

## VII.A.4 Electrocatalyst Supports and Electrode Structures

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*Projected End Date: Project continuation and direction determined annually by DOE*

### Objectives

- Substantially reduce the amount of Pt (and platinum group metal, PGM) required.
- Improve Pt catalyst stability/durability.
- Improve electrode manufacturability and performance.

### 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

### Technical Targets

**Table 1.** Progress Towards Meeting DOE Electrocatalyst Technical Targets

Characteristic	Units	Targets			This Project	
		2005	2010	2015	a	b
PGM Total Content (Electrocatalyst)	g/kW (rated)	2.67	0.5	0.4	3.7	0.33
PGM Total Loading (Electrocatalyst)	mg PGM/cm <sup>2</sup> electrode area	0.7	0.3	0.2	0.92	0.13
Total Catalyst Loading (Membrane Electrode Assembly)	g/kW (rated)	2.7	0.33	0.2	3.7	0.33

a - demonstrated for 1000 h in a single cell [Brookhaven National Laboratory (BNL) catalyst].

b - stability issues, but demonstrates sufficient activity (BNL catalyst).

### Approach

- Support Pt monolayers on other metals (e.g., Group VIII) that maintain Pt stability and activity (Los Alamos National Laboratory fuel cell testing of BNL catalysts).

- Develop “interactive” ceramic supports (CSs) that provide stability and oxygen reduction reaction (ORR) activity to highly dispersed Pt catalysts (e.g., monolayers or sub-crystallite particles).
- Develop theoretical models to understand support/catalyst interactions.

### **Accomplishments**

- Demonstrated long-term fuel cell (FC) performances of low-Pt-content (BNL) catalysts.
- Demonstrated in FC testing that low-PGM-content (BNL) catalysts are intrinsically active enough to exceed long-term technical targets.
- Discovered spontaneous deposition of precious metals on certain CS materials.
- Demonstrated ORR activity with sub-crystalline Pt on CS.
- Synthesized CS materials with particle sizes significantly smaller than commercially available or in the literature.

### **Future Directions**

- Conduct fuel cell testing of BNL and CS-based catalysts.
- Screen additional CS materials for spontaneous deposition and other properties.
- Synthesize additional and better CS and catalyzed CS materials.
- Expand theoretical models to encompass CSs, etc.
- Develop electrode structures that take advantage of CS properties.
- Characterize CS-based catalysts using X-ray absorption and rotating ring disk electrode (RRDE) techniques.

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### **Introduction**

While platinum is the most effective catalyst for polymer electrolyte fuel cells (PEFCs), its cost and availability limits commercial applications using current technology. Fully eliminating platinum will require the development of either platinum or acid-electrolyte alternatives, both of which are formidable challenges. Another approach is to maximize the utilization of platinum, as the majority of the platinum in the nanoparticles of the current technologies does not directly contribute to the electrochemical reactions. On the other hand, this “bulk” platinum provides an environment that maintains the properties of the surface platinum that are necessary for maximum activity, particularly for the ORR. Pt particles with smaller or thinner (monolayers) structures that increasingly diverge from bulk-like electronic properties have lower surface activity. Even if active, free-standing structures readily coalesce into larger particles, an “inactive” support, such as carbon, will only impede and not prevent the particle growth. For high Pt dispersions, then, a support is required that is “interactive” in the sense that some level of

connectivity exists between support and catalyst that stabilizes and maintains the activity of the latter. Other criteria are electrochemical stability, electronic conductivity, and low cost.

### **Approach**

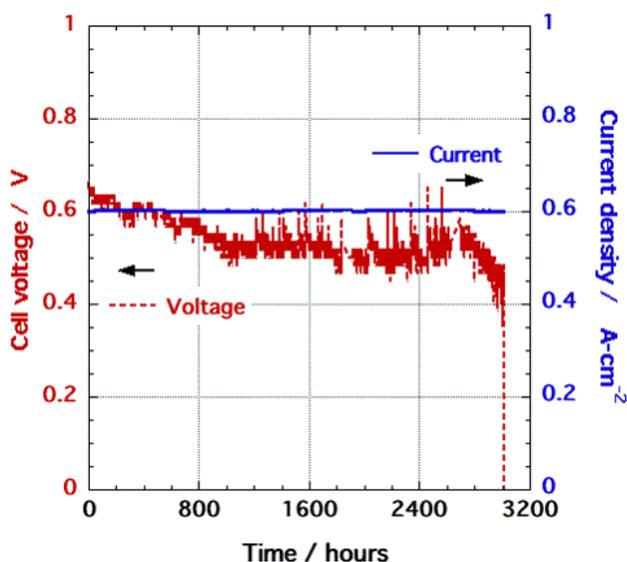
In the first approach to attain an “interactive” support, R. Adzic and co-workers from Brookhaven National Laboratory (BNL) deposit highly dispersed Pt onto other metal particles possessing similar enough properties that the Pt retains bulk-like activity and stability (see “Publications”). Los Alamos National Laboratory (LANL) performs fuel cell testing of the BNL catalysts, and some key results will be discussed below.

