V.D.4 Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes

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Project Start Date: July 20, 2009
Project End Date: 2013

Fiscal Year (FY) 2011 Objectives
• Produce novel catalysts based on extended Pt surfaces with increased activity and durability.
• Further increase electrochemically available surface area (ECA) and mass activity of extended surface catalysts.
• Effectively incorporate extended Pt catalysts into more traditional dispersed electrodes for mass transport/water management.
• Demonstrate and validate models for catalysts and electrodes based on extended surfaces.

Technical Barriers
This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program’s Multi-Year Research, Development and Demonstration Plan:
(A) Durability (of catalysts and membrane electrode assemblies)
(B) Cost (of catalysts and membrane electrode assemblies)
(C) Performance (of catalysts and membrane electrode assemblies)
(D) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets
This project synthesizes novel extended thin film electrocatalyst structures (ETFECS) and incorporates these catalysts into electrodes with and without carbon for further study. The project has targets outlined in the Multi-Year Research, Development and Demonstration Plan for both electrocatalysts for transportation applications (Table 3.4.12) and membrane electrode assemblies (MEAs) (Table 3.4.13). The specific targets and status of highest relevance are presented in Table 1.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2010/2015 Targets</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical Area Loss</td>
<td>%</td>
<td>&lt;40%/&lt;40%</td>
<td></td>
</tr>
<tr>
<td>Mass Activity (150 kPa H_2/O_2 80°C 100% RH)</td>
<td>A/mg-Pt @ 900mV</td>
<td>0.44/0.44</td>
<td>0.33</td>
</tr>
<tr>
<td>Specific Activity (150 kPa H_2/O_2 80°C 100% RH)</td>
<td>µA/cm²-Pt @ 900 mV</td>
<td>720/720</td>
<td>800-1,300</td>
</tr>
</tbody>
</table>

RH – relative humidity

FY 2011 Accomplishments
• Synthesized novel ETFECS that routinely surpass DOE 2015 target for specific activity.
• Demonstrated ETFECS with ECA as high as 40 m²/gₚt and mass activities of 330 mA/mgₚt far beyond the surface area of most extended surface catalysts with a mass activity approaching the 2015 DOE target.
• Demonstrated significantly improved durability of ETFECS towards potential cycling in rotating disc electrode (RDE) studies for both the Pt dissolution (0.6-1.0 V) and carbon corrosion region (1.0-1.6 V).
- Incorporated carbon into electrode structures that contain ETFECS while maintaining durability and activity.
- Demonstrated high specific activities of ETFECS in fuel cells.

**Introduction**

Pt remains a primary limitation for the widespread commercialization of polymer electrolyte fuel cells. To date, approaches looking to replace Pt with a non-platinum-group metal have met with limited success. “Thrifting” of Pt (i.e., ultra-low Pt loadings) seems to be the most likely (near-term) option for meeting cost, performance and durability targets. Typical Pt catalysts for fuel cell applications are small nanoparticles (such as cubooctahedron) that have high surface areas, and therefore significant fractions of Pt atoms are surface accessible. Clearly, having as many Pt atoms on the surface as possible is advantageous. However, catalytic activity and durability of extended surfaces can outweigh the surface area advantages of smaller particles, particularly if these advantages can be maintained at thin wall thickness, as highlighted by the promising work done on nanostructured thin film catalysts based on Pt or Pt alloys at 3M [1] and Pt and Pt alloy nanotubes at UC Riverside [2]. The synthesis of catalysts with high mass activity and the effective implementation of these catalysts in high performance, durable and robust MEAs will help enable fuel cell commercialization on a significant scale.

**Approach**

Our approach involves synthesizing novel ETFECS using either a nanostructured support material such as carbon nanotubes (CNTs), metal oxide nanoparticles, or perylene red nanowhiskers, or a sacrificial metal template. Pt is deposited on these materials either through vapor deposition (including sputtering and atomic layer deposition (ALD)) or solution deposition (including galvanic displacement). Our goal is to produce nanostructures with thin, continuous films of Pt because similar structures have shown high catalytic activity and durability. The materials synthesized are characterized by several techniques with a strong focus on microscopy and electrochemistry. To date, extended surface catalysts have not been demonstrated in traditional, thick catalyst layers that include Nafion® and have been shown to exhibit good tolerance to a wide range of operating conditions including cold-start. The novel catalysts produced in this project are being implemented in thick, dispersed electrodes to investigate the production of high performance, robust electrodes from these materials. Modeling is being used in support of our catalyst synthesis studies and our electrode studies, extending established models involving wetting of Pt on supports, simulating electrode architecture, and evaluating criteria that impact electrode performance.

