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Title

Use of Bipolar Membranes for Maintaining Steady-State pH Gradients in Membrane-Supported, Solar-Driven Water Splitting

Permalink https://escholarship.org/uc/item/9rs4k0nz

Journal ChemSusChem, 7(11)

ISSN 1864-5631

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Publication Date 2014-11-01

DOI 10.1002/cssc.201402288

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Peer reviewed

DOI: 10.1002/cssc.201402288



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A bipolar membrane can maintain a steady-state pH difference between the sites of oxidation and reduction in membranesupported, solar-driven water-splitting systems without changing the overall thermodynamics required to split water. A commercially available bipolar membrane that can serve this purpose has been identified, its performance has been evaluated quantitatively, and is demonstrated to meet the requirements for this application. For effective utilization in integrated solardriven water-splitting systems, such bipolar membranes must, however, be modified to simultaneously optimize their physical properties such as optical transparency, electronic conductivity and kinetics of water dissociation.

In one approach to artificial photosynthesis, a tandem structure involving two light absorbers and electrocatalysts for the oxygen-evolution reaction (OER) and the hydrogen-evolution reaction (HER) are imbedded in a membrane that allows for passive product separation and proton management (Figure 1). A conceptually straightforward implementation of such a system involves operation of all of the components of the system at a mutually common pH. This implementation, however, imposes constraints on the materials that can be beneficially utilized in a complete, operational system. For example, silicon is a desirable photocathode but is unstable under alkaline conditions, whereas most metal oxide photoanodes dissolve under acidic conditions. Similarly, earth-abundant electrocatalysts for water splitting function well under alkaline conditions, but relatively few membranes are stable and can manage protons under such conditions. Hence, methods that could allow operation of the oxidative and reductive compo-

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Figure 1. Proposed model for an integrated solar water-splitting device. (a) Cross-section, showing high-aspect-ratio photoelectrodes with mounted catalysts embedded in a membrane. (b) A single photoelectrode pair, depicting light absorption leading to charge separation. Holes (h^+) in the n-type photoanode are transported radially to the catalyst to perform the oxygenevolution reaction from water while electrons (e^-) in the p-type cathode perform the hydrogen-evolution reaction using protons. The membrane is a conduit for the dissipation of ionic and electronic charge.

nents of the solar-driven water-splitting assembly at their individually optimal pH values are desirable.^[1]

Operation of a solar-driven water electrolysis cell with a transient pH gradient has been used as a strategy to decrease the voltage requirements of the photoelectrolysis.^[2] This approach is, however, only feasible for short-term operation because the pH gradient will dissipate rapidly. For long-term application, the pH gradient must be maintained, and we describe herein the use of bipolar membranes (BPMs), utilized traditionally in electrodialysis processes, for this purpose. A commercially available BPM will maintain a large (i.e., 14 pH unit) difference in steady-state pH while operating efficiently, and it is feasible to translate such a system to photoelectrochemical (PEC) devices. This concept has been evaluated in congruence with Mallouk et al.^[3]

A BPM is formed by lamination of an anion-exchange layer (AEL) that is permselective to anions with a cation-exchange layer (CEL) that is permselective to cations.^[4] With the anode facing the AEL and the cathode facing the CEL (Figure 2a), when a potential is applied such that a small current flows, because the ion-exchange permselectivity is non-ideal, ions in solution that have the same polarity as the fixed charges in the corresponding membrane layer (co-ions) will carry the ionic current against the electrostatic repulsion of the membrane. This will occur until the applied bias cannot increase the co-ion current significantly. As the potential is further increased, water molecules in the interfacial layer become sufficiently polarized and dissociate to form OH^- and H^+ [Eq. (1)]. These ions migrate through the AEL and CEL, respectively, and facilitate larger currents (> 100 mA cm⁻²). In the electrodialysis literature,



