

## V.J.7 Engineered Nanostructured MEA Technology for Low Temperature Fuel Cells\*

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\* Congressionally directed project

### Project Objective

The objective of this project is to develop a novel catalyst support technology based on unique engineered nanostructures for low temperature fuel cells which:

- Achieves high catalyst activity and performance
- Improves catalyst durability over current technologies
- Reduces catalyst cost

### 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 (HFCIT):

- (A) Performance
- (B) Durability

### Technical Targets

This project is directed at the development of durable catalysts supported by novel support that improves the catalyst utilization and hence reduce

the catalyst loading. This project will develop a solid fundamental knowledge base necessary for the synthetic effort while at the same time demonstrating the catalyst advantages in direct methanol fuel cells (DMFCs). If successful, the project will address the following DOE technical targets as outlined in the HFCIT Multi-Year Research, Development and Demonstration Plan:

This project is conducting fundamental studies of nanowire supported catalysts applied in fuel cells. Insights gained from these studies will be applied to DMFCs first to demonstrate the catalyst advantages over commercial carbon supported catalysts, prior to eventual demonstration in hydrogen fuel cells:

- $>60 \text{ mW/cm}^2$  at  $40^\circ\text{C}$ , ambient condition
- Demonstrate durability advantage,  $<60 \mu\text{A/hr}$

### Accomplishments

- Produced Si nanowire with a diameter as small as 30 nm.
- Converted Si nanowire to graphite/SiC nanowire with high surface area of  $125 \text{ m}^2/\text{g}$  (Brunauer-Emmett-Teller, BET).
- Controlled Pt alloy particle size in the range of 1.5~3 nm, average 2 nm.
- Uniformly deposited Pt alloy nanoparticles on nanowire support.
- Achieved  $>112 \text{ mW/cm}^2$  (2x of target) with nanowire catalysts-based membrane electrode assembly (MEA) at ambient condition and  $40^\circ\text{C}$  for 3M DMFCs, which is  $45 \text{ mW/cm}^2$  better than that with a commercial catalyst.
- Achieved durability of over 1,000 hours with  $9 \mu\text{V/hr}$  decay rate (equiv. 6.5x of target).



### Introduction

The MEA in a fuel cell contains the catalysts critical to the process which promote the electrochemical reactions such as oxidation of hydrogen or methanol and reduction of oxygen. In today's fuel cells, the level of precious metal catalyst utilization using supported catalysts in the MEA is extremely low, around 20-30%. This low catalyst utilization represents a major barrier towards lowering the cost and improving the performance of fuel cells. Additional efficiency is lost when catalyst particles are located such that they are in poor electrolytic contact with the proton exchange

membrane or poor electrical contact with the electrode through the support matrix. Each of these elements impacts overall efficiency of the MEA and therefore the resulting fuel cell. The U.S. DOE outlined four strategies to address challenges in catalysts and support materials, which are: lower precious group metal content – improved Pt utilization and durability; Pt alloys – maintain/improve performance and reduce cost; novel support structures – non-carbon supports and alternative carbon structures; non-Pt catalysts – maintain performance and durability.

For this project, we are to develop a novel catalyst support technology based on unique engineered nanostructures for low temperature fuel cells which achieves high catalyst activity and performance, as well as improves catalyst durability over current technologies. Through precise control of the nanowire density, diameter, length, surface chemistry, catalyst deposition density and sulfonic acid group density of polymer electrolyte, we will be able to independently control and optimize each of the most important elements of the MEA, including porosity, electrical connectivity, electrolyte connectivity and catalyst accessibility. This level of control is not possible with traditional packed-bed MEAs and will allow us to fabricate MEAs in which majority of the catalyst material is accessible and active.

