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Suppression of current-induced membrane discharge of bipolar membranes by regulating ion crossover transport

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ABSTRACT

Bipolar membranes (BPMs) exhibit the unique capability to regulate the operating environment of electrochemical system through the water dissociation-combination processes. However, the industrial utilization of BPMs is limited by instability and serious energy consumption. The current-induced membrane discharge (CIMD) at high-current conditions has a negative influence on the performance of anion-exchange membranes, but the underlying ion transport mechanisms in the BPMs remain unclear. Here, the CIMD-coupled Poisson-Nernst-Planck (PNP) equations are used to explore the ion transport mechanisms in the BPMs for both reverse bias and forward bias at neutral and acid-base conditions. It is demonstrated that the CIMD effect in the reverse-bias mode can be suppressed by enhancing the diffusive transport of salt counter-ions (Na^+ and Cl^-) into the BPMs, and that in the forward-bias mode with acid-base electrolytes can be suppressed by matching the transport rate of water counterions (H_3O^+ and OH^-). Suppressing the CIMD can promote the water dissociation in the reverse-bias mode, as well as overcome the plateau of limiting current density and reduce the interfacial blockage of salt coions (Cl⁻) in the anion-exchange layer in the forward-bias mode with acid-base electrolytes. Our work highlights the importance of regulating ion crossover transport on improving the performance of BPMs. © 2024 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by ELSEVIER B.V. and Science Press. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

1. Introduction

Bipolar membranes (BPMs) have been widely used in energy conversion technologies [1–3], such as water electrolysis for hydrogen production [4,5], fuel cells [6], acid-base flow batteries [7,8], electrochemical CO₂ reduction [9], and synthetic ammonia [10]. BPMs are typically composed of a cation exchange layer (CEL) and an anion exchange layer (AEL), and selectively transfer H₃O⁺ and OH⁻ through the water dissociation (WD) and recombination at the interface layer (IL) between CEL and AEL. Therefore, they can maintain different pH conditions on two sides of the BPMs and prevent the crossover of salt ions [11,12], promoting the kinetics of half-reactions and the selection of economically efficient catalysts [13–16]. Currently, most of the commercialized BPMs are developed for traditional electrodialysis processes with a working current density usually less than 100 mA cm⁻² [17,18]. However, industrial-scale application of BPMs is limited by the relatively and mechanical deformation [20,21] at large current densities. Some fabricating strategies have been proposed for solving the

high membrane resistance [19], co-ion leakage [12], delamination,

instability and high energy consumption of BPMs [22,23]. Xu et al. designed interlocked BPMs with the three-dimensional "mortisetenon joint" structure of the AEL-CEL interface, achieving a high current (1000 mA cm⁻²) in the electrochemical synthesis of ammonia [24]. Chen et al. illustrated the role of electronic conductivity of WD catalysts in screening and focusing the interfacial electric field, which can modulate the performance of BPMs [25]. Shehzad et al. employed a systematic catalyst shielding strategy to guide the design of new WD catalysts for the durable BPMs, which can operate stably under limiting current density (300–600 mA cm⁻²) [26]. These works highlight the importance of optimizing the interfacial structure and enhancing the electric field effect, and the key is to regulate ion transport mechanisms through the CEL, AEL, and AEL-CEL interface at practical operating conditions.

When the BPMs are operated at high current conditions, the amphoteric nature of the fixed charge in BPMs is highly sensitive to the local pH and electric field within the membrane, inducing the phenomenon of current-induced membrane discharge (CIMD)

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[27]. The CIMD is caused by the equilibrium reactions of membrane (de)protonation and water dissociation, resulting in the screening of partial fixed charges and the decrease in the conductivity of the BPMs [28]. For instance, using an electrochemical impedance spectroscopy, Blommaert et al. found that BPMs suffered from a 10% increase in ohmic resistance at an open-circuit voltage as well as a 32% increase in ohmic resistance at an operating current during the long-term operation of electrochemical cells [29]. The effective suppression of CIMD requires a deep understanding of the kinetic and transport processes of ions at the CEL, AEL, and AEL-CEL interface under high current conditions [30,31]. Lin et al. performed a one-dimensional (1D) continuum model to successfully investigate the electrochemical behavior in BPMs and emphasized the role of WD kinetics in BPMs [32]. Bui et al. revealed the significance of salt-ion crossover in the electrochemical performance, extending the understanding of ion transport processes in BPMs in the different electrolyte environments [33,34]. However, previous models defined the fixed charge of BPMs as a function of membrane spatial position, disregarding the influence of CIMD on the transmembrane ion transport. Incorporating the proton transfer reaction between the functional groups of BPMs and water molecules into the developed continuum model can explore the effects of different electrolyte environments and the membrane properties on CIMD, subsequently capturing the effect of CIMD on the electrochemical properties of BPMs at high current densities.

