

Supporting Information for
Understanding Multi-Ion Transport Mechanisms in Bipolar Membranes

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S1: Model Sensitivity to Electrolyte Boundary Layer Thickness, Meshing, and Buffer Recombination Rate Constants

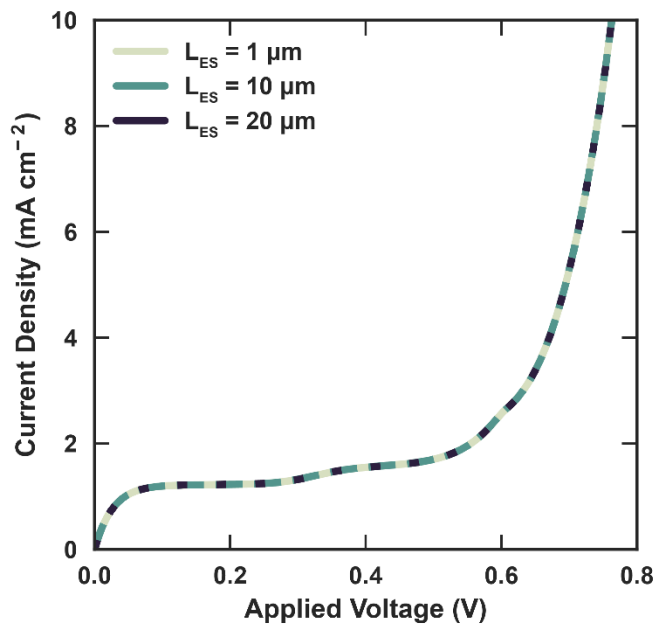


Figure S1: Sensitivity of modeled polarization curves to exchange solution layer thickness (L_{ES}). As shown, the modeled polarization curves remain consistent regardless of the value of L_{ES} .

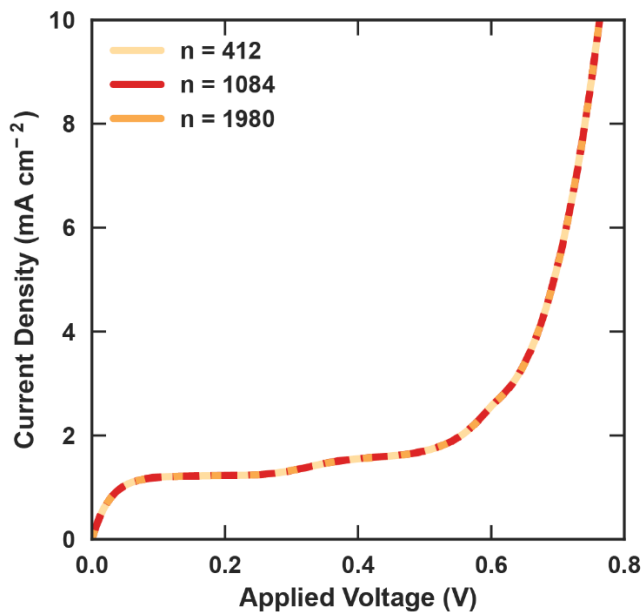


Figure S2: Sensitivity of modeled polarization curves to domain meshing. As shown, the modeled polarization curves remain consistent regardless of the number of domain mesh elements.

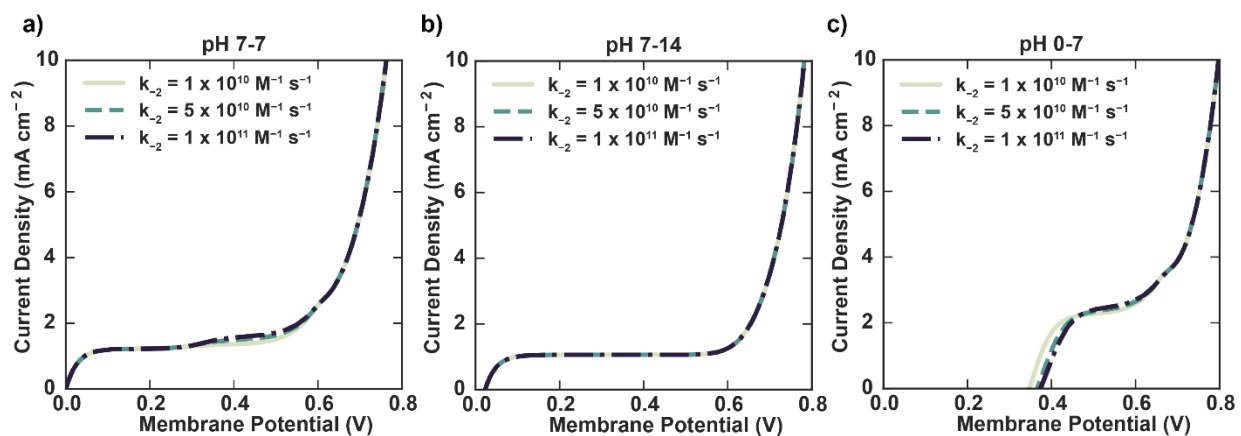


Figure S3: Sensitivity of modeled polarization curves to k_{-2} for (a) pH 7-7, (b) pH 0-7, and (c) pH 7-14. As shown, the overall polarization curve is relatively insensitive to the choice of k_{-2} .

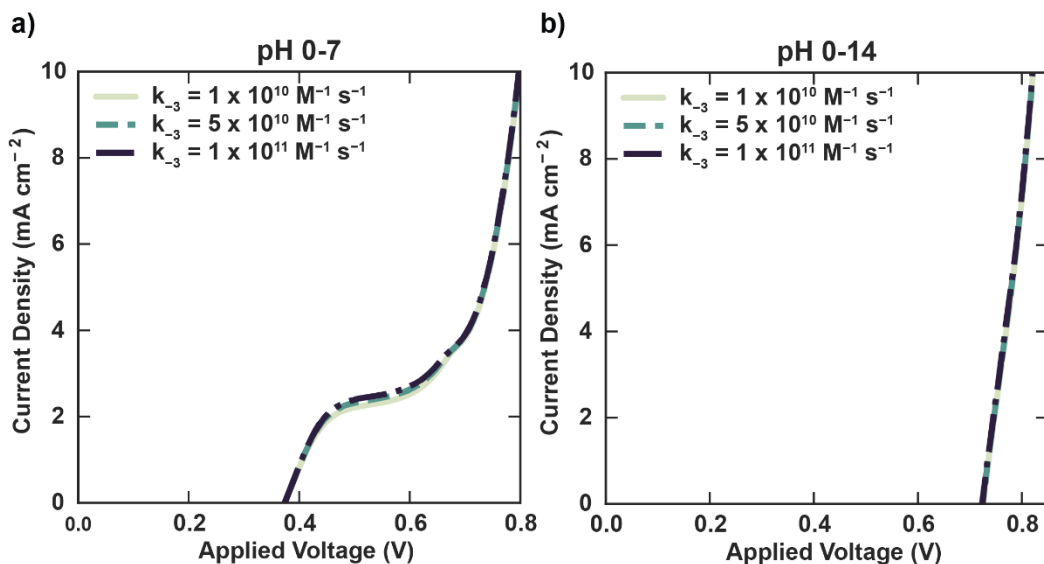


Figure S4: (a-b) Sensitivity of modeled polarization curves to k_{-3} for (a) pH 0-7 and (b) pH 0-14. As shown, the overall polarization curve is relatively insensitive to the choice of k_{-3} .

S2: Derivation of Equilibrium Constants in a Molar Ratio Reference

2.1 For Bimolecular Water Dissociation:



$$\mu_{\text{H}_3\text{O}^+} + \mu_{\text{OH}^-} = 2\mu_{\text{H}_2\text{O}} \quad (2)$$

The chemical potentials for H_3O^+ and OH^- based on the standard reference states ($c_{\text{H}_3\text{O}^+, \text{standard}}^0 = 1 \text{ M H}_3\text{O}^+$, $c_{\text{OH}^-, \text{standard}}^0 = 1 \text{ M OH}^-$, $c_{\text{H}_2\text{O}}^0 = 55 \text{ M H}_2\text{O}$) are given by:

$$\begin{aligned} \mu_{\text{H}_3\text{O}^+}^0 + RT \ln \left(\frac{c_{\text{H}_3\text{O}^+}}{c_{\text{H}_3\text{O}^+, \text{standard}}^0} \right) + \mu_{\text{OH}^-}^0 + RT \ln \left(\frac{c_{\text{OH}^-}}{c_{\text{OH}^-, \text{standard}}^0} \right) \\ = 2\mu_{\text{H}_2\text{O}}^0 + 2RT \ln \left(\frac{c_{\text{H}_2\text{O}}}{c_{\text{H}_2\text{O}}^0} \right) \end{aligned} \quad (3)$$

