

V.A.4 Applied Science for Electrode Cost, Performance, and Durability

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Accomplishments

- Applied micro-electrodes to the study of the ORR on smooth polycrystalline Pt and rough platinized surfaces; found Nafion[®] reorganization on rough platinized surfaces was significantly inhibited, giving insight into the platinum-ionomer interface of real electrode systems.
- Quantified peroxide production rates for smooth polycrystalline platinum in contact with Nafion[®] as a function of temperature and relative humidity (RH).
- Demonstrated that processing significantly affects the fraction of the platinum surface area available in a fuel cell. For the systems investigated less than one-quarter of the heterogeneous surface area was electrochemically accessible in the membrane electrode assembly (MEA), suggesting significant improvements in utilization could be achieved.



Objectives

- Model oxygen reduction reactions (ORRs) using reactive adsorption mechanism.
- Use micro-electrodes to study the platinum-ionomer interface, ORR and peroxide generation.
- Elucidate catalyst utilization and durability of electrodes.

Technical Barriers

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

- (A) Durability
- (B) Cost
- (C) 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/kWe
- Durability with cycling: 5,000 hours

Introduction

Fuel cells will need to address issues of cost, durability and performance in order to meet commercialization requirements. The goal of this project is to provide the fundamental understanding of processes necessary to assist the DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program to meet DOE milestones for cost, performance and durability. This effort focuses on development of ORR models, investigation of the platinum-ionomer interface and the impact of electrode design and processing in order to decrease cost, and improve performance and durability.

Approach

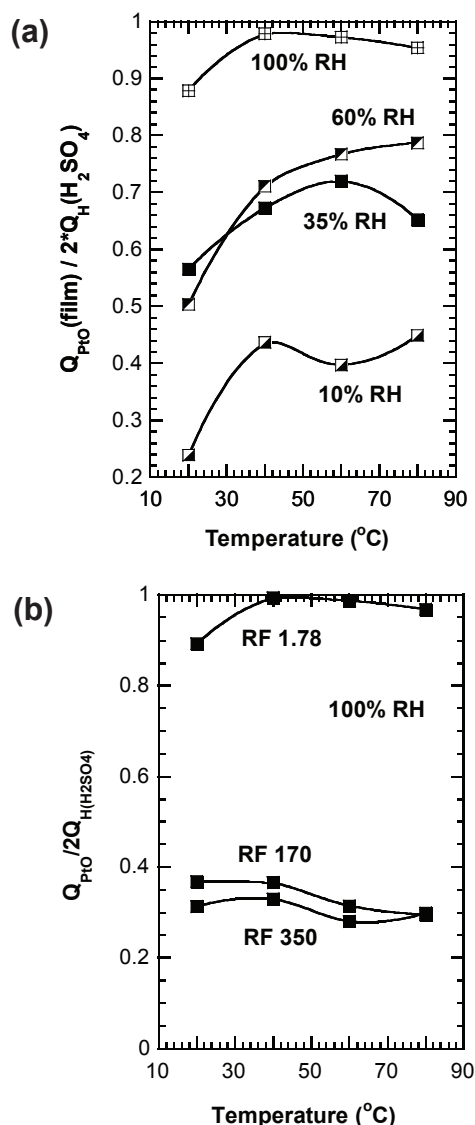
The project centers on exploring electrodes (primarily cathodes) in order to better understand how to address issues such as cost, performance and durability. Electrodes were chosen for this project as cost projections suggest that Pt may represent almost half of large volume production costs based on current technology fuel cells, and are known to be critical for performance and durability [1]. We have applied micro-electrodes, including interdigitated micro-electrode arrays to the study of ORR and peroxide generation for ionomers in contact with platinum. We have studied catalyst particle size, heterogeneously accessible surface area and electrochemically accessible surface area as a function of processing of catalyst and catalyst-ionomer mixtures. We have also collaborated with Brookhaven

National Laboratory in order to develop reactive adsorption-based models for ORR.

Results

Micro-electrode investigations into the platinum-ionomer interface have shown that the platinum-ionomer interface is much more complicated and dynamic than traditionally considered [2]. This work has been expanded to include roughened platinized surfaces and interdigitated micro-arrays for the study of peroxide generation. Figures 1a and 1b show a ratio of the charge associated with the reduction of platinum oxide (PtO) after holding the Pt-ionomer sample at 1.4 V (vs. the reference hydrogen electrode, RHE) for 10 seconds to twice the charge associated with hydrogen adsorption of an ionomer-free sample in contact with sulfuric acid as a function of temperature as determined by voltammetry. The ratio plotted in Figures 1a and 1b gives information about the accessibility of platinum when in contact with ionomer. Figure 1a shows that for a smooth sample (roughness factor [RF] = 1.78, where roughness factor equals platinum surface area/geometric surface area) at high RH almost all of the platinum is available for oxidation, whereas at low RH significantly less platinum is oxidized. The amount of surface area at a given RH increases with temperature and is consistent with our prior observations of ionomer rearrangement increasing with either temperature or RH. Figure 1b shows data at 100% RH for three different samples: the smooth sample (RF=1.78, also shown in Figure 1a) and two rough samples obtained by electrodepositing platinum from solution (RF = 170 and 350). The high RF samples show significantly decreased available surface area even at high RH, suggesting that ionomer reorganization is significantly inhibited by the increased interface between the platinum and ionomer. This system is closer to that of actual high catalyst surface area electrodes and suggests that much of the Pt surface in real electrodes may not be effectively accessible when in contact with the ionomer.