Figure 2. (a) BPM structure with anion-exchange layer (AEL) facing the anode and cation-exchange layer (CEL) facing the cathode in NaClO₄ aqueous solutions. Ions migrate toward the oppositely charged electrodes. Na⁺ and ClO₄⁻ transport through the AEL and CEL, respectively (faded arrows), is greatly attenuated due to electrostatics (dashed lines indicate some leakage of these ions through the BPM). To maintain electroneutrality at large biases, water is dissociated in the AEL–CEL junction (the interfacial layer) and the dissociation products (OH⁻ and H⁺) migrate toward the electrode of opposite charge. Water that is consumed in the interfacial layer is replenished. (b) *J*–*E* relationship for the current density as a function of potential across the bipolar membrane, E_{BPM} , for the configuration shown in panel (a) with 1 m electrolyte. Inset: Small current-density region depicting co-ion leakage current and the limiting region.

this phenomenon is known as the enhanced field effect.^[5]

$$H_2 O \rightarrow O H^- + H^+ \tag{1}$$

The fixed charges in the CEL and AEL resemble the dopants in p- and n-type semiconductors, respectively. For this reason, the overall structure has been compared to that of a p-n junction.^[6] The current-voltage behavior is similar for both types of systems in that under a reverse-bias condition, the current is rectified until a breakdown voltage is reached, at which point the current is then facilitated by the charge carriers generated by polarization.^[7] Figure 2b shows the relationship between the potential across a commercially available BPM (fumasep FBM, FuMa-Tech) in 1 \bowtie NaClO₄(aq) and the current passed under the conditions shown in Figure 2a. Small current densities (< 1 mA cm⁻²) are transported by co-ion leakage until a limiting magnitude is reached.^[8] At potentials > 0.8 V, the water dissociation mechanism is engaged and an additional current is observed. At these higher potentials, bubbles could be observed on the external-bias platinum electrodes, indicating that O_2 and H_2 were the products of the redox reactions and water electrolysis was successfully effected. At current densities > 120 mA cm⁻², a second limiting region is approached, resulting from mass-transport limitations under which the influx of water from the solutions is not sufficient to replace the water consumed in the interfacial layer.^[9]

As depicted in Figure 3a, this BPM configuration could in principle be exploited to sustain a pH gradient in a water-splitting system. Water dissociation in the interfacial layer recycles OH^- and H^+ ions that are consumed at the anode via the OER and at the cathode via the HER, respectively. These pH conditions are optimal in terms of thermodynamics and stability for earth-abundant materials that drive and catalyze the OER and HER, because hydroxide ions are more readily oxidized than water molecules. Similarly, photoanodes are generally more stable in alkaline media and photocathodes are generally more stable under acidic conditions. The *J*–*E* behavior of fumasep FBM during water electrolysis with the anode immersed in 1 M NaOH(aq) and the cathode immersed in 1 M HClO₄(aq) exhibits



Figure 3. (a) BPM configuration shown in Figure 2 a with base (1 mu NaOH) in the anode (AEL) compartment and acid (1 mu HCIO₄) in the cathode (CEL) compartment. OH⁻ is consumed at the anode and H⁺ is consumed at the cathode. Na⁺ and CIO₄⁻ transport is electrostatically attenuated and the ionic current is enabled by water dissociation in the interfacial layer. (b) *J*–*E* relationship for the current density as a function of potential across the bipolar membrane, *E*_{BPM}, for the configuration shown in panel (a) with 1 mu base and acid solutions. A likely target operational current density of 20 mA cm⁻² is highlighted. Inset: Small current density region depicting a measured open-circuit potential difference of ~0.8 V.

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a behavior similar to that observed with no pH gradient (Figure 2b) but displays an open-circuit potential of ~0.8 V and no co-ion leakage current region. This behavior is consistent with previous reports of such membranes examined under similar conditions.^[8,10] An incipient current density of ~20 mA cm⁻² is required for operation of efficient solar-driven water-splitting under 1 sun illumination,^[11] which clearly entails significant water dissociation in the interfacial layer of the BPM.

