

Supporting Information for

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

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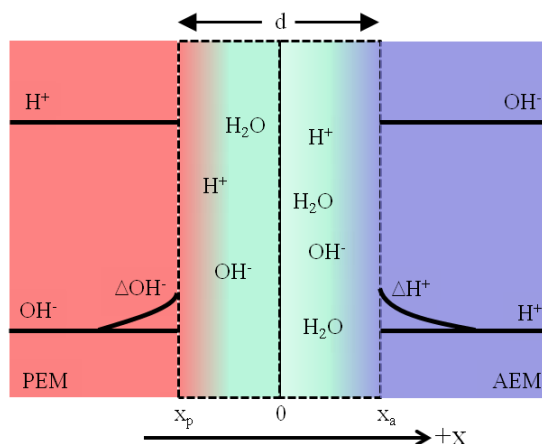
Experiment

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

Properties	sQAPSF	Nafion
Functional group	$-\text{N}^+(\text{CH}_3)_3\text{OH}^-$	$-\text{SO}_3\text{H}$
conductivity (σ , $\text{mS}\cdot\text{cm}^{-1}$)	23.0	45.0
Swelling ratio (%)	3.00	23.0
IEC ($\text{mmol}\cdot\text{g}^{-1}$)	1.34	0.90
density (ρ , $\text{g}\cdot\text{cm}^{-3}$)	1.10	1.87

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 $\text{mg}\cdot\text{cm}^{-2}$. 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_{dif})

The wide of depletion region on each side in the interface ¹:

$$d_a = \frac{N_p d}{N_a + N_p},$$

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

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 ($x_a = d_a$) are:

$$c_H(x_a) = c_H^{AEM} \exp\left(\frac{q\eta}{kT}\right) \quad (S4)$$

$$\Delta c_H (x_a) = c_H (x_a) - c_H^{AEM} \quad (S5)$$

The diffusion current density can be expressed as:

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

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 (τ) as $L = \sqrt{D\tau}$. For the reaction (1) under the φ_{eq} , the rate of water formation ($v_f^0 = k_f c_H^0 c_{OH}^0$, k_f is rate constant for water formation) is equal to the rate of water dissociation (v_d^0). It assumed that the rate of water dissociation in the membranes hardly alters. Hence,

$$v_d = v_d^0 = v_f^0 \quad (S7)$$

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

$$v = v_f - v_d = k_f (c_H c_{OH} - c_H^0 c_{OH}^0) \quad (S8)$$

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 electroneutral conditions. Thus the Eq. S8 can be derived into:

$$v = k_f (c_H^0 + c_{OH}^0 + \Delta c_{OH}) \Delta c_{OH} = \frac{\Delta c_{OH}}{\tau} \quad (S9)$$

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

In the PEM, as $c_H^0 \gg c_{OH}^0$, Δc_{OH} is valid, then the decay time of OH^- in PEM is:

$$\tau_{\text{PEM}} = \frac{1}{k_f c_H^0} = \frac{1}{k_f c_H^{\text{PEM}}} \quad (\text{S10})$$

In the AEM $c_{OH}^0 \gg c_H^0, \Delta c_H$ is valid, then the decay time of H^+ in AEM is:

$$\tau_{\text{AEM}} = \frac{1}{k_f c_{OH}^0} = \frac{1}{k_f c_{OH}^{\text{AEM}}} \quad (\text{S11})$$

Therefore, the diffusion lengths are obtained.

$$L_{OH} = \sqrt{D_{OH} \tau_{\text{PEM}}},$$

$$L_H = \sqrt{D_H \tau_{\text{AEM}}} \quad (\text{S12})$$

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

$$i_{\text{diff}} = F \sqrt{k_f} \left[\exp\left(\frac{q\eta}{kT}\right) - 1 \right] \left[\sqrt{D_{OH} c_H^{\text{PEM}} c_{OH}^{\text{PEM}}} + \sqrt{D_H c_{OH}^{\text{AEM}} c_H^{\text{AEM}}} \right] \quad (\text{S13})$$

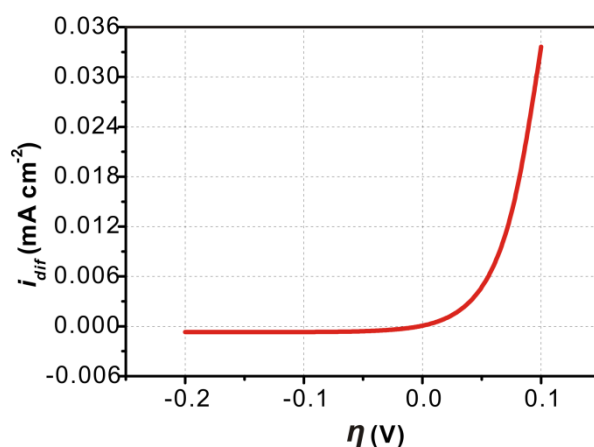


Fig. S1 Calculated diffusion current according to Eq. S13 with parameters in Table S1.

