Spatially Resolved Modeling of Electric Double Layers and Surface Chemistry for the Hydrogen Oxidation Reaction in Water-Filled Platinum—Carbon Electrodes

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Supporting Information

ABSTRACT: We present a multidimensional model that spatially resolves transport, surface chemistry, and electrochemical kinetics within water-filled pores of a porous electrode with an adjacent Nafion polymer electrolyte. A novel aspect of this model is the simultaneous capturing of the electric double layers (EDLs) at the water/Nafion and water/electrode interfaces. In addition, the model incorporates discrete domains to spatially resolve specific adsorption at the inner Helmholtz plane (IHP); surface charging due to functional groups; and multistep, multipathway electrochemical reactions at the outer Helmholtz plane (OHP). Herein, we apply the model to the hydrogen oxidation reaction (HOR) in water-filled mesopores of a platinum—(Pt—) carbon electrode, similar to a polymer electrolyte fuel cell (PEFC)’s anode. This work was motivated by the limited understanding of how incomplete polymer electrolyte coverage of a catalyst affects the kinetics and transport in these electrodes. Our results indicate that the Pt within a water-filled pore is only 5% effective for an applied potential of 20 mV. At low potentials (<150 mV), the current is limited by the low H2 solubility in water according to the Tafel—Volmer HOR pathway. At higher potentials, the current is reduced by proton exclusion by the overlapping EDLs and the Donnan potential at the water/polymer electrolyte interface, suppressing the Heyrovsky—Volmer pathway. Our analysis includes a parametric study of the pore radius and length.

INTRODUCTION

Conventional polymer electrolyte fuel cell (PEFC) electrodes with carbon-supported platinum catalysts rely on ionomers for proton conduction. In some instances, the ionomer does not percolate through the entire electrode and does not contact all of the Pt nanoparticle catalyst because of size exclusion. This was shown in an early work by Uchida et al.,1 who used mercury intrusion porosimetry while varying the ionomer concentration in water, there can be increased activation losses showing decreased electrochemically active surface area and electrode performance as a result of high proton-transport resistance at low relative humidity (RH). Shinozaki et al.6 measured a large Pt utilization decrease at low RH for high-surface-area carbon black (Ketjenblack), where a significant amount of the Pt particles reside in the micropores and small mesopores. In contrast, they reported high Pt utilization when using lower surface area carbon black supports (Vulcan XC72R) even at low RH. The authors concluded that the Pt utilization decrease for Ketjenblack is due to protons being transported to the catalyst by adsorbed water in the micropores at higher levels of RH. Ikeda et al.7 observed a similar behavior at low RH in an analysis of the capacitance current during cyclic voltammetry. Pt/Ketjenblack electrodes showed a dramatic drop in capacitance current at low RH, whereas the Pt/Vulcan electrode current was more consistent. The authors suggested that the Pt/Ketjenblack electrode had more water-filled micropores that were inaccessible to ionomer because of size exclusion. Sinha et al.8 recently studied the performance of NSTF electrodes under dry operating conditions and observed significantly higher losses compared to conventional Pt/C electrodes at lower RH levels. These losses were attributed to the substantially decreased proton conductivity in the ionomer-free NSTF electrodes.

A small number of experimental and modeling works have focused on the physics of proton conduction within ionomer-free regions of these electrodes. In an early work, McBreen9 observed notable proton transport over carbon surfaces when using sufficiently humidified gases, suggesting proton transport...
through adsorbed water films. Tominaka et al.\textsuperscript{10,11} observed significant losses in the proton conductivity and electrochemical performance of ionomer-free Pt/C and mesoporous Pt catalysts. For Pt/C catalyst,\textsuperscript{10} the measured ionic resistance was significantly lower than that of bulk water, indicating that acidic surface groups on the carbon black might assist proton transport. Thompson et al.\textsuperscript{12} measured ac impedance spectra for polytetrafluoroethylene (PTFE) and ionomer-bound Pt-black electrodes and for unbound (ionomer-free) Pt-black electrodes. They identified a single mechanism as responsible for the proton conduction in the unbound electrodes and attributed it to conduction through water adsorbed on the Pt surface. Although the values of conductivity were 1–2 orders of magnitude lower than in conventional electrodes they were 2–3 orders of magnitude higher than that of bulk water exposed to CO$_2$.

Typically, proton transport in PEFC electrodes is modeled with a current conservation equation by assuming proton transport only in the polymer electrolyte, charge neutrality, and uniform proton concentration. In one variant, Berg et al.\textsuperscript{13} considered the water content dependence for Nafton’s acid dissociation (resulting in a nonuniform proton concentration) and modeled the proton flux with the Nernst–Planck equation. Alternatively, Wang et al.\textsuperscript{14,15} modeled water-filled agglomerates and ultrathin electrodes saturated with water. For cathode transfer coefficients less than one, they observed nonuniform reaction rates and decreases in effectiveness factor with greater agglomerate radius or electrode thickness. Chan and Eikerling\textsuperscript{16} studied transport and reaction kinetics in water-filled ultrathin cathode electrodes with an extended Pt surface. They described the proton transport in the water pores mainly as electromigration in the diffuse layer with the proton concentration controlled by the Pt’s surface charge. They estimated the surface charge according to the potential of zero charge.

Bazant and co-workers have published multiple works on modeling transport and kinetics in electrochemical cells including the EDL effects and Frumkin correction to the Butler–Volmer equation (FBV).\textsuperscript{17–22} Their works included an application of FBV theory to porous electrodes\textsuperscript{22} and the coupling of Donnan and Stern potentials in modeling ion transport in porous electrodes at the macro- and nanoscales.\textsuperscript{23} In addition, Sprague and Dutta\textsuperscript{4,23} recently used the FBV equation along with Navier–Stokes and Poisson–Nernst–Planck equations to evaluate the diffuse layer effects in laminar flow fuel-cells.

Although many works have studied the oxygen reduction reaction (ORR) in PEFC cathodes because of its sluggish kinetics, recent experimental and modeling studies of the hydrogen oxidation reaction (HOR) suggest that the anode should be revisited. Neyelin et al.\textsuperscript{24} used a hydrogen pump configuration to characterize the exchange current density of the HOR in ionomer-bound Pt/C electrodes. They found the exchange current densities to be in the range of 200–600 mA/cm$^2$, which is 10–100 times larger than commonly reported. Chen and Kucernak\textsuperscript{25} studied transport and kinetics of the HOR on single Pt particles with diameters as low as 72 nm that were adhered to a carbon support. This configuration enabled mass-transport rates that far exceed those possible with a rotating disk electrode (RDE). With these high mass-transport rates, they measured two plateaus in steady-state polarization curves that corresponded to adsorption and diffusion limiting reaction rate steps. This suggested the need for a dual-pathway, multistep HOR model, which was implemented by Wang et al.\textsuperscript{26,27}

Herein, we present a model to resolve the ion-transport mechanisms and reaction kinetics in water-filled pores of porous electrodes. We implemented our model in a multi-dimensional numerical framework that spatially resolves the nonequilibrium double layers at the water/electrode and water/Nafion interfaces. The model also includes the physics for specific adsorption at the inner Helmholtz plane (IHP); the chemistry of surface functional groups, electron dipoles, and the space-charge layer in the solid electrode; and multistep, multipathway electrochemical reactions. In this article, we apply the model to the HOR in a water-filled pore with an adjacent layer of polymer electrolyte, resembling a carbon-supported Pt anode in a PEFC. Throughout the article, we use comparisons to a Nafion-filled pore to highlight the transport and reaction hindrances due to water.