Beyond the other PGM metals, there are few options that meet the support criteria. Stability, low cost and conductivity can be attained with a number of refractory or “ceramic” materials. Thus, in the second approach, ceramic materials are being pursued that meet these criteria as well as serve as “interactive” hosts for Pt.

Starting this year, a quantum-mechanical modeling effort has been initiated in the Theoretical Division at LANL with the purpose of understanding and predicting the behavior and activity of Pt monolayers on non-Pt substrates. The effort builds upon recent work that shows the anticipated advantages of Ru substrates over others in mitigating CO poisoning (Hammerberg et al.).

## Results

A number of fuel cell tests with BNL catalysts were performed this past year at LANL. Those described here will highlight key aspects of the approach. First, Figure 1 depicts the FC life test results for a cell with a BNL cathode catalyst over 3000 h. Some loss of activity is apparent over the first ~1000 h which correlates with a loss in electrochemical surface area over this time period. Further cell performance variations appear to be the result of non-catalyst factors, such as the cross-over which ultimately destroyed the cell at 3000 h. Despite some initial loss of activity, the important result is that the stability and activity of the sub-crystalline Pt structures can be maintained for a length of time relevant for transportation applications. Another test (not shown) with total cell

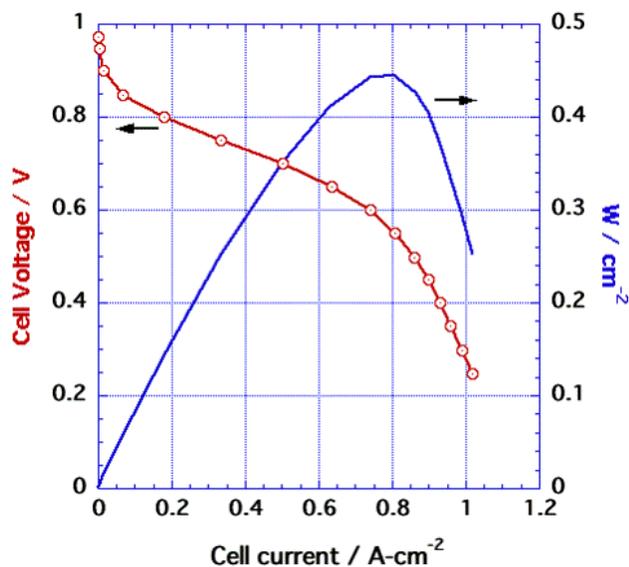


**Figure 1.** 50 cm<sup>2</sup> H<sub>2</sub>/Air FC (N1135) Operated at Constant Current at 80°C; Anode: 0.18 mg Pt/cm<sup>2</sup> (20% Pt-C, ETEK); Cathode: 0.077 mg Pt/cm<sup>2</sup> (20% Pd-4% Pt, BNL) (Total metal at cathode: 0.45 mg/cm<sup>2</sup>), Stoich: H<sub>2</sub>/air = 1.3/2.0.

PGM loadings close to the 2005 technical targets (shown as “a” in the technical target progress table) provided even better 1000 h results.

The second illustration of key results with BNL catalysts is shown in Figure 2. Here, a BNL cathode catalyst consisting of Pt deposited on Au-coated Ni particles provides good fuel cell performance while using a PGM loading below even the 2015 technical targets (shown as “b” in the technical target progress table). While there are stability issues, it unambiguously demonstrates that the sub-crystalline Pt alone is responsible for activity, as Au and Ni are not ORR active (in acidic media). This shows that the long-term technical targets are in principle achievable, thus validating the general approach behind these efforts.

Substantial progress was made this past year in the effort to develop ceramic supports (CSs) that are appropriate hosts for sub-crystallite Pt as well as meet the other criteria. While screening a particular family of potential CS materials, the unexpected discovery was made that certain members of this family are able to spontaneously deposit Pt and several other precious metals from solution. By screening commercial low-surface-area powders, three CSs with this property have so far been



**Figure 2.** FC Polarization and Power Plots with Ultra-Low Pt Content; 5 cm<sup>2</sup> H<sub>2</sub>/Air FC (N1135) at 80°C, Anode: 0.077 mg Pt/cm<sup>2</sup> (20% Pt/C, ETEK), Cathode: 0.169 mg total metal/cm<sup>2</sup> (19 μg Pt; 37 μg Au; 0.113 mg Ni)

identified. Steps in the process are depicted in Figure 3. First is shown an uncoated glassy carbon electrode, then an electrode coated with a film of CS1 powder, and finally a gold layer formed on a CS1 film coated electrode. In the last case, a drop of chloroauric acid solution was added to the film, spontaneous deposition commenced until the solution was depleted, and the electrode was rinsed and dried.

