

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

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Project Start Date: July 20, 2009

Project End Date: September 30, 2011

Fiscal Year (FY) 2011 Objectives

Our primary 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 of highly oriented pyrolytic graphite (HOPG) on the catalyst activity and stability of PtRu catalyst nanoparticles deposited by vapor or solution phase processes.
- Determine the effect of doping level and type of dopants (e.g., n or p) on the catalytic activity and durability of the PtRu/HOPG model catalyst system.
- Apply the understanding established from the dopant-engineering approach of the model HOPG planar materials to high surface area carbon supports. The goal is to improve catalyst utilization, activity, and durability for membrane electrode assemblies (MEAs).

Technical Barriers

This project addresses the following technical barriers from the consumer electronics section of the Fuel Cell Technologies Program 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

FY 2011 Accomplishments

- Established the effect of nitrogen dosage and nitrogen functionalities on catalyst durability using the model HOPG system.
- Determined that the dopant type (N_2^- , N_2/H_2 - CF_4 , O_2^- and I_2 -doped HOPG) affects MOR activity and durability.
- Developed a tool and process for effective ion implantation and sputter deposition processes applicable to high surface area carbon materials.
- Developed and optimized PtRu sputter deposition methods from a single composition PtRu alloy target to produce highly dispersed PtRu nanoparticles of a desired catalyst composition and metal loading on high surface area carbon supports.
- Demonstrated that in-house magnetron sputter deposited PtRu/N-doped Vulcan carbon catalysts are more durable than both the undoped in-house catalysts and commercial PtRu/C catalysts.
- Demonstrated that in-house sputter deposited PtRu/C catalyst outperforms a commercial catalyst in a DMFC.



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.

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 performance and long-term durability of the anode catalyst for the MOR. Our approach is to modify and optimize 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 as demonstrated by a series of recent publications [1-6] on PtRu catalysts. These well-defined systems allow us to assess dopant effects and provide a test-bed for exploring new dopant/catalyst combinations. These undoped and doped, via ion implantation, carbon substrates are decorated with PtRu using both aqueous solution and physical vapor methods. The catalysts are characterized with various techniques such as microscopy, Raman spectroscopy, X-ray diffraction (XRD), 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 performance and transferred to high surface area carbon studies for further study. The highest performing materials are used in DMFC testing.

Results

We demonstrated that nitrogen implantation on HOPG has a beneficial effect of improved methanol oxidation catalytic activity and durability. XRD results showed no difference in the PtRu composition, structure, or crystallite size for PtRu on N-doped HOPG, Ar-HOPG or undoped HOPG. However, the methanol oxidation activity was higher for PtRu on N-HOPG. Nitrogen doping resulted in an inherent chemical effect and an improved stability as was predicted by theory [2-3].

We also established the role of nitrogen in the durability of PtRu/HOPG catalyst via microscopy and XPS analysis. Figure 1 shows PtRu nanoparticles on N-doped HOPG samples before and after 300 cycles between 0 and 1.1 V vs. Ag/AgCl, at 250 mV/s in 1 M H₂SO₄, for different levels of N-doping. Before cycling, the transmission electron microscope (TEM) images show that PtRu coverage and