Rearranging and assuming $c_{\text{H}_2\text{O}} = c_{\text{H}_2\text{O}}^0 = 55 \text{ M H}_2\text{O}$, the equilibrium constant in the standard reference is evaluated as follows:

$$\begin{aligned} K_1^{0, \text{standard}} &= \exp \left(\frac{2\mu_{\text{H}_2\text{O}}^0 - \mu_{\text{H}_3\text{O}^+}^0 - \mu_{\text{OH}^-}^0}{RT} \right) \\ &= \left(\frac{c_{\text{H}_3\text{O}^+} c_{\text{OH}^-}}{c_{\text{H}_2\text{O}}^2} \right) \left(\frac{c_{\text{H}_2\text{O}}^0{}^2}{c_{\text{H}_3\text{O}^+, \text{standard}}^0 c_{\text{OH}^-, \text{standard}}^0} \right) = 1 \times 10^{-14} \end{aligned} \quad (4)$$

For consistency with Craig¹, we define our chemical potential based on molar ratios with the following reference state ($\frac{c_{\text{H}_3\text{O}^+}^0}{c_{\text{H}_2\text{O}}^0} = 1$, $\frac{c_{\text{OH}^-}^0}{c_{\text{H}_2\text{O}}^0} = 1$, $c_{\text{H}_2\text{O}}^0 = 55 \text{ M H}_2\text{O}$). $\mu_{\text{H}_3\text{O}^+}^\theta$, and $\mu_{\text{OH}^-}^\theta$ are the reference chemical potentials based on the same molar ratio reference state:

$$\mu_{\text{H}_3\text{O}^+} = \mu_{\text{H}_3\text{O}^+}^\theta + RT \ln \left(\frac{c_{\text{H}_3\text{O}^+} c_{\text{H}_2\text{O}}^0}{c_{\text{H}_2\text{O}}^0 c_{\text{H}_3\text{O}^+}^0} \right) \quad (5)$$

$$\mu_{\text{OH}^-} = \mu_{\text{OH}^-}^\theta + RT \ln \left(\frac{c_{\text{OH}^-} c_{\text{H}_2\text{O}}^0}{c_{\text{H}_2\text{O}}^0 c_{\text{OH}^-}^0} \right) \quad (6)$$

Since the chemical potentials must be equal independent of the choice of reference state, we can determine the reference potential in the molar ratio reference by equating the chemical potential in the molar ratio reference to that in the standard reference.

$$\mu_{H_3O^+}^0 + RT \ln \left(\frac{c_{H_3O^+}}{c_{H_3O^+,standard}^0} \right) = \mu_{H_3O^+}^\theta + RT \ln \left(\frac{c_{H_3O^+}}{c_{H_2O}^0} \frac{c_{H_2O}^0}{c_{H_3O^+}^0} \right) \quad (7)$$

$$\mu_{OH^-}^0 + RT \ln \left(\frac{c_{OH^-}}{c_{OH^-,standard}^0} \right) = \mu_{OH^-}^\theta + RT \ln \left(\frac{c_{OH^-}}{c_{H_2O}^0} \frac{c_{H_2O}^0}{c_{OH^-}^0} \right) \quad (8)$$

Rearranging, leads to

$$\mu_{H_3O^+}^0 = \mu_{H_3O^+}^\theta + RT \ln \left(\frac{c_{H_3O^+,standard}^0}{c_{H_2O}^0} \right) \quad (9)$$

$$\mu_{OH^-}^0 = \mu_{OH^-}^\theta + RT \ln \left(\frac{c_{OH^-,standard}^0}{c_{H_2O}^0} \right) \quad (10)$$

Substitution of $\mu_{H_3O^+}^0$ and $\mu_{OH^-}^0$ into eq. (4) results in a statement of the equilibrium constant defined with respect to the standard reference state:

$$\begin{aligned} K_1^{0,standard} & \quad (11) \\ &= \exp \left(\frac{2\mu_{H_2O}^0 - \mu_{H_3O^+}^\theta - RT \ln \left(\frac{c_{H_3O^+,standard}^0}{c_{H_2O}^0} \right) - \mu_{OH^-}^\theta - RT \ln \left(\frac{c_{OH^-,standard}^0}{c_{H_2O}^0} \right)}{RT} \right) \\ &= \left(\frac{c_{H_3O^+} c_{OH^-}}{c_{H_2O}^2} \right) \left(\frac{c_{H_2O}^0{}^2}{c_{H_3O^+,standard}^0 c_{OH^-,standard}^0} \right) \end{aligned}$$

Rearranging eq. (11) to solve for the equilibrium constant defined in terms of the molar ratio reference state, K_1^0 :

$$\begin{aligned} K_1^0 &= \exp \left(\frac{2\mu_{H_2O}^0 - \mu_{H_3O^+}^\theta - \mu_{OH^-}^\theta}{RT} \right) \quad (12) \\ &= \left(\frac{c_{H_3O^+,standard}^0 c_{OH^-,standard}^0}{c_{H_2O}^0{}^2} \right) \left(\frac{c_{H_3O^+} c_{OH^-}}{c_{H_2O}^2} \right) \left(\frac{c_{H_2O}^0{}^2}{c_{H_3O^+,standard}^0 c_{OH^-,standard}^0} \right) \end{aligned}$$

$$K_1^0 = K_1^{0,standard} \frac{c_{H_3O^+,standard}^0 c_{OH^-,standard}^0}{c_{H_2O}^0{}^2} = \frac{1 \times 10^{-14}}{55^2} = \frac{c_{H_3O^+} c_{OH^-}}{c_{H_2O}^2} \quad (13)$$

2.2 For Bimolecular Dissociation of a Generic Acid:



To evaluate the equilibrium constant based on the standard reference state ($c_{\text{H}_3\text{O}^+, \text{standard}}^0 = 1 \text{ M}$, $c_{\text{A}^-, \text{standard}}^0 = 1 \text{ M}$, $c_{\text{HA}, \text{standard}}^0 = 1 \text{ M}$), we begin with eqns. (15) and (16):

$$\begin{aligned} \mu_{\text{H}_3\text{O}^+}^0 + RT \ln \left(\frac{c_{\text{H}_3\text{O}^+}}{c_{\text{H}_3\text{O}^+, \text{standard}}^0} \right) + \mu_{\text{OH}^-}^0 + RT \ln \left(\frac{c_{\text{OH}^-}}{c_{\text{OH}^-, \text{standard}}^0} \right) \\ = \mu_{\text{HA}}^0 + RT \ln \left(\frac{c_{\text{HA}}}{c_{\text{HA}, \text{standard}}^0} \right) + \mu_{\text{H}_2\text{O}}^0 + RT \ln \left(\frac{c_{\text{H}_2\text{O}}}{c_{\text{H}_2\text{O}}^0} \right) \end{aligned} \quad (15)$$

$$K_a^{0, \text{standard}} = \exp \left(\frac{\mu_{\text{H}_2\text{O}}^0 + \mu_{\text{HA}}^0 - \mu_{\text{H}_3\text{O}^+}^0 - \mu_{\text{OH}^-}^0}{RT} \right) = \left(\frac{c_{\text{H}_3\text{O}^+} c_{\text{A}^-}}{c_{\text{H}_2\text{O}} c_{\text{HA}}} \right) \left(\frac{c_{\text{H}_2\text{O}}^0 c_{\text{HA}}^0}{c_{\text{H}_3\text{O}^+}^0 c_{\text{A}^-}^0} \right) \quad (16)$$

For consistency with Craig¹, we instead choose to define our chemical potential instead based off of molar ratio with the following reference state ($\frac{c_{\text{H}_3\text{O}^+}^0}{c_{\text{H}_2\text{O}}^0} = 1$, $\frac{c_{\text{A}^-}^0}{c_{\text{H}_2\text{O}}^0} = 1$, $\frac{c_{\text{HA}}^0}{c_{\text{H}_2\text{O}}^0} = 1$). $\mu_{\text{H}_3\text{O}^+}^\theta$, and $\mu_{\text{OH}^-}^\theta$ are the reference chemical potentials with a molar ratio reference.

$$\mu_{\text{H}_3\text{O}^+} = \mu_{\text{H}_3\text{O}^+}^\theta + RT \ln \left(\frac{c_{\text{H}_3\text{O}^+} c_{\text{H}_2\text{O}}^0}{c_{\text{H}_2\text{O}}^0 c_{\text{H}_3\text{O}^+}^0} \right) \quad (17)$$

$$\mu_{\text{A}^-} = \mu_{\text{A}^-}^\theta + RT \ln \left(\frac{c_{\text{A}^-} c_{\text{H}_2\text{O}}^0}{c_{\text{H}_2\text{O}}^0 c_{\text{A}^-}^0} \right) \quad (18)$$

$$\mu_{\text{HA}} = \mu_{\text{HA}}^\theta + RT \ln \left(\frac{c_{\text{HA}} c_{\text{H}_2\text{O}}^0}{c_{\text{H}_2\text{O}}^0 c_{\text{HA}}^0} \right) \quad (19)$$

Because the chemical potentials must be equal independent of choice of reference state, we can determine the reference potential in the molar ratio reference by equating the chemical potential in the molar ratio reference to that in the standard reference.

