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Modeling ion conduction and electrochemical reactions in water films on thin-film metal electrodes with application to low temperature fuel cells

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ABSTRACT

Transport-regulated electrochemical reactions in thin-film platinum (Pt) electrodes for polymer electrolyte fuel cells (PEFCs) is theoretically investigated with a meso-scale modeling framework. These electrodes are of interest for their potential to reduce low temperature fuel cell costs, but the mechanisms governing their operation are not well-understood at this time. A primary question arising from experimental data is the origin of the high ion conductivity and oxygen reduction reaction (ORR) activity on ionomer-free Pt during PEFC operation when typical ORR potentials are well above commonly measured potentials of zero charge (PZC) for Pt surfaces. These ORR potentials should result in low proton conductivity and high activation losses. Herein, we address these questions with a model that considers both polymer electrolyte and water-covered portions of the Pt electrocatalysts similar to the experimental electrodes. Local electroneutrality is not assumed and the ion transport in water- and polymer electrolyte-covered regions of the Pt is modeled using the continuum Poisson- Nernst- Planck (PNP) equations including spatially-resolved domains for the compact (Stern) portions of the double layer. In addition, the model incorporates the water dissociation reaction (WDR) and both the acidic and alkaline ORR mechanisms. In water-covered regions, the ionic conductivity is highly dependent on the Pt surface charge, local pH, and transport-regulated ORR pathway. The model predicts the experimentally observed high ionic conductivity for Pt thin films in water and attributes it to high hydroxide concentration.

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1. Introduction

For polymer electrolyte fuel cells (PEFCs) to be a viable commercial option for automotive and portable applications the cost barrier of high platinum (Pt) loading in the fuel cell stack has to be overcome. To compete with combustion engines, an estimated Pt loading of less than 15 g is required [1]. Optimizing PEFC's electrode to achieve this low Pt loading target, while maintaining the high power densities and durability requirements is a challenging task. Conventional high-surface area carbon-supported Pt electrodes have proven to meet many of the PEFC's electrode design requirements. However, challenges of low Pt utilization [2], durability and increased mass transport losses at low Pt loadings remain key issues to be resolved for broad PEFC commercialization [1,3]. Thin-film Pt electrodes, such as the nano-structured thin-film

(NSTF) electrodes being developed by the 3 M Corporation [4], have demonstrated the desired power densities and durability, and at the same time having reduced Pt loading. NSTF electrodes are prepared by vacuum deposition of Pt and Pt-alloy electrocatalyst on crystalline organic perylene red whiskers [4]. NSTF electrodes are distinct from conventional carbon-supported Pt PEFC electrodes because they are not mixed, coated, or impregnated with a polymer electrolyte and are roughly an order of magnitude thinner. One major challenge in optimizing structural design of these state-of-the-art electrodes is understanding the mode of proton transport over the ionomer-free Pt surface. In conventional electrodes, the polymer electrolyte binder percolates within meso- and macro-pores of the electrode's porous matrix. Polymer electrolyte binders, such as Nafion ionomer, introduce fixed, high proton concentrations for the oxygen reduction reaction (ORR) and at the same time acts as a proton conducting phase. In NSTF electrodes there is no polymer electrolyte to aid in proton conduction and the current understanding of the proton transport in the NSTF electrodes remains limited. It has been observed that the performance of the NSTF electrodes is severely hindered at low

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relative humidity (RH) operation conditions [5], especially at high current densities due to low ionic conductivity. This experimental evidence suggests that adsorbed water films formed at high RH aid in proton conduction within NSTF electrodes, however at low RH ion transport is hindered due to lack of adsorbed water films. Moreover, recent experimental studies find the ionic conductivity of ionomer-free Pt electrodes to be many orders of magnitude higher than that of bulk water and to be highly dependent on RH [6–8]. Over the past two decades, two major transport mechanisms have been proposed to explain ion transport in ionomer-free electrodes: 1) adsorbed hydrogen ad-atom surface diffusion along the Pt surface [9–13] and 2) water-mediated conduction of protons [14,15]. In the next few paragraphs, we outline previous works that support either of the two mechanisms and propose our hypothesis to explain the observations of high ion conductivity.

The first transport mechanism has been widely studied and is mainly proposed by authors in order to explain cyclic voltammetry (CV) results. In an early study, McBreen et al. [9] performed voltammetric studies of Pt mesh in contact with Nafion in a highly-humidified atmosphere. When adding an additional Pt mesh on top of the first one they observed a doubling of hydrogen charge in the under-potential deposition (UPD) region of the CV. Hence, Pt, which was not in direct contact with Nafion contributed to the CV measurements. The authors proposed H-adatom surface diffusion to be one of the possible mechanisms to explain high Pt utilization. Tu et al. [10] observed similar phenomena when comparing the CVs for 10-40 μm thick Pt-black powder electrodes immersed in 0.5 M H_2SO_4 to the same electrodes pressed against Nafion and filled with water. Pt utilization values were high for both electrodes. Most likely, H-adatom surface diffusion mechanism is responsible for high Pt utilization in these studies. While H-adatom surface diffusion and spillover mechanisms are viable at potential windows of < 0.4 V they are hard to justify as the transport mechanism for hydrogen at the high ORR potentials where the UPD hydrogen is desorbed.

