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Challenges and Opportunities for Ion-Exchange Membranes in Solar Fuels Devices

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ABSTRACT

Separators or membranes are required in all electrochemical devices to prevent product crossover while maintaining a large ionic conductance. In solar fuels devices, and electrolyzers and fuel cells, separators must also support pressure differentials and serve as robust barriers to reactive chemical intermediates. Many different ion-exchange materials exist for this purpose but no single material has been identified as a clear front-runner for solar fuels applications. Described herein are state-of-the-art ion-exchange membranes, including cation conducting, anion conducting, mixed conducting, proton selective, and electron conducting, which may be useful in solar fuels devices. In addition, porous separators that afford mixing of electrolyte are also discussed in the context of near-neutral pH electrolytes. Analogous to fuel cells, solar fuels devices that are fed with water vapor are described, and possible membrane requirements for integrated tandem solar fuels devices are presented and discussed. Interfaces between the membrane and other components of solar fuels devices are briefly described as a new field with many opportunities for additional research.

KEYWORDS: Solar Fuels, Ion-Exchange Membranes, Bipolar Membranes, Water Splitting, Nafion.

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1. INTRODUCTION

Solar fuels devices store sunlight energy in chemical bonds by driving a reduction and an oxidation reaction (e.g., $4e^- + 4H_3O^+ \rightarrow 2H_2 + 4H_2O$ and $6H_2O \rightarrow O_2 + 4H_3O^+ +$ $4e^-$, respectively) that push the system away from thermodynamic equilibrium. In the absence of illumination, e.g., at night, performing these two fuel-forming redox reactions is thermodynamically unfavorable, and so the reverse reactions occur to re-equilibrate the system as mandated by the second law of thermodynamics. This, however, results

*Author to whom correspondence should be addressed. Email: ardo@uci.edu Received: 30 April 2014 Accepted: 6 June 2014 in no net storage of solar energy. To attenuate this equilibration, in practical solar fuels devices a separator is incorporated with the purpose of slowing the intermixing of the reaction products and subsequent reactions that release the stored electrochemical potential as heat (Fig. 1). This review focuses on possible separators and their properties that are specific to solar fuels devices.

Ion-exchange membranes are a specific type of separator that is used industrially for the purpose of preventing equilibration of reaction species produced by electrolysis and other electrochemical reactions, while allowing conduction of ions. Nafion[®] is the state-of-the-art ion-exchange membrane used in most electrochemical devices. Historically, it replaced the toxic Na-Hg amalgam and asbestos diaphragm separators formerly used in the chlor-alkali process (i.e., the production of Cl₂ and NaOH from brine).^{1,2} Nafion is a fluorinated copolymer membrane that was conceived by Dr. Frank Gresham of DuPont[™] in the early 1960s.² It consists of a polytetrafluoroethylene (PTFE) backbone decorated with perfluorinated vinyl ethers and terminal sulfonate ionic functional groups, and was first synthesized by Dr. Walther Grot of DuPont in the mid-1960s.² The benefits of Nafion are its extreme chemical, thermal, and mechanical robustness, and its ability to maintain large pressure differentials, while also affording a large and selective room-temperature cationic conductivity of $\sim 100 \text{ mS cm}^{-1}$, which increases slightly at elevated



Fig. 1. Schemes of hypothetical solar water splitting devices consisting of (a) an integrated form factor with a composite material that contains the light absorber(s), electrocatalysts, and a cation-exchange membrane, and (b) an electrode-based form factor with a separate (photo)anode (top), (photo)cathode (bottom), and a cation-exchange membrane (middle). The membrane greatly attenuates crossover of O_2 and H_2 between the top and the bottom compartments, and their subsequent exothermic reaction to generate water and waste the stored potential as heat.

temperatures.^{2.3} When hydrated, the sulfonate-lined waterfilled channels exclude negatively charged salt species due in part to Donnan exclusion,⁴ but allow positively charged species to pass.⁵ Even cations as large as [Ru^{II}(bpy)₃]²⁺, methyl viologen, and ferrocene derivatives can enter and conduct through Nafion.⁶⁻⁹

A stable separator such as Nafion is desired for aqueous electrochemical reactions that can generate highly reactive side products, such as hydroxyl radicals from the partial oxidation of water to hydrogen peroxide.¹⁰ As most solar fuels devices propose to drive overall water splitting, or at least oxygen evolution through water oxidation, it is likely that hydroxyl radicals will form during operation of solar fuels devices, necessitating the use of Nafion, or a membrane with similar chemical resistance. Additionally, when the fuel is a gas at practical temperatures and pressures, (photo)electrochemical pressurization may be advantageous, again supporting the use of Nafion, which can withstand large pressure differentials.¹¹

With the conjecture that Nafion is the state-of-the-art membrane, is appropriate for solar fuels devices, and has been proven as an industrial technology in various electrochemical devices for nearly half a century, why should there be interest in a review paper on the subject of ionexchange membranes for solar fuels devices? The answer is that there are several additional membrane properties that may be desired in a solar fuels device beyond simply a stable ion-exchange membrane, including compatibility with non-platinum-group metal electrocatalysts, and for tandem devices, the ability to electrically conduct and optically transmit nearly all above-band-gap sunlight. In addition, the design and evaluation of a completely engineered solar fuels reactor has yet to be performed and may raise unforeseen additional requirements and challenges for the device, electrolyte, and/or materials. For example, using numerical device physics modeling and simulations it was shown that for a solar water splitting device operating at 20 mA/cm² at room temperature, which equates to a \sim 25% efficient device, and with a light-absorber shortest dimension of ~ 1 cm, a ~ 50 mV average ohmic potential



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drop (V_{drop}) existed when immersed in a 1 M aqueous salt solution (Fig. 2).12 For this membrane-integrated device, less than 1% of the distance that protons conducted was through the Nafion membrane, the rest being through the liquid electrolyte, and thus the conductivity of Nafion is completely sufficient for application in solar fuels devices immersed in strong liquid electrolytes. A recent technoeconomic analysis commissioned by the United States Department of Energy compared various fixed-electrode panel-based arrays and determined that in order to be cost competitive with current fossil fuel technologies, a tandem solar water splitting device with a near-ideal energyconversion efficiency of ~25% would be required.^{13,14} Thus, even a 50 mV membrane V_{drop} is problematic,¹⁵ and consequently a sub-centimeter-sized light absorber is most likely required for membrane-integrated devices. This puts additional constraints on the membrane, such as providing physical support for the small light absorbers.