**MODEL DESCRIPTION**

Figure 1 shows a schematic of a conventional PEFC anode with Pt/C catalyst and Nafion ionomer binder. It is assumed that the electron-conducting Pt/C particles form agglomerates that are bound by Nafion and filled with water during operation. Figure 1 also illustrates the idealized model domains for a single water-filled pore in an agglomerate with an adjacent Nafion film. As Figure 2 shows in detail, the model is two-dimensional, axisymmetric, and divided into two major domains: the Nafion film and the cylindrical water-filled pore bounded by the polarized Pt/C surface. We simulate Nafion with mobile protons and stationary negative SO$_3^-$ ions at a concentration consistent with Nafion. Because the surface area of the Pt/C particles is primarily that of carbon black, we model the pore wall considering only the carbon black surface properties. The ratio of Pt area to carbon area is approximately 0.06 for the catalysts we consider. Rather than distinguishing individual Pt particles, we uniformly distribute the electrochemical reactions using the area-average Pt surface area.

We model the EDLs at the carbon black water/pore wall interface according to Gouy–Chapman–Stern–Grahame (GCSG) theory, dividing it into three subdomains: (1) the diffuse layer and the (2) outer and (3) inner portions of the Stern layer on either side of the IHP.\textsuperscript{30} The outer Helmholtz...
plane (OHP) separates the diffuse layer from the Stern layer and is the plane of closest approach to the wall for fully solvated ions. We model the Nafion and the diffuse layer as continuum domains where the Nernst–Planck and Poisson equations describe the H\(^+\) and OH\(^-\) diffusion and electromigration. The Poisson equation is also used to describe the electrostatics in the Stern layer. The charge in the Stern layer is constrained to a thin volume corresponding to the IHP, the plane of closest approach to the wall for specifically adsorbed ions. We model the chemistry of the functional groups on the carbon black surface using the 2-pK surface complexation model,\(^3\) where the surface can be covered with positively charged, negatively charged, or neutral surface complexes depending on the pH of the solution and the surface polarization. It is worth mentioning the differences between the specific adsorption at the IHP and the charging due to surface group reactions on the carbon wall. We assume that the specific adsorption occurs at the graphitic basal planes of carbon black and is controlled by chemical and electrostatic forces at the electrode/solution interface. Alternatively, the surface group reactions are assumed to take place at the edges of the graphitic basal planes and are due to native surface complexes. Thus, we locate the charge of these surface complexes at the wall, rather than at the IHP. These surface complexes are either impurities or different functional groups created after oxygen exposure at high temperatures during fabrication.\(^3\)\(^2\),\(^3\)\(^3\)

To account for the potential difference due to preferentially arranged dipoles at the interface we apply a highly simplified version of a jellium model to the carbon surface where the charge density and capacitance correspond to those observed at the potential of zero charge (pzc). We model the electron spillover effect as the charge separation across a finite spacing between two thin volumes, where the separation distance is equivalent to the screening length of the solid carbon. We refer to this domain as the carbon space-charge layer. The Poisson equation describes the electrostatics of the charge separation at the carbon surface, where the applied potential is specified at the interior of the carbon and is equivalent to the inner (Galvani) potential. Here, we neglect the contribution of water dipoles to the pzc, because it has been suggested that roughly two-thirds of the interface water molecules are dimers.\(^3\)\(^4\) Thus, the water has a minor effect relative to the carbon space-charge layer.

### KEY ASSUMPTIONS

In developing the set of model equations described in this work, we relied on the following key assumptions:

- We model electrochemical reactions at the OHP with uniformly distributed electrocatalyst (i.e., we do not locally resolve the Pt surfaces, and instead, we distribute the reaction over the entire pore wall area).
- We treat the activation overpotential of the HOR as the potential difference between the wall and the OHP less the same potential difference at equilibrium.
- We neglect the effect of Pt on the surface properties and zeta potential measurements.
- We neglect impurities in the solution and exposure to CO\(_2\).
- We assume that the Volmer reaction step is much faster than the Tafel or Heyrovsky step in modeling a multistep, dual-pathway HOR.
- The coverage of the reaction intermediate (H–Pt) and the equilibrium coverage are small.
- We use bulk Nafion properties for the Nafion domain.
- We neglect the water dipole contribution to the pzc.

**Model Equations.** The Nernst–Planck equation with the dilute solution approximation describes the H\(^+\) and OH\(^-\) transport in water and Nafion

\[
\frac{\partial c}{\partial t} + \nabla \cdot (-D \nabla c - z u_m F \nabla \psi) = k_f c_{H_2O} - k_b c_{H^+} c_{OH^-}
\]  

(1)

where \(c\) is the ion concentration, \(\psi\) is the potential, \(F\) is Faraday’s constant, \(D\) is the diffusion coefficient, \(z\) is the charge number, and \(u_m\) is the mobility. The diffusion coefficient and mobility values are for transport in water at \(T = 353\) K. In the Nafion domain, those values are adjusted with a factor of 0.2 to account for the Nafion morphology that reduces proton mobility; the factor is based on measured Nafion conductivity. The right-hand side of the equation represents the water dissociation reaction,\(^3\)\(^6\) where \(k_f\) and \(k_b\) are the forward and backward reaction rate constants, respectively.

We resolve electrostatics with the Poisson equation

\[
-\varepsilon_\varepsilon_0 \nabla \nabla \psi = (z c_{H^+} + z c_{OH^-} c_{OH^+} + z c_{SO_3^-} c_{SO_3^-}^+) F
\]

(2)

where \(\varepsilon_\varepsilon_0\) is the vacuum permittivity and \(\varepsilon_\varepsilon\) is the relative permittivity for a particular domain. The Stern layer domains, not including the thin IHP volume, have zero charge density. The value of the relative permittivity of the diffuse layer is adjusted for water at \(T = 353\) K, and the Stern layer permittivity is reduced by oriented water dipoles at the interface. The right-hand side of the equation is the charge density, which is zero for the sulfonylic acid groups in Nafion. \(z c_{SO_3^-} c_{SO_3^-}\) is zero in the water domain.

Fick’s law describes hydrogen diffusion within the Nafion and water.
\[ \frac{\partial c_{\text{H}_2}}{\partial t} + \nabla \cdot (-D_{\text{H}_2} \nabla c_{\text{H}_2}) = 0 \]  

(3)

where \( D_{\text{H}_2} \) is the diffusion coefficient.

**Specific Adsorption.** To incorporate specific adsorption into the numerical model, we model the IHP as a finite, thin volume. The computational domain for the IHP is sufficiently thin that it acts as an interface. The effective surface charge density due to specific adsorption is computed with a revised version of Stern’s modified Langmuir adsorption isotherm

\[ \sigma_{\text{IHP}} = \frac{zeN_{\text{IHP}}}{1 + x_{\text{ads}} \exp \left( \frac{ze(\psi_{\text{IHP}} - \psi_{\text{ads}}) + \theta_{\text{ads}}}{kT} \right)} \]

(4)

where \( e \) is the electron charge; \( k \) is the Boltzmann constant; \( N_{\text{IHP}} \) is the number of sites for adsorption; \( \theta_{\text{ads}} \) is the chemical specific adsorption potential; \( \psi_{\text{IHP}} \) and \( \psi_{\text{ads}} \) are the electric potentials at the IHP and OHP, respectively; and \( x_{\text{ads}} \) is the ion mole fraction at the OHP.

The version of Stern’s isotherm commonly used in the literature relates the probability of ion adsorption to the molar fraction of the ions in the bulk of a solution. When dealing with overlapping double layers in pores or nanochannels, it is more useful to relate the probability of ion adsorption to the centerline concentration or to the concentration at another nearby plane (e.g., the OHP). This is especially true if the ion concentration varies with the axial distance along the pore as it does in our model. To resolve the axial dependence of ion-specific adsorption, we have revised Stern’s isotherm to arrive at eq 4 by considering two possible energy states for ions: (1) adsorbed ions at the IHP and (2) desorbed ions at the OHP. The probability of the ion being in either state is partially determined by the Boltzmann factor with electrostatic and chemical contributions. The chemical specific energy of adsorption, \( \theta_{\text{ads}} \), is a function of pressure, temperature, ionic activity, and pH. The value of \( \theta_{\text{ads}} \) can be measured experimentally with titrations and electrophoresis for a specific solid/electrolyte interface and it varies in magnitude within a few multiples of \( \pm kT \). Here, we assume \( \theta_{\text{IHP}} = 0 \) because of a present lack of experimental data.