In this work, the CIMD-coupled PNP equations are performed to study the effect of CIMD on the current-voltage relation and underlying ion transport mechanisms under both reverse bias and forward bias of BPMs in neutral and acid-base solutions. We found that increasing the diffusive transport of salt counter-ions into the BPMs with the reverse-bias mode is favorable for the inhibition of CIMD to promote water dissociation. The current-voltage response of the BPMs with the forward-bias mode in acid-base electrolyte undergoes a plateau of limiting current density, which is related to the limitation of OH⁻ transport at the interface layer and the blockage of salt co-ions. Matching the transport rate of water counter-ions (H_3O^+ and OH^-) into BPMs can reduce the membrane potential and lower the energy consumption. The work

provides theoretical insights into suppressing the CIMD from the perspectives of electrolyte composition and membrane functional groups to improve the electrochemical performance of BPMs.

2. Model and methods

2.1. Model description

The four-electrode experimental setup can capture the electrostatic potential of BPMs and decouple the transmembrane potential drop from the electrode surface reaction kinetics. Previous studies typically considered a computational domain containing two reference electrodes. As shown in Fig. 1, on the two sides of the diffusion layer, different electrolyte environments are considered, including the neutral electrolyte (NaCl/NaCl solution) and the acid-base electrolyte (HCl/NaOH solution). The voltage is set to 0 V at the leftmost side of the diffusion laver near the CEL and a membrane voltage (E_{Mem}) is applied at the rightmost side of the diffusion layer near the AEL. The direction of current from right to the left is specified to be positive, indicating that the BPMs are in the reverse-bias mode, accompanied by the interfacial WD reaction to produce H_3O^+ and OH^- ions moving from the interface to bulk. When the BPMs are in forward-bias mode, the H_3O^+ and OH^- ions move from bulk to the interface to undergo the interfacial waterrecombination reaction. The effect of the interfacial electric field and the catalyst on the water dissociation-recombination reaction is considered in the model. Furthermore, we incorporated proton transfer reactions between membrane surface groups and water molecules to consider the effect of CIMD on the amphoteric nature of the BPMs. Furthermore, some necessary assumptions are included in the model, as shown in Table S1. The equations and references are given to facilitate the subsequent development of the model and to ensure the interchangeability of the corresponding equations.

2.2. Poisson-Nernst-Planck (PNP) equations

The PNP-based equations are used to solve the coupling processes of diffusion, migration, water transport, and reactions in



Fig. 1. Schematic of the mass transport of solution species within bipolar membranes under forward bias and reverse bias. The diffusion layer (20 μm), cation exchange layer (80 μm), anion exchange layer (80 μm), and interfacial layer (2 nm) are included in the continuum model of BPMs.

the model of BPMs self-consistently. The general equation for the mass conservation is expressed as

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot J_i + \sum R_i \tag{1}$$

where c_i is the concentration of the solution species (H₃O⁺, OH⁻, Na⁺, and Cl⁻), and R_i is the rate of reaction of species *i*. The flux J_i of solution species *i* within the solution is given by the following constitutive equation

$$J_{i} = -D_{i}\nabla c_{i} - \frac{D_{i}z_{i}Fc_{i}}{RT}\nabla\phi + \frac{D_{i}c_{i}}{c_{H_{2}O}}\nabla c_{H_{2}O} - \frac{D_{i}c_{i}}{\gamma_{E}}\nabla\gamma_{E}$$
(2)

Here, D_i , c_i , and z_i are the diffusion coefficient, the concentration, and the charge valency. The correction approach of diffusion coefficient within the ionomer can be found in Section S1. In addition, *F*, *R*, and *T* represent the Faraday constant, gas constant, and absolute temperature, respectively. The γ_E is the electric-field dependent activity coefficient, maintaining thermodynamic consistency, expressed by

$$\gamma_E = \left(\frac{f_{\rm E,-1}}{f_{\rm E,1}}\right)^{0.5} \tag{3}$$

Here, $f_{\rm E,1}$ and $f_{\rm E,-1}$ are the correction coefficient of electric field on water dissociation-combination reactions (details in Fig. S1). The concentration of water is expressed by

$$c_{\rm H_2O}(x) = \frac{c_{\rm H_2O,0}}{2} \left(2 - \tanh\left(\frac{x - x_1}{L_{\rm char}}\right) + \tanh\left(\frac{x - x_4}{L_{\rm char}}\right) \right) \\ + \frac{c_{\rm H_2O,m}}{2} \left(\tanh\left(\frac{x - x_1}{L_{\rm char}}\right) - \tanh\left(\frac{x - x_4}{L_{\rm char}}\right) \right)$$
(4)

where $c_{\rm H_2O,0}$ is the concentration of water in bulk solution (55.56 M), $L_{\rm char}$ = 0.58 nm is the characteristic bond length for water dissociation [33,34], and $c_{\rm H_2O,m}$ is the concentration of water in membranes.