Optimal design criteria for solar fuels devices can be determined with a rather straightforward analysis. For most electrochemical devices the potential drop/loss in the electrolyte can be approximated using Ohm's law,

$$V_{\rm drop} = I_{\rm device} \times R_{\rm electrolyte} \tag{1}$$

where V_{drop} is the potential drop (V), I_{device} is the steadystate current in the device (A), and $R_{electrolyte}$ is the resistance of the electrolyte (Ω). Thus, V_{drop} increases linearly as the resistance of the conductive components increases, and/or as the operating current increases, such as with increasing optical solar concentration. Thus, for all cases described herein, if the device operates under optical concentration, then the resistance must be decreased in order to minimize V_{drop} , which will naturally occur to some extent due to the resulting increase in temperature. The resistance is a product of the inverse of the conductivity of a phase, the distance over which the current flows, and the inverse of the area through which the current flows,

$$R = \sigma^{-1} \times d \times a^{-1} \tag{2}$$



Fig. 2. Scheme of a hypothetical solar water splitting device consisting of a regular square pattern of light absorbers containing electrocatalysts (black) alternating with cation-exchange membranes (light grey), and with an intervening material that can conduct both protons (purple) and electrons (red).

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where σ is conductivity (S/cm), *d* is distance (cm), and *a* is area (cm²). Combined with Eq. (1), this dictates that V_{drop} increases when the conductivity of the materials and/or electrolyte decrease, when the minimum distance over which current flows increases, and/or when the cross-sectional area confining the flow of current decreases, respectively. Said another way, V_{drop} decreases when the volume of the material and/or electrolyte increase while the minimum distance current must flow remains unchanged.¹² Thus, in order to minimize V_{drop} , and maximize energy-conversion efficiency, in practice the conductivity and the volume of the materials and/or electrolyte should be large, while the distance over which current must flow should be small.

Prior to 2011, no studies had reported specific properties of the ion-exchange membrane for use in solar fuels assemblies,¹⁶ even though such membranes had been described decades prior,¹⁷ Because the functions of solar fuels devices are the sum of those from an electrolyzer and a photovoltaic, it seemed reasonable that the knowledge garnered from the photovoltaic and polymerelectrolytemembrane electrolyzer (and fuel cell) communities could be leveraged for solar fuels devices. However, photovoltaics and electrolyzers operate at drastically different current densities, and were engineered to perform best under specific conditions. (Photovoltaics under unconcentrated solar illumination operate at 10-45 mA/cm².¹⁸ while electrolyzers operate at ~ 1 A/cm²).¹⁹ Thus, for an efficient solar fuels device that has properties of a photovoltaic and an electrolyzer, either the active area of the photovoltaic materials must be one to two orders of magnitude larger than that of the electrolyzer materials or the electrolyzer materials (i.e., electrocatalysts and ion-exchange membrane) must operate at a drastically smaller current density than they were intended to operate. Alternatively, the photovoltaic materials could operate under 10-100 times optical concentration but this then requires that the resistance of the materials decreases by this same factor. At these current densities, weaknesses in the membrane will become more apparent because small shunt currents will no longer be masked by large fuel-forming reaction currents.

Commercial polymer-electrolyte-membrane electrolyzers and fuel cells both incorporate Nafion as their ion-exchange membrane.^{19, 20} However, both electrolyzers and fuel cells operate at much larger current densities ($\sim 1 \text{ A/cm}^2$)^{19, 20} than solar fuels devices, which are projected to operate at 10--20 mA/cm².²¹ The membrane placement, electrode geometry, and electrode materials in electrolyzers and fuel cells have been engineered for these specific rates. This is an important point because the rate of product crossover, i.e., H₂ and O₂, does not often scale with the amount of product present; thus, although an electrolyzer or fuel cell with 1% fuel loss due to product crossover (i.e., 1 A/cm² operational current density and 10 mA/cm² rate of loss) is not a problem, for a solar fuels device generating products at 10 mA/cm², a 10 mA/cm² product crossover rate will result in no net product formation and an overall zero percent efficiency.

Because acid-stable membranes were already presented above, i.e., Nafion, the remainder of the review is organized to present classes of solar fuels devices based on the membrane properties as follows: liquid bulk electrolyte at an alkaline pH, liquid bulk electrolyte with a pH gradient, liquid bulk electrolyte with a buffered non-extreme pH, highly porous and highly selective separators, polymer electrolyte with vapor-phase fuel feeds, dual-conducting membranes, and membrane–light-absorber contacts. Each subsection describes state-of-the-art materials in each class, new and interesting applications, and opportunities for additional research and development. The purpose is to bring to the attention of the readers the challenges and opportunities for ion-exchange membranes in solar fuels devices.