**Results**

In the past year, we added a number of additional substrates to our studies probing supports as extended surface Pt hosts. Included on our list of substrate nanomaterials to date are: carbon nanotubes, inorganic oxides, metals, and perylene red whiskers. Examples of novel templates synthesized this past year are shown in Figure 1.

In the area of Pt deposition, we focused on sputtering, ALD, and spontaneous galvanic displacement (SGD). Sputtering remains an area of interest, as we and 3M [1] have shown it to be a viable technique for depositing thin, continuous Pt layers. We have focused on deposition onto mats and short (>2 µm) vertically aligned CNTs. Transmission electron microscopy close-ups of Pt sputtered CNT mats show a transition between discrete particles and continuous Pt coating. These micrographs suggest that continuous coatings can be obtained at thicknesses of ~2 nm. Unfortunately, our ability to generate these
materials consistently and in higher yields has been poor. We have continued to investigate ALD for its ability to produce thin continuous Pt films. The most promising results have focused on using TiO₂ as a bonding layer. We found that a minimum thickness of TiO₂ followed by thermal treatment (annealing) results in the conversion of amorphous TiO₂ to anatase. The anatase form showed the fastest and most consistent Pt nucleation rates and is now being explored at ultra-thin (>5 nm) coating thicknesses and on nanostructured substrates. In the area of SGD we used Ag and Cu nanowires and Ag nanoplates as templates for Pt displacement and performed studies that have also included Pd or Au.

Our electrochemical characterization and electrode studies made significant strides in the past year. We established agreement with literature and demonstrated a high degree of reproducibility. We quantified the increases in specific activity from our novel materials and showed reasonably high surface areas (up to 40 m²/g Pt) in ETFECS. While a few studies with CNTs were performed, our primary focus of electrochemical characterization was on materials synthesized by SGD, because we obtained higher yields and higher performance with these materials. A select portion of our data is highlighted in Figure 2. The three different colors/symbols represent a systematic series of novel materials based on SGD of either Cu or Ag nanowires investigating features including: reactant delivery rate, stoichiometry, temperature, reaction solvent, and post-processing. While we commonly surpass the DOE 2015 target for specific activity (720 µA/cm² Pt), highlighted in Figure 3, we have not yet achieved the 2015 target for mass activity. Although extended surface catalysts have typically been limited to ECAs around 10 m²/gPt we demonstrated ETFECS with ECA up to ~40 m²/g Pt. This high ECA material resulted in a novel catalyst with mass activity of 330 µA/gPt, approaching the 440 µA/gPt DOE 2015 target. Continued investigations will seek to further increase both specific activity and ECA.

Beyond the improvements in electrochemical properties determined for the SGD ETFECS already highlighted, we also explored the impact of carbon incorporation on the electrochemical performance of these materials, tested the materials in fuel cells, and investigated the durability of these materials. All of these studies showed the promise of extended surfaces as novel fuel cell catalysts. Highlights from our studies are shown in Figure 4. The specific and mass activities of our ETFECS have essentially no impact on the observed specific and mass activity. Normalized ECAs show that traditional catalysts, as expected, show much poorer durability with potential cycling. Similar results were observed in the Pt dissolution region (0.6-1.0 V) in similar potential cycling studies.

Conclusions and Future Direction

We demonstrated for the first time conformal Pt coatings on CNTs and Pt nanostructures from Cu nanowires. We performed controlled growth of CNTs. We investigated Pt ALD, sputtering, SGD and other solution based routes as Pt deposition techniques. Future work, broken down by topical area, includes:

Templates/Cores:
- Metal oxide substrate development.

Pt Deposition:
- SGD process further optimization focusing on post-processing parameters.
- ALD studies investigating Pt growth on carbon and with reduced thickness/decreased nucleation cycles.
Electrode Studies:

- Electrochemical (RDE) durability screening of ETFECS as a function of initial ECA.
- Incorporation of highest performing catalyst (350 mA/mgPt) into electrode studies.
- Expanded MEA fabrication and fuel cell testing of ETFECS.

Modeling:

- Advancement of models to electrode structures incorporating model ETFECS – PtNT of 150 nm diameter, 2 micron length.
- Expansion of porous electrode models to ETFECS incorporated electrodes.

FY 2011 Publications/Presentations


References
