

## V.J.1 Novel Approach to Advanced Direct Methanol Fuel Cell (DMFC) Anode Catalysts

Huyen N. Dinh (Primary Contact),  
Thomas Gennett, David Ginley, Bryan Pivovar,  
Katherine Hurst, Arrelaine Dameron, Kevin  
O'Neill, Jennifer Leisch, Justin Bult, Tim Olson,  
KC Neyerlin

National Renewable Energy Laboratory (NREL)  
1617 Cole Blvd.  
Golden, CO 80401-3393  
Phone: (303) 275-3605  
E-mail: Huyen.Dinh@nrel.gov

DOE Technology Development Manager:  
Kathi Epping Martin  
Phone: (202) 586-7425  
E-mail: Kathi.Epping@ee.doe.gov

### Subcontractors:

- Ryan O'Hayre, Colorado School of Mines (CSM), Golden, CO
- Charles Hays and Sri.R. Narayan, Jet Propulsion Laboratory (JPL), Pasadena, CA

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### Objectives

Our objective is to improve the catalytic activity and durability of PtRu for the methanol oxidation reaction (MOR) via optimized catalyst-support interactions.

- Determine the effect of ion implantation on the catalytic activity and stability of PtRu catalyst nanoparticles deposited on highly-oriented pyrolytic graphite (HOPG) supports. Implantation will cause n- or p- doping via incorporation of various species, initially focusing on nitrogen.
- Determine the effect of *doping level* and *dopants* type (n or p) on the catalytic activity and durability of the PtRu/HOPG model catalyst system that improve catalyst-substrate interaction resulting in an improved catalyst material for the methanol oxidation reaction.
- Apply this dopant-engineering approach to high surface area carbon supports. The goal is to improve catalyst utilization, activity, and durability for membrane electrode assemblies.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program's Multi-Year Research, Development and Demonstration Plan (section 3.4.4):

- (A) Durability
- (B) Cost
- (C) Performance

### Technical Targets

This project aims to improve the catalytic activity and durability of PtRu for the MOR via optimized catalyst-support interactions. Insights gained from these studies will be applied toward the development and demonstration of DMFC anode catalyst systems that meet or exceed the following DOE 2010 Consumer Electronics targets:

- Cost: \$3/W
- Specific Power: 100 W/kg
- Power Density: 100 W/L
- Lifetime: 5,000 hours

### Accomplishments

- (1) Established an optimal N-implantation parameter set for HOPG, which resulted in enhanced PtRu catalytic activity for MOR.
- (2) Obtained experimental results demonstrating an increase in durability on N-doped samples.
- (3) Sputter deposited PtRu alloy with controlled composition, phase, and orientation from a single PtRu alloy target.
- (4) Built a chamber that allows for ion-implantation and sputter deposition of powders.
- (5) Established protocol for deposition of uniform PtRu catalyst particles on commercial and chemical vapor deposition synthesized B-doped and N-doped powders.



### Introduction

High material cost and insufficient catalytic activity and durability are key barriers to the commercial deployment of DMFCs – the most advanced fuel cell technology for consumer electronics application. DMFCs

are attractive for portable commercial and military applications because they offer extremely high theoretical energy density (~10x better than Li-ion batteries).

To accelerate the commercialization of DMFCs for consumer electronics applications, next generation materials based on leap-frog technology are needed. In DMFCs, the MOR on the anode limits the performance and durability. Breakthroughs in DMFC anode catalysis with respect to performance, cost and durability will help enable and accelerate the commercialization of DMFCs.