$$c_{\rm H_2O,m} = \lambda c_{\rm fix} \tag{5}$$

Here, λ is the water content, which is a function of the concentrations of H₃O⁺ and OH⁻ ions (Eqs. (S6) and (S7)), and c_{fix} is the fixed charge concentration in the BPMs, whose initial concentration is expressed as

$$c_{\text{fix},0}(x) = \frac{\rho_{\text{Mwet}} \times \text{IEC}}{2} \left(\tanh\left(\frac{x-x_3}{L_{\text{char}}}\right) - \tanh\left(\frac{x-x_4}{L_{\text{char}}}\right) + \tanh\left(\frac{x-x_2}{L_{\text{char}}}\right) - \tanh\left(\frac{x-x_1}{L_{\text{char}}}\right) \right)$$
(6)

The electrostatic potential ϕ satisfies the Poisson equation

$$\nabla \cdot (\varepsilon_0 \varepsilon_r \nabla \phi) = -F\left(\sum_{i=1}^n z_i c_i + c_{\text{fix}}\right)$$
(7)

where ε_0 is the permittivity of vacuum and ε_r is the relative permittivity of water.

2.3. CIMD mechanism

The proton transfer reaction between functional groups and water molecules induced by changes in ion concentration and pH in the membrane at high currents is the origin of CIMD. The fixed functional groups and water molecules in the CEL are expressed as [35–38]

$$A^{-} + H_2 O \stackrel{k_{f/r}^1}{\leftrightarrow} AH + OH^{-}$$
(8)

$$AH + H_2 O \stackrel{k_{\it f/r}^2}{\leftrightarrow} A^- + H_3 O^+ \tag{9}$$

where AH is a neutral acid, such as sulfo group $-SO_3H$, and $c_{A^-} + c_{AH} = c_{fix,0}$. In the AEL,

$$\mathbf{B} + \mathbf{H}_2 \mathbf{O} \stackrel{k_{f/r}^r}{\leftrightarrow} \mathbf{B} \mathbf{H}^+ + \mathbf{O} \mathbf{H}^- \tag{10}$$

$$\mathbf{B}\mathbf{H}^{+} + \mathbf{H}_{2}\mathbf{O} \stackrel{k_{J/r}^{\ell}}{\leftrightarrow} \mathbf{B} + \mathbf{H}_{3}\mathbf{O}^{+}$$
(11)

where B is a neutral base, such as secondary amine $-NH_2$, and $c_B + c_{BH^+} = c_{fix,0}$.

2.4. Interfacial water dissociation and recombination

An improved micro-kinetic model for field-enhanced water dissociation and recombination was proposed by Bui et al. [34], which includes three pathways. The first type is called the "direct" pathway.

$$2H_2O \stackrel{\kappa_{f/r}}{\leftrightarrow} H_3O^+ + OH^-$$
(12)

The second type is the "acidic" pathway where active sites are more likely to react with water molecules in acidic environments.

$$H_2O + s - OH \stackrel{k_{f/r}^{o}}{\leftrightarrow} s - OH_2^+ + OH^-$$
(13)

$$H_2O + s - OH_2^+ \stackrel{k_{\mathcal{I}r}^{dr}}{\leftrightarrow} s - OH + H_3O^+$$
(14)

To characterize WD catalysts, the pK_a of the surface reactions on the WD catalyst is typically employed. For "acidic" pathway, $pK_{a1} = -\log_{10}(\frac{k_{a1}^{p_1}}{k^{p_1}} \times c_{H_20,0})$ [34].

The third type is the "alkaline" pathway where active sites are more likely to react with water molecules in alkaline environments.

$$H_2 O + s - OH \stackrel{k_{f/r}^{b_1}}{\leftrightarrow} s - O^- + H_3 O^+$$

$$\tag{15}$$

$$H_2O + s - O^{-} \stackrel{k_{D_T}^{b_2}}{\leftrightarrow} s - OH + OH^{-}$$
(16)

For "alkaline" pathway, $pK_{a2} = -\log_{10}\left(\frac{k_f^{b1}}{k_f^{b1}} \times c_{H_20,0}\right)$ [34].

