Kinetic model of platinum dissolution in PEM fuel cells

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Introduction

Supported platinum electrocatalysts are commonly used in state-of-the-art PEM fuel cells to enhance the rates of the hydrogen oxidation and oxygen reduction reactions. In such catalysts, the high surface-to-volume ratios of the platinum particles maximize the area of the surfaces available for reaction. It is the structure and proper dispersal of these platinum particles that make low-loading catalysts feasible for PEM operation. If the platinum particles cannot maintain their structure over the lifetime of the fuel cell, changes in the morphology of the catalyst layer from the initial state will result in a loss of electrochemical activity. In this paper, we develop a mathematical model for the kinetics of platinum dissolution and examine model predictions under a range of PEM fuel cell operating conditions.

Description of the model

Three reactions are considered in the kinetic model: platinum dissolution

$$Pt = Pt^{2+} + 2e^{-}$$

platinum oxide film formation,

$$Pt + H_2O = PtO + 2H^{+} + 2e^{-}$$

and the chemical dissolution of platinum oxide

$$PtO + 2H^{+} = Pt^{2+} + H_2O$$

The dissolution reaction is described via Butler-Volmer kinetics, with a factor related to the surface coverage that allows the reaction to occur only on uncovered platinum surfaces. The kinetic expression for platinum oxidation is based on the models of Conway and co-workers; their model is augmented with a cathodic term added to describe the conversion of platinum oxide to bare platinum. This term allows us to define an equilibrium oxide coverage. Our model for platinum oxidation accounts for only a single platinum oxidation state. This is doubtless a simplified view, but it captures the characteristic interactions between the dissolution reaction and oxide formation, as they pertain to platinum stability. The final reaction is a chemical reaction that allows PtO to convert to Pt^{2+}. This reaction is assumed to be slow, but is necessary for the model to relax to equilibrium at high potentials where Pt^{2+} and PtO are in equilibrium.

These kinetic reactions are combined with material balances to describe the changing nature of the platinum particles as a function of time and electrode potential. We account for growth and shrinkage of the platinum crystals as platinum is dissolved and re-crystallized, multilayer formation and removal of platinum oxides, and accumulation of ionic platinum species in solution.

Results and Discussion

The model is used to fit the relevant portions of a cyclic voltammogram, taken of a commercially available MEA with supported Pt electrocatalysts. The model and data indicate that, at lower potentials (i.e., under the conditions of normal H_2/air fuel-cell operation), the solubility of platinum in acid is quite low. At higher potentials; that is, at the potential an electrode will reach when exposed to air in the absence of hydrogen crossover, the oxide layer effectively insulates the platinum particle from dissolution. At intermediate potentials, however, the uncovered surface is prone to high rates of platinum dissolution. Under some modes of fuel-cell operation, the electrodes will undergo transients that expose them to this intermediate potential window and thereby aggressively dissolve platinum from the surface. The implications of this phenomenon are discussed in the paper.

References

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