**Surface Complexation Model.** Similarly to the IHP, we model the carbon wall as a finite, thin volume. In this case, the charge in this thin volume reflects the ionic surface groups at the carbon surface. As shown by Figure 3, we model the wall charging mechanism with the 2-pK site-binding model. We choose the 2-pK model instead of the 1-pK or MUSIC model because of its better compatibility with the triple-layer structure of the EDL when experimental zeta-potential measurements are used. As Figure 3 shows, the surface species can be in three protonation states: zero, one, or two protons per site. It was previously shown that carbon blacks are likely to have acidic surface oxides at the edges of graphene layers. Assuming the free sites to be acidic, the charge of the surface complexes with zero protons is negative, SO\(^-\), those with one proton are neutral, SOH\(^+\), and those with two protons are positive, SOH\(_2\)\(^+\), where S denotes the functional surface group. Here, we implement the 2-pK model following the methodology of Piasecki et al. Specifically, we implement the model such that the surface charge is evaluated according to the conditions at the OHP rather than in the bulk solution. In the following discussion, we describe how measurements of the dependence of the zeta potential on the bulk pH are used to evaluate the 2-pK model constants and how the typical bulk solution model inputs are evaluated from properties at the OHP.

The following equilibrium reactions describe the formation of surface complexes from free sites

\[ \text{SO}^- + \text{H}^+ \leftrightarrow \text{SOH}^0 \quad (5) \]

\[ \text{SO}^- + 2\text{H}^+ \leftrightarrow \text{SOH}_2^+ \quad (6) \]

The reaction equilibrium constants \( K_0 \) and \( K_+ \) can be found from the expressions

\[ K_{\text{aH}} \exp \left( \frac{ze(\psi_{\text{wall}} - \zeta)}{kT} \right) = \frac{\theta_0}{\theta_-} \quad (7) \]

\[ K_{\text{aH}}^2 \exp \left( \frac{2ze(\psi_{\text{wall}} - \zeta)}{kT} \right) = \frac{\theta_+}{\theta_-} \quad (8) \]

where the proton activity in the equilibrium bulk solution is \( a_H = \exp(-2.3 \times \text{pH}) \); \( \zeta \) is the zeta potential; \( \psi_{\text{wall}} \) is the potential at the plane of the functional surface groups; and \( \theta_0, \theta_+, \) and \( \theta_- \) are the fractional surface coverages corresponding to \( \text{SOH}^0 \), \( \text{SOH}_2^+ \), and \( \text{SO}^- \), respectively, and can be found from

\[ \theta_0 = \frac{[\text{SOH}^0]/N_{\text{n_wall}}}{[\text{SOH}^0]} \quad \theta_+ = \frac{[\text{SOH}_2^+]/N_{\text{n_wall}}}{[\text{SOH}^0]} \]

\[ \theta_- = \frac{[\text{SO}^-]/N_{\text{n_wall}}}{[\text{SOH}^0]} \quad (9) \]

where the brackets indicate concentrations and \( N_{\text{n_wall}} \) is the total number of sites on the carbon surface. Given the total number of sites and the fractional surface coverage for every charged surface complex group, the surface charge density is

\[ \sigma_{\text{wall}} = eN_{\text{n_wall}}(\theta_0 - \theta_-) \quad (10) \]

Rearranging eqs 7 and 8 into an isotherm form using the constraint \( \theta_+ + \theta_- + \theta_0 = 1 \) and substituting the result into eq 10 yields the equation

\[ \sigma_{\text{wall}} = eN_{\text{n_wall}} \frac{K_{f_+} - 1}{1 + K_{f_0} + K_{f_+}} \quad (11) \]

where
\[ f_0 = \exp \left[ \frac{-e(\psi_{wall} - \zeta)}{kT} - 2.3 \times pH \right] \]  
\[ f_e = f_0^2 \]  

Equation 11 relates the wall charge to the bulk solution’s pH, where the coefficients \( K_v \) and \( K_o \) can be obtained if the relationship between the wall potential or surface charge and the pH is known. Here, we use experimental measurements of zeta potential for different solution pH values (see the Experimental Section) to obtain the wall potential’s dependence on pH. More specifically, we use classical double-layer theory for a planar surface to relate the zeta potential to the wall adsorption during the zeta potential measurements\(^{31}\).

\[ \zeta = \frac{2kT}{lz_e} \ln \left( \frac{\sigma_{wall}}{8e_0\varepsilon_F kT} + \left( \frac{\sigma_{wall}^2}{8e_0\varepsilon_F kT} + 1 \right)^{1/2} \right) \]  

where the ionic strength of the solution is \( I = 0.5(n_{Na^+} + n_{OH^-} + n_{H^+} + n_{Cl^-}) \) and \( n \) is the ion number density. The aforementioned assumption of the thin double layers is reasonable given the typical 200-nm and larger particle agglomerate diameters and the moderate background salt concentration used during the zeta potential measurements. We iteratively solve for \( \sigma_{wall} \) as a function of pH using eq 14 and \( \zeta \) values from a hyperbolic tangent fit to the zeta potential versus pH data. Treating the capacitance within the regions between the Stern layer planes as constants, we arrive at the following expressions relating the wall charge to the wall potential:

\[ \psi_{wall} = \zeta + \sigma_{wall} \frac{(x_3 - x_1)}{e_2} + \sigma_{wall} \frac{x_1}{e_1} \]  
\[ \sigma_{wall} = \left( \frac{\psi_{wall} - \zeta}{(x_2 - x_1)} + \frac{x_2}{x_1} \right) \]  

Equation 15 relates the potential at the wall of carbon to the pH of the solution (the values of \( \zeta \) and consequently \( \sigma_{wall} \) depend on pH). By equating eq 16 to eq 11, we obtain best-fits to the parameters \( K_v \) and \( K_o \). Equation 11 is directly used in the model to determine the wall charge. We use eq 17 to obtain an effective bulk pH input into eq 11 based on the local pH at the OHP by assuming a Boltzmann distribution for the proton concentration. This correction is required because our \( K_v \) and \( K_o \) values are based on the bulk solution pH values in our experiments:

\[ pH = pH_{OHP} = \frac{1}{2.3} \frac{ze\psi_{wall}}{kT} \]  

\[ f_0 = \exp \left[ \frac{-e(\psi_{wall} - \zeta)}{kT} - 2.3 \times pH \right] \]  
\[ f_e = f_0^2 \]  

Finally, the dipole space-charge density at pzc, \( \rho_{pzc} \) is found with an expression for a metal-like conductor with a conductivity, \( k_{pzc} \) proportional to the mobility, \( \mu_{pzc} \) and density of states:

\[ \rho_{pzc} = \frac{k_{pzc}}{\mu_{pzc}} = eD(\psi_p)kT \]

Barbieri et al.\(^{41}\) reported the values of \( C_{ac} \) for different carbons using eq 18. We calculated the corresponding densities of states and observed that they vary within 1 order of magnitude. In the model, we used the value of \( D(\psi_p) = 7.2 \times 10^{-1} \) cm\(^{-3}\) eV\(^{-1}\), which is based on the measured carbon space-charge layer capacitance for Vulcan XC72R.\(^{31}\)

**Hydrogen Oxidation Reaction.** Using single-particle electrodes, Chen and Kucernak were able to measure HOR limiting currents up to 1170 mA/cm\(^2\).\(^{27}\) This value is 2 orders of magnitude larger than the typical limiting current for RDEs. In this high-limiting-current regime, the common Butler–Volmer equation fails to correctly reproduce the HOR polarization curve, resulting in a need for a multistep, dual-pathway HOR model. Similarly to Wang et al.,\(^{28}\) we model the HOR with the Tafel, Heyrovsky, and Volmer mechanisms as the three elementary steps for hydrogen oxidation on the Pt surface:

\[ H_2 + 2Pt \Leftrightarrow 2(H-Pt) \quad \text{Tafel reaction} \]  
\[ H_2 + Pt \Leftrightarrow (H-Pt) + H^+ + e^- \quad \text{Heyrovsky reaction} \]  
\[ (H-Pt) \Leftrightarrow Pt + H^+ + e^- \quad \text{Volmer reaction} \]

The key difference between our approach and that of Wang et al. is that we apply the model at the OHP rather than for the bulk. This is similar to the Frumkin correction for the Butler–Volmer equation.\(^{42}\) Here, we provide the salient details of the derivation of this reaction model. The full derivation is provided in the Supporting Information.

