Communication—Electrochemical Characterization of Commercial Bipolar Membranes under Electrolyte Conditions Relevant to Solar Fuels Technologies

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Water electrolysis using a catholyte and anolyte at different pH values requires a bipolar membrane to sustain the pH difference and 1.23 V to electrolyze water. Bipolar membranes that separated concentrated aqueous acid and base exhibited an open-circuit potential consistent with the Nernst equation and rapid transport of protons and hydroxide ions. When excess supporting electrolyte was added to both solutions the membrane potential was measured to be ~0 V, which suggested that water electrolysis occurred at <1.23 V and therefore, protons and hydroxide ions were not the majority ionic charge carriers.

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Monopolar ion-exchange membranes attenuate mixing of fuel species while bipolar ion-exchange membranes (BPMs) also attenuate mixing of ions. BPMs consist of a cation-exchange layer (CEL) and an anion-exchange layer (AEL), and sustain pH differences across the membrane even during the passage of large reverse-bias currents, where electric-field-enhanced water dissociation generates the majority of mobile ions (Figure 1).1 Each proton or hydroxide ion that migrates from (to) the CEL/AEL interfacial region is consumed (replenished) by proton-coupled-electron-transfer reactions at the electrodes. Differences in pH are useful for electrochemical technologies that incorporate materials that are inherently unstable in a single pH electrolyte.2

Ului, Zhou, and Kohl reported use of a BPM in a polymer-electrolyte-membrane H2/O2 fuel cell.3 The overall thermodynamic potential for water formation (i.e. H2 oxidation and O2 reduction; 1.23 V) remained the same as when a monopolar ion-exchange membrane was used. Mallouk and colleagues and Freund, Lewis, and colleagues independently demonstrated that this behavior also occurred when liquid electrolytes were used.4,5 They showed that BPMs wetted by aqueous acidic electrolyte on the CEL side and alkaline electrolyte on the AEL side supported and maintained pH differences across the membrane. In general, their reported theories and results were similar to those of Ului, Zhou, and Kohl; however, use of a liquid electrolyte allowed the potential difference across the membrane to be measured selectively using four-electrode electrochemical techniques,6 which are analogous to solid-state four-point-probe methods.7 The open-circuit (resting) potential measured across the membrane (E_{BPM}) when wetted by 1 M acid and base and using two saturated calomel electrodes (SCEs) was reported to be E_{BPM,SCE} ≈ 0.8 V,8 which is consistent with the value of 0.83 V calculated using a Nernst-like equation,

\[ E_{BPM,SCE} = \frac{RT}{nF} \ln \left( \frac{[H^+]_{AEL}}{[H^+]_{CEL}} \right) \approx \frac{2.303RT}{nF} \log \left( \frac{[H^+]_{AEL}}{[H^+]_{CEL}} \right) + 0.05916 \Delta pH \]

where R, T, n, F, [H^+], and ΔpH are the ideal gas constant (8.314 J/K), (room) temperature (298.15 K), charge of a proton 1, Faraday’s constant (96,485 C/mol), activity of protons in phase i, concentration of protons in phase i, and pH difference across the membrane, respectively. Using these data, and the redox potentials of the Nernstian half-reactions for water electrolysis (i.e. E_{H+/H2} = 0 V vs NHE and E_{O2/H2O/2} = +0.40 V vs NHE), the potential of the cell, E_{cell}, was calculated per the following equations.

\[ E_{cell} = -E_{ws} + E_{BPM,SCE} = -E_{H+/H2} + E_{O2/H2O/2} + E_{BPM,SCE} \]

\[ E_{BPM,SCE} = 1.23 V \]

where E_{ws} is the potential for water electrolysis.

Several studies have characterized BPMs wetted by aqueous acid on the CEL side and base on the AEL side.4,5,8,9 However, no studies have reported electrochemical behavior when additional supporting electrolyte was present. These experimental conditions are important because supporting electrolyte is likely necessary in solar fuels devices that utilize two different, but non-extreme, pH conditions, where the ionic strength is low. Data under these conditions, and our interpretations, are reported in this communication.

Experimental

All protocols have been reported previously in the literature,5,6 and are described in more detail in the Supplementary Information.

Results and Discussion

Shown in Figure 2a is the current density vs potential (J–E) behavior of a BPM wetted by concentrated aqueous acid on the CEL side and base on the AEL side, i.e. 1 M HCl/NaOH. The data obtained under reverse-bias conditions resembled that reported previously in the literature; E_{BPM,SCE} = 798 ± 5 mV using two SCEs, which is close to the value of ~0.83 V calculated using Equation 1.5,7 Assuming the BPM equilibrated with the liquid electrolytes, by definition the electrochemical potential difference across the membrane would be zero. Because E_{BPM,SCE} was non-zero, it suggests the SCEs do not sense the electrochemical potential difference and instead only sense the electric potential difference,3 which is equal in magnitude but opposite in sign to the chemical potential difference that is not being sensed. This same behavior underpins why pH can be measured across glass membranes and patch-clamp techniques measure electric potential differences across biological membranes.10,11

This was experimentally validated by measurements of E_{cell} using two reversible hydrogen electrodes (RHEs, i.e. Pt in contact with the
H$_2$/H$^+$ (aq) redox couple), where $E_{\text{BPM,SCE}}$ was measured to be $\sim 0$ V, consistent with zero difference in electrochemical potential across the membrane. Like SCEs, RHEs are sensitive to the electric potential difference, which was 798 mV ($E_{\text{BPM,SCE}}$); however, RHEs are also sensitive to the chemical potential of protons such that the chemical potential difference is equal to $-E_{\text{BPM,SCE}}$ and the sum of these potentials is zero, as observed experimentally.

