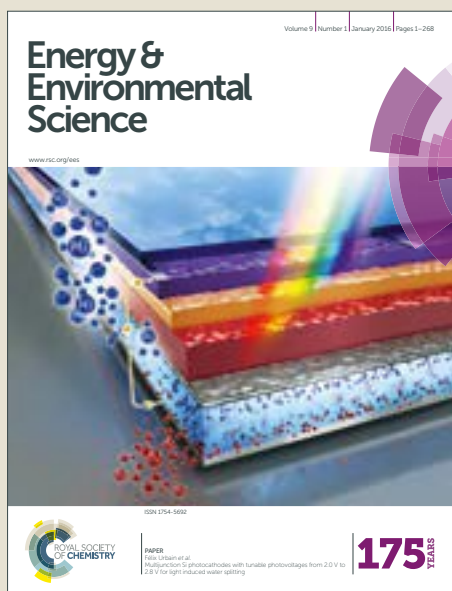


# Energy & Environmental Science

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# Pathways to Electrochemical Solar-Hydrogen Technologies

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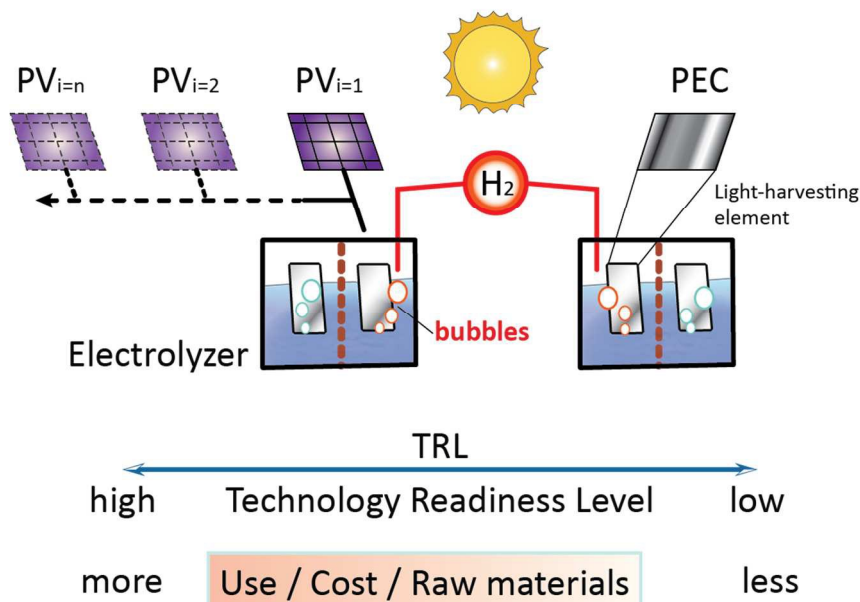
## 1 **1. Introduction**

2 Solar-powered technologies for the electrochemical production of hydrogen through water  
3 electrolysis are of significant immediate interest. These so-called “solar hydrogen” technologies are able  
4 to capture solar energy and efficiently store it as hydrogen for widespread use when demand is high,  
5 uniquely for stationary applications, as a mobile transportation fuel, and as a reductant for various  
6 chemical transformations. This application space complements others covered by alternative technologies  
7 that capture solar energy and generate electricity (e.g. photovoltaics) or heat (e.g. solar-thermal systems).  
8 Over the past decade, several large research programs around the globe have been implemented with the  
9 aim of accelerating the development of the science and technology of solar-hydrogen devices: The  
10 Swedish Consortium for Artificial Photosynthesis, NSF Center for Chemical Innovation in Solar Fuels,  
11 the Joint Center for Artificial Photosynthesis, The Korean Center for Artificial Photosynthesis, the  
12 Institute for Solar Fuels at the Helmholtz Center in Berlin, the Japan Technological Research Association  
13 of Artificial Photosynthetic Chemical Process, The VILLUM Center for the Science of Sustainable Fuels  
14 and Chemicals in Denmark, the Center for Multiscale Catalytic Energy Conversion and the Towards  
15 BioSolar Cells program in The Netherlands, the PEC House and Solar Hydrogen Integrated  
16 Nanoelectrolysis Project (SHINE) in Switzerland, the UK Solar Fuels Network, among others. These  
17 large-scale programs, in conjunction with the efforts of small teams of researchers worldwide, have  
18 contributed to a clearer understanding of the requirements and challenges of solar-hydrogen  
19 technologies,<sup>1-10</sup> placing us in an appropriate position, to perform an informed assessment on the  
20 feasibility of their future deployment. On June 13–17, 2016, fifty-two participants from 10 countries and  
21 32 different organizations with expertise in multiple areas of solar hydrogen gathered at the Lorentz  
22 Center in Leiden, The Netherlands (<http://www.lorentzcenter.nl/>). Participants represented leading  
23 research institutions, the industrial sector, social scientists evaluating the societal impact and perception  
24 of solar-hydrogen technologies, and delegates from several governments. Attendees with this breadth in  
25 expertise and experience in solar hydrogen and broad topic discussions made this workshop unique. Over



1 the five days of the workshop multiple topics were discussed and debated, including the state-of-the-art  
2 and limitations of materials, device architectures, early-stage market opportunities, and a roadmap for the  
3 implementation of solar-hydrogen technologies into large-scale energy markets. Several coupled  
4 considerations were examined for successful implementation of solar-hydrogen devices: (1) technical  
5 constraints for the robust and stable long-term operation of the system, (2) economic viability and  
6 environmental sustainability, and (3) societal impacts and political drivers. The most important outcome  
7 from the workshop was a specific technology roadmap for solar hydrogen devices, which had not  
8 previously existed.