Using a steady-state reaction approximation, where the reaction intermediate (H–Pt) coverage, \( \theta \), does not change with time, we describe the total current as a combination of Tafel–Volmer (\( j_{TV} \)) and Heyrovsky–Volmer (\( j_{HV} \)) pathways.
\[ j_{\text{HOR}} = 2(j_{TV} + j_{IV}) \]
\[ = 2Fk_{TV}c_{0}^{\text{HOR}} \left[ (1 - \theta)^2 - (1 - \theta\theta) (\theta / \theta_0)^2 \right] \]
\[ + 2Fk_{IV}c_{0}^{\text{HOR}} \exp \left( \frac{(1 - \alpha)\Delta\psi_{eq}}{RT} \right) \]
\[ \{ (1 - \theta)\exp \left( \frac{(1 - \alpha)\Delta\psi_{eq}}{RT} \right) - (1 - \theta\theta) (\theta / \theta_0)^2 \exp \left( -\alpha\theta_0 \right) \} \]
\[ \exp \left( -\alpha\theta_0 \right) \]  
\[ \text{(24)} \]

where \( k_{TV} \) and \( k_{IV} \) are the rate constants for the Tafel and Heyrovsky pathways, respectively; \( \alpha \) is the transfer coefficient; \( c_{0}^{\text{HOR}} \) is the local hydrogen concentration at the OHP, and \( \theta_0 \) is the equilibrium intermediate coverage at the wall. We define the overpotential, \( \eta \), for the Heyrovsky reaction step as the difference between the electrode potential, \( \psi_{ad} \) and that at the OHP, \( \psi_{OHP} \), less their difference at equilibrium

\[ \eta = \Delta\psi - \Delta\psi \]  
\[ = (\psi_{m} - \psi_{OHP}) - (\psi_{m} - \psi_{OHP})_{eq} \]  
\[ \text{(25)} \]

Because of the nonlinear conditions, the equilibrium HOR potential is not 0 but, rather, is dependent on the local proton concentration at the OHP. By applying the Nernst equation to the Heyrovsky reaction step, we arrive at the following equation for the equilibrium electrochemical potential

\[ \Delta\psi_{eq} = \Delta\psi_{eq}^0 + \frac{RT}{nF} \ln \left( \frac{c_{H^+}^{\text{OHP}}/c_{H^+}^0}{c_{H^+}^{\text{OHP}}/c_{H^+}^0} \right) \]  
\[ + \frac{RT}{nF} \ln \left( \frac{\theta_0/\theta_0^{\text{nd}}}{(1 - \theta_0)(1 - \theta_0^{\text{nd}})} \right) \]  
\[ \text{(26)} \]

where \( \Delta\psi_{eq}^0 \) is the standard-state potential, proton and hydrogen concentrations, and equilibrium coverage, respectively. Similarly, by applying the Nernst equation to the Tafel reaction step, the equilibrium intermediate coverage is related to the hydrogen adsorption energy, \( \Delta G_{ads}^0 \) and the hydrogen concentration at the OHP

\[ \frac{\theta_0}{1 - \theta_0} = \exp \left( -\Delta G_{ads}^0 / RT \right) \frac{c_{H^+}^{\text{OHP}}}{c_{H^+}^0} \theta_0^{\text{nd}} / (1 - \theta_0^{\text{nd}}) \]  
\[ \text{(27)} \]

We separate the standard-state potential of the Heyrovsky step, \( \Delta\psi_{eq}^0 \), into two components corresponding to hydrogen adsorption and oxidative charge transfer. The standard-state potential for hydrogen oxidation is 0 V, whereas the standard-state potential for hydrogen adsorption is related to the free energy of adsorption, making the overall equilibrium potential for adsorption equal to \( \Delta\psi_{eq} = \Delta G_{ads}/nF \). Inserting this relation along with eq 27 into eq 26, we obtain the relation for the equilibrium potential of the Heyrovsky step as

\[ \Delta\psi_{eq} = \frac{RT}{nF} \ln \left( c_{H^+}^{\text{OHP}} / c_{H^+}^0 \right) \]  
\[ \text{(28)} \]

We use the following expression derived by Wang et al.\textsuperscript{28} to describe the ratio between the intermediate concentration and that at equilibrium

\[ \theta = \frac{\exp(-F\eta/\gamma RT)}{1 - \theta_0 + \theta_0 \exp(-F\eta/\gamma RT)} \]  
\[ \text{(29)} \]

where \( \gamma \) is the potential range constant found with the exchange currents of the three reactions. Inserting eqs 28 and 29 into eq 24 yields the following general expression for the total current

\[ j_{\text{HOR}} = 2Fk_{IV}c_{0}^{\text{HOR}} \]  
\[ \left\{ k_{IV} \left( \frac{\exp(-F\eta/\gamma RT)}{1 - \theta_0 + \theta_0 \exp(-F\eta/\gamma RT)} \right)^2 \right\} \]  
\[ + k_{IV} \left( \frac{c_{H^+}^{\text{OHP}}}{c_{H^+}^0} \right)^{1/a} \left\{ \exp \left( (1 - \alpha)\psi_{ad}/RT \right) \right\} \]  
\[ - \frac{\exp(-(\alpha + \gamma^{-1})F\eta/RT)}{1 - \theta_0 + \theta_0 \exp(-F\eta/\gamma RT)} \} \]  
\[ \text{(30)} \]

**Initial and Boundary Conditions.** Figure 2b shows the two-dimensional cross section of the axisymmetric domain and the boundary conditions. In the numerical model, we run a transient solver for times that are sufficiently long to obtain steady-state solutions. We set the initial potential across all the domains to be 0 V. Initial concentrations of H\(^+\) and OH\(^-\) in the diffuse layer are those in water at pH 7. Assuming that there is no adsorption at the IHP at \( t = 0 \), the ion concentrations at the IHP is set to 0. In the Nafion domain, the initial OH\(^-\) concentration is 0, whereas the H\(^+\) concentration is set to the bulk Nafion concentration, \( c_{\text{Naf}} \) which is equal to the concentration of the sulfonic acid sites, \( c_{\text{SO3}} \). In the wall domain, we assume that all of the surface groups are initially neutral (SO\textsuperscript{2-}). The charge in the carbon space-charge layer due to electron dipoles is set to \( \rho_{\text{vac}} \) in the outer domain and to \( -\rho_{\text{vac}} \) in the inner domain of the carbon surface, so that the net charge of the carbon’s electron-slippery dipole is 0.

