

## V.G.4 Advanced Materials and Concepts for Portable Power Fuel Cells

P. Zelenay (Primary Contact), H. Chung, Z. Ding, C.M. Johnston, Y.S. Kim, Q. Li, A. Trendewicz, P. Turner, G. Wu

Materials Physics and Applications Division  
Los Alamos National Laboratory  
Los Alamos, NM 87545  
Phone: (505) 667-0197  
E-mail: zelenay@lanl.gov

### DOE Manager

HQ: Nancy Garland  
Phone: (202) 586-5673  
E-mail: Nancy.Garland@ee.doe.gov

### Subcontractors:

- R.R. Adzic, M. Li, K. Sasaki, M. Vukmirovic  
Brookhaven National Laboratory, Upton, NY
- Y. Yan, S. Alia  
University of California, Riverside, CA
- J. McGrath, Y. Chen, C. H. Lee, M. Lee  
Virginia Polytechnic Institute and State University,  
Blacksburg, VA
- N. Permogorov, G. Hards, G. Spikes  
Johnson Matthey Fuel Cells, Swindon, United Kingdom
- V. Graf, C. Böhm, J. Stephens  
SFC Energy, Brunenthal, Germany
- K. More  
Oak Ridge National Laboratory, Oak Ridge, TN  
(no-cost partner)

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established by DOE for portable fuel cell systems; assure path to large-scale fabrication of successful materials.

Individual objectives of this research are as follows:

- Synthesize and thoroughly evaluate direct methanol fuel cell (DMFC) anode catalysts with enhanced activity, reduced cost and improved durability.
- Design and implement in fuel cells innovative electrode structures for better activity and durability of portable power systems.
- Develop new hydrocarbon membranes based on (i) multiblock copolymers and (ii) copolymers with cross-linkable end-groups to assure lower MEA cost and enhanced fuel cell performance.
- Develop novel electrocatalysts and evaluate viability of portable power systems based on fuels alternative to methanol: ethanol and dimethyl ether.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Multi-Year Research, Development and Demonstration Plan: Planned Program Activities for 2005-2015 [1]:

- (A) Durability (catalysts and electrode layers)
- (B) Cost (catalysts and MEAs)
- (C) Performance (including fuel oxidation kinetics and the impact of fuel crossover on cathode performance)

### Fiscal Year (FY) 2011 Objectives

The main objective of this project is to:

- Develop advanced materials (catalysts, membranes, electrode structures, membrane electrode assemblies [MEA]) and fuel cell operating concepts capable of fulfilling cost, performance, and durability requirements

### Technical Targets

Portable fuel cell research in this project focuses on DOE's technical targets specified in Table 3.4.7 (Consumer Electronics) of the Multi-Year Research, Development and Demonstration Plan [1]. Table 3.4.7 defines DOE's Fuel Cell Technologies Program 2010 targets (soon to be modified).

Table 3.4.7 Technical Targets: Consumer Electronics (sub-Watt to 50-Watt)				
Characteristic	Units	2005 Status <sup>a, b</sup>	2006	2010
Specific power	W / kg	20	30	100
Power density	W / L	20	30	100
Energy density	Wh / L	300	500	1,000
Cost	\$ / W	40 <sup>c</sup>	5	3
Lifetime	hours	>500	1,000	5,000

<sup>a</sup> First year for which status was available.

<sup>b</sup> Unless otherwise noted, status is based on average of available data.

<sup>c</sup> Fuel Cell Seminar Abstracts, 2004, p. 290.

Using DOE's Table 3.4.7 solely as guidance relevant to the portable power system as a whole, we have devised the following specific technical targets for the project:

