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Modeling the electrochemical behavior and interfacial junction profiles of bipolar membranes at solar flux relevant operating current densities†

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A 1-dimensional, multi-physics model that accounts for the migration and diffusion of solution species, electrostatics, and chemical reactions, in particular water dissociation (WD), at bipolar membrane (BPM) interfaces was developed to study the electrochemical behavior of bipolar membranes (BPMs) at solar flux relevant operating current densities (tens of mA cm⁻²). Significant partial current densities for WD were observed at BPM voltages much less than the equilibrium voltage, e.g., 59 mV × ΔpH from both experiments and modeling. The co-ion leakage across the BPM at pH differentials accounted for the early presence of the partial current density for WD. Two distinctive electric field dependent WD pathways, the un-catalyzed pathway and the catalyzed pathway, were quantitatively and parametrically studied to improve the turn-on potential of the BPM. The catalyzed pathway accounted for the majority of the partial current density for WD at low voltages, while the un-catalyzed pathway dominated the WD at relatively high voltages. Significant WD was observed only within the interfacial CL (<5 nm), in which a large electric field was present. To improve the electrochemical behavior and the turn-on potential of BPMs, the impacts of the pK_a of the immobilized WD catalysts, the electric-field dependent rate constant, the thickness of the catalyst layer and fixed charge density in BPMs on the partial current densities for WD were studied systematically. In addition, the electrochemical behavior and concentration profiles of BPMs in a buffered electrolyte were studied and contrasted with those in an un-buffered electrolyte from both modeling and experiments.

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Introduction

Bipolar membranes (BPMs) have been used in many device configurations in solar fuel applications, including solar-driven water-splitting cells^{1,2} and solar-driven CO₂ reduction (CO₂R) cells.^{3–5} The use of BPMs in solar-fuel devices can achieve many unique operating conditions that cannot be obtained by using cation exchange membranes (CEM) or anion exchange membranes (AEM) alone. First of all, BPMs can sustain pH differentials between the catholyte and anolyte and hence offered unique opportunities to different electrolyte combinations for more efficient and stable solar fuel devices.⁶ Secondly, the use of both CEMs and AEMs can effectively block the crossover of bicarbonate ions between the catholyte and anolyte, which was the main origin for CO₂ loss in aqueous based

electrochemical cells for the CO₂R.^{7,8} In addition, BPM based electrochemical cell configurations that leveraged the local acidification of the electrolyte and local generation of CO₂ have shown promise in bicarbonate/carbonate feed CO₂R devices.^{9,10} While BPMs are widely used in electro dialysis and electrolysis applications,^{11–13} the operating current densities as well as the electrolyte combinations are quite different from those of solar fuel applications, e.g., the operating current density in electrolysis or electro dialysis systems is often a couple orders of magnitude higher than in solar fuel devices. In addition, most electrolysis and electro dialysis systems leverage the low transport loss and high water dissociation rates of BPMs at high pH differentials, e.g., pH = 0/pH = 14, and the BPM resistive loss accounts for the majority of the voltage loss in the system. In comparison, solar fuel devices, in particular for the CO₂R, rarely operate at extreme pH values due to catalyst selectivity, and often required to minimize the pH gradients and the concentration overpotential related to fuel forming reactions.^{14,15} As a result, large voltage losses were observed experimentally in various electrolyte combinations even at a relatively low operating current density in the range of tens of mA cm⁻².^{16,17}

The operating principle of BPMs was often compared and contrasted with that of solid-state semiconductor p–n junctions.¹⁸ However, the electric-field dependent WD kinetics¹⁹ and

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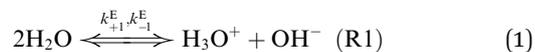
impacts of WD catalysts at a reverse bias²⁰ were often not considered. A recent report showed that at high operating current densities (>100 mA cm⁻²), WD catalysts played a governing role relative to the electric field at the interface, and BPMs with engineered 3D junctions exhibited lower potential drops.²¹ In addition, the inclusion of WD catalyst materials with different points of zero charge at the BPM interface has shown a significant impact on the overall current-voltage characteristics in a water-feed electrolysis cell without any co-ions.²² The dissociation of weak electrolytes under an applied electric field was studied by Onsager²³ and an analytical expression was obtained without the consideration of the length of the chemical bond in the paired ions. An improved model developed by Craig indicates that the WD rates can be varied by many orders of magnitude with small changes in the length of the chemical bond.²⁴ In this study, the electrochemical behavior of BPMs as well as the potential and net charge profiles at the BPM interface in both un-buffered electrolytes and buffered electrolytes were modeled and studied with a 1D multiphysics model that accounted for the migration and diffusion of solution species, electrostatics and chemical reactions, in particular the WD kinetics using the improved model developed by Craig and others.^{21,24,25} The effects of the WD kinetics, the thickness of the catalyst layer and fixed charge densities on the voltage across the BPM at current densities that are relevant to solar fuel devices were modeled and simulated.

Physical-based model development

Fig. 1a shows a schematic illustration of the modeling domain for the BPM. The simulation domain includes, a CEM layer (CEL), a catalyst layer (CL), an AEM layer (AEL), and two electrolyte boundary layers (BL) on each side of the BPM. For an electrolyte with extreme pH differentials (pH = 0/pH = 14), 1 M HCl and 1 M KOH were used, while for an electrolyte at the same pH (pH = 7/pH = 7), 0.5 M K₂SO₄ was used on both sides of the BPM. The thickness of CEL and AEL layers was set to 75 μm. The thickness of the CL was set to 10 nm for the reference case.²⁴

The BL thickness was set to 50 μm to account for moderate stirring or recirculation in the cell.

Two pathways of water disassociation (*i.e.*, the un-catalyzed pathway and the catalyzed pathway) were included in this study. The electric field dependent, un-catalyzed water disassociation reaction (R1) was modeled across the whole simulation domain:



where $k_{+1}^E = f_{E,\text{enhance},f} k_{+1}^0$ and $k_{-1}^E = f_{E,\text{enhance},b} k_{-1}^0$ are the forward and backward reaction rate constants.

The equilibrium constant of the un-catalyzed pathway was defined as

$$K_1^E = \frac{k_{+1}^E}{k_{-1}^E} = \frac{c_{\text{H}_3\text{O}^+} c_{\text{OH}^-}}{c_{\text{H}_2\text{O}}^2} \quad (2)$$

The equilibrium constant of the un-catalyzed pathway at zero electric field was defined as

$$K_1^0 = \frac{k_{+1}^0}{k_{-1}^0} \quad (3)$$

The intrinsic reaction rate constants (*i.e.*, k_{+1}^0 and k_{-1}^0) were set to $3.67 \times 10^{-10} \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$ and $1.11 \times 10^8 \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$ based on the analytical correlation proposed by Craig.²⁴ As a result, $K_1^0 = \frac{k_{+1}^0}{k_{-1}^0} = 3.3 \times 10^{-18}$. Considering a bulk water concentration of 55.34 M, $c_{\text{H}_3\text{O}^+} c_{\text{OH}^-}$ gives 10^{-14} M^2 at zero electric field. As a result, $\text{p}K_a + \text{p}K_b = 14$ for the water dissociation reaction (eqn (1)) at zero electric field.