## Approach

To achieve the objectives, novel inorganic nanowire supported catalysts are being developed by utilizing the Nanosys nanowire synthesis technology and nanoparticle synthesis technology. This includes, in particular, SiC nanowire as well as PtRu and Pt nanoparticles. This includes:

- Create nanowires using vapor-liquid-solid (VLS) synthesis method for synthesizing Si nanowires and then carburizing them to form SiC/nano-graphite core/shell nanowires;
- Create catalyst nano-particles using colloidal method;
- Integrate catalyst onto nanowire support with improved stability and activity;
- Fabricate catalyst coated membrane with nanowire supported PtRu and Pt catalysts and control the porosity of catalyst layers as well as catalyst and ionomer distribution in MEA;
- Optimize cell performance and perform durability evaluation.

## Results

We have grown silicon nanowires on the surface of a substrate using a colloidal catalyst based VLS synthesis method.  $\text{SiH}_4$  is used as the growth gas. The diameter is controlled within 30~40 nm. Then, the silicon

nanowires are directly converted at high temperature into SiC coated with nanographite shell. The nanowires have been characterized using transmission electron microscopy (TEM) and/or scanning electron microscopy. After the high temperature process the crystallinity and nanowire structure are retained. TEM studies have indicated this graphite shell is covalently bonded onto the surface of the SiC nanowires. The high crystallinity and covalent bonding between nanographite and SiC make this support much more stable than poorly crystallized carbon black. The final core-shell nanowires have diameters as small as 30 nanometers and aspect ratios of ~100:1. The rough nanographite shell makes the nanowire material have good electrical conductivity. This also results in a large surface area of ca. 125  $\text{m}^2/\text{g}$ , measured by BET.

We have prepared free-standing well-dispersed nanoparticles using a solution phase process method. By controlling the reaction temperature profile and ratio of starting reagents and conditions, the particle size, size-distribution and composition have been tuned independently. Energy dispersive X-ray analysis has confirmed the ratio of Pt and Ru is ca. 1 to 1. X-ray diffraction results indicate that the particle size of the metallic PtRu particles can be controlled from 1 to 5 nm, typically, 2 nm.

We have successfully developed a method to integrate the nanoparticle catalysts onto the nanowire supports by dispersing the nanowire support materials in ethylene glycol and then adding the nanoparticles. By inducing electrostatic attraction between the nanoparticles and the nanowires, this integration is quite strong for the relative size of the nanoparticles and nanowires. Typically 30% PtRu can be easily deposited on the nanowire support. The uniform distribution of nanoparticles on the surface of the nanowire support has been observed by TEM, as shown in Figure 1.

The activity and performance for a methanol oxidation reaction at the nanowire supported PtRu catalyst has been characterized in an electrochemical cell at 40°C. At 0.5 V, the mass current for methanol oxidation at PtRu/NW is ca. 2.5x higher than that at PtRu/C (commercial), which clearly indicates PtRu/NW advantage in activity for methanol oxidation over PtRu/C.

The stability of PtRu/NW catalyst for methanol oxidation has been measured by cycling potential between 0.05 V and 0.6 V for 3,200 cycles. The loss in mass current measured at 0.5 V (27%) is much lower than that of 69% for commercial PtRu/C catalyst under the identical condition. The losses in electrochemically active surface area are similar for both PtRu/NW and PtRu/C catalysts (~22%), which may indicate comparable defoliating and coalescing of the catalysts. We may assume the net loss in mass activity can be evaluated by the difference between the measured mass current loss and the surface area loss. Therefore, only

