Understanding Transport at the Acid-Alkaline Interface of Bipolar Membranes

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The combination of cation exchange membrane (CEM) and anion exchange membrane (AEM) electrolytes to form a hybrid, or bipolar membrane (BPM) electrolyte, can have unique advantages for electrochemical systems including fuel cells, electrolysers, electrodialysis, and photovoltaic solar-to-fuel devices. However, a major challenge for this approach is the development of a stable and active interfacial region (i.e., junction) that adjoins the CEM and AEM layers. Moreover, a fundamental understanding of transport at the CEM-AEM interface is lacking. Therefore, the present study focuses on the theoretical development and analysis of the nature of the BPM interface. A Poisson-Nernst-Planck (PNP) theory is formalized and applied to a representative BPM interface. The findings are reported in terms of bias (i.e., overpotential) in a galvanic device with respect to CEM and AEM material requirements. Specific attention is paid to our interests in the application of the BPM to a fuel cell device with an acidic (CEM) anode and alkaline (AEM) cathode. We demonstrate that a BPM with an acidic CEM anode and alkaline AEM cathode must promote a trap-assisted type of recombination mechanism under forward bias. Without such a mechanism, large overpotentials are needed to drive ionic recombination processes.

Low temperature fuel cells have had difficulty in reaching the mass market despite promise as an efficient and scalable power source. Issues associated with costs, reliability, and ease of integration have made it difficult to disrupt established energy storage and conversion technologies. Fuel cell costs are often driven by the use of noble metal catalysts and fluorinated polymeric electrolytes. Numerous research groups exploit catalyst materials in search of methods to remove platinum (Pt) and other precious metal electrocatalysts from low temperature fuel cell systems. To their credit, Pt content in polymer electrolyte membrane hydrogen/air fuel cells have dropped from upwards of 5 mg/cm² in the 1980s to approximately 0.125–0.3 mg/cm² at present. Other portions of the research community have turned their attention from acidic polymer electrolytes, a type form of cation exchange membrane (CEM), to alkaline anion exchange membrane (AEM) materials.

The motivation for the move to AEM materials is the recognition that oxygen reduction reaction (ORR) can be performed without Pt-based electrocatalysts. However, the hydrogen and methanol oxidation reaction at an alkaline anion-catalyst interface can also experience a voltage penalty associated with specific adsorption of cationic groups and/or other intermediates. In addition to challenges with catalysts, a fuel cell system’s balance of plant (BoP) can turn a simple device into a complex system. The BoP, which is typically comprised of radiators or heat exchangers, humidifiers, flow regulators, and power conditioning components, can also contribute to challenges associated with a fuel cell system’s size, cost, and reliability.

The incorporation of a bipolar membrane (BPM) electrolyte may be one way to circumvent many challenges associated with low temperature fuel cells’ electrocatalyst costs and BoP. The BPM is a hybrid material, which adjoins a cation conducting CEM with an anion conducting AEM. This is shown for a fuel cell (or electrolyzer) in Fig. 1. In Fig. 1a, oxidation occurs at an acidic CEM electrode and reduction occurs at an alkaline AEM electrode so that hydrogen ions and hydroxide ions migrate to the CEM-AEM interface where they recombine. In Fig. 1b, the electrode reactions are reversed so that water is split into hydrogen and hydroxide ions at the CEM-AEM interface. The intent of the approach shown in Fig. 1a, a focus of the present study, is two-fold. First, an acidic (CEM) anode for hydrogen or methanol oxidation and an alkaline (AEM) cathode for oxygen reduction reactions are electrochemically favorable and require significantly less Pt-based catalysts. Second, there is promise for the approach to simplify the low temperature fuel cell system’s BoP, where components that perform water and fuel management operations may be minimized. There are numerous large components to (i) capture the water by-product and

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Figure 1. Bipolar membrane fuel cell employing a hybrid acid- and alkaline-membrane are shown. These include: (a) an acidic (CEM) anode and alkaline (AEM) cathode with water generated at the bipolar interface and (b) alkaline (AEM) anode and acidic (CEM) cathode with water split at the bipolar interface. Figures are shown for H₂/air.

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recycle it for diluting a concentrated liquid fuel, such as methanol, or (ii) humidify the fuel and oxidant streams such that the membrane electrolyte is sufficiently hydrated. The BPM approach shown in the Fig. 1a is intrinsically self-hydrating. The creation of a BPM junction (i.e., at CEM-AEM interface) close to the water-consuming cathode can reduce the need for active water management because water is being needed. While further system development efforts are needed, Kohl et al. have shown that hydrogen/oxygen fuel cells employing such a configuration operate most efficiently without any humidification of the fuel and/or oxidant.10,11

The history of BPM material systems date to discussions on weak acid and base solutions as chemical analogs to impurity-containing semiconductors by H. Reiss.12 J. Bockris clarified this perspective by noting the electrochemical requirements for such a configuration and demonstrated rectification-like behavior using acidic and alkaline polyelectrolytes.13 Since these early efforts, bipolar electrolytes have been examined for numerous processes and applications including electrodialysis, acid/base chemical production and purification, chlor-alkali electrolysis, analogous to biological systems, macromolecular systems.14–21–23 However, there have been relatively few attempts to extend this theory to implementation in fuel cell devices.24,25

In the present study, we explore the application of the hybrid acid-alkaline BPM to fuel cells. The theory formalized in this study is applicable to other BPM configurations and applications, making it more general than the present discussions. A consistent framework could be used to study interfacial phenomena in a wide range of electrochemical systems including electro-osmosis, colloids, electrodialysis, acid/base chemical production, chlor-alkali electrolysis, bioelectrochemical systems, and capacitive electrodes to name a few.14–20,26–28

The strength of the present model is that a consistent framework can be used for acid- and base-solutions with a consistent potential scale; making it straightforward to implement with other potential- and field-dependent analyses.

Nevertheless, the present effort focusses on the investigation of the BPM fuel cell configuration with an acidic anode and alkaline cathode (Fig. 1a), which has similarities to that of a semiconductor p-n junction under forward bias. For completeness, the reverse configuration (Fig. 1b) (i.e., alkaline anode and acidic cathode) is also considered with similarities to a p-n junction under reverse bias. Thermodynamic and transport theories are formalized for the examination of the BPM under equilibrium and non-equilibrium conditions. This includes a discussion on the thermodynamics associated with the formation of a bipolar junction and the corresponding built-in junction voltage. The theory governing the space charge region and ionic transport at the BPM interface under bias (overpotential) are discussed. And the reactive processes that result in ionic charge generation and recombination at the BPM interface are examined. We find that trap-like mechanisms are needed to provide a low-loss junction for galvanic currents typical of a fuel cell. Moreover, the BPM system discussed has unique constraints relative to a semiconductor device. This is supported using evidence in the published literature as well as some key figures of merit on what are seen as the most likely (contributing) factors to the rates of the recombination reactions that dictate the magnitude of the losses associated with the bipolar interface. Finally, fabrication approaches to tailor the acid-alkaline interface to further reduce losses associated with the BPM interface are discussed.

Theoretical Development

Junction thermodynamics at thermal equilibrium. —A thermodynamic approach is used to examine the effect of marrying an acidic CEM with an alkaline AEM, which provides relationships for the “built-in” or “junction” potential. This analysis is analogous to the thermodynamic relationships for a p-n junction in a semiconductor at thermal equilibrium. For simplicity, we use a hydrogen/oxygen (H₂/O₂) fuel cell, where the global reaction is well known.

\[ H_2 + \frac{1}{2} O_2 = H_2O \]  

[1]

The open circuit voltage (OCV), \( V_{OCV} \), may be calculated according to the change in Gibbs free energy, \( \Delta G_f \), for the overall reaction.

\[ nFV_{OCV} = -\Delta G_f \]  

[2]

Considering an acidic (CEM) anode and an alkaline (AEM) cathode, the electrochemical hydrogen oxidation reaction (HOR) and ORR are typical.

\[ H_2 \rightleftharpoons 2H^+ + 2e^- \]  

[3]

\[ \frac{1}{2} O_2 + H_2O + 2e^- \rightleftharpoons 2OH^- \]  

[4]

During fuel cell operation, the protons (H⁺) in a CEM migrate from the anode to the cathode and the hydroxide (OH⁻) in an AEM migrate from the cathode to the anode. Therefore it seems to reason that water will be formed in the vicinity of the junction in the bipolar configuration.

\[ 2H^+ + 2OH^- \rightleftharpoons 2H_2O \]  

[5]

The combination of protons and hydroxide at the junction not only makes intuitive sense, its inclusion yields the standard global reaction for the full fuel cell. This observation is important for two reasons. First, we have a stable system at steady-state operation. Second, there are no additional entropic terms from the application of the junction; we have the same global reaction and corresponding changes in enthalpy and free energy. This implies there shouldn’t be anomalous exothermic heating effects from the proton and hydroxide recombination (i.e., as would typically accompany the “mixing” of an acid and base in solution). Therefore, as Kohl et al. have shown experimentally, we have the same potential at open circuit.20 It is important to clarify that this does not imply there won’t be additional losses associated with the junction as we depart from equilibrium. For completeness, the interfacial reactions for four distinct H₂/O₂ fuel cell configurations are provided in Table I. These include the standard CEM- and AEM-based polymer electrolyte fuel cells, as well as the two bipolar membrane fuel cell configurations shown in Fig. 1.