$$\mu_{\text{H}_3\text{O}^+}^0 + RT \ln \left(\frac{c_{\text{H}_3\text{O}^+}}{c_{\text{H}_3\text{O}^+, \text{standard}}^0} \right) = \mu_{\text{H}_3\text{O}^+}^\theta + RT \ln \left(\frac{c_{\text{H}_3\text{O}^+} c_{\text{H}_2\text{O}}^0}{c_{\text{H}_2\text{O}}^0 c_{\text{H}_3\text{O}^+}^0} \right) \quad (20)$$

$$\mu_{\text{A}^-}^0 + RT \ln \left(\frac{c_{\text{A}^-}}{c_{\text{A}^-, \text{standard}}^0} \right) = \mu_{\text{A}^-}^\theta + RT \ln \left(\frac{c_{\text{A}^-} c_{\text{H}_2\text{O}}^0}{c_{\text{H}_2\text{O}}^0 c_{\text{A}^-}^0} \right) \quad (21)$$

$$\mu_{HA}^0 + RT \ln \left(\frac{c_{HA}}{c_{HA,standard}^0} \right) = \mu_{HA}^\theta + RT \ln \left(\frac{c_{HA}}{c_{H_2O}^0} \frac{c_{H_2O}^0}{c_{HA}^0} \right) \quad (22)$$

Rearranging, we obtain:

$$\mu_{H_3O^+}^0 = \mu_{H_3O^+}^\theta + RT \ln \left(\frac{c_{H_3O^+,standard}^0}{c_{H_2O}^0} \right) \quad (23)$$

$$\mu_{A^-}^0 = \mu_{A^-}^\theta + RT \ln \left(\frac{c_{A^-,standard}^0}{c_{H_2O}^0} \right) \quad (24)$$

$$\mu_{HA}^0 = \mu_{HA}^\theta + RT \ln \left(\frac{c_{HA,standard}^0}{c_{H_2O}^0} \right) \quad (25)$$

Substituting $\mu_{H_3O^+}^0$, $\mu_{A^-}^0$, and μ_{HA}^0 into eq. (16), we obtain the following expression for the equilibrium constant in the standard reference state:

$$K_a^{0,standard} = \exp \left(\frac{\mu_{H_2O}^0 + \mu_{HA}^0 + RT \ln \left(\frac{c_{HA,standard}^0}{c_{H_2O}^0} \right) - \mu_{H_3O^+}^\theta - RT \ln \left(\frac{c_{H_3O^+,standard}^0}{c_{H_2O}^0} \right) - \mu_{A^-}^\theta - RT \ln \left(\frac{c_{A^-,standard}^0}{c_{H_2O}^0} \right)}{RT} \right) \quad (26)$$

Rearranging this expression to solve for the equilibrium constant in the molar ratio refence, K_a^0 , gives:

$$K_a^0 = \exp \left(\frac{\mu_{H_2O}^0 + \mu_{HA}^\theta - \mu_{H_3O^+}^\theta - \mu_{A^-}^\theta}{RT} \right) \quad (27)$$

$$= \left(\frac{c_{H_3O^+,standard}^0 c_{A^-,standard}^0 c_{H_2O}^0}{c_{H_2O}^0{}^2 c_{HA,standard}^0} \right) \left(\frac{c_{H_3O^+} c_{A^-}}{c_{H_2O} c_{HA}} \right) \left(\frac{c_{HA,standard}^0 c_{H_2O}^0}{c_{H_3O^+,standard}^0 c_{A^-,standard}^0} \right)$$

$$K_a^0 = K_a^{0,standard} \frac{c_{H_3O^+,standard}^0 c_{A^-,standard}^0}{c_{H_2O}^0 c_{HA,standard}^0} = \frac{K_a^{0,standard}}{55} = \frac{c_{H_3O^+} c_{A^-}}{c_{H_2O} c_{HA}} \quad (28)$$

S3: Membrane Fixed Charge Distribution

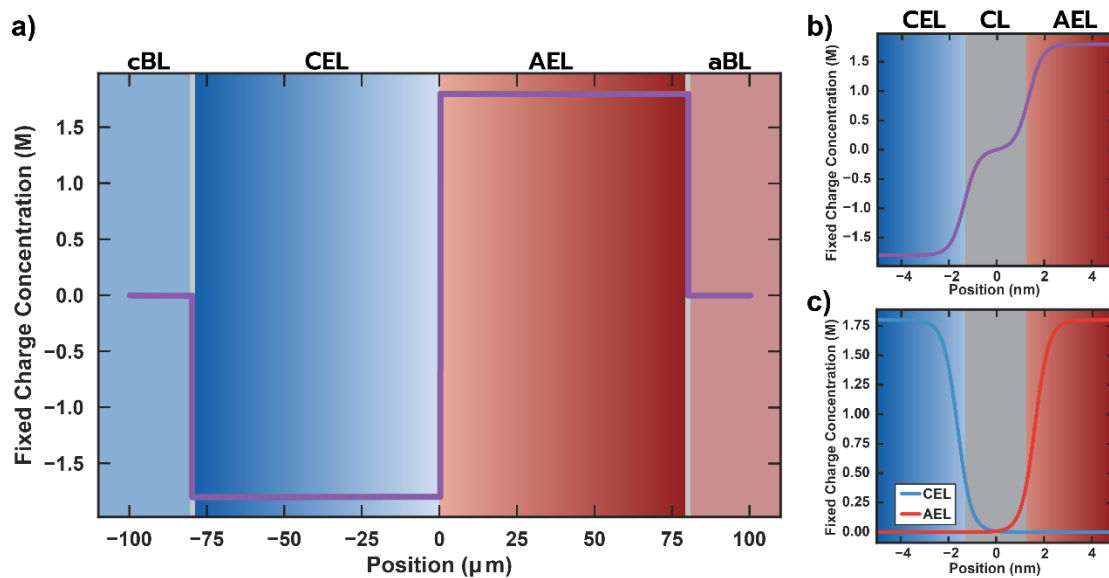


Figure S5: (a) Membrane fixed charge distribution across modeled domain. (b) Membrane fixed charge zoomed in to view junction region. (c) Contributions to membrane fixed charge from both AEL and CEL near the junction

S4: Donnan Equilibrium Between Membrane and Electrolyte

Set chemical potential of species equal across phases, assuming no electric field effects in the bulk phase:

$$\tilde{\mu}_i^M - \tilde{\mu}_i^{ES} = RT \ln \left(\frac{c_i^M c_{H_2O}^{ES}}{c_i^{ES} c_{H_2O}^M} \right) + z_i F \Delta \Phi = 0 \quad (29)$$

Rearrange:

$$c_i^M = c_i^{ES} \frac{c_{H_2O}^M}{c_{H_2O}^{ES}} \exp \left(\frac{-z_i F \Delta \Phi}{RT} \right) \quad (30)$$

Apply electroneutrality condition in ionomer, correct for the background charge, plug in Eq (25) for all ionic species and solve for $\Delta \Phi$:

$$z_M c_M + \sum_i z_i c_i^M = 0 \quad (31)$$

Plug $\Delta \Phi$ and bulk electrolyte concentrations back into Eq (25) to solve for all ionomer phase ionic species concentrations.

S5: Membrane Hydration Hydronium/Hydroxide Content Dependence

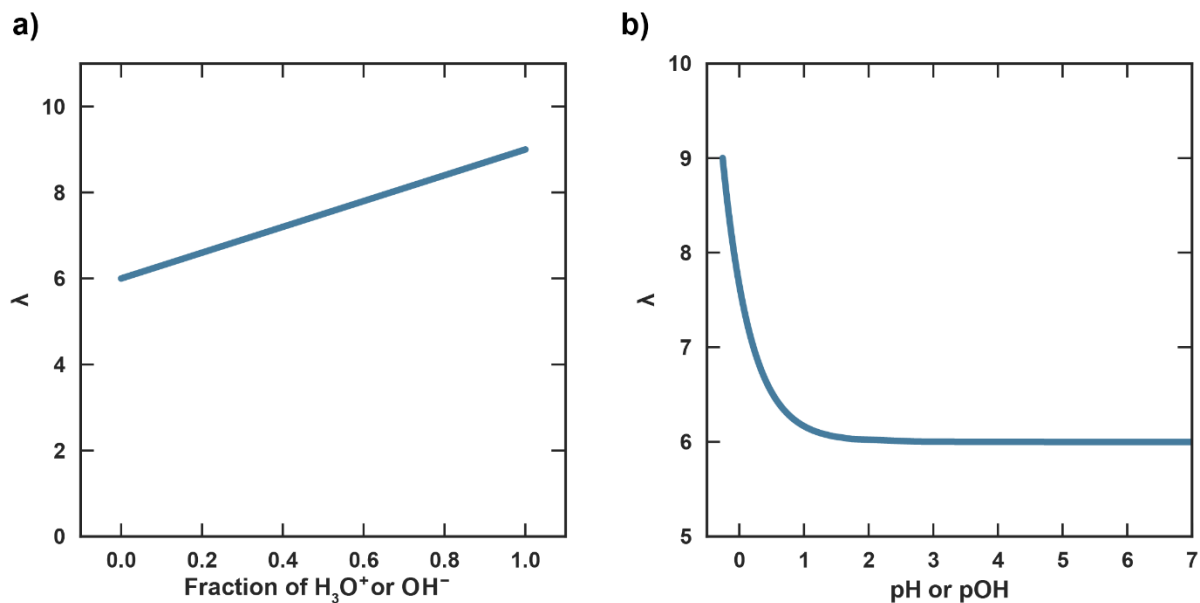


Figure S6: (a) Plot of membrane hydration dependence on the fraction of protons or hydroxides present in the ionomer, and (b) equivalent hydration data plotted instead against local pH or pOH in the ionomer.

