V.G.6 Applied Science for Performance, Cost and Durability

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Objectives

- Model membrane-electrode delamination.
- Model hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR).
- Investigate the effect of the platinum-iomomer interface on ORR.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost
(C) Electrode Performance

Technical Targets

This project is conducting fundamental studies for cost, performance and durability. Insights gained from these studies will be applied toward the design and synthesis of fuel cell materials that meet the following DOE 2010 targets (Table 3.4.4):

- Precious metal loading: 0.3 g/kW
- Cost: $30/kW$_e$
- Durability with cycling: 5,000 hours

Accomplishments

- Developed and validated a delamination model to explain membrane-electrode interfacial resistance, of particular interest for alternative ionomers.
- Developed a model for anode kinetics based on Tafel-Heyrovsky mechanism, applied this model with good qualitative agreement to fuel cells operated with hydrogen impurities.
- Applied micro-electrodes to the study of ORR on polycrystalline Pt, found Pt-ionomer interface depends on potential, relative humidity (RH), ionomer type and temperature.
- These approaches are leading to a better understanding of the effects of impurities, catalyst loading, ORR inefficiencies, and the enablement of novel ionomers that will help meet DOE fuel cell targets.

Introduction

Issues of cost, durability and performance in order to meet commercialization requirements will need to be addressed. The goal of this project is to provide the fundamental understanding of processes necessary to assist the DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program meet DOE targets for cost, performance and durability. This effort focuses on phenomenological modeling of the membrane-electrode interface, development of hydrogen oxidation reaction models, and investigation of the platinum-ionomer interface in order to decrease cost, and improve performance and durability.

Approach

The approach of this project is three-pronged. First, we develop and validate a model to interpret performance losses due to membrane-electrode delamination. This model combines phenomenological and computational fluid dynamics (CFD) models in an attempt to validate membrane-electrode delamination as a degradation mechanism. Second, we refine kinetic models of the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) in order to better understand cost-performance trade-offs and durability issues in membrane electrode assemblies. Third, we explore platinum-ionomer interface using micro-electrodes and rotating ring disc electrodes. The oxygen reduction reaction has been explored as a function of humidity, temperature and ionomer type.

Results

Membrane-electrode delamination modeling is essentially complete. Figure 1 shows the qualitative agreement between experimental data for an alternative membrane sample with electrode delamination, compared to model results of fuel cell performance with different delamination sizes (at fixed 36% surface delamination) as a function of membrane thickness. The results of this work qualitatively agree with experimentally observed performance and high frequency resistance, and stress the importance of avoiding membrane-electrode delamination in operating systems.

Most fuel cell models use Butler-Volmer kinetics at the anode. These models cannot explain anode behavior at high overpotential of concern for low loadings, in dilute H_2 streams, and in the presence of impurities. In collaboration with Brookhaven National Lab (BNL) we have helped elucidate anode kinetics by using Tafel-Volmer at low- and Heyrovsky-Volmer models at high-potential. Figure 2 shows the Tafel-Heyrovsky mechanism. Figure 3a and 3b compare experimental data to modeled data using LANL-BNL developed Tafel-Heyrovsky kinetics. The good qualitative agreement between these complex figures shows the potential application this model for the study of impurities, the effects of aging or ultra low anode loadings.

