Supporting Information for

Evaluating the interfacial reaction kinetics of the bipolar membrane interface in the bipolar membrane fuel cell

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Experiment

Table S1 The physical properties of sQAPSF and Nafion membranes under room temperature.

<table>
<thead>
<tr>
<th>Properties</th>
<th>sQAPSF</th>
<th>Nafion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional group</td>
<td>-N+(CH₃)₃OH</td>
<td>-SO₃H</td>
</tr>
<tr>
<td>conductivity (σ, mS·cm⁻¹)</td>
<td>23.0</td>
<td>45.0</td>
</tr>
<tr>
<td>Swelling ratio (%)</td>
<td>3.00</td>
<td>23.0</td>
</tr>
<tr>
<td>IEC (mmol·g⁻¹)</td>
<td>1.34</td>
<td>0.90</td>
</tr>
<tr>
<td>density (ρ, g·cm⁻³)</td>
<td>1.10</td>
<td>1.87</td>
</tr>
</tbody>
</table>

The electrodes were made by a conventional thin hydrophilic electrode method consisting of painting a catalyst ink onto carbon paper. The ink for PEM (low-pH) electrode was prepared by mixing a Nafion solution (10 wt%), Pt/C catalyst (50 wt%, E-TEK), isopropyl alcohol, and pure water, while the ink for AEM (high-pH) electrode was a mixture of sQAPSF solution (2.0 wt%) and Pt/C catalyst (50 wt%, E-TEK). The inks were sonicated for 30 min and then cast onto Toray carbon paper (TGP-H-060) with gas diffusion layer and dried at 40 °C. The Pt loading for both PEM and AEM electrodes were 0.5 mg·cm⁻². Then, the AEM electrodes were immersed in aqueous 1.0 M KOH solution to exchange Cl⁻ into OH⁻ in the alkaline ionomer. Finally, 50 μL of sQAPSF solution (2.0 wt%) was sprayed onto the AEM electrodes and dried at 40 °C for 30 minutes. The BPMFC MEAs were assembled into two steps. First, the PEM electrode was hot pressed with pretreated Nafion 212 membrane at 135 °C and 4 MPa for 90 s. Then, the AEM electrode was pressed with as-synthesized MEA at room temperature and 4 MPa for 180 s.
Model description

Scheme S1 Schematic of the bipolar membrane interface.

**Diffusion current density (i_{diff})**

The width of depletion region on each side in the interface $^{1}$:

$$d_s = \frac{N_p d}{N_s + N_p},$$

$$d_p = \frac{N_s d}{N_s + N_p} \quad (S1)$$

At the PEM/SCR boundary ($x_p = -d_p$), the concentration of hydroxide ions and its variation can be expressed as:

$$c_{OH} (x_p) = c_{OH}^{PEM} \exp \left( \frac{q\eta}{kT} \right) \quad (S2)$$

$$\Delta c_{OH} (x_p) = c_{OH} (x_p) - c_{OH}^{PEM} \quad (S3)$$

In the same way, the concentration of proton and its variation at the SCR/AEM boundary ($x_s = d_s$) are:

$$c_H (x_s) = c_H^{AEM} \exp \left( \frac{q\eta}{kT} \right) \quad (S4)$$
\[ \Delta c_H (x_s) = c_H (x_s) - c_H^{EM} \]  
(S5)

The diffusion current density can be expressed as:

\[ i_{sd} = F \left[ D_{OH} \frac{\Delta c_{OH} (x_p)}{L_{OH}} + D_H \frac{\Delta c_H (x_s)}{L_H} \right] \]  
(S6)

where \( D_H, D_{OH} \) are the diffusion coefficients of proton and hydroxide ions in membranes, \( L_H, L_{OH} \) are the diffusion lengths. Moreover, the diffusion length \( L \) of \( H^+/OH^- \) is determined by the decay time (\( \tau \)) as \( L = \sqrt{D \tau} \). For the reaction (1) under the \( \varphi_{eq} \), the rate of water formation \( (\nu_f = k_f c_H^0 c_{OH}^0) \), \( k_f \) is rate constant for water formation) is equal to the rate of water dissociation \( (\nu_d^0) \). It assumed that the rate of water dissociation in the membranes hardly alters. Hence,

\[ \nu_d = \nu_d^0 = \nu_f \]  
(S7)

Then the net reaction rate \( (\nu) \) can be expressed as:

\[ \nu = \nu_f - \nu_d = k_f \left( c_H c_{OH} - c_H^0 c_{OH}^0 \right) \]  
(S8)

with \( c_H = c_H^0 + \Delta c_H \), \( c_{OH} = c_{OH}^0 + \Delta c_{OH} \) and \( \Delta c_H = \Delta c_{OH} \) according to the eletroneutral conditions. Thus the \( Eq. \) S8 can be derived into:

\[ \nu = k_f (c_H^0 + c_{OH}^0 + \Delta c_{OH}) \Delta c_{OH} = \frac{\Delta c_{OH}}{\tau} \]  
(S9)

with the decay time \( \tau = \frac{1}{k_f (c_H^0 + c_{OH}^0 + \Delta c_{OH})} \).