- System cost target: \$3/W
- Performance target: Overall fuel conversion efficiency ( $\eta_{\Sigma}$ ) of 2.0-2.5 kWh/L
- In the specific case of a DMFC, the above assumption translates into a total fuel conversion efficiency ( $\eta_{\Sigma}$ ) of 0.42-0.52, corresponding to a 1.620-fold improvement over the state of the art (ca. 1.250 kWh/L). Assuming fuel utilization ( $\eta_{\text{fuel}}$ ) and balance-of-plant efficiency ( $\eta_{\text{BOP}}$ ) of 0.96 and 0.90, respectively (efficiency numbers based on information obtained from DMFC systems developers), and using theoretical voltage ( $V_{\text{th}}$ ) of 1.21 V at 25°C, the cell voltage ( $V_{\text{cell}}$ ) targeted in this project can be calculated as:

$$V_{\text{cell}} = V_{\text{th}} [\eta_{\Sigma} (\eta_{\text{fuel}} \eta_{\text{BOP}})^{-1}] = 0.6-0.7 \text{ V}$$

Thus, the ultimate target of the materials development effort in the DMFC part of this project is to assure an operating single fuel cell voltage of at least 0.6 V. Very similar voltage targets have been calculated for the fuel cells operating on the two other fuels, ethanol (EtOH) and dimethyl ether (DME).

### FY 2011 Accomplishments (in the first nine months of the project)

- Activity of "thrifed" PtRu catalyst of methanol (MeOH) oxidation significantly increased, much above that defined by an interim 2011 mass activity target of 200 mA/mg<sub>Pt</sub>.
- PtRu-nanotube catalysts demonstrated with high specific MeOH oxidation activity.
- Lower MeOH permeability and better DMFC performance than that of Nafion<sup>®</sup> shown with hexafluoro bisphenol A benzonitrile-biphenyl sulfone (6FPAEB-BPS100) multiblock copolymers.
- PtRhSnO<sub>2</sub> electrocatalysts with unprecedented activity for ethanol oxidation designed, synthesized and demonstrated in electrochemical cell.
- Highest ever performance of gas-fed direct dimethyl ether fuel cell (DDMEFC) demonstrated with a Pt<sub>50</sub>Ru<sub>50</sub> anode catalyst at 80°C.



### Introduction

This multitask, multi-partner project targets advancements to portable fuel cell technology through the development and implementation of novel materials and concepts for (i) enhancing performance, (ii) lowering cost, (iii) minimizing size, and (iv) improving durability of fuel cell power systems for consumer electronics and other

mobile and off-grid applications. The primary focus of the materials research in this project is on electrocatalysts for the oxidation of MeOH, EtOH, and DME, on innovative nanostructures for fuel cell electrodes, and on hydrocarbon membranes for lower cost of the MEA and enhanced fuel cell performance (fuel crossover, proton conductivity). In parallel with new materials, this project targets development of various operational and materials-treatment concepts, concentrating among others on improvements to the long-term performance of individual components and the complete MEA.

### Approach

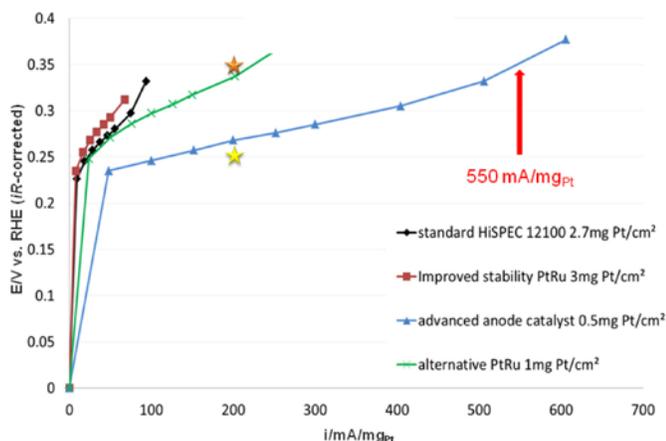
The two primary research goals of this project are (i) the development of binary and ternary catalysts for the oxidation of MeOH, EtOH, and DME and (ii) synthesis of hydrocarbon polymers (multiblock copolymers, copolymers with cross-linkable functional groups) for lower cost and better fuel cell performance through reduced fuel crossover and increased protonic conductivity. Better understanding of the key factors impacting the performance of both catalysts and polymers is also pursued through a major characterization effort including X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, nuclear magnetic resonance (NMR), and transmission electron microscopy (TEM).