Irrespective of the reference electrodes, biasing the membrane several hundred millivolts positive or negative of $E_{\text{BPM,SCE}}$ resulted in a nearly ohmic $J$–$E$ response with an area-specific resistance of $\sim 8.5$ Ohm-$cm^2$ from contributions of the membrane and two liquid electrolytes. This means that net transport of H$^+$ and OH$^-$ to the CEL/AEL interface and water formation (forward bias) and net water dissociation and transport of H$^+$ and OH$^-$ away from the CEL/AEL interface (reverse bias) are rapid and reversible processes.$^{12}$

The $J$–$E$ behavior of a BPM wetted by dilute aqueous acid on the CEL side and base on the AEL side, i.e. 10 mM HCl/NaOH, was similar to that of a BPM wetted by concentrated acid/base (Figure 2a, inset), except that the current was about two orders-of-magnitude smaller, with a forward-bias limiting current density ($j_{\text{lim}}$) $\approx -0.6$ mA/cm$^2$ vs $-50$ mA/cm$^2$ in concentrated acid/base. Moreover, $E_{\text{BPM,SCE}} = 555 \pm 8$ mV, which is close to the value of $-0.59$ V calculated using Equation 1, and is about four Nernstian shifts ($\sim 60$ mV) smaller than $E_{\text{BPM,SCE}}$ measured in concentrated acid/base. $E_{\text{app}} \approx -0.64$ V, calculated using Equations 2 and 3 and experimentally measured as $-0.69$ V using two three-electrode measurements; therefore, $E_{\text{cell}} = 1.23$ V, the minimum potential required to drive net water electrolysis.

The $J$–$E$ behavior of a BPM wetted by 1 M NaCl(aq) on both sides is displayed in Figure 2b and resembles that reported previously in the literature.$^{2-5}$ At membrane potentials between $-1.0$ V and $-0.8$ V the BPM rectified ionic current with $j_{\text{lim}} \approx 0.5$ mA/cm$^2$, which, typically arises from co-ion transport through the BPM (Figure 1), and its magnitude is a measure of the perselectivity of the ion-exchange layers.$^{1,6,13}$ Similar to Figure 2a, at reverse-bias potentials greater than $-0.8$ V the current increased with applied potential, which has been ascribed to an increase in the rate constant for water dissociation at the CEL/AEL interface, and therefore an increase in $K_w$, an increase in the equilibrium concentrations of H$^+$ and OH$^-$, and a decrease in the limiting resistance at the CEL/AEL interface.$^1$

The $J$–$E$ behavior of a BPM wetted by 10 mM HCl/NaOH, including 1 M NaCl on both sides, resembled that of a BPM in 1 M NaCl with $E_{\text{BPM,SCE}} \approx 0$ V (Figure 2b), and thus the chemical potential difference of protons across the membrane was not sensed. However, $E_{\text{app}} \approx -1.23$ V in 1 M NaCl whereas here $E_{\text{app}} \approx -0.64$ V, and therefore using Equation 3, $E_{\text{cell}} \approx 0.64$ V which violates the second law of thermodynamics! Of course, this cannot be the case. Instead, this implies that protons have not equilibrated across the BPM and that the electric potential is dictated primarily by other excess salt species. A similar situation occurs across biological membranes and can be calculated using the Goldman equation;$^{11}$ the electric potential difference generated from ions present at large concentrations dictates the direction for migration of ions present at small concentrations which remain far from the equilibrium. Notwithstanding, this suggests that water electrolysis can be driven at an applied bias potential of $\sim 0.64$ V but that the majority ions transported by the BPM are not protons and hydroxide ions, which must be transported for sustainable water electrolysis (see Supplementary Information). Like BPMs wetted by 1 M NaCl only, we hypothesize that supporting electrolyte is responsible for the ionic current until the potential difference at the CEL/AEL interface ($E_{\text{CEL/AEL}}$) $>$ $0.8$ V, where protons and hydroxide ions become the majority ionic charge carriers.$^1$ Calculations using Donnan theory for the NaCl only data and Goldman theory for the acid–base–salt data support that under initial open-circuit conditions, $E_{\text{CEL/AEL}} \ll 0.8$ V (see Supplementary Information).

**Summary**

The $J$–$E$ behavior of BPMs under conditions relevant to solar fuels devices was characterized. When 10 mM aqueous acid and base were used, $E_{\text{app}} \approx -0.64$ V and $E_{\text{BPM,SCE}}$ varied from 0.59 V to 0 V depending on the concentration of supporting electrolyte: therefore, $E_{\text{app}}$ ranged from 0.64 V to 1.23 V. Because it is thermodynamically impossible to electrolyze water at standard state when $E_{\text{app}} < 1.23$ V, net water dissociation must not accompany H$_2$ and O$_2$ evolution. While a holistic theory of the behavior of BPMs wetted by acid and

**Figure 1.** Scheme depicting directions of migration for each ion, under conditions of (a) forward bias ($E_{\text{app}} < 0$) and (b) large reverse bias ($E_{\text{app}} >> 0$), and where a thick arrow qualitatively indicates that the transport number of that ion(s) is large.

**Figure 2.** (a) $J$–$E$ behavior of BPMs wetted by HCl(aq) on the CEL side and NaOH(aq) on the AEL side: 1 M of each (red circles) and 10 mM of each (blue triangles). (b) $J$–$E$ behavior of BPMs wetted on both sides by 1 M NaCl(aq) with (green triangles) and without (orange squares) 10 mM HCl(aq) on the CEL side and 10 mM NaOH(aq) on the AEL side.
base is beyond the scope of this communication, these data and preliminary hypotheses suggest that care must be taken when interpreting experimental data for BPMs.

Acknowledgments

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