Interdigitated micro-arrays consisting of 25 intermeshing (smooth) platinum “fingers” (5 microns wide and 100 nm high, separated by 5 microns and covered by a 6.8 micron film of Nafion[®]) were used to determine peroxide production rates during oxygen reduction. To this point peroxide or other radical species have been blamed as a primary culprit in membrane degradation, but few studies have directly quantified these species existence *in situ*. Figure 2a shows oxygen reduction current and peroxide generation as a function of potential and scan direction at 60% RH, 40°C. The ORR current shows a large hysteresis based on the scan direction and peroxide representing between 1% and 5% of the total current, shown in Figure 2b as Icollector/ Igenerator. Results (not shown) of temperature and RH studies show peroxide generation



FIGURES 1. Ratio of PtO Reduction Charge after Oxidation at 1.4 V to Twice the H Adsorption Charge in Sulfuric Acid as a Function of Temperature as Determined by Voltammetry for (a) Smooth Platinum (RF=1.78) at Various RH, and (b) for Various RF Samples at 100% RH

increases with both RH and temperature. These results taken with the large hysteresis shown in Figure 2b, concordant with micro-electrode studies, suggest that ionomer reorganization at the platinum interface may be important in peroxide generation rates.

Platinum utilization in electrodes has not been reported extensively, although a notable exception would be a study reported by General Motors (GM) for a specific set of processing conditions and several different catalysts [3]. Here, we move beyond this work investigating processing conditions more thoroughly and adding other surface area measurements. The amount of platinum electro-chemically accessible is a primary concern for increasing performance while limiting cost

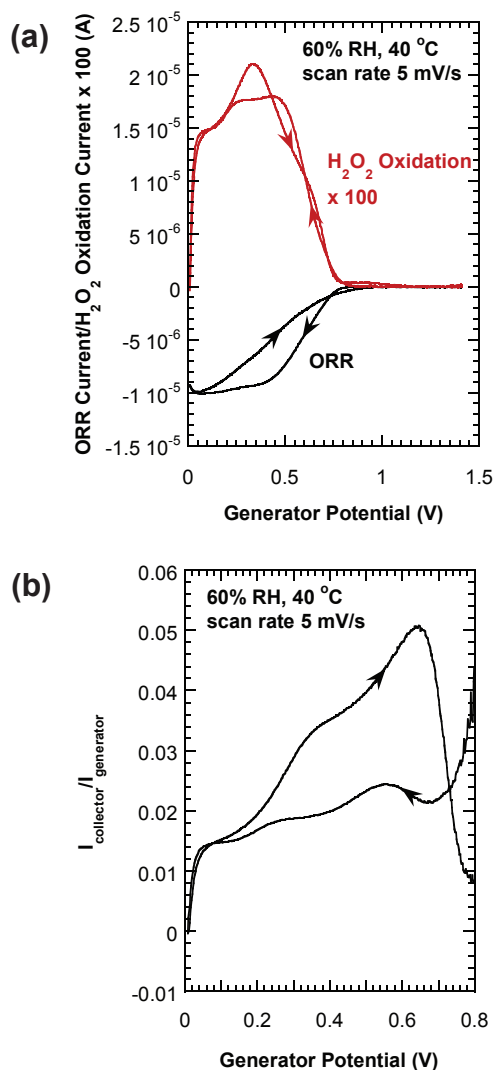


FIGURE 2. (a) Peroxide Production Rates and Oxygen Reduction Rates, and (b) the Ratio of Peroxide Production Rates to Oxygen Reduction Rates as Determined by Interdigitated Micro-Array Micro-Electrodes as a Function of Potential at 60% RH and 40°C

and also has implications for durability. The studies undertaken here have looked at platinum surface area by a number of techniques: X-ray diffraction (by particle size), heterogeneous surface area measurement (adsorption of chemical species on active surface), half cell techniques and fuel cell measurements. Figure 3 demonstrates the heterogeneous surface area probe we developed for estimating surface area. Figure 3 shows the response of a sulfide ion selective probe for an 1,010 ppm H₂S containing gas mixture that has been fed through a 20% Pt on carbon sample and a blank showing the response of the system when fed through a carbon sample without Pt (inset). The amount of sulfur adsorbed on this Pt sample was calculated from this data to be 110 m²/g of Pt. Figure 4 shows the estimated surface area for the same 20% Pt on carbon catalyst as a

