

## V.G.14 Electrode Stability

Xiaoping Wang (Primary Contact),  
Deborah Myers, and Romesh Kumar

Argonne National Laboratory  
9700 S. Cass Avenue  
Argonne, IL 60439  
Phone: (630) 252-1182; Fax: (630) 252-4176  
E-mail: wangx@cmt.anl.gov

DOE Technology Development Manager:  
Nancy Garland

Phone: (202) 586-5673; Fax: (202) 586-9811  
E-mail: Nancy.Garland@ee.doe.gov

Start Date: October 2005

Projected End Date: September 2009

### Objectives

- Elucidate the rates and mechanisms of the loss of electrochemically active surface area (EASA) of polymer electrolyte fuel cell platinum electrodes

### 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
- (C) Electrode Performance

### Technical Targets

This project focuses on fundamental studies of electrocatalyst degradation mechanisms. Insights gained from these studies will be applied toward the definition of operating conditions and the development of improved materials to achieve the following DOE electrocatalyst durability requirements:

- 5,000 operating hours under load cycling at  $\leq 80^\circ\text{C}$
- 2,000 operating hours under load cycling at  $> 80^\circ\text{C}$

### Accomplishments

- Determined dissolution behavior of bulk platinum as a function of potential and potential cycling
- Determined the dissolution behavior of platinum nano-particles on a high-surface-area carbon

support and determined the platinum particle size change

---

### Introduction

One of the challenges facing the development of polymer electrolyte fuel cells (PEFCs) for automotive and stationary power applications is the durability of the fuel cell materials [1]. PEFC performance loss under steady-state and cycling conditions has been attributed in part to a loss of electrochemically active surface area of the platinum cathode electrocatalyst [2–5]. 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 [1,6,7]. This dissolved platinum can then either deposit on existing platinum particles to form larger particles (Ostwald ripening) [5] or diffuse into an electrochemically inaccessible portion of the membrane-electrode assembly (e.g., into the gas diffusion layer) [8]. It has been speculated that platinum dissolution may be quite prevalent, not only during potential cycling typical of varying load conditions, but also during potential holds at high potentials typical of idling in the automotive application [1]. Such dissolution may be a significant cause of limited PEFC lifetimes. The purpose of this project is to determine the mechanisms and rates of loss of electrochemically active surface area of platinum and platinum alloy electrocatalysts under conditions relevant to PEFCs in the automotive application. The data from this study can be used to predict electrocatalyst lifetimes and to define conditions (e.g., potentials) that accelerate or mitigate catalyst degradation.

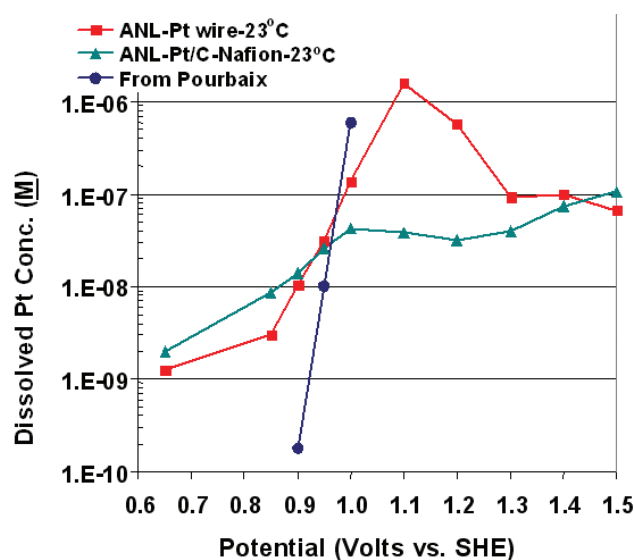
### Approach

The overall approach of this project is a combination of measurements of platinum dissolution rates, pre- and post-polarization *ex situ* analyses of membrane-electrode assemblies (MEAs), and *in situ* x-ray scattering and fluorescence studies of operating MEAs. This year's research focused on the measurement of the equilibrium concentration of dissolved platinum and dissolution rates as a function of form of the electrode, potential, and potential cycling. The electrode was platinum wire or platinum nano-particles on high-surface-area carbon (10-wt% Pt/C, E-Tek). The electrolyte was perchloric acid, chosen because it mimics the non-adsorbing characteristics of Nafion® [9].