2.5. Model validation

We validate the model by making a comparison between our calculation and the experimental data from Pärnamäe et al. [39]. Three electrolyte environments are considered (0.1/1 M NaCl and 0.5 M HCl/NaOH) and the calculated results are consistent with the experimental data, as shown in Fig. 2(a). In the model, all parameters are same as the experiments, as listed in Table S2. When employing the diffusion coefficients of H₃O⁺ and OH⁻ from the research of Craig et al. [40], the results still match the experimental observations (Fig. S2), indicating that it is meaningful in the same order of magnitude. Notably, the acid-base electrolyte system exhibits sensitivity to membrane voltage (E_{Mem}), thus serving as the basis for parameter fitting. We calibrated the fitting parameters listed in Table S2 by comparing the calculation results with the experimental data presented in Fig. 2(b-d).

The CIMD-coupled PNP equations are solved using COMSOL Multiphysics with specific boundary conditions in a 1D model. The Dirichlet boundary condition specifies the concentration and potential in bulk. The meshes are set to be the densest at the IL, membrane-membrane boundary, and membrane-solution boundary, with the maximum component size being 0.5 nm. In other parts that do not require high precision, such as in bulk electrolytes and host membranes, the fixed number of units is 1000.



Fig. 2. Model validation. (a) Calculated (solid lines) and experimental (markers) current-voltage curves of BPMs for both reverse-bias and forward-bias in neutral and acidbase electrolytes. Effect of modifying (b) interfacial layer thickness, (c) pK_a of the surface reactions on the WD catalyst, and (d) ion exchange capacity (IEC) of the BPMs in acidbase electrolytes.

3. Results and discussion

3.1. Suppression of CIMD promoting water dissociation in neutral electrolytes

As illustrated in Fig. 3(a), the occurrence of CIMD in the BPMs under reverse-bias mode ($I_{Mem} > 0$) causes a serious reduction of current density. Notably, when the current density reaches 400 mA cm⁻², a membrane voltage of 1.5 V is necessitated (Solid line). However, if the influence of CIMD is totally suppressed, only 1.06 V is required (Dashed line). It indicates a significant relation between high membrane voltage challenges in industrial processes and membrane (de)protonation. Further insights can be obtained from the contributions of the partial current density for each ionic species to the total current density in Fig. 3(b). It is worth noting that this phenomenon is primarily due to the reduction in the current carried by H_3O^+/OH^- ions. In the reverse-bias mode, the H_3O^+/OH^- OH⁻ ions are generated from the interfacial water dissociation. When the generated H_3O^+/OH^- ions enter the membrane, they will react with the functional groups of polymers through the proton transfer reactions (Eqs. (9) and (10)), leading to the screening of fixed charges in some polymer groups under high currents. The fixed charge concentration of the BPMs in the presence and suppression of CIMD at E_{Mem} = 1.2 V is shown in Fig. 3(c). The average concentration of fixed charges inside the membrane with CIMD is 0.4 M, leaving only 12% of the initial charge capacity when the CIMD is totally suppressed. It will largely reduce the ability of BPMs to attract the counter-ions and repel the co-ions, thus hindering the leave of generated H_3O^+/OH^- ions from the interface layer (Fig. 3b). Moreover, it is found that the electric field at the interface layer is 3.9×10^8 V m⁻¹ at $E_{Mem} = 1.2$ V, but if the CIMD is totally suppressed, the electric field increases to 5.9×10^8 V m⁻¹ with broadening the space charge region (SCR), which can lead to a significant improvement in the activity of water dissociation (Fig. S3).

By contrast, the current-voltage response at the forward-bias mode ($I_{Mem} < 0$) in the NaCl solution is completely unaffected by the CIMD. In the forward-bias mode, the H_3O^+/OH^- ions undergo water recombination at the interface layer. At $E_{\text{Mem}} = -0.1$ V, the average concentration of H_3O^{\ast} in CEL is about $3.1\,\times\,10^{-7}$ M and the average concentration of OH^- in AEL is about 1.7×10^{-7} M (Fig. S4). Since the concentration of H_3O^+/OH^- ions is exceptionally low, the CIMD is suppressed, and the current inside the CEL and AEL is mainly carried by Na⁺/Cl⁻ ions (Fig. S5). Therefore, the fixed charge density of the BPMs remains unchanged (Fig. S6). However, when $E_{\text{Mem}} = -0.1$ V, the average concentration of Na⁺ ions inside the membrane is 3.64 M, indicating that the concentration of salt ions in the membrane can reach 3-5 times of the bulk concentration, which can lead to a serious co-ion leakage at the interface layer, resulting in the salt precipitation and subsequently damaging the stability of the BPMs (Fig. S7).