9 The minimum requirement for a practical solar-hydrogen system is that it uses sunlight to convert  
10 water to a hydrogen stream that contains oxygen at a concentration below the flammability limit.<sup>11, 12</sup>  
11 Here, we only consider devices and systems that generate H<sub>2</sub> via proton/electron-transfer redox reactions  
12 driven by gradients in electrochemical potential formed by non-thermal photovoltaic action resulting from  
13 sunlight absorption. While this includes processes such as solar photovoltaic plus electrolyzers,  
14 photoelectrochemistry, photocatalysis, and molecular approaches, we recognize that other processes are  
15 possible as well (e.g., using light to drive thermochemical hydrogen generation). For clarity and  
16 simplicity, we classify device architectures into two broad categories as described in Figure 1 and Table  
17 1: photovoltaic-driven electrolysis (PV–Electrolysis) and photo-electrochemistry (PEC).<sup>13-15</sup>



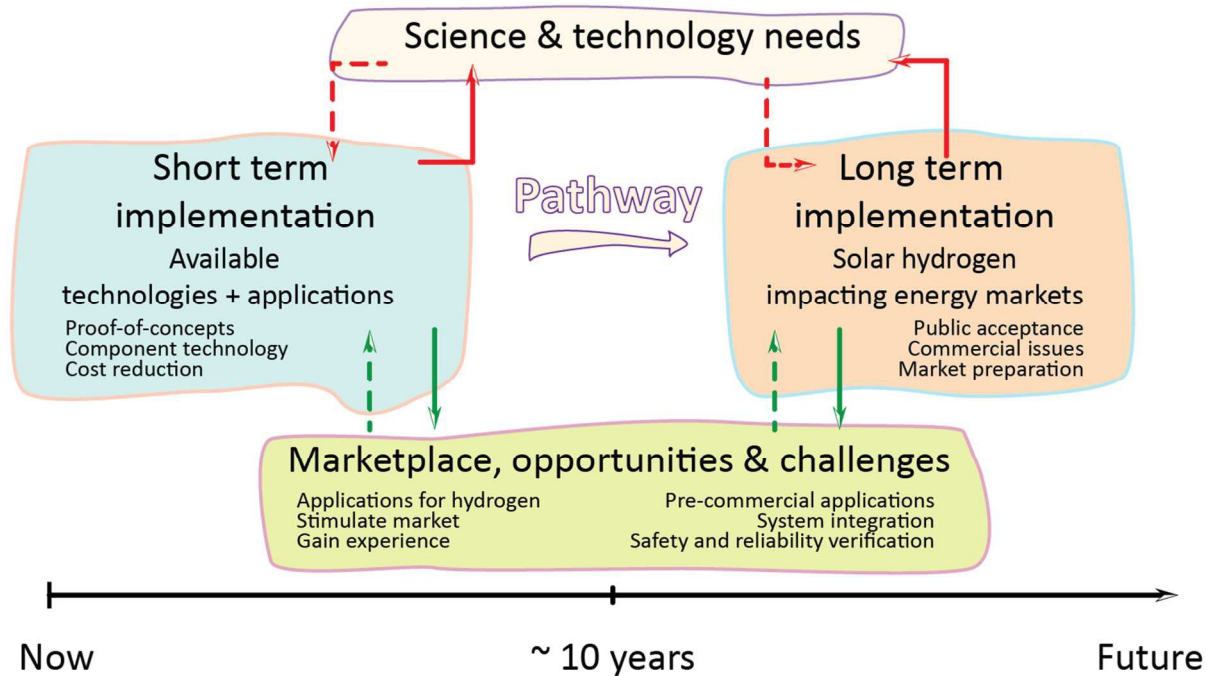
- 1
- 2 **Figure 1.** Scheme representing PEC and PV–Electrolysis device concepts, including current use, projected costs,
- 3 amount of raw materials, and current relative level of technology readiness. For more details, see Table 1.
- 4 **Table 1. PV–Electrolysis versus PEC systems.** Overview of general concepts, and comparison of unique
- 5 characteristics, technological considerations, economic challenges and political factors for each device type.

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

<b>Solar-to-Hydrogen efficiency<sup>†</sup></b>		
<b>Economic challenges</b>	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	
<b>Socio-political factors</b>	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)	

1 <sup>†</sup>Based on laboratory-scale device demonstrations capable of producing nearly pure H<sub>2</sub>.

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



1  
2 **Figure 2.** Schematic representation of a pathway and timeline for solar H<sub>2</sub> technologies and interrelated aspects  
3 discussed in this article.  
4

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

14

## 15 **2. General considerations**

## 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.<sup>19</sup> 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.<sup>20</sup> Power electronics add to the cost of the system and decrease system efficiency,

1 while transmitting electricity through the grid results in additional costs which are defined by the  
2 electricity markets. A specific option for distributed approaches is the implementation of alternative  
3 electricity grids that are exclusively used for PV–Electrolysis (possibly operated under direct current, like  
4 those envisioned in Europe and China and only requiring DC–DC converters).<sup>21, 22</sup> If new infrastructure is  
5 needed for these DC grids, this approach requires a large upfront capital investment but saves operational  
6 expenses related with electricity grid transmission costs and management.

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

17 PV–Electrolysis devices have a higher technology readiness level than PEC devices.<sup>23, 24</sup> PV panels  
18 and electrolyzers are already established in the market and are continually optimized (as independent  
19 installations). PEC devices are still in the early stage of development and could enter the market in the  
20 medium-to-long-term (> 10 years) (Figure 2). In the medium-term, the technologies most likely to  
21 succeed are those that leverage semiconductor manufacturing techniques to fabricate planar  
22 photoelectrodes. In the long-term, advanced structural designs may be cost-effective where the PEC units  
23 are micro-/nano-structured, inexpensive flexible substrates are used, or particles or molecules are  
24 suspended or dissolved in liquid electrolytes. Complex PEC structures may ultimately enhance  
25 performance of solar-hydrogen devices, including light absorption, catalysis, and mass transport.<sup>25, 26</sup>

1 Suspensions could benefit from economic advantages associated with low-cost plastic reactors that do not  
2 require electrical wiring or framing required to physically support heavy electrically conductive  
3 substrates.<sup>27</sup>