S6: Experimental Methods for 4-Probe Measurement

6.1 Preparation of electrodes

The cathode and the anode were titanium (Ti) plates with a platinum (Pt) coating. Pt films were deposited onto Ti plates (0.89 mm thick, annealed, 99.7% metal basis, Alfa Aesar) using AJA radio frequency (rf) magnetron sputtering from a Pt target (Kur J. Lesker, 99.95%, 2-inch diameter). The argon (Ar) flow was kept at 20 sccm and the working pressure was held at 5 μ bar. The rf power was 100 W and the deposition rate was approximately 0.667 \AA s^{-1} . The deposition time was set to 25 min, and the thickness of the resulting Pt film was approximately 100 nm.

6.2 Electrochemical measurement

BPM voltage measurements were performed in a home-built flow electrochemical cell consisting of a cathode, a catholyte compartment, a BPM (Fumasep[®] FBM), an anolyte compartment and an anode. The spacing of the catholyte and the anolyte compartment was 1 cm, and the active area of the cathode, the anode and the BPM was 4 cm². The catholyte and the anolyte were flowed to the electrochemical cell each at a rate of 43 mL min⁻¹ using a peristaltic pump (Masterflex[®] C/L[®] Analog Variable-Speed Pump Systems with Dual Channel Pump Head, Cole-Parmer). 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 electrical current to the anode and the cathode using Keithley 2400 (Tektronix[®]) in a 4-wire sensing mode. BPM voltage measurements were carried in multistep chronopotentiometry mode from high current density (11 mA cm⁻²) to 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. Electrical current control and voltage measurements were performed out using I-V software (developed by Michael Kelzenberg, Caltech). The data were shown as measured without correction for ohmic losses.

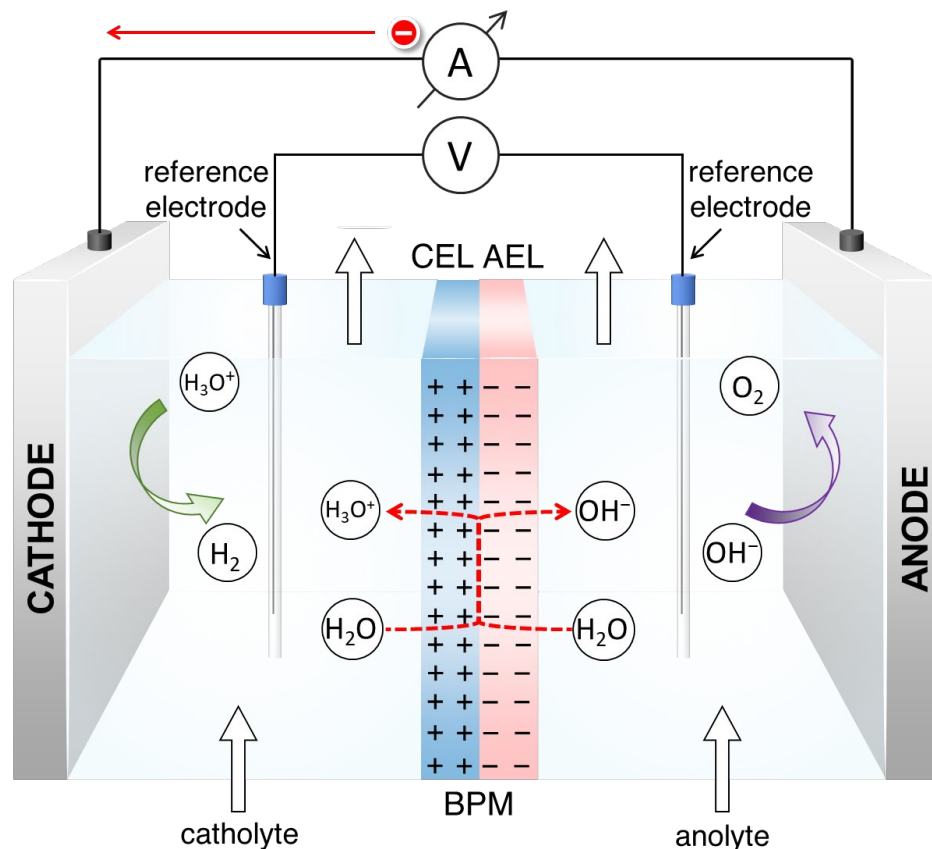


Figure S7: Schematic of 4-probe set up used for experiments.

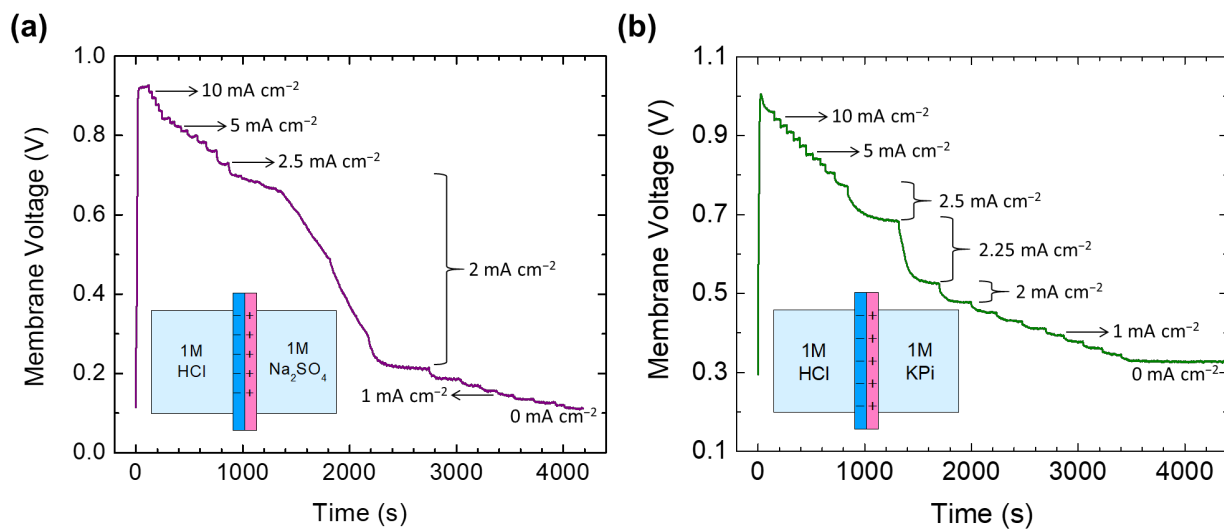


Figure S8: Time dependence of measured polarization curves, demonstrating steady state for all measured current densities in the 1 M HCl | 1 M Na₂SO₄ and 1 M HCl | 1 M K_iH_jPO₄ electrolytes.

S7: Model Equation Set

Table S1: Summary of governing equations.

H₃O⁺	$R_{H_3O^+} = \frac{d}{dx} \left(-D_{H_3O^+} \frac{dc_{H_3O^+}}{dx} + D_{H_3O^+} c_{H_3O^+} \frac{d(\ln(c_{H_2O}))}{dx} + D_{H_3O^+} c_{H_3O^+} \frac{FE}{RT} - D_{H_3O^+} c_{H_3O^+} \frac{d(\ln(\gamma_{\pm}^E))}{dx} \right)$
OH⁻	$R_{OH^-} = \frac{d}{dx} \left(-D_{OH^-} \frac{dc_{OH^-}}{dx} + D_{OH^-} c_{OH^-} \frac{d(\ln(c_{H_2O}))}{dx} - D_{OH^-} c_{OH^-} \frac{FE}{RT} - D_{OH^-} c_{OH^-} \frac{d(\ln(\gamma_{\pm}^E))}{dx} \right)$
Co- and Counter-ions	$R_i = \frac{d}{dx} \left(-D_i \frac{dc_i}{dx} + D_i c_i \frac{d(\ln(c_{H_2O}))}{dx} - D_i c_i \frac{FE}{RT} - D_i c_i \frac{d(\ln(\gamma_{\pm}^E))}{dx} \right)$
Electrostatic Potential	$-\frac{d^2\Phi}{dx^2} = \frac{F}{\varepsilon} \left(c_M(x) + \sum_i z_i c_i \right)$

Table S2: Summary of constitutive relationships.