Prior modeling work by Chan and Eikerling [14] has suggested that the second proposed mechanism of water-mediated proton conduction is viable only if potential of zero charge (PZC) of Pt is higher than 0.7 V. Here it is important to distinguish the two types of PZCs referred in literature: potential of zero free charge (PZFC) and potential of zero total charge (PZTC) [17]. The PZFC is defined at a point where the metal's free, electronic excess charge density is zero, whereas the PZTC is defined at a point where the sum of metal free and a charge that is transferred to surface due to species adsorption equals to zero. Here, and in further discussion the PZC we are referring to is the PZFC. Considering the PZC of Pt in a PEFC, if Pt has a high PZC then the PEFC's operating condition of 0.6 V falls into negative polarization [18], where protons accumulate in the water-covered pores due to the negatively-charged Pt surface. However, if the Pt PZC is lower than the electrode's potential, the metal's surface charge is positive and water-filled pores are proton depleted [19]. The experimental studies of in-situ CO displacement and ex-situ UHV PZC measurements agree that PZC of Pt is roughly 0.26 V on a standard hydrogen electrode (SHE) scale [20,21]. Recent work on polycrystalline Pt nano-particles also indicates PZC values below 0.3 V [22]. If electrostatic accumulation of protons at the Pt is responsible for measured high proton conductivities, then the PZC is likely rather high and these conductivities should show potential dependence as observed for meso-porous gold electrode filled with water [23]. However, recent in-situ experimental measurements for unsupported Pt-black catalyst do not show significant potential dependence of the ionic conductivity on applied potential [8].

In the present work, we aim to explain the high ionic conductivities and the strong dependence of performance on RH that are experimentally observed in water-filled Pt electrodes. The strong RH dependence indicates that ion conduction in water films is an important part of these electrodes' operation. It is important to note that the experimentally measured ionic conductivities do not differentiate between positive and negative ions and it has been widely assumed that the measured ionic conductivities are those of protons. For Pt covered by ionomer this holds true due to the high concentration of fixed anions, but for the electrodes filled with water one also has to consider counter-ion contributions to the total conductivity. This is especially true under high ORR potentials, where protons are expelled from the water-filled portions of the electrode if the PZC is in the expected range, yielding local environments of high pH. At high pH, the commonly assumed acidic ORR will be limited due to the negligible presence of the proton reactant. However, under high pH an alkaline ORR mechanism can become dominant, where hydroxide ions are a product of the reaction. To the best of our knowledge no previous works have considered the alkaline and acidic ORR mechanisms in parallel within porous electrodes. In this work we apply previously developed modeling framework, previously applied to a carbon-supported Pt anode [19] and water-filled Pt electrode [24], to the ORR in a NSTF-type cathode. We incorporate alkaline along with acidic ORR mechanisms in order to resolve kinetics of the ORR within the water-covered portion of the pore where large variations in pH exist. In the following sections we outline the model's theory and present our results for the spatial distributions of ORR acidic and alkaline mechanisms inside NSTF Pt electrodes and the results for the proton and hydroxide conductivities. We additionally evaluate the effect the Pt PZC has on the electrode properties in order to establish the impact that PZC has on PEFC performance.

2. Model Description

Fig. 1 shows a schematic of the model, which considers a thin-film Pt catalyst partially submerged into Nafion with the larger portion having adsorbed water-film. This arrangement is chosen to reflect NSTF whiskers being partially embedded into the Nafion membrane during membrane electrode assembly (MEA) fabrication. As Fig. 1 shows, the model is two-dimensional and axisymmetric, and is divided into four major domains that incorporate a Nafion film, and a cylindrical Pt pore having internal void space with a water film present on the surface of the Pt. We model the Nafion as having a fixed concentration of immobile negative sulfonic acid groups that are charge-balanced by mobile protons. We use continuum equations to describe long-range of ion and gas transport. The Poisson-Nernst-Plank equations describe the diffusion and electromigration of H^+ and OH^- species inside the Nafion domain and the water's diffuse layer domain. As the Fig. 1 inset depicts, we resolve electric double layers (EDLs) at water|electrode interface with Gouy-Chapman-Stern-Grahame (GCSG) theory applied in discrete finite domains. The EDLs are divided into three sub-domains: i) the diffuse layer, and the ii) outer and iii) inner domains of the Stern layer [25]. The plane of the closest approach to the Pt surface for fully-solvated ions is the outer Helmholtz plane (OHP), which is also where we apply the kinetic models for the ORR. We also implicitly resolve Donnan potential drop at the water|Nafion interface due to significant ion concentration differences between water and Nafion domains. The water dissociation reaction (WDR) is incorporated into the model in both water and Nafion domains. Fick's law for diffusion describes the oxygen transport within the pore space, water, and Nafion domains.

Key Assumptions

- Electrochemical reactions are modeled at the OHP with Pt uniformly distributed over the pore walls.