
Novel Intermetallic Catalysts to Enhance PEM Membrane Durability

Francis J. DiSalvo (Primary Contact),
Neal M. Abrams, Paul F. Mutolo (Cornell
University); Mallika Gummalla,
Thomas H. Madden (UTRC)

Cornell University
102 Baker Laboratory
Ithaca, NY 14850
Phone: (607) 255-7238; Fax: (607) 255-4137
E-mail: fjd3@cornell.edu

DOE Program Officer: Aravinda Kini
Phone: (301) 903-3565
E-mail: aravinda.kini@science.doe.gov

Objectives

The Cornell collaboration with scientists at the United Technology Research Center focuses on incorporating novel fuel cell anode catalysts into the matrix of current industrial fuel cell technology. The goal to move to lower anode electrocatalyst loadings in real membrane electrode assemblies (MEAs), plus the ability of these electrodes to operate for longer times on dirtier hydrogen fuel, requires an understanding of the fundamental processes leading to an observed platinum catalyst degradation. The primary challenge is to determine the source of anode dissolution in the polymer electrolyte membrane (PEM). Once that has been defined, changes in the catalyst and/or operating condition can be studied in an effort to mitigate these effects. The overall goal is to add more detail to understand the nature of the dissolution processes (e.g., equilibrium vs. kinetic).

Technical Barriers

The current state-of-the-art PEM fuel cells suffer from failure over long term use due to materials breakdown. Generally, electrodes perform well with ultra-pure hydrogen, but still require recovery mechanisms to reverse degradation processes. Incorporating intermetallic nanoparticles into the MEA will allow introduction of dirty fuel as well as carbon-based fuels such as methanol and ethanol. At the same time, these new electrocatalysts will potentially mitigate degradation effects common to platinum-containing MEAs.

Abstract

The goal to move to lower anode electrocatalyst loading in real MEAs, plus the ability of these electrodes

to operate for longer times on dirtier hydrogen fuel, require an understanding of the fundamental processes leading to the observed degradation. Research at the Cornell Fuel Cell Institute (CFCI) focuses on the ability of Pt-containing intermetallics to be resistant to poisons such as sulfur and CO commonly found in dirty hydrogen. Preliminary data reports no changes in catalyst size or electrochemical activity when operated under potentiostatic conditions.

Progress Report and Future Directions

The Cornell collaboration with scientists at the United Technology Research Center focuses on incorporating novel fuel cell anode catalysts into the matrix of current industrial fuel cell technology. The current state-of-the-art PEM fuel cells suffer from failure over long term use due to materials breakdown. In laboratory electrochemical cells, ultra-low anode electrocatalyst loadings have been achieved. In the case of the actual MEA, loadings of approximately 0.5 mg/cm² are still required to permit operation with thousands of hours between recovery cycles. Generally, electrodes perform well with ultra-pure hydrogen, but still require recovery mechanisms to reverse degradation processes. These processes occur on the order of hundreds of hours.

In this work, the fate of the nanoparticle anode electrocatalyst electrode is being measured quantitatively over time for varied operating conditions, including: temperature, relative humidity and particle size. Literature reports and studies at UTRC point to three likely outcomes for the aging of catalyst particles: (1) coalescence of platinum nanoparticles via migration, (2) dissolution and redeposition (Ostwald ripening), and (3) catalyst agglomeration triggered by corrosion of the carbon support.¹

The project began by hiring a postdoc at Cornell, Dr. Neal Abrams, in October 2005. Since its inception, collaboration with UTRC has taken place by one on-site visit to the UTRC facility. Bi-weekly to monthly phone conferences take place between UTRC/UTC and Dr. Abrams and the associate director of CFCI (Dr. Paul Mutolo). Through these conferences, experimental designs and protocols have been established so this collaboration is as beneficial as possible to both UTRC and the CFCI. Subsequently, an electrochemical rotating ring-disk system has been setup in the DiSalvo lab for half-cell hydrogen fuel oxidation. Continuous feedback from the UTRC team has led to positive results and maintained focus in the project. Initial studies of the behavior of supported Pt catalysts in hydrogen oxidation have been performed as a benchmark

for planned studies of intermetallic compounds. A variety of characterization methods (SEM, TEM, EDX, XRD) have also been employed.

Catalyst ripening/dissolution is being studied using supported catalysts with an emphasis on accelerated lifetime testing. This includes operating at high temperatures (70–80 °C) with high relative humidity (RH) and results compared to low temp/low RH conditions. Continuous load testing is carried out for >100 hours as literature reports have found platinum dissolution/ripening effects to take place on this time scale.² A considerable hurdle in this research is the need to maintain a clean, high temperature environment for electrochemical testing. Ultrapure conditions are required given the proclivity for platinum poisoning, far beyond those originally anticipated by the research team. By maintaining clean conditions, chronoamperometric studies show relatively zero loss in catalytic activity over 7 days (168 hours), the anticipated timescale for catalyst degradation. Figure 1 illustrates the catalyst activity in hydrogen fuel and 0.1 M sulfuric acid where the high current at the beginning of day 1 and 7 constitute a single cleaning cycle. The small amount of remaining impurities in these high purity solutions decrease activity but do not entirely block the surface catalyst sites. Transmission electron microscopy (TEM) images of the carbon supported platinum catalyst are shown in Figure 2 before and after testing for 7 days. As can be seen, there is no perceptible change in particle size or agglomeration. This is expected since the experiment was maintained under potentiostatic conditions. In real-life fuel cell operations, anode potentials can reach near 1.2 V, well within the thermodynamic region of platinum dissolution.^{3,4} At this point, initial and background studies have concluded and we are moving into the next phase of understanding catalysts migration and dissolution. Potential cycling will be introduced into the chronoamperometry scans, enhancing the effect of catalyst dissolution. It is expected that very observable changes will take place, notably growth of single crystal platinum particles, loss of active electrochemical surface area, and migration of platinum particles into the membrane structure.¹