The enhancement factor of the forward reaction ($f_{E,\text{enhance},f}$) and backward reaction ($f_{E,\text{enhance},b}$) based on the extended Onsager method for chemical bonds with empirical fitting was given as²⁴

$$f_{E,\text{enhance},f} = \left(\sum_{n=0}^{\infty} \frac{(2E_d)^n}{n!(n+1)!} \right) \cosh(\tau E_d) (\cosh(\tau))^{E_d} \quad (4)$$

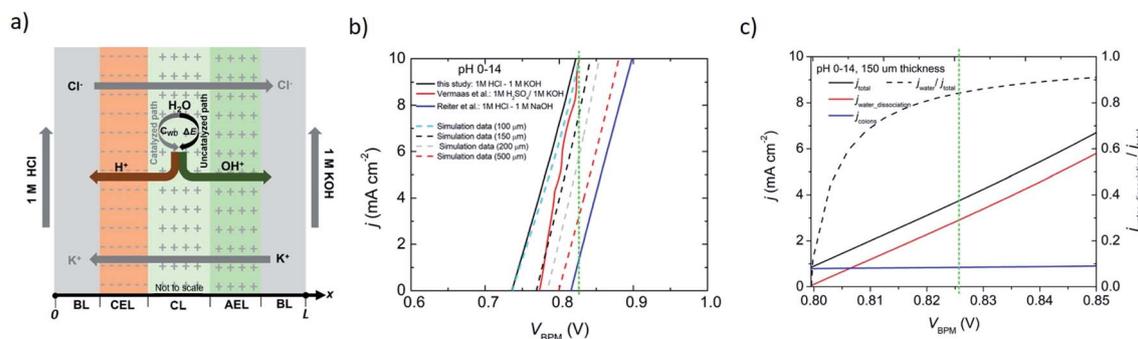


Fig. 1 (a) A schematic illustration of the modeling domain in a bipolar membrane. (b) The experimental and modeling comparison of the electrochemical behavior of the BPM in the pH = 0/pH = 14 electrolyte combination. Four membrane thicknesses (100, 150, 200, and 500 μm) are shown as dashed lines. (c) The simulated partial current density for WD and co-ion leakage as a function of voltage across the BPM. $j_{\text{water_dissociation}}$ is the partial current density due to water dissociation and j_{coions} is for co-ion crossover. The vertical dotted line (green) indicates that $V_{\text{BPM, equilibrium}} = 826 \text{ mV}$ in the pH = 0/pH = 14 electrolyte combination.

$$f_{E,\text{enhance,b}} = \frac{1 - \exp\left(-\frac{1}{\alpha}\right)}{1 + \frac{\exp\left(-\frac{1}{\alpha}\right)}{2}} \left(\alpha^2 E_d + 4.97\alpha \frac{\sinh(0.0835\alpha E_d)}{\cosh(0.0835\alpha E_d)^2} \right) \quad (5)$$

where $\tau = 0.128 \ln(\cos(0.235\alpha)) + 5.72\alpha^2$ is a fitting parameter with $\alpha = \frac{7.28\epsilon_{\text{H}_2\text{O}}RT}{eF}$, and $E_d = \frac{0.29}{\alpha} \left| \frac{eE}{k_B T} \right|$ is the dimensionless electric field. It is important to note that in the presence of an electric field, $c_{\text{H}_3\text{O}^+}c_{\text{OH}^-}$ is no longer equal to a constant (10^{-14} M^2). The product of the hydronium concentration and the hydroxide concentration during active WD reactions under the electric field was given by:

$$c_{\text{H}_3\text{O}^+}c_{\text{OH}^-} = 10^{-14} \text{ M}^2 \times f_{E,\text{enhance,f}}/f_{E,\text{enhance,b}} \quad (6)$$

When the simulation reached a steady state, in which the concentrations of all species stopping changing, the generation rate of hydronium and hydroxide ions is equal to their recombination rate, which yielded eqn (6). The catalyzed pathway included two sequential chemical reactions, eqn (7) and eqn (9) (denoted as (R2) and (R3)). The first chemical reaction, eqn (7), was the WD reaction in the presence of a WD catalyst (denoted as C_{WD}) or the protonation of the WD catalyst, and the second chemical reaction, eqn (9), was the deprotonation of the WD catalyst. The first chemical reaction has the same electric-field dependent WD enhancement factors, $f_{E,\text{enhance,f}}$ and $f_{E,\text{enhance,b}}$, as the un-catalyzed pathway, while the equilibrium constant at zero electric field was significantly higher than that of the un-catalyzed WD pathway. The second chemical reaction was assumed to be electric-field independent because no net production of charges took place in eqn (7).²⁴



$$\frac{k_{+2}^E}{k_{-2}^E} = \frac{c_{C_{\text{WD}}\text{H}^+} c_{\text{OH}^-}}{c_{C_{\text{WD}}} c_{\text{H}_2\text{O}}} \quad (8)$$



$$\frac{k_{+3}^E}{k_{-3}^E} = \frac{c_{C_{\text{WD}}} c_{\text{H}_3\text{O}^+}}{c_{C_{\text{WD}}\text{H}^+} c_{\text{H}_2\text{O}}} \quad (10)$$

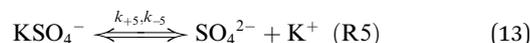
The intrinsic reaction rate constants for (R2) and (R3) were set as follows: $k_{+2}^0 = 83.9 \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$, $k_{-2}^0 = 2.13 \times 10^7 \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$, $k_{+3}^0 = 1.8 \times 10^{-5} \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$, and $k_{-3}^0 = 2.15 \times 10^7 \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$.²⁴ The reaction rates for (R2) were also dependent on the electric field due to net charge generation in the reaction. The reaction enhancement factor for (R2) followed the same relationship as (R1) (eqn (4) and (5)). In this study, the concentration of the total concentration of the catalyst ($C_{\text{WD}} + C_{\text{WD}}\text{H}^+$) was set to 1.0 M (equal to the fixed charge concentration for the BPM) over the 10 nm CL. It is important to note that the catalyzed pathway and un-catalyzed pathway are not thermodynamically independent; from eqn (3), (8) and (10), the general rate relationship follows:

$$\frac{k_{+3}^E}{k_{-3}^E} \frac{k_{+2}^E}{k_{-2}^E} = \frac{k_{+1}^E}{k_{-1}^E} \quad (11)$$

For the cases with buffer solution, the phosphate buffer reaction (R4) in the electrolyte was estimated based on its $\text{p}K_a$ (6.62 at 1.0 M)²⁶



where k_{+4} and k_{-4} were set to 10^2 s^{-1} and $4.17 \times 10^3 \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$, respectively. The protonation and deprotonation of the buffer species were sufficiently fast, and the simulation results were only dependent of the $\text{p}K_a$ of the buffer and were not dependent on k_{+4} and k_{-4} used in the study. In addition to the WD reactions, homogeneous reactions due to ion-pairing (R5) were also considered as follows:



Note that (R5) was only considered for the un-buffered electrolyte with the K_2SO_4 electrolyte. The equilibrium constant for ion pairing (K_5) for (R5) at 25 °C was set to 0.483 M,²⁷ where k_{+5} and k_{-5} were set to 10^2 s^{-1} and $0.21 \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$, respectively. Full disassociation was assumed for HCl and KOH electrolytes at the extreme pH differential ($\text{pH} = 0/\text{pH} = 14$).

