Artificial Solar-Fuel Generators

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We have experienced significant growth and interest in increasing the share of renewable energy sources into the world energy landscape.[1] These technologies span the generation or capture of energy from carbon neutral sources, storage of the energy so that it can be used when and where is needed, and utilization of energy supplies in more efficient ways. Within the set of alternatives available for power generation from renewable sources, solar energy conversion is ubiquitous in the discussion, given the vast amount of energy that we have access to. Despite the scale of this energy resource, its fractional portion of the global energy portfolio is relatively small (0.06 % of the global energy generation).[2, 3] While economic factors account for a significant part of the barrier towards implementation, significant technological challenges stem from the inherently intermittent nature of the solar generation process. One alternative to mitigate the intermittency of solar energy generation is the incorporation of energy storage capacity into grid, so that fluctuations in energy generations can be buffered and not affect the operation of the electricity distribution channels. The large scale implementation of energy storage also faces both technological and economic hurdles requiring significant research and development. Alternatively, one could take inspiration from nature in which energy is stored in the form of chemical bonds. In the case of artificial photosynthesis, this means the generation of fuels directly from solar energy.[1, 4-8] Integrated solar-fuel generators are photoelectrochemical (PEC) cells that can capture solar energy and catalytically convert low energy reactants into energy dense fuels. Of particular interest, water splitting systems take water as a feed and produce hydrogen fuel and oxygen as byproduct. A general representation of these systems is presented in **Figure 1**. Practical systems would need to take water and solar energy as inputs, and produce in a safe and scalable manner output streams of hydrogen and oxygen. In this way pure fuel streams can be collected and used in electrochemical energy conversion devices (i.e. fuel cells), or in chemical processes to synthesize or enhance the energy content of liquid fuels (e.g. Fisher-Tropsch process). The concept of solar fuel generators can be further extended to the electrochemical reduction of CO_2 that can generate carbon containing fuels, but represents a closed cycle from the carbon perspective making these new fuels truly carbon neutral. Solar driven CO_2 reduction poses more significant technical challenges, as the number of electron transfer steps in the reactions is increased, the concentration of CO_2 in electrolytes is generally low, and the diversity of products generated imposes more stringent requirements for separation.

As shown in Figure 1, the solar fuels generation process begins with the absorption of light to form charges which are then used to drive oxidation and reduction reactions. This could be done in separate units, for example a photovoltaic cell to generate electricity which is then used to power an electrolyzer which incorporates the catalysts, but could also be done in a fully integrated device. Comparisons between these two scenarios are largely dependent on gains that can be obtained in the integrated device in terms of the economics and flexibility of deployment. All of these variables largely depend on research and development currently underway in a variety of academic, government, and industrial laboratories.

In this article, we will focus largely on the aspects of an integrated system that are the focus of current exploration and development. A fully integrated solar hydrogen generator, as shown in Figure 1(B) would consist of integrally connected photovoltaic and catalytic units. Ideally, the oxidation and reduction sites would be physically separated so that the product (H_2 in the case of water splitting) is generated in a space different than the byproduct (O_2 in this case). Further, the size scale of the photovoltaic unit is generally set by the solar absorption depth of the material and is on the order of microns to millimeters. In many ways, it makes sense to have an array of photovoltaic units held together by a mechanically robust membrane. This membrane could also serve the role of keeping the product gases physically separated and shuttling the ions from one catalyst site to the other. Under acidic conditions, water will be dissociated into O_2 and

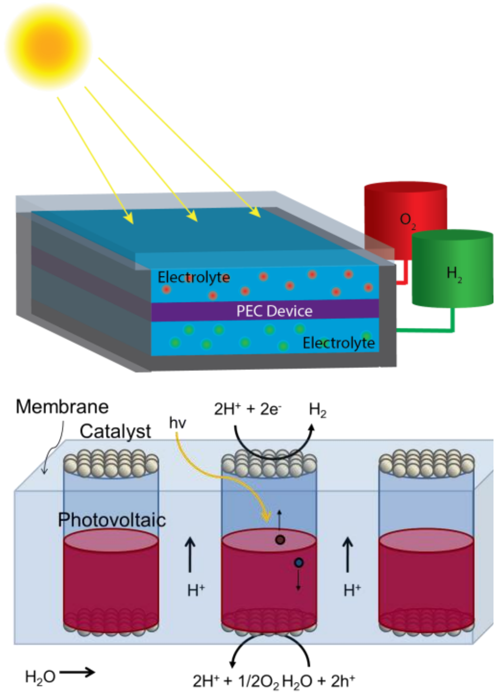

Figure Error! No text of specified style in document. General representation of integrated solar hydrogen generation system(A) and a protons in the oxidation side of the membrane. The protons generated will then be transported through the membrane to the reduction side, where H_2 will be evolved. In this way both oxidation and reduction products will be generated in separated regions of the membrane, preventing the need for further separation. As described in the picture below, PEC units need to be uniaxially aligned and oriented in a way that oxidation and reduction sites are in opposite sides of the membranes. Achieving this configuration can be simple for macroscopic units, but in the case of micrometer to nanometer scale systems significant advances are required in terms of both membrane and PEC unit self-assembly. The subsections below will touch upon some of the advances in achieving practical solar-fuel generators, implications for membranes used in these systems as well as overall system design considerations.