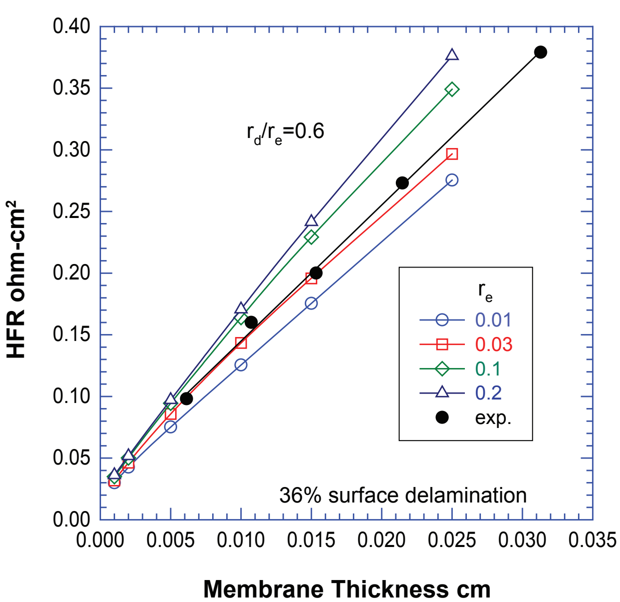

FIGURE 1. High frequency resistance (HFR) versus membrane thickness for experimental data (black line added to guide the eye) versus model comparisons at a fixed 36% surface delamination assuming homogeneous delamination. r_e represents the repeat unit size (in cm) for the grid on which the delaminations have been modeled.

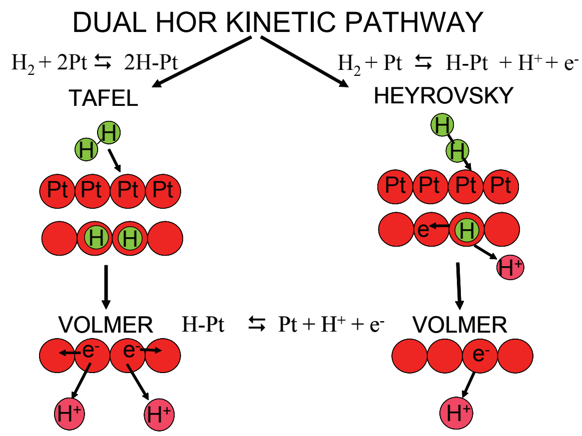

FIGURE 2. Tafel-Heyrovsky mechanism for hydrogen oxidation reaction.

Investigations into the platinum-ionomer interface have shown that the interface is much more complicated than traditionally considered and this has major implications for fuel cell performance, particularly when operated outside of normal operating regimes. In particular, the nature of the interface has been found to be highly dependent on potential and time. Figure 4a and 4b show voltammetry and chronoamperometry, respectively, of Nafion® (1100 equivalent weight) coated on a polycrystalline micro-electrode. The dependence of the voltammogram shape (in Figure 4a) on scan rate suggests ionomer reorganization at the interface. This ionomer reorganization is further supported by chronoamperometry (Figure 4b). Other data show important changes in performance and overpotential as a function of ionomer type, temperature and relative humidity, and increased peroxide production in the presence of Nafion®.

Conclusions & Future Directions

- Delamination Model
  - Experimentally observed performance losses have good qualitative agreement with delamination model predictions.
  - Minimal future work on this task (correlate performance losses with delaminations and prepare publication).
- Catalytic Models
  - Tafel-Heyrovsky model for HOR has been applied to fuel cell models to show predictive value for the case of impurities such as CO and H_2S.
  - Further refine anode poisoning models, explore loading level influence, correspond with impurities task for hydrogen purity.