To study the thermodynamics associated with the bipolar membrane we introduce a definition for the electrochemical potential \( \mu_i \) of species \( i \) in phase \( \alpha \), which is consistent with Bard and Faulkner.30

\[ \mu_i = \mu_i^0 + RT \ln (a_i^0) + \psi_i \]  

[6]

In this definition, the reference chemical potential, \( \mu_i^0 \), ionic activity \( a_i^0 \), and electrical potential of the phase/material in question \( \psi_i \) are used. The bar over electrochemical potential designates the difference between a chemical and electrochemical potentials.

To describe the BPM configurations shown in Fig. 1, we must describe the equilibrium process relating the protons and hydroxide ions to water.

\[ \mu_{{H^+}} + \mu_{OH^-} = \mu_{H_2O} \]  

[7]

If we expand the electrochemical potentials and note that the hydrogen proton is the predominant carrier in the CEM-phase and the hydroxide anion is the predominant carrier in the AEM-phase, we arrive at an expression for the junction potential.

\[ \mu_{{H^+}} + RT \ln (a_{{H^+}}^{CEM}) + F\psi_{{H^+}}^{CEM} + \mu_{{OH^-}} + RT \ln (a_{{OH^-}}^{AEM}) - F\psi_{{OH^-}}^{AEM} = \mu_{{H_2O}} + RT \ln (a_{{H_2O}}) \]  

[8]

This is a highly non-ideal system, where the potential differences between the phases are very large. The resulting calculation of this equilibrium process will yield a set of algebraic equations that can be solved for the unknown electrochemical potentials and chemical activities.
Recognizing that \( \mu_{an}^H + \mu_{OH}^O = \mu_{H,O}^O \), Eq. 8 may be simplified to a Nernst-like expression for the potential difference across the interface, referred to as a junction potential, \( V_j \), where \( a_{an}^j = \frac{K_w}{a_{H,O}} \).

\[
V_j = (\psi^{AEM} - \psi^{CEM}) = \frac{RT}{F} \cdot \ln \left( \frac{a_{H,O}^{CEM}}{a_{H,O}^{AEM}} \right)
\]

\[
= \frac{RT}{F} \cdot \ln \left( \frac{a_{H,O}^{CEM}}{a_{H,O}^{AEM}} \right) = \frac{RT}{F} \cdot \ln \left( \frac{a_{H,O}^{CEM}}{a_{H,O}^{AEM}} \right) [9]
\]

It should be noted that in our definition of Eq. 9, the junction potential was taken as \( \psi^{AEM} - \psi^{CEM} \). This is a sign specific designation which yields a positive junction potential value for the configuration shown in Fig 1a. The configuration shown in Fig 1b, is simply the negative of that which is derived in Eq. 9 (i.e. \( V_j = \psi^{CEM} - \psi^{AEM} \)). These expressions are consistent with the values provided in Table I.

To confirm this expression and demonstrate its generality, an entire fuel cell may be considered with the junction momentarily treated as a black box. For this exercise, we consider the configuration shown in Fig. 1a. The acidic HOR and alkaline ORR may be written using Eqs. 10 and 11.

\[
\mu_{H}^{an} = 2\mu_{H,O}^{an} + 2F\psi^{an} = 0 [10]
\]

\[
\frac{1}{2} \mu_{cat}^{an} - \mu_{H,O}^{an} + 2F\psi^{cat} + 2\mu_{OH}^{an} = 0 [11]
\]

A fuel cell’s voltage is dictated by the difference in electric potential (i.e., \( V = [\psi^{cat} - \psi^{an}] \)).

\[
2FV = 2F \left( \psi^{cat} - \psi^{an} \right) = \mu_{H}^{an} + \frac{1}{2} \mu_{cat}^{an} + \mu_{H,O}^{an} - 2\mu_{H}^{an} + \mu_{OH}^{an} - 2\mu_{H}^{an} + 2\mu_{OH}^{an} [12]
\]

Expanding the electrochemical potential terms and simplifying Eq. 12, an expression is obtained that relates the chemical potential of the fuel and oxidant processes at the junction.

\[
2FV = \mu_{H}^{an} + \frac{1}{2} \mu_{cat}^{an} + \mu_{H,O}^{an} - 2 \left( \mu_{H}^{an} + \mu_{OH}^{an} \right) + 2F \left( \psi^{cat} - \psi^{an} \right) [13]
\]

The last two groups of terms are equivalent to our previous derivation of the relation between potential, protons, hydroxide, and water at the junction.

\[
-2\mu_{H,O}^{an} = -2 \left( \mu_{H}^{an} + \mu_{OH}^{an} \right) + 2F \left( \psi^{cat} - \psi^{an} \right) [14]
\]

Substituting Eq. 14 into Eq. 13, an expression for analyzing the voltage in a H₂/O₂ fuel cell is found.

\[
2FV = \mu_{H}^{an} + \frac{1}{2} \mu_{cat}^{an} + \mu_{H,O}^{an} - 2\mu_{H,O}^{an} [15]
\]

This expression may be analyzed by equating the chemical potentials to the change in free energy within the system; effectively defining a Nernst equation.

\[
-2FV = \Delta G_j + RT \cdot \ln \left( \frac{a_{H,O}^{an} \cdot a_{H,O}^{cat} \cdot a_{H,O}^{j}}{a_{H,O}^{an}} \right) [16]
\]

Under equilibrium conditions, the chemical potential of water at the cathode can be assumed into the chemical potential of the water produced at the junction at equilibrium, yielding.

\[
2FV = \mu_{H}^{an} + \frac{1}{2} \mu_{cat}^{an} - \mu_{H,O}^{an} [17]
\]

and

\[
-2FV = \left( G_{H,O} + \frac{1}{2} G_{O_2} - G_{H,O} \right) + RT \cdot \ln \left( \frac{a_{H,O}^{an} \cdot a_{H,O}^{cat} \cdot a_{H,O}^{j}}{a_{H,O}^{an}} \right) [18]
\]

These expressions are equivalent to those for a H₂/O₂ fuel cell.

\[
2FV = \mu_{H}^{an} + \frac{1}{2} \mu_{cat}^{an} - \mu_{H,O}^{an} [19]
\]

Both of the approaches shown provide thermodynamic evidence that the potential difference arising from the bipolar junction satisfies the global reaction. From the perspective of calculating the cell potential, the junction potential may be considered additive to the typical definition, which is consistent for either configuration shown in Fig. 1.

\[
V = \psi^{cat} - \psi^{an} + V_j [20]
\]

It is also worth noting that there are alternative means by which we can show the validity of this expression. For example, the expressions shown in Eq. 8 and Eq. 9 are in effect a simple analysis of the Donnan potential difference between the membranes. Likewise, the Nernst-Planck equation at thermal equilibrium (i.e., zero current) yields a similar expression.29

**Thermal equilibrium & analogy to semiconductors.—**To access the characteristics of the mobile ionic species and intrinsic (electrostatic) or junction potentials, an analogy to intrinsic semiconductor
Figure 2. Band energy and carrier considerations of semiconductor materials. The semiconductor baseline serves as an analogy to the polyelectrolyte system.

\[ n = n_i \cdot \exp \left( \frac{q}{kT} (\psi - \psi_n) \right) \] [23]

\[ p = n_i \cdot \exp \left( \frac{q}{kT} (\psi_p - \psi) \right) \] [24]

As shown in Fig. 2, an \( n \)- or \( p \)-type material can be created by doping the semiconductor with donors and/or acceptors, respectively. When the semiconductor is doped, it skews the availability of mobile \( p \)- and \( n \)-carriers by introducing fixed ionized cores into the material. The doping effectively shifts the quasi-Fermi potential toward the conduction or valence band, and the equilibrium mobile electron and hole concentrations approach the corresponding doping number density (i.e., \( N_D \) and \( N_A \)).