The Nernst–Planck–Poisson relationship was used for solving the mass balance, species transport, and electrostatics. The general form for Nernst–Planck is given as

$$N_i = -D_i c_i \frac{1}{RT} \frac{d\mu_i}{dx} \quad (14)$$

where D_i is the diffusion coefficient for species i (the D_i values used in this study are tabulated in Table S1†), c_i is the local concentration, and μ_i is the electrochemical potential. For the pH 0/pH 14 case, the involved solution species were H_3O^+ , OH^- , K^+ , and Cl^- . For the pH 7/pH 7 case, the involved solution species were H_3O^+ , OH^- , K^+ , SO_4^{2-} , and NaSO_4^- . For the case with phosphate buffer, the involved solution species were H_3O^+ , OH^- , K^+ , HPO_4^{2-} , H_2PO_4^- , NaHPO_4^- , and NaH_2PO_4 . For H_3O^+ and OH^- , eqn (15) was used with an additional term accounting for the electric field dependence. For all other mobile species, a common Nernst–Planck eqn (16) was employed. The electrochemical potentials for different species were calculated using

$$\mu_i = \mu_i^0 + RT \ln\left(\frac{c_i}{c_{\text{H}_2\text{O}}}\right) + nF\phi - \frac{1}{2} RT \ln\left(\frac{k_{-}^E}{k_{+}^E}\right) \quad (15)$$

$$(i = \text{H}_3\text{O}^+, \text{OH}^-, c_{\text{WD}}\text{H}^+, c_{\text{WD}}),$$

$$\mu_i = \mu_i^0 + RT \ln\left(\frac{c_i}{c_{\text{H}_2\text{O}}}\right) + nF\phi \quad (i \neq \text{H}_3\text{O}^+, \text{OH}^-), \quad (16)$$

where μ_i^0 is the reference state for species i in water at 1 bar, n is the charge number for species i , ϕ is the electric field, and k_{+}^E and k_{-}^E are the electric field dependent dissociation and recombination rate constants, which only applied to H_3O^+ and OH^- . In this model, the electrochemical potentials for

hydronium and hydroxide included an explicit dependence on the electric field (eqn (15)). As a result, the transport equation based on (eqn (14)) was modified from the traditional Nernst–Planck relationship. Note that for the buffer reactions used in the simulation, such as protonation and deprotonation of phosphate ions, the reaction rate is already at the diffusional limit, and further increase of the backward and forward reaction rates did not change the simulation results. Combining eqn (14)–(16), a general form of the species molar flux equation was obtained as follows:

$$N_i = -D_i \frac{dc_i}{dx} + nD_i c_i \frac{FE}{RT} + D_i c_i \frac{dc_{\text{H}_2\text{O}}}{dx} + 0.5D_i c_i \frac{d \ln \left(\frac{k_-^E}{k_+^E} \right)}{dx} \quad (17)$$

($i = \text{H}_3\text{O}^+, \text{OH}^-$).

$$N_i = -D_i \frac{dc_i}{dx} + nD_i c_i \frac{FE}{RT} + D_i c_i \frac{dc_{\text{H}_2\text{O}}}{dx} \quad (i \neq \text{H}_3\text{O}^+, \text{OH}^-), \quad (18)$$

The mass balance was solved using

$$\frac{dN_i}{dx} = R_i \quad (19)$$

where R_i represents the reaction mass source terms due to chemical reactions ((R1)–(R5)). The immobile species, *i.e.*, C_{WD} and $C_{\text{WD}}\text{H}^+$, were not solved with the Nernst–Planck formulation. The mass balance of C_{WD} and $C_{\text{WD}}\text{H}^+$ was computed with two additional algebraic equations with a fixed catalyst concentration of 1 M for the reference case. The partition of C_{WD} and $C_{\text{WD}}\text{H}^+$ was determined by the catalytical reactions (R2) and (R3):

$$c_{C_{\text{WD}}} = \frac{k_2^- c_{\text{OH}^-} + k_3^+ c_{\text{H}_2\text{O}}}{k_2^+ c_{\text{H}_2\text{O}} + k_2^- c_{\text{OH}^-} + k_3^+ c_{\text{H}_2\text{O}} + k_3^- c_{\text{H}_3\text{O}^+}} c_{\text{fix}} \quad (20)$$

$$c_{C_{\text{WD}}\text{H}^+} = \frac{k_2^+ c_{\text{H}_2\text{O}} + k_3^- c_{\text{H}_3\text{O}^+}}{k_2^+ c_{\text{H}_2\text{O}} + k_2^- c_{\text{OH}^-} + k_3^+ c_{\text{H}_2\text{O}} + k_3^- c_{\text{H}_3\text{O}^+}} c_{\text{fix}} \quad (21)$$

Poisson's equation was utilized for solving electrostatics:

$$\frac{d(\varepsilon E)}{dx} = F \sum_i c_i \quad (22)$$

$$-\frac{d\phi}{dx} = E \quad (23)$$

where i is the index for difference species, E is the electrical field, and the ϕ is the electrostatics potential. $c_{\text{H}_2\text{O}}^0$ in the electrolyte is 55.34 M. The $c_{\text{H}_2\text{O}}$ in the BPM was corrected with its volumetric water fraction ($c_{\text{H}_2\text{O}} = f_{\text{water}} c_{\text{H}_2\text{O}}^0$, $f_{\text{water}} = 0.215$ in this study (experimentally fitted value)). The f_{water} in the membrane was assumed to be a constant value in this study due to small current densities ($\sim 10 \text{ mA cm}^{-2}$). At high operating current densities, typically $>100 \text{ mA cm}^{-2}$, the dehydration of BPM interface limits the attainable water dissociation rates and causes irreversible damage to the BPM interface.¹ However, at solar flux relevant current densities (tens of mA cm^{-2}), water

transport does not pose a limitation as shown in Fig. S1.† For example, at a current density of $\sim 10 \text{ mA cm}^{-2}$, the junction water concentration is only $\sim 1\%$ lower than that of the case without applied current. Fig. S2.† shows the effect of f_{water} on the current voltage characteristics of the BPM. We used f_{water} as one of the fitting parameters to fit the experimental BPM current–voltage curves.