Integrated solar hydrogen generation systems

Since the first demonstration of solar-driven water splitting by Fujishima and Honda in the 1970's,[9] the prospect of using PEC cells for solar fuel generation has motivated the quest for components and integrated systems that can continuously and robustly produce hydrogen fuels directly from sunlight. In the past 40 years, many studies have attempted to tackle parts of the problem, and fuel generating systems have been built reaching solar hydrogen generation efficiencies of up to 18%.[10] Although, solar hydrogen generation units have been demonstrated, they fall short in satisfying the stability and cost-effectiveness requirements. Some high efficiency systems rely on III-V multijunction photovoltaic components that have prohibitively high costs and have significant photocorrosion challenges at the interface between the semiconductor and the electrolyte.[10-12] Other systems based on silicon light absorbing components; including earth abundant catalysts face significant stability problems when operated under basic or acidic electrolytes. Recently, Nocera's group at MIT demonstrated integrated systems that incorporate earth abundant components that can stably operate under buffered electrolytes at moderate pH.[13] This promising demonstration can open avenues for the implementation of cost-effective solar-hydrogen generators, but significant challenges for the management of ion and mass transport remain unsolved. These challenges arise from the need to separate the gaseous products that are generated while providing conductive pathways for ion conduction at steady state.[14, 15] When systems are operated at moderate pH regimes, the low concentration of proton or hydroxide conduction in solution results into a high solution resistance for these ions, and most of the ionic current is carried by supporting ions present in solution (i.e. dissociated ions from buffer molecules). Under these circumstances, as the conducting ions are not part of the electrode reactions, concentration gradients will evolve and the overall system will not be able to operate continuously. Lastly, achieving efficient solar hydrogen generation would represent a large step to increase the share of renewable fuel sources but implementation would be challenging as our current infrastructure is based on liquid carbon based fuels. An alternative to solar water splitting lies in the direct reduction of CO_2 for the generation of carbon containing fuels that can be more easily implemented.[6, 16, 17] Significant research is being done in this field, but the challenges are greater as requirements for catalyst selectivity, CO_2 absorption and product separation are more stringent.

Membrane materials for Artificial Photosynthesis

Membranes in solar-hydrogen generators serve two basic functions: provide pathways for ion-conduction and maintain gaseous products separated (as shown in Figure 2). Ion-conducting membranes have been investigated for several decades, and are important components not only in artificial photosynthesis applications but also in a variety of energy conversion devices.[2, 33] The fundamental similarities in membrane requirements between solar fuels devices, hydrogen fuel-cells, and electrolyzers suggest an existing set of candidate materials.

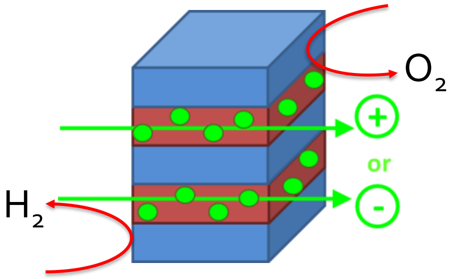

Figure 2: Diagram of membrane material used for solar water splitting

In the case of artificial photosynthesis applications, the operating current density is dictated by the solar absorption rate and is relatively low when compared to the requirements for other similar devices, but are very sensitive to crossover due to the relatively small quantity of product. Moreover, the presence of a large number of interfaces between the polymer and inorganic PEC components can severely affect the structure and transport properties of common nanostructured fuel cell membrane materials. Perflourosulfonic acid ionomer (PSFA) membranes such as Nafion® are the most prominent alternatives for proton conduction, given their high ionic conductivity and remarkable chemical and structural stability. In the case of artificial photosynthesis membranes, high levels of conductivity are not required and a stronger emphasis should be given to a balance between the ionic and gas transport properties of materials. The development of ion-conducting block copolymers (BCPs) represent a promising route to decouple these two properties, wherein different blocks can be designed to provide complimentary structural and gas barrier properties as well as ionic conductivity. Furthermore, properties of these systems can be easily tuned and optimized by altering the molecular weight and volume fraction of each phase.[34] BCP membranes based on blends with ionic liquids (ILs) as well as polymerized ILs have been considered because of their good ionic conductivity and tunability.[35-39][40][40-43] Recent work has demonstrated the potential of PIL BCP materials for tuning transport properties in membranes used for solar-fuel applications.[44, 45]

Balancing Transport Processes in Solar Hydrogen Generators

In practical systems, all the components need also to operate stably and perform efficiently under the same conditions (i.e. temperature, electrolyte). Additionally, the photovoltage generated by the light-absorbing units need to be sufficient to support the water splitting reaction (1.23 V), the catalyst overpotential requirement, the ohmic drop associated with transporting both electrons and ions across the device, and any additional overpotential introduced in the system arising from chemical potential differences (i.e. concentration overpotential). Furthermore, all the transport processes in the system need to occur in parallel so that the electronic current matches the ionic current across reaction sites. Several electrochemical modeling studies have approached this topic directly and provide some guidance on the optimal arrangements and dimensions of each of the components within an integrated solar hydrogen generator.[14, 46-48] In general, a device will operate at the point at which the output from the photovoltaic component matches the electrochemical load from the catalytic and ion transport components of the device. By controlling the dimensions and component architecture, it is possible to optimize the performance of the device so that it operates near the maximum possible efficiency. Furthermore, optimizing the topology of the components in the device can help overcome some of the component stability limitations, achieve operations under a wide range of conditions, and increase the efficiency of devices overall. As new components become available, significant ongoing work is necessary in this design area is necessary to understand what shape and form will lead to overall optimization of cost, efficiency, and stability.

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