The OHP is specified as the reaction plane for the HOR.\textsuperscript{16} In addition, the OHP is where ions are removed from or introduced into the diffuse layer to account for adsorption and desorption, respectively, at the IHP and for protonation and deprotonation, respectively, of surface groups at the wall. We describe these ion-transfer processes at the OHP with flux boundary conditions. Thus, there are three ion fluxes at the OHP: (1) a proton flux due to the HOR, (2) a flux of H\(^+\) and OH\(^-\) due to ion adsorption at the IHP, and (3) a flux for protons protonating or deprotonating the carbon’s functional surface groups. The total proton flux in the diffuse layer at the OHP can be written as

\[ \vec{n}_{H^+,\text{HOR}} = \vec{n}_{H^+,\text{HOR}} - \vec{n}_{H^+,\text{ads}} + \vec{n}_{H^+,\text{wall}} \]  
\[ \text{(31)} \]

where \( \vec{n} \) is the outward normal vector of the diffuse layer boundary at the OHP and

\[ \vec{n}_{H^+,\text{HOR}} = \frac{j_{\text{HOR}}}{F} \]  
\[ \text{(32)} \]

The flux due to proton adsorption at the IHP is driven by the difference between the equilibrium charge density, \( \sigma_{\text{HOR}} \), calculated from eq 4 and the actual charge density at the IHP, \( \sigma_{\text{HOR}}^{\text{act}} \) using a kinetic rate coefficient, \( k_{\text{act}} \), that is set sufficiently high for equilibrium conditions to persist\textsuperscript{85}

\[ \vec{n}_{H^+,\text{ads}} = k_{\text{ads}}(\sigma_{\text{HOR}} - \sigma_{\text{HOR}}^{\text{act}})/F \]  
\[ \text{(33)} \]
The surface-group protonation/deprotonation flux in eq 31 is similarly due to the difference between the equilibrium wall charge density, \( \sigma_{wall} \), computed with eq 11 and the actual, instantaneous charge density at the wall, \( \sigma_{wall}^{act} \):

\[
\dot{n}_{H^+}^{wall} = k_{ads}(\sigma_{wall} - \sigma_{wall}^{act})/F
\]  

(34)

The rate of protons entering the IHP is set equal to the adsorption rate of protons leaving the OHP:

\[
-\dot{n}_{H^+} = \dot{n}_{H^+}^{ads}
\]  

(35)

Likewise, the rate of protons entering/leaving the wall is set equal to the wall adsorption/desorption rate of protons leaving/entering the OHP:

\[
-\dot{n}_{H^+} = \dot{n}_{H^+}^{wall}
\]  

(36)

In eqs 35 and 36, \( \ddot{n} \) is the outward normal vector of the thin IHP and wall volumes, respectively.

The proton concentration at the outer perimeter of the Nafton is set to the bulk Nafton concentration:

\[
\varepsilon_{H^+} = \varepsilon_{Nafton}
\]  

(37)

Because OH\(^-\) ions are assumed to be electrochemically inactive, the only flux at the OHP is that due to the specific adsorption at the IHP:

\[
\dot{n}_{OH^-}^{wall} = \dot{n}_{OH^-}^{ads}
\]  

(38)

where \( \dot{n}_{OH^-}^{ads} \) is calculated analogously to eq 33. All other boundary conditions for H\(^+\) and OH\(^-\) transport are zero-flux conditions:

\[
-\dot{n}_{H^+} = -\dot{n}_{OH^-} = 0
\]  

(39)

Figure 2b also shows boundary conditions for the electric potential in the Poisson equation. We apply uniform potential relative to the reversible hydrogen electrode (RHE) at the outer carbon perimeter:

\[
\psi_{wall} = V - V_{RHE}
\]  

(40)

The potential at the Nafton's outer perimeter is assumed to be 0 V relative to a RHE. The concentration of Nafton at the outer perimeter corresponds to that of bulk Nafton at 1100 mol/m\(^3\), and the hydrogen pressure for all of the results is set at 1 atm. Using a dilute-solution approximation and the Nernst equation, the potential difference at the outer Nafton/RHE interface is equal to 0.0025 V, which we approximate as 0 V in our model:

\[
\psi_{wall}^{Nafton} = 0
\]  

(41)

All of the other boundary conditions in the Poisson equation are zero-charge conditions.

For hydrogen, we apply a constant concentration to the upper Nafton boundary. This value corresponds to the equilibrium hydrogen solubility in Nafton at 100% RH for 1 atm gas pressure:

\[
\varepsilon_{H_2} = \varepsilon_{H_2,eq}^{Nafton}
\]  

(42)

Because the hydrogen solubility in water, \( \varepsilon_{H_2,eq} \), is roughly 2 orders of magnitude lower than that in bulk Nafton, \( \varepsilon_{H_2,eq}^{Nafton} \), there is a need to specify an internal interfacial condition for hydrogen at the water/Nafton interface. We set a hydrogen-flux boundary condition at the Nafton side with the equation:

\[
\varepsilon_{H_2}^{Nafton} = k_{H_2}^{Nafton} \left( \varepsilon_{H_2,eq}^{Nafton} - \varepsilon_{H_2}^{Nafton} \right)
\]  

(43)

where \( k_{H_2}^{Nafton} \) is the kinetic rate coefficient and \( \varepsilon_{H_2,eq}^{Nafton} \) and \( \varepsilon_{H_2}^{Nafton} \) are local hydrogen concentrations at the interfaces in water and in Nafton, respectively. The kinetic rate coefficient is set sufficiently high for equilibrium conditions. The hydrogen flux at the water side of the interface is equal in magnitude to that on the Nafton side of the interface: \( \dot{n}_{H_2}^{wall} = -\dot{n}_{H_2}^{Nafton} \). The hydrogen boundary condition at the OHP is that for the HOR: \( \dot{n}_{H_2,HOR} = -\dot{n}_{H_2}^{wall} = 0 \). All of the other boundary conditions are zero-flux conditions.

### Numerical Model

The model was implemented in a commercial, multiphysics finite-element software package (COMSOL 3.5a, COMSOL, Inc., Palo Alto, CA). The coupled physics was solved with the transient direct solver (UMFPACK). For a 50-nm-long pore, the commercial, multiphysics finite-element mesh had 12130 rectangular elements. The mesh density was selected following a grid convergence study that verified mesh independence and species conservation.

### EXPERIMENTAL SECTION

Vulcan XC72R (Cabot Corp., Boston, MA) carbon black, which is commonly used in fuel cell electrodes, was rinsed three times with deionized water and dried to remove impurities. The carbon black was then dispersed in 2.5 mM NaCl aqueous solution at a weight loading of 0.01% wt. Sis et al.\(^{44}\) showed that the ionic strength of the NaCl solution does not impact the measured zeta potential of carbon black. The solution was stirred with a magnetic stirrer for 2 h. Afterward, the solution was divided into 20 mL samples, and the pH of each sample was adjusted with HCl or NaOH to obtain a pH range from 2 to 10. The pH was measured before and after the zeta potential measurements. Laser Doppler microelectrophoresis with phase analysis light scattering (Zetasizer Nano ZS, Malvern Instruments Ltd., Worcestershire, U.K.) was used to measure the zeta potential of the dispersed carbon particles. Each measurement was repeated three times.

### RESULTS

Figure 4 presents the experimental zeta potential measurements for Vulcan XC72R over a pH range of 2–10. At low pH, the zeta potential ranges between 20 and 30 mV, whereas at high pH, the zeta potential is approximately –40 mV. We observed the zeta potential sign reversal, the isoelectric point (IEP), at a pH of roughly 5. This value agrees well with those reported in literature.\(^{44–46}\) Figure 4 also shows the hyperbolic tangent curve fit used in estimating the 2-pK surface complexation model parameters.