The effective diffusion coefficients for each species within the BPM were corrected with the Bruggeman model ($D = D^0 f_{\text{water}}^\theta$, $\theta = 1.5$).²⁸ Note that in addition to the mobile species considered in eqn (17) and (18), immobile fixed charges within the BPM and charged catalytical $C_{\text{WD}}\text{H}^+$ for the CL were included in eqn (22). The detailed dielectric constant (ε) as a function of the x -position is included in Table S2.† Fig. S3.† illustrates the dielectric constant change across the simulation domain.

The boundary conditions for the Nernst–Planck equations (eqn (17)–(19)) on both sides of the membrane are Dirichlet boundary conditions with the concentrations of each species given as the values in bulk electrolytes. For Poisson equations (eqn (22) and (23)), an electrical ground ($\phi = 0 \text{ V}$) is considered at $x = 0$ and a constant electrolyte potential is applied at $x = L$. The model was solved numerically using the finite element method *via* Newton's method in COMSOL Multiphysics. The relative tolerance was set to be 10^{-4} with a mesh number of 6500. A mesh independent study was conducted to minimize the effect of the mesh on the results. A list of governing equations and unknowns is tabulated in Table S3.† The total number of governing PDEs is 10 for the pH 0/pH 14 case, 12 for the pH 7/pH 7 case, and 16 for the phosphate buffer case. Model parameters including diffusion coefficients and fitting parameters for f_{water} and θ in the Bruggeman model (Table S1.†), dielectric constants (Table S2.†), and reaction constants (Table S4.†) are provided.

Results and discussion

Fig. 1b shows the experimental and modeling comparison of the electrochemical behavior of the BPM in the pH = 0/pH = 14 electrolyte combination. BPM voltage measurements were performed in a flow electrochemical cell consisting of a cathode, a catholyte compartment, a BPM, an anolyte compartment and an anode compartment (see Fig. S4.†). The spacing between the catholyte and the anolyte compartment was 1 cm, and the active area of the cathode, the anode and the BPM was 4 cm^2 . The catholyte and the anolyte were fed into the electrochemical cell at a rate of 43 ml min^{-1} using a peristaltic pump. The BPMs used in the experiments are commercial Fumasep bipolar membranes from Fuma-Tech. All the experimental current–voltage measurements were carried out using fresh BPMs that were cut from the same membrane sheet. The BPM voltage was determined by measuring the voltage difference between two Ag/AgCl reference electrodes (1 M KCl, CH instruments); each was placed in the catholyte and the anolyte compartment while applying an electrical current to the anode and the cathode using a Keithley 2400 in a 4-wire sensing mode.^{22,29} The distance between each reference electrode and the BPM was 0.5 cm. The

BPM voltage measurements were carried in multistep chronopotentiometry mode from a high current density (11 mA cm^{-2}) to a low current density (0 mA cm^{-2}). The voltage at each applied current density was recorded once the voltage stabilized to ensure that the BPM voltage was not underestimated. All experimental measurements were carried using fresh BPMs that were cut from the same membrane sheet. Typical transients of the BPM voltages as a function of time at different operating current densities are included in Fig. S5†. Note that it can take hundreds of seconds for the solution species and the BPM voltage to reach equilibrium, especially when the operating current density was low (Fig. S5†). No IR correction was performed on the data presented in this study. The conductivity of infinitely diluted K_2SO_4 is $0.0306 \text{ S m}^2 \text{ mol}^{-1}$.³⁰ Considering the 0.5 M concentration and 1 cm distance between two reference electrodes, the resistance is estimated to be 6.54Ω . The IR corrected IV curve is compared with no IR correction curve in Fig. S6† for the pH 7/7 case.

The vertical dotted line (green) in Fig. 1b and c indicates that $V_{\text{BPM_equilibrium}} = 826 \text{ mV}$ in the pH = 0/pH = 14 electrolyte combination. Different voltages across BPMs at zero operating current density ranging from 0.74 V to 0.81 V were observed experimentally. The variation of the electrochemical behavior was likely due to the different batches of BPMs from commercial vendors. Note that appreciable current densities were observed at voltages less than the $V_{\text{BPM_equilibrium}}$ in all

experimental measurements. Co-ion leakage was often accounted for the current densities at voltages less than the $V_{\text{BPM_equilibrium}}$, and WD was not supposed to take place at voltages less than the $V_{\text{BPM_equilibrium}}$.¹⁶ In this case, the co-ion leakage includes the transport of K^+ from the alkaline chamber to the acid chamber and the transport of SO_4^{2-} from the acid chamber to the alkaline chamber.³¹ However, the simulated partial current density for WD and co-ion leakage at different voltages across the BPM (Fig. 1c) showed that significant WD took place at voltages equal to or less than the $V_{\text{BPM_equilibrium}}$. $j_{\text{water_dissociation}}$ is the partial current density due to water dissociation, and j_{coions} is the current density for the co-ion crossover. For example, at the $V_{\text{BPM_equilibrium}}$ (dashed line in Fig. 1c), the WD current density accounted for 77.4% of the total current density, where the co-ion leakage only accounted for 23.6% of the total current density. This phenomenon was not only observed in the pH = 0/pH = 14 electrolyte combination. In other pH combinations, significant partial current density related to WD was also observed (see Fig. S7†) at voltages less than the $V_{\text{BPM_equilibrium}}$. Note that $V_{\text{BPM_equilibrium}}$ in different pH combinations was defined as $V_{\text{BPM_equilibrium}} = \Delta\text{pH} \times 59 \text{ mV}$, where ΔpH was the pH differential between the two electrolytes,¹⁶ and $V_{\text{BPM_equilibrium}}$ is the thermodynamic voltage that is needed to perform WD reactions in BPMs.^{3,6,22} In the presence of co-ion leakage, the electrochemical free energy generated by neutralizing the pH gradients between the two