In an \( n \)- or \( p \)-type semiconductor, the electron and hole concentrations are defined using the difference between the quasi-Fermi potentials for the electrons \( \psi_n \) and holes \( \psi_p \), as well as the electrostatic potential \( \psi \). The Fermi energies may also be mapped to the electrochemical potential \( \mu_i \left( = \frac{q}{kT} \psi \right) \):

\[ n = n_i \cdot \exp \left( \frac{q}{kT} (\psi - \psi_n) \right) \] [23]

\[ p = n_i \cdot \exp \left( \frac{q}{kT} (\psi_p - \psi) \right) \] [24]

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If a \( p \)-type semiconductor is placed in intimate contact with an \( n \)-type semiconductor, as shown in Fig. 3, an equilibration process takes place. An electrochemical potential difference between the (majority) mobile \( p \)- and \( n \)-type carriers (i.e., difference in the quasi-Fermi potential) exists when the materials are brought together. This potential difference drives the transport of mobile charge carriers near the interface. Mobile electrons and holes near the \( p-n \) interface recombine until the quasi-Fermi potential difference is nullified and the system reaches thermal equilibrium. At thermal equilibrium, the quasi-Fermi potentials for the \( n \) - and \( p \)-type carriers align to zero potential. However, this equilibration process also results in a local departure from electroneutrality near the \( p-n \) junction. A depletion, or space-charge, region is formed near the interface and there is
compensatory bending of the conduction and valence bands. The intrinsic energy, $E_i(-q\psi)$, which is related to the electrostatic potential $\psi$, results from this band bending. Moreover, an electrostatic potential difference and electric field across the space-charge region to compensate the departure from electroneutrality. This potential difference is the built-in voltage $V_{BI}$, and is dependent upon the band-gap and donor/acceptor concentrations in the respective materials.

$$V_{BI} = \frac{k_B T}{q} \ln \left( \frac{n_D}{n_p} \right) = \frac{k_B T}{q} \ln \left( \frac{p_n^0}{n_p^0} \right) = \frac{k_B T}{q} \ln \left( \frac{N_A N_D}{n_i^2} \right)$$

[25]

The variations in electrostatic potential and mobile carrier concentrations can also be calculated by solving Poisson’s equation, which requires the dielectric properties of the system, $\epsilon(=\epsilon_r\epsilon_0)$.

$$\frac{d}{dx} \left( \epsilon \frac{d\psi}{dx} \right) = -q \sum_i z_i n_i$$

$$= q \left( N_A - N_a + n_i \cdot \exp \left( \frac{q}{k_B T} (\psi_p - \psi) \right) - n_i \cdot \exp \left( \frac{q}{k_B T} (\psi_p - \phi_p) \right) \right)$$

[26]

This provides a Poisson-Boltzmann description of the $p-n$ interface, and its definition provides a convenient departure point for examining analogy to the electrolytic system.

The extension of the chemical physics associated with a semiconductor to an electrolytic system is not rigorous. The discrete size and mass of ions is different from the elementary charges in a semiconductor. And, the concentration and mobility of the mobile charge carriers present in electrolytes can be drastically different than those in semiconductors. Undoubtedly, certain phenomena which are observed with semiconductors are not likely to extend to electrolytic membranes and vice-versa. Nevertheless, many of the underlying descriptions of the systems are consistent from the perspective of thermodynamics and transport phenomena. The analogy to semiconductors provides a convenient framework for examining a membrane electrolyte system.

For the electrolytic system, we no longer have elementary charges relegated to a band structure. Nonetheless, the $H^+$ and $OH^-$ concentrations are intrinsically linked via the thermal water auto-ionization constant, $K_w$, where brackets are used to denote molar concentration.

$$[H^+] [OH^-] = K_w (T)$$

[27]

The $K_w$ provides an analog to the relationship between mobile hole and electron concentrations in the intrinsic semiconductor. However, unlike semiconductor materials, additional mobile ionic species may be able to participate; a prospect which is discussed in more detail later.

Within this framework, a quasi-Fermi (electrochemical) potential for the mobile ionic carriers may be defined by an excess electrochemical potential, $\mu_i^e$.

$$\mu_i^e = \mu_i^e(C, \psi) - \mu_i^e(C_i^0) = RT \cdot \ln \left( \frac{C_i}{C_i^0} \right) + \frac{z_i F \psi}{RT}$$

[28]

As is typical of thermodynamic systems, the excess electrochemical potential represents the difference between the actual electrochemical potential, $\bar{\mu}_i$, and that at defined state (e.g., an ideal system at equilibrium). We define this reference electrochemical potential $\mu_i^e$ as that of the neutral aqueous solution at thermal equilibrium and spatially separated from any space-charge inducing interfaces (i.e., $\bar{\mu}_i^e = f(C_i^0) = \sqrt{K_w} \cdot \psi (\psi = 0)$). The excess electrochemical potential defines the quasi-Fermi electrochemical potential of the mobile ionic species and therefore goes to zero for a system at thermal equilibrium.

$$[OH^-] = \sqrt{K_w} \cdot \exp \left[ \frac{1}{RT} (F \psi - \sqrt{K_w} \cdot \psi) \right]$$

[29]

$$[H^+] = \sqrt{K_w} \cdot \exp \left[ \frac{1}{RT} (\sqrt{K_w} \cdot \psi) \right]$$

[30]

The definition of the reference concentration and potential are critical to a proper treatment of the bipolar membrane. Other theories developed within the community, which are used for understanding a variety of electrochemical phenomena at interfaces, are built upon electrochemical potential definitions that reference the bulk electrolyte concentration. While the approaches used by these groups lead to more compact forms of Poisson-Boltzmann relationships (i.e., analytically solvable), it is not appropriate for the present study if we are to depart from equilibrium conditions.

The relationship between the mobile ionic species is highlighted in Fig. 4 for the application to polymer electrolyte membranes. At the most basic level, parallels between the intrinsic semiconductor in Fig. 2 and electrolyte solutions in Fig. 4 are straightforward. Whereas the bandgap and doping effectively dictate the balance between the available electron and hole carrier concentration in semiconductors, the water auto-ionization constant and concentration of the fixed ionic head-groups does so for polymer electrolytes. A typical CEM has fixed perflurosulfonic acid groups, which provide an acceptor-like behavior (i.e., donates excess hydrogen protons to the solution) whereas the AEM has fixed cationic groups (e.g., trimethylammonium) that provides donor like behavior (i.e., provides excess hydroxide to the solution). The acidic perflurosulfonic acid (-SO3H) and basic trimethylammonium (-TMA+) groups are used as general proxies for the respective ionic head-groups in this study with the ‘-‘ denoting the tether; however, other ionic groups are also prevalent. The tethered head-groups within the AEM and CEM can have a degree of flexibility due to mobility of the tether segment, which does not occur within a crystalline semiconductor. The balance between the $H^+$ and $OH^-$ carriers in both of these systems are still governed by the water constant $K_w$ (i.e., Eq. 27). In Fig. 4, the system shown assumes that the CEM and AEM polyelectrolyte materials are fully dissociated, which is not always the case. Nonetheless, this donor/acceptor behavior has a similar effect on the polyelectrolyte as it does in the semiconductor. The availability of the respective carriers are skewed and the quasi-Fermi electrochemical potential is pulled toward an acid or alkaline limit.

**Figure 4.** A polyelectrolyte system may be viewed from a similar carrier perspective as the semiconductor materials. Note: Brackets indicate molar concentration.
bipolar junction formation

\[ [H^+] \equiv [-SO_3]_{CEM} \quad [H^+] \equiv K_w/[TMA^+]_{AEM} \]

\[ \frac{\mu_F}{\mu^*_{H^+}} = \mu_i + RT \ln \left( \frac{[H^+]}{K_w} \right) \]

\[ \frac{\mu^*_{OH^-}}{\mu^*_{OH^+}} = \mu_i - RT \ln \left( \frac{[OH^-]}{[OH^+]} \right) \]

CEM

Proton

\[ \mu_i = q\psi \]

Hydroxide

AEM

\[ \frac{\mu^*_{H^+}}{\mu^*_{OH^+}} = \mu_i + RT \ln \left( \frac{[H^+]}{K_w} \right) \]

\[ \frac{\mu^*_{OH^-}}{\mu^*_{OH^+}} = \mu_i - RT \ln \left( \frac{[OH^-]}{[OH^+]} \right) \]

Figure 5. Formation of built-in, or junction potential, at thermal equilibrium in a bipolar membrane.