The thermodynamic potential of this configuration will be the sum of the Nernst electrode potentials ΔE_{Nernst} and the junction potential at the BPM interfacial layer E_j due to the pH gradient [Eq. (2)].

$$\Delta E_{\text{cell}} = \Delta E_{\text{Nernst}} + E_{\text{j}} = [E_{\text{H}^+/\text{H}_2} - E_{\text{O}_2/\text{OH}^-}] + E_{\text{j}}$$
(2)

Assuming that water is in equilibrium with OH^- and H^+ throughout the cell in Figure 3 a, an expression for the junction potential using $K_W = a_{OH^-}a_{H^+}$ is obtained [Eq. (3)]:^[12]

$$E_{j} = \frac{RT}{F} \ln \frac{\left(a_{\text{OH}}^{\text{AEL}} a_{\text{H}^{+}}^{\text{CEL}}\right)}{K_{\text{w}}}$$
(3)

Expansion of Equation (2), including Equation (3), and assuming 1 bar of H_2 and O_2 at standard state, gives Equation (4).

$$\Delta E_{\text{cell}} = [E^{0}_{\text{H}^{+}/\text{H}_{2}} - E^{0}_{\text{O}_{2}/\text{OH}^{-}} + \frac{RT}{F} \ln(a^{\text{anode}}_{\text{OH}^{-}}a^{\text{cathode}}_{\text{H}^{+}})] + \frac{RT}{F} \ln\frac{K_{\text{w}}}{(a^{\text{AEL}}_{\text{OH}^{-}}a^{\text{CEL}}_{\text{H}^{+}})}$$
(4)

Under conditions where the OH^- and H^+ activities in the membrane are the same as in the adjacent solutions, the activity terms sum to zero, resulting in Equation (5).

$$\Delta E_{\text{cell}} = [E^{0}_{\text{H}^{+}/\text{H}_{2}} - E^{0}_{\text{O}_{2}/\text{OH}^{-}}] + \frac{RT}{F} \ln(K_{\text{w}})$$
(5)

At room temperature, 1 bar H₂ and O₂, and 1 m base and 1 m acid at unit activity (realistic for a practical artificial photosynthesis device), the standard potentials for the OER and HER are $E^{0}_{O_{2}/OH^{-}} = 0.40 \text{ V}$ and $EO_{H^{+}/H_{2}} = 0.00 \text{ V}$, respectively (Figure 3 a). Under these conditions $K_{\rm W}$ is 10^{-14} , hence $E_{\rm j} = -0.83$ V, which is the thermodynamic potential for water dissociation in the interfacial layer^[10] and is consistent with the experimentally determined value of ca. 0.8 V (Figure 3b). Thus, the potential difference for such a cell, ΔE_{cell} , is -1.23 V. This is the same potential difference as that required to perform water electrolysis with no pH gradient in the absence of a membrane. Hence, the overpotential, and total applied potential, at steady-state for water splitting is not affected by the presence of the pH differential when an appropriate BPM configuration is used. Equivalently, since splitting of H₂O stoichiometrically to H₂ and $\frac{1}{2}O_2$ can be associated with a thermodynamic set of state functions, if water is the only reagent required and the only net products are H_2 and $\frac{1}{2}O_2$, the potentials, free energies, and all other state functions required to drive this process must be the same regardless of the internal details of the system.

To confirm this analysis, the potential difference across two platinum electrodes spanning the configuration depicted in Figure 3a was measured as the system performed electrocatalytic water-splitting (see Supporting Information for calculations). Although not ideal for the solar-driven process in terms of electrode configuration and materials (such as Figure 1), this system models the potential drop across a membrane while the relevant half reactions occur on known electrocatalysts that are on opposite sides of the membrane. Figure 4 shows



Figure 4. Overall (orange) *J–E* relationship of two water-splitting cells consisting of the OER (purple) and the HER (blue) on platinum electrocatalyst across a) fumasep FBM, for which OER occurs in 1 M NaOH and HER in 1 M HClO₄; and b) Nafion, for which both OER and HER occur in 1 M HClO₄. Additionally, OER, HER, and membrane (not shown) data were added (green dashed). Current density and potential are shown as absolute values to eliminate the sign of each data set, for simplified comparison. All data are compensated for Ohmic resistance losses.

the corresponding unsigned J-E data, which compare the behavior of this cell, consisting of alkaline oxidation and acidic reduction across a BPM (Figure 4a), to that of a uniform pH system utilizing a cation exchange membrane (Nafion) (Figure 4b) as the separator (see Supporting Information for data manipulation details). At the target current density of 20 mA cm⁻², the measured potential of platinum effecting the HER in 1 \bowtie HClO₄ is ~0.5 V vs. SCE. The measured potential for effecting OER in 1 \bowtie NaOH, the case for the BPM-gradient system, is ~1.1 V vs. SCE while the potential of platinum effecting the OER in 1 \bowtie HClO₄, the case for Nafion-acid water-splitting, is considerably larger, at ~1.8 V vs. SCE. This difference is