## 4 **2.2. Economic challenges**

5 In comparison to the technical options, the economic feasibility requirements are broader and depend  
6 on the ultimate application of the technology. Applications in the energy sector provide opportunity for  
7 the largest and most impactful implementations of solar-hydrogen technologies. The scale of these  
8 markets is massive (> 28,000 Terawatt-hours (TWh) per year in the US alone). In the energy share, solar-  
9 hydrogen technologies can be used for direct energy generation, as a fuel for transportation, or for  
10 temporary storage and ultimate electricity production. To date, hydrogen's direct contribution to energy  
11 markets is almost negligible, with hydrogen being almost exclusively produced from non-renewable  
12 energy sources, and small-scale uses of hydrogen that include demonstrations of grid-level energy  
13 storage, hydrogen fuel cell vehicles, and crude oil refining.<sup>28, 29</sup> The multiple orders-of-magnitude  
14 difference between the current scale of the energy markets and the hydrogen market represents a clear  
15 opportunity for solar-hydrogen technologies. For solar-hydrogen devices to be deployable at the energy-  
16 market scale, however, the conditions of cost competitiveness and availability must be satisfied;  
17 specifically, solar-hydrogen technologies must be scalable so that collectively they have the potential to  
18 supply a significant fraction of the future global hydrogen needs (likely hundreds of GW) at a competitive  
19 price point on a "per kWh" basis. In terms of the active components of the technology, the scalability  
20 requirement is related to the current and projected ease of accessibility and processability of the  
21 materials.<sup>30, 31</sup> While noble-metal catalysts that are currently implemented in state-of-the-art electrolyzers  
22 allow production of systems at a scale approaching GW/year, research on the development of improved  
23 utilization of precious metals and use of non-precious-metal electrocatalysts and low-cost light absorbers  
24 and ancillaries, such as transparent-conductive oxides and protective coatings, could enable production at  
25 larger scales.<sup>32</sup> This is a classic trade-off between cost and efficiency; the challenge is to optimize these



1 aspects to improve the desired metric (\$/kWh or \$/kg H<sub>2</sub>). This cost metric needs to account for not only  
2 the cost of the device and its balance-of-system costs, but also the costs associated with the operation and  
3 maintenance (O&M) of the technology. O&M costs may include, for example, energy costs associated  
4 with feeding water to reaction sites, cleaning of the system, gas collection, compression and  
5 transportation to distribution centers, each which are likely to cost more in integrated systems that operate  
6 at low current densities and therefore occupy large areas.

7 The bottom line for cost-competitiveness in the hydrogen market (where hydrogen is used not only  
8 for energy purposes, but also for chemical processing such as petroleum refining and ammonia and  
9 methanol production) is that solar hydrogen will need to compete ultimately with hydrogen from fossil  
10 fuels (i.e. usually produced from methane reforming and coal gasification routes, which tend to be  
11 situated in close proximity to points of utilization, such as ammonia production plants, thus reducing  
12 transportation costs). In the broader energy markets scale, the cost of energy produced via solar-hydrogen  
13 routes will need to compete with energy produced from other sources, e.g. fossil, nuclear, hydroelectric,  
14 wind. These non-solar energy sources define the baseline cost that determines the viability of solar-  
15 hydrogen technologies. At early stages of technological development, smaller-scale applications may  
16 benefit from use of solar hydrogen when the characteristics of the technology pose an advantage over  
17 other technologies. Below, a series of potentially viable market opportunities where solar hydrogen could  
18 be impactful in the short-term (i.e. within the next 10 years) are presented, and a critical assessment of the  
19 requirements for inclusion in large-scale energy markets in the long-term is made. For completeness,  
20 “cost” includes not only the monetary value of energy, but also any other value that society assigns to the  
21 externalities associated with different energy production mechanisms (e.g. CO<sub>2</sub> emissions, nuclear  
22 disasters, ecological damage).<sup>33</sup> In anticipation of the future global energy markets, the costs of  
23 externalities are incompletely internalized by either energy producers or energy consumers, and instead  
24 the monetary value of their impact is shared over many entities that may not have been involved in the  
25 energy-generation process or have not derived any benefit from the energy use. Although new successful



1 applications of solar-hydrogen technologies will need to stand alone without heavily relying on  
2 regulation, advanced energy policies could incorporate the costs of externalities via various market  
3 mechanisms (e.g. carbon taxes, emission limits, incentives).<sup>34</sup> In practice, this could render polluting or  
4 risky technologies costlier on a monetary basis than safe renewable energy technologies, such as solar  
5 hydrogen.

### 6 ***2.3. Societal and political impacts***

7 In addition to technical and economic challenges, other unknown or emerging societal and political  
8 events will influence the deployment of solar-hydrogen technologies. Building an adequate physical  
9 infrastructure (e.g., pipelines, fuel stations, two-way electricity grids) could favor the deployment of  
10 particular new technologies, including solar hydrogen. On the other hand, events such as oil spills,  
11 nuclear disasters, or hydrogen explosions can change public perception and the political agenda of  
12 specific governments, and therefore the funding scheme. The Fukushima nuclear accident in 2011, for  
13 example, received intense media coverage and led to demonstrations against nuclear power in Germany.<sup>35</sup>  
14 The growing public concern and resistance resulted in requests for more transparency and into a drastic  
15 change of the German national policy toward more renewable energy.<sup>36, 37</sup> The awareness and perception  
16 of risks and advantages of a new technology can thus influence the acceptance of the public for new  
17 technological or infrastructural changes which are crucial for its deployment. As social studies show,  
18 safety and price are the main concerns for public acceptance of hydrogen technologies.<sup>38</sup> However, the  
19 general attitude of people towards technology and the types of information they are given also greatly  
20 influences their opinion about hydrogen technology.<sup>39, 40</sup> In addition to public acceptance, political  
21 decisions can have an impact on technological development. In 1990 for example, the California Air  
22 Resources Board obliged major car manufacturers to bring zero emission vehicles to the market by 2003,  
23 which led to an increase in funding for research and development activities and pushed the development  
24 of new technologies in this field.<sup>41</sup> The political agenda in several countries support emerging  
25 technologies via funding schemes, e.g. in large programs on renewable energy. For example, Norway will

1 ban the sale of fossil fuel cars by 2025.<sup>42</sup> Political and public attention around a particular topic thus help  
2 to mobilize research funding and relevant actors, while unfulfilled research promises can lead to a shift to  
3 other technological options. Hydrogen-based technologies for example have already seen major ups and  
4 downs in political and public attention in the past.<sup>43, 44</sup> Specific to solar-hydrogen technologies is that they  
5 must also compete with other research activities not only in the field of renewable energy but also with  
6 technologies that promise to reduce energy consumption or net CO<sub>2</sub> emissions. The scientific community  
7 will likely have more influence on the opinion of policy-makers if applied research goals are focused on  
8 realistic research targets that can be delivered in a timely fashion and that satisfy society's evolving  
9 expectations. Of course, realistic research targets are mostly based on pre-existing long-term fundamental  
10 research products.<sup>45</sup> Understanding how to continue to fund fundamental research, while yielding tangible  
11 deliverables that have social impact, constitutes a challenge for all stakeholders in the hydrogen  
12 technology sector.