2. LIQUID BULK ELECTROLYTE AT AN ALKALINE pH

Electrolyzers and fuel cells containing anion-exchange membranes would be of great commercial and practical benefit. Then, the precious-metal electrocatalysts used with acid-stable cation-exchange membranes like Nafion (e.g., those that contain the platinum group metals Pt, Ru, Ir)¹⁹ could be replaced by inexpensive and abundant first-row transition-metal electrocatalysts which are stable when in contact with alkaline electrolytes.^{22,23} Historically, quaternary-ammonium-based anion-exchange membranes have been used for this purpose, but most are unstable due to Hofmann elimination through beta-proton abstraction and other side reactions, such as nucleophilic substitutions.^{24,25} In addition, polybenzimidazole doped with concentrated aqueous KOH has been used as an anion-exchange membrane for higher temperature operation, and exhibited an ionic conductivity similar to that of Nafion.^{24, 25} Cations based on phosphorus, sulfur, and transition metals have recently been utilized as fixed-charge groups in anion-exchange membranes, and include quaternary phosphonium (PR⁺₄),²⁶ quaternary phosphazenium $(P(NR)_4^+)$,^{27,28} quaternary phosphatranium,²⁹ tertiary sulfonium (SR_3^+) ,³⁰ and tris(amino) sulfonium $(S(NR)_3^+)$;²⁷ in addition, ruthenium bis-terpyridine and copper dications have each been coordinated into separate crosslinked polymers to serve as anion-exchange membranes.³¹⁻³³ The best anion-exchange membranes based on phosphorus, sulfur, and Ru(II) cations were shown to exhibit rapid hydroxide conduction, roughly five times smaller than the proton conductivity of Nafion which is sufficient given that Nafion is far from the limiting resistive component in the path of charge conduction in solar fuels devices, and excellent stability over weeks to months when immersed in strong alkaline electrolytes at room temperature, and up

to 80 °C.^{26, 28, 30, 31} The challenge that remains for anionexchange membranes is to engineer a membrane material that is also forgiving to a small concentration of hydroxyl radicals, like Nafion is. Functionalization of Nafion precursor materials with anion-conducting functional groups has been explored with limited successes.^{34,35} Alternatively a membrane design that occluded hydroxyl radicals or hydrogen peroxide from entering the membrane would be beneficial. Then, less expensive organic membranes that do not incorporate synthetically demanding fluoropolymers could be used. In addition, for electrochemical systems that utilize carbon-based precursors, such as solar fuels devices that reduce CO₂ to liquid fuels, precipitation of carbonate salts in the alkaline polymer electrolyte results in degradation and clogging of pores in the membrane.24,25 Physical occlusion of free cations or CO2 and carbonate from the membrane would, again, be a possible solution. One means to occlude free cations and prevent carbonate salt formation is to operate the solar fuels device using a feed of deionized liquid water or vapor-phase water (see Polymer Electrolyte with Vapor-Phase Fuel Feeds section below).

3. LIQUID BULK ELECTROLYTE WITH A pH GRADIENT

As described above, catalyst stability is the impetus for using an alkaline-stable anion-exchange membrane. This is most important for electrocatalysts of the oxygen-evolution reaction (OER), because IrO_x is the only acid-stable and somewhat efficient OER electrocatalyst.36 However, alkaline electrolytes are not always desired. Although silicon is a widespread industrially produced material and has a nearly ideal bandgap energy for use in a tandem solar fuels device,^{21,37-39} it corrodes in alkaline electrolytes. Thus, even if an extremely robust anion-exchange membrane were to exist, silicon, a likely candidate material for a scalable and efficient solar fuels device, could not be in contact with the membrane. One solution to this is a mixed conducting ion-exchange membrane. It can be used in place of a proton-exchange membrane or hydroxide-exchange membrane so that the OER compartment is in contact with an alkaline electrolyte while the hydrogen-evolution reaction (HER) compartment is in contact with an acidic electrolyte. Then Si could be used to drive the HER in the acidic compartment and a non-IrO, electrocatalyst could be incorporated to drive the OER in the alkaline compartment. This type of membrane is known as a bipolar membrane, and has been used for over half a century in commercial electrodialvsis devices.40 Stable pH differences can be maintained across bipolar exchange membranes while affording ionic conduction, as protons through the cation-exchange region and hydroxides through the anion-exchange region, generated by water dissociation at the membrane interface (Fig. 3). Protons liberated (consumed) by water splitting at



Fig. 3. Scheme depicting ion migration through three different types of membranes: proton conduction through a cation-exchange membrane (CEM), hydroxide conduction through an anion-exchange membrane (AEM), and mixed proton and hydroxide conduction within a bipolar membrane (BPM). The bipolar membrane shown here is under a reversebias applied potential such that water dissociates at the interface of the anion-exchange region (top) and cation-exchange region (bottom).

the anode (cathode) are balanced by hydroxides (protons) gained through this water dissociation phenomenon.

In addition to the challenges with H₂ and O₂ product crossover described above, bipolar membranes must also consider proton and hydroxide crossover. Different from H₂ and O₂ reaction products, the electrolyte is not continuously removed from the system, and thus as proton and hydroxide crossover occurs there exists a slow loss in the pH gradient that cannot be reformed without expenditure of energy by adding exogenous acid and/or base, which constitutes an overall loss in the energy-conversion efficiency. More significant crossover of protons and hydroxides is required to convert the liquid electrolyte from pH 14 to 13 (or 0 to 1) than to convert the liquid electrolyte from pH 13 to 12, or 12 to 1 l, etc. (or 1 to 2, or 2 to 3, etc.), due to the logarithmic nature of the pH (Fig. 4). However, this also means that after the pH has changed by one unit, it will quickly change over the full pH range, and the electrodes will rapidly become unstable. A figure-of-merit can be defined, in units of distance per time, which defines the thickness of the liquid electrolyte on either side of the membrane required to maintain the pH, initially at the extremes of 1 M H_3O^+ and 1 M OH⁻, to within one pH value (and thus essentially all pH values) over a given time period. Based on the 89% current efficiency for water dissociation at 20 mA/cm² using state-of-the-art bipolar membranes and 1 M HCl and 1 M NaOH at room temperature,⁴¹ the figure-of-merit is \sim 2.7 m/year per side (assuming 8 hours of sunlight, i.e., operation per day), implying that a total of ~ 5.3 m of electrolyte is required to minimize the net change in the pH gradient to two pH units after one year.