Development of new catalysts and polymers is closely tied to novel electrode nanostructures tailored to minimize precious metal content, maximize mass activity, and enhance durability. The electrode-structure component of the effort concentrates on two groups of materials: (i) solid-metal nanostructures (e.g., nanowires and nanotubes) and (ii) carbon-based nanostructures acting as metal catalyst supports.

In addition to short-term testing and initial performance assessment, the catalysts, membranes, supports, electrode structures, and membrane-electrode assemblies developed in this project are subject to long-term performance (durability) testing. Performance limiting factors and degradation mechanisms are being identified and, if possible, addressed. Fabrication and scale up of viable catalysts, membranes, and supports is also being tackled through collaboration between partners in this project.

### Results

DMFC Catalysts — New methanol oxidation catalysts were developed through "thrifing" of Pt in the binary PtRu catalysts. As shown by the anode polarization data in Figure 1, the "advanced MeOH catalyst" matched the performance of a benchmark HiSPEC<sup>®</sup> 12100 catalyst used at a much higher loading. The mass activity of 550 mA/mg<sub>Pt</sub> was reached at 0.35 V (80°C), exceeding by 175% the interim 2011 mass-activity target (200 mA/mg<sub>Pt</sub> at 0.35 V; orange star in the Figure 1). The anode catalyst research using the "thrifing" approach is on track to reach the project goals of 200 mA/mg<sub>Pt</sub> at an anode potential of 0.25 V (Figure 1;



**FIGURE 1.** DMFC anode polarization plots recorded with three “Pt-thrifted” PtRu catalysts and a benchmark HiSPEC® 12100 PtRu catalyst in 0.5 M MeOH at 80°C.

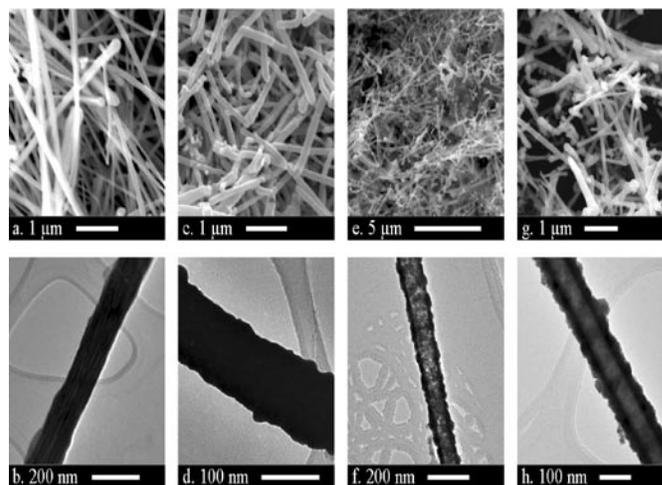
yellow star) and 150 mA/cm<sup>2</sup> in a DMFC MEA at a voltage of 0.60 V.

In addition to the performance testing, the newly developed DMFC catalysts were subject to stability testing under cyclic voltammetry (CV) conditions. An increase in the Pt-character was observed during the first 200 cycles (0.0-0.85 V, 20 mV/s, 80°C), with virtually no change thereafter. 300 CV cycles resulted in 20-30 mV fuel cell performance loss at 0.50 V, attributable to the anode (based on the anode polarization data).

**Innovative Electrode Structures —** PtRu nanotube catalysts of MeOH oxidation were obtained using (i) displacement of Ag in an Ag nanowire template to form PtNT, followed by Ru deposition and reduction via a chemical method, followed by annealing to form a PtRu alloy; (ii) displacement of Ag in an Ag nanowire template to form PtNT, followed by electrochemical deposition of Ru; and (iii) simultaneous displacement of Cu in a Cu nanowire template to create PtRuNT, followed by annealing to form a PtRu alloy. Scanning electron microscope (SEM) and TEM images of Cu nanowires and PtRu nanotube catalysts, obtained using the last of the three methods, are shown in Figure 2.

Excellent specific activity for MeOH oxidation was demonstrated with several PtRuNT catalysts, with the onset potential of methanol oxidation of 0.33 V matching the one measured with a state-of-the-art commercial catalyst (HiSPEC® 12100). However, the mass activity of PtRu nanotube catalysts was relatively low.