When the CEM and AEM material are brought into intimate contact, as shown in Fig. 5, a difference in the excess electrochemical potential of the (majority) mobile ionic species (i.e., quasi-Fermi electrochemical potential) results in a recombination process at the junction. During recombination, the excess electrochemical potentials drive toward zero and a depletion, or space charge, region forms. A built-in or junction voltage, \( V_j \), is formed in an analogous manner for the semiconductor interface (and as was also shown from a thermodynamic perspective in the Junction thermodynamics at thermal equilibrium section).

\[ V_j = \frac{RT}{F} \ln \left( \frac{[H^+]_{CEM}}{[H^+]_{AEM}} \right) = \frac{RT}{F} \ln \left( \frac{[OH^-]_{AEM}}{[H^+]_{CEM}} \right) \]

\[ \approx \frac{RT}{F} \ln \left( \frac{\alpha_{CEM}}{\alpha_{AEM}} \right) \]

[31]

With the mobile ionic species defined according to the excess electrochemical potentials, Poisson’s equation may also be defined to describe variations in electrostatic potential and mobile ionic species.

\[ \frac{d}{dx} \left( \epsilon \frac{d\psi}{dx} \right) = \rho_f - F \left( \sqrt{K_w} \cdot \exp \left[ \frac{1}{RT} \left( F\psi - \frac{\mu^*_{OH^-}}{K_w} \right) \right] \right. 

\left. - \sqrt{K_w} \cdot \exp \left[ \frac{1}{RT} \left( \mu^*_{H^+} - F\psi \right) \right] \right) \]

[32]

In Eq. 32, \( \rho_f \) is the local (signed) charge density associated with the fixed ionic head-groups in the CEM and AEM. This effectively represents a Poisson-Boltzmann formalism and provides a mean field description of a concentrated electrolytic system. The present study relies on the use of a Boltzmann distribution, which implicitly assumes point-like charges; a noted problem for electrolytic systems which have finite ion size and mass. Several research groups, have addressed this problem for electrochemical interfaces via variational approaches, which re-evaluates the system with additional entropic considerations (e.g., ion size) in the free-energy formulation.36-39,41-44 From this perspective, ionic specificity and steric effects on phenomena including dielectric decre-

ment, solvation, double-layer structure, and surface tension, among others, continue to be an area of active research.

Effects of carbon dioxide and carbonates.—AEM materials can undergo an exchange from OH\(^-\) to (bi)carbonate (CO\(_3^2-\), HCO\(_3^-\)) in the presence of carbon dioxide (CO\(_2\)). CO\(_2\) is present at about 400 ppm in ambient air and is also a by-product of many electrochemical oxidation reactions for carbon-containing fuels like methanol.

\[ H^+ + O H^- \rightarrow H_2O \]

[33]

\[ H^+ + H CO_3^- = CO_2 + H_2O \]

[34]

\[ 2H^+ + CO_3^- = CO_2 + H_2O \]

[35]

Because CO\(_2\) is soluble in the water which hydrates AEM materials, it has a direct path into the AEM and fuel cell.

This phenomena has been studied in some detail.45,46 The impact of CO\(_2\) on fuel cells and electrolysis devices is typically two-fold. First, the formation of (bi)carbons reduce the ionic conductivity of the AEM material. Second, the formation of (bi)carbonates can reduce the pH in the AEM materials. This drop in pH results in a thermodynamic loss; typically on the order of 200 mV at room temperature (i.e., 59 mV/decade in pH decrease) in ambient air. The CO\(_2\) solubility in water decreases with temperature. Elevated temperatures may be used to reduce the magnitude of such losses. Additional methods to separate and/or scrub CO\(_2\) from water can also be used. For example, in electrolyzers for the production of dry hydrogen gas, waste hydrated oxygen gas is also produced and it is used to purge the incoming water feed.

In the present study, the presence of CO\(_2\), CO\(_3^2-\), and HCO\(_3^-\) reduces the pH difference (i.e., OH\(^-\) activity) across the bipolar junction. This results in a lower equilibrium junction potential, as may be described with Eq. 9. Moreover, additional anions and recombination at the junction changes the problem because CO\(_2\) (or H\(_2\)CO\(_3\)) is produced in addition to H\(_2\)O. Therefore, the BPM system has mixed potentials and multiple mobile carriers (majority), which is a departure from the analogy of a traditional p-n junction. However, the framework is sufficiently robust to address this problem. The thermal auto-ionization properties of water remain valid and typical charge conservation principles still apply outside of the bipolar interface’s space charge region. Therefore, if we hypothesize that the CO\(_3^2-\) and HCO\(_3^-\) can also directly recombine with the H\(^+\), there is no loss in consistency. The liberation of CO\(_2\) at the junction will require further examination in future studies to ensure that the solvent does not become saturated and generate internal CO\(_2\) pressures (i.e., evolve gaseous CO\(_2\) internal to the membrane).

Transport equations.—Non-equilibrium processes must be considered and understood for the implementation of a BPM into a practical device. Figure 6 highlights the relationships in a BPM fuel cell employing an acidic anode at a potential negative of its potential of zero charge (PZC) and alkaline cathode at a potential positive of its PZC. At equilibrium, each electrochemical interface has a double-layer associated with the distinct phases and corresponding electrochemical potential differences. This double-layer is represented by charge accumulation across the interfaces (i.e., relative to point of zero charge, PZC). The double-layer results in an electric field as well as variations in electrical potential. The magnitude of the electric field and potential variations are dependent upon the polarizability (dielectric) of the media as well as the physical properties. However, as shown in Fig. 6, we are also interested in the response under galvanic conditions where a bias, or overpotential, is necessary for the recombination (or generation) of H\(^+\) and OH\(^-\) at the BPM interface.

Transport and continuity equations are necessary to analyze the system under bias. In semiconductor materials, the drift-diffusion equations are used in conjunction with Poisson’s equation (Eq. 26).

There are numerous treatises on this subject, which are not repeated here.33 In the electrolytic framework, a Nernst-Planck framework exists for describing transport in the CEM and AEM.
The Nernst-Planck transport equations provided in Eqs. 36–37 relate the mobile ionic current densities (shown for $H^+$ being conserved. It is found by summing that of the respective mobile carriers. The mechanisms and rates are discussed in more detail in the subsequent section; however, it suffices to say that they are a function of the local mobile ionic concentrations and quasi-Fermi-Fermi electrochemical potentials in the vicinity of the space charge region.

An interesting observation is made by introducing a bias (overpotential) and tracking its influence, whereby the product of the mobile carriers is scaled by the overpotential in the vicinity of the junction.

$$[H^+] \left[ OH^- \right] = K_w \cdot \exp \left( \frac{F \eta}{RT} \right) \quad [41]$$

This type of expression is shown analytically using Eqs. 29–30, and holds when the difference between the $H^+$ and $OH^-$ quasi-Fermi electrochemical potentials is equal to $F \eta$. Accordingly, Eq. 41 holds identically at the metallurgical junction (i.e., position of maximum charge recombination rate) and generally through much of the space charge regions. It provides a useful point of verification for the implementation of the numeric model.

Numerical solutions are needed to study the effects of bias on the BPM interface response. A bias, or overpotential $\eta$, must be applied to the coupled system of the transport, continuity, and Poisson’s equations. This is handled by applying the bias to the intrinsic (electrostatic) potential and the corresponding quasi-Fermi electrochemical potentials. It should occur at the boundary of the BPM junction at a location that is sufficiently far from the depletion region that the gradients of the electrostatic potential and mobile carrier concentrations effectively go to zero. Figure 7 highlights concentration, quasi-Fermi electrochemical potentials and intrinsic potentials in a BPM fuel cell of the type represented in Fig. 1a. Specifically, the potentials of a system at thermal equilibrium in Fig. 7b are contrasted with those in a system with a forward bias (overpotential) $\eta$ applied across the membrane in Fig. 7c. The bias reduces the electrostatic potential difference across the space charge region and introduces a difference between the quasi-Fermi electrochemical potentials. Far from the junction, these quasi-Fermi electrochemical potentials take on the same value. However, in the vicinity of the space-charge region, there is a difference between the quasi-Fermi electrochemical potentials which drives ionic recombination (or generation in a reverse bias scenario). To this effect, corresponding results predicted by the model for a symmetric bipolar membrane are also shown in Fig. 7. Disregarding the mechanism associated with ionic recombination, Fig. 7d provides model predictions for the fixed and mobile (carrier) ionic concentrations and Fig. 7e provides the corresponding potentials at thermal equilibrium for a bipolar membrane with symmetric fixed charge concentrations of 1.5 M and assuming comparable ionic diffusivities. These assumptions are not necessary within the model construct, but provide a simpler demonstration of the physical phenomena being described. Under forward bias, the model results in Fig. 7f shows a decrease of the electrostatic (intrinsic) potential within the material as well as bending of the $H^+$ and $OH^-$ quasi-Fermi potentials (shown on a voltage scale).