Water Concentration	$c_{H_2O}(x) = \frac{c_{H_2O}^0}{2} \left(2 - \tanh\left(\frac{x-x_1}{L_{char}}\right) + \tanh\left(\frac{x-x_4}{L_{char}}\right) \right) + \frac{c_{H_2O}^M}{2} \left(\tanh\left(\frac{x-x_1}{L_{char}}\right) - \tanh\left(\frac{x-x_4}{L_{char}}\right) \right)$
Membrane Fixed Charge Concentration	$c_M(x) = \frac{\rho_{M,wet} \times IEC}{2} \left(\tanh\left(\frac{x-x_3}{L_{char}}\right) - \tanh\left(\frac{x-x_4}{L_{char}}\right) + \tanh\left(\frac{x-x_2}{L_{char}}\right) - \tanh\left(\frac{x-x_1}{L_{char}}\right) \right)$
Electric Field	$\frac{d\Phi}{dx} = -E$
Hydration	$\lambda_{CEL} = \lambda_{f_{H_3O^+=0}} + f_{H_3O^+} \lambda_{f_{H_3O^+=1}}$ $\lambda_{AEL} = \lambda_{f_{OH^-=0}} + f_{OH^-} \lambda_{f_{OH^-=1}}$

Degree of Freedom Analysis

1. Unsolved Variables: c_{H_3O} , c_{OH} , Φ , c_i (from $i = 1$ to n : all salt ion concentrations), E , c_M , c_{H_2O} , $\lambda \Rightarrow 7 + n$ unsolved variables
2. Governing Equations: H₃O continuity, OH continuity, Poisson Equation, Salt Ion Continuities $\Rightarrow 3 + n$ equations
3. Constitutive Relationships: Membrane Fixed Charge Definition, Water Concentration Definition, Electric Field relationship, Hydration dependence $\Rightarrow 4$

$$\text{Degrees of Freedom: } (7 + n) - (3 + n) - (4) = 0$$

S8: Tables of Fitting Parameters

Table S3: Vermaas Dataset²

Parameter	Value	Unit
L_{CL}	2.7	nm
α	1.8	
q	1.0	
$\lambda_{f_{H_3O^+}=0}, \lambda_{f_{OH^-}=0}$	6	

Table S4: 1 M HCl | 1 M Na₂SO₄ and 1 M HCl | 1 M K_iH_jPO₄ Dataset

Parameter	Value	Unit
L_{CL}	2.7	nm
α	1.6	
q	1.1	
$\lambda_{f_{H_3O^+}=0}, \lambda_{f_{OH^-}=0}$	6	

S9: Plot of $\text{H}_3\text{O}^+/\text{OH}^-$ Fraction of Current

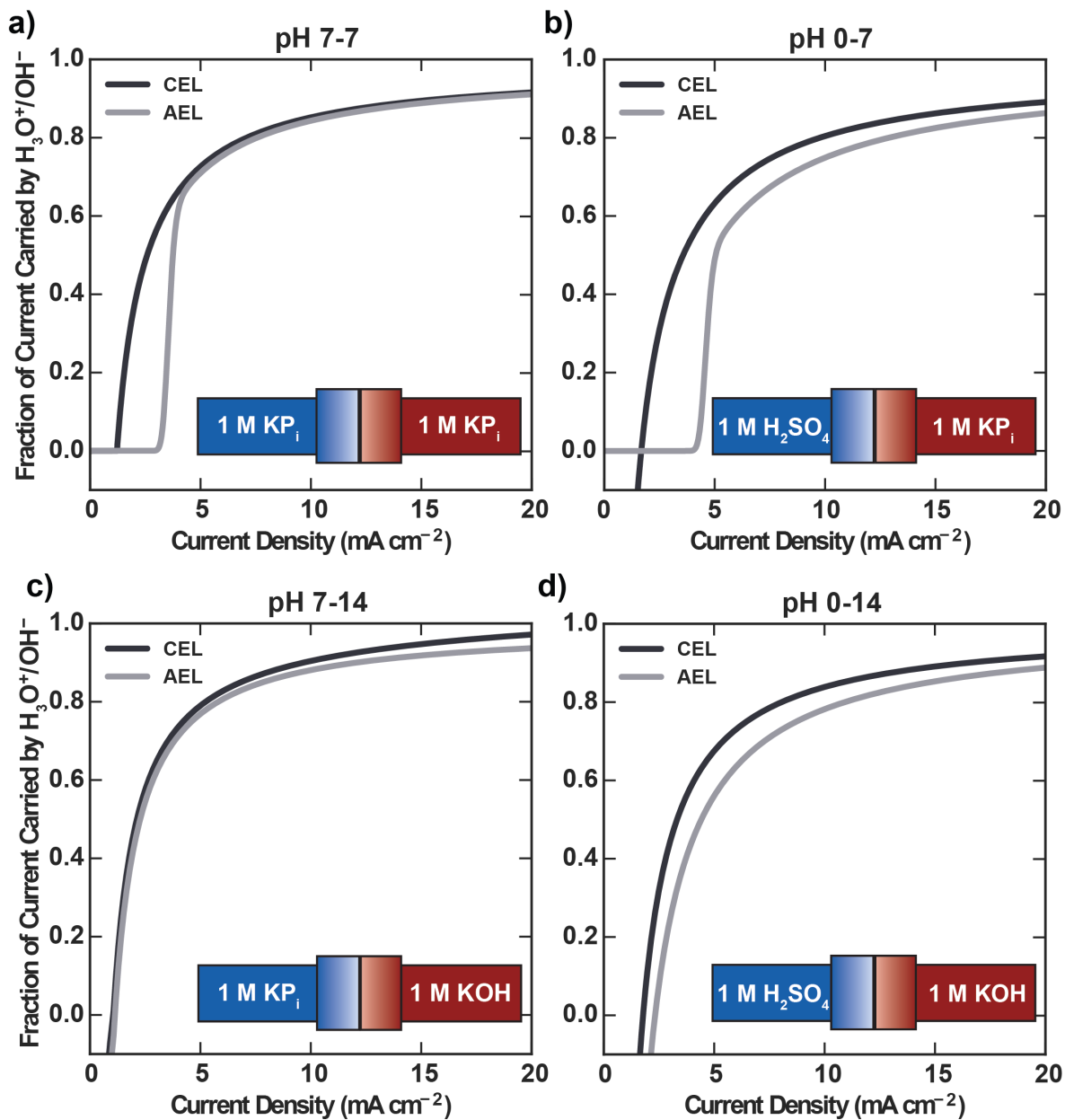


Figure S9: (a-d) Fraction of current carried by hydronium or hydroxide ions plotted against total current for various applied pH gradients: **(a)** pH 7-7, **(b)** pH 0-7, **(c)** pH 7-14, and **(d)** pH 0-14.