Considering different transport driving forces of H₃O⁺ and Na⁺ ions, the contributions of diffusion $(D_i \nabla c_i)$, migration $(\frac{D_i z_i F c_i}{RT} \nabla \phi)$, and water transport $(\frac{D_i c_i}{c_{H_2O}} \nabla c_{H_2O})$ to the current in the presence and suppression of CIMD at E_{Mem} = 1.2 V (reverse-bias mode) are shown in Fig. 3(d). In the presence of CIMD, the partial current den-



Fig. 3. Effect of CIMD on the electrochemical performance of BPMs in neutral electrolytes (1 M NaCl) in the presence and suppression of CIMD. (a) Current-voltage curves of BPMs for both reverse-bias (Current density > 0) and forward-bias (Current density < 0). (b) The voltage-response of partial current densities for each ionic species in CEL and AEL when the voltage interval of reverse-bias is 0–1.5 V. (c) Fixed charge profiles within the BPMs at $E_{Mem} = 1.2$ V. (d) Partial current densities of H₃O⁺ and Na⁺ in CEL at $E_{Mem} = 1.2$ V, which depicts the contributions of diffusive transport ($D_i \nabla c_i$), migration ($\frac{D_{iz_i}E_{iz_i}}{C_{H_2O}} \nabla \phi_i$), and water transport ($\frac{D_{ic_i}}{C_{H_2O}} \nabla c_{H_2O}$). (e) Concentration profiles of H₃O⁺/OH⁻ ions and Na⁺/Cl⁻ ions within the BPMs at $E_{Mem} = 1.2$ V. The coordinate x = 0 µm represents the BPMs junction.

sity of H_3O^+ contributed by diffusion decreases from 550.2 to 43.5 mA cm⁻², while that contributed by migration decreases from 328.3 to 109.6 mA cm⁻². The CIMD alters the main transport mechanism of H_3O^+ , shifting from diffusion dominated to migration dominated. The ion concentration within the BPMs at $E_{Mem} = 1.2$ V (reverse-bias mode) is plotted in Fig. 3(e) to further understand the ion transport mechanisms. When the CIMD is totally suppressed, the concentration of all ions is largely increased, leading to the rise of the current contributed by both diffusion and migration (Fig. 3d). The concentration gradients of H_3O^+/OH^- and Na⁺/Cl⁻ ions inside the membrane show opposite directions, with the diffusion-induced current direction, but that of Na⁺/Cl⁻ being converse.

3.2. Suppression of CIMD to overcome limiting current density in acidbase electrolytes

The polarization curves of BPMs in 1 M HCl/NaOH electrolyte are plotted in Fig. 4(a). When CIMD is completely suppressed, the current density of BPMs at E_{Mem} = 1.2 V increases from 269 to 736 mA cm⁻², also indicating that suppressing CIMD can significantly improve the electrochemical performance of BPMs. The current response in the reverse-bias mode is similar to that observed in 1 M NaCl solution. However, in the forward-bias mode, the BPMs present a current plateau with a limiting current density observed at -91 mA cm⁻². Fig. 4(b) illustrates the behavior that arises from the variation of the partial current density of $H_2O^+/$ OH⁻ ions. It is significantly different from the forward-bias mode in NaCl solution, where the current is mainly contributed by Na⁺/ Cl^{-} ions. As illustrated in Fig. 4(c), the CIMD induces a reduction in the concentration of fixed charges within the BPMs, unlike the forward-bias mode in NaCl solution with almost no loss of fixed charges.

To explain the plateau of limiting current density in the forward-bias mode, we plot the concentration distribution of $H_3O^+/OH^-/Na^+/Cl^-$ near the IL within BPMs (Fig. 4d and e). At $E_{Mem} = 0.6$ V, the average concentration of OH^- ions in the AEL is 0.23 M in the presence of CIMD and 3.55 M when the CIMD is totally suppressed. Due to the water recombination process at the IL, the concentration of OH^- ions becomes lower near the IL. To monitor the OH^- ions that are crucial due to its slower diffusion rate compared to H_3O^+ ions, OH^- ions are more susceptible to mass transfer limitations. When $E_{Mem} = 0.3$ V (within the platform region), the concentration of H_3O^+ ions at the IL/CEL interface and that of OH^- ions at the IL/AEL interface are 2.6×10^{-4} and 1.3×10^{-8} M, respectively, indicating that OH^- ions have entered the mass transfer restricted region. Consequently, reactive OH^- ions, serving as the only base species susceptible to protonation, are gradually depleted at the interface layer with decreasing voltage until the limiting current density is reached.

