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Molecular modeling of the proton density distribution in a water-filled slab-like nanopore bounded by Pt oxide and ionomer

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ABSTRACT

A slab-like pore model consisting of a thin water slab that is confined by a metal wall on one side and a dense ionomer skin layer on the other side was simulated with classical molecular dynamics. The model mimics thin-film structures of Pt/support (referred to as the metal), water layer, and ionomer phase encountered in cathode catalyst layers of polymer electrolyte fuel cells. The equilibrium proton density near the metal surface is the key variable required to predict the ORR activity and the Pt dissolution rate under fuel cell operating conditions. Here, we explored the equilibrium proton density distribution in the confined water layer as a function of oxide coverage at the metal surface, excess surface charge density, water layer thickness, and ionomer film structure. The effect of ionomer hydrophobicity on the water dynamics in the nanopore was also investigated. The electric dipole field created by the oxide layer on the Pt surface interacts strongly with protons, and concentrates protons at the metal surface. A direct relation was found between the surface proton concentration and the oxide layer dipole moment. Performing simulations with different ionomer structures and pore widths clarified the sensitivity of the proton density distribution to properties that are specific for the structure and distribution of the ionomer phase in catalyst layers.

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1. Introduction

Platinum continues to be the best-performing and most stable catalyst for polymer electrolyte fuel cells (PEFC). However, in the current generation of PEFC, Pt still accounts for 30–70% of the total materials costs for the fuel cell stack [1]. A drastic reduction of the Pt loading, while meeting stringent demands in performance and durability, remains the primary objective of on-going efforts in fuel cell electrocatalysis and electrode design [2,3]

The density distribution of protons in the cathode catalyst layer (CCL) is a vital factor in determining performance, durability and lifetime. Due to the sluggish kinetics of the oxygen reduction reaction (ORR), the proton density distribution in the CCL does not deviate significantly from the equilibrium distribution over the normal range of fuel cell operating conditions [4]. Hence, the equilibrium proton distribution can be used in physical models of PEFC operation [5]. Fuel cell degradation models also incorporate the local pH in the CCL [6–10]. Hence, finding the values of the local proton density in the CCL is vital for studying the impact of degradation processes on PEFC performance, and rationalizing their dependence on the Pt oxidation state as well as on the structure and composition of the layer.

Molecular dynamics (MD) simulations are a valuable tool to study ion density distributions and dynamics in nanoscopic media. MD has been used extensively in simulations of electrostatically-controlled ion distribution and transport phenomena in biological channels, see Ref. [11] for a review, and similar electrostatic phenomena in electrocatalytic nanomaterials can be captured using this technique as well. The equilibration time of protons in a solvated system resembling nanopores in fuel cell CLs is on the order of hundreds of picoseconds. Hence, obtaining a sufficient number of statistically independent proton density distributions requires a few nanoseconds of simulation time. A similar simulation setup for Pt nanochannels in ionomer-free ultrathin CLs has affirmed the reliability of this technique [12].

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The presence of oxide on the Pt catalyst surface and its effect on fundamental interfacial charging phenomena has garnered the attention of researchers for decades [7,13,14]. Surface oxides act as intermediate species for both ORR and Pt dissolution [15,16]. It is thus important to establish the relationships between oxide formation, electrostatic charging, as well as reaction mechanisms and pathways involved in the ORR and Pt dissolution. A fully self-consistent calculation of these relationships remains a primary challenge for *ab initio* electrochemical modeling; while the development of such approaches is heavily pursued, it is beyond the scope of this article. Instead, we provide a parametric study to elucidate the importance of these coupled effects.

In this work, we use molecular dynamics simulations to study the equilibrium proton density distribution in a slab-like water-filled pore, bound on one side by a PtO catalyst surface and on the other side by a skin-type ionomer film. In Section 2, we describe the model and computational details of the simulation system. In Section 3, we investigate the effects of Pt oxidation state and excess surface charge density, pore width, and ionomer structure on the proton distribution and water transport in the nanopore.

2. Model description and computational details

The model schematic is shown in Fig. 1. It consists of a five-layer Pt slab with Pt(111) surface structure at a set excess surface charge density, a set amount of oxide adsorbed at the Pt surface, and a pre-formed ionomer layer. The space in between the ionomer film and the Pt/O surface is filled with a water slab that contains a sufficient amount of hydronium ions to exactly counterbalance the electric charge on ionomer and Pt/O surface.