Recently, bipolar membranes were used in fuel cells, where there was no bulk supporting liquid electrolyte and the pH was determined by the pH of the ion-exchange membranes.⁴² The results indicated that the pH gradient could be utilized with little to no thermodynamic penalty. The potential required to drive water splitting in the different polymer electrolytes was nullified by the potential



Fig. 4. Relationship between the proton (hydroxide) crossover, and thus pH change, versus the thickness of the electrolyte on each side of the membrane per operation time, for state-of-the-art bipolar membranes and assuming an initial acid (base) activity of I, i.e., pH 0 (pH 14).

required to drive ions up or down the pH gradient. To mimic a typical embodiment of a solar fuels device, bipolar membranes and accompanying electrolytes with the appropriate pH values have been used for electrodialysis⁴¹ and proposed solar fuels applications.⁴³

The bipolar membrane systems described herein are akin to that described in the initial Fujishima and Honda demonstration of photoelectrochemical water splitting in 1971,^{44, 45} and more clearly in a follow-up study where a pH gradient was described that chemically biased the device.⁴⁶ Instead of a bipolar membrane, Fujishima and Honda used a salt bridge which afforded rapid ion conduction and low product crossover. However, because salt bridges are non-specific and not ion selective, a rapid loss in the pH gradient was inevitable, due to diametric proton and cation counterion diffusion, e.g., Na⁺, or hydroxide and anion counter ion diffusion, e.g., Cl⁻, resulting in an unstable photoelectrochemical device.

4. LIQUID BULK ELECTROLYTE WITH A BUFFERED, NON-EXTREME pH

A solar fuels device that operates at near-neutral pH would be advantageous because the bulk electrolyte could be noncorrosive and benign. In addition, such a device could use seawater as the water source assuming the electrocatalysis of chloride was slow and that fresh electrolyte displaced the used electrolyte that contained concentrated seawater. Integrated solar fuels devices operating at near-neutral pH have been demonstrated,⁴⁷⁻⁵⁰ but none have incorporated a membrane. If a membrane had been incorporated, a pH gradient would have formed over time, due to proton liberation (consumption) and buffer or counterion migration through the membrane that would have resulted in a larger required potential to drive the water splitting redox chemistry. This added thermodynamic penalty (59.2 mV× Δ pH,

•1



Fig. 5. (a) Scheme depicting the transport processes present across an anion-exchange membrane when used in an electrochemical cell containing phosphate-buffered near-neutral pH water.⁵¹ (b) Values of the pH in the anode and cathode compartment of a cell, each containing 4 mL of 3.5 M of the indicated buffers, and separated by an anion-exchange membrane.⁵¹ Reprinted with permission from [51], E. A. Hernández-Pagán, et al., *Energy Environ. Sci.* 5, 7582 (2012). © 2012, The Royal Society of Chemistry.

at room temperature) would have to be supplied from the light absorbers and would result in a lower efficiency than when no pH gradient was present.

The magnitude of the pH gradient formed during simulated solar fuels device operation was recently explored experimentally to elucidate the complex ion transport that occurs when neutral pH conditions are utilized.⁵¹ Many buffers are negatively charged and thus when a cationexchange membrane was used, e.g., Nafion, the counter ions, e.g., Na⁺, K⁺, Ca²⁺, were shown to carry nearly the entire ionic current (i.e., their transport number was large), whereas when an anion-exchange membrane was used, the buffer anions were shown to carry nearly the entire ionic current (Fig. 5(a)). After three days of sunlight-simulated operation, a phosphate or acetate buffer species on one side of the membrane had moved almost entirely to the other side; the resulting less buffered side of the device was shown to exhibit erratic changes in pH with continued device operation (Fig. 5(b)). Akin to the bipolar membranes described above, a figure-of-merit can be determined for these systems, also with units of distance per year, again where the distance is the thickness of the liquid electrolyte on each side of the membrane required to result in a change in the concentration of the buffer from 1 M to 100 mM over a year (assuming 8 hours of sunlight, i.e., operation, per day). Given the reported nearunity ionic current efficiency and transport number for the phosphate buffer, the figure-of-merit is ~ 24 m/year per side and thus every year a total of \sim 49 m of electrolyte would be required!

An alternative means to maintain the buffer concentration and near-neutral pH conditions is to continually mix the electrolytes in a controlled manner through a small via.⁵² For solar fuels devices in buffered solutions at nearneutral pH, as before the pH was shown to change drastically during operation in quiescent solutions, and the

efficiency dropped to zero. When recirculation was introduced to mix the system through a small via, this was shown to be sufficient to maintain the concentration of protons and buffer to within one order-of-magnitude of the initial values, and the resulting water splitting efficiency remained nearly constant over time, although there is an energetic cost to mix (Fig. 6(a)). The maximum dissolved concentration of O2 and H2 at room temperature is so small, i.e., $\sim 1 \text{ mM}$ for each,⁵³ that there is little fear of generating an explosive mixture in the headspace, as long as the recirculation flow rate is not too rapid. One consideration not discussed was the effect of pressurization of one compartment over the other. Given the stoichiometry of the reaction (i.e., 2:1 v/v of H₂:O₂) the cathode side would pressurize more rapidly than the anode side and force the liquid electrolyte from the cathode to the anode. Tight control over the pressure is required; in the absence of any material in the via, extremely small pressure differentials must be maintained.¹² One means to circumvent this is to keep both sides at atmospheric pressure through incorporation of flexible containers that raise and lower with increased pressure, but do not stretch, such as baggietype reactors, described previously,^{13, 14}

