# V.A.15 Highly Robust Low PGM MEAs Based upon Composite Supports (SBIR I)

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### **Overall and Fiscal Year (FY) 2017 Objectives**

- Demonstrate a successful overcoat method on commercial low platinum group metal Pt/C catalysts, specifically targeting uniform coverage of the carbon support with gas phase access to the Pt catalysts.
- Evaluate the activity, ohmic resistance and cycling stability of overcoated catalyst materials by rotating disk electrode (RDE) and membrane electrode assembly (MEA) testing.
- Demonstrate improved cycling durability with MEA testing of optimized encapsulated catalysts without significant loss in activity.
- Down-select to a viable encapsulated Pt/C catalyst material based on performance, process scalability and techno-economic considerations.

#### **Technical Barriers**

This project addresses the following technical barrier from the Fuel Cell section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) Durability

#### **Technical Targets**

Achieve the 2020 MEA targets:

- \$40/kW at the system level, \$14/kW at the MEA level.
- Greater than 5,000 start-stop cycles with less than 5% loss in voltage.
- Less than 10% loss in power after 5,000 hours of normal operation and less than 40% loss in mass activity under start-stop conditions at the electrocatalyst level.

#### FY 2017 Accomplishments

- Demonstrated a variety of atomic layer deposition (ALD) overcoats onto commercial Pt/C catalysts with 1–10 wt% coating added.
- Preliminary RDE measurements indicate an unoptimized durability retention of >70% for both mass activity and specific activity after 5,000 electrochemical cycles (1–1.5 V at 500 mV/s, compared to ~25% for the baseline).



#### INTRODUCTION

The proton exchange membrane fuel cell platinum catalyst is deposited at the nanoscale on high surface area carbon, with a goal of achieving very high catalytic surface area and dispersion. However, well documented aging processes tend to increase catalyst particle size, with corresponding decrease in available surface area and catalytic activity. Aging appears to be the result of the combined effects of catalyst migration, Ostwald ripening (particle dissolution followed by redepositing on larger particles), and significant corrosion of the high surface area carbon catalyst support. Cell durability is degraded by corrosion of the carbon support through carbon oxidation that occurs through the electrochemical formation of CO<sub>2</sub> and/or through the water gas shift reaction, producing CO. As carbon is consumed via these reactions, the sites which accommodate the platinum electrocatalyst are eliminated, thereby decreasing the surface area for electrochemical reaction, and which in turn decreases the performance of the fuel cell, becoming a dominant durability limiting mechanism.

Approaches that promise to eliminate catalyst substrate corrosion will improve fuel cell durability dramatically, but must do so without negatively effecting other attributes of the substrate and current cell construct. These include the conductivity and low cost of the catalyst support, catalytic activity, and the ability to achieve catalyst dispersion and substrate adhesion. The Forge Nano approach achieves protection of the carbon via nanolayer coatings which will not significantly impact conductivity and which can be tailored to ensure catalyst application. ALD coatings are very thin, yet can be tailored in thickness, can change composition and materials through the depth of the coating (by applying coating layers), are uniform in thickness and are defect free. In addition, the high-throughput ALD technology developed by Forge Nano is very low cost, and may even lower the cost of the electrode by enabling further reductions in catalyst loading. These attributes promise to facilitate use of the current inexpensive carbon material, yet solving the durability issues experienced today.

#### APPROACH

The ideal catalyst system will promote Pt stability, reduce Pt mobility, increase Pt dispersion with ideal-sized nanoparticles, and reduce Pt induced carbon corrosion. Several studies have focused on increasing Pt-carbon support interactions and developing Pt alloys to reduce Pt mobility and reduce Pt dissolution. However, the successful strategies to increase Pt stability are largely ineffective at reducing carbon corrosion. This is because the presence of the Pt near the C-H<sub>2</sub>O interface likely catalyzes the oxidation of the carbon support under start-stop conditions. In contrast, ceramic catalyst supports have demonstrated fantastic cycling durability. However ceramic supports generally have lower specific activities because of mass differences relative to carbon, lower surface areas of the supports, less dispersion and larger Pt size that combined lead to reduced electrochemical surface area, and because the supports are not inherently conductive so binders or conductive additives are implemented. To mitigate the carbon corrosion reaction, we have demonstrated an overcoat on the Pt/C catalyst materials with an ultrathin ceramic ALD encapsulation layer. The ideal encapsulation layer will provide a barrier to water and oxygen at the carbon interface, without impeding electron flow in the electrode or gas diffusion to the Pt particles. As such, our Phase I technical approach also includes implementing ALD over-coating layers with high conductivity through the incorporation of dopants to explore the impacts of and mitigate added electrical resistance from the coating.

The ALD coatings were found to uniformly coat the commercial catalyst, and through process design the total surface area (as measured by Brunauer–Emmet–Teller [BET]) could also be refined by filling progressively larger pores in the underlying substrate (see Figure 1). Preliminary RDE measurements targeting carbon corrosion (1–1.5 V cycling) show improved durability of the ALD overcoated samples compared to the baseline (uncoated) catalyst (Figures 2 and 3).



**FIGURE 1.** Physical surface area (BET) modification as a function of the number of ALD cycles



**FIGURE 2.** Normalized electrochemical surface area, current density, and activities for the unmodified catalysts before and after electrochemical cycling (17 ugPt/cm<sup>2</sup>; 1-1.5 V at 500 mV/s)





## CONCLUSIONS AND UPCOMING ACTIVITIES

MEA testing of the ALD overcoated catalysts will be performed, specifically investigating activities, mass transport and conductance changes as a function of the coating parameters. Additional RDE measurements will be made to understand the impacts of process parameters during the coatings process. Ex situ analysis of catalysts and cast catalyst films will be performed to understand coating quality and crystallinity of the ALD films and any porosity changes as a result of the ALD. Finally, technoeconomic analysis will be performed to determine the cost of ALD overcoats for the best coatings with respect to the savings from their implementation.