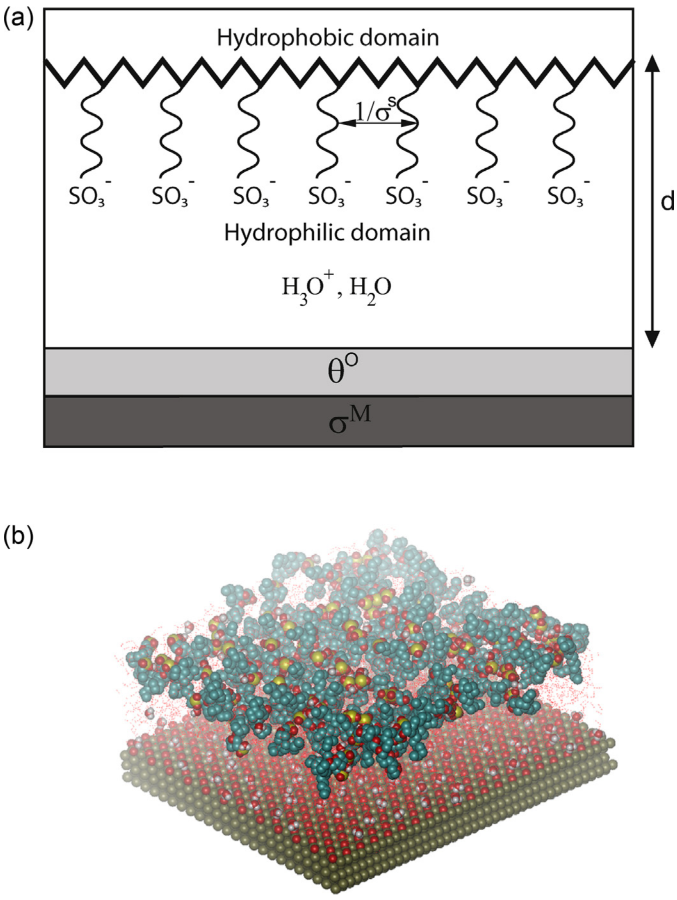

Fig. 1. (a) Model schematics; the model variables are metal surface charge density, oxide surface coverage, nanopore diameter, and ionomer sidechain density. (b) Snapshot of the system during the simulation.

Table 1
Model variables and ranges.

Variable	Symbol (unit)	Range
Oxide coverage	θ^O	6.25–69%
Excess PtO surface charge density	$\sigma^M \left(\frac{\mu C}{cm^2}\right)$	−16 to 16
Ionomer sidechain number density	$\sigma^S \left(\frac{1}{nm^2}\right)$	1.1–2.1
PtO surface-ionomer layer distance	d (nm)	2–8

The model system has four independent variables: surface oxide coverage (θ^O), PtO excess surface charge density (σ^M), ionomer sidechain density (σ^S), and width of the slab-like water-filled pore (d). Table 1 shows the ranges of variation for each of the parameters.

PtO configurations at different oxide coverage values were obtained from *ab initio* DFT calculations. Hawkins et al. [17] showed for Pt(111) that surface oxide forms on three-fold hollow adsorption sites with fcc symmetry at coverage values below 0.5 ML, and more stable phases will be formed at oxygen coverages above 0.5 ML. Coverage is defined as the ratio of oxide atoms to surface Pt atoms. Here, we obtained the relaxed atomic structure and the surface charge density distribution for the Pt oxide layer at zero total charge of the slab from density functional theory (DFT) calculations. The DFT calculations were carried out with the plane-wave based Vienna *Ab initio* Simulation Package (VASP) [18,19]. For a comparative study, we have used two generalized-gradient approximation (GGA) functionals that are widely used in surface science, *viz.* the PW91 functional and the revised Perdew–Burke–Ernzerhof (revPBE) functional [20,21]. Pt lattice constants of 3.99 Å and 4.02 Å were used with PW91 and revPBE functionals, respectively.

The PW91 and PBE functionals are found to have very similar gradient-dependent exchange correlation energy contributions, which causes the very similar chemisorption energies of different atomic and molecular adsorbates on metal surfaces [22]. RevPBE modifies PBE functional and has been found to improve the atomization energies of atoms and molecules closer to experimentally measured values. The interaction between atomic cores and electrons was described by the projector augmented wave (PAW) method [23,24]. The optimization was performed on a five-layer Pt(111) slab with the three top layers relaxed. The valence wave functions were expanded in a plane wave basis with cut-off energy of 400 eV. A 2 × 2 × 1 Monkhorst-Pack *k*-point mesh was used to sample the Brillouin zone. The convergence criteria for the electronic self-consistent iteration and the ionic relaxation loop were set to 10^{-5} eV and 0.02 eV/Å, respectively. The vacuum spacing between periodically repeated slabs was set to be 15 Å. A dipole correction was applied in the direction perpendicular to the surface. The dipole moment in the direction normal to the Pt surface (z-direction) was obtained from DFT calculations as

$$\mu_z = \int_V z\rho^{el}(\mathbf{r})\mathrm{d}V + \sum_{atoms} z^{nu} n^{nu}(\mathbf{r}),$$

where $\rho^{e1}(r)$ is the negative charge density of electrons, V is the slab volume, z^{nu} is position of atoms, and $n^{nu}(r)$ is the positive charge of the atomic cores.

Pt oxidation state and net surface charge density are dependent upon each other in reality; however, due to the lack of reliable quantitative information relating the two parameters, we treated them as independent variables in this work. In the absence of DFT calculations of charged PtO surfaces, an excess surface charge was distributed uniformly over all surface Pt atoms.

To initialize the classical MD studies of the slab configuration, a 10 nm × 10 nm area of PtO was simulated by replicating the final configuration from the DFT simulation. This surface area was

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