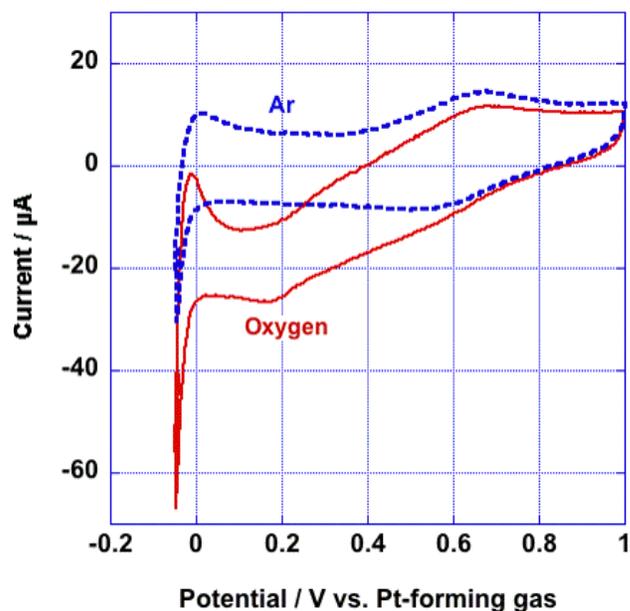
While spontaneous deposition is of considerable interest for catalyst layer and membrane electrode assembly (MEA) fabrication, it does not assure usefulness as a Pt support. Cyclic voltammograms (CVs) in acidic media were performed to evaluate stability and activity of the commercial low-surface-area CS samples alone and Pt-deposited. CV testing with wide voltage windows and numerous cycles indicates that the CS materials are quite stable, but long-term FC testing will ultimately be required. CVs were also performed on CSs with varying amounts of spontaneously deposited precious metals. Because of the large CS particle sizes, very low loadings were required to attain sub-crystallite Pt particles. The results for one sample are shown in Figure 4. Here, a 0.3 wt% Pt loading provided a high dispersion (monolayers or sub-crystalline particles as determined by x-ray diffraction, XRD) on the low-



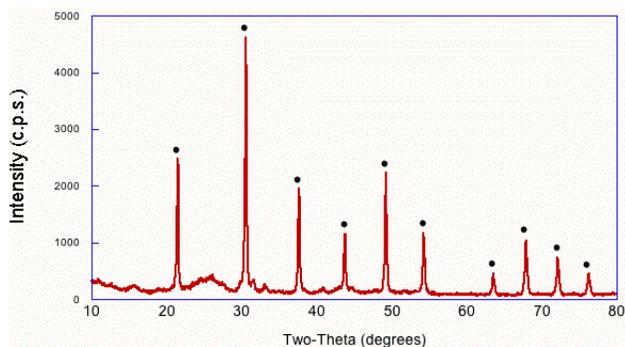
**Figure 3.** A Series of Glassy Carbon Disk Electrodes Depicting Steps in the Spontaneous Deposition Process (From left to right; uncoated, CS1 coated, and heavily gold deposited microelectrodes.)

surface-area CS1 support. The two CVs in the figure contrast the results under argon and oxygen purge gases, with the offset indicating that the Pt was ORR active. These CS materials are the first refractory supports that we have tested that have the “interactivity” to sustain ORR activity with sub-crystalline Pt. This would suggest that there is some level of chemical interaction between support and catalyst, which is desirable not only for catalytic purposes, but also for minimizing the mobility of the Pt and hopefully increasing the durability and stability of the catalyst in the fuel cell. Both fuel cell testing and catalyst-support characterization are needed to further understand these issues.

The deposition screening and the CS results described thus far were achieved using commercially procured materials. Unfortunately, the particles’ sizes (about 10 microns) and, in some cases, purity, are not appropriate for FCs. FC catalyst supports need to be much smaller to provide sufficient surface area in a thin catalyst layer. Ball-milling is ineffective in reducing particle sizes, as the CS materials are very hard and abrasive. Very little information exists in the literature on the synthesis of sub-micron CS particles, and the few studies that address the issue tend to use exotic precursors that



**Figure 4.** CVs of a Pt/CS1 Electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> (0.03 µg of Pt was spontaneously deposited on a CS1 coated microelectrode. Results are for room temperature and a 100 mV/s scan rate.)