13

### 14 **3. Identifying pathways for implementation of solar-hydrogen technologies**

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

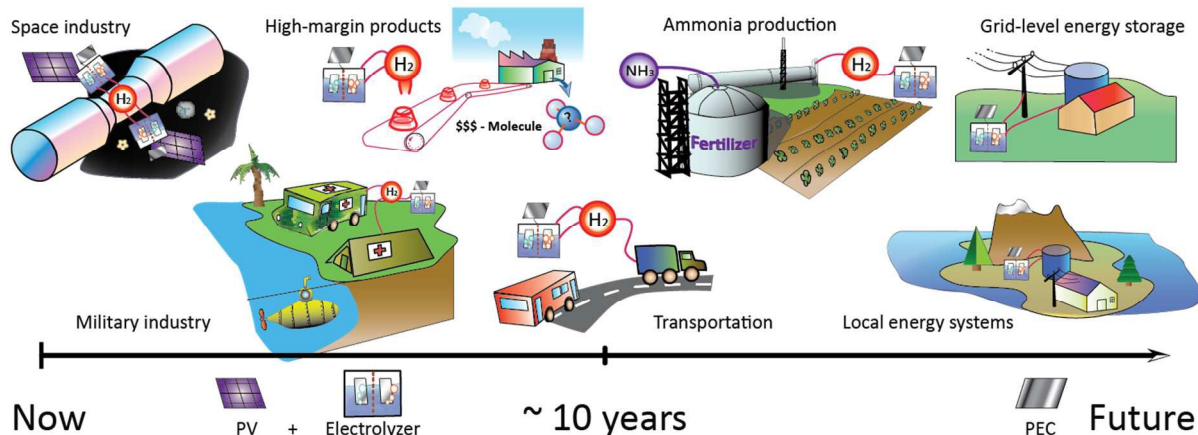
#### 20 ***3.1. Short-term implementation (10-year timeframe)***

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

### 1           3.1.1. Market opportunities

2           Although solar-hydrogen technologies use sunlight and water to generate hydrogen directly, under  
3           current market conditions they must compete with hydrogen generated from methane reforming or from  
4           grid-powered electrolysis. As long as fossil fuels remain as the predominant source of grid-level  
5           electricity, hydrogen produced by either of these non-solar routes has a substantial CO<sub>2</sub> footprint, and  
6           therefore, has clear environmental costs. Moreover, while hydrogen can be obtained inexpensively from  
7           methane reforming at large-scale plants, its use in the transportation sector could be hampered by the  
8           additional costs and added emissions from delivery to consumer locations. In addition, reformer-produced  
9           H<sub>2</sub> must have carbon species (e.g., CO, CO<sub>2</sub>, CH<sub>4</sub>), as well as trace sulfur in natural gas, removed from  
10          the reaction products at an additional cost.

11          While generating H<sub>2</sub> from a pure water feedstock does not require removal of carbonaceous reaction  
12          products, residual water must be removed in both cases. Given these product differentiators, application  
13          areas where solar-hydrogen technologies could potentially succeed in the near-term should aim at  
14          exploiting *a) environmental aspects of the production processes, b) generation of hydrogen close to the*  
15          *point of utilization, and c) purity of the produced hydrogen.* This would aid in the competitiveness of the  
16          technology in cost-inelastic markets that require high-purity hydrogen, production (decentralized) near the  
17          point of application, and with low environmental impacts that solar-based technologies can provide.  
18          Broadly speaking, plausible early-stage application fields can be divided in to seven distinct areas that are  
19          depicted in Figure 3: (i) grid-level energy storage, (ii) local or isolated permanent energy systems, (iii)  
20          transportation, (iv) as a precursor for the production of high-margin products, (v) the military industry,  
21          (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

1 high prices of electrolysis units and large energy losses incurred during both generation of  
2 hydrogen from water and recombination of hydrogen and oxygen, grid-level energy storage  
3 would be a difficult market to access and build a profitable business case.<sup>46, 47</sup> Under current  
4 market conditions, batteries are economically more viable for short-term energy storage due to  
5 their high round-trip efficiencies. Despite their own challenges, batteries would serve in the same  
6 role as hydrogen in grid-level energy storage, where, in general, most storage requirements are on  
7 the scale of days.<sup>48-50</sup> Additionally, gas peaker plants that operate on methane combustion are able  
8 to rapidly adapt to different electricity production levels, and can be used to smooth intermittent  
9 energy produced by solar or wind power installations both for short- and long-term energy  
10 storage needs.<sup>51</sup> In summary, the current alternatives (i.e. battery energy storage and natural gas  
11 fired power generation) tend to be more cost effective than solar-hydrogen technologies and  
12 therefore, it is unlikely that grid-level energy-storage solutions based on solar-hydrogen  
13 technologies will be economically viable in the short-term, although even small impacts represent  
14 large opportunities.