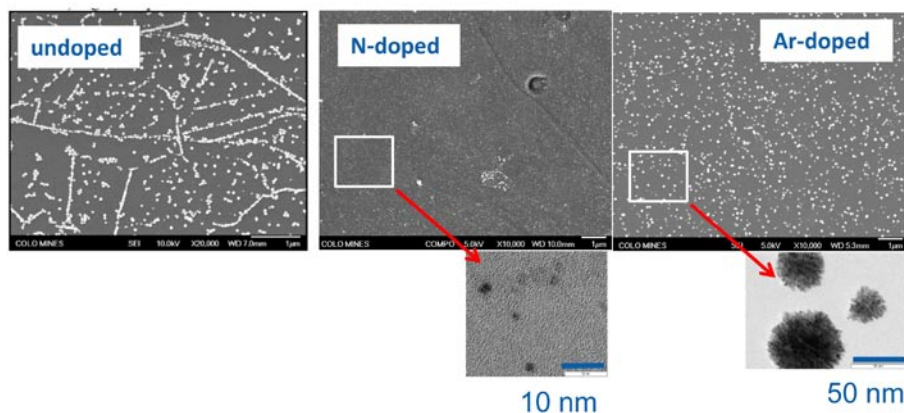
## Approach

This project focuses on improving the catalytic and durability of the anode catalyst for the MOR. Our approach is to modify and improve catalyst-support interactions in order to substantially increase activity, selectivity, and durability of PtRu catalytic systems. The team systematically investigated the effects of ion-implantation on HOPG, as a model support analogue [1-3], on PtRu catalysts. These well-defined systems allowed us to assess dopant effects and provide a test-bed for exploring new dopant/catalyst combinations. These doped and undoped carbon substrates are decorated with PtRu using both aqueous solution and physical vapor methods. The catalysts are characterized with various techniques such as microscopy, X-ray diffraction, X-ray photoelectron spectroscopy (XPS) and electrochemistry to determine the catalyst particle size, dispersion, composition, structure, degree of alloying, MOR activity and electrochemical durability. The catalyst synthesis process and materials are down-selected based on best performance and transferred to high surface area carbon studies for further study. The highest performing materials will be used in DMFC testing.

## Results

We demonstrated enhanced PtRu catalytic activity for methanol oxidation by achieving smaller particle size and more uniform dispersion of PtRu on N-doped HOPG. For the N-implantation conditions investigated, we determined 45 seconds as optimal for N-doping. Nitrogen was found to incorporate into the carbon network, resulting in the formation of  $sp^3$ - $sp^2$  bonding disrupting the graphitic structure of the undoped HOPG. Various oxygen groups, including C-O, C=O and N-C=O, were also observed after implantation. Ion implantation of  $N_2$  longer than 45 seconds resulted in no additional surface structural disorder. The relative amount of nitrogen (7%, determined by XPS) introduced into the carbon substrate also saturated after 30-45 seconds. Electrochemical data obtained by project partner, JPL, confirmed NREL results. (Argon implanted HOPG was used to establish benchmark performance caused by structural defects.)

Figure 1 shows examples of PtRu deposited on various HOPG samples. It is apparent from Figure 1 that the most uniform and smallest particles of PtRu catalyst were obtained using N-doped HOPG samples. Ar-doping improved the dispersion compared to undoped HOPG but resulted in a more pronounced agglomeration of catalyst particles as compared to N-doping. Similar samples to those shown in Figure 1 at higher PtRu loadings were used to measure methanol oxidation activity. Table 1 shows that nitrogen doping resulted in the highest MOR activity and highest surface roughness factor as compared to undoped and Ar-doped HOPG. Table 1 also shows that our microwave deposition of Pt and Ru onto N-HOPG gave comparable activity to commercial PtRu catalysts on a per metal surface area basis.



**FIGURE 1.** Scanning electron micrograph images of PtRu electrochemically deposited on an undoped HOPG, N-doped HOPG, and Ar-doped HOPG. The transmission electron micrographs show that Ar doping resulted in more PtRu particle agglomeration compared to N-doping.

**TABLE 1.** Roughness factor and methanol oxidation activity, at 0.65 V vs. the reference hydrogen electrode, measured for high loading of PtRu, electrochemically deposited (20-40 pulses), on different substrates: undoped, N-doped, and Ar-doped HOPG. The table also compares the roughness factor and methanol oxidation current density for microwave deposited PtRu on N-HOPG and commercial Johnson Matthey (JM) PtRu/C catalyst. ( $\text{cm}^2_{\text{metal}}$  = area determined from CO stripping voltammetry and  $\text{cm}^2_{\text{electrode}}$  = geometric area).

	Roughness Factor ( $\text{cm}^2_{\text{metal}}/\text{cm}^2_{\text{electrode}}$ )	Methanol oxidation activity ( $i @ 650 \text{ mV}$ $\mu\text{A}/\text{cm}^2_{\text{metal}}$ )
Echem PtRu/HOPG	0.24	1.5
Echem PtRu/Ar-HOPG	1.1	5.4
Echem PtRu/N-HOPG	1.5	21
Microwave PtRu/N-HOPG	1.1	72
JM HiSPEC 10000 PtRu/C	22.5	58