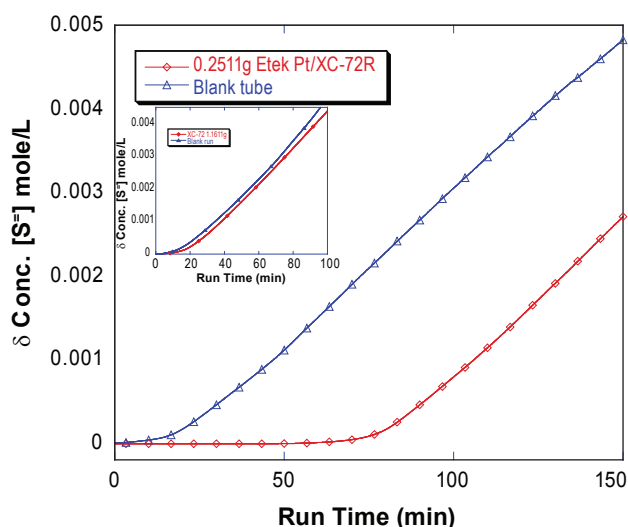


FIGURE 3. Response of Sulfide Selective Ion Probe Versus Time for H₂S Containing Gas Mixture Flowing Past 20% Pt on Carbon and Carbon (Inset)

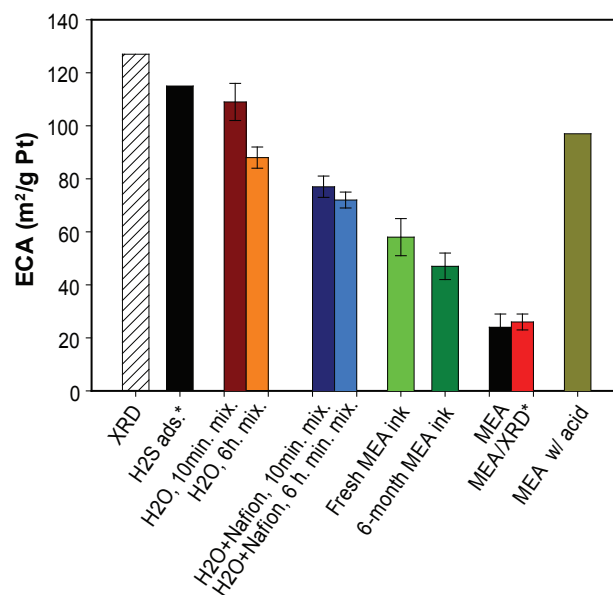


FIGURE 4. Estimated Surface Area (ECA) as a Function of Processing Condition for Various Measurement Techniques of 20% Pt on Carbon

function of processing conditions as estimated by various techniques (MEA ink composition given in Ref. 4). The data show clear trends in decreasing surface area with increased processing, and X-ray diffraction and X-ray fluorescence measurements confirm that a large fraction of the Pt surface area is inaccessible in the final MEA. These studies show the importance of processing on available surface area. Further processing studies will be carried out, along with studies on the implications on performance and durability.

Conclusions & Future Directions

- Kinetic Studies
 - Discerning activity within accessible Pt (not all sites are equal).
 - Can accessible sites be made more active?
- Electrode Design/Processing Studies
 - Differences in processing of electrodes.
 - Coupling performance and durability with structure.
- Tool Development
 - Atomic force microscopy (phase mode plus conductivity/reaction).
 - Ionic/electronic conductivity decoupling.

FY 2007 Publications/Presentations

1. J. X. Wang, T. E. Springer, and R. R. Adzic, "Dual-Pathway Kinetic Equations for the Hydrogen Oxidation Reaction on Pt Electrodes," *J. Electrochem. Soc.* (2006), 153, no. 9, p. A1732-40.
2. J.Chlistunoff, F.Uribe, B.Pivovar, *Oxygen Reduction at the Pt/Recast-Nafion[®] Film Interface at Different Temperatures and Relative Humidities.*, ECS Trans. 1, (6) 137 (2006).
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5. J.Chlistunoff, F.Uribe, B.Pivovar, *ULTRAMICROELECTRODE STUDY OF OXYGEN REDUCTION AT THE PLATINUM/IONOMER INTERFACE AT LOW RELATIVE HUMIDITY*, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 2006, 51 (2).

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2. 2006 DOE Report on this project, http://www.hydrogen.energy.gov/pdfs/review06/fc_22_pivovar.pdf.
3. Gasteiger, HA; Kocha, SS; Sompalli, B; Wagner, FT, *App.Cat. B*, 56, 9-35, 2005.
4. Wilson, MS; Valerio, JA; Gottesfeld, S, *Electrochimica Acta*, 40, 1995, 355.