In this work, we applied the model to the case of a Pt/C PEFC anode with Nafton binder, operating at a temperature of 353 K with hydrogen at a gas pressure of 1 atm and 100% relative humidity. The parameters were selected so as to simulate state-of-the-art PEFC electrodes under normal operating conditions. Table 1 lists the key model input parameters used in this model. In the following sections, we present the predicted polarization curves and then analyze the distributions of the proton and hydrogen concentrations, potential, pH, and surface charge densities for the case of a 24-nm-diameter pore that is 50 nm in length. Finally, we present a parametric study of the morphological parameters:
Figure 4. Zeta potential of Vulcan XC72R as a function of pH for a 2.5 mM NaCl background electrolyte. The tanh curve fit used in calculating the 2-pK model’s parameters is also included. The horizontal error bars are standard deviations for the measured pH values before and after the zeta potential measurements. The vertical error bars are standard deviations for the measured pH values before and after the zeta potential measurements.

Figure 5 presents the HOR polarization curves predicted with this model. Figure 5a shows the kinetic current results for a water-filled pore and a Nafion-filled pore. The kinetic current was found using the total current relation (eq 30), where we neglect diffusive hydrogen transport and fix the hydrogen concentration to the equilibrium solubility value, \( c_{\text{H}_2,\text{eq}} \). To compare the kinetic performance of the Nafion-filled pore to the water-filled pore, we fictitiously set the Nafion \( \text{H}_2 \) solubility equal to that of water, \( c_{\text{H}_2,\text{eq}} \). The first term of eq 30 corresponds to the Tafel-Volmer pathway current, \( j_{\text{T-V}} \), at high overpotentials, the isotherm-like term for intermediate coverage, \( \theta/\theta_0 \), approaches zero, forcing the overall \( j_{\text{HOR}} \) to asymptotically approach its maximum value. From Figure 5a, it is evident that the Tafel-Volmer current, \( j_{\text{T-V}} \), dominates at low potential for both the water-filled and Nafion-filled pores. In addition, the Tafel-Volmer current magnitudes are almost equal for the two cases. This is expected because there is no kinetic proton concentration dependence for this pathway. The second term in eq 30 describes the current of the Heyrovsky-Volmer pathway, \( j_{\text{HV}} \), which depends on the potential difference \( \psi_{\text{a}} - \psi_{\text{OHP}} \). In contrast, the Heyrovsky-Volmer current in the water-filled pore is significant only at potentials greater than 0.5 V, which is very high for the HOR. Thus, there are significant kinetic limitations to the HOR in the water-filled pore at applied potentials greater than 0.2 V because of the limited value of \( j_{\text{HV}} \). We investigate the cause for this difference in the subsequent analyses.

To partially validate the model, we compared our results for the Nafion-filled pore to the experimental data of Chen and Kucernak and the modeling results of Wang et al. who focused on modeling the Chen and Kucernak data. A unique feature of the Chen and Kucernak work is the very high mass-transport rates that were obtained using a Pt nanoelectrode in a 0.1 M sulfuric acid electrolyte rather than an RDE apparatus. Here we compare our results to Chen and Kucernak’s results for their smallest, 72-nm-diameter Pt particle, which gave a limiting current density of \( \sim 1.5 \text{ A/cm}^2 \), an approximate Tafel-Volmer asymptotic maximum current density of 0.5–0.6 A/cm\(^2\), and an onset potential for the Heyrovsky-Volmer pathway in the range of 0.1–0.2 V. We compared these data to the kinetic current results for the Nafion pore because it has a proton concentration closer to that of 0.1 M sulfuric acid and uses the hydrogen concentration based on the solubility of \( \text{H}_2 \) in water, which is within 2% of that in sulfuric acid. We can reasonably compare these results with this version of our model in the low current regime where mass-transport effects in the experiment are small (\( \text{H}_2 \) mass transport is not considered in the models for the kinetic current results in Figure 5a.)

Table 1. Model Input Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Source(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, ( T )</td>
<td>353</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>Relative permittivity of water, ( \varepsilon_1 )</td>
<td>61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative permittivity between the wall and IHP, ( \varepsilon_2 )</td>
<td>6</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Relative permittivity between the OHP and IHP, ( \varepsilon_s )</td>
<td>20</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Relative permittivity in carbon, ( \varepsilon_m )</td>
<td>3.3</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Bulk Nafton concentration, ( c_{\text{Nafton}} )</td>
<td>1100</td>
<td>mol/m(^3)</td>
<td>52</td>
</tr>
<tr>
<td>Initial water concentration, ( c_0 )</td>
<td>10(^{-4})</td>
<td>mol/m(^3)</td>
<td></td>
</tr>
<tr>
<td>Pore radius, ( a )</td>
<td>12</td>
<td>nm</td>
<td></td>
</tr>
<tr>
<td>Pore length, ( L )</td>
<td>50</td>
<td>nm</td>
<td>53, 54</td>
</tr>
<tr>
<td>Forward water dissociation reaction rate constant, ( k_c )</td>
<td>2 \times 10(^{-5})</td>
<td>A/m(^2)</td>
<td>36</td>
</tr>
<tr>
<td>Backward water dissociation reaction rate constant, ( k_b )</td>
<td>1.5 \times 10(^3)</td>
<td>1/s</td>
<td>36</td>
</tr>
<tr>
<td>Chemical adsorption potential, ( \theta_{\text{ads}} )</td>
<td>0kT</td>
<td>m(^2)/(s mol)</td>
<td></td>
</tr>
<tr>
<td>IHP adsorption rate constant, ( k_{\text{ads}} )</td>
<td>5 \times 10(^4)</td>
<td>1/s</td>
<td></td>
</tr>
<tr>
<td>Number of adsorption sites at IHP, ( N_{\text{n,IHP}} )</td>
<td>7.08 \times 10(^{15})</td>
<td>sites/m(^2)</td>
<td></td>
</tr>
<tr>
<td>Distance from the wall to IHP, ( y_1 )</td>
<td>0.15</td>
<td>nm</td>
<td>55</td>
</tr>
<tr>
<td>Distance from the wall to OHP, ( y_2 )</td>
<td>0.6</td>
<td>nm</td>
<td>30</td>
</tr>
<tr>
<td>Density of states at Fermi level, ( (E_F) )</td>
<td>7.2 \times 10(^{31})</td>
<td>1/(cm(^3) eV)</td>
<td>41</td>
</tr>
<tr>
<td>Electric field screening length, ( \delta_\alpha )</td>
<td>0.16</td>
<td>nm</td>
<td>41</td>
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<tr>
<td>Transfer coefficients, ( \alpha_1 )</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wall adsorption fitting parameter, ( K_s )</td>
<td>2 \times 10(^9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen solubility in water, ( c_{\text{H}_2,\text{eq}} )</td>
<td>0.74</td>
<td>mol/m(^3)</td>
<td>47</td>
</tr>
<tr>
<td>Hydrogen solubility in Nafton, ( c_{\text{H}_2,\text{Nafton}} )</td>
<td>12.9</td>
<td>mol/m(^3)</td>
<td>47</td>
</tr>
<tr>
<td>Reference hydrogen solubility, ( c_{\text{H}_2,\text{ref}} )</td>
<td>0.59</td>
<td>mol/m(^3)</td>
<td>27</td>
</tr>
<tr>
<td>Hydrogen rate constant, ( D_{\text{H}_2} )</td>
<td>10(^7)</td>
<td>m/s</td>
<td></td>
</tr>
<tr>
<td>Hydrogen diffusion coefficient in water, ( D_{\text{H}_2} )</td>
<td>1.4 \times 10(^{-6})</td>
<td>m(^2)/s</td>
<td>56</td>
</tr>
<tr>
<td>Hydrogen diffusion coefficient in Nafton, ( D_{\text{H}_2} )</td>
<td>2.34 \times 10(^{-10})</td>
<td>m(^2)/s</td>
<td>57</td>
</tr>
<tr>
<td>Hydrogen partial pressure</td>
<td>0.533</td>
<td>atm</td>
<td></td>
</tr>
<tr>
<td>Tafel-Volmer rate constant, ( k_T )</td>
<td>37.4</td>
<td>m/s</td>
<td>28</td>
</tr>
<tr>
<td>Heyrovsky-Volmer rate constant, ( k_H )</td>
<td>0.83</td>
<td>m/s</td>
<td>28</td>
</tr>
<tr>
<td>Equilibrium coverage of the reaction intermediate, ( \theta_0 )</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potential range constant, ( \gamma )</td>
<td>1.22</td>
<td></td>
<td>28</td>
</tr>
</tbody>
</table>