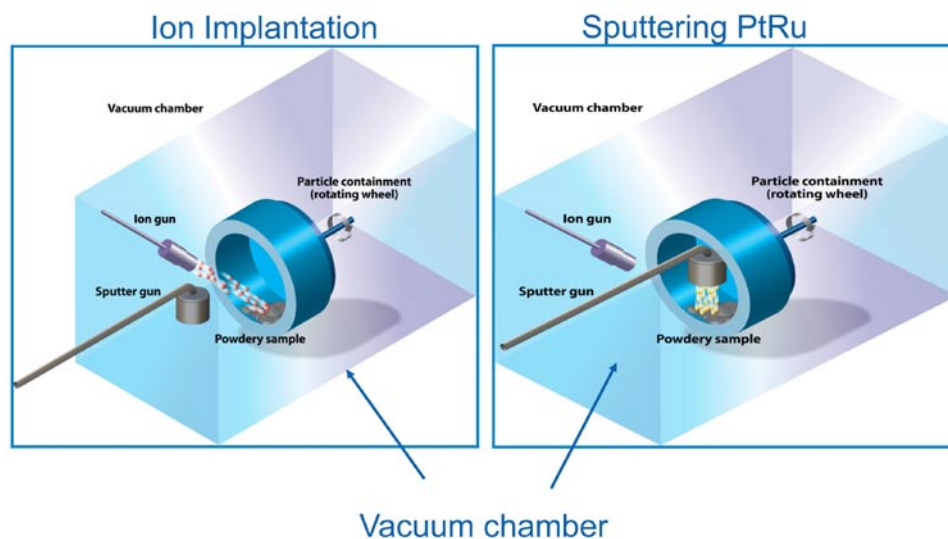
We developed a novel method to deposit  $\text{Pt}_{1-x}\text{Ru}_x$  alloy or amorphous films/particles by sputtering from a single, alloyed PtRu target. We were able to control the PtRu composition with sputtering power and chamber oxygen concentration. We can also demonstrate a dependence of the orientation and phases (hexagonal close packed/face centered cubic) of  $\text{Pt}_{1-x}\text{Ru}_x$  with overall chamber pressure. Finally, we designed and built a new chamber for ion implantation and sputter deposition of catalyst on high surface area carbon materials (Figure 2). Preliminary experiments were performed and the resultant materials are being characterized.

## Conclusions and Future Direction

- Demonstrated that nitrogen implantation on HOPG enhanced MOR activity.
- Established different PtRu deposition methodologies.
- Established optimized N-doping level on HOPG via ion implantation.
- Initiated a preliminary study of the effect of different dopants.
- Developed a processing system for ion implantation of high surface area carbon materials, and initiated study of high surface area carbon.
- We will conduct studies of other dopants on HOPG (B, S, I).
- We will investigate different methods to dope high surface area carbon (in situ and ex situ) (e.g., ion implantation, chemical vapor deposition, and pyrolysis).
- We will characterize and measure methanol oxidation performance of PtRu/doped high surface area carbon.
- We will optimize materials and measure DMFC performance and durability of optimized catalysts.

## FY 2010 Publications/Presentations

1. A. Dameron, S. Pylypenko, S. Studer, J. Leisch, K. Neyerlin, T. Olson, K. O'Neill, A. Queen, R. O'Hayre, H.N. Dinh, T. Gennett "Sputtering  $\text{Pt}_{1-x}\text{Ru}_x$  Alloyed Particles for Direct Methanol Fuel Cell Catalysts", American Chemical Society Spring 2010 Meeting, March, 2010.



**FIGURE 2.** Schematic of the new powder implantation chamber built at NREL. The ion implantation occurs as the sample is either rotated or agitated (rapid shake) with the circular can. The sputter gun is on a translational axis and can be inserted into the can as the sample is being agitated or rotated, and magnetron sputter deposition of the PtRu is achieved.

2. S. Studer, “Electrochemical Analysis of Single Source Sputtered PtRu”, Case Study Defense Presentation, Colorado School of Mines, March 2010.
3. Y. Zhou, K.C Neyerlin, T. Olson, S. Pylypenko, J. Bult, H.N. Dinh, T. Gennett, Z. Shao, R. O’Hayre, “Enhancement of Pt and Pt-Alloy Fuel Cell Catalyst Activity and Durability via Nitrogen-Modified Carbon Supports”, Review paper for Energy & Environmental Science, submitted Jan. 2010.
2. Y. Zhou, R. Pasquarelli, J. Berry, D. Ginley, R. O’Hayre, “Improving PEM Fuel Cell Catalysts Using Nitrogen-doped Carbon Supports,” Proceedings of the 6<sup>th</sup> ASME Fuel Cell Science, Engineering, and Technology Conference, Denver, CO, June 16–18, 2008.
3. O’Hayre, Yingke Zhou, Robert Pasquarelli, Joe Berry, and David Ginley, “Doped-Carbon Supports for Enhanced Catalysis” Presented at the MRS International Materials Research Conference, Chongqing, China, June 9<sup>th</sup>, 2008.

## References

1. Y. Zhou, R. Pasquarelli, J. J. Berry, D. Ginley, R. O’Hayre, “Improving PEM Fuel Cell Catalyst Activity and Durability Using Nitrogen-Doped Carbon Supports”, submitted, *Nature Materials*.