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expected given that the thermodynamic potential for this half reaction is of greater magnitude (1.23 V vs. 0.40 V). Nafion has a measured potential drop of ~0 V while fumasep FBM, in the presence of a 14-unit pH gradient, has a measured potential drop of ~0.8 V (closely matching the thermodynamic junction potential E_j magnitude of 0.83 V) with 1 M base and acid on each side, respectively (not shown). In accord with predictions, the junction potential induced by the pH gradient across the BPM offsets the difference in potential between OER in base versus OER in acid (the key difference between the two systems examined).

According to Equation (2), the total cell potential can be determined using the OER, HER, and membrane potentials. These resultant performance curves are shown in Figure 4 (green dashed) for both systems, and are in excellent agreement with the measured overall cell potential curves (orange) for the pH gradient system (Figure 4a) and generally within 100 mV variance for the uniform pH system (Figure 4b). According to Equation (5), a cell involving a sustained pH gradient should have the same overall potential difference as a system that is operated at a uniform pH. The measured value of ~2.4 V is similar to that measured for the Nafion–acid system, demonstrating that a BPM maintaining a pH difference has the same overall potential difference requirements as a system employing a typical ion exchange membrane that operates at a uniform pH.

The flow of ions depicted in Figure 3a implies that the number of H⁺ and OH⁻ ions on each side will remain constant. A BPM that is not capable of water dissociation will not replenish the OH⁻ and H⁺ consumed by the electrode reactions, and a BPM that does not have ideal permselectivity will allow the counterions of the base and acid solutions (i.e., $\ensuremath{\mathsf{Na}^+}$ and ClO₄⁻, respectively) to carry a portion of the current, dissipating the pH gradient. The capability of maintaining a pH gradient was tested by passing 20 mA cm⁻² across fumasep FBM with the anode in 1 M NaOH and cathode in 1 M HClO₄ for a length of time required to convert the alkaline compartment to 1 m acid and the acidic compartment to 1 m base, respectively, if no mechanism were otherwise in place to maintain the pH difference (8.36 h, see Supporting Information). The water volume was replaced at the same rate as water was consumed, because water was the only overall reactant (Figure 3 a). No measurable pH change of the solutions was observed after the experiment, so the commercially available BPM was thus able to maintain a pH difference of 14 units while incorporated in a cell actively effecting water-splitting for a length of time where the pH gradient would have been entirely reversed with a regular ion-exchange membrane.

For efficient operation, the resistances in the cell must be minimized. An analysis of PEC-based conversion devices for hydrogen production indicates that losses should optimally be $< 2 \text{ V}.^{[13]}$ Systems that utilize membranes are subject to the additional potentials associated with the CEL, AEL, and interfacial layer, and thus will require additional optimization, but with the added benefits of material stability, effective separation of the product gases, and maintenance of pH gradients. Commercial BPMs, such as fumasep FBM, have been designed for use

in electrodialysis applications, whereas BPMs have only recently been considered for energy-related applications such as fuel cells.^[12] BPMs suitable for PEC-based systems will have yet additional constraints, such as optical transparency and electrical conductivity of the membrane (see Figure 1).

The challenges of optimization of the AEL/CEL are primarily associated with their ionic current resistance and membrane permselectivity. The state-of-the-art fuel cell membrane material, Nafion, has a pore structure that is permselective for cations, affording a large proton conductivity, and its perfluorinated structure forms a mechanically and chemically durable barrier to H₂ and O₂ crossover.^[14] Nafion is an attractive CEL for PEC conversion applications because it is transparent and solvent-processable, thereby permitting scaled-up manufacturing. Nafion can also be easily blended with materials such as conducting polymers to form composites and to thereby impart suitable electronic conductivity to the composite material.^[11]

A desirable AEL would possess qualities similar to Nafion, but would have facile hydroxide transport properties and permselectivity to anions. Current state-of-the-art materials often possess aromatic ring-containing polymers for stability, and quaternary ammonium groups for anion exchange.^[15] One such AEL candidate, fluorinated quaternary ammonium poly(arylene ether sulfone) (QAPSF), has been developed specifically for alkaline fuel cells,^[16] and has been applied as an anion-exchange membrane for PEC conversion by solution casting the material into arrays of silicon microwires.^[11] Given this material's transparency, high hydroxide conductivity, and stability, such AEL materials would seem to be well-suited for use in BPMs.

