Spatially-Resolved Modeling of Electric Double Layers for the Oxygen Reduction Reaction in Water-Filled Platinum Electrodes Iryna V. Zenyuk and Shawn Litster^{*}

Department of Mechanical Engineering Carnegie Mellon University, Pittsburgh, PA, USA 15213 *Corresponding Author: litster@andrew.cmu.edu

There is increased interest in developing polymer electrolyte fuel cells (PEFCs) electrodes without polymer electrolyte binder given the mass transport losses the films can introduce with low Pt loadings. However, the ion conduction mechanisms in state-of-the-art thin film, extended surface Pt electrodes are not well-resolved. In recent experimental studies it has been observed that ionic conductivity is many orders of magnitude higher than that of bulk water and is highly dependent on RH (1, 2). For the acidic oxygen reduction reaction (ORR) to proceed without significant kinetic limitations, the proton concentration in ionomer-free electrodes should be high. For nanostructured thin film (NSTF) electrodes it has been suggested that surface charging is the mechanism for proton migration along the Pt support (3). However, our recent study shows that at high applied potentials waterfilled pores are proton depleted unless there is a very high potential zero charge (4).

Herein, we apply previously developed modeling framework, previously applied to a carbon supported Pt anode (4), to the ORR in a Pt cathode. The twodimensional, axisymmetric, multi-domain model resolves electric double layers (EDLs) at the water-Pt and water-Nafion interfaces using the Poisson-Nernst-Planck equations and discrete zones for the electrode surface. Figure 1a shows the modeling domains for a single cylindrical pore. The proton concentration distribution in Figure 1b shows that even for low applied potentials water-filled pore is proton depleted. Due to positive potentials applied at the wall hydroxide ions are attracted, while protons are repulsed from the wall. This creates an environment of high pH right next to the Pt surface. Thus, we incorporated alkaline ORR mechanism within the model along with the ORR mechanism for acidic media, in order to resolve kinetics of the ORR in a pore with large variations in pH.



Figure 1: (a) Schematic of the modeling domains and (b) spatial proton concentration distribution at applied potential of 0.5 V.

Figure 2 shows average proton and hydroxide concentration along the centerline of the pore with and

without including alkaline ORR mechanism in model. We observe significant increase of hydroxyl ion concentration with alkaline ORR mechanism due to OH^- being generated during the reaction. The inset shows that at the outer Helmholtz plane (OHP) the concentration of OH^- ions is about four or more orders of magnitude higher compared to H^+ concentration.

Figure 3 shows polarization curves comparing the performance of water-filled pore with or without alkaline ORR mechanism included to that of a Nafionfilled pore. With only acidic ORR mechanism the current decays rapidly at high potentials in the water-filled pore due to low proton concentration at the interface. When the OH⁻ generating alkaline ORR mechanism is included for the total current in a water-filled pore, there is 2-3 orders of magnitude greater current at high potentials. Therefore, the alkaline ORR mechanism is an important consideration when modeling ionomer-free electrodes.



Figure 2: Average centerline proton and hydroxide concentrations for different applied potentials with and without alkaline ORR mechanism included. The inset shows ion concentrations at the OHP.



Figure 3: A comparison of the kinetic currents for the Nafion and water-filled pores with and without ORR in alkaline media included.

In this paper and presentation, we will outline the model's theory and present our results of ORR acidic and alkaline mechanisms inside the water-filled Pt electrodes.

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