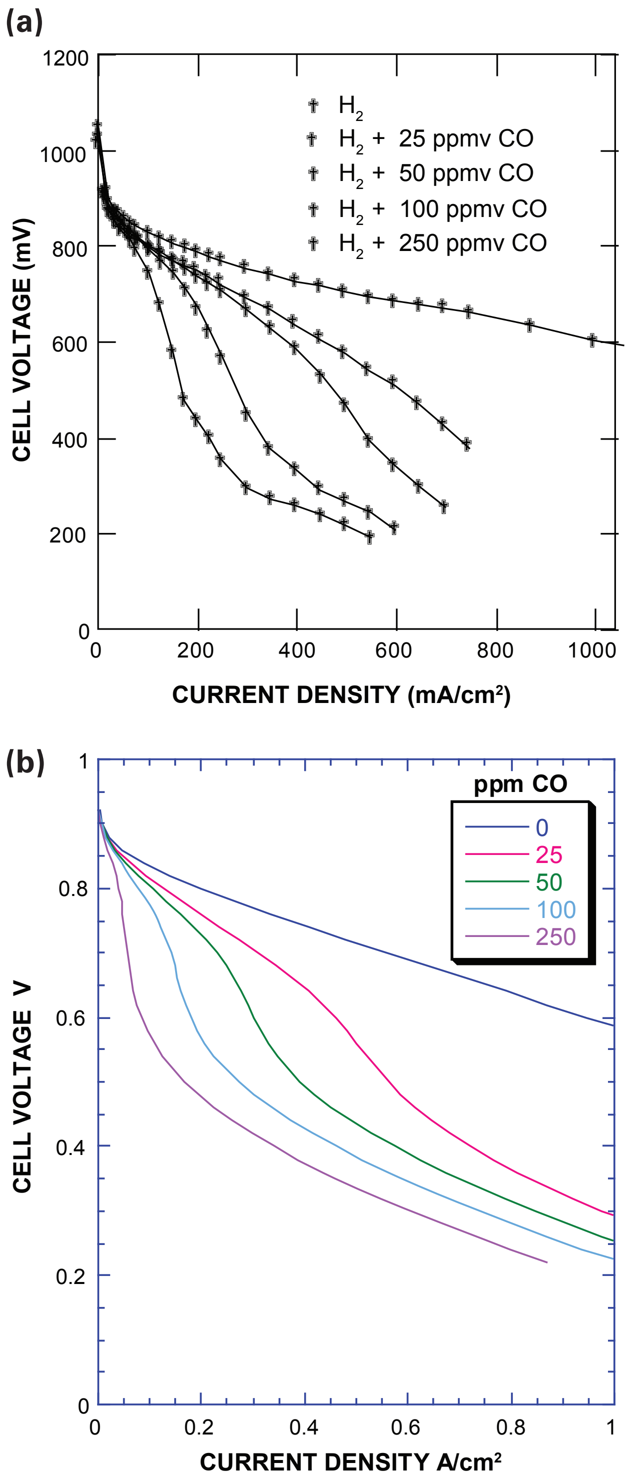

FIGURE 3. LANL data for fuel cell performance as a function of CO concentration (a). Tafel-Heyrovsky anode model for qualitative prediction of fuel cell performance (b). The line is used to guide the eye.