The interfacial layer of the BPM contains the potential drop (due to the pH gradient), overpotential for water dissociation catalysis, as well as resistance. The key features of the interfacial layer include the structure of the junction, the ion-exchange capacity, and the presence of a water dissociation catalyst.^[17] The interfacial layer must be thin enough to allow for adequate conductivity with minimal charge-carrier depletion. Additionally, a planar topography with a large degree of abruptness is desired to minimize the charge-separation distance, as in conventional solid-state semiconducting p-n junctions. Water molecules that enter the electric field in the interfacial layer must be rapidly oriented^[18] and dissociated into H⁺ and OH⁻ to facilitate migration through their respective ion-exchange layers. Inclusion of dissociable groups for ion-exchange capacity, not unlike those composing the AEL and CEL, have been found to increase the hydrophilicity of the interfacial region and therefore promote rapid water replacement while additionally favoring the reaction in Equation (1).^[19] Increasing the density of fixed charge groups in the interfacial layer also increases the local magnitude of the electric field, and therefore also enhances the polarization of water molecules.^[20]

Modern BPMs often incorporate catalysts to facilitate the dissociation of water. Table 1 presents a survey of recently disclosed interfacial layer materials. The figure of merit for application of BPMs in PEC conversion is E_{BPM} at the current density typically produced by appropriate band gap semiconductors exposed to the solar photon flux (20 mA cm⁻²). The E_{BPM} values in Table 1 are subject to significant variation due to inconsis
 Table 1. Literature survey of some recently studied BPM interfacial layer materials.

Material	Е _{врм} ^[а] (20 mA cm ⁻²) [V]	Ref.	
Neosepta BP-1 (Tokuyama Ltd.)	0.8	[21]	
No interfacial layer	6.4	[22]	
TiOH	5.7	[22]	
ZrOH	4.2	[22]	
SiOH	3.4	[22]	
S-PEEK 2.1 + poly(ferrocenyl dimethylsilane)	5.8	[17]	
S-PEEK 2.1 $+$ 2 wt % Fe(OH) ₃ (sol gel)	6.6	[17]	
S-PEEK 2.1 + 2-3 wt % Fe(OH) ₃ (electrodeposition)	2.8	[17]	
S-PEEK 2.1 + 80 nm poly(4-vinylpyridine)	1.5	[17]	
PEG-3400	2.3	[23]	
SPPO-poly(acrylamide) (6 % graft) ^[b]	< 0.5	[24]	
5 mM FeCl ₃ /5 g dm ⁻³ palygorskite composite ^(b)	0.5	[25]	
Boltorn H40 (1 mg mL ^{-1})	0.5	[26]	
(hyperbranched polyester molecules) ^(b)			
PVA-SA/TiO ₂ -ZnO-CS (irradiation) ^[c]	4.1	[27]	
PVA-CMC/nano-ZnO-CeO ₂ -CS (irradiation) ^[c]	3.7	[28]	
graphene oxide (2 mg mL $^{-1}$, 500 rpm)	1.1	[29]	
[a] Estimated from current-voltage curve figures with 2 M NaCl on both			

sides of BPM, except [b], [c] and [d]. [b] $0.5 \text{ M} \text{ Na}_2\text{SO}_4$ on both sides of BPM. [c] $1 \text{ M} \text{ Na}_2\text{SO}_4$ on both sides of BPM. [d] $1 \text{ M} \text{ Na}_2\text{SO}_4$ on both sides of BPM.