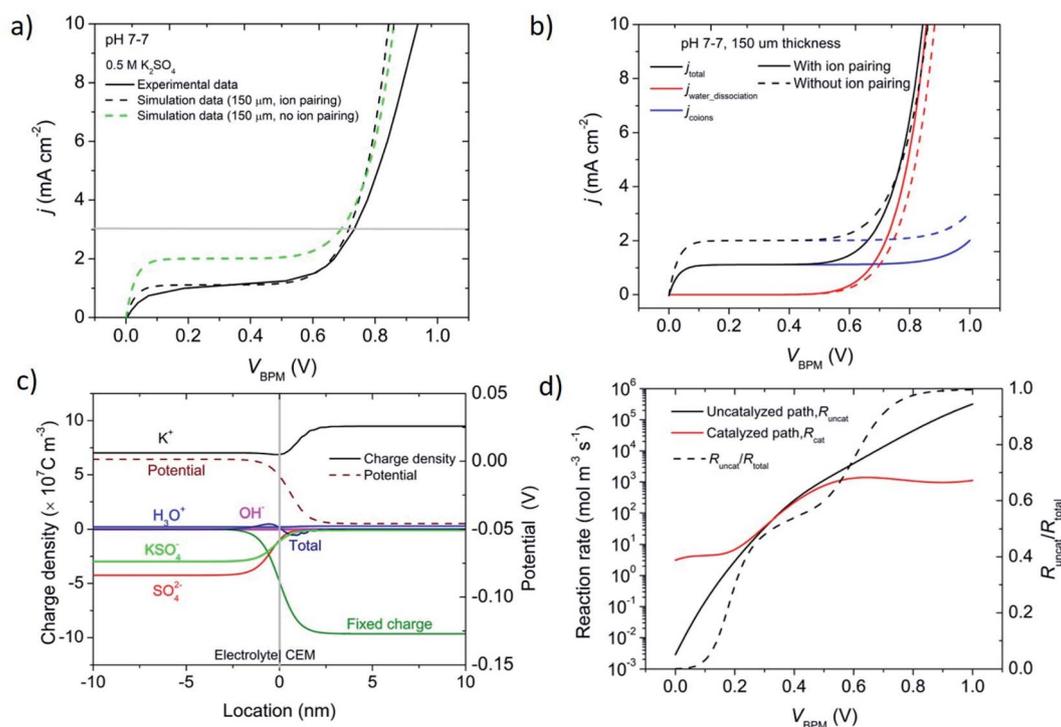


Fig. 2 (a) The experimental and modeling comparison of the electrochemical behavior of the BPM in the pH = 7/pH = 7 electrolyte combination, i.e. $0.5 \text{ M K}_2\text{SO}_4$. (b) The simulated partial current density for WD and co-ion leakage as a function of the applied potential with or without the consideration of ion pairing using a $0.5 \text{ M K}_2\text{SO}_4$ electrolyte. (c) The charge density of various species and the potential across the membrane/electrolyte interface at a current density of 3 mA cm^{-2} . (d) The simulated contribution of the catalyzed pathway and uncatalyzed pathway of WD as a function of voltage across the BPM.

sides of the BPM accounted for the voltage shift observed in the simulation. Effectively, a small leaky concentration cell was operated in parallel at low current density to drive the WD at the BPM interface. The relatively small shift at turn-on voltage < 100 mV observed here did not contradict with the thermodynamics of water dissociation within the BPM, but instead an additional process, in this case, the co-ion leakage which resulted in gradual neutralization of pH across the BPM, needs to be considered during the BPM operation, especially at low current densities. As shown in Fig. 1b and S8,[†] as the thickness of the membrane increased and the co-ion leakage decreased, the turn-on potential for the water dissociation reaction moved to voltage values closer to $V_{\text{BPM_equilibrium}}$.

The electrochemical energy dissipated by co-ion leakage at two different pH differentials and effectively neutralizing the pH gradients in the system accounted for the early initiation of the WD reaction. For the BPM operated without any co-ions, for example, in a vapor-fed electrolysis system without any liquid/mobile electrolytes, the WD reaction would take place at voltages equal to or larger than the $V_{\text{BPM_equilibrium}}$. Fig. 2a shows the experimental and modeling comparison of the electrochemical behavior of the BPM in the pH = 7/pH = 7 electrolyte combination. The experimental curves and the simulated

curves matched relatively well. The effect of the BPM thickness on the electrochemical behavior is presented in Fig. S9.[†] The thinner BPM thickness leads to larger co-ion leakage with smaller ohmic losses. The consideration of the ion pairing reaction in the 0.5 M K_2SO_4 electrolyte resulted in a reduced leaking current density in the flat region compared to the case without the ion pairing reaction. As shown in Fig. S10[†] the change of the CEL or AEL thickness or the use of asymmetric thicknesses had small effects on the current density–voltage characteristics of the BPM, mainly because the resistive loss across the CEL or AEL was small at low operating current densities. The reduced leaking current density due to the reduced concentration of mobile ions better matched with the experimental results. Fig. 2b shows the simulated partial current density for WD and co-ion leakage as a function of the applied potential with or without the consideration of ion pairing. Two distinctive regions, one relatively flat region at voltage < 0.6 V, and one exponential turn-on region at voltage > 0.6 V, were observed, which corresponds to co-ion leakage and the WD reaction at the BPM interface, respectively. The total concentration as well as the size of the mobile ions due to ion pairing changed the co-ion leaking current density significantly. The flat region shows a limited current density with increasing