5. HIGHLY POROUS AND HIGHLY SELECTIVE SEPARATORS

Ion-exchange membranes hold back large pressure differentials; porous separators cannot, however, they can be much less expensive.¹⁹ Thus, if one could control small pressure differentials during water splitting then a porous separator would provide a clear cost advantage for solar fuels devices. To this end, a porous benzoylated cellulose membrane has been used in a water electrolysis cell where $H_3PMo_{12}O_{40}$ polyoxometalates were used to buffer electrons and protons delivered from one water-splitting half reaction so that later they could be used for the



Fig. 6. (a) Scheme depicting a solar fuels device consisting of a light absorber(s) (PV), electrocatalysts for the O_2 evolution reaction (OER) and H_2 evolution reaction (HER), and a membrane, with recirculation of the electrolyte to attenuate the formation of gradients in pH and buffer concentration.⁵² (b) Two-step scheme for water electrolysis using polyoxometalates as an intermediate electron-coupled-proton buffer, and a benzoylated cellulose schemator.⁵⁴ (c) Model image of a solar fuels device that is encapsulated in Nafion, and relics on H_2 diffusion through Nafion for product collection.⁶¹

other water-splitting half reaction (Fig. 6(b)).⁵⁴ Over the timescale of weeks there was < 2% shunting current due to O_2 reacting with reduced polyoxometalates, and thus this suggests that an intermediate storage mechanism may be useful in solar fuels devices.

Water splitting is a desirable reaction because water is abundant, safe, and easy to transport, and O_2 is a slowly reactive and physiologically safe waste product. In order to access our current energy infrastructure, however, some research groups are exploring solar fuels devices that directly reduce CO₂ to fuels such as methanol. Notwithstanding, methanol diffusive crossover through Nafion is very rapid,⁵⁵ with an activation energy only two times larger than for proton diffusion through Nafion,⁵⁶ and thus a new non-Nafion polymer-electrolyte membrane is required for carbon-based fuels. The fuel cell community has yet to identify a membrane with sufficiently low methanol crossover for their application,²⁴ and due to the \sim 100-fold smaller current densities present in solar fuels devices, identification of an acceptable, low-permeability membrane for this application is even more unlikely.

An alternative to a methanol-impermeable membrane is a system whereby a proton-selective material is inserted in the ion conduction path. Thus, by definition, methanol, methane, and any non-proton species is entirely excluded from crossing over. Palladium metal serves this role. Pd foils are used in electrochemical hydrogen separators and purifiers, and as membranes to filter water out of wet

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 H_2 gas streams.⁵⁷ An efficient polymer-electrolyte fuel cell with methanol contaminants has been demonstrated, whereby a Pd foil was sandwiched between two Nafion membranes to serve as the membrane.⁵⁸ Pd is one of several materials known to conduct protons and/or hydrogen atoms, including FeS₂ and polythiophene,⁵⁹ and thus there exists several opportunities for new proton-selective ion-exchange materials.

6. POLYMER ELECTROLYTE WITH VAPOR-PHASE FUEL FEEDS

Akin to solar fuels devices, electrolyzers generate H₂ and O₂ through water splitting of liquid water. In fuel cell devices, the reverse net chemical reaction occurs whereby H_2 and O_2 in the gas phase combine to generate water vapor. Can water vapor be used as the water source for an electrolyzer or a solar fuels device? For an electrolyzer reacting with vapor-phase water, the challenge is to feed water vapor at a fast enough rate to maintain the large $\sim 1 \text{ A/cm}^2$ current densities. However, because solar fuels devices operate at ~ 100 -fold smaller current densities, water vapor is a plausible reactant feed even at ambient humidity. It was recently demonstrated that a polymer-electrolyte-membrane fuel cell could electrolyze water vapor at solar-photon-flux-relevant current densities and over potentials similar to those present in liquid electrolyzers suggesting that a solar fuels device being fed by

water vapor was feasible.⁶⁰ In addition, numerical device physics modeling and simulation studies concluded that efficient, integrated solar fuels devices could incorporate a Nafion thin film that completely covered the electrocatalyst layers and relied on diffusion of H₂ through the Nafion to release the H₂ fuel reaction product (Fig. 6(c)).⁶¹ For this design it was imperative that the ion-exchange membrane had a substantial permeability to H₂ and/or that the membrane was thin. No integrated devices for solar water splitting using a vapor-phase water feed have been reported to date.

7. DUAL-CONDUCTING MEMBRANES

The membranes discussed thus far could have been implemented in electrolyzers, fuel cells, or solar fuels devices. That is, the engineering designs were not specific solely to applications in solar fuels devices, although the crossover requirements were \sim 100-fold more stringent and the ionic conductivities were \sim 100-fold less stringent. A form factor akin to that of a membrane-electrode assembly fuel cell or a zero-gap electrolyzer is beneficial in order to minimize V_{drop} and maximize efficiency.⁶² These designs were engineered to minimize ion transport distances in relation to electron transport distances because the resistivity of most ion-conductive materials (i.e., electrolytes) is orders of magnitude larger than the resistivity of most electron-conductive materials (e.g., metals). Because solar fuels devices pass much less current than electrolyzers and fuel cells, the design requirements for conductive pathways are relaxed and this allows alternatives whereby the ion-conductive pathways are not smaller than the electron-conductive pathways. For example, a checkerboard/snakeskin design with alternating patches of ion-conductive membranes and electron-conductive lightabsorbing materials has been described (Fig. 2),^{12, 17, 63} as well as a similar water-vapor-fed design with a polymer electrolyte.61

An alternative design consists of a composite material that contains the light absorber(s), electrocatalysts, and a cation-exchange membrane (Fig. 1(a)). For such a design, an intervening material is required to connect the two sides that must be both electrically and ionically conductive. For this dual-function membrane, various polymeric materials have been investigated. The first demonstration in a solar fuels device used poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS),¹⁶ which is a common hole-conducting material used in flexible electrically conductive organic devices. The PEDOT:PSS layer had to be made as thin as possible because PEDOT+ absorbs visible light strongly and thus filters light to the second absorber. Because the functional groups in the PSS counterions are the same as those that form the charged pores in Nafion (i.e., sulfonates/sulfonic acids), this dual-conducting material also conducted protons, with a conductivity that was about three times smaller than that of Nafion and was in the range of conductivities observed for state-of-the-art anion-exchange membranes.⁶⁴