Toh et al. have previously posited, in their analysis of BPMs electrolyzers containing weak acid/base, that the ionic blockage enforced by inactive counter ions may contribute to the occurrence of limiting current density [41]. However, our study demonstrates that even in the absence of additional non-reactive anions, Cl- ions from the outside of CEL can diffuse into the interface layer when the CIMD occurs in AEL, leading to the accumulation of nonreactive Cl⁻ ions at the IL (Fig. 4d). The depletion of OH⁻ ions at the IL results in the ionic blockage of Cl- ions to maintain electroneutrality. A place-exchange mechanism exists for the transport of OH^- ions, wherein OH^- ions diffuse towards the interface exchange sites with Cl⁻ ions diffusing away from the interface, ultimately forming a polarization curve independent of potential (the plateau of limiting current density). As the E_{Mem} decreases further, it disrupts the linear diffusion of OH⁻ of the plateau region (Fig. S8) that limits current density by strengthening the electromigration effect, leading to a further increase of current density. When the CIMD is totally suppressed, the concentration of OHat the interface layer remains relatively high, and thus the limited current density cannot be observed. However, with the further decrease of E_{Mem} , the accumulation of Cl⁻ ions at the interface



Fig. 4. Effect of CIMD on the electrochemical performance of BPM in acid-base electrolytes (1 M HCl/NaOH) in the presence and suppression of CIMD. (a) Current-voltage curves of BPMs for both reverse-bias (Current density > 0) and forward-bias (Current density < 0). (b) The voltage-response of partial current densities for each ionic species in CEL and AEL at the voltage interval of reverse-bias below 0.6 V. (c) Fixed charge profiles within the BPMs at $E_{Mem} = 0.3$ V. Concentration profiles of (d) H_3O^+/OH^- ions and (e) Na^+/CI^- ions within the BPMs at $E_{Mem} = 0.3$ and 0.6 V. The coordinate $x = 0 \ \mu m$ represents the BPMs junction.

layer also becomes evident gradually (Fig. 4e). It is speculated that with the over-high absolute current density, the plateau of limiting current density can still appear even though the CIMD is totally suppressed. Therefore, the blockage of salt co-ions is the inherent characteristic of BPMs, but the CIMD will accelerate the emergence of this phenomenon.

3.3. Suppression of CIMD vs. electric field screening

The effect of neutral electrolyte concentration on the electrochemical performance of BPMs is further investigated in the reverse-bias mode. As the interfacial field strength plotted at low-voltage region in Fig. 5(a), the interface in 1 M NaCl exhibited a lower field strength than that in 0.1 M NaCl, thus suppressing the water dissociation. At high-voltage region, the electric field screening is also enhanced at high NaCl concentration, but more NaCl ions inside the BPMs suppress the CIMD and thus maintain the fixed charge concentration (Fig. 5b). Therefore, at the highvoltage region (E_{Mem} = 1–1.5 V), BPMs exhibit a larger current density with a higher concentration of electrolyte, which is different from that at low-voltage region of $E_{\text{Mem}} = 0.6-1$ V (Fig. 5c). When the CIMD is totally suppressed, the water dissociation rate decreases by 5.7×10^6 mol m⁻³ s⁻¹ with the NaCl concentration from 0.1 to 1 M (Fig. S9). Therefore, the salt co-ions at the IL can reduce the water dissociation rate by partially screening the interface electric field. But when the CIMD becomes serious at high voltages, the salt counter-ions in CEL (Na⁺) and AEL (Cl⁻) can maintain the fixed charge density of the BPMs to improve the performance

of the BPMs, even at the cost of increasing the salt ion crossover. Based on this conclusion, a possible practical approach has been proposed to introduce additional salt counter-ions into the membrane by running a high-concentration electrolyte before pure water electrolysis or by alternating between electrolytes of different concentrations. Furthermore, our findings can be extended to specific areas of electrochemistry. For inorganic salt ion recovery or acid-base production, ion selectivity is an important production metric, and the crossover of salt ions may instead reduce production efficiency [42]. But for the CO₂ reduction process, the introduction of salt ions not only inhibits CIMD, but also modulates the local environment and pH to increase the faraday efficiency of the reaction [43]. As for the aqueous acid-base redox flow batteries, the introduction of salt ions in the AEL might be able to modulate the pH near the anode to inhibit the generation of highly oxidized substances that would oxidize the functional groups, such as Br₂ [8].