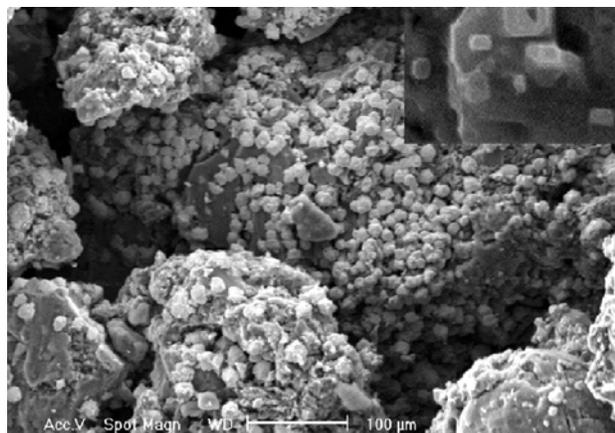


**Figure 5.** An XRD Pattern of As-Made CS3 (Dots designate literature CS3 diffraction angles. Refined particle sizes are about 70-80 nm.)

are impractical for low-cost processing. We proceeded to develop a process to synthesize smaller CS particles that primarily hinged on two aspects: first, the use of high-surface-area carbon as a “diluent” to initiate and partition particle formation at high synthesis temperatures, and second, the use of precursors that are easily prepared from inexpensive materials.

Eventually, a process was developed that yielded CS crystallite sizes less than 100 nm in diameter. The XRD pattern for an as-made CS3 sample is shown in Figure 5. The pattern replicates the literature angles (black dots), and only very minor impurity peaks are evident. A scanning electron microscope (SEM) micrograph of the as-made sample is shown in Figure 6. Lighter colored spheres populate the surface of a larger and darker substrate. Microanalysis indicates that the spheres are CS3 material and the substrate a mixture of CS3 and carbon. The inset of Figure 6 shows a close-up of one of the spheres, showing the crystalline structure of individual surface CS3 particles. The apparent contradiction between sphere and XRD-derived crystallite sizes was resolved after brief ball-milling, as the spheres and substrates readily broke up and a relatively unstructured material was attained (at SEM resolution levels).

Preliminary electrochemical testing of CS3 synthesized powders has been performed and appears to generally replicate the results obtained with low-surface-area commercial materials, albeit at proportionally higher currents attributable to the substantial increase in surface area. A noticeable



**Figure 6.** Micrographs of As-Made CS3 (Spheres are CS3, substrate is a mixture of CS3 and carbon (sample about 20 wt% carbon. Inset is a close-up of a CS3 sphere showing cubic microcrystals.)

amount of ORR activity is evident with the high-surface-area CS3, though more rigorous RRDE measurements are needed for this and the catalyzed samples to quantify performance. Additional work is also needed in the areas of support and catalyst preparation and characterization, fuel cell testing, and the development of electrodes and MEAs that capitalize on these new materials.

## Conclusions

This year we have demonstrated several key elements important to the general approach of “interactively” supported sub-crystalline Pt catalysts. Fuel cell testing of BNL catalysts has shown that appropriately supported sub-crystalline Pt structures have first, the durability to support several thousand hour lifetimes, and second, the intrinsic ORR activity to provide the required performance. The third key element demonstrated was the ability to attain ORR activity with sub-crystalline Pt on certain ceramic materials, thus introducing a potential source of low-cost, stable, and “interactive” supports.

Of significant further importance to this effort was the discovery that the “interactive” CS materials also spontaneously deposit precious metals. This phenomenon is of particular interest for the future development and production of more cost-effective and efficient catalyst layers and MEAs.

**Publications**

1. K. Sasaki, J. X. Wang, M. Balasubramanian, J. McBreen, F. Uribe, R. R. Adzic, "Ultra-low Platinum Content Fuel Cell Anode Electrocatalyst with a Long-term Performance Stability." *Electrochim. Acta*, 49, 3873 (2004).
2. K. Sasaki, M. Vukmirovic, F. Uribe and R. Adzic, "Ultra-low Pt Loading Electrocatalysts for H<sub>2</sub>/CO and Methanol Oxidation." 206th Meeting of The Electrochemical Society. Hawaii, October 2004. Abstract No. 1502.
3. F. A. Uribe, T. Rockward, J. A. Valerio and R. R. Adzic, "Performance of PEMFC Electrodes Containing Low-Pt Loadings." 206<sup>th</sup> Meeting of The Electrochemical Society. Hawaii, October 2004. Abstract No. 1857.

**References**

1. J. E. Hammerberg, R. Ravelo, T. C. Germann, J. D. Kress, and B. L. Holian, AIP Conference Proceedings, 706, 565 (2004).