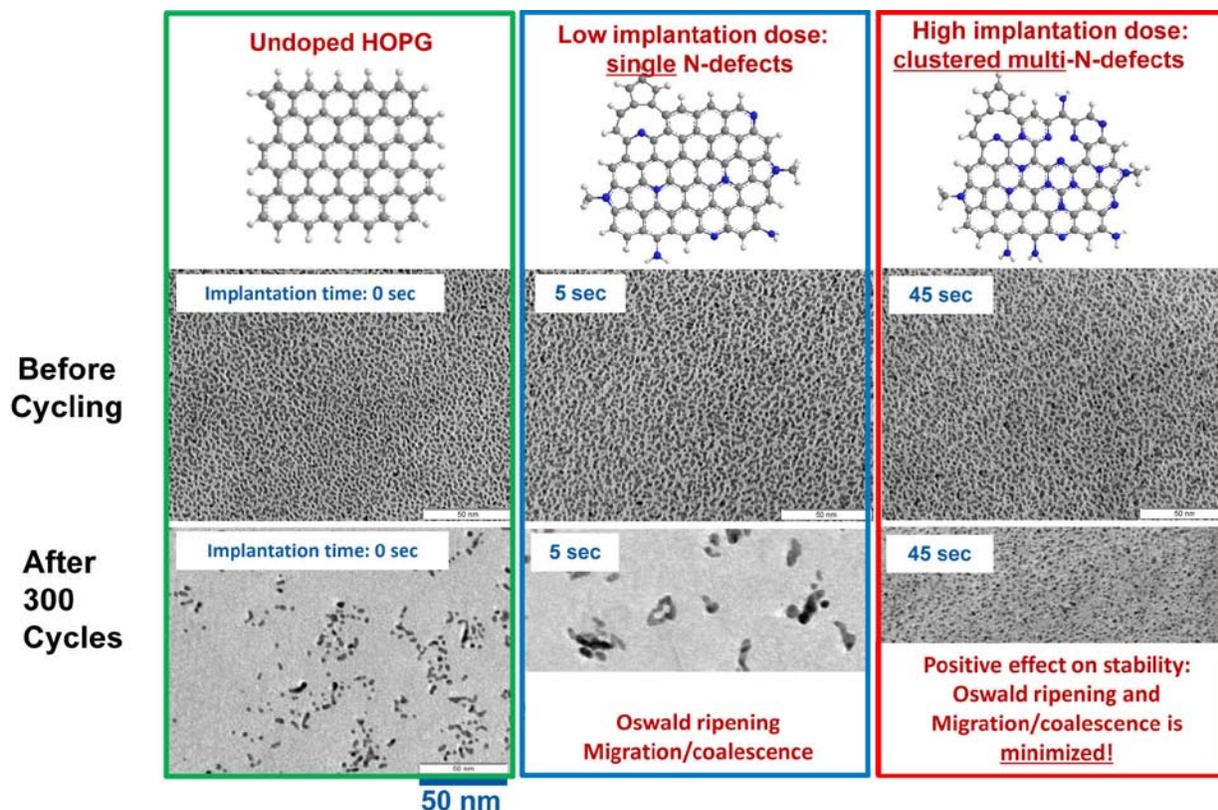


FIGURE 1. TEM images showing the effect of N-dosage on catalyst durability following potential cycling. High N-dosage results in clustered multi-N-defects, which have a positive effect on the stability of PtRu nanoparticles on N-doped HOPG.

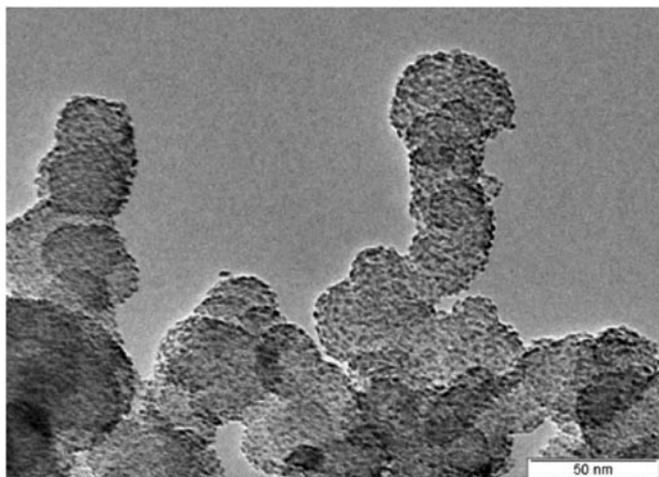


FIGURE 2. Representative TEM sputter-deposited PtRu/Vulcan carbon materials.

composition are independent of the amount of nitrogen present. After cycling to 1.1 V, low implantation dose (5-15 s) resulted in poor stability while high implantation dose (45, 100s) seemed to have greatly increased particle stability. The results indicate that a high amount of N is needed to form clustered multi-N-defects, which appears to minimize coalescence/migration of the PtRu catalyst. Density functional theory (DFT) was used to infer the effect of specific N functionalities on the stability of PtRu. DFT calculations show that N-defects such as pyrrolic and pyridinic N enhances the stability of Pt in PtRu and that pyrrolic N improves the stability of PtRu by stabilizing both Pt and Ru. Hence, a balance between pyrrolic and pyridinic N is needed to stabilize PtRu catalyst.