By contrast, in the forward-bias model, the current densities corresponding to HCl/NaOH electrolytes of 0.1, 0.5, and 1 M are -260, -176, and -91 mA cm⁻² at $E_{\text{Mem}} = 0.3$ V, respectively (Fig. 5d). The reduction can be attributed to the enhanced ion blockage of salt co-ions at the interface layer, resulting from an increased gradient of ions within the BPMs (Fig. S10), thereby prompting BPMs to enter the plateau of limiting current density and consequently diminishing its electrochemical performance. In the absence of CIMD, increasing the HCl/NaOH concentration leads to a reduction in the current density of BPMs, which is attributed to the electric field screening as discussed above.



Fig. 5. (a) The profiles of electric field strength at the interface layer of the BPMs at $E_{Mem} = 0.8$ V for different concentrations of NaCl in the presence of CIMD. (b) The profiles of fixed charge concentration within the BPMs at $E_{Mem} = 1.5$ V for different concentrations of NaCl in the presence of CIMD. Current-voltage curves (c) in the reverse-bias mode at different NaCl concentrations and (d) in the forward-bias mode at different HCl/NaOH concentrations with the presence and suppression of CIMD.

3.4. Potential strategies for suppressing CIMD

As discussed above, increasing the concentration of salt counter-ions in the BPMs is a potential strategy to suppress the CIMD in the reverse-bias mode, but may result in the unfavorable crossover of salt co-ions at the IL. Nikonenko et al. highlighted that water splitting rate can be improved by matching the dissociation constant of the functional groups in the CEL and AEL of BPMs [38]. The viewpoint emphasizes that optimizing the properties of functional groups in BPMs to mitigate CIMD holds promise for enhancing the performance of BPMs. Accordingly, the data in Fig. 6(a and b) illustrate that high K_a in CEL and high K_b in AEL are more favorable for suppressing the CIMD, where the equilibrium constant K is defined as $K_a = \frac{C_A - C_{H_3O^+}}{C_{AH}}$ in CEL and $K_b = \frac{C_{BH^+} - C_{OH^-}}{C_B}$ in AEL. The materials of such membrane layers are usually strongly acidic or basic, such as sulfonic acid groups, quaternary ammonium groups, or quaternary pyridine groups, thereby maintaining the concentration of fixed charges within BPMs and improving their electrochemical performance.

The performance of BPMs can be enhanced by increasing the transport rate of OH^- ions within the AEL to overcome the limiting current density in the forward-bias mode of BPMs at acid-base conditions. However, as the polarization curve of BPMs at different diffusion coefficients of OH^- ions is presented in Fig. 6(c), it is found that when the diffusion coefficient of OH^- ions is doubled

over the bulk diffusion coefficient $(2D_{OH^-})$, the performance of BPMs is decreased unexpectedly. It stems from the diffusion rate of OH⁻ ions surpassing that of H₃O⁺ ions, potentially resulting in H_3O^+ being limited by mass transfer. Ion selectivity in the AEL is likewise considered, with selectivity represented by the percentage of partial current density carried by OH-. Fig. S11 demonstrates that the effect of the OH- diffusion coefficient on ion selectivity is consistent with its effect on current density, indicating that modulating the ion transport of OH⁻ not only improves the current density but also suppresses the co-ions leakage. Consequently, optimizing BPMs performance under forward-bias necessitates the efforts to achieve consistent transport rates of water coions (H₃O⁺ and OH⁻) within BPMs. In practice, enhancing the diffusion coefficient of OH⁻ in AEL often necessitates membrane modifications. For instance, Wei et al. improved ion transport by introducing host-guest interactions into AEM [44], and Yang et al. constructed an efficient OH⁻ transport channel inside the AEM utilizing the self-aggregation advantage of phthalocyanine [45]. However, these strategies may elevate the membrane costs.

