VII.C.6 Cathode Electrocatalysis: Platinum Stability and Non-Platinum Electrocatalysts

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Objectives

- Elucidate rates and mechanisms of the degradation of polymer electrolyte fuel cell (PEFC) platinum electrode performance
  - Effect of electrolyte, potential (holding and cycling), time, and temperature
- Develop non-platinum cathode electrocatalysts for PEFCs
  - Transition metal carbides and nitrides
  - Bi-metallic systems
  - Metal centers attached to electron-conducting polymer backbones

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. Electrode Performance

Approach

<u>Determine the mechanisms and rates of the loss of electrochemically active surface area for PEFC platinum electrodes</u>

- Potentiostatic dissolution measurements in adsorbing (phosphoric acid) and non-adsorbing (perchloric acid and Nafion®) electrolytes, effect of temperature and potential
- Potential step dissolution rate measurements (cf. drive cycles)
- Electrochemical and *ex situ* microscopic analyses of membrane-electrode assemblies
  - *In situ* x-ray fluorescence (Pt oxidation state) and wide-angle diffraction (Pt particle size) of operating membrane-electrode assemblies

<u>Develop non-platinum oxygen reduction electrocatalysts</u>

- Transition metal carbides and nitrides
- Bi-metallic systems (e.g., base metal, noble metal) on carbon and transition metal oxide supports
- Metal centers attached to electron-conducting polymer backbones

Accomplishments

- Determined the dissolved platinum equilibrium concentrations for polycrystalline platinum immersed in room-temperature phosphoric acid and perchloric acid electrolyte
- Evaluated the oxygen reduction reaction (ORR) activity and stability of carbides and nitrides
- Evaluated the ORR activity and stability of gold and gold bi-metallics supported on carbon and titania

Future Directions

- Determine the effect of potential, potential cycling (cf. drive cycles), temperature, atmosphere, and the presence of Nafion® on the dissolution of high-surface-area Pt/C and Pt-Co electrodes
- Prepare and test the ORR activity of select bi- or tri-metallic systems
  - Conduct surface and bulk characterization to verify the desired catalyst composition/structure, particle size, and electronic properties
  - Explore different synthesis methods and temperature treatments
  - Continue synthesis and characterization of metal centers attached to polymer backbones
- Incorporate higher-temperature ORR kinetic measurements and ring electrode to detect intermediates
- Fabricate and test a membrane-electrode assembly using newly developed cathode electrocatalyst

Introduction

The performance of polymer electrolyte fuel cells with platinum or platinum alloy electrocatalysts degrades with time, with the observed performance loss being on the order of 54 microvolts/hour at 1 A/cm² and 80°C [1]. This has been attributed to a loss of the electrochemically active surface area of the platinum alloy cathode electrocatalyst (25 to 17 m²/gram after 1000 hours) [1]. One of the proposed mechanisms for the loss of electrochemically active surface area is oxidation and dissolution of platinum at the high potentials typical of the PEFC cathode [2,3]. This dissolved platinum can then either deposit on existing Pt particles to form larger particles or diffuse into an electrochemically inaccessible portion of the membrane-electrode assembly (e.g., into the gas diffusion layer). It has been speculated [4], based on potentiostatic platinum solubility data measured in phosphoric acid [5], that dissolution and loss of platinum may occur at a significant rate at the high potentials encountered on the cathode of the PEFC at low power output (e.g., 0.9 V during idling).

One of the main barriers to commercialization of polymer electrolyte fuel cell power systems is cost. The cost of the membrane-electrode assembly constitutes approximately 84% of the total fuel cell stack cost, with the anode and cathode contributing almost 50% of this cost. The high cost of the electrodes is largely due to the use of platinum-containing electrocatalysts [6]. In the past decade, there have been significant advances in reducing the platinum metal loading of both the anode and cathode. However, any further substantial cost reductions will require the replacement of platinum with a less expensive electrocatalytic material.