**Multiblock Copolymers for Reduced MeOH Crossover —** Partial fluorination of a hydrophobic block was used to enhance proton conductivity via better phase separation and to improve adhesion (intactness) to the Nafion® ionomer used in the electrodes. In turn, benzonitrile was employed to reduce MeOH permeability via complexation reaction



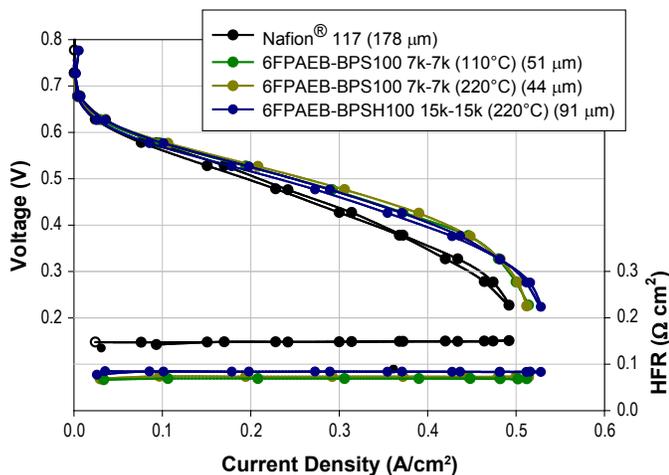
**FIGURE 2.** Top: SEM images of (a) CuNW; (c) PtNT; (e) Pt<sub>80</sub>Ru<sub>20</sub>; (g) Pt<sub>50</sub>Ru<sub>50</sub>. Bottom: TEM images of (b) CuNW; (d) PtNT; (f) Pt<sub>80</sub>Ru<sub>20</sub>; (h) Pt<sub>50</sub>Ru<sub>50</sub>.

with H<sub>2</sub>O molecules, and highly-sulfonated hydrophilic block was used to increase proton conductivity. <sup>1</sup>H-NMR confirmed the intended chemical structure of the multiblock copolymer. Higher water uptake (undesirable) and proton conductivity (desirable) than in random copolymer were observed with multiblock copolymer. By controlling the block length of multiblock copolymers improved conductivity was achieved while maintaining the level of water uptake similar to that of random copolymers.

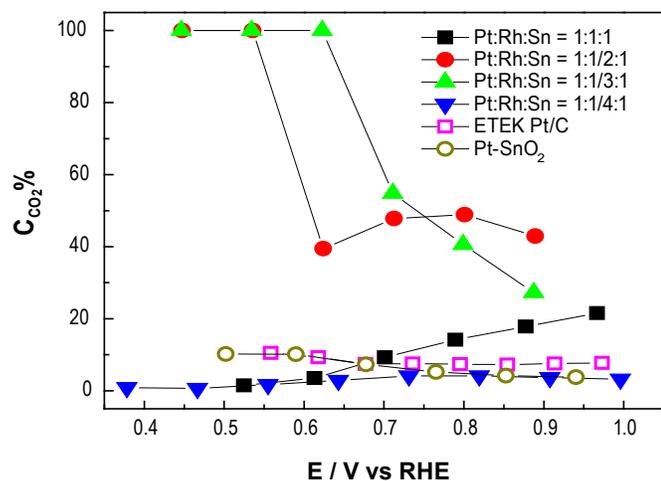
Good adhesion of multiblock-copolymer membranes and Nafion®-bonded electrodes was observed during MEA processing and in DMFC testing. MeOH permeability of multiblock-copolymer membranes was found to be three times lower than that of Nafion®, allowing for the use of thinner membranes. As a result, multiblock-copolymer membranes were found to outperform Nafion® 117 in DMFC testing, even at a relatively low MeOH concentration of 0.5 M MeOH (Figure 3). Even larger improvement relative to Nafion® is expected at higher MeOH concentrations.