From the above discussion, it can be seen that matching the transport rates of water counter-ions $(H_3O^+ \text{ and } OH^-)$ in the forward-bias mode with acid-base solutions can significantly increase the electrochemical performance of BPMs, and thus we design a suitable asymmetric BPMs system to maintain the low cost while improving the current density. Fig. 6(d-f) illustrates the effect of membrane thickness, ion exchange capacity, and bulk



Fig. 6. Influence of equilibrium constants for the proton-transfer reaction between water molecules and functional groups on current density for (a) CEL and (b) AEL under the reverse-bias mode in neutral electrolytes. Influence of the (c) diffusion rate of OH⁻ ions on current density under the reverse-bias mode in acid-base electrolytes. Influence of (d) ion exchange layer thickness, (e) ion exchange capacity, and (f) electrolyte concentration on current density in acid-base electrolytes for asymmetric BPMs design.

electrolyte concentration on the current-voltage curves of BPMs. Asymmetric BPMs have been developed to adjust the thickness of AEL. Rathod et al. demonstrated that reducing AEL thickness minimizes co-ion leakage and improves product recovery [46], coinciding with the trend observed in Fig. 6(d). However, instead of reducing the AEL thickness only, our model adjusts the relative thicknesses of AEL and CEL to maintain the mechanical properties and stability of the BPMs while keeping the total thickness of the BPMs constant. Therefore, our findings suggest that further reducing AEL thickness to 40 µm significantly decreases the current density, potentially due to a shift in transport-limited ions from OH⁻ to H₃O⁺. The addition of the ion exchange capacity (IEC) is also proved to be effective, as demonstrated in Fig. 6(e). Increasing the IEC of AEL increases current density, whereas enhancing the IEC of CEL yields no significant change. However, it is important to note that in practical production, increasing the IEC may escalate the production expenses of the membrane. Thus, a judicious approach to regulating the IEC ratio of AEL to CEL can enhance current density while maintaining a low cost. Fig. 6(f) illustrates the influence of asymmetric electrolytes on BPMs, and the combination of 1 M NaOH and 0.1 M HCl exhibits the best performance, while that of 0.1 M NaOH and 1 M HCl shows the worst performance. Therefore, we recommend using a combination of high-concentration bases and low-concentration acids to improve the current density of BPMs. The application of high alkali concentrations is desired to increase the mass transport rate of OH⁻ within the AEL, while the low concentration of acid is applied to reduce the accessibility of the salt ion (Cl⁻) to the interface of BPMs. It can be seen that when 0.1 M HCl is employed, no significant limiting current density is present in the polarization curves, and as we discussed in Section 3.2, the blockage of Cl⁻ at the interface is an important cause to the reduction of current density. Moreover, the pH change of the paired electrolyte not only affects the performance of BPMs, but also has an impact on the reaction kinetics and selectivity of the electrode reactions, and thus the design of the nextgeneration BPMs should be comprehensively considered in conjunction with the electrode reactions.

4. Conclusions

In this work, the CIMD-coupled PNP equations, which include the proton-transfer reactions of fixed functional groups in BPMs and the kinetics of interfacial water dissociation, are used to solve the diffusion, migration, water transport, and reaction processes of ions self-consistently for investigating the effect of CIMD on the current-voltage curve of BPMs. The inhibition of CIMD on the performance of BPMs originates from the alterations of local environment in the CEL and AEL, including the interfacial electric field and ion concentration distribution, which is induced by the reduction of fixed charges at high current densities. In the reverse-bias mode, when the salt co-ions enter the interfacial layer, the space charge density and electric field are partially screened, thereby reducing the rate of interfacial water dissociation and impeding the performance of BPMs. But at larger current densities, the serious CIMD can be suppressed by the salt counter-ions to enhance the current density through the BPMs. Consequently, in the reverse-bias mode, enhancing the electrochemical performance of BPMs at industrial current densities may be achieved by increasing the transport of salt counterions. For specific electrochemical processes, the selection of electrolytes must strike a balance between high membrane voltage and salt ion crossover. In the forward-bias of BPMs at acid-base conditions, a plateau of limiting current density is observed, which is caused by the diffusion limitation of H₃O⁺/OH⁻. It is proven that the ion blockage phenomenon that occurs in acid-base solution systems is an inherent characteristic of BPMs. Finally, potential strategies for suppressing CIMD are proposed for both reverse-bias and forward-bias modes. Optimizing the properties of fixed functional groups to maintain charge density is suggested. In addition, matching the transport rate of water counter-ions (H⁺ and OH⁻) to avoid mass-transfer limitations is also an important approach to increase the current density of BPMs. Our work provides a deep understanding of the CIMD in BPMs, highlighting the importance of regulating ion crossover transport in improving electrochemical performance of BPMs.

CRediT authorship contribution statement

Tingting Yu: Writing – review & editing. Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Haolan Tao: Writing review & editing, Writing - original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization. Jingkun Li: Supervision, Project administration, Formal analysis. Cheng Lian: Writing - review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. Honglai Liu: Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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