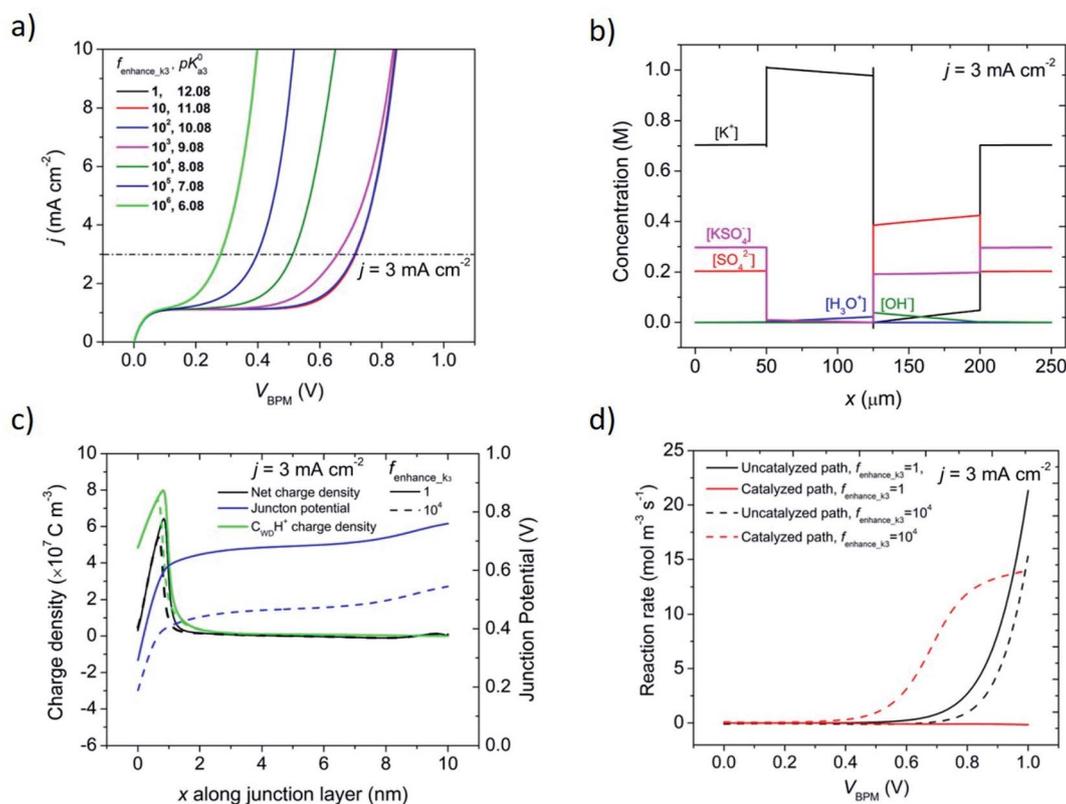


Fig. 3 Improving the turn-on potential of the BPM by optimizing the pK_a of the immobilized WD catalyst. (a) The simulated total current density as a function of the BPM voltage with different pK_a of the WD catalyst. (b) The concentration profile of H_3O^+ , OH^- and other co-ions across the BPM at different pK_a of the WD catalyst at a current density of 3 mA cm^{-2} . (c) The net charge density, the charge density of the WD catalyst, and the junction potential across the CL within the BPM at 3 mA cm^{-2} with two different pK_a of the WD catalysts. (d) The simulated contribution of the catalyzed pathway and uncatalyzed pathway of WD as a function of voltage across the BPM with two different pK_a of the WD catalysts at a current density of 3 mA cm^{-2} .

applied voltage due to a limited water dissociation rate at the CL with only leaking current from co-ion movement through the BPM (Fig. 2b). The co-ion leaking current density was found to be $\sim 1 \text{ mA cm}^{-2}$ in this study and this value can reach $\sim 2 \text{ mA cm}^{-2}$ if the ion pairing effect is neglected. The membrane/electrolyte interface was modeled and simulated to understand the transport and junction profile across the interface as illustrated in Fig. 2c. The selected case is $\text{pH} = 7/\text{pH} = 7$ with an operating current density of 3 mA cm^{-2} . The net charge (dark blue curve) from both mobile ions and fixed ions in the system accounted for the abrupt potential change (dotted brown curve) across the BPM/electrolyte interface. Note that the width of the space charge region within the CEL at an operating current density of 3 mA cm^{-2} was $\sim 3 \text{ nm}$ from the simulation, and the width of the double layer in the aqueous electrolyte was typically smaller than 50 nm , both of which agreed with literature values. At different applied voltages across the BPM, the contribution of the catalyzed pathway and uncatalyzed pathway of WD is simulated in Fig. 2d. WD from the un-catalyzed pathway (eqn (1), black curve) played a major role at $V_{\text{BPM}} > 0.6 \text{ V}$ during the operation. Because the intrinsic forward reaction rate of the catalyzed pathway was larger than that of the un-catalyzed pathway and both reactions had the same electric-field dependence, the WD rates from the catalyzed pathway dominated at small membrane voltages. At higher membrane voltages, the protonation and deprotonation of the WD catalyst (eqn (7) and (9)) became the rate determining step, which significantly constrained the overall WD in the catalyzed pathway. As shown in Fig. 2d, the catalyzed pathway exhibited a sigmoidal behavior, where the reaction rate remained relatively unchanged between 0 and 0.2 V and between 0.6 V and 1 V . The electric field enhancement for (R2) was minimum at voltage smaller than $\sim 0.2 \text{ V}$, and the high rate constants at zero field for the catalyzed pathway (*i.e.*, k_{+2}^0 and k_{-2}^0) accounted for the flat region between 0 and 0.2 V . As the voltage increased beyond 0.6 V , the electric field independent (R3) became the rate limiting step, which accounted for the flat region between 0.6 V and 1 V . To improve the electrochemical behavior of BPMs, in particular, at operating current densities relevant to areal-

matched solar fluxes, several simulation strategies were applied to show the impact on the turn-on potential of the BPMs. Fig. 3a shows the simulated total current density as a function of the BPM voltage with different $\text{p}K_{\text{a}}$ of the WD catalyst. To operate at 10 mA cm^{-2} , the voltage across the BPMs decreased from 0.875 V to 0.29 V , when the $\text{p}K_{\text{a}}$ of the WD catalyst decreased from 12.08 to 6.08 .

While the electrochemical behavior of the BPMs showed a dramatic difference at different $\text{p}K_{\text{a}}$ of WD catalysts, the concentration profile of H^+ , OH^- , and other co-ions across the BPM remained the same as illustrated in Fig. 3b at the same operating current density. The concentrations of each species are quite flat at two boundary layers. The low H^+ concentration is mainly due to the low operating current density at 3 mA cm^{-2} , as the H^+ concentration is dependent on the current density, and the H^+ peak concentration increased from 0.022 M to 0.4 M when the current density increased from 3 mA cm^{-2} to 40 mA cm^{-2} (Fig. S11[†]). A logarithm concentration profile for 3 mA cm^{-2} is also shown in Fig. S12.[†] Fig. 3c shows the net charge density, the charge density of the WD catalyst, and the junction potential across the CL within the BPM at 3 mA cm^{-2} with two different $\text{p}K_{\text{a}}$ values of the WD catalysts. The decrease of the net charge density (black curve) at the BPM interface accounted for the decrease of the potential change with the WD catalyst at a low $\text{p}K_{\text{a}}$ value. The net charge density difference between two cases was attributed to higher $C_{\text{WD}}\text{H}^+$ charge density at a higher (R3) forward reaction rate. A space charge region of $\sim 3 \text{ nm}$ can also be seen in Fig. 3c. As shown in Fig. 3d, by decreasing the $\text{p}K_{\text{a}}$ value of the WD catalyst, the catalyzed pathway (dotted red curve) was enhanced significantly and became the dominating contribution to the total current density. For example, at $V_{\text{BPM}} = 0.8 \text{ V}$, the contribution of catalyst pathway to the total water dissociation rate for non-enhanced case was only $2.76 \text{ mol m}^{-3} \text{ s}^{-1}$ and increased to $11.86 \text{ mol m}^{-3} \text{ s}^{-1}$ when enhanced by a factor of 10^4 . A detailed schematic showing the two-pathway water dissociation is presented in Fig. S13.[†]

Fig. 4a shows the impact of the enhancement of the field dependent WD rate, k_{+2}^0 , in the catalyzed pathway. A relatively small change in the turn-on potential was observed when the