The electronic properties of this dual-conducting membrane are similar to those for transparent conductive oxides (TCOs), such as fluorine-doped tin oxide (FTO) or indium-tin oxide (ITO), because large conductivity and small sunlight absorption are beneficial to both. However, there is one very important difference; in the dualconducting membrane described herein, the charges must conduct through the plane of the material and not in the plane, like in a typical TCO (Fig. 7). Thus, the goal for application in solar fuels devices is to minimize the transverse area-specific resistance and not necessarily the sheet resistance. For TCOs there is a tradeoff in minimizing desired properties (i.e., sheet resistance and light absorption), because as the thickness decreases the sheet resistance increases and the absorption decreases. However, for the dual-conducting membrane described herein, as the thickness decreases the area-specific resistance also decreases, and so both the absorption and resistance decrease as the membrane is made thinner. Making the dual-conducting membrane as thin as possible is a goal for solar fuels devices.

To decrease light absorption by PEDOT:PSS, it has been mixed with Nafion, which is transparent, resulting in a composite material with decreased visible absorption coefficients, increased ionic conductivity, and sufficient electronic conductivity.⁶⁵ Using a two-point-probe electrical technique this composite polymer was shown to form highly conductive contacts to Si microwires.^{66–68} In addition, a layer-by-layer process was used to fabricate a membrane that did not contain Nafion but still afforded substantial proton conductivity and electrical conductivity.⁶⁹ It was a composite membrane consisting of PEDOT:sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (PEDOT:sPPO), and thus was similar in chemical structure to PEDOT:PSS and had a conductivity about five times smaller than that of Nafion.

A question that remains is whether a dual-conducting membrane can be in contact with liquid electrolytes in both



Fig. 7. Scheme depicting the orthogonal directions of electronic charge conduction in the dual-conducting membrane (DM) of a solar fuels device (left) and in a transparent conductive oxide (TCO) of a thin-film solar cell (right).

compartments. While such a structure would afford ionic conduction between each electrolyte compartment, it would also supply pathways for electronic conduction between each electrolyte compartment. In a photovoltaic, this type of contact is termed a shunt and results in decreased energy-conversion efficiency.⁷⁰ However, for the devices described herein, a shunt will not exist if there are no species in the electrolyte to react with the charge. That is, if the dual-conducting composite membrane consists of materials that are not electrocatalytic for the reverse reactions of H₂ oxidation and O₂ reduction, then it should not form shunts even if the materials are electronically conductive. This has yet to be reported in the literature but is an interesting point that deserves further study.

8. MEMBRANE-LIGHT-ABSORBER CONTACTS

A subtlety of the designs shown in Figures 1(a) and 2 is that contacts are required between the light absorbers and the membranes. This is a new consideration in solar fuels devices because micron-sized light-absorbing structures embedded in Nafion have only recently been investigated for solar fuels applications,¹⁶ yet they provide a straightforward means to investigate interfacial effects. Nation and a poly(arylene-ether-sulfone) anion-exchange membrane have been cast between micron-sized light absorbers to form a robust, interpenetrating membranesemiconductor system that exhibited conductivities similar to the bulk ion-exchange membrane materials.¹⁶ To investigate the strength of the membrane-light-absorber interface, a technique to mechanically pull these micron-sized light absorbers consisting of silicon was developed. The silicon surface was functionalized with different organic groups and the interaction with an insulating polydimethylsiloxane (PDMS) polymer was investigated.⁷¹ A feature on the top of a micron-sized light absorber was fabricated using a focused ion beam (FIB), and served as the handle for tensile tests so that the shear strength of the membrane-semiconductor interaction could be guantified. No interfacial tests have been performed using ion-exchange membrane polymers. However, the interface between planar silicon wafers and Nafion was studied by grazing-incidence small-angle X-ray scattering to determine the pore and interfacial film morphology.^{72, 73} It was shown that interfacial wetting interactions greatly affect the bulk membrane morphology which in turn affects the ionic conductivity.

9. CONCLUSIONS

Nafion is the membrane of choice in commercial electrochemical systems due to its ability to withstand harsh chemical environments, hold back large pressure differentials, prevent rapid product crossover, and rapidly conduct cations. Thus, membranes for solar fuels devices will likely use this same type of membrane. However, some interesting non-Nafion demonstration systems and new separators exist that may represent opportunities for exploration of alternative membranes for solar fuels devices. Specifically, the following types of membranes and systems have yet to be incorporated into integrated solar fuels devices:

• Anion-exchange membranes with fixed-charge groups based on phosphorus, sulfur, or Ru(II) cations, which have recently been shown to be stable and conductive.

• Bipolar membranes, which allow each half reaction of water electrolysis to be performed in different pH environments.

• Proton-selective ion-exchange-membrane materials, which allow fuels such as methanol to be generated and/or used with no product crossover.

• Vapor-phase reactions, which may prove beneficial in solar fuels devices because all of the charged species, besides protons, are fixed in the solid electrolyte and thus buffer species cannot crossover and carbonates will not precipitate in anion-exchange membranes.

Several aspects of solar fuels devices related to the membrane have been explored but no consensus exists as to optimal designs, and so unanswered challenges in the field include the following:

• Solar fuels devices operating at near-neutral pH conditions cannot simultaneously attenuate buffer crossover, due to migration, and prevent mixing of the anolyte and catholyte when a porous separator is used, due to small pressure differentials arising from gaseous product formation; a device architecture and materials to overcome these challenges could greatly impact the solar fuels field.