## Results

The equilibrium concentration of dissolved platinum in perchloric acid was determined as a function of potential for potentiostatic conditions and at room temperature for both platinum wire and Pt/C. These results are summarized in Figure 1. These data show that the equilibrium concentration of dissolved platinum for Pt wire increases with increasing potential from 0.65 to 1.1 V (vs. standard hydrogen electrode, SHE) and is logarithmically dependent on potential in the 0.85 to 1.1 V region. The potential dependence observed in this region translates to a ten-fold increase in dissolved platinum concentration for every 92 mV increase in potential. The equilibrium concentration of dissolved platinum for Pt wire was found to decrease at potentials above 1.1 V. This decrease has been attributed to the formation of a passivating oxide film on the platinum surface. The invariant concentration of dissolved platinum in the 1.3 to 1.4 V region indicates that the platinum metal is fully covered by a protective PtO film and that the equilibrium  $\text{Pt}^{2+}$  concentration in the electrolyte is governed by the chemical dissolution of PtO.

The equilibrium concentration of dissolved platinum for Pt/C was found to be less dependent on potential than for platinum wire, and it was found to decrease at potentials between 1.0 and 1.2 V. Unlike the Pt wire, however, the Pt/C did not passivate above 1.2 V and showed a further increase in dissolved Pt when held at potentials  $>1.2$  V. This behavior has been attributed to corrosion of the carbon support at these high



**FIGURE 1.** Equilibrium concentration of dissolved platinum as a function of potential for Pt wire and Pt/C. Also shown for comparison is the expected concentration from thermodynamic calculations for dissolution to  $\text{Pt}^{2+}$  (ref. 10).

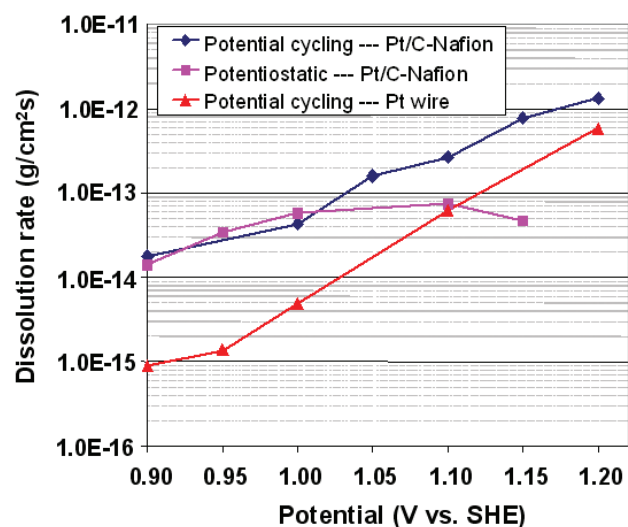
potentials, resulting in the loss of Pt to the electrolyte. Transmission electron microscopic examination of the Pt/C before and after the potentiostatic treatment showed that there was no strong effect of the treatment on Pt particle size.

This year we also determined the rates of Pt dissolution under potentiostatic and potential cycling conditions. These results are shown in Figure 2. Conclusions from these results are that the dissolution rate for Pt/C is much higher than that for Pt wire under potential cycling conditions and that cycling the potential to  $>1.0$  V accelerates potential cycling-related Pt dissolution compared to potentiostatic dissolution rates. It was also found that the steady-state dissolved platinum concentration for both polycrystalline Pt and Pt/C increase with increasing upper potential limit of the potential cycles.

## Conclusions and Future Directions

### Conclusions

The dependences of the equilibrium concentration of dissolved platinum on potential for both the bulk platinum and Pt/C electrodes are consistent with platinum dissolution concurrent with oxide layer formation. At potentials of 1.1 and 1.0 V, for Pt wire and Pt/C, respectively, the oxide forms a passivating film, inhibiting further platinum dissolution. At potentials  $>1.2$  V, which can be encountered during PEFC start-up and shut-down procedures [11] the equilibrium concentration of dissolved platinum increases further for the Pt/C electrode, most likely due to concurrent corrosion of the carbon support.



**FIGURE 2.** Platinum dissolution rates for Pt wire and Pt/C under potentiostatic and potential cycling conditions. Potential cycling was from 0.4 V to potentials shown at a rate of 10 mV/s.