Approach

Our approach for elucidating the mechanism and rates for the loss of electrochemically active surface area of platinum and platinum alloy PEFC electrocatalysts is to use a combination of measurements of platinum dissolution rates, pre- and post-polarization *ex situ* analyses of membrane-electrode assemblies, and *in situ* x-ray scattering and fluorescence studies of operating membrane-electrode assemblies. We are determining the mechanisms and rates of platinum dissolution from platinum and platinum alloys as a function of potential and temperature using potentiostatic and potential step dissolution measurements in adsorbing (phosphoric acid) and non-adsorbing (perchloric acid and Nafion®) electrolytes. The change in particle size, the oxidation state, and the distribution of platinum will be determined using a combination of *in situ* electrochemical measurements, *ex situ* microscopic analyses of aged fuel cells, and *in situ*

x-ray fluorescence and wide-angle diffraction studies of operating fuel cells.

Our approach to developing non-Pt ORR electrocatalysts involves three systems: (1) transition metal carbides and nitrides, (2) bi-metallic base metal-noble metal systems using conventional carbon and alternative supports, and (3) metal centers attached to electron-conducting polymer backbones. The rationale for studying transition metal carbides and nitrides is that they contain surface vacancies and defects to adsorb and dissociate oxygen, they can be isoelectronic with platinum (e.g., tungsten carbide), they have been found to be catalytically active in hydro-treating and dehydration reactions, they are resistant to acidic corrosion, and they are electronically conducting. The choice of metals for the bi-metallic systems is based on surface energy calculations by Ruban et al. [7] giving the propensity of one metal to segregate to the surface of a bi-metallic combination. We are studying systems where the Ruban et al. calculations show that the minor noble metal component will tend to segregate to the surface of a particle with a predominantly base metal core to form a protective layer. The base metal component was chosen to modify the d-band center of the noble metal, making it more "Pt-like". We have also examined the use of titania as an alternative support to modify the electronic properties of nano-scale gold particles. Finally, we are investigating the use of metal centers attached to electron-conducting polymer backbones to allow precise control of the spacing between the metal centers and to promote high catalyst utilization by having an electron conductor in close proximity to the reaction site. The oxygen reduction kinetics of the candidate materials are determined using the thin-film rotating ring-disk electrode technique. This technique allows determination of the reaction kinetic parameters (exchange current density and transfer coefficient) independent of mass-transfer effects.

Results and Conclusions

In FY 2005, we determined the equilibrium concentration of dissolved platinum as a function of potential in non-adsorbing perchloric acid electrolyte, as a Nafion® mimic, and in adsorbing phosphoric acid electrolyte. A summary of the results from this study is shown in Figure 1.
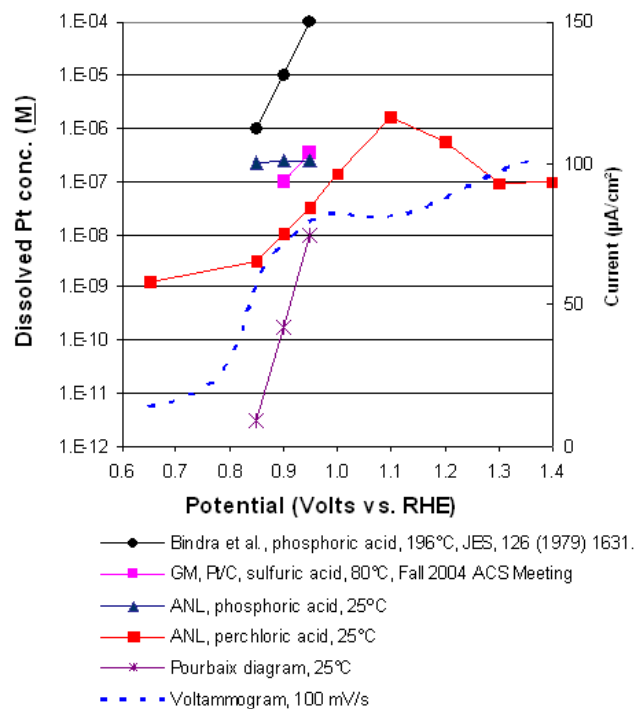

Figure 1. Dissolved Platinum Equilibrium Concentrations from a Polycrystalline Platinum Wire Immersed in Room-Temperature Phosphoric Acid or Perchloric Acid Electrolyte (ANL data) (Also shown for comparison are data from Ref. 5, polycrystalline Pt in phosphoric acid at 196°C, and from Ref. 4, Pt/C in sulfuric acid at 80°C. The voltammetric profile for polycrystalline Pt in perchloric acid electrolyte (right-hand axis) is also shown.)