• Tandem integrated solar fuels devices could be fabricated by laminating two materials together if the membranes conducted both ions and electrons; electronically conductive polymers with sulfonate-based counterions are well-suited for this purpose but most still absorb sunlight too strongly.

• The mechanical properties of the contacts between the light-absorbing materials and the polymer membranes are just beginning to be explored, but understanding interfaces is important to attaining stable solar fuels devices, especially in the presence of large H_2 pressures.

Using the above as starting points, it is our hope that experts in ion-exchange membrane technologies can identify specific interests to investigate further that will ultimately benefit solar fuels devices.

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References and Notes

- 1. T. F. O'Brien, T. V. Bommaraju, and F. Hine, Handbook of Chlor-Alkali Technology, Springer US, New York (2005), Vol. 1.
- W. Grot, Fluorinated Ionomers, William Andrew Publishing, Norwich (2007).
- S. Slade, S. A. Campbell, T. R. Ralph, and F. C. Walsh, J. Electrochem. Soc. 149, A1556 (2002).
- A. J. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd edn., John Wiley and Sons, Inc., New York (2001).
- 5. K. A. Mauritz and R. B. Moore, Chem. Rev. 104, 4535 (2004).
- 6. I. Rubinstein and A. J. Bard, J. Am. Chem. Soc. 102, 6641 (1980).
- 7. I. Rubinstein and A. J. Bard, J. Am. Chem. Soc. 103, 5007 (1981).
- 8. H. S. White, J. Leddy, and A. J. Bard, J. Am. Chem. Soc. 104, 4811 (1982).
- 9. C. R. Martin, I. Rubinstein, and A. J. Bard, J. Am. Chem. Soc. 104, 4817 (1982).
- T. H. Yu, Y. Sha, W.-G. Liu, B. V. Merinov, P. Shirvanian, I. Goddard, and A. William, J. Am. Chem. Soc. 133, 19857 (2011).
- L. Lipp (ed.), Development of Highly Efficient Solid State Electrochemical Hydrogen Compressor (EHC). Arlington: Fuel Cell Energy; (2008) Contract No.: PDP29. Sponsored by the U.S. Department of Energy.
- S. Haussener, C. Xiang, J. M. Spurgeon, S. Ardo, N. S. Lewis, and A. Z. Weber, *Energy Environ. Sci.* 5, 9922 (2012).
- B. D. James, G. N. Baum, J. Perez, and K. N. Baum (eds.), Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production. Arlington: Directed Technologies, Inc. (2009). Contract No.: GS-10F-009J. Sponsored by the U.S. Department of Energy.
- 14. 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 Environ. Sci.* 6, 1983 (2013).
- M. T. Winkler, C. R. Cox, D. G. Nocera, and T. Buonassisi, *Proc. Natl. Acad. Sci. U. S. A.* 110, E1076 (2013).
- J. M. Spurgeon, M. G. Walter, J. Zhou, P. A. Kohl, and N. S. Lewis, Energy Environ. Sci. 4, 1772 (2011).
- H. Gerischer, Solar Energy Conversion, Topics in Applied Physics, edited by B. O. Seraphin, Springer Berlin Heidelberg, Heidelberg (1979), Vol. 31, pp. 115–172.
- M. A. Green, K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop, Prog. Photovolt. Res. Appl. 22, 1 (2014).
- M. Carmo, D. L. Fritz, J. Mergel, and D. Stolten, *Int. J. Hydrogen Energy* 38, 4901 (2013).
- 20. Y. Wang, K. S. Chen, J. Mishler, S. C. Cho, and X. C. Adroher, Applied Energy 88, 981 (2011).
- 21. S. Hu, C. Xiang, S. Haussener, A. D. Berger, and N. S. Lewis, Energy Environ. Sci. 6, 2984 (2013).
- M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, and N. S. Lewis, *Chem. Rev.* 110, 6446 (2010).
- 23. J. R. McKone, N. S. Lewis, and H. B. Gray, *Chem. Mater.* 26, 407 (2013).
- 24. J. R. Varcoe and R. C. T. Slade, Fuel Cells 5, 189 (2005).
- 25. R. C. T. Slade, J. P. Kizewski, S. D. Poynton, R. Zeng, and J. R. Varcoe, Fuel Cells: Selected Entries from the Encyclopedia of Sustainability Science and Technology, edited by K. D. Kreuer, Springer, New York (2013), pp. 9–29.
- 26. S. Gu, R. Cai, T. Luo, Z. Chen, M. Sun, Y. Liu, G. He, and Y. Yan, Angew. Chem., Int. Ed. Engl. 48, 6499 (2009).
- B. S. Pivovar and D. L. Thorn, Anion'-conducting polymer, composition, and membrane, U.S. Patent 7,439,275, October (2008).
- K. J. T. Noonan, K. M. Hugar, H. A. Kostalik IV, E. B. Lobkovsky, H. C. D. AbrunÞa, and G. W. Coates, J. Am. Chem. Soc. 134, 18161 (2012).
- X. Kong, K. Wadhwa, J. G. Verkade, and K. Schmidt-Rohr, Macromolecules 42, 1659 (2009).