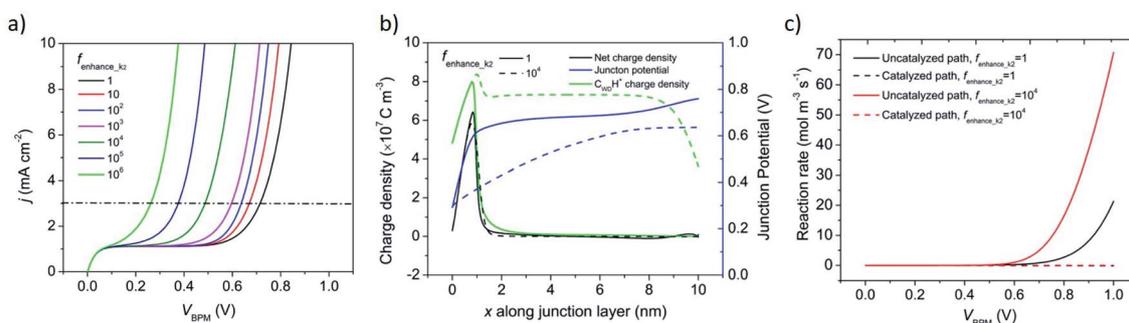


Fig. 4 Improving the turn-on potential of the BPM by improving the electric field dependent WD rate, k_{+2} , in the catalyzed pathway. The electrolytes on both sides of the BPM are $0.5 \text{ M K}_2\text{SO}_4$. (a) The simulated total current density as a function of the BPM voltage with different enhancement factors of k_{+2} ($f_{\text{enhance_}k_2}$). (b) The net charge density, the charge density of the WD catalyst, and the junction potential across the CL within the BPM at 3 mA cm^{-2} with two different $f_{\text{enhance_}k_2}$. (c) The simulated contribution of the catalyzed pathway and uncatalyzed pathway of WD as a function of BPM voltage with two different $f_{\text{enhance_}k_2}$.

enhancement factor for k_{+2}^0 was parametrically swept from 1 to 10 000. As shown in Fig. 4b, the fixed charge density due to the WD catalyst exhibited a very different profile within the BPM junction layer, which gave rise to the potential profile. As noted previously, the protonation and deprotonation of the WD catalyst (eqn (7) and (9)) was the rate determining step for WD; as a result, enhancing k_{+2}^0 does not increase the contribution from the catalyzed pathway as shown in Fig. 4c. However, the change of the potential gradient between 0 nm and ~ 1.5 nm at the junction was enhanced by the change of k_{+2}^0 , which improved the turn-on potential for the un-catalyzed WD pathway.

Furthermore, the impact of the width of the junction as well as the fixed charge density of the BPM on the electrochemical behavior of the BPM was modeled and simulated. Fig. 5 shows the effects of the width of the CL and the fixed charge density in the BPM. When the CL thickness was varied from 5 nm to 100 nm, the current voltage characteristics of the BPM remained unchanged. As shown in Fig. 5b, the net charge density and the potential profile in the CL were almost identical at the two different CL thicknesses. The majority of the electric field enhancement and the associated WD reactions took place within the first few nanometers in the CL, and as a result, the

increase of the CL thickness played a very minimal role in the electrochemical behavior of the BPM. In contrast, when the fixed charge in the BPM was increased from 0.5 M to 2.5 M, a noticeable difference in the current voltage characteristics of BPM was observed (Fig. 5c). The voltage across the BPM decreased from 1.21 V to 0.67 V at an operating current density of 10 mA cm^{-2} when the fixed charge in the BPM increased from 0.5 M to 2.5 M. The water dissociation turn-on voltage also reduced from ~ 0.7 V to ~ 0.5 V with increased fixed charge density from 0.5 M to 2.5 M due to increased net charge density generated at the CL layer at increased fixed charge density (see Fig. S14[†]). In addition, the increase of the fixed charge in the BPM also decreased the co-ion leakage between the cathode and anode chamber. The co-ion leaking current density decreased from 1.78 mA cm^{-2} to 0.9 mA cm^{-2} when the fixed charge in the BPM increased from 0.5 M to 2.5 M. This was a result of the reduced migration of co-ions (K^+) due to decreased mobile cations within the CEL (see Fig. S15[†]) with increasing fixed charge density.

Fig. 6a shows the experimental and modeling comparison of the electrochemical behavior of the BPM using a buffered electrolyte in the $\text{pH} = 7/\text{pH} = 7$ electrolyte combination. To fit the experimental curve (only for the buffer case), the

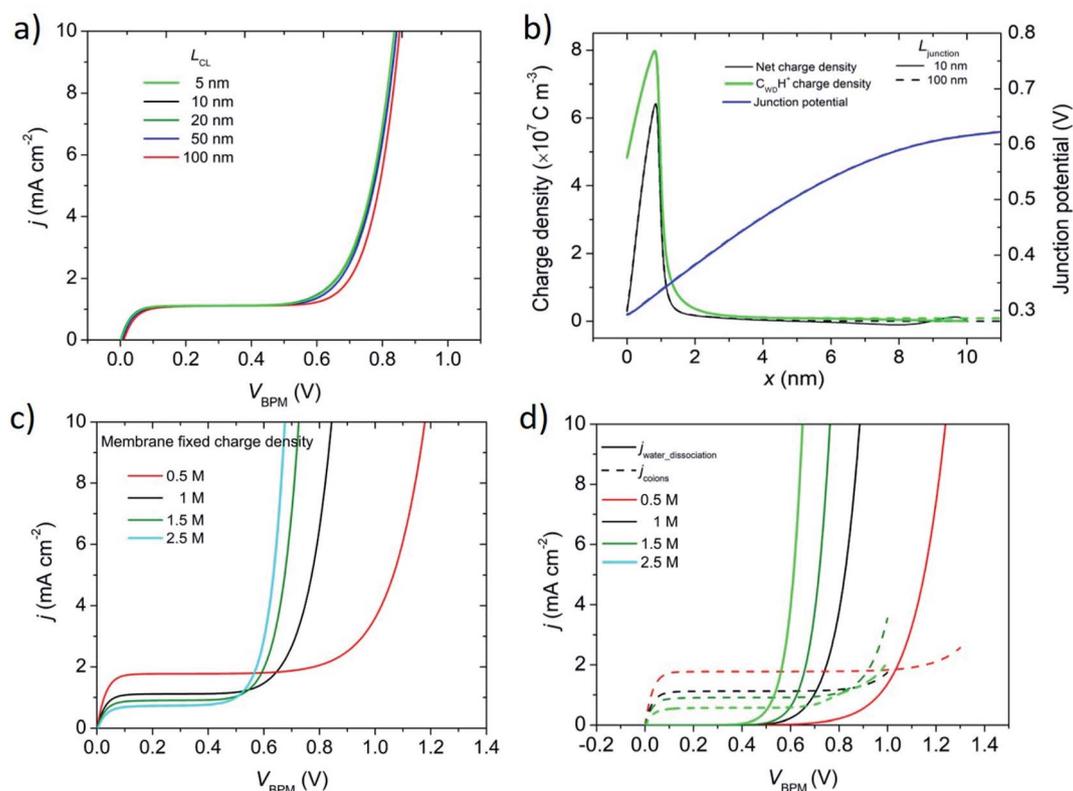


Fig. 5 Improving the turn-on potential of the BPM by improving the width of the CL and the fixed charge density in the BPM. The electrolytes on both sides of the BPM are 0.5 M K_2SO_4 . (a) The simulated total current density as a function of the BPM voltage with different widths of the CL. (b) The simulated net charge density, the charge density of the WD catalyst, and the junction potential across the CL within the BPM at two different widths of the CL. (c) The simulated total current density as a function of the BPM voltage with different fixed charge densities in the AEM and CEM. (d) The simulated partial current density for WD and co-ion leakage as a function of the BPM voltage at different fixed charge densities in the AEM and CEM.