In the PEM, as \( c_H^0 >> c_{OH}^0, \Delta c_{OH} \) is valid, then the decay time of \( OH^- \) in PEM is:
\[ \tau_{PEM} = \frac{1}{k_f c^0_H} = \frac{1}{k_f c^{PEM}_H} \]  

In the AEM \( c^0_{OH} \gg c^0_H, \Delta c_H \) is valid, then the decay time of \( H^+ \) in AEM is:

\[ \tau_{AEM} = \frac{1}{k_f c^0_{OH}} = \frac{1}{k_f c^{AEM}_{OH}} \]  

Therefore, the diffusion lengths are obtained.

\[ L_{OH} = \sqrt{D_{OH} \tau_{PEM}}, \quad L_H = \sqrt{D_H \tau_{AEM}} \]  

Then the diffusion current density in the BPM interface can be obtained by combining the Eq. S3,S5,S6 and S10~S12, yielding:

\[ i_{diff} = F \sqrt{k_f} \left[ \exp \left( \frac{q \eta}{kT} \right) - 1 \right] \left[ \sqrt{D_{OH} c^0_{OH}} c^{PEM}_{OH} + \sqrt{D_H c^0_{OH}} c^{AEM}_H \right] \]  

Fig. S1 Calculated diffusion current according to Eq. S13 with parameters in Table S1.

Positive value for water formation and negative for water dissociation
### Table S2 Parameters used for simulation

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
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<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q$</td>
<td>$1.60 \times 10^{-19}$ C</td>
<td>$IEC_p$</td>
<td>0.90 mmol·g$^{-1}$</td>
</tr>
<tr>
<td>$k$</td>
<td>$1.38 \times 10^{-23}$ J·K$^{-1}$</td>
<td>$IEC_a$</td>
<td>1.34 mmol·g$^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>$8.85 \times 10^{-14}$ F·cm$^{-1}$</td>
<td>$\rho_p$</td>
<td>1.87 g·cm$^{-3}$</td>
</tr>
<tr>
<td>$N_A$</td>
<td>$6.02 \times 10^{23}$ mol$^{-1}$</td>
<td>$\rho_a$</td>
<td>1.10 g·cm$^{-3}$</td>
</tr>
<tr>
<td>$F$</td>
<td>96485 C·mol$^{-1}$</td>
<td>$D_H^a$</td>
<td>1.20 $\times 10^{-5}$ cm$^2$·s$^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>35$^1$</td>
<td>$D_{OH}^a$</td>
<td>6.13 $\times 10^{-6}$ cm$^2$·s$^{-1}$</td>
</tr>
<tr>
<td>$R$</td>
<td>8.314 J·K$^{-1}$·mol$^{-1}$</td>
<td>$c_{H^+}^{PEM}$</td>
<td>1.00 mol·L$^{-1}$</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>79.89 kJ·mol$^{-1}$</td>
<td>$c_{OH}^{ARM}$</td>
<td>1.00 mol·L$^{-1}$</td>
</tr>
<tr>
<td>$T$</td>
<td>298.15 K</td>
<td>$k_f^b$</td>
<td>8.00 $\times 10^{15}$ L·mol$^{-1}$·s$^{-1}$</td>
</tr>
</tbody>
</table>

$^a$ The diffusion coefficient $D$ was estimated using the conductivity ($\sigma$) of membranes through considering the molar conductivity ($\Lambda$) and the Einstein relationship. It expressed as $D = \frac{kT}{q_c F} \sigma$.

$^b$ The forward reaction constant $k_f$ was obtained by model fitting, which could be different with different membrane systems.

**Reaction current density ($i_{\text{react}}$)**
The forward and reverse reaction rates of reaction (1):

\[
v_f = A_f c_{\text{H}_2\text{O}} \exp\left(-\frac{E_f}{kT}\right) = k_f c_{\text{H}_2\text{O}} ,
\]

\[
v_d = A_d c_{\text{H}_2\text{O}} \exp\left(-\frac{E_d}{kT}\right) = k_d c_{\text{H}_2\text{O}}
\]

with \(A_f, A_d\) are the pre-exponential factors.