Positive value for water formation and negative for water dissociation

Table S2 Parameters used for simulation

Parameters	Value	Parameters	Value
q	$1.60 \times 10^{-19} \text{ C}$	IEC_p	$0.90 \text{ mmol} \cdot \text{g}^{-1}$
k	$1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$	IEC_a	$1.34 \text{ mmol} \cdot \text{g}^{-1}$
ε_0	$8.85 \times 10^{-14} \text{ F} \cdot \text{cm}^{-1}$	ρ_p	$1.87 \text{ g} \cdot \text{cm}^{-3}$
N_A	$6.02 \times 10^{23} \text{ mol}^{-1}$	ρ_a	$1.10 \text{ g} \cdot \text{cm}^{-3}$
F	$96485 \text{ C} \cdot \text{mol}^{-1}$	D_H^a	$1.20 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$
ε_r	35^1	D_{OH}^a	$6.13 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$
R	$8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	c_H^{PEM}	$1.00 \text{ mol} \cdot \text{L}^{-1}$
ΔG	$79.89 \text{ kJ} \cdot \text{mol}^{-1}$	c_{OH}^{AEM}	$1.00 \text{ mol} \cdot \text{L}^{-1}$
T	298.15 K	k_f^b	$8.00 \times 10^{15} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$

^aThe diffusion coefficient D was estimated using the conductivity (σ) of membranes through considering the molar conductivity (Λ) and the Einstein relationship. It

expressed as $D \approx \frac{kT}{qcF} \sigma$.

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

Reaction current density (i_{reac})

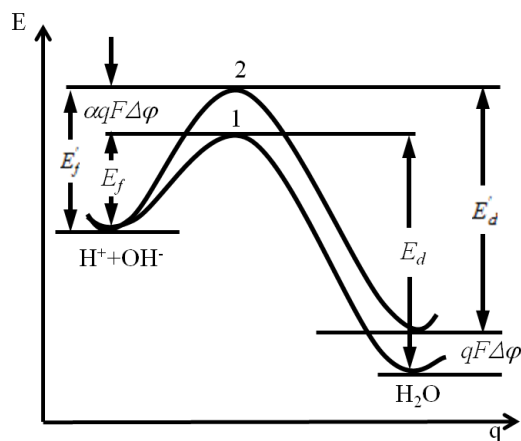


Fig. S2 Energy diagram of the water formation/dissociation reaction.

The forward and reverse reaction rates of reaction (1):

$$v_f = A_f c_H c_{OH} \exp\left(-\frac{E_f}{kT}\right) = k_f c_H c_{OH},$$

$$v_d = A_d c_{H_2O} \exp\left(-\frac{E_d}{kT}\right) = k_d c_{H_2O} \quad (\text{S14})$$

with A_f , A_d are the pre-exponential factors.

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

$$E_f^* = E_f + \alpha q \Delta \varphi,$$

$$E_d^* = E_d - (1 - \alpha) q \Delta \varphi \quad (\text{S15})$$

where α is the symmetry factor (transfer coefficient).

Then the reaction rate for forward and backward reactions and the net reaction rate are derived to be

$$v_f = A_f c_H c_{OH} \exp\left(-\frac{E_f'}{kT}\right) = k_f c_H c_{OH} \exp\left(-\frac{\alpha F \Delta \varphi}{RT}\right),$$

$$v_d = A_d c_{H_2O} \exp\left(-\frac{E_d'}{kT}\right) = k_d c_{H_2O} \exp\left[\frac{(1-\alpha)F \Delta \varphi}{RT}\right] \quad (\text{S16})$$

$$v = v_f - v_d = k_f c_H c_{OH} \exp\left(-\frac{\alpha F \Delta \varphi}{RT}\right) - k_d c_{H_2O} \exp\left[\frac{(1-\alpha)F \Delta \varphi}{RT}\right] \quad (\text{S17})$$