- 30. B. Zhang, S. Gu, J. Wang, Y. Liu, A. M. Herring, and Y. Yan, *RSC Adv.* 2, 12683 (2012).
- 31. Y. Zha, M. L. Disabb-Miller, Z. D. Johnson, M. A. Hickner, and G. N. Tew, J. Am. Chem. Soc. 134, 4493 (2012).
- 32. M. L. Disabb-Miller, Y. Zha, A. J. DeCarlo, M. Pawar, G. N. Tew, and M. A. Hickner, *Macromolecules* 46, 9279 (2013).
- 33. P. Y. Xu, C. H. Zhao, and Q. L. Liu, J. Appl. Polym. Sci. 130, 1172 (2013).
- 34. D. M. Hillman, S. H. Stephens, S. D. Poynton, S. Murphy, A. L. Ong, and J. R. Varcoe, J. Mater. Chem. A 1, 1018 (2013).
- D. S. Kim, C. H. Fujimoto, M. R. Hibbs, A. Labouriau, Y.-K. Choe, and Y. S. Kim, *Macromolecules* 46, 7826 (2013).
- 36. C. C. L. McCrory, S. Jung, J. C. Peter, and T. F. Jaramillo, J. Am. Chem. Soc. 135, 16977 (2013).
- M. F. Weber and M. J. Dignam, J. Electrochem. Soc. 131, 1258 (1984).
- 38. J. R. Bolton, S. J. Strickler, and J. S. Connolly, *Nature* 316, 495 (1985).
- 39. L. C. Seitz, Z. Chen, A. J. Forman, B. A. Pinaud, J. D. Benck, and T. F. Jaramillo, *ChemSusChem* 7, 1372 (2014).
- 40. L. M. Raff, F. A. Iddings, and G. W. Murphy, J. Phys. Chem. 64, 127 (1960).
- 41. R. Simons, J. Membr. Sci. 78, 13 (1993).
- 42. M. Ünlü, J. Zhou, and P. A. Kohl, J. Phys. Chem. C 113, 11416 (2009).
- **43.** M. B. McDonald, S. Ardo, N. S. Lewis, and M. S. Freund (unpublished observations).
- 44. A. Fujishima and K. Honda, Bull. Chem. Soc. Jpn. 44, 1148 (1971).
- 45. A. Fujishima and K. Honda, Nature 238, 37 (1972).
- A. Fujishima, K. Kohayakawa, and K. Honda, Bull. Chem. Soc. Jpn-48, 1041 (1975).
- E. L. Miller, D. Paluselli, B. Marsen, and R. E. Rocheleau, Sol. Energy Mater. Sol. Cells 88, 131 (2005).
- S. Y. Reece, J. A. Hamel, K. Sung, T. D. Jarvi, A. J. Esswein, J. J. H. Pijpers, and D. G. Nocera, *Science* 334, 645 (2011).
- 49. C.-Y. Lin, Y.-H. Lai, D. Mersch, and E. Reisner, *Chem. Sci.* 3, 3482 (2012).
- P. Bornoz, F. F. Adbi, S. D. Tilley, B. Dam, R. van de Krol, M. Grätzel, and K. Sivula, J. Phys. Chem. C in press, Doi: 10.1021/jp500441h.
- E. A. Hernández-Pagán, N. M. Vargas-Barbosa, T. Wang, Y. Zhao, E. S. Smotkin, and T. E. Mallouk, *Energy Environ. Sci.* 5, 7582 (2012).
- 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 Environ. Sci.* 7, 297 (2014).
- W. M. Haynes (ed.), CRC Handbook of *Chemistry and Physics*, 94th edn., CRC Press, Boca Raton (2013).
- 54. M. D. Symes and L. Cronin, Nature Chem. 5, 403 (2013).
- 55. B. Gurau and E. S. Smotkin, J. Power Sources 112, 339 (2002).
- X. Ren, T. E. Springer, T. A. Zawodzinski, and S. Gottesfeld, J. Electrochem. Soc. 147, 466 (2000).
- V. S. Bagotsky, Fuel Cells: Problems and Solutions, 2nd edn., John Wiley and Sons, Inc. Hoboken (2012).
- C. Pu, W. Huang, K. L. Ley, and E. S. Smotkin, J. Electrochem. Soc. 142, L119 (1995).
- 59. H. Tributsch, Ionics 6, 161 (2000).
- J. M. Spurgeon and N. S. Lewis, *Energy Environ. Sci.* 4, 2993 (2011).
- 61. C. Xiang, Y. Chen, and N. S. Lewis, *Energy Environ. Sci.* 6, 3713 (2013).
- H. Wendt and G. Kreysa, Electrochemical Engineering: Science and Technology in Chemical and Other Industries, Springer-Verlag-Berlin (1999).
- R. D. Rauh and R. A. Boudreau, Photoelectrochemical cell, U.S. Patent 4,388,384, June (1983).

- 64. M. Lefebvre, Z. Qi, D. Rana, and P. G. Pickup, *Chem. Mater.* 11, 262 (1999).
- 65. S. L. McFarlane, B. A. Day, K. McEleney, M. S. Freund, and N. S. Lewis, *Energy Environ. Sci.* 4, 1700 (2011).
- 66. I. Yahyaie, K. McEleney, M. Walter, D. R. Oliver, D. J. Thomson, M. S. Freund, and N. S. Lewis, J. Phys. Chem. Lett. 2, 675 (2011).
- I. Yahyaie, K. McEleney, M. G. Walter, D. R. Oliver, D. J. Thomson, M. S. Freund, and N. S. Lewis, J. Phys. Chem. C 115, 24945 (2011).
- I. Yahyaie, S. Ardo, D. R. Oliver, D. J. Thomson, M. S. Freund, and N. S. Lewis, *Energy Environ. Sci.* 5, 9789 (2012).
- 69. J. Liu, N. R. Davis, D. S. Liu, and P. T. Hammond, J. Mater. Chem. 22, 15534 (2012).
- 70. S. M. Sze and K. K. Ng, *Physics of Semiconductor Devices*, 3rdedn., John Wiley and Sons, Inc., New York (2006).
- 71. C. J. Cho, L. O'Leary, N. S. Lewis, and J. R. Greer, *Nano Lett* 12, 3296 (2012).
- 72. M. A. Modestino, A. Kusoglu, A. Hexemer, A. Z. Weber, and R. A. Segalman, *Macromolecules* 45, 4681 (2012).
- M. A. Modestino, D. K. Paul, S. Dishari, S. A. Petrina, F. I. Allen, M. A. Hickner, K. Karan, R. A. Segalman, and A. Z. Weber, *Macromolecules* 46, 867 (2013).