Platinum migration in PEM Fuel Cells

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In a previous paper[1], the kinetics of platinum dissolution and oxidation were combined in a lumped-parameter model to study the stability of Pt crystallites in a PEM fuel-cell catalyst layer. It has been shown that this dissolution process can result in large changes in ECA under PEM fuel-cell operation.[2] In this work, these kinetic expressions are used in a model of a fuel cell cross section. This model allows us to simulate the movement of platinum through the different regions of a PEM fuel cell.

Variations in concentration and potential are considered in the direction normal to the membrane. The partial pressures of oxygen and hydrogen have been added to the variables used to describe platinum oxidation and dissolution so that the mixed potentials that exist during typical fuel cell operation may be simulated. Kinetic parameters for hydrogen oxidation and oxygen reduction were fit to experimental data.

Two platinum particle sizes are permitted in each electrode. This makes it possible to simulate sintering, albeit crudely, with the model. Currently, the model only describes electrochemically driven sintering. That is to say that material can only be exchanged between platinum particles by dissolution and recrystallization; the model does not describe transfer of platinum in the solid.

Fick's law governs the movement of hydrogen and oxygen.

$$N_i = -\varepsilon D_i \nabla c_i$$

where ε is the porosity. The diffusion coefficients, D_i, in the diffusion media are taken from the literature and corrected for tortuosity; in the other regions the diffusion coefficient was matched to experimentally measured permeabilities.

Dilute-solution theory without convection is used to describe the movement of dissolved platinum ions within the membrane. Thus,

$$N_i = -\varepsilon D_i \nabla c_i - \varepsilon z_i u_i F c_i \nabla \Phi_2$$

where D_i is the diffusion coefficient, u_i is the ionic mobility, z_i is the valence of platinum ions, c_i is the concentration of platinum ions in the membrane phase, and Φ_2 is the potential in the membrane phase. Under normal fuel-cell operating conditions, platinum ions will tend to diffuse from the cathode to the anode because the concentration of platinum ions in solution will be higher at the cathode, due to the higher solubility of platinum at the higher potential. Conversely, the potential drop in the solution phase will tend to force platinum to migrate from the anode to the cathode. The net flux represents a balance between these competing forces. The diffusion coefficient and ionic mobility for Pt^{2+} in Nafion were assumed, rather arbitrarily, to be a factor of 10 less than in water, with a tortuosity correction. Convection of Pt^{2+} was neglected because the movement of water through the membrane was not treated.

The conservation equations were solved in control-volume form with Crank-Nicholson time stepping. This approach does a very good job at conserving the total amount of platinum in the system. This is a very important consideration because simulations of complicated cycling profiles for realistic times may involve hundreds of thousands of time steps.

The rate constant for the platinum dissolution reaction was fit to a potentiostatic hold experiment at 1.05 V. No parameters were adjusted to fit the remaining experiments. Such an effort would be difficult given the long run times of the cycling simulations.

The figure shows the ECA loss predicted during square-wave cycling between 0.87 and 1.2 V with hydrogen and air continuously supplied. These potentials are consistent with a high efficiency operating point on hydrogen-air and air-air open-circuit, respectively. Because the hydrogen sink is always on at the anode, this experiment probably exaggerates the rate of degradation beyond that of a real system. The ECA linearly decreases in both cases. Aragane et al.[4] present a qualitatively similar picture of platinum redistribution in a phosphoric acid fuel cell

ECA loss during potential cycling
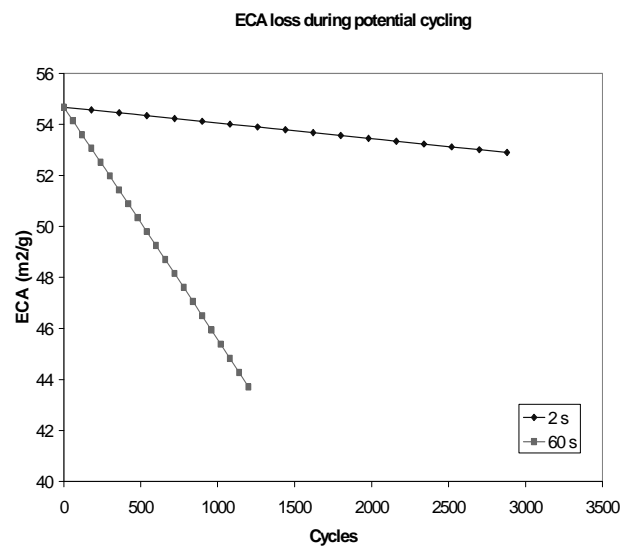
References:
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2. T. Patterson, "Effect of Potential Cycling on Loss of Electrochemical Surface Area of Platinum Catalyst in Polymer Electrolyte Membrane Fuel Cell," *Fuel Cell Technology Topical Conference Proceedings,* 2002 AIChE Spring National Meeting, March 10-14, 2002.
3. K. Kinoshita, J. T. Lundquist, and P. Stonehart, "Potential cycling effects on platinum electrocatalyst surfaces", *Electroanal Chem. and Interfacial Electrochem.*, **48**, 157-166 (1973).
4. J. Aragane, T. Murahashi, and T. Odaka, *J. Electrochem. Soc.*, **135**, 844 (1988).