. Jung and R. Lahdelma, *International Journal of Sustainable Built Environment*, 2013, **2**, 89-98.
84. L. C. Stokes, *Energy Policy*, 2013, **56**, 490-500.
85. D. Barstow, D. Rohde and S. Saul, Deepwater Horizon's Final Hours, http://www.nytimes.com/2010/12/26/us/26spill.html?pagewanted=all, (accessed 12/20/2017).
86. C. Krauss, Oil Prices: What to Make of the Volatility, https://www.nytimes.com/interactive/2017/business/energy-environment/oil-prices.html, (accessed 12/20/2017).
87. A. H. Fathima and K. Palanisamy, *Renewable and Sustainable Energy Reviews*, 2015, **45**, 431-446.
88. P. Denholm, K. Clark and M. O'Connell, *On the Path to SunShot: Emerging Issues and Challenges in Integrating High Levels of Solar into the Electrical Generation and Transmission System*, National Renewable Energy Laboratory, 2016.
89. W. J. Chang, K.-H. Lee, H. Ha, K. Jin, G. Kim, S.-T. Hwang, H.-m. Lee, S.-W. Ahn, W. Yoon, H. Seo, J. S. Hong, Y. K. Go, J.-I. Ha and K. T. Nam, *ACS Omega*, 2017, **2**, 1009-1018.
90. M. A. Green, *Journal of Materials Science: Materials in Electronics*, 2007, **18**, 15-19.
91. J. Hill, GTM Forecasting More Than 85 Gigawatts of Solar PV to be Installed in 2017, https://cleantechnica.com/2017/04/05/gtm-forecasting-85-gw-solar-pv-installed-2017/, (accessed 11/14/2017).
92. S. M. H. Hashemi, M. A. Modestino and D. Psaltis, *Energy & Environmental Science*, 2015, **8**, 2003-2009.
93. D. V. Esposito, *Joule*, DOI: 10.1016/j.joule.2017.07.003.

94. G. D. O'Neil, C. D. Christian, D. E. Brown and D. V. Esposito, *Journal of The Electrochemical Society*, 2016, **163**, F3012-F3019.
95. M. I. Gillespie, F. van der Merwe and R. J. Kriek, *J Power Sources*, 2015, **293**, 228-235.
96. G. Merle, M. Wessling and K. Nijmeijer, *Journal of Membrane Science*, 2011, **377**, 1-35.
97. J. R. Varcoe, P. Atanassov, D. R. Dekel, A. M. Herring, M. A. Hickner, P. A. Kohl, A. R. Kucernak, W. E. Mustain, K. Nijmeijer and K. Scott, *Energy & Environmental Science*, 2014, **7**, 3135-3191.
98. M. Carmo, D. L. Fritz, J. Mergel and D. Stolten, *International Journal of Hydrogen Energy*, 2013, **38**, 4901-4934.
99. Q. Wang, T. Hisatomi, Q. Jia, H. Tokudome, M. Zhong, C. Wang, Z. Pan, T. Takata, M. Nakabayashi, N. Shibata, Y. Li, I. D. Sharp, A. Kudo, T. Yamada and K. Domen, *Nature Materials*, 2016, **15**, 611.
100. D. M. Fabian, S. Hu, N. Singh, F. A. Houle, T. Hisatomi, K. Domen, F. E. Osterloh and S. Ardo, *Energy & Environmental Science*, 2015, **8**, 2825-2850.
101. J. W. Ager, M. R. Shaner, K. A. Walczak, I. D. Sharp and S. Ardo, *Energy & Environmental Science*, 2015, **8**, 2811-2824.
102. D. Mersch, C.-Y. Lee, J. Z. Zhang, K. Brinkert, J. C. Fontecilla-Camps, A. W. Rutherford and E. Reisner, *Journal of the American Chemical Society*, 2015, **137**, 8541-8549.
103. P. van der Linde, Á. Moreno Soto, P. Peñas-López, J. Rodríguez-Rodríguez, D. Lohse, H. Gardeniers, D. van der Meer and D. Fernández Rivas, *Langmuir*, 2017, **33**, 12873-12886.
104. S. Haussener, C. Xiang, J. M. Spurgeon, S. Ardo, N. S. Lewis and A. Z. Weber, *Energy & Environmental Science*, 2012, **5**, 9922-9922.
105. S. Haussener, S. Hu, C. Xiang, A. Z. Weber and N. S. Lewis, *Energy & Environmental Science*, 2013, **6**, 3605-3618.
106. S. Hu, C. Xiang, S. Haussener, A. D. Berger and N. S. Lewis, *Energy & Environmental Science*, 2013, **6**, 2984-2993.
107. M. Dumortier and S. Haussener, *Energy & Environmental Science*, 2015, **8**, 3069-3082.
108. C. Xiang, A. Z. Weber, S. Ardo, A. Berger, Y. Chen, R. Coridan, K. T. Fountaine, S. Haussener, S. Hu, R. Liu, N. S. Lewis, M. A. Modestino, M. M. Shaner, M. R. Singh, J. C. Stevens, K. Sun and K. Walczak, *Angewandte Chemie International Edition*, 2016, **55**, 12974-12988.
109. L. C. Seitz, Z. Chen, A. J. Forman, B. A. Pinaud, J. D. Benck and T. F. Jaramillo, *ChemSusChem*, 2014, **7**, 1372-1385.
110. M. R. Singh, K. Papadantonakis, C. Xiang and N. S. Lewis, *Energy & Environmental Science*, 2015, **8**, 2760-2767.
111. M. R. Singh, C. Xiang and N. S. Lewis, *Sustainable Energy & Fuels*, 2017, **1**, 458-466.
112. R. Sathre, C. D. Scown, W. R. Morrow, J. C. Stevens, I. D. Sharp, J. W. Ager, K. Walczak, F. A. Houle and J. B. Greenblatt, *Energy & Environmental Science*, 2014, **7**, 3264-3278.
113. R. Sathre, J. B. Greenblatt, K. Walczak, I. D. Sharp, J. C. Stevens, J. W. Ager and F. A. Houle, *Energy & Environmental Science*, 2016, **9**, 803-819.
114. D. W. Wakerley and E. Reisner, *Energy & Environmental Science*, 2015, **8**, 2283-2295.
115. N. Kaeffer, A. Morozan and V. Artero, *The Journal of Physical Chemistry B*, 2015, **119**, 13707-13713.
116. K. Maeda, K. Teramura, D. Lu, N. Saito, Y. Inoue and K. Domen, *Angewandte Chemie International Edition*, 2006, **45**, 7806-7809.
117. M. A. Modestino, K. A. Walczak, A. Berger, C. M. Evans, S. Haussener, C. Koval, J. S. Newman, J. W. Ager and R. A. Segalman, *Energy & Environmental Science*, 2014, **7**, 297-301.
118. E. L. Miller, Hydrogen Production and Delivery Program, https://www.hydrogen.energy.gov/pdfs/review17/pd000_miller_2017_o.pdf, (accessed 11/14/2017).

119. U.S. DOE Energy Efficiency and Renewable Energy Office, Fuel Cell Technologies Office, Multi-Year Research, Development, and Demonstration Plan 2015, https://www.energy.gov/sites/prod/files/2015/06/f23/fcto_myrdd_production.pdf, (accessed 06/04/2018).