Conclusions from our FY 2005 work are as follows: (1) Pt dissolution is more severe in phosphoric acid than in perchloric acid; (2) the dissolved Pt equilibrium concentration is less dependent on potential than predicted by the Pourbaix diagram, although the concentration is higher than that predicted by the Pourbaix diagram [8]; and (3) the concentration of dissolved Pt increases monotonically up to 1.1 V and decreases at potentials >1.1 V, presumably due to the formation of a protective oxide film. In FY 2006, we will determine the effect of potential, potential cycling (cf. drive cycles), temperature, atmosphere, and the presence of Nafion® on the dissolution of high-surface-area Pt/C and Pt-Co electrodes.

We have completed our studies of carbides and nitrides as non-platinum oxygen reduction

electrocatalysts. We found that these materials were stable in an acidic environment and were active for oxygen reduction. However, these materials showed oxygen reduction activity at potentials far too low for the fuel cell application (e.g., 0.23 V vs. reversible hydrogen electrode, RHE), even after greatly increasing the catalyst surface area. During FY 2005, we began two new approaches, developing electrocatalysts with well-controlled spacing between catalytic sites and close proximity to an electron conductor by attaching active metal centers to an electron-conducting polymer backbone, and developing bi-metallic transition metal alloys and transition metals supported on carbon or metal oxide supports. We have synthesized and tested several gold bi-metallic formulations supported on Vulcan XC-72R carbon, including gold-nickel, gold-iron, gold-cobalt, and gold-iridium. We have also synthesized and tested gold supported on titania. These electrocatalysts have metal particle sizes ranging from 5 to 40 nm and are stable in the acidic environment. As shown in Figure 2, iridium enhances the ORR activity of gold. However, these materials have oxygen reduction activity at potentials of 0.4–0.6 V, which are too low for the fuel cell application. In FY 2006, we will complete the gold bi-metallic systems and focus our efforts on bi-metallics of rhodium, ruthenium, and palladium. We will alloy these noble metals with base metals to alter their electronic properties such that they are similar to those of the most active ORR catalyst, Pt_3Co.

References

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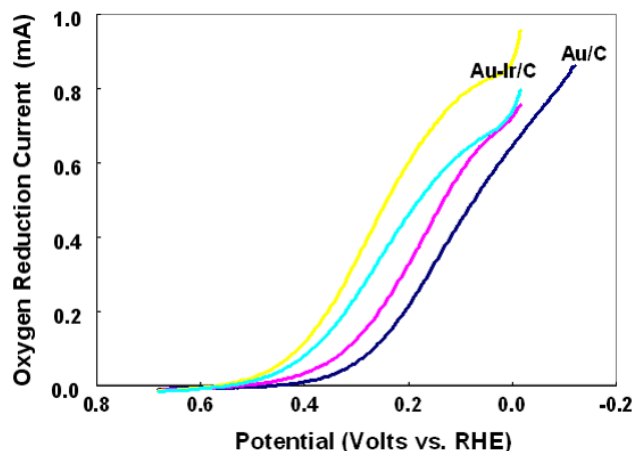2. E. G¸lzow, *J. Power Sources*, 127 (2004) 213-221.

Figure 2. Oxygen Reduction Reaction Current for Nafion®-Bonded Gold and Gold-Iridium Electrocatalysts Supported on Vulcan XC-72R High-Surface-Area Carbon (The electrodes were rotated at 1600 rpm in an oxygen-saturated perchloric acid electrolyte; potential scan rate 10 mV/s.)

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