In equilibrium, net reaction rate v is zero. That is, $v_f = v_d$

$$\Delta \varphi_{eq} = \frac{RT}{F} \ln \frac{k_f c_H c_{OH}}{k_d c_{H_2O}} \quad (\text{S18})$$

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

$$k_d c_{H_2O} = k_f K_w \quad (\text{S19})$$

In the BPMFC, we can apply the interfacial overpotential, the activation overpotential

η ($\eta = \Delta \varphi_{eq} - \Delta \varphi$) rather than $\Delta \varphi$. This is the “extra voltage” which drives the

reaction current. In terms of overpotential, the reaction rate is

$$v = k_f c_H c_{OH} \exp\left[-\frac{\alpha F (\Delta \varphi_{eq} - \eta)}{RT}\right] - k_d c_{H_2O} \exp\left[\frac{(1-\alpha)F (\Delta \varphi_{eq} - \eta)}{RT}\right] \quad (\text{S20})$$

Using Eq. S18, it yields

$$v = k_f c_H c_{OH} \left(\frac{k_f c_H c_{OH}}{k_d c_{H_2O}}\right)^{-\alpha} \exp\left[\frac{\alpha F \eta}{RT}\right] - k_d c_{H_2O} \left(\frac{k_f c_H c_{OH}}{k_d c_{H_2O}}\right)^{1-\alpha} \exp\left[-\frac{(1-\alpha)F \eta}{RT}\right] \quad (\text{S21})$$

Then combining Eq. S19, Eq. S21 and $c_H c_{OH} = K_w \exp\left(\frac{q\eta}{kT}\right)$ with the assumption for

simplification that the water content in the BPM interface is saturated, thus

$$v = K_w k_f \exp\left[\frac{(1-\alpha)F\eta}{RT}\right] \left\{ \exp\left(\frac{\alpha F\eta}{RT}\right) - \exp\left[-\frac{(1-\alpha)F\eta}{RT}\right] \right\} \quad (\text{S22})$$

Therefore,

$$i_{\text{reac}} = Fvd = FdK_w k_f \exp\left[\frac{(1-\alpha)F\eta}{RT}\right] \left\{ \exp\left(\frac{\alpha F\eta}{RT}\right) - \exp\left[-\frac{(1-\alpha)F\eta}{RT}\right] \right\} \quad (\text{S23})$$

$$i_{\text{reac}} = i_0 \left\{ \exp\left(\frac{\alpha F\eta}{RT}\right) - \exp\left[-\frac{(1-\alpha)F\eta}{RT}\right] \right\} \quad \text{with: } i_0 = FdK_w k_f \exp\left[\frac{(1-\alpha)F\eta}{RT}\right]$$

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

Simulation

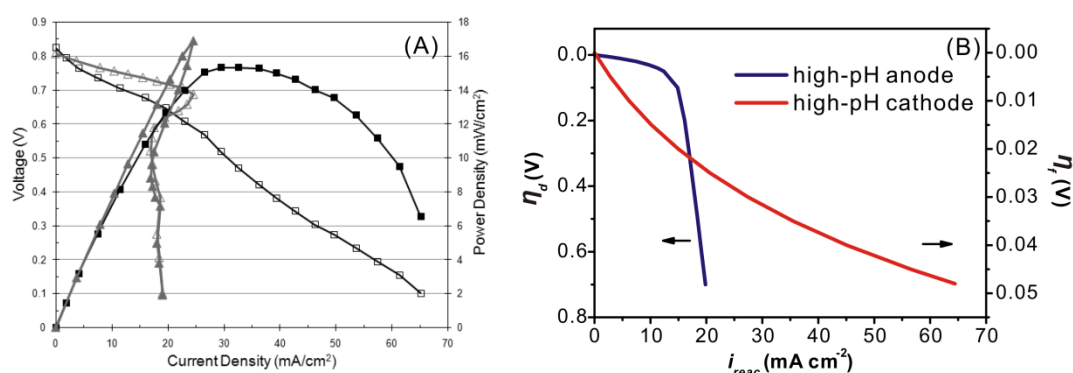


Fig. S3 (A) Polarization curves of a BPMFC by Ünlü *et al.*¹ Cells comprised with a high-pH anode (Δ) or a high-pH cathode (\square) with a Nafion 212 membrane at 50 °C. Solid symbols correspond to the power density. (B) Model fitted polarization curves calculated with Eq. 2 by replacing the parameters 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 $5.0 \times 10^{15} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$.

Reference

1. M. Ünlü, J. F. Zhou and P. A. Kohl, *Journal of Physical Chemistry C*, 2009, **113**, 11416-11423.