When the reaction system of reaction (1) is influenced by a potential difference \(\Delta \varphi\), the overall activation barriers and their dependence on the potential difference are derived based on the energy diagram shown in Fig. S2. Hence,

\[
E'_f = E_f + \alpha q \Delta \varphi ,
\]

\[
E'_d = E_d - (1 - \alpha) q \Delta \varphi
\]

where \(\alpha\) is the symmetry factor (transfer coefficient).

Then the reaction rate for forward and backward reactions and the net reaction rate are derived to be
\[
v_f = A_f c_{H_{2}O} \exp \left( -\frac{E_f}{kT} \right) = k_f c_{H_{2}O} \exp \left( -\frac{\varphi \Delta \varphi}{RT} \right),
\]

\[
v_d = A_d c_{H_{2}O} \exp \left( -\frac{E_d}{kT} \right) = k_d c_{H_{2}O} \exp \left[ \frac{(1 - \alpha) \varphi \Delta \varphi}{RT} \right]
\]

\[
v = v_f - v_d = k_f c_{H_{2}O} \exp \left( -\frac{\varphi \Delta \varphi}{RT} \right) - k_d c_{H_{2}O} \exp \left[ \frac{(1 - \alpha) \varphi \Delta \varphi}{RT} \right]
\]

In equilibrium, net reaction rate \( v \) is zero. That is, \( v_f = v_d \)

\[
\Delta \varphi_{eq} = \frac{RT}{F} \ln \frac{k_f c_{H_{2}O}}{k_d c_{H_{2}O}}
\]

Under standard equilibrium potential, the \( \Delta \varphi_{eq} = 0 \), thus

\[ k_d c_{H_{2}O} = k_f K_* \]

In the BPMFC, we can apply the interfacial overpotential, the activation overpotential \( \eta \) \((\eta = \Delta \varphi_{eq} - \Delta \varphi)\) rather than \( \Delta \varphi \). This is the “extra voltage” which drives the reaction current. In terms of overpotential, the reaction rate is

\[
v = k_f c_{H_{2}O} \exp \left( -\frac{\alpha F (\Delta \varphi_{eq} - \eta)}{RT} \right) - k_d c_{H_{2}O} \exp \left[ \frac{(1 - \alpha) F (\Delta \varphi_{eq} - \eta)}{RT} \right]
\]

Using Eq. S18, it yields

\[
v = k_f c_{H_{2}O} \frac{k_f c_{H_{2}O}}{k_d c_{H_{2}O}} \exp \left( -\frac{\alpha F \eta}{RT} \right) - k_d c_{H_{2}O} \frac{k_f c_{H_{2}O}}{k_d c_{H_{2}O}} \exp \left[ -\frac{(1 - \alpha) F \eta}{RT} \right]
\]

Then combining Eq. S19, Eq. S21 and \( c_{H_{2}O} = K_\omega \exp \left( \frac{\eta}{kT} \right) \) with the assumption for simplification that the water content in the BPM interface is saturated, thus
\[ v = K_\alpha k_f \exp\left(\frac{(1-\alpha)F\eta}{RT}\right)\exp\left(\frac{\alpha F\eta}{RT}\right) - \exp\left(-\frac{(1-\alpha)F\eta}{RT}\right) \]  
(S22)

Therefore,

\[ i_{rec} = Fvd = FdK_\alpha k_f \exp\left(\frac{(1-\alpha)F\eta}{RT}\right)\exp\left(\frac{\alpha F\eta}{RT}\right) - \exp\left(-\frac{(1-\alpha)F\eta}{RT}\right) \]  
(S23)

\[ i_{rec} = i_0 \exp\left(\frac{\alpha F\eta}{RT}\right) - \exp\left(-\frac{(1-\alpha)F\eta}{RT}\right) \] with: \[ i_0 = FdK_\alpha k_f \exp\left(\frac{(1-\alpha)F\eta}{RT}\right) \]

i.e. to the Eq. 2 in the main text.

Simulation

Fig. S3 (A) Polarization curves of a BPMFC by Ünlü et al. Cells comprised with a high-pH anode (Δ) or a high-pH cathode (□) with a Nafion 212 membrane at 50 °C. Solid symbols correspond to the power density. (B) Model fitted polarization curves calculated with Eq. 2 by replacing the parameters of AEM properties and temperature in Table S2 with that applied by Ünlü et al.. In this case, the \( k_f \) was estimated to be about 5.0 \times 10^{15} \text{ L \cdot mol}^{-1} \cdot \text{s}^{-1}.

Reference