tencies in the reported CEL, AEL, fabrication, electrolyte composition, and experimental techniques. $E_{\rm BPM}$ values near the thermodynamic limit for water dissociation have been reported using commercial fumasep FBM and Neosepta BP-1^[21] BPMs, suggesting that the overpotential is minimal in these commercially available systems. The most impactful materials for efficient water dissociation to date are weak organic acids and bases, as well as metals and metal oxides, hydroxides, complexes, and minerals. It has also been recently demonstrated that a graphene oxide is a prime water dissociation catalyst for BPMs in electrodialysis applications.^[29]

Interfacial layers that contain organic acid and/or base groups are advantageous because these polymeric materials act as proton buffers and are typically processable, flexible, ionically conductive, and often transparent; hence they are well-suited to PEC applications. In addition, these charged groups serve as counterions in doped electrically conducting polymers,^[30] which may facilitate the incorporation of electronic conductivity into BPMs. Inorganic materials have also been investigated in Table 1 as components for the interfacial layer because such materials afford many surface sites to facilitate rapid water dissociation. However, the overpotential for water dissociation at these inorganic materials is larger than for materials that are purely organic, except for one membrane that utilized ferric chloride and palygorskite, a mineral containing aluminum, magnesium, and silicon.^[25] Larger overpotentials have been shown to be reduced through illumination of photoactive inorganic water-dissociation catalysts in BPMs.^[27, 28] If BPMs for PEC-based energy conversion are expected to suffer some losses due to parasitic light absorption by the water dissociation catalysts, this loss could in principle be recovered through utilization of such materials. Traditional transparent electrically conductive oxides, such as indium- or fluorinedoped tin oxide and aluminum-doped zinc oxide,^[31] may be well-suited for application as water dissociation catalysts for PEC conversion applications due to their optical transparency and electrical conductivity. Figure 5 depicts a structure for the incorporation of a BPM into the PEC conversion device shown in Figure 1, and includes examples of materials that should yield rapid water dissociation and charge transport.



Figure 5. A proposed PEC conversion configuration for hydrogen production using a BPM, where OH⁻ and H⁺ are consumed at the high-aspect-ratio photoanodes and photocathodes, respectively, and are replaced through water dissociation in the interfacial layer. The electrically insulating AEL faces the alkaline half cell and CEL faces the acidic half cell to attenuate crossover of co-ions through an electrically conductive interfacial layer. This layer is enlarged on the right, and shows a proposed composition of low-absorbance metallic compound particles (e.g., Al:ZnO) to dissociate water and conduct electrical current between photoelectrodes, and a polymeric base to attract water and facilitate proton transfer using, for example, poly(4-vinylpyridine), as reported in Table 1.

BPMs can allow for the sustained existence of a pH gradient for PEC-based solar-driven water-splitting applications without any overall thermodynamic penalty on the voltage required to drive the water-splitting process. The requirements for efficient BPMs are similar regardless of their application; however, the performance of a BPM in a PEC-based device will be dictated by a number of factors. As a BPM-based PEC device described herein has not yet been constructed or tested, the discerning issues associated with PEC cannot yet be proven solved. Critical design restraints for PEC-BPM include transparency and electronic conductivity. The AEL/CEL can in principle be composed of stable, permselective, transparent, and highly ionconductive Nafion-like materials that are processable. The materials to be included in the interfacial layer must accelerate the water dissociation kinetics and provide minimal resistance to ion transport. Water transport must be managed to allow sufficient hydration of the interfacial layer as water is consumed, yet not so much as to form an electrically insulating region. As such, future bipolar membranes for artificial photosynthesis will likely contain the best polymeric interfacial layer materials available for maintaining a well-hydrated, polarizing layer with catalysts imbedded to facilitate water dissociation. Catalytic, conductive inorganic compounds that are also transmissive may be promising, and photocatalysts may beneficially enhance water dissociation yet further.

Experimental Section

Materials: A fumasep FBM bipolar membrane was purchased from FuMA-Tech GmbH (Germany); platinum foil (99.9%, 0.025 mm

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thickness) was purchased from Sigma–Aldrich; and Ag conductive epoxy was purchased from MG Chemicals. Sodium hydroxide was purchased from Fisher Scientific and sodium perchlorate and perchloric acid (ca. 70%) were purchased from Sigma–Aldrich. All electrolytes were prepared as 1 μ solutions using distilled and ion exchanged water (18.2 M Ω cm) obtained from a Milli-Q Academic (model A10) water purifier.