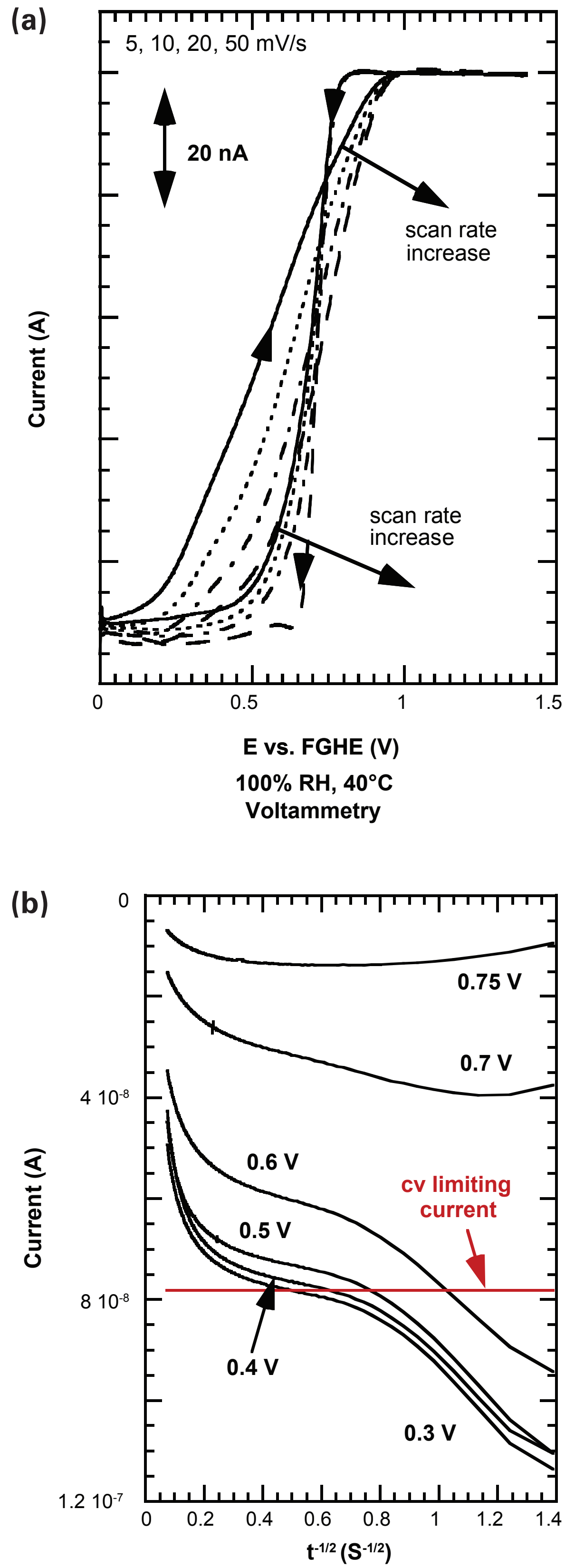

FIGURE 4. Voltammogram of platinum coated with Nafion® in presence of air at 100% RH, 40°C at different scan rates (a). Chronoamperometry of platinum coated with Nafion® in presence of air at 60% RH, 40°C at different potentials (b).

  - Investigate cathode kinetics using similar models (explore Pt/PtO, PtO, PtOH, PtOOH intermediates and peroxide generation).
- Platinum-Ionomer Interface
  - The platinum-ionomer interface has been found to be dynamic and important for the observed overpotentials at a fuel cell cathode.
  - Expand studies in peroxide generation.
  - Implement non-electrochemical techniques (neutron reflectivity, etc).
  - Extend studies to other polymer systems.

FY 2006 Publications/Presentations

1. Jia X. Wang, Thomas E. Springer, and Radoslav R. Adzic, "Dual-Pathway Kinetic Equations for the Hydrogen Oxidation Reaction on Pt Electrodes," *J. Electrochem. Soc.* (2006) in press.

2. Jia X. Wang, Thomas E. Springer, and Radoslav R. Adzic, "Dual-Pathway Kinetic Equations for the Hydrogen Oxidation Reaction on Pt Electrodes," Electrochemical Society Meeting, Denver, CO, May 10, 2006.

3. J.Chlistunoff, F.Uribe, B.Pivovar, "Oxygen Reduction at the Pt/Recast-Nafion® Film Interface at Different Temperatures and Relative Humidities" – accepted for publication in *Transactions of the Electrochemical Society.*

4. J. Chlistunoff, F.Uribe and B.Pivovar, *Oxygen Reduction at the Pt/Recast-Nafion® Film Interface at Different Temperatures and Relative Humidities.*, presentation at the 208th Meeting of the Electrochemical Society, Los Angeles, October 16–21, 2005.

5. J. Chlistunoff, F.Uribe and B.Pivovar, *Oxygen Reduction at the Pt/Recast-Nafion® Film Interface. Effect of the Polymer Equivalent Weight*, presentation at the 209th Meeting of the Electrochemical Society, Denver, May 7–12, 2006.

6. B. Pivovar, "LANL Fuel Cell Research: Freeze Studies and Fundamental Catalysis", Lawrence Berkeley National Lab, April 20, 2006.

7. B. Pivovar, "Optimizing Alternative Polymer Performance in Fuel Cells," Pacific Polymer Conference IX, Ka'anapali, HI, December 12, 2005.