The theoretical formalism presented in this study is complementary to other Nernst-Planck based studies dealing with multicomponent transport in electrochemical systems, for example.26,28,45-47 In the present model, the coupling of Eq. 32 with Eqs. 39–40 provides additional fidelity via the (i) explicit coupling of the Nernst-Planck model to Poisson’s equation to account for space charge at interfaces, and (ii) use of the intrinsic concentration scale $K_w$ to consistently account for potential-based effects in acidic- and alkaline-media. As this present model transitions from the charged interfaces, local electroneutrality regains its validity. In this limit, when coupled with typical conservation principles, the model becomes equivalent with the noted studies (and numerous others) which utilize PNP formalism and/or a Nernst-Planck model in conjunction with a thermodynamic treatment (e.g., Donnan equilibrium, Henry’s law, etc.) of the interfaces.

Mechanisms of charge generation & recombination in the space-charge region.—To address the characteristics of the bipolar membrane interface, it is necessary to identify the mechanisms which participate in the ionic recombination and/or generation. There are significant differences between the polymer electrolytes forming the BPM and the semiconductor materials in the $p-n$ junction. Four of the most significant include the (i) type and mass of the mobile carriers, (ii) doping and fixed charge concentrations, (iii) diffusivity or mobility of the mobile carriers, and (iv) chain segment mobility of

![Figure 6. Interactions between the space-charge (relative to point of zero charge, PZC), electric-field, and electric potential in a bipolar membrane of the kind shown in Fig. 1a. The potential is shown at both thermal equilibrium (i.e., open circuit, or OCV), as well as with a galvanic current (e.g., in a fuel cell with faradaic current being produced).](image-url)
the head-groups in the AEM and CEM. There are severe implications of these deviations. The transition from elementary charge carriers to ions suggest that factors including the differences in momentum (mass), thermal motion (Brownian), steric (ionic radii), and chemical (solvation) aspects of the mobile charge carriers uniquely influence the respective systems. Moreover, polymer electrolytes support large fixation or diffusivity) tend to be much smaller than the elementary charges in semiconductors.

In an ideal p-n junction, minority charge injection dominates the charge transfer process (i.e., via low level injection), which is typically characterized by small band gaps as well as relatively large minority carrier lifetimes and diffusion lengths (i.e., relative to the depletion region widths). This scenario does not seem to hold for a p-n junction, minority charge injection dominates the charge transfer process (i.e., via low level injection), which is typically characterized by small band gaps as well as relatively large minority carrier lifetimes and diffusion lengths (i.e., relative to the depletion region widths). This scenario does not seem to hold for a BPM. The acid-base reactions $H^+ + OH^- \rightarrow H_2O$ are among the fastest known reactions in aqueous chemistry with a recombination (forward) rate constant of $k_{\text{recomb}} (= 1.3 \times 10^{11} M^{-1} s^{-1})$ and an equilibrium constant of $K_p$. The fast recombination process yields carrier lifetimes and diffusion lengths on the order of $\tau = 7 \times 10^{-12}$ s and $L_c = \sqrt{D\tau}$ = 0.3 nm for conditions that are typical of the polymer electrolytes in the BPM. The depletion layer widths may also be calculated for our system:

$$W_T = W_{CEM} + W_{AEM} = \frac{2 \varepsilon V_f}{F} \left( \frac{1}{[-SO_3]_{CEM}} + \frac{1}{[-TMA^+]_{AEM}} \right)$$

$$[-SO_3]_{CEM} \cdot W_{CEM} = [-TMA^+]_{AEM} \cdot W_{AEM}$$

Eq. 42–43 approximate the depletion layer widths by assuming that the space charge region is effectively depleted of mobile ionic charge carriers. It is an approximation, but provides a useful characteristic length. Our detailed transport model does not utilize such an approximation, and must be solved numerically. However, because the concentrations of the mobile ionic species is significantly depressed in the space charge region, the detailed model yields nearly identical values for the depletion layer width as those in Eq. 42–43. Values for the overall and relative depletion layer widths for a BPM at thermal equilibrium (i.e., $\eta \rightarrow 0$) are provided in Fig. 8. The fixed charge concentration scales reported in Fig. 8 are analogous to a volume-based ion exchange capacity. These values can be converted to the traditional mass-specific ion exchange capacity using corresponding membrane electrolyte density. Regardless of the scale used, it is apparent that the space-charge region is compact for the BPM as is typical of double-layers in condensed phases. This is due in large part to the head-group density within the AEM or CEM (i.e., fixed charge concentration).

It may be noted that the characteristic diffusion lengths for the mobile ionic charges is roughly an order of magnitude smaller than

Figure 7. Notional representation of the anticipated (a) charge distribution and (b) intrinsic (electrostatic) and quasi-Fermi potentials in a bipolar membrane at thermal equilibrium. Under (c) forward bias $\eta$, the intrinsic and quasi-Fermi (electrochemical) potentials are lowered resulting in differences between the $H^+$ and $OH^-$ quasi-Fermi electrochemical potentials. Predicted trends for equilibrium (d) charge distribution and (e) potentials, as well as (f) system under forward bias are also provided for reference.

Figure 8. Predicted (a) absolute and (b) relative depletion layer widths for the acid-alkaline interface as a function of the relative ion-exchange capacity (fixed charge) values for the CEM and AEM materials. Analysis assumes the interface is fully depleted and complete dissociation (ionization) of the respective fixed ionic groups. Surface plots are shown with the fixed charge concentrations spaced with a log distribution.
the calculated depletion layer widths. That is to say that the diffusive minority carrier (low-level) injection that is characteristic of an ideal p-n junction is not expected to be appreciable for our BPM interface. This is actually an encouraging observation for the use of BPM materials in electrochemical devices. Low-level injection at an ideal p-n junction is typically characterized by large biases to drive diffusion limited current. The small characteristic ionic diffusion length for the BPM (relative to the depletion layer width) is indicative that there are faster recombination processes at play which have lower losses.

As a result, our attention turns to an analogue of band-to-band recombination. From an intuitive standpoint, this mechanism is the most satisfying. It is characterized by the direct interaction of the mobile species as they traverse the space charge region. Effectively, this is a bimolecular acid-base reaction and may be viewed from the perspective of mass-action kinetics. Bimolecular reaction processes (Langevin) have been recognized as being significant in organic semiconducting materials when the characteristic carrier transport length is smaller than critical distance \( r_c = q^2/4\pi\epsilon_0kT \). The characteristic mobile carrier diffusion length is roughly an order of magnitude smaller than \( r_c \) for our BPM, substantiating its presence. The overall rate of recombination for a Langevin mechanism has been noted as being proportional to the transport coefficients for the mobile carriers.

\[
\dot{R}_{re} \approx \frac{F^2(D_{H^+} + D_{OH^-})}{\tau} \cdot \left\{ [H^+] [OH^-] - K_w \right\}
\]

It is interesting that an alternative expression for the bimolecular mechanism may be calculated according to the noted mass-action kinetics approach (i.e., via using the acid-base recombination rate constant, \( K_{recomb} \)).

\[
\dot{R}_{re} \approx F K_{recomb} \left\{ [H^+] [OH^-] - K_w \right\} = F K_{recomb} K_w \left\{ \exp \left( \frac{\mu_{H^+} - \mu_{OH^-}}{RT} \right) - 1 \right\}
\]

Evaluation of these rate expression reveals that the rate coefficient terms are identical; a product of the acid-base type reactions being responsible for this mechanism. The characteristic of many acid-base reactions terms are identical; a product of the acid-base type reactions being known as a Shockley-Read-Hall (SRH) trap-assisted recombination kinetics approach (i.e., via using the acid-base recombination rate mechanism may be calculated according to the noted mass-action kinetics approach (i.e., via using the acid-base recombination rate constant, \( K_{recomb} \)).

\[
\dot{R}_{re} = F K_{recomb} \left\{ \exp \left( \frac{\mu_{H^+} - \mu_{OH^-}}{RT} \right) - 1 \right\}
\]

Eq. 46 is a direct ionic analogy to the well-known SRH recombination rates. The concentrations of the protons and hydroxide when the quasi-Fermi potential correspond to that of the trap. We assume that the traps fall at the intrinsic energy level for this study (i.e., follow the electrostatic potential). Therefore, these concentrations take on that of the intrinsic system (i.e., \([H^+] = [OH^-] = \sqrt{K_{W}}\). The minority mobile ionic species life time values, \( \tau_{OH^-} \) and \( \tau_{H^+} \), also appear in Eq. 46. These values represent the mean lifetime of the respective mobile ionic species in the opposite membrane material (i.e., OH\(^-\) ions in the CEM). Accordingly, the lifetime is implicitly linked to the ion exchange capacity (IEC) via the concentration of the fixed ionic groups which we hypothesize can promote a trap-like behavior. We take the lifetime values to be that of the diffusion-limited acid-base reaction, \( \tau_{OH^-} \sim k_{recomb} [-SO_4^2^-]^{-1} \) \( \tau_{H^+} \sim k_{recomb} [-TMA]^+ \). As a point of reference, lifetimes c.a. \( \tau_{OH^-} = \tau_{H^+} = 7 \times 10^{-12} \) s correspond to a one molar system; however, we note that these lifetime values could be different for other systems including weak acids/bases and/or with other counterions. Implementing the discussed assumptions, and substituting Eqs. 29–30 into Eq. 46, we arrive at a trap-assisted recombination rate which corresponds to our dependent variables (i.e., \( \mu_{H^+}, \mu_{OH^-}, \text{and } \psi \)).