Future Directions

Novel System: Ordered Intermetallics

Once the protocols for studying electrocatalyst particle fate have been established for Pt, they will be applied to ordered intermetallic (OI) nanoparticle electrocatalysts. These electrocatalysts were developed at CFCI, where the superior poison tolerance and enhanced electrocatalytic activity for small organic

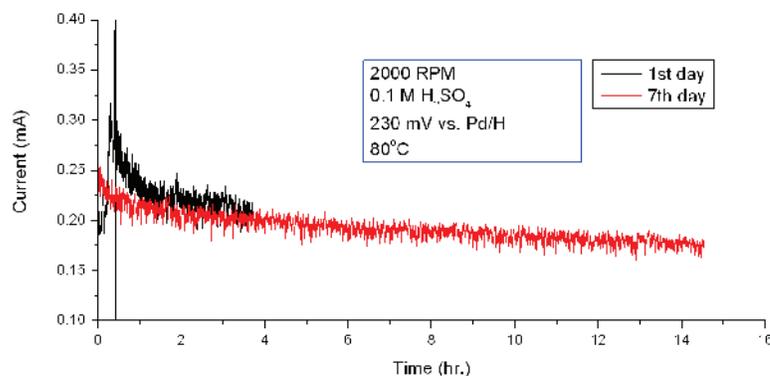


FIGURE 1. Chronoamperometry scan of hydrogen oxidation on a carbon-supported platinum catalyst in 0.1 M sulfuric acid. Data shows data from day 1 and day 7. Initial high current at $t \approx 0$ results from a single cleaning scan.

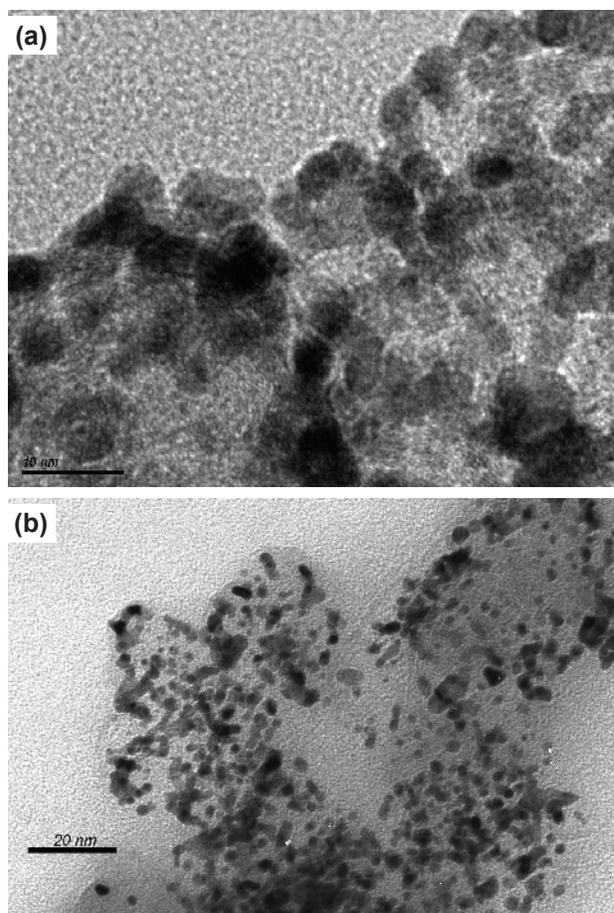


FIGURE 2. Carbon supported platinum nanoparticles, (a) before electrochemical testing and (b) after 7 days of testing at 80 °C.

molecule oxidation of these electrocatalysts was demonstrated.⁵ The mechanisms by which molecules undergo electro-oxidation on these surfaces are often different than those on Pt or PtRu. Of interest is quantifying any mitigation (compared to Pt) in (i) the

catalyst degrading aging mechanisms, and (ii) peroxide formation, plus (iii) tracking differences in catalytic activity over time.

Catalyst morphology will continue to be characterized by TEM, HR-TEM, and STEM for changes in particle size and morphology, as well as for crystallinity. Powder XRD is also used to determine bulk changes in crystallinity.

Though this project is still developing, a well-defined statement of work has been established between Cornell and UTRC that will direct future milestones. As the initial learning curve for this project has reached a plateau, the research planned for the following year will bring new results based upon the promise of continued collaborative efforts.

Endnotes

1. Ferreira, P.J.; la O', G. J.; Shao-Horn, Y.; Morgan, D.; Makharia, R.; Kocha, S.; Gasteiger, H A. *J. Electrochem. Soc.* **2005**, *152*, A2256.
2. Xie, J.; Wood, D. L.; More, K. L.; Atanassov, P.; Borup, R. L. *J. Electro. Chem. Soc.* **2005**, *152*, A1011.
3. Internal discussion, UTRC and Cornell University
4. Porbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Permagon Press, Oxford, 1966.
5. as reference: Casado-Rivera, E.; Volpe, D.J.; Alden, L. R.; Lind, C.; Downie, C.; Vazquez-Alvarez, T.; Angelo, A. C. D.; DiSalvo, F. J.; Abruna, H. D. *J. Am. Chem. Soc.*, **2004**, *126*, 4043. Alden, L. R.; Roychowdhury, C.; Matsumoto, F.; Han, D. K.; Zeldovich, V. B.; Abruna, H. D.; DiSalvo, F. J. *Langmuir*, **2006**, *22*, 10465.