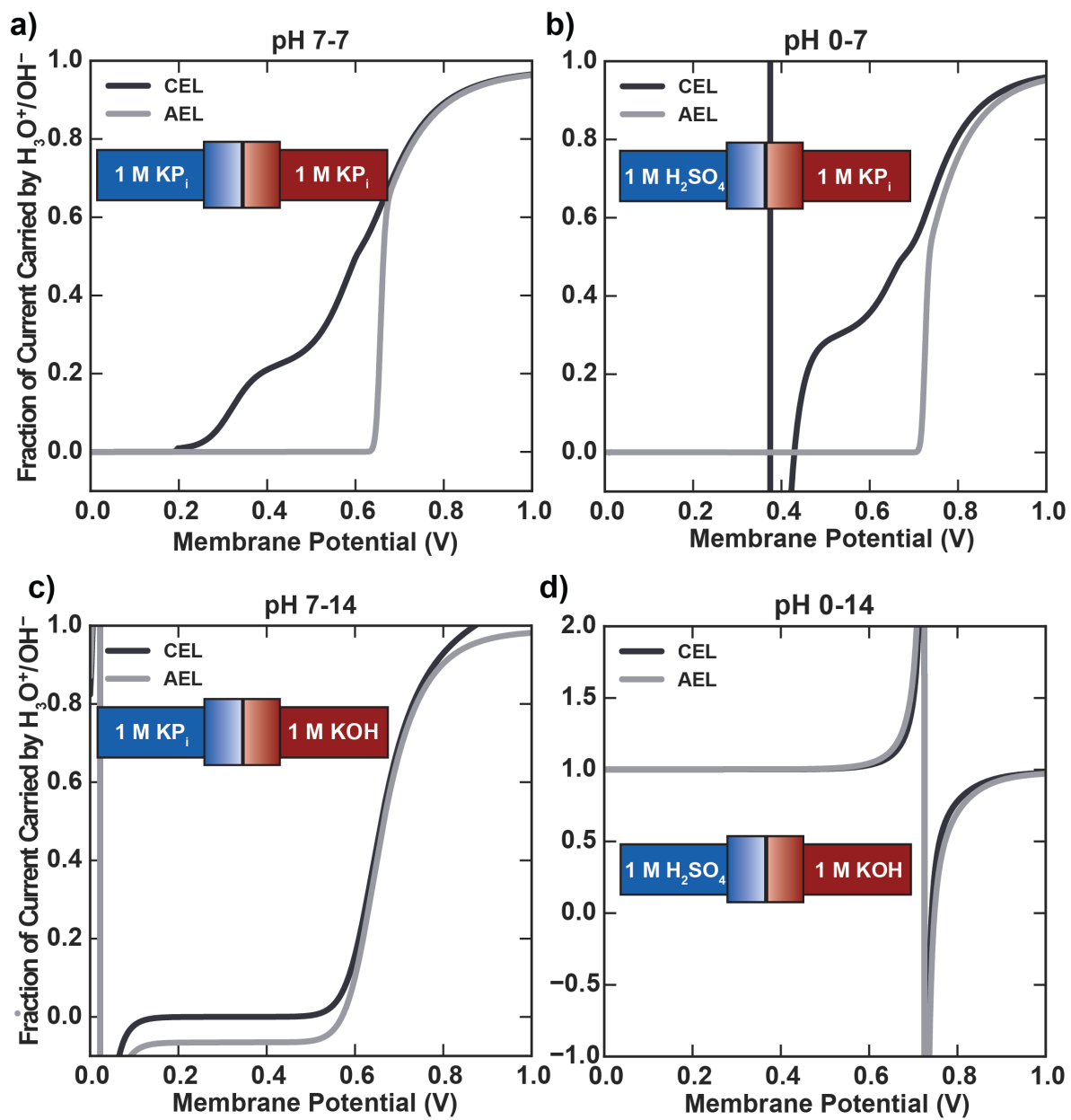


Figure S10: Fraction of current carried by hydronium or hydroxide ions plotted against membrane potential for various applied pH gradients: (a) pH 7-7, (b) pH 0-7, (c) pH 7-14, and (d) pH 0-14.

S10: Electrostatic Potential Profiles

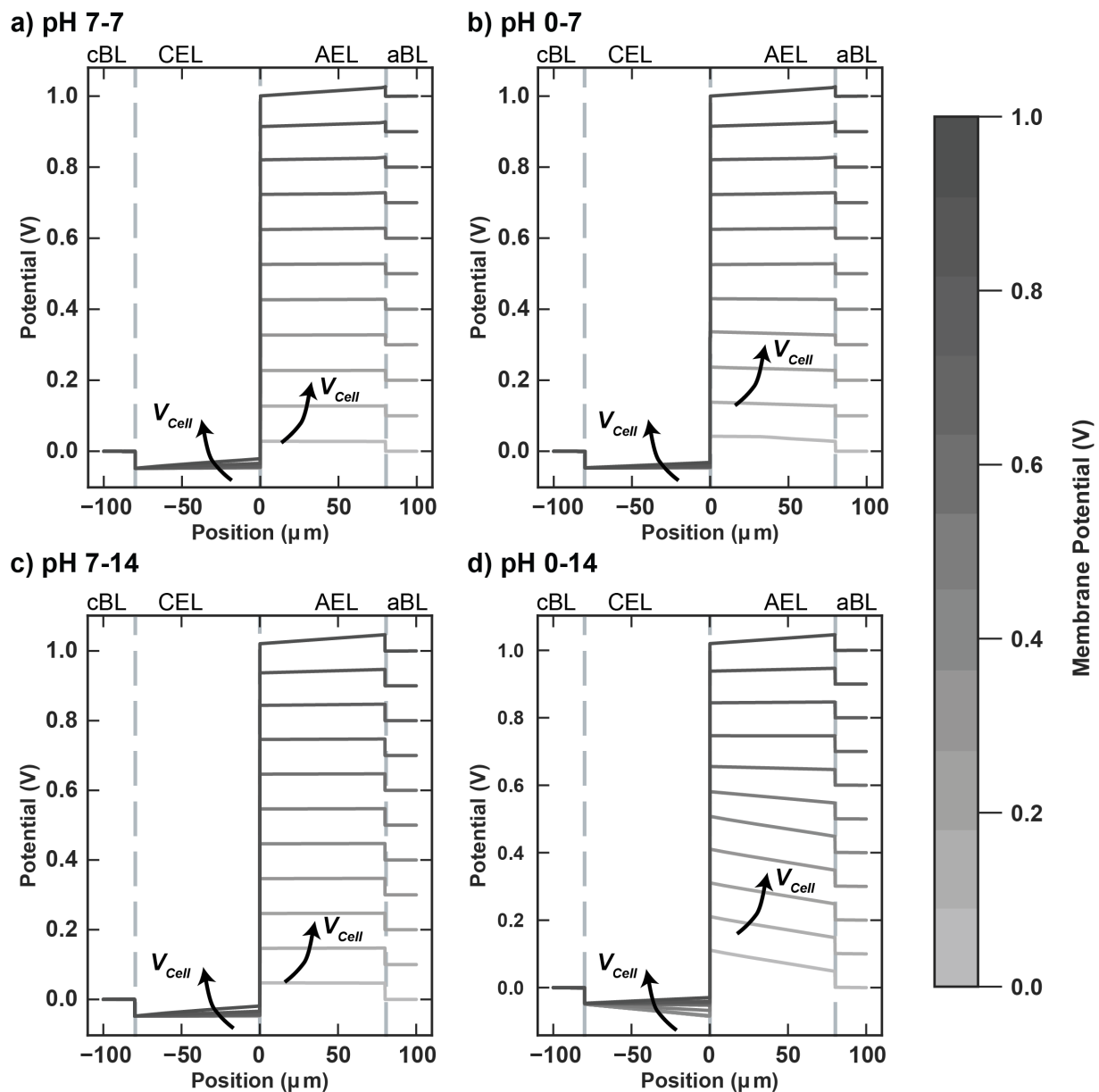


Figure S11: Electrostatic potential profiles at various applied voltages for four modeled pH environments: (a) pH 7-7, (b) pH 0-7, (c) pH 7-14, and (d) pH 0-14. Arrows represent direction of increasing membrane voltage.