\[
\dot{R}_{re} = F \sqrt{K_w} \left\{ \exp \left( \frac{\mu_{H^+} - \mu_{OH^-}}{RT} \right) - 1 \right\}
\]

Prior to implementing such a mechanism, a critical question arises. Can such a mechanism be present in a system comprised of polymer electrolytes, whereby the discrepancies in the mass and thermal motion associated with the ionic species (i.e., relative to elementary charges) become significant? Specifically, are there centers within the BPM’s space charge region which can serve as de-facto traps for mobile ions? We speculate that dopants (i.e., fixed ionic charge groups) are persistent throughout the material and there are numerous additional heterogeneities due to the polymeric nature of the materials, phase segregation, and other material interfaces. However, is counterion condensation and/or the presence of other heterogeneities’ sufficient for promoting trap-like behavior? This issue will be discussed in further detail within our results.

The reverse bias case is not examined in detail within this study; however, some comments are merited. Under the conditions of reverse bias, as would be the case for an electronic device where water splitting occurs at the CEM-AEM interface, Fig. 1b, the issue is no longer relevant. Under the conditions of reverse bias, the other mechanisms described may still be participating in either the generation and/or recombination process; however, they are typically suppressed and do not significantly contribute to the reverse current.

**Numeric methods & solution procedures.** The described equations represent a set of coupled, non-linear ordinary differential equations, which take the form of a boundary value problem. Two methods were used to obtain solutions. The first method uses the boundary value problem solver in Matlab, which utilizes a colocation methodology.
Second, the identical equations were also programmed into and solved with COMSOL v.5.1, which uses a finite element methodology. The results were examined to ensure mesh independence and compared for verification purposes. All Matlab results were completed on a personal desktop computer (Dell T7500 with two Intel Xeon 2.67 GHz processors and 12 GB of RAM) while COMSOL results were generated on a single node of a Cray XC40. Results presented in this study were consistently taken from COMSOL.

Results and Discussion

The analysis of the BPM for fuel cell applications begins with predictions of the junction potential and depletion layer widths at thermal equilibrium. As may be inferred from Eq. 9 and described in Eqs. 42–43, both of these factors are dependent upon the fixed charge concentration of the respective polymer electrolytes. As noted in Table I, the nominal junction potential is on the order of 830 mV for typical acidic CEM and alkaline AEM materials at room temperature, when the activity of all the majority mobile ionic species equals unity. This corresponds to the standard potential difference between the HOR in acidic and alkaline media (vs. SHE, 25 °C). Given the Nernst-like nature of Eq. 9, reduction in either or both electrolyte concentration(s) (i.e., IEC) lowers the junction potential. This is a result of a reduction in ionic activity, but the effect is small considering typical IEC values for AEM and CEM materials. One of the items noted in the thermodynamic analysis of the CEM-AEM interface, Fig. 1, is that the interface is stable and there are no new or additional entropic terms relative to a standard fuel cell. This observation has also been reported experimentally, where stable open circuit voltage values were demonstrated in BPM fuel cells in both of the configurations highlighted in Fig. 1.29

The depletion layer widths shown in Fig. 8 were calculated with Eqs. 42 and 43. The depletion layer widths are shown as contour plots, with the CEM and AEM volume-specific IEC values independently varied and shown with log-spacing in Fig. 8. It is immediately apparent that the depletion layer width is extremely compact at typical IEC values, i.e. 4 to 10 nm. This is important because it highlights the relatively small region of the BPM which is responsible for ionic recombination or water splitting. By comparison, the size of conductive channels in a typical AEM or CEM are on the order of 2 to 20 nm and the length of the tether between the ionic head-group and the polymer backbone is on the order of 1 nm. The present study also assumes that the CEM and AEM employ strong acid and base head-groups, respectively. They were treated as being fully dissociated with a hydrated head-group and hydrated mobile conductive ion, but this need not be the case. A polymer electrolyte material where a weak acid or base head-group were used would result in a partially dissociated fixed ion head-group. Such a scenario would reduce the corresponding ionic activity (i.e., junction potential) as well as the unscreened head-group concentration (i.e., effective doping level) that establishes the depletion layer width.

The ion concentrations within the CEM-AEM depletion region are shown for two cases in Fig. 9, which provides the electrostatic potential Fig. 9a, electric-field Fig. 9b, space charge Fig. 9c, and mobile ion concentrations for a BPM which has been exposed to 400 ppm CO2 Fig. 9d as well as a CO2-free junction Fig. 9e. In Fig. 9, the red vertical lines depict the width of the depletion region according to Eqs. 42 and 43. They were calculated for the condition with ambient CO2 present, which are more compact than the CO2-free case (i.e., by approximately 10% because the pH difference between the two sides of the junction is lower with CO2). The agreement between the predictions from Eqs. 42 and 43 are apparent in Fig. 9c, which provides the space charge accumulation in the depletion region. The baseline properties used throughout this study consist of a system at standard ambient conditions (i.e., T = 300 K, P = 1 atm) with a relative dielectric permittivity εr(=35) as is typical of a strong electrolyte. More robust treatments which account for the large electric fields are available, such as Booth’s approach, but have minimal impact on the observed response.54 The fixed charge concentration of the CEM [−SO3]C,CM(=1.5 M) and AEM [−TMA+]A,AM(=1.5 M) as well as the proton DpH(=6.0×10−9 m2/s) and hydroxide ionic diffusivity DOH(=6.0×10−9 m2/s) values were used so as to provide...
symmetric properties across the BPM interface. These values deviate slightly from those which are expected for a real system; however, they simplify the interpretation of the results. This issue will be discussed in additional detail momentarily.

Two additional observations can be made regarding Fig. 9. The first is that the CO$_2$-free system exhibits an electrical potential difference, or junction potential, in excess of 800 mV. This junction potential is the result of the large electric field created by the depletion of mobile ionic charge and resulting charge separation for the head-groups within the space charge region. The theory is sufficiently robust to treat this scenario where ambient CO$_2$ (400 ppm) has equilibrated with the membrane and equilibrium between CO$_2$, HCO$_3^-$, CO$_3^{2-}$, and OH$^-$ has been achieved. As was previously noted, the difference in the junction potential (c.a. 200 mV) and electric field relative to the pristine case is a direct result of the suppression of the OH$^-$ concentration and activity in the AEM materials. The second observation in regard to Fig. 9 is the magnitude of the space charge and electric fields that are present within the depletion region. These extreme conditions are not unprecedented for electrochemical interfaces, such as electrode/electrolyte interfaces. However, they do play an important role and their influence extends beyond the voltage-current response of the BPM materials.

With an appreciation for the nature of the BPM system at thermal equilibrium, it is prudent to move to galvanic conditions. The primary focus of the present study is for a BPM fuel cell which employs an acidic anode and alkaline cathode as is shown in Fig. 1a. This is representative of forward-bias condition and implies that the bias, or overpotential, reduces the electrostatic potential across the junction. This decreases the electric field at the junction and causes the depletion region to narrow. Additional mobile ions enter the space charge region (Eq. 41) where they can recombine. The opposite is true of the reverse configuration, which would be representative of a galvanic device in the configuration shown in Fig. 1b. Operation in this configuration would involve a reverse bias condition, where the bias would increase the potential across the BPM junction, increase the electric field, and force water splitting to occur.

Focusing on the configuration in Fig. 1a, one of the interesting aspects of the theoretical approach is that it may be used to explore the effects of different mechanisms. We take this approach by exploring the differences between a system with bimolecular recombination processes relative to those involving a combined bimolecular and trap-assisted recombination processes. A sampling of results at different forward biases are shown in Fig. 10 and Fig. 11, respectively.

The bias reduces the potential difference across the bipolar junction, which in turn reduces the electric field and forms a more compact space charge region. As shown in Figs. 10a–10b and Figs. 11a–11b, these processes are nearly identical regardless of the recombination mechanism being considered. However, there is a dramatic difference in current density (c.a. three orders of magnitude) achieved for the BPM with the bimolecular, or mass action, based mechanism in Fig. 10c relative to that of the combined bimolecular and trap-assisted mechanism in Fig. 11c. The higher current density is the result of the differences in the net recombination rates between the mechanisms. This manifestation is especially apparent in the tails of the minority carrier concentration in Fig. 10d and Fig. 11d as well as the area between the H$^+$ and OH$^-$ quasi-Fermi electrochemical potential windows.