4-electrode current-voltage measurements: Membrane potentials were evaluated by placing the membrane between two custom-made Pyrex half-cells filled with 30 mL of solution. Haber-Luggin capillaries were affixed 2.5 cm from the membrane. Two working (applied current) electrodes (ca. 4.5 cm² each) were constructed by attaching insulated wires to one side of the platinum foil using conductive Ag epoxy. The electrodes were then insulated using polyethylene from a hot glue gun. The assembled electrodes were positioned 8.5 cm from each side of the membrane. To ensure a leak-free seal, the membrane was clamped between each half-cell using a thin layer of drop-coated solubilized electrical tape on the cell flanges. Saturated calomel reference electrodes (SCE, CH Instruments) were placed in each Haber-Luggin chamber, and the reference electrodes were back-filled with the solution added to each side, to isolate the membrane potential measurement. Current was applied across the platinum electrodes and the membrane potential was measured between the reference electrodes. using a Solartron 1287 electrochemical interface. Galvanostatic steps were applied for 20 min each, and the measured potential was recorded as the final value at 20 min for each step. Some experiments were performed galvanodynamically at a scan rate of 0.2 mAs^{-1} . The current density was defined with respect to the geometric area (1.66 cm²) of the membrane that was exposed to the solution.

2- and 3-electrode current-voltage measurements: Individual electrode and overall cell potentials were evaluated using the same apparatus described above, but without the use of reference electrodes in the Haber-Luggin compartments. In this situation, the current density was defined by the area of the platinum electrodes. For 3-electrode measurements, the appropriate reference lead was connected to the working electrode, and the other reference lead was connected to a SCE reference electrode that was placed as close to the working electrode as possible. For 2-electrode measurements, the reference leads were connected to the appropriate working or counter electrode. Current was applied either galvano-dynamically (1 mAs⁻¹) or by galvanostatic steps (as described for 4-electrode measurements). The potential was measured across the points where the potentiostat leads were connected to the electrodes, and thus included all regions of the cell.

BPM pH-maintaining capability: An Electrolyser 5 (h-tec Wasserstoff-Energie-Systeme GmbH; Lübeck, Germany) apparatus was modified to replace the membrane to be examined. The original metal grate electrodes (16 cm² face, including vacancies) were modified by masking the backside of each grate to expose 21.5 cm² (including vacancy walls). Ca. 200 nm of platinum (210 mC cm^{-2}) was then galvanostatically (0.1 mA cm^{-2}) plated from an aqueous solution that contained 10 mMK₂PtCl₄ and 100 mм NaClO₄. A fumasep FBM BPM was then inserted between the electrode scaffold and was tightened between two Pyrex glass plates. Solution chambers (50 mL) were connected to feed 1 m NaOH(aq) and 1 M HClO₄(aq) to the anodic and cathodic sides, respectively. A current density of 20 mA cm⁻² (defined by the geometric membrane area in contact with the face of the electrodes, 16 cm²) was applied for 8.36 h (see below) by a Solartron 1287 electrochemical interface. Tubes connected to two syringes in a kd Scientific (model 230) syringe pump continually replaced the water consumed by the electrolysis cell (0.9 μ Lmin⁻¹×2 syringes) with de-ionized water to the solution chambers. The pH of each solution was measured before and after the experiment, using a sympHony (model SB90M5, VWR) pH electrode.

Acknowledgements

M.S.F. and M.B.M. acknowledge support by the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Canada Research Chair program, the Province of Manitoba's Science and Technology International Collaboration Fund, and the University of Manitoba. This research made use of the Manitoba Institute for Materials facility, which is supported by the Canada Foundation for Innovation (CFI), the Manitoba Research and Innovation Fund, and the University of Manitoba. N.S.L. and S.A. acknowledge support by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993. S.A. also acknowledges partial support from the United States Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE) Postdoctoral Research Award under the EERE Fuel Cell Technologies Program. We also acknowledge Nathan Craig, Adam Nielander, and Carl Koval for helpful discussions.

Keywords: artificial photosynthesis · bipolar membranes · earth-abundant materials · PEC membranes · pH gradients

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Received: April 11, 2014 Published online on September 22, 2014