Pt surface area per unit carbon wall area, \( A \) | 0.0621 | | |
hydrophobic phase of the Na
high solubility has been attributed to hydrogen present in the hydrogen solubility in Na
Na
Figure 5. Comparison of the (a) kinetic and (b) total currents for Na
Na
Figure 5b presents the polarization curves for the water- and Na
Na
A/cm
A/cm
2, they measured HOR overpotentials of approximately 15, 30, and 45 mV, respectively (see Figure 5 of Neyerlin et al.). This linear behavior is consistent with the initial regions of \( j_{TV} \) polarization curves. Those values are more consistent with our results for the water-filled pores than the Naﬁon-ﬁlled pores; they are the same order of magnitude. The difference between the measured overpotential of 45 mV at 0.75 A/cm
A/cm
2 and model’s potential of 500 mV at 0.72 A/cm
A/cm
2 is not a major concern considering the high sensitivity of the model’s applied potential to current at potentials greater than 50 mV. In light of this comparison, it is possible that water between the Naﬁon and the Pt catalyst could be hindering the HOR in PEFCs.

One can also evaluate the effectiveness factor of the Pt catalyst in the water-ﬁlled pore.49,50 The effectiveness factor typically represents the ratio of the actual current to the current with ideal transport. Here, we deﬁne the effectiveness factor, \( \chi \), to evaluate the kinetic and \( \text{H}_2 \)-transport limitations in the water-ﬁlled pore. We express it as the ratio of the total current for the water-ﬁlled pore to the kinetic current of the Naﬁon-ﬁlled pore in Figure 5b

\[
\chi = \frac{j_{\text{total}}}{j_{\text{kinetic}}}
\]

As an example, at a potential of 20 mV, the water-ﬁlled pore has a total current of 0.15 A/cm
A/cm
2, and the Naﬁon-ﬁlled pore has a kinetic current of 2.70 A/cm
A/cm
2. Thus, the effectiveness factor of the water-ﬁlled pore at this potential is 5.6%. The inset of Figure 5b shows a plot of \( \chi \) as a function of the wall potential. Again, this demonstrates the signiﬁcant penalty associated with incomplete Naﬁon coverage. In practical terms for a PEFC, if all of the Pt resided within water-ﬁlled pores, 20 times more Pt would be needed relative to the amount required for the same PEFC current if all of the Pt were covered with a thin ﬁlm of Naﬁon.

Spatial Distributions. We now present an analysis of the distributions of charges, concentrations, and potentials within the pore, wall, and Naﬁon. Figure 6a shows the two-dimensional proton and potential distributions in the Naﬁon film and in the water-ﬁlled pore for a low wall potential of 0.02 V. The proton concentration of Naﬁon is 1100 mol/m
3—orders of magnitude larger than the proton concentration of water at pH 7. Having such a large discrepancy in proton concentration between water and Naﬁon causes protons to diffuse from the Naﬁon into the water, creating a charge separation and an EDL at this interface. As protons diffuse into potential value of the Tafel—Volmer current. Thus, the water-ﬁlled pore is kinetically limited.

These polarization curves can also be related to the speciﬁc current densities required by high-performance PEFC operation. As an example, if one considers the operation of an ultralow-Pt-loading anode (0.003 mgPt/cm
2) with a typical electrochemically active Pt surface area of 92 m
2/gPt, for typical PEFC geometric current densities of 1 and 2 A/cm
2, the Pt speciﬁc current densities are 0.36 and 0.72 A/cm
2, respectively. For the case of the Nafion-ﬁlled pore, these PEFC current densities result in anode potentials of less than 10 mV (on the order of 1 mV). However, for the water-ﬁlled pores, these PEFC current densities result in potentials of 10 and 500 mV.

We can compare our results to Neyerlin et al.’s26 hydrogen pump characterizations of the HOR in a PEFC with vapor-saturated gases considering the same loading and active Pt surface area. At speciﬁc current densities of 0.25, 0.5, and 0.75 A/cm
2, they measured HOR overpotentials of approximately 15, 30, and 45 mV, respectively (see Figure 5 of Neyerlin et al.). This linear behavior is consistent with the initial regions of \( j_{TV} \) polarization curves. Those values are more consistent with our results for the water-ﬁlled pores than the Naﬁon-ﬁlled pores; they are the same order of magnitude. The difference between the measured overpotential of 45 mV at 0.75 A/cm
2 and model’s potential of 500 mV at 0.72 A/cm
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\[
\chi = \frac{j_{\text{total}}}{j_{\text{kinetic}}}
\]
the pore, the unshielded negative sulfonic groups generate a Coulomb force that prevents further diffusion of the protons. Most of the changes in the concentration happen within a few nanometers of the water-Nafion interface. The proton concentration along the pore centerline away from the interface remains constant at around 3.9 mol/m$^3$ (pH 2.4).

The theoretical equilibrium Donnan potential for the interface of infinite water and Nafion domains is 0.49 V. When modeling this scenario, the numerical model's results show good agreement with the theoretical interface prediction. As shown by Figure 6a, for the water-filled pore model with a wall potential of 0.02 V, the potential difference over the water-Nafion interface is 0.171 V. This difference from the simplified interface Donnan potential of 0.171 V is partially due to the confined geometry of the pore and the potential difference between the carbon and the outer surface of the Nafion. More importantly, however, the Donnan potential is reduced because the proton concentration in the pore is much higher than that in the bulk water due to charging of the wall.

The HOR's charging of the electrode's EDL occurs because of the substantial equilibrium $\Delta G$ value for the HOR given the very low initial proton concentration. Thus, H$_2$ oxidizes and injects protons into the water and introduces a negative charge onto the electrode surface ($H_2 + 2H^+_{\text{solution}} + 2e^-_{\text{electrode}} \rightarrow 2H_2O$). Upon reaching quasi-equilibrium, the charging stops, and additional protons from the continuing HOR leave the pore, the electrons conduct out of the electrode, and the current reaches the steady-state value reported here. At quasi-equilibrium, the Donnan potential is equal to 0.171 V.

The HOR charging is also the cause for the high proton concentrations in the pore compared to pure water (3.9 versus 1 $\times$ 10$^{-4}$ mol/m$^3$). For a proton concentration of 3.9 mol/m$^3$, the theoretical Donnan potential is 0.164 V instead of 0.49 V, which is in good agreement with the value of 0.171 V.

In contrast to Figure 6a, for an applied wall potential of 0.4 V (see Figure 6b), the potentials in the pore are below that of the wall. This arises because the applied potential is much greater than the nearly equilibrium Donnan potential of 0.171 V. The concentration and potential distributions for the Nafion-filled pore are not presented because the proton concentration is uniform at the value for bulk Nafion and the potential remains roughly at the reference potential of 0 V (the exception being very thin EDLs at the pore walls).

Figure 7 shows the two-dimensional, axisymmetric hydrogen distribution in the Nafion- and water-filled pores for applied wall potentials of 0.02 and 0.4 V. Because of the high current within the Nafion-filled pore and its high hydrogen-transport resistance, the Nafion-filled pore exhibits significant H$_2$ depletion even at a low potential of 0.02 V. This is consistent with the findings from the quasi-equilibrium model.
domains along the line of axisymmetry, \( r = 0 \), for applied potentials of 0.02, 0.1, and 0.4 V. At the end of the pore, the potential lines are almost flat, but toward the Nafion interface, the potential decreases until it asymptotically approaches zero a few nanometers into the Nafion. For applied potentials of 0.02 and 0.1 V, the axial potential profiles differ very little because the Donnan potential has the dominant effect at low wall potentials. As the wall potential passes the equilibrium Donnan potential, the centerline potential near the end of the pore approaches the value of the wall potential. The water-filled pore’s proton concentration distribution results from the combined proton diffusion from the Nafion and the wall charging by hydrogen oxidation. At 0.4 V the pore becomes proton depleted down to a concentration of nearly 0.01 mol/m² (pH 5) because of high wall potentials and overlapping double layers. In contrast, at lower wall potentials, the concentration within the pore is on the order of 10 mol/m³ (pH 2).