**EtOH Oxidation Catalysts —** The effort here focused on the development of ternary catalysts, PtRhSnO<sub>2</sub> in particular. The ternary PtRhSnO<sub>2</sub> catalyst was found capable of oxidizing EtOH to CO<sub>2</sub> thanks to its multifunctional character. In that catalyst, Pt assists in the abstraction and oxidation of H atoms; SnO<sub>2</sub> serves as a source of OH for the oxidation of strongly bound intermediates; and Rh, placed either on SbO<sub>2</sub> or on Pt itself, aids in C-C bond scission. As a result of such an in-concert action of the three components, the optimized PtRhSnO<sub>2</sub> catalysts (Pt:Rh:Sn atomic ratios of 1:1/3:1 and 1:1/2:1) showed unprecedented activity in the oxidation of EtOH to CO<sub>2</sub> (Figure 4). The activity in complete oxidation of EtOH to CO<sub>2</sub> is especially evident at low potentials – a highly desirable property.

Other ternary catalysts were also studied, including PtIrSnO<sub>2</sub>. The Ir-based ternary catalysts showed significant



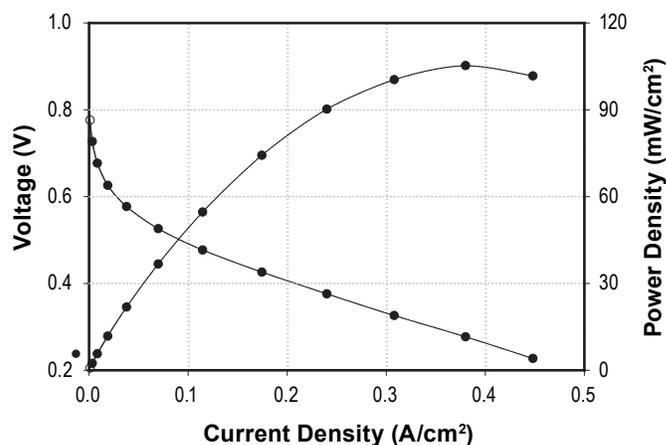
**FIGURE 3.** DMFC polarization and high-frequency resistance plots of MEAs using Nafion® and 6FPAEB-BPS100 multiblock copolymer membranes at 80°C. Numbers in parenthesis stand for the heat treatment temperature and membrane thickness. Anode: 6 mg/cm<sup>2</sup> Pt<sub>50</sub>Ru<sub>50</sub> black, 1.8 mL/min 0.5 M MeOH solution; Cathode: 4 mg/cm<sup>2</sup> Pt black, 20 psig, 500 sccm air.



**FIGURE 4.** Carbon monoxide yields determined from infrared absorption spectra for four ternary PtRhSnO<sub>2</sub> catalysts, an Rh-free PtSnO<sub>2</sub> catalyst and a Pt/C reference catalyst from E-TEK.

activity in EtOH oxidation to acetic acid (CH<sub>3</sub>COOH) but their selectivity for CO<sub>2</sub> formation was much lower than that of the best PtRhSnO<sub>2</sub> catalysts. Also studied were catalysts obtained via deposition of a Pt monolayer on gold single crystals, Au(111) in particular, these catalysts revealed promising activity in both EtOH and MeOH oxidation.

DME Fuel Cell Research — In general, DDMEFC exhibits lower performance than DMFC with MEAs optimized for methanol (but not yet for DME). DDMEFC performance was found to strongly depend on pressure but not much on the fuel flow rate (40-200 sccm; 5 cm<sup>2</sup> test cell). A wide range of Pt-to-Ru atomic ratios was screened



**FIGURE 5.** DDMEFC polarization and power density plots at 80°C. Anode: 6 mg/cm<sup>2</sup> Pt<sub>80</sub>Ru<sub>20</sub> black, 40 sccm DME gas, 30 psig; Cathode: 4 mg/cm<sup>2</sup> Pt black, 20 psig, 500 sccm air; Membrane: Nafion® 117.

for DME anode performance for the first time. Although a Pt<sub>50</sub>Ru<sub>50</sub> catalyst exhibited overall the best performance in high and middle voltage ranges, Pt-rich catalysts performed better at low voltages (near peak power), together attesting to a behavior much more complex than that of DMFC anode catalysts.

The above limitations notwithstanding, careful optimization of the anode catalyst and DDMEFC operating conditions allowed the achievement of a specific power density in excess of 100 mW/cm<sup>2</sup> (Figure 5). In spite of using gaseous DME feed, this result represents the best performance ever published for a DDMEFC at 80°C, surpassing that of Im et al. [2].