Both Fig. 10 and Fig. 11 considered the symmetric bipolar conditions noted at the beginning of the results and discussion. However,

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**Figure 10.** Predicted BPM response as a function of overpotential (i.e., forward bias) for the bimolecular, or mass-action-kinetic, recombination mechanism. Results include the (a) electrical potential, (b) electric field, (c) current density, (d) mobile carrier concentrations, (e) quasi-Fermi potentials on the voltage scale (e), and (f) volumetric ionic recombination rates.
we expect both the ionic diffusivity and fixed charge concentrations to be different in the CEM and AEM materials for a real system. From a heuristic perspective, the hydroxide and proton diffusivity values have a modest impact on the trap-assisted recombination rates. For example, a five-fold decrease in $D_{OHS}$ only changes the current response by a few percent. An asymmetric fixed charge concentrations, (e.g., considering $[-SO_{4}]_{CEM}(=1.5\ M)$ and $[-TMA^{+}]_{AEM}(=1.0\ M)$) increases the current by about 20% at a given overpotential. However, a lower ionic conductivity typically accompanies a lower fixed charge concentration. If we consider a concurrent decrease in $D_{i}$ (i.e., for the majority ionic species in the membrane with the reduced fixed charge concentration) the current response falls back to within 10% of the baseline (symmetric) case noted above. Both of these parameters will necessarily influence the membrane resistance and associated transport processes, which are not explicitly discussed. Different characteristics are likely to occur if the bimolecular recombination process is rate limiting. Reduced fixed charge concentrations can increase concentration of minority carriers within the space charge region and therefore the current response; however, care needs to be taken as the diffusivity values are also coefficients to the diffusion-limited bimolecular rate expression in Eq. 44.

In addition to the details shown in Fig. 10 and Fig. 11, simplified representations of the voltage-current characteristics are informative. For diodes, saturation equations are used to describe the behavior and can be used to simplify the representation of our system. An analogous expression may be used for the BPM using an exchange current density $i_{ex}$ in place of a saturation current.

$$i = i_{ex} \left[ \exp \left( \frac{\alpha_j F}{RT} \eta \right) - 1 \right]$$ [48]

Because we are dealing with an ionic system, a reaction symmetry factor $\alpha_j$ is included. This expression is typically valid for any forward bias as well as reverse biases up to some critical value. For example, it is not valid when dielectric breakdown occurs in semiconductors under extreme reverse bias. The same is true of the spontaneous splitting of water under large electric fields for galvanic devices. The current-voltage result at conditions consistent with Fig. 10 and Fig. 11 is shown in Fig. 12a, where the symbols represent the detailed PNP analysis and the lines correspond to Eq. 48. These results are shown on a semi-log and standard scale in Fig. 12a and Fig. 12b, respectively. While not shown, the expression also satisfactorily describes the reverse bias up to the aforementioned critical potential, which is characterized by very small reverse current densities that are typical of a diffusion limited system. The exchange current density and symmetry factors for the respective mechanisms are noted. The trap-assisted recombination mechanism has an exchange current density roughly 5 orders of magnitude larger than that of the bimolecular recombination. The difference in the losses associated with a BPM interface in a fuel cell for the respective mechanisms is readily apparent in Fig. 12b. The trapping mechanism yields reasonable overpotential values whereas those associated with the bimolecular mechanism are over-burdensome and will result in a low-current or inefficient device.

**Figure 11.** Predicted BPM response as a function of overpotential (i.e., forward bias) for the combined bimolecular and trap-assisted recombination mechanism. Results include the (a) electrical potential, (b) electric field, (c) current density, (d) mobile carrier concentrations, (e) quasi-Fermi potentials on the voltage scale, and (f) volumetric ionic recombination rates.

**Figure 12.** Analysis of the BPM current-voltage characteristics as a function of recombination mechanism, which compares the detailed PNP results (symbols) to the simple saturation model (lines) provided in Eq. 48. Results include a (a) semi-log plot as well as a (b) linear plot.
Both of the exchange current characteristics used in Fig. 12 may be improved by tailoring the BPM interface making the real surface area greater than the superficial area. For example, sub-micrometer electrospun polymer electrolyte fibers can provide acid-alkaline interfaces with significantly higher interfacial area than the nominal cell area. However, given the length scales of the depletion layer widths, the full interfacial area may not be active. This suggests that a realistic increase in CEM-AEM junction area needs to have a period which is greater than the depletion layer thickness.

This observation leads to the obvious question of what other materials-based modifications and/or structures may be used to further increase the current density at modest bias in a BPM-based device under galvanic conditions. Results from two concepts are provided in Figs. 13 with graphical representation of these materials configurations in Fig. 14. The exchange current density and symmetry factors for these studies are provided in Table II. The first concept is to reduce the doping level (i.e., lower the AEM and/or CEM IECs), as shown in Figs. 14a–14c. The second approach is to intermix regions of the CEM and AEM material, as shown in Figs. 14d–14e. This may be achieved through attaching both AEM and CEM head-groups to the polymer in the depletion region or co-electrospinning CEM and AEM materials. On the basis of these approaches, results for the combined trapping and bimolecular recombination processes are shown in Fig. 13a while those for the isolated bimolecular recombination processes are shown in Fig. 13b. Complementary linear scales are additionally provided in Fig. 13c and Fig. 13d, respectively.

Interestingly, Fig. 13 shows that a BPM interface employing the lowest fixed charge concentrations (i.e., 1/10 the baseline case), have the highest bimolecular recombination rate and current density at a given bias. On the other hand, the results for the combined bimolecular and trap assisted recombination processes only exhibit modest variations in current density at a given bias. The lower fixed ion concentrations will inherently influence the junction potential as well as...
the ionic conductivity, water transport, and accessibility of the fixed charges within these polymeric materials. It is beyond the scope of this work to explore the tradeoffs between all of these dependencies. Instead, we focus on their effect on the recombination processes. The lower fixed charge concentrations effectively increase the concentration of minority mobile ionic species, which is leading to the higher exchange current density values. One can envision a system with a thin BPM interface region employing polymer electrolyte materials with low IECs, sandwiched by more typical CEM and AEM materials. The question which arises is whether sufficient rates of ionic and water transport through a BPM interface with low IEC materials can be accomplished in a stable manner. Other intracellular catalysts and modifications can also be considered. Weak acid and base materials have been used at the BPM interface in commercial applications to produce acids and bases from salt solutions. These systems increase the minority carrier concentration and can improve interactions within the junction region. As noted in Table II, these types of approaches yield modest variations in the exchange current density for the trap-assisted recombination mechanism. However, the exchange current density for the bimolecular recombination mechanism increases by nearly an order of magnitude.

The results of the analysis provided in Fig. 13 are two-fold. First, this suggests that if the bimolecular recombination process is rate limiting, these types of approaches are needed in order to achieve a high-current BPM fuel cell device. Such an approach is less prudent if the trap-assisted mechanism is at play. The second is that we need to better understand which recombination mechanism(s) are rate-limiting for the BPM materials. The immediate question is whether a trap-assisted mechanism is practical for an ionic system? There are several important pieces of evidence which may be pointed to in order to suggest that such a mechanism is possible and rate limiting for this system.

One of the few existing efforts associated with understanding the recombination kinetics in a BPM fuel cell within the literature, was recently presented by Xiang and coworkers who utilized transition state theory (TST). Their study used TST with published experimental data to fit rate constants and examine transport in a BPM fuel cell. Several implicit assumptions were made in this study, including the use of Butler-Volmer kinetics to form the saturation current-voltage curve (i.e. similar to Eq. 48) and that the minority ionic concentrations in the entire space charge region are governed by Eq. 41, which has its own limitations. Nevertheless, examination of the exchange current densities predicted with this approach (c.a. 20 A/m²) support the values we predict with the use of the trap-assisted mechanism within the BPM.

Having already hypothesized that Coulombic interactions for the fixed charges and/or a counterion condensation process could promote a trap-assisted recombination mechanism, a comparison between the nature of the space charge region and bulk polymer electrolyte materials can be made. The characteristic lengths of physical processes within the vicinity of the acid-alkaline BPM junction are compared to those in the bulk membranes (i.e., away from any space charge effects). The Bjerrum length \( l_{Bjerrum} \) is often used is often used to calculate ionic association in chemical systems. It is attributed to Coulombic interactions between ions and defined related to the thermal energy \( k_B T \). Its values typically range which from about 0.7 nm at room temperature in pure liquid water to 1.6 nm for a typical CEM or AEM.

\[
l_{Bjerrum} = \frac{q^2}{4\pi k_B T \epsilon}
\]

A characteristic electric field length \( l_E \) may also be defined.