Figure 9 illustrates the corresponding distribution of charges at the pore wall along its length for potentials of 0.1 and 0.4 V. These charges include the charges due to specific adsorption at the IHP (\( \sigma_{\text{IHP}} \)), the surface charge due to functional groups on the carbon surface (\( \sigma_{\text{wall}} \)), and the wall charge of the electron-conducting Pt–carbon phase due to excess or depleted electrons (\( \sigma_m \)). The \( \sigma_m \) value is calculated by the potential gradient between the wall and the IHP, minus the surface charge of the functional groups.
along the length of the Nafton pore is due to hydrogen mass-transport limitations.

Figure 11a,b shows the radial potential profiles in water for the same conditions as the axial current distributions in Figure 10 for two different distances along the pore: (a) at the end of the pore (z = 0) and (b) 2 nm away from the water/Nafton interface (z = 48 nm). For comparison purposes, Figure 11c shows the radial potential profiles at the end of the Nafton-filled pore. For the Nafton-filled pore, the largest potential drop occurs across the Stern layer, creating a large positive difference between $\psi_m$ and $\psi_{OHP}$ yielding high HOR rates through the Heyrovsky−Volmer pathway. The radial distributions show the thin (on the order of 0.1−1 nm) diffuse layers due to the high proton concentration in the Nafton. In comparison, the plots for the water-filled pore in Figure 11a,b show overlapping double layers and, in most cases, an inverted potential profile where the potential increases with distance into the pore. The increased potential into the pore occurs in all plots except for the cases of the 0.1 and 0.4 V wall potentials adjacent to the Nafton in Figure 11b. As discussed before, the high centerline potential in the pore is due to the Donnan potential at the water/Nafton interface. These regions where the potential in the pore is greater than at the wall are also those where the Heyrovsky−Volmer pathway is suppressed. Likewise, the Heyrovsky−Volmer current becomes significant in regions where the wall potential is greater than that at the OHP. This arises because this pathway is driven by an electric potential drop from the wall to the OHP (cf. eq 30). We note that, although the negative difference between the $\psi_m$ and $\psi_{OHP}$ at distances far from the Nafton would normally suggest the hydrogen evolution reaction (HER), the currents in Figure 10a are all positive and indicate the HOR. This is because the kinetic current depends on the potential difference relative to the equilibrium potential difference for this nonstandard state. Consider eq 25 for the overpotential: Because of the low H$^+$ concentration, the equilibrium values of $(\psi_m - \psi_{OHP})_{eq}$ are negative. Thus, in computing $\eta$, the nonequilibrium, negative values $(\psi_m - \psi_{OHP})$ are compensated by the negative equilibrium values, and $\eta$ becomes small. Furthermore, the Tafel hydrogen-adsorption step is considered the rate-determining step in the Tafel−Volmer pathway and does not directly depend on the interfacial polarization.

**Parametric Study of Pore Morphology.** In this section, we present an analysis on how a water-filled pore’s geometry affects the HOR. In this parametric study, we investigate the pore morphology for an applied potential of 0.4 V so that the effects of the Heyrovsky−Volmer pathway are significant. Figure 12 presents the kinetic and total current densities for a parametric study of the pore radius and length. First, we consider the effects on the kinetic current. As the radius is increased, we observe increasing kinetic currents. Note that the current has been normalized by Pt area, so this increased...
current density is not due to the greater perimeter length. Rather, the larger pore diameter results in less overlap of the pore wall EDLs and increased proton concentration (reduced proton exclusion), which increases the kinetic currents due to the lower Donnan and equilibrium HOR potentials. We also observe that the specific current density increases for shorter pores. This increase is due to a greater proportion of the pore being near the Nafion and within the EDL of the water/Nafion interface where the Heyrovsky–Volmer current is significant. These results show that, at 0.4 V, the increases in kinetic current are significant only for pores shorter than 40 nm in length with radii greater than 6 nm. In longer pores, the Heyrovsky–Volmer mechanism is suppressed for the majority of the Pt. For pores with smaller diameters, the proton exclusion is more dominant and quenches the Heyrovsky–Volmer pathway.

For the total current with H₂ transport, we observed a significant decrease in the current due to H₂-transport resistances. In Figure 12, it is apparent that the pore length and radius both influence the severity of the mass-transport loss. As expected, longer pores increase the transport length scale from the Nafion and within the EDL of the water/Nafion interface where the Heyrovsky–Volmer current is significant. These results show that, at 0.4 V, the increases in kinetic current are significant only for pores shorter than 40 nm in length with radii greater than 6 nm. In longer pores, the Heyrovsky–Volmer mechanism is suppressed for the majority of the Pt. For pores with smaller diameters, the proton exclusion is more dominant and quenches the Heyrovsky–Volmer pathway.

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CONCLUSIONS

In this article, we have presented a model that describes the H₂ and H⁺ transport and HOR kinetics within a water-filled pore of a Pt–carbon electrode resembling a PEFC anode. The key and novel aspects of the model include the coupling of water/Nafion and water/carbon wall EDLs. The model incorporates nanometer and subnanometer physics using a continuum modeling approach by applying discrete domains for the distinct zones within the Stern layer and wall. These physics include the specific adsorption at the IHP; the dual-pathway, multistep HOR; the 2-pK surface complexation model for the functional groups on the carbon wall; and the space-charge layer within carbon. Thus, the model is able to capture a variety complex, coupled phenomena, such as the wall charging due to the large HOR equilibrium potential for these conditions.

We compared the performance of a water-filled pore to that of a Nafion-filled pore and identified significant kinetic limitations in the water-filled pore not observed for the Nafion-filled pore. It was found that the Tafel–Volmer mechanism, which dominates at low potentials, is primarily hindered by the low H₂ solubility in water because H adsorption is the rate-determining step for this pathway. At high potentials, we observed a suppression of the Heyrovsky–Volmer pathway current. For sulfuric acid and Nafion electrolytes, the Heyrovsky–Volmer pathway can yield high currents at moderate potentials (>200 mV). However, the proton exclusion of the overlapping EDLs in the pore and the Donnan potential due to the water/Nafion interface cause a severe suppression of this pathway, moving the onset of the Heyrovsky–Volmer current to a potentials of roughly 500 mV. It was also found that the mass-transport losses due to hydrogen diffusion were significantly less important for the kinetically limited, water-filled pores.

In terms of the PEFC anode application, we found that the catalyst in the water-filled pore has an effectiveness factor in the range of 5%. Further, we identified that, for ultralow anode Pt loadings (~0.01 mgPt/cm²), the anode overpotential could reach values as high as 600 mV at a current density of 3 A/cm² if there were poor Nafion coverage. In that case, the anode would become the limiting loss factor for a state-of-the-art, high-power-density PEFC, and therefore, high Nafion coverage is crucial for achieving ultralow Pt loadings in the anode. Future extensions of the model include modeling of the transport and kinetics for the ORR in nanopores of the cathode catalyst layer and coupling of the nanoscale geometry to the macroscale in a multiscale modeling framework. In addition, this modeling approach could prove valuable in evaluating the effects of ionic impurities and poisoning on the performance PEFCs and other electrochemical cells.

ASSOCIATED CONTENT

Supporting Information
Detailed derivation of the dual-pathway, multistep HOR. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES