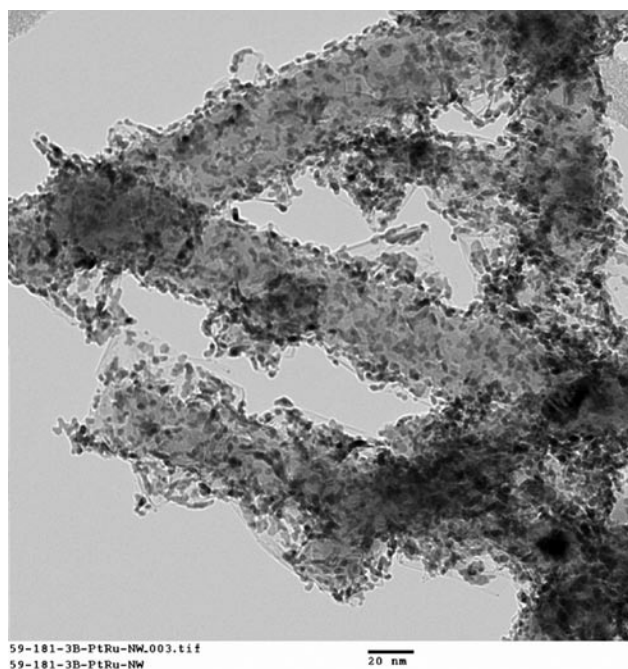


FIGURE 1. TEM Image for PtRu Distribution on Nanowire Support

5% loss is for PtRu/NW, which is much lower than that of 47% for the PtRu/C catalyst.

Using the nanowire catalysts, commercially available gas diffusion layers and Polyfuel hydrocarbon membranes, MEAs of 5 cm<sup>2</sup> active area are fabricated for the catalyst performance evaluation. A catalyst coated membrane method is used to fabricate MEAs. Formulation of nanowire catalyst, ionomer, and dispersion solvents have been optimized. The Nafion<sup>®</sup> ionomer with lower equivalent weight (EW1000) has been used for the nanowire supported catalyst.

The porosity of the nanowire supported catalyst layer is comparatively larger than that of the carbon supported catalyst layer; consequently the ionomer can be uniformly distributed in the layer with nanowire supported catalysts. In contrast, large ionomer agglomerates can be observed in the catalyst layer with carbon supported catalysts. These features result in a higher triple phase boundary (TPB) area for the nanowire supported catalysts over the carbon supported catalysts, and hence result in a higher catalyst utilization and a higher performance.

Anode polarization and fuel cell polarization performance have been evaluated. To compare and evaluate the nanowire anode catalyst, a commercial Pt/C cathode catalyst is used. The anode in an MEA made with nanowire catalyst shows that the improvement in anode polarization is ca. 47 mV at 100 mA/mg-PtRu and 71 mV at 200 mA/mg-PtRu, as shown in Figure 2. We have also achieved a maximum power density of 112 W/cm<sup>2</sup> in DMFC with nanowire anode catalyst and

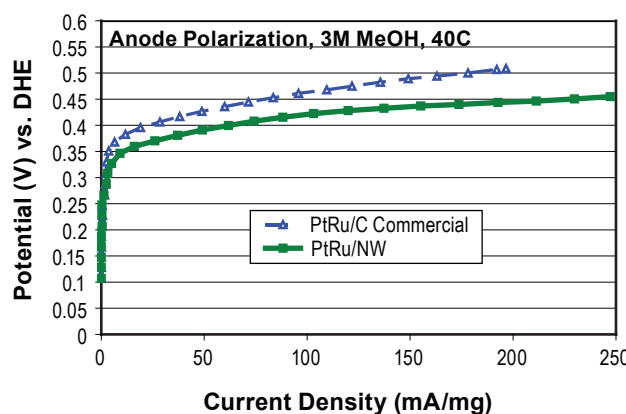


FIGURE 2. Anode Polarizations for Methanol Oxidation, PtRu/NW (Nanosys) vs. PtRu/C (commercial)

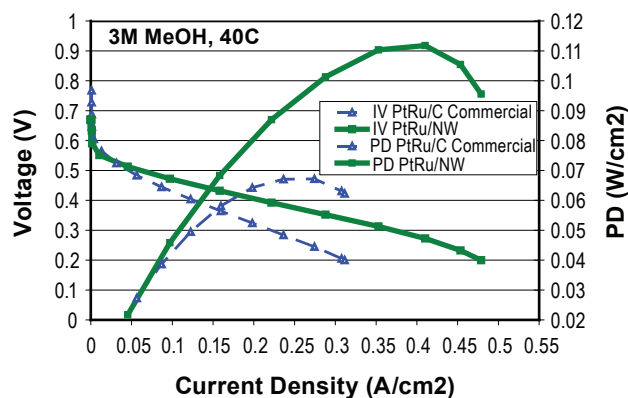


FIGURE 3. Fuel Cell Polarization and Power Density (PD) Curves, PtRu/NW (Nanosys) vs. PtRu/C (commercial)

3M methanol at 40°C, which is 45 mW/cm<sup>2</sup> higher than that with commercial PtRu/C anode catalyst (68 mW/cm<sup>2</sup>), see Figure 3.