- 15 ii. Local or isolated permanent energy systems: Communities without grid access, including those  
16 on small islands, could benefit from localized, independent energy systems where the  
17 implementation of renewable energy sources may be advantageous. As such, solar-hydrogen  
18 technologies could play a key role in these energy solutions, especially when these communities  
19 or military bases receive high solar insolation. These implementations would also likely benefit  
20 from a local electricity microgrid that contains photovoltaics and energy-storage systems. As  
21 described above, battery economics favor short-term energy storage while electrolyzers coupled  
22 to use as a fuel cell compare favorably to batteries for larger periods of storage.<sup>52</sup> Unlike grid-  
23 level energy storage, which is backed by enormous baseload power that can adjust to seasonal  
24 variability, isolated permanent electrolysis units would serve the purpose of buffering long-term  
25 fluctuations in photovoltaic output (i.e. weeks to seasons). This time frame and scale are not

1 practical for battery energy storage due to slow self-discharge that becomes significant over long  
2 timescales and unit size because battery mass scales proportionally with energy needs.<sup>53</sup> The  
3 distribution of batteries and hydrogen storage units would depend on seasonal fluctuations in  
4 local-specific resources. For example, desert locations would require fewer electrolysis units due  
5 to small seasonal fluctuations in solar insolation, while temperate regions would require larger  
6 and/or more electrolysis units due to more seasonal variability in the solar resource.

7 iii. Transportation: In the short-term, solar-hydrogen technologies can directly impact the  
8 transportation sector. Hydrogen can be mixed into natural gas pipelines to provide some of the  
9 available energy during combustion, even in internal combustion engines.<sup>54</sup> In addition, small  
10 fleets of hydrogen fuel-cell vehicles (HFCVs) recently entered the market, and they have been  
11 allocated in local communities with hydrogen fueling capabilities. Early adopters of HFCVs are  
12 predominantly environmentally conscious and technologically knowledgeable individuals with  
13 the appropriate economical means. Currently, the vast majority of hydrogen available for fueling  
14 is produced via CO<sub>2</sub>-emitting methane reforming. This method is implemented because the cost  
15 of hydrogen production from a centralized methane reforming plant, while variable, is lower than  
16 via electrolysis methods. Also, large capital investments are required for compression, storage,  
17 and dispensing in hydrogen fueling stations which deters the additional investment required to  
18 produce renewable hydrogen locally. Nonetheless, given the low supply of hydrogen fuel, the  
19 price charged at hydrogen fueling stations must be significantly higher than the cost to produce  
20 and distribute hydrogen. A non-negligible subset of the population would be willing to pay a  
21 premium for hydrogen from clean sources, just as a subset of the population is willing to pay for a  
22 HFCV.

23 Public transportation represents a logical opportunity for implementation of HFCVs and use  
24 of solar-hydrogen technologies to generate hydrogen fuel. Already some example demonstration  
25 projects have been implemented in the US, Germany, Switzerland, Japan among others.<sup>55-59</sup> These

1 projects are easier to implement than infrastructure changes required for personal HFCVs,  
2 because vehicles for public transportation have predetermined and limited routes, and require  
3 access to fueling stations in close proximity to their service route. Depots for public  
4 transportation vehicles can even be co-located with solar-hydrogen technologies so that the solar-  
5 hydrogen light absorbers can shade the vehicles from sunlight, thus keeping the vehicles cooler  
6 when not in use and ultimately saving on air conditioning needs. Furthermore, public  
7 transportation is often government regulated, and therefore a direct and rapid pathway to  
8 implementation may exist due to pressures from clean-energy policy. For similar reasons, long-  
9 distance shipping and transportation may benefit from HFCVs and solar-hydrogen technologies.

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



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

19 v. Military industry: Military applications provide another specialized market entry point for solar-  
20 hydrogen technologies. Small-scale, easily deployable, portable, and robust microgrid energy  
21 systems are of interest to deployed troops in isolated locations. Larger installations could supply  
22 power for grid-independent bases, which are therefore less vulnerable to cybersecurity hacks or  
23 attacks on the electrical grid. Again, for remote and isolated applications, reliability, mass, and  
24 volume are often more important than the cost of the technology. In addition, remote generation  
25 of hydrogen is useful for powering fuel cells for aeromedical evacuations, which enable longer



1 flight times compared to those powered by batteries. Similar to use for respiration during space  
2 exploration, the generation of medical grade oxygen from water splitting is also of importance for  
3 military hospital installations and any people who are involved in remote projects and  
4 expeditions.

- 5 vi. Space industry: Specialized applications in the space industry might also be a viable entry point  
6 for solar-hydrogen technologies. The cost of devices to generate hydrogen and oxygen are of  
7 minor importance, while the most important factors are reliability and the mass and volume of the  
8 systems, including feedstocks. For space applications, this is because enormous amounts of fuel  
9 are required to transport payloads and therefore the mass of the fuel, and oxidant for return  
10 missions, dominate the cost of space missions. Onboard generation of fuel (by reaction of H<sub>2</sub> with  
11 CO<sub>2</sub>) and for prolonged and distant space missions (e.g. between Earth and Mars), generation of  
12 an oxidant (O<sub>2</sub>) to release the energy stored in the fuel in space and create thrust, would result in a  
13 much lighter payload and therefore, a lower mission cost. For this reason, lightweight and flexible  
14 designs for on-demand energy production and storage are extremely beneficial strategies.  
15 Moreover, recycling water and electrolyzing it for direct onboard oxygen generation for  
16 respiration is a common approach used in space applications, and driving the process with  
17 sunlight affords a reliable, low-mass option for energy generation and storage. Lightweight solar  
18 panels consisting of thin films of III-V materials deposited on Kapton supports are already used  
19 in space applications, and lightweight designs for solar-hydrogen technologies have also recently  
20 been proposed.<sup>16, 60</sup> For these applications, it is even more critical that devices operate at the  
21 highest possible efficiency, and that is why the highest-performing photovoltaics are preferred  
22 over low-cost alternatives. In addition, the solar spectrum differs between space and earth, and  
23 terrestrial size constraints for deployed devices are often relaxed for implementations in space  
24 where vast regions are unoccupied, as long as the devices can be effectively bundled for delivery.