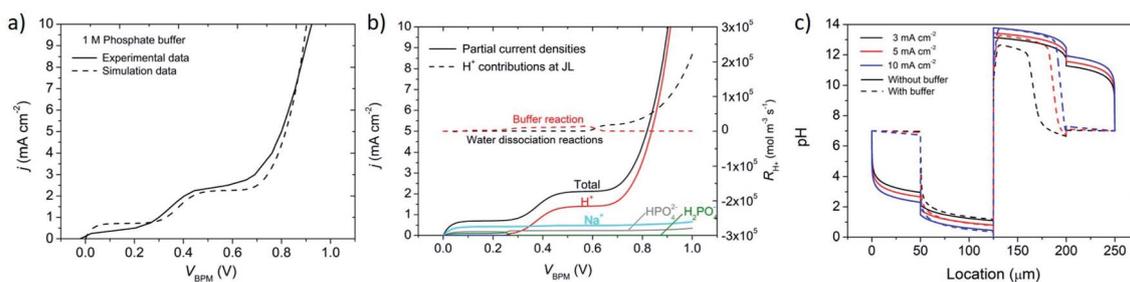


Fig. 6 Modeling electrochemical behavior of the BPM in buffered electrolytes (a) The experimental and modeling comparison of the electrochemical behavior of the BPM in the pH = 7/pH = 7 combination with 1 M buffered electrolytes. (b) Partial current densities of different charged species for the buffer case and CL H^+ generation rates differentiating the contribution of the buffer reaction and water dissociation reaction. (c) The pH profile along the BPM for the cases without buffer (solid lines) and with buffer (dashed lines) at 3, 5, and 10 mA cm^{-2} .

exponential factor, θ , in the Bruggeman model for K^+ , $H_2PO_4^-$ and HPO_4^{2-} was set to 2.1, 1.0 and 1.0, respectively, and f_{water} was set to 0.158. The change of fitting is used accounting for the relative diffusion coefficient in the presence of phosphate ions. The interaction between the buffer ions and polymer membranes with fixed charges can significantly alter the effective diffusion coefficient of solution species within the BPM. In contrast with the un-buffered electrolyte (Fig. 2a), two distinctive plateaus of current densities, one between 0 and ~ 250 mV and one between ~ 400 mV and ~ 500 mV (see Fig. 6a), were observed reproducibly in the steady-state measurements. From 0 to 250 mV, the major current carrier was the K^+ leakage (Fig. 6b); for instance, the K^+ leakage accounted for $\sim 60.6\%$ of the total current at 0.2 V. Two other major partial current densities were carried by HPO_4^{2-} and $H_2PO_4^-$ accounting for 26.2% and 12.7%. While H^+ only carried $\sim 0.5\%$ of the total current density, indicating a limited water dissociation rate in this regime. The further increase in current density in the range of ~ 250 mV to ~ 500 mV attributed to the increased H^+ generation from the buffer reaction, as shown in Fig. 6b. As the current density continued to increase, significant pH gradients were observed within the BPM (Fig. 6c), and the buffer species were fully deprotonated under high pH conditions in the catalyst layer, and as a result, a significant decrease of the proton current density from the buffered reaction was observed, ~ 600 mV. Further exponential increase in current density with increasing voltage beyond ~ 650 mV was accounted by the WD reaction due to the large electrical gradients. Two distinctive pH profiles were observed between the buffered case and un-buffered case, as shown in Fig. 6c. At three different operating current densities, the buffered electrolyte was able to maintain the pH relatively constant within the BLs, while the majority of the pH drop took place within the AEM or CEM layers. In contrast, in the un-buffered electrolyte, a relatively small change of pH was observed within the AEM or CEM layers, and significant pH drops took place within the BLs. Note that the pH values at the BPM interfaces were almost identical between the buffered or non-buffered cases. The pH gradients across the simulation domain in both the buffered electrolyte and un-buffered electrolyte accounted for very small voltage drops during the operation, and the majority of the voltage drops took

place within the CL. However, in solar-fuel devices, the detailed pH profiles would be an important factor for the placement of electrocatalysts to minimize the Nernstian potential loss and to optimize the activity and selectivity of the catalyst under specific pH conditions.

Summary

In summary, the 1D multiphysics model that accounts for WD kinetics and species transport in BPMs successfully predicted the electrochemical behavior of BPMs under solar flux relevant current densities in various electrolyte, buffered or unbuffered, combinations. Significant partial current densities for WD were observed at BPM voltages much less than the equilibrium voltage, *e.g.*, $59 \text{ mV} \times \Delta\text{pH}$ from both experiments and modeling. The co-ion leakage across the BPM at pH differentials accounted for the early presence of the partial current density for WD. Two distinctive electric field dependent WD pathways, the un-catalyzed pathway and the catalyzed pathway, were quantitatively and parametrically studied to improve the turn-on potential of the BPM. The catalyzed pathway accounted for the majority of the partial current density for WD at low voltages, while the un-catalyzed pathway dominated the WD at relatively high voltages. By lowering the pK_a of the WD catalysts and improving the rate limiting step in the catalyzed pathway, *e.g.*, the deprotonation step associated with the WD catalyst, a significant improvement in the turn-on potential was observed. For example, by lowering the pK_a of the WD catalysts from 12.08 to 4.08, the voltage required to operate at 10 mA cm^{-2} lowered from 875 mV to 290 mV. Improvements in the turn-on potentials were also observed when the electric field dependent WD rate, K_2 , in the catalyzed pathway was enhanced. The increase of the electric field strength at the interfacial CL, which enhanced the un-catalyzed pathway, accounted for the turn-on potential improvements. The width of the CL exhibited minimal effects on the BPM current voltage behavior since the majority of the net charge density and the rapid change of the potential profile took place within the first few nanometer in the CL. The increase of the fixed charge density in the BPM improved the turn-on potential and at the same time decreased the co-ion leakage in low voltage regions. A two plateau, titration-like behavior in the current voltage characteristics with

a buffered electrolyte was observed experimentally under steady state conditions. In the buffered electrolyte, the majority of the pH drops took place within the CEM and AEM, while in the unbuffered electrolyte, the majority of the pH drops took place at the aqueous electrolyte layer. The voltage penalty associated with WD, even at relatively low operating current density, accounted for the majority of the voltage loss in the BPM system. The development and implementation of WD catalysts with optimal pK_a under operation conditions as well as fundamental understanding of the electric field dependent water dissociation constant can guide and improve the electrochemical behavior of the BPM system.

Conflicts of interest

There are no conflicts to declare.

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