The upper potential limit dramatically affects both the steady-state dissolved Pt concentration and the rate of dissolution when cycling the potential in the 0.4 to 1.2 V range. The threshold potential for potential cycling-accelerated dissolution of platinum is 1.02 V. This observation indicates that formation and reduction of the passivating oxide film are responsible for the increased degradation rates of fuel cell electrodes under potential cycling conditions. Cycling the PEFC between potentials typical of open circuit conditions (~1 V) and potentials typical of load conditions should be avoided in order to mitigate cycling-related acceleration of platinum dissolution.

### Future Work

Our near-term future work will focus on measurement of platinum dissolution for Pt/C and Pt<sub>3</sub>Co/C:

- Pt/C high surface area electrode (E-Tek) in perchloric acid electrolyte
  - Finish determining potential cycling effects on dissolution with higher upper-limit potentials (1.3–1.5 V)
    - Transmission electron microscopy for changes in Pt particle size and support
  - Effect of atmosphere (air and hydrogen)
  - Effect of temperature (room temperature to 120°C)
- Pt<sub>3</sub>Co/C high surface area electrode (Tanaka) in perchloric acid electrolyte
  - Potential (0.65–1.4 V)
  - Potential cycling (0.4 to 1.4 V)
  - Atmosphere (air and hydrogen)
  - Temperature (room temperature to 120°C)
- Particle size, oxidation state, and distribution of platinum in MEAs under varied experimental conditions (e.g., potentiostatic, potential cycling, different atmospheres and temperatures)

### FY 2006 Publications/Presentations

1. “Effect of Voltage on Dissolution of Pt, Relevance to Polymer Electrolyte Fuel Cells,” Xiaoping Wang, Romesh Kumar, and Deborah J. Myers, *Electrochem and Solid-State Letters*, **9**(5), A225-A227 (2006).
2. “Fundamental Studies of Platinum Electrocatalyst Degradation,” Xiaoping Wang, Deborah J. Myers, and Romesh Kumar, *Fuel Cell Durability 2005*, Washington, D.C., December 8–9, 2005.
3. “Polymer Electrolyte Fuel Cell Cathode Electrocatalysts,” Xiaoping Wang, Romesh Kumar, and Deborah J. Myers, Poster and Abstract, 2005 Fuel Cell Seminar, Palm Springs, CA, November 14–18, 2005.

### References

1. M. Mathias, H. Gasteiger, R. Makharia, S. Kocha, T. Fuller, T. Xie, and J. Pisco, *Fuel Chemistry Division Preprints, 2004*, American Chemical Society Fall National Meeting, 46, ACS, Philadelphia (2004).
2. M. S. Wilson, F. H. Garzon, K. E. Sickafus, and S. Gottesfeld, *J. Electrochem. Soc.*, **140**, 2872 (1993).
3. T. Patterson, *Fuel Cell Technology: Opportunities and Challenges*, Topical Conference Proceedings, 2002 AIChE Spring National Meeting, G. J. Igwe and D. Mah, Eds., pp. 313–318, AIChE, New York (2002).
4. E. Antolini, *J. Materials Science*, **38**, 2995 (2003).
5. J. Xie, D. L. Wood III, K. L. More, P. Atanassov, and R. Borup, *J. Electrochem. Soc.*, **152**, A1011 (2005).
6. R. M. Darling and J. P. Meyers, *J. Electrochem. Soc.*, **126**, A1523 (2003).
7. P. J. Ferreira, G. J. Ia O', Y. Shao-Horn, D. Morgan, R. Makharia, S. Kocha, and H. A. Gasteiger, *J. Electrochem. Soc.*, **152**, A2256 (2005).
8. E. Gülzow, *J. Power Sources*, **127**, 213 (2004).
9. U. A. Paulus, T. J. Schmidt, H. A. Gasteiger, and R. J. Behm, *J. Electroanal. Chem.*, **495**, 134 (2001).
10. M. Pourbaix, “Atlas of Electrochemical Equilibrium in Aqueous Solutions,” 1st ed., Pergamon Press (1966).
11. P. T. Yu, S. Kocha, L. Paine, W. Gu, and F. T. Wagner, *Conference Proceedings, 2004 AIChE Spring National Meeting*, AIChE, New Orleans, LA (2004).