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

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

### 16     3.1.2. *Technological implementation*

17    The technology readiness of solar-hydrogen technologies is low; the readiness of the specific subset  
18    of PEC solar-hydrogen technologies is even lower. Generally, for applications where cost is a significant  
19    market driver, the cost of the PV–Electrolysis device would be the most important factor. Because > 90%  
20    of the PV market consists of solar cells made from silicon (either mono-crystalline or multi-crystalline),<sup>64</sup>  
21    they are likely to be the most appropriate light absorbers to implement, although other commercially  
22    available light absorbers could compete with silicon based on the application. CdTe and CIGS  
23    photovoltaics represent a viable option which is likely to result in solar-hydrogen costs in a similar range  
24    to those achievable using silicon photovoltaics.<sup>65</sup> In most cases, PV modules based on III-V

1 semiconductors are currently not economically viable for terrestrial applications, but are predominant in  
2 space applications where their efficiency and thin lightweight designs offset their capital cost. There are  
3 also active research programs aimed at lowering the cost of III-V solar cells and PEC devices while  
4 maintaining their conversion efficiency, thus enabling their use in conventional flat-plate and low-  
5 concentration applications.<sup>66-68</sup>

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

10 *Liquid electrolyte alkaline electrolyzers* have been deployed commercially for more than 100 years.<sup>69</sup>  
11 <sup>70</sup> Because of this, they have already been developed and implemented on larger scales than PEM  
12 electrolyzers, but they require additional attention and safety considerations due to the use of a strongly  
13 corrosive *liquid* alkaline electrolyte and the need for tightly balanced pressures of H<sub>2</sub> and O<sub>2</sub>. Alkaline  
14 electrolyzers also tend to be less efficient than the acidic PEM electrolyzers at a given current density.  
15 This is due to the larger overpotential required for the alkaline-stable Ni-based electrocatalysts for  
16 hydrogen evolution and the larger ohmic losses caused by the lower conductivity of the electrolyte and  
17 the larger inter-electrode gap. Alkaline electrolyzers are also less amenable to changes in their operation  
18 conditions, because they usually implement porous separators between the electrodes with higher gas  
19 permeability and hence high crossover rates. Contrarily, PEM electrolyzers implement highly selective  
20 gas-separating ion-exchange membranes.

21 *PEM electrolyzers* are the state-of-the-art for most small-scale hydrogen generation applications.  
22 They implement ion-conducting polymer membranes as *solid* acid electrolytes that are selective for  
23 cations, allowing proton transport from the site of water oxidation to the site of hydrogen generation. Use  
24 of a solid electrolyte and liquid deionized water as a feedstock is much less of a safety concern than the

1 corrosive liquid electrolytes needed in alkaline electrolyzers. Yet, because PEM electrocatalysts are in  
2 direct contact with the solid electrolyte membrane, which is acidic and corrosive, the only efficient  
3 catalyst materials that remain bound and stable are those based on noble metals (e.g. Pt and IrO<sub>x</sub> are the  
4 state-of-the-art). While the terrestrial scarcity of noble metals could preclude the implementation of PEM  
5 electrolyzers on large TW scales, their implementation at early stages on GW scales is not expected to be  
6 limited by the availability of specific raw materials. In comparison to alkaline electrolyzers, PEM  
7 electrolyzers are in many ways more amenable to PV–Electrolysis devices. The use of state-of-the-art  
8 electrocatalysts in PEM electrolyzers allow for more efficient operation. Moreover, PEM electrolyzers  
9 operate more effectively under conditions of fluctuating power input, particularly when intermittent solar  
10 insolation drives electrolysis consistently outputting a pressurized hydrogen product (up to 30 bar).<sup>71</sup>  
11 While PEM electrolyzers do have significant technical advantages over alkaline electrolyzers, they still  
12 tend to be more costly (currently costing ~1.2 USD/W)<sup>72</sup> partly because of lower production volumes and  
13 limited system sizes, with the largest planned systems being on the order of several MW.<sup>73, 74</sup> As their  
14 production volumes increase, it is likely that their costs will continue to decrease due to economies of  
15 scale and technological advances.

### 16 3.1.3. *Science and technology opportunities*

17 There are significant challenges for the implementation of PV–Electrolysis devices, mainly arising  
18 from complications caused by the PV-driven intermittent use of electrolyzers. These challenges can at  
19 least in part be mitigated using today's electrolyzer technologies if electronic buffering mechanisms are in  
20 place to maintain operation above a threshold and therefore avoid large amounts of gas crossover and  
21 formation of explosive gas mixtures.<sup>12</sup> Buffering approaches include incorporation of an array of batteries  
22 or capacitors, or utilization of grid electricity, where available. An alternative to buffering is removal of  
23 the hydrogen and oxygen reaction products from the reaction chambers during periods of slow operation,  
24 for example, by flushing the system with water, or to implement other engineering approaches to avoid  
25 the formation of explosive gas mixtures.<sup>75</sup> Additionally, electrical circuits of photovoltaic arrays and AC-

1 driven peripheral components (e.g. pumps, fans and control systems) could be re-designed to directly  
2 drive water electrolyzers without the need for power electronics (i.e. maximum power trackers or DC–DC  
3 converters).<sup>16, 76</sup> If electricity buffers, product removal, and power electronics could be avoided, a  
4 scenario that seems reasonable within the next decade, solar-hydrogen technologies will be simplified,  
5 therefore ensuring smooth operation and ultimately driving down their cost.

### 6 ***3.2. Long-term deployment in energy markets***

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

#### 12 ***3.2.1. Societal, economic, and policy changes and drivers***

13 Environmental challenges associated with burning large quantities of fossil fuels to generate energy  
14 have triggered a strong interest in implementation of renewable-energy systems.<sup>77, 78</sup> As a testimony to  
15 this, the number of energy-conversion installations driven by sunlight or wind has experienced  
16 exponential growth over the past decade. In the case of solar energy, this growth is directly apparent from  
17 the enormous increase in the production capacity of photovoltaics, which has resulted in significant  
18 reductions in their cost.<sup>79</sup> On the production side, government incentives facilitated this market increase  
19 by providing strong investment that led to the rapid increase in production. An increase in demand was  
20 propelled by policy drivers that aimed to curtail use of non-renewable energy sources. For example,  
21 China, India, and even smaller size countries all have policies to promote renewable energy technologies.  
22 Further policy drivers such as controls on CO<sub>2</sub> emission as well as incentives for clean-energy  
23 technologies will help increase penetration of renewables into the energy markets and raise awareness for  
24 the need to realize accessible, reliable and affordable supply of energy. The Paris Climate Agreement

1 helped set the stage for this development.<sup>80</sup> The Dutch government, for example, targets 40% renewable  
2 energy by 2030 and a > 80% reduction in CO<sub>2</sub> emissions by 2050.<sup>81</sup> Societal aspects can also trigger the  
3 large-scale adoption of clean energy technologies. Changes to the environment, violent and more frequent  
4 natural disasters, and local pollution can favor the adoption of clean technologies on the basis of world  
5 energy and global transportation scenarios created by the World Energy Council.<sup>82</sup> Additionally,  
6 investment in education and in accessible and accurate information regarding environmental effects of  
7 various energy sources can help shape society's perceptions of the energy markets. Ultimately, these  
8 changes in public perception can decisively lead to the enactment of long-lasting clean energy policies.<sup>83</sup>

9 <sup>84</sup>

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

1 for PV phase out, soft costs must continue to decrease to keep PV competitive with fossil sources of  
2 electricity.