PtRu anode deactivation was found to occur at high potentials, likely due to the surface oxide formation (more oxophilic and thus less active surface). Fuel crossover experiments revealed much lower DME oxidation current at the cathode than that of MeOH, especially at higher potentials, indicating lower DME crossover and possibly inactivity of the oxidized Pt surface in DME oxidation.

## Conclusions

- Selected “thrifty” PtRu catalysts of MeOH oxidation meet and significantly exceed 2011 interim mass activity target for methanol oxidation (200 mA/mg<sub>Pt</sub>); PtRu nanotube catalysts exhibit promising methanol oxidation activity, however, mass activity needs to be increased by, for example, thinning tube walls.
- Ternary PtRhSnO<sub>2</sub> electrocatalysts of EtOH oxidation show unprecedented activity for ethanol oxidation, producing large amounts of CO<sub>2</sub>; ternary catalysts with a Rh-to-Pt ratio between 1:3 and 1:2 exhibit the highest activity in EtOH oxidation; an increase in the catalyst particle size may be required for efficient EtOH adsorption and dehydrogenation; Au represents

potentially promising support for EtOH and MeOH oxidation catalysts.

- Multiblock copolymers with improved mechanical properties and high proton conductivity show lower MeOH permeability and better DMFC performance than Nafion<sup>®</sup>-based membranes.
- Unlike in MeOH oxidation, the optimal PtRu catalyst composition varies depending on the operating voltage of the DME fuel cell (anode potential); DME crossover is less than that of MeOH under typical testing conditions; a DDMEFC operating with a Pt<sub>50</sub>Ru<sub>50</sub> anode catalyst has shown the highest performance reported to date at 80°C.

### Future Directions

- MeOH Oxidation Catalysis: Perform comprehensive activity and stability study of advanced MeOH oxidation catalysts versus HiSPEC<sup>®</sup> 12100 as a benchmark; complete evaluation of PtSnX catalysts for upcoming Go/Go-No decision on PtSn catalysts in FY 2012; evaluate the degree of Ru crossover resulting from advanced MeOH oxidation catalysts.
- Innovative Membranes and Electrode Structures: Determine durability of multiblock copolymers in an operating fuel cell; reduce polymer water uptake; improve dimension control and eliminate oxidation of CuNW (before galvanic displacement); significantly reduce wall thickness of PtRu nanotubes to at least double the catalyst surface area.
- EtOH Oxidation Catalysis: Increase the size of PtRh nanoparticles to enhance the size of Pt ensembles in PtRhSnO<sub>2</sub> catalyst and thus facilitate adsorption and dehydrogenation of the EtOH molecule; scale up the synthesis of a selected ternary catalyst to 2 g per batch for MEA testing; evaluate Au clusters and/or supported Au-monolayers as catalyst supports; complete differential electrochemical mass spectroscopy instrument set up.
- DME Research: Determine the effect of anode catalyst composition on Ru crossover and cathode performance (relevant to both DDMEFC and DMFC); complete half-cell DME studies with PtRu catalysts; assess DDMEFC feasibility versus DMFC following full optimization of the DME anode (Go/No-Go decision on DME research in FY 2012).

### References

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2. "Ethanol electrooxidation on the ternary Pt-Rh-SnO<sub>2</sub>/C electrocatalysts with varied Pt:Rh:Sn ratios;" M. Li, A. Kowal, K. Sasaki, N.S. Marinkovic, D. Su, E. Korach, P. Liu, R.R. Adzic, *Electrochim. Acta*, **55**, 4331 (2010).
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2. 4<sup>th</sup> Santa Fe Workshop on Materials and Energy Conversion, Catalysts for Ethanol Oxidation and Electro-oxidation, Santa Fe, New Mexico, November 4–6, 2010. Title: "Catalyst Crossover in Polymer Electrolyte Fuel Cells;" P. He, T.T.H. Cheng, R. Bashyam, A.P. Young, S. Knights, Y.S. Kim, and P. Zelenay.