S11: Interfacial Electric Fields

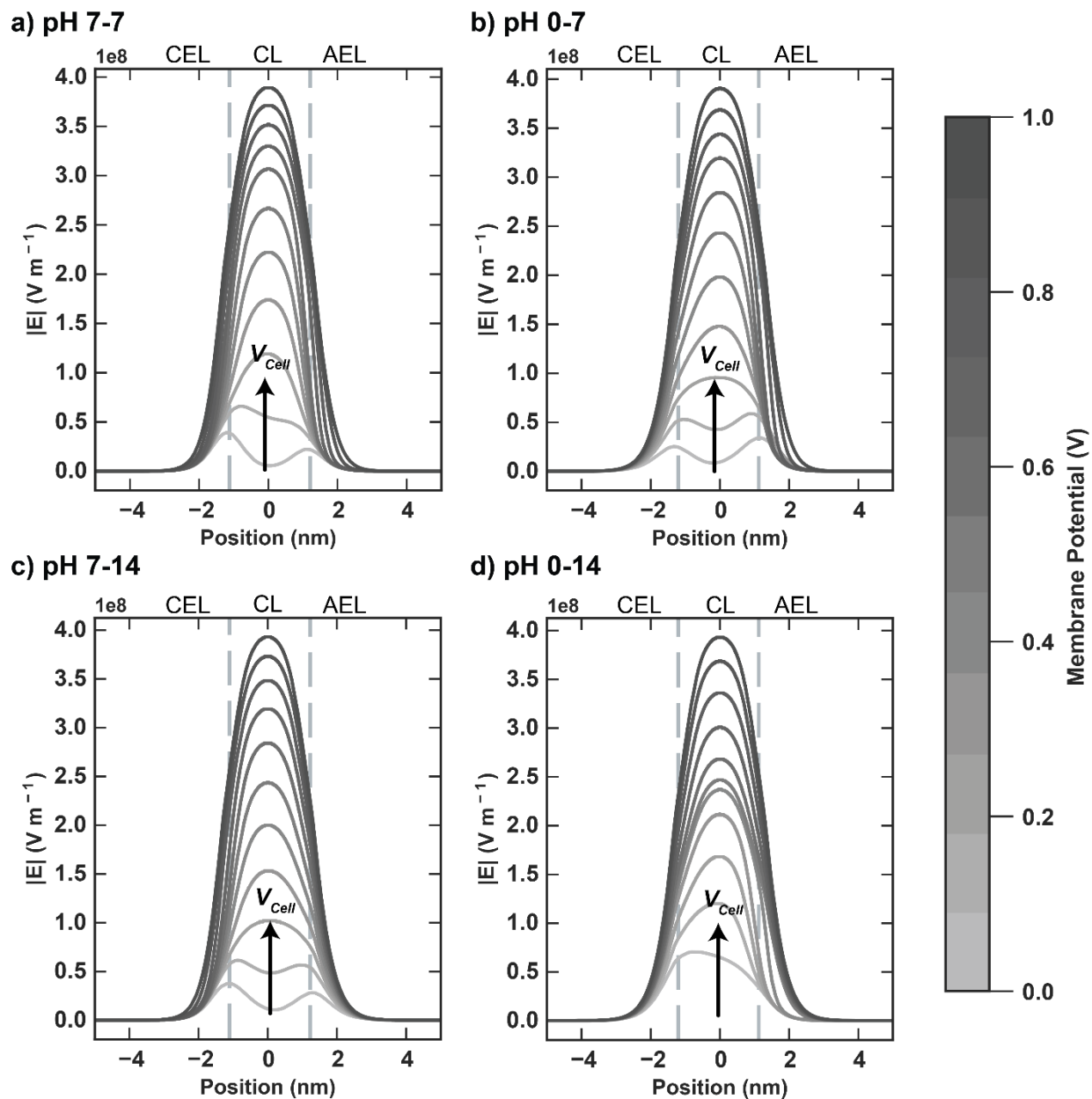


Figure S12: Electric field profiles at the AEL-CEL junction at various applied voltages for four modeled pH environments: (a) pH 7-7, (b) pH 0-7, (c) pH 7-14, and (d) pH 0-14. Arrows represent direction of increasing membrane voltage.

S12: Full pH 0-14 Polarization Curve

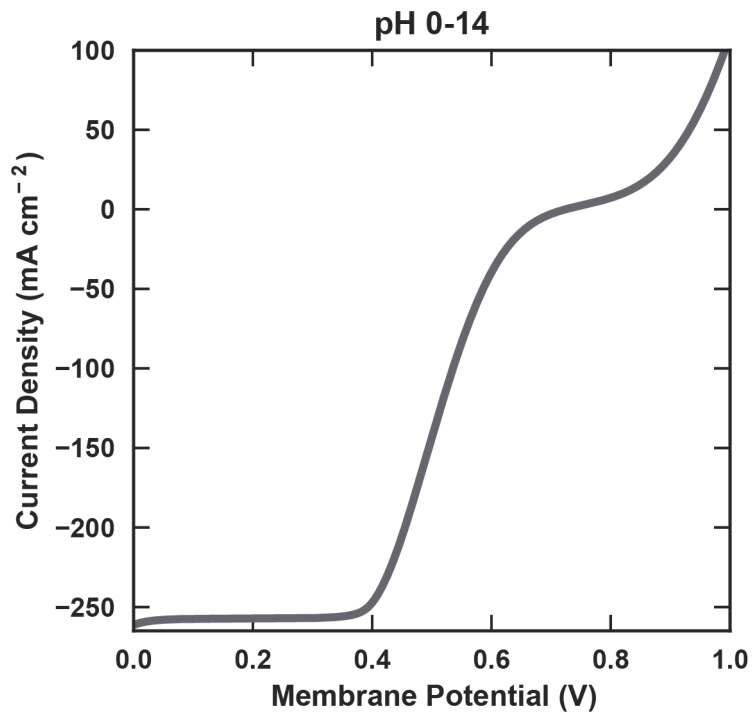


Figure S13: Full simulated polarization curve for pH 0-14, demonstrating high recombination current densities at low applied biases.

S13: Simplified Counterion Concentration Profiles

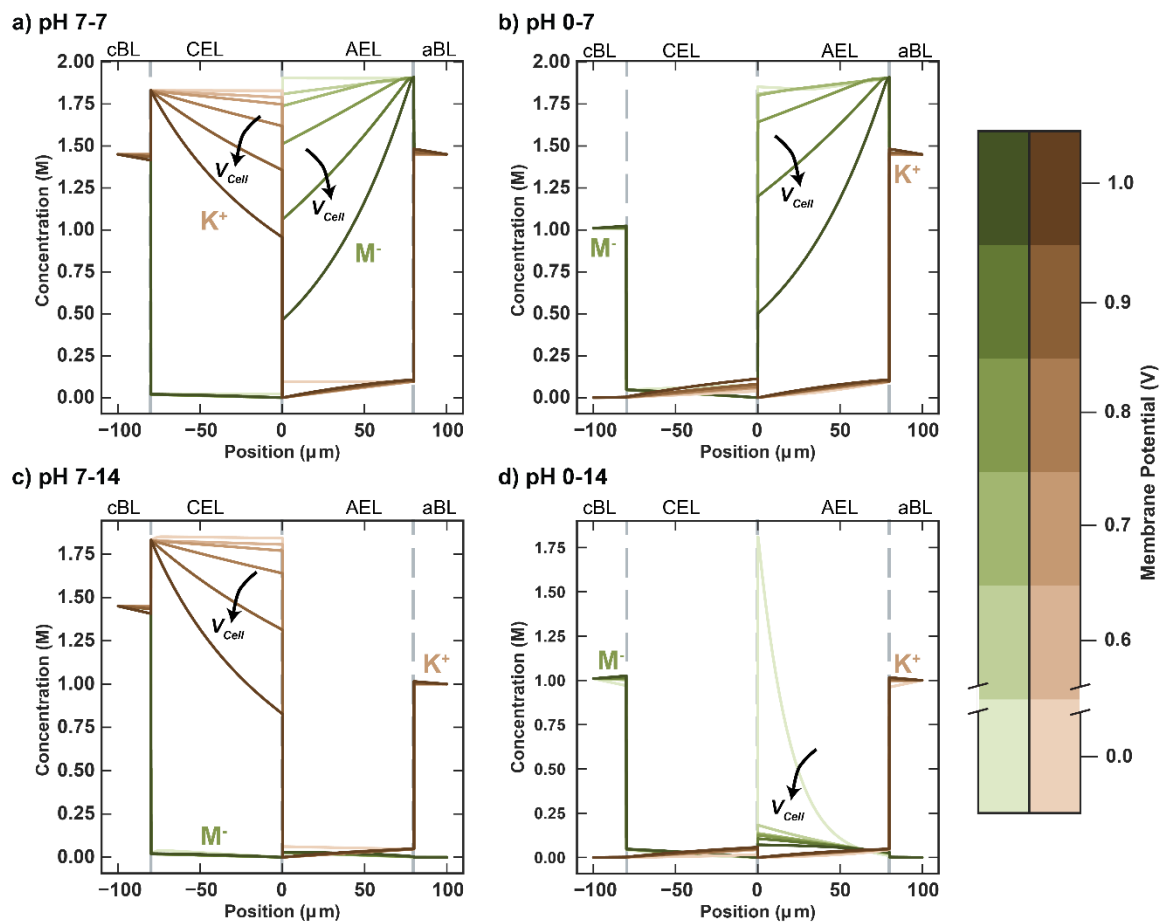


Figure S14: Simplified counterion concentration profiles at various applied voltages for four modeled pH environments: (a) pH 7-7, (b) pH 0-7, (c) pH 7-14, and (d) pH 0-14. Anions are summed by charge. Arrows represent direction of increasing membrane voltage.