### 3 *3.2.2. Science and technology opportunities*

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

### 12 *3.3. Pathways for PV–Electrolysis*

13 To a large extent, PV–Electrolysis advances can be commercialized by independently optimizing  
14 each of the constituent components,<sup>10</sup> i.e. the PV module, the cell stack materials, and the electrolyzer  
15 design. However, the ultimate goal of a practical system coupling the two components must be kept in  
16 mind while performing this independent optimization. Although at a first glance this statement might  
17 seem obvious and non-constraining, there is a significant number of peripheral components (mainly  
18 power electronics) that are incorporated into PV installations and electrolysis units to couple their  
19 operation with the electrical grid. These components account for a non-trivial fraction of the overall  
20 capital costs of the equipment, and furthermore poor integration will result in efficiency decreases on the  
21 order of at least 10%, with ~5% losses on each of the two AC/DC conversion steps, and even larger losses  
22 at low power output. While under some circumstances PV–Electrolysis will operate in conjunction with  
23 the grid to maximize the utilization of the electrolyzer unit, lean alternatives with fewer peripheral  
24 components and a more integrated operation will likely be preferred as the technology progresses and

1 electrolyzers become more capable of operating with fluctuating loads. This integrated PV–Electrolysis  
2 approach would not require that power electronics be incorporated in current electrolyzers systems, as PV  
3 arrays may be designed to directly power electrolyzers units with the appropriate DC characteristics. The  
4 reduced balance-of-system costs of integrated PV–Electrolysis devices and the higher efficiencies  
5 achievable due to short transmission distances could favor their implementation in the long term,  
6 assuming that no new durability challenges emerge during intermittent or fluctuating operation.<sup>5, 7, 8</sup> In the  
7 short term the value proposition of on-site or wastewater-derived solar-hydrogen generation can be  
8 realized in niche markets. Those gains would need to compensate for the economic losses from the low  
9 utilization of the electrolyzer units if powered exclusively with solar energy.

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



1 impact on solar-hydrogen devices. Lastly, inexpensive optical concentration or light management  
2 schemes and heat and mass transfer optimizations that enhance efficiency and materials utilization of PV–  
3 Electrolysis over PV or electrolyzers alone, could improve the viability of PV–Electrolysis.

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

22 In addition to economies of scale, cost reductions in electrolyzers may arise from lowering the capital  
23 cost requirements of the system (currently at ~1/3 of the total cost), or by reducing costs associated with  
24 the electricity feedstock required for their operation. Solar-to-hydrogen efficiency improvements will  
25 directly affect electricity feedstock expenses, as less electricity will be needed for a given rate of solar-

1 hydrogen production. Important sources of efficiency improvements in current PEM electrolyzers may  
2 come from reduction of ionic resistances in membranes, improvement in electrocatalyst activity, and  
3 mitigation of mass transport limitations in catalyst and porous transport layers.<sup>98</sup> If the efficiency  
4 improvements lead to larger operating current densities, electrolyzer units could be designed with smaller  
5 footprints for a given production level, thus reducing their capital costs. Additionally, the feedstock costs  
6 could be reduced if the electrical grid is circumvented in a direct PV–Electrolysis configuration. In this  
7 configuration, the costs associated with electricity transmission and distribution through the grid would be  
8 eliminated. Opportunities exist for defining application-specific guidelines for membranes used for direct  
9 PV–Electrolysis. Research and development of membranes for direct PV–Electrolysis configurations  
10 include identifying those with lower gas permeability and optimal ion-transport and mechanical  
11 properties, information on the molecular and morphological characteristics of membranes during mass  
12 transport processes, and ion-conducting membranes that can operate under intermittent electrolysis  
13 conditions. These fundamental science developments can lead to advances in the long term that ultimately  
14 may brighten the economic prospects of PV–Electrolysis technologies.

### 15 ***3.4. Pathways for PEC***

16 Even if all the advancements in component performance and cost of coupled PV–Electrolysis systems  
17 are achieved, the nature of their design will require significant cost reduction of the auxiliary components  
18 in order for them to be cost-competitive with other hydrogen production pathways. This is similar to the  
19 case of current PV plants where the cost of the PV does not dominate system cost. Such cost reductions  
20 might not even be possible given the inherent system architecture of coupled PV–Electrolysis systems.  
21 For this reason, PEC systems could provide an opportunity for this necessary cost reduction, given that  
22 their design can be completely different than PV–Electrolysis systems and therefore could lead to  
23 disruptive and significant cost reduction. Opening up the design space to a broader set of architectures can  
24 only have a positive impact on the potential to identify a cost-optimal option. One example is systems  
25 based on photocatalyst particles.<sup>4, 99, 100</sup> However, to date, large-scale deployment of PEC-based solar-