Within the bulk electrolyte, electric fields with magnitudes on the order of \( 10^3 \) V/m are typical which yield electric field length values on the order of \( 10^4 \) nm. However, as shown in the preceding figures, the magnitude of the electric fields can significantly exceed \( 10^7 \) V/m within the space charge region at the acid-alkaline BPM interface. This yields characteristic electric field length values on the order of \( 10^{-2} \) nm. By comparing the ratio of Eq. 49 and Eq. 50, it becomes apparent that different physical effects apply. The ratio \( \chi(= l_{Bjerrum}/l_E) \) tells us that the local Coulombic interactions play a different role in the space charge region than in bulk polymer electrolytes. Inspection shows that \( \chi \) ranges from 10 to 100 in the BPM's space charge region and \( 10^{-4} \) to \( 10^{-5} \) in the bulk electrolyte. This highlights the different role that local Coulombic interactions are playing within the space charge region. It is these unique characteristics which could facilitate a trap-like recombination mechanism as a direct result of a physical process similar to counterion condensation or local screening of the mobile ions.

With evidence of unique physical interactions in the space charge region, we next turn our attention to evidence within the published literature. The first is Nyquist plots from in situ electrochemical impedance spectroscopy (EIS) performed on BPM fuel cells at a variety of conditions. Several publications have shown consistent trends associated with the high frequency resistance (HFR) of BPM fuel cell membrane electrode assemblies (MEAs), which is typically associated with MEA resistance, across a range of humidification, stoichiometry, and operational conditions.(10,29) The fact that the HFR is consistent is indicative that the resistance within the MEA is constant/stable and that there is not an additional condition-dependent interfacial junction resistance. This does not preclude an intrinsic interfacial resistance, such as may occur from phase segregation or the presence of an interfacial film (e.g., from processing). The same Nyquist plots which show consistent HFR values, exhibit a charge transfer resistance that is on the order of 1 to 4 Ohm cm² depending upon the cell potential, humidification, and fuel/oxidant flow rate.(10,11,29,55) The reported in situ AC impedance spectra exhibited a single loop characteristic in these studies and do not show any diffusion limited tails, characteristic of a Warburg impedance element. While small cells were used in those studies (c.a. 2 cm³), the overall charge transfer resistance can be compared to those which would be caused by the recombination mechanisms discussed here. The exchange current densities for the trap-assisted recombination mechanism correspond to charge transfer resistances on the order of 1 Ohm cm² for a MEA of comparable size. Those which are characteristic of the bimolecular reaction process would be orders of magnitude larger. Given the magnitude of the

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Trapping + Bimolecular</th>
<th>Bimolecular Only</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( i_0 ) [A/m²]</td>
<td>( \alpha )</td>
</tr>
<tr>
<td>Abrupt: 1.5P/1.5A [M]</td>
<td>52.5</td>
<td>0.53</td>
</tr>
<tr>
<td>Abrupt: 0.75P/0.75A [M]</td>
<td>33.5</td>
<td>0.54</td>
</tr>
<tr>
<td>Abrupt: 0.15P/0.15A [M]</td>
<td>15.9</td>
<td>0.54</td>
</tr>
<tr>
<td>Mixed: 0.75P &amp; 0.75A (20 nm) [M]</td>
<td>33.5</td>
<td>0.54</td>
</tr>
<tr>
<td>Mixed: 0.15P &amp; 0.15A (20 nm) [M]</td>
<td>15.5</td>
<td>0.54</td>
</tr>
</tbody>
</table>
charge transfer resistance predicted for the respective recombination mechanisms, as well as the clear dependence of the experimentally reported EIS spectra do not exhibit distinct features for the electrode and junction processes. Undoubtedly, additional EIS study of these systems including a broader frequency range as well as the development of an impedance model for the BPM fuel cell are needed. However, the fact that the EIS spectra exhibit clear charge-transfer behavior and that the magnitude of the charge transfer resistances for a trap-assisted mechanisms are of the appropriate order of magnitude for these spectra (along with the electrode processes) provides compelling evidence that such a mechanism is rate limiting.

The final experimental evidence which suggests that a mechanism similar to the trap-assisted recombination mechanism is occurring within the BPM is the corresponding fuel cell voltage-current density characteristics which have been achieved. The current-voltage characteristics calculated for a BPM which is rate limited by a bimolecular (mass-action kinetics) recombination mechanism are simply not sufficient to generate the fuel cell current-voltage characteristics shown in these studies.

Conclusions

In conclusion, we have introduced a theoretical framework for addressing transport in BPM materials for fuel cell applications. The theoretical framework was developed in an analogous manner to the p-n junction in semiconductor devices, with major discrepancies between the systems being directly addressed. The most critical step in the development of this analogy-based model was the development of the Poisson's and the transport equations relative to the water auto ionization constant. Emphasis was placed on identification of a detailed mechanism associated with ionic recombination under forward bias (overpotential). The configuration is representative of a fuel cell device with an acidic anode, alkaline cathode, and water generated at the bipolar interface. Both a bimolecular mechanism, which is analogous to band-to-band recombination or mass-action kinetics, and a trap-assisted mechanism were identified as possible. Based on the analyses and associated rates, a trap-assisted recombination mechanism would be needed to produce a practical galvanic device such as a fuel cell device. On the basis of characteristic forces in the bulk electrolyte relative to the bipolar space charge region, it was argued that the Coulombic interactions between the mobile ionic species and the fixed ionic charges would promote such a mechanism through counterion condensation and/or screening processes. The presence of a low-loss mechanism is supported by a range of published experimental data, and based on the present findings, the response characteristics could only be explained by a mechanism similar to the trap-assisted process. Nonetheless, additional efforts are needed to better understand and explain these processes. Finally, several materials-based methods are needed to further reduce the losses associated with ionic recombination at the BPM interface.

Acknowledgments

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List of Symbols

\[ a \]
Chemical activity of species i [#]

\[ A \]
Area [m²]

\[ C_i \]
Molar concentration of species i [mol/m³]

\[ D_i \]
Diffusivity of species i [m²/s]

\[ E \]
Energy [eV]

\[ \bar{E} \]
Electric field [V/m]

\[ F \]
Faraday’s constant \( = 96485.333 \text{ C/mol} \)

\[ G \]
Gibbs free energy [J/mol]

\[ \Gamma \]
Current density [A/m²]

\[ \theta \]
Exchange current density [A/m²]

\[ k_{\text{recomb}} \]
Acid-base reaction rate [m³/mol/s]

\[ K_W \]
Water auto-ionization constant [mol²/m⁶]

\[ k_b \]
Boltzmann constant [J/K]

\[ l \]
Length [m]

\[ L \]
Characteristic diffusion length [m]

\[ n \]
Electron number density [#/m³]

\[ n_i \]
Intrinsic carrier number density [#/m³]

\[ N_D \]
Number density of donor, acceptor, or density of states [#/m³]

\[ N_A \]
Avogadro’s number = 6.022141 × 10²³ [#/mol]

\[ p \]
Hole number density [#/m³]

\[ \rho \]
Elementary charge \( = 1.602 \times 10^{-19} \text{ C} \)

\[ \rho \]
Universal gas constant \( = 8.3145 \text{ J/mol/K} \)

\[ R_i \]
Volumetric rate [m³/mol/s]

\[ T \]
Temperature [K]

\[ V \]
Voltage [V]

\[ W \]
Depletion layer width [m]

\[ x \]
Position [m]

\[ z \]
Charge number [#]

Greek

\[ \alpha \]
Electrochemical symmetry factor [#]

\[ \epsilon_{\text{o}} \]
Vacuum permittivity \( = 8.8542 \times 10^{-12} \text{ F/m} \)

\[ \epsilon_{\text{r}} \]
Medium specific relative permittivity [#]

\[ \varepsilon \]
Total dielectric permittivity \( = \epsilon_{\text{r}} \epsilon_{\text{o}} \) [F/m]

\[ \eta \]
Bias or overpotential [V]

\[ \mu_i \]
Chemical potential of species i [J]

\[ \nu_i \]
Electrochemical potential of species i [J]

\[ \nu_i^{\text{ex}} \]
Excess electrochemical potential of species i [J]

\[ \rho \]
Space charge density [C/m³]

\[ \sigma \]
Conductivity [S/m]

\[ \tau_i \]
Lifetime of carrier species i [s]

\[ \psi_i \]
Quasi-Fermi potential of species i [V]

\[ \chi \]
Ratio of characteristic lengths [#]

\[ \psi \]
Electric potential [V]

References


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