Nanowire supported catalysts have advantages over commercial carbon supported catalysts, which have high catalyst utilization (1.6x > PtRu/C), high activity (2.6x > PtRu/C), high accessibility, and high stability/durability, as shown in Table 1. These differentiate nanowire-based catalysts from carbon supported catalysts. For anode polarization, the mass current of PtRu/NW is 3.4 times

TABLE 1. Nanowire Supported Catalyst Advantages

	TPB Area (m <sup>2</sup> /g)	Catalyst Utilization (%)	AP, I (mA/mg) @ 0.45 V, 40°C	AP, I (mA/mg) @ 0.3 V, 40°C
Nanosys PtRu/Nanowire	47	61	260	9.8
Commercial PtRu/Carbon	23	39	76	3.8

**Nanosys Advantage** 2x 1.6x 3.4x 2.6x  
 AP – Anode polarization

higher than that of PtRu/C at 0.45 V, 40°C. This mass current is attributed to improvement in both activity and accessibility. In contrast, at lower potential of 0.3 V, the activity-dominant mass current for PtRu/NW is 2.6 times higher than that of PtRu/C. The difference in mass current gain between 0.45 V and 0.3 V is an indication of improvement in accessibility for PtRu/NW. In addition, we achieved durability of over 1,000 hours with 9  $\mu$ V/hr decay rate, by operating the DMFC with 3M MeOH and ambient air at 40°C.

## Conclusions and Future Directions

Nanosys has developed durable fuel cell catalysts, which outperform the state-of-the-art catalysts:

- The project demonstrated novel inorganic nanowire catalyst support and catalysts. This may fundamentally overcome the catalyst durability problems, in particular, carbon corrosion problem.
  - Unique features of the nanowire supported catalysts are firstly demonstrated for methanol oxidation prior to hydrogen oxidation. It turned out that PtRu/NW catalysts have higher activity, utilization and accessibility over commercial PtRu/C catalysts.
  - Nanowire supported catalysts have superior stability over carbon supported catalysts.
  - The results have been presented in 2009 Small Fuel Cells and 2009 DOE Annual Review meetings.
- For the remainder of project, we will fulfill reporting obligations, most notably the final report, and prepare manuscripts for publications. As for future directions, we will explore further applications in hydrogen fuel cells and develop more active catalysts for cathode. (This effort will continue at Nanosys after completion of the project.)

## Patents Issued

1. Nanostructured Catalyst Supports, 01-007440US, filed in April of 2009, Yimin Zhu, Jay Goldman, Baixin Qian and Ionel Stefan, portions of this invention may have been made pursuant to a contract with the US DOE, Hydrogen, Fuel Cells & Infrastructure Technologies Program (# DE-FG36-08G088097).

## FY 2009 Publications/Presentations

1. **DMFC Inorganic-Nano-Fiber-Based Catalyst with Superior Performance and Lifetime** *Yimin Zhu, Ionel Stefan, Baixin Qian, Jay Goldman, Jurgen Hofler and Jason Hartlove*, 11th Annual International Conference for Small Fuel Cells 2009 - May 7-8, 2009.
2. **Engineered Nanostructured MEA Technology for Low Temperature Fuel Cells** *Yimin Zhu, Ionel Stefan, Baixin Qian, Jay Goldman, Jurgen Hofler and Jason Hartlove*, 2009 DOE ANNUAL MERIT REVIEW and PEER EVALUATION MEETING, May 18, 2009; fcp\_09\_zhu.