1 hydrogen technologies appears to be disadvantaged with respect to PV–Electrolysis approaches. PEC  
2 devices are significantly less developed, and their efficiencies are generally worse than for coupled PV–  
3 Electrolysis devices.<sup>101</sup> Moreover, they suffer from poor stability due to the requirement of light  
4 absorbing materials to be in contact or close proximity with often caustic electrolytes. Despite great  
5 efforts to develop protection strategies, this challenge remains largely unsolved and precludes deployment  
6 of PEC technologies.<sup>101</sup> One important development challenge is the scale: for PEC devices to reach the  
7 same rate of H<sub>2</sub> output as PV–Electrolysis technologies the projected electrochemically active H<sub>2</sub>  
8 production area would have to be at least ~50 times larger.<sup>5, 14</sup> These large electrochemical areas would  
9 lead to significant challenges in product handling due to the low current density at the photoelectrode  
10 surface, but could result in higher operating efficiencies and less stringent catalytic requirements.  
11 Enabling large-scale efficient PEC devices requires advances in materials durability and the ability to  
12 control at the atomic-level reproducible material engineering across macroscopic areas.<sup>102</sup> From a  
13 topological viewpoint, PEC devices are a subset of PV–Electrolysis devices where the electrocatalytic  
14 components are collocated with the light absorbers, and in fact can then be the same material. However,  
15 viable implementation pathways for PEC architectures will require the discovery of a PEC system that  
16 can perform solar water-splitting at a cost per kg of H<sub>2</sub> that is equal to or lower than available PV–  
17 Electrolysis systems, and as a consequence, PEC devices cannot be based on components that could also  
18 be used to fabricate a PV–Electrolysis device with equivalent or higher economic benefits. If this goal is  
19 not achieved, long-term solar-hydrogen technologies will tend toward PV–Electrolysis architectures. In a  
20 PV–Electrolysis configuration, each of the device components (e.g. light-absorber and water-splitting  
21 units) can be independently engineered so that the overall device is optimized, often with the aid of power  
22 electronics. Furthermore, there are significant fundamental advantages of decoupling the light-absorption  
23 and water-splitting functions in solar-hydrogen devices, which arise from increased flexibility in device  
24 design, optimization, and operation. For example, in a PEC configuration, the light absorbers will require  
25 innovative electrode designs to minimize shading due to optical absorption and scattering by the catalysts

1 and to facilitate gas evolution and mitigate occlusion of electrocatalytic sites, for example, due to evolved  
2 bubbles that can block mass transfer and light incidence.<sup>103</sup>

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

#### 21 **4. Conclusions and perspectives**

22 This article presented a broad perspective on pathways for the implementation of solar-hydrogen  
23 technologies. Several niche market opportunities were identified for solar hydrogen implementation on  
24 the short-term ( $\leq 10$  years). In this time frame, it is anticipated that PV–Electrolysis systems will be the

1 only approach that could be implemented for such applications and still be economical. In the long term,  
2 solar-hydrogen technologies could be deployed more broadly in the energy markets. For that to happen,  
3 hydrogen produced via solar routes might need to be competitive against other energy carriers, such as  
4 fossil fuels. This is a daunting challenge, as the cost of energy from fossil sources has been historically  
5 low, even though extremely volatile, and it suggests that hydrogen production costs today would need to  
6 sum to less than \$2/kg hydrogen.<sup>118</sup> Despite the scale of the challenge, solar-hydrogen technologies  
7 provide a promising path to clean alternative fuels, and if externalities from fossil fuel utilization were  
8 internalized, the prospects for hydrogen fuel implementation would be greatly enhanced. Implementing  
9 PV–Electrolysis units manufactured using currently available commercial devices would lead to costs of  
10 hydrogen that exceed this value by at least a factor of three.<sup>7</sup> Therefore, achieving that cost target with  
11 PV–electrolysis devices would require significant technology advances, cost reductions, and possibly also  
12 political/policy measures, such as a CO<sub>2</sub> tax. Currently, one high-impact research focus is to advance  
13 electrolysis that is directly driven by PV installations. Under this mode of operation, electrolyzers will  
14 need to accommodate the natural intermittency of solar irradiation, in a stable way over lifetimes  
15 comparable to current PV technologies. This approach would result in significant capital cost reductions  
16 due to elimination of power electronics required in existing systems, and would increase overall  
17 efficiency; at the expense of a reduced capacity factor of the electrolyzer. Important long-term goals  
18 include the ability to operate PV–Electrolysis devices using inexpensive and efficient electrocatalysts.  
19 This will require the development of new catalytic materials that are stable under acidic electrolytes or  
20 anion-exchange membranes with significantly improved stability. PEC routes present even more  
21 significant challenges but have a significantly more disruptive potential. For a PEC system to be  
22 implemented, it would have to perform at least equally as well as available PV–Electrolysis alternative  
23 systems on economic grounds. Additionally, if the components used for the fabrication of such a PEC  
24 device could be utilized in a PV–Electrolysis arrangement, the integrated PEC architecture would need to  
25 be economically preferable to an alternative PV–Electrolysis arrangement and also show advantages in  
26 terms of sustainability even while it is less flexible in design, optimization, and operation. Understanding

1 fundamental science aspects and developing reactor engineering design guidelines can help to achieve  
2 these goals.

3 Even if the scientific community achieves all of the advances in PV–Electrolysis or PEC devices  
4 outlined in this report, it is uncertain whether solar-hydrogen technologies will be competitive in large-  
5 scale energy markets in the long term. This will depend on a variety of factors that include, but are not  
6 limited to, system efficiencies, materials cost, balance-of-system costs, lifetime, externalities, social  
7 acceptance, and price of energy or hydrogen from alternative sources. The possible impact of some of  
8 these factors have been described in more detail in recent DOE reports.<sup>119</sup> Economic policy mechanisms  
9 to account for the environmental effects of CO<sub>2</sub> emissions can help facilitate this prospect. As a  
10 worldwide community, we should emphasize the development of CO<sub>2</sub>-free, sustainable energy  
11 technologies at comparable cost than today's CO<sub>2</sub>-heavy alternatives. While scientific curiosity should  
12 never be hindered by economic considerations, cost can and should be considered at a stage when more  
13 applied research programs or policy decisions need to be designed. There has been tremendous progress  
14 in the fundamental understanding of solar-hydrogen systems in the past decades and the interdisciplinary  
15 knowledge accumulated can be implemented in new electrochemical processes, wastewater treatment, or  
16 applications for which the purity or sustainability of the hydrogen is more important than the price, with  
17 greater prospects for profitability, sustainability, and societal impact. The creativity of the scientific  
18 community and its ability to pivot into new promising application areas will have a decisive effect on the  
19 future societal and environmental impacts of solar-hydrogen technologies.

20

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