S14: Complete Counterion Concentration Profiles

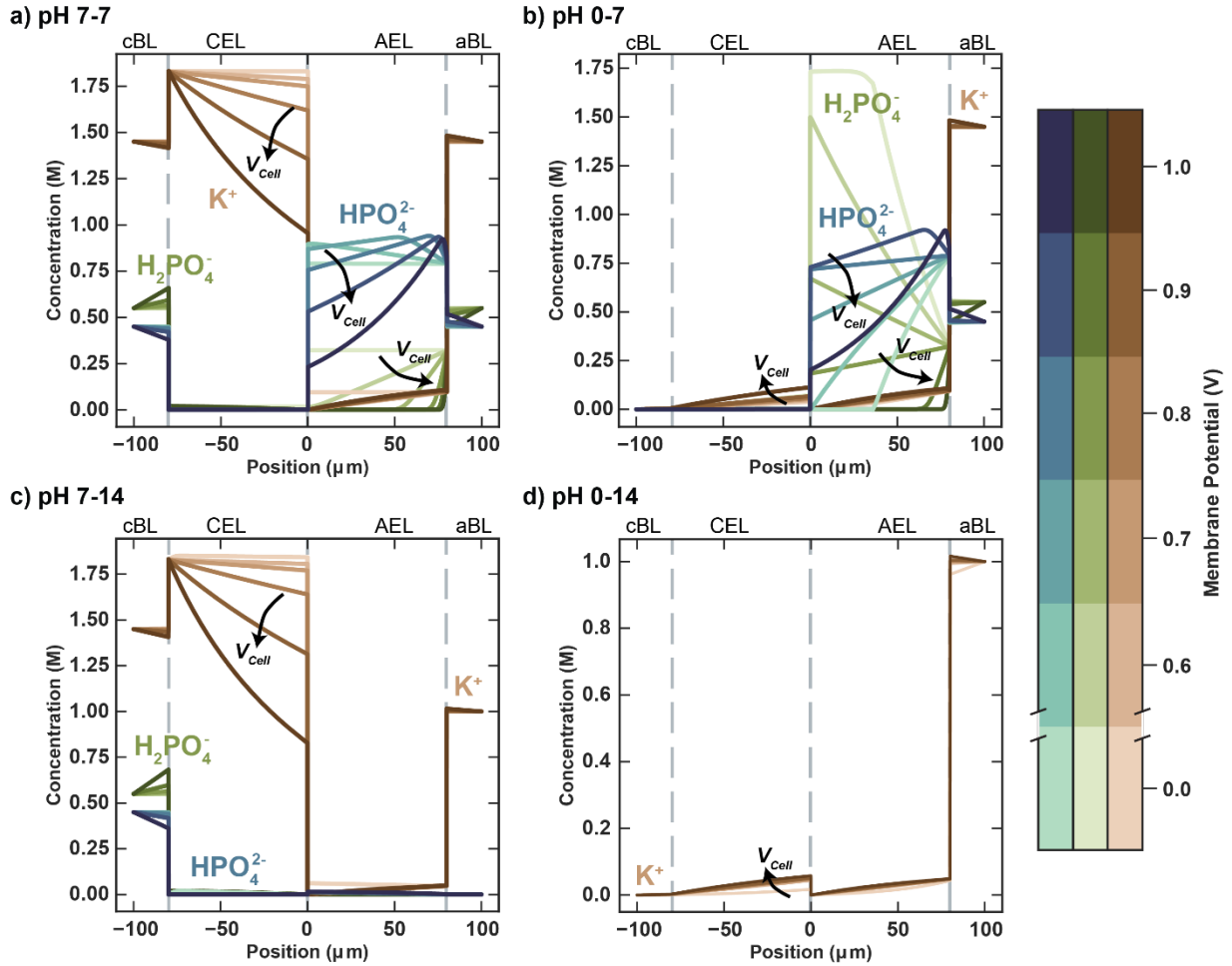


Figure S15: Complete counterion concentration profiles for potassium and phosphates at various applied voltages for four modeled pH environments: **(a)** pH 7-7, **(b)** pH 0-7, **(c)** pH 7-14, and **(d)** pH 0-14. Arrows represent direction of increasing membrane voltage.

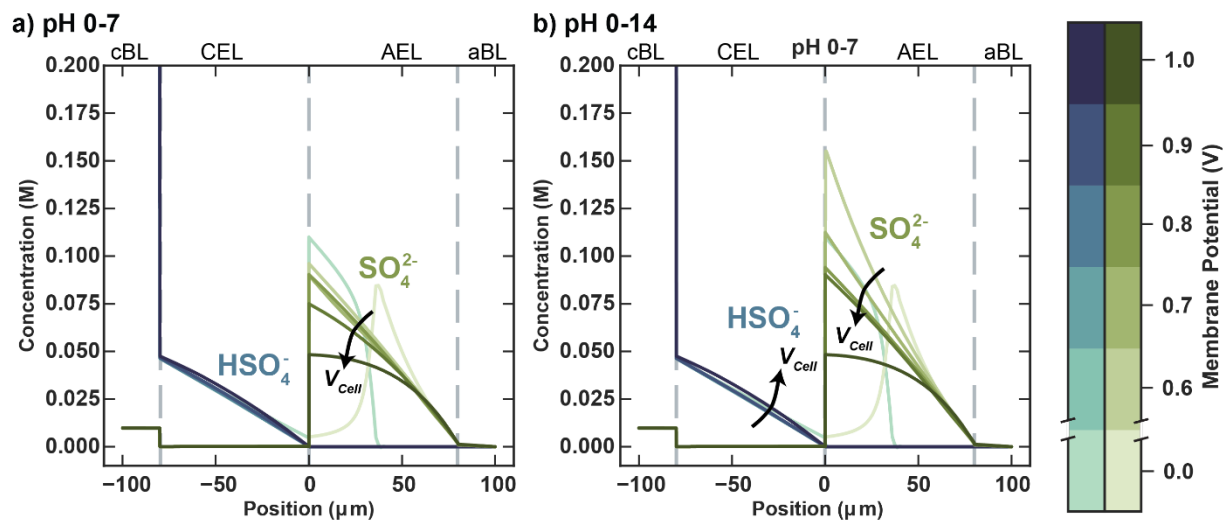


Figure S16: Complete counterion concentration profiles for sulfates at various applied voltages for two modeled pH environments: **(a)** pH 0-7 and **(b)** pH 0-14. Arrows represent direction of increasing membrane voltage.

S15: Depletion Region Hydration Profiles

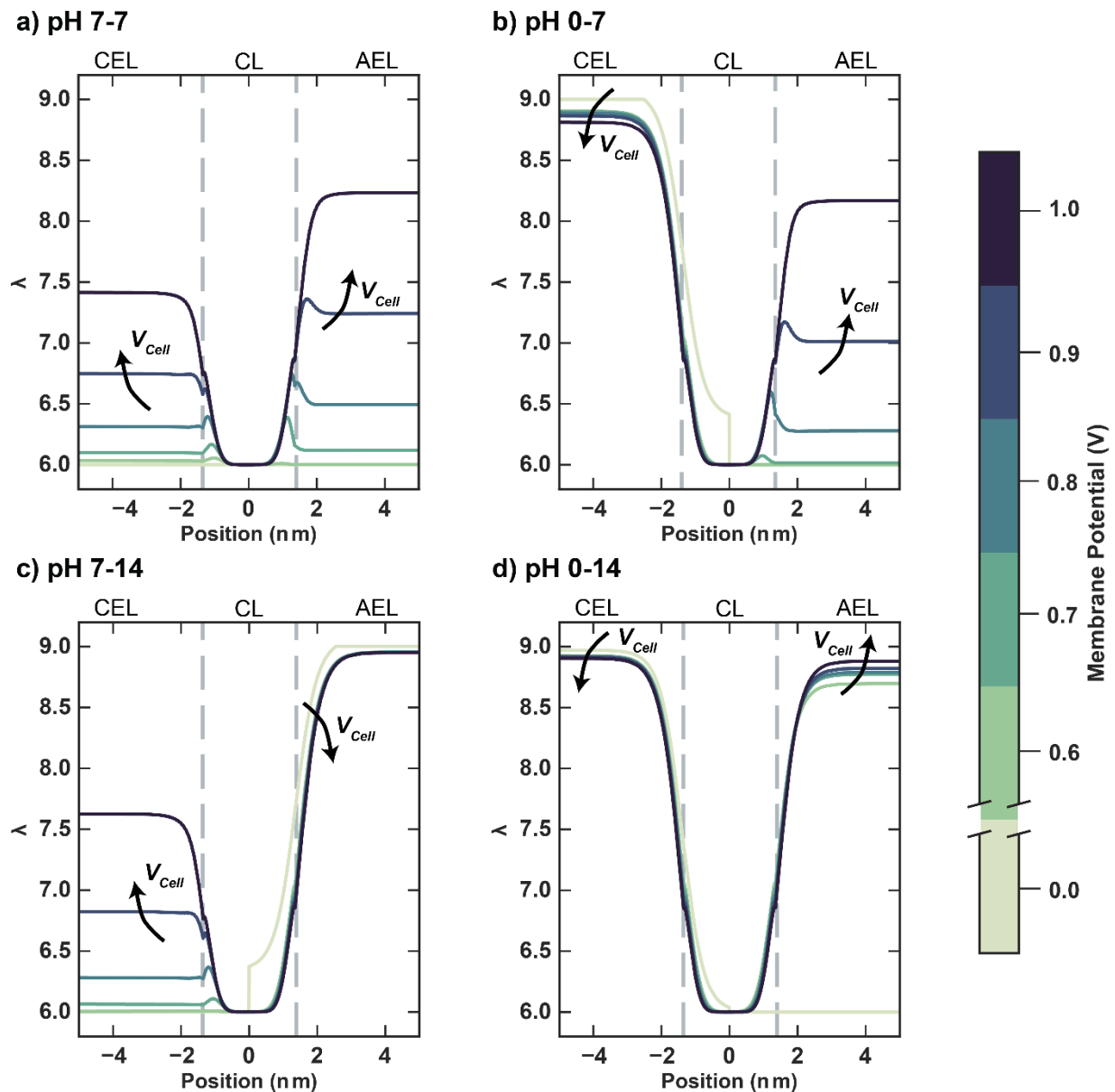


Figure S17: Water hydration profiles in the depletion region at various applied voltages for four modeled pH environments: (a) pH 7-7, (b) pH 0-7, (c) pH 7-14, and (d) pH 0-14. Arrows represent direction of increasing membrane voltage.

References:

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- (2) Vermaas, D. A.; Wiegman, S.; Smith, W. A. Ion Transport Mechanisms in Bipolar Membranes for (Photo)Electrochemical Water Splitting. *Sustain. Energy Fuels* **2018**, No. 9, 2006–2015. <https://doi.org/10.1039/c8se00118a>.