We established an entirely vapor-phase process for PtRu catalyst material development. By controlling specific, yet interdependent, sputter deposition parameters, we were able to generate high performing and highly dispersed PtRu nanoparticles (Figure 2) of a desired composition, particle size and electroactive surface area on Vulcan carbon support. Table 1 compares the half-cell MOR specific and mass activity of in-house catalysts and a commercial catalyst of a similar metal loading (30 wt%) and PtRu composition (1:1 atomic%). Our in-house sputtered PtRu/C catalysts consistently showed 20%–30% improvement in MOR activity as compared to commercial catalyst of comparable composition. Furthermore, the NREL in-house PtRu

on N-doped carbon catalyst proved more durable than the undoped catalyst and commercial catalyst. Further optimization is needed to improve the MOR activity for the in-house N-doped catalysts.

Table 1 compares the electrochemical surface area (ECA), the MOR specific and mass activity, and durability of two in-house and one commercial 30 wt% PtRu/C catalysts. JM5000 is a commercial catalyst purchased from Johnson Matthey. PtRu/N-C is a catalyst that has about 5% N-incorporated in the Vulcan carbon via implantation, followed by sputter deposition of PtRu. The ECA was obtained from CO stripping voltammetry. The MOR activity was measured in a half-cell set up in 1 mol/L methanol + 1 mol/L H₂SO₄. The durability test was done by cycling between 0.23 and 0.80 V vs. reference hydrogen electrode at 20 mV/s in 1 M H₂SO₄. All measurements were carried out at room temperature.

TABLE 1. Half-Cell Catalyst Performance and Durability Comparison

Catalyst	ECA (m ² /g)	Specific Activity @ 0.4 V (μA/cm ² _{metal})	Mass Activity @ 0.4 V (A/mg _{metal}) X 10 ³	% of ECA after 100x Durability cycles	% of ECA after 5,000x Durability cycles
30 wt% PtRu/C (sputter)	73	33	24	51	10
28 wt% PtRu/N-C (sputter not optimized)	55	30	17	60	40
30 wt% PtRu/C JM5000	69	29	20	48	17

The non-solution process was scaled up to generate a sufficient amount of the best performing in-house catalyst for DMFC testing. Table 2 shows that the in-house sputter 30 wt% PtRu/C outperforms the DMFC commercial catalyst JM5000. MEA preparation method needs to be optimized to improve the DMFC performance further.

Table 2 shows that in-house sputtered PtRu/C catalyst outperforms the commercial JM5000 catalyst of the same catalyst loading (1 mg/cm²). DMFC testing was carried out at 50°C using a 5 cm² MEA, 1 mol/L methanol and humidified air. Anode polarization was carried out using 1 mol/L methanol on the anode and hydrogen on the cathode. ECA was measured using CO stripping voltammetry.

TABLE 2. Catalyst DMFC Performance Comparison

Catalyst	PtRu ECA (m ² /g)	DMFC Current Density @ 0.4 V			Anode Polarization @ 0.4 V	
		(mA/cm ²) Geometric Surface Area	(μA/cm ² _{metal})	(mA/mg)	(μA/cm ² _{metal})	(mA/mg)
JM500	55	25	45	25	48	26
Sputtered PtRu/C	41	30	73	30	83	34

Conclusions and Future Direction

- We demonstrated that nitrogen implantation has an inherent beneficial effect on MOR activity and durability and that nitrogen dosage and functionalities play a role on these effects.
- We established an entirely non-solution, scalable process that produced highly dispersed PtRu/C catalyst that outperformed commercial catalysts in both MOR specific and mass activity.
- We demonstrated that PtRu on N-doped Vulcan carbon catalysts are more durable than PtRu on undoped carbon and commercial catalysts.
- We screened several different chemical dopants and determined that dopant level of interaction with carbon matrix affects MOR activity and durability.
- We will continue to optimize catalyst utilization through sputter-implantation parameter control.
- We will evaluate the DMFC performance and durability of PtRu/implanted carbon catalyst materials.
- We will establish catalyst degradation mechanisms, e.g., extent of ruthenium dissolution and catalyst coarsening.
- We will perform soft X-ray and hard X-ray scattering studies in situ during electrochemical analysis to determine the sites for PtRu attachment and study the degradation of PtRu during cycling (at the SLAC National Accelerator Laboratory).

Patents Issued

1. “Advanced Vacuum Deposition of Catalyst Materials,” Dameron, T. Olson, H.N. Dinh, D. Ginley, T. Gennett, Preliminary Patent Application, March 2011.

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