

V.I.2 Advanced Materials and Concepts for Portable Power Fuel Cells

P. Zelenay (Primary Contact), H. Chung, Y.S. Kim, Q. Li, G. Purdy, D. Spornjak, X. Wen, G. Wu
Materials Physics and Applications Division
Los Alamos National Laboratory
Los Alamos, NM 87545
Phone: (505) 667-0197
Email: zelenay@lanl.gov

DOE Manager

Nancy Garland
Phone: (202) 586-5673
Email: Nancy.Garland@ee.doe.gov

Subcontractors:

- R.R. Adzic, M. Li, M. Vukmirovic
Brookhaven National Laboratory, Upton, NY
- Y. Yan, J. Zheng
University of Delaware, Newark, DE
- J.E. McGrath, Y. Chen, J. Rowlett, A. Shaver
Virginia Polytechnic and State University, Blacksburg, VA
- A.M. Bonastre, N.C. Moreno, G. Hards, E. Price, J. Sharman, G. Spikes
Johnson Matthey Fuel Cells, Swindon, United Kingdom
- C. Böhm
SFC Energy, Brunthal, Germany
- K.L. More, D. Cullen
Oak Ridge National Laboratory, Oak Ridge, TN (no-cost partner)

Project Start Date: September 2010

Project End Date: August 2014

Overall Objective

Develop advanced materials (catalysts, membranes, electrode structures, membrane electrode assemblies [MEAs]) and fuel cell operating concepts capable of fulfilling cost, performance, and durability requirements established by DOE for portable fuel cell systems; assure path to large-scale fabrication of successful materials.

Fiscal Year (FY) 2013 Objectives

- Demonstrate PtRu or PtRuSn methanol oxidation catalyst that exceeds final project anode mass activity target of $200 \text{ mA mg}_{\text{Pt}}^{-1} \text{ cm}^{-2}$ at $\leq 0.25 \text{ V}$ at 80°C (internal resistance [iR]-corrected), with durability at least matching that of the state-of-the-art methanol oxidation catalyst (HiSPEC[®] 12100).
- Develop PtRu/CuNWS-based methanol oxidation catalysts with the onset potential $< 0.3 \text{ V}$ vs. the reference hydrogen electrode (RHE) and mass activity at 0.40 V

vs. RHE at least matching that of the benchmark PtRu catalyst (HiSPEC[®] 12100).

- Synthesize multi-block copolymer with methanol permeability reduced by at least 50% relative to Nafion[®] and maintained ionic conductivity and water uptake.
- Improve selectivity of the ternary PtRhSnO₂ electrocatalyst for 12-electron oxidation of ethanol to CO₂ up to 30% at $E = 0.4 \text{ V}$, $60\text{--}80^\circ\text{C}$.
- Demonstrate 150 mA cm^{-2} at 0.50 V in a direct dimethyl ether fuel cell (DDMEFC) operating with a new-generation PtRuPd/C anode catalyst at a loading of $< 3.0 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ (80°C).
- Characterize the most promising new direct methanol fuel cell (DMFC) anode catalyst and/or membrane developed in the project in a short stack under conditions simulating SFC Energy's commercial products.

Technical Barriers

This project addresses the following technical barriers in the Fuel Cells section (3.4.5, Technical Barriers) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan [1]:

- (A) Durability (catalysts, membranes, electrode layers)
- (B) Cost (catalysts, MEAs)
- (C) Performance (catalysts, membranes, electrodes, MEAs)

Technical Targets

Portable fuel cell research in this project focuses on the DOE technical targets specified in Tables 3.4.7a, 3.4.7b, and 3.4.7c in Section 3.4.4 (Technical Challenges) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan [1]. Table 1 summarizes the latest DOE performance targets for portable power fuel cell systems in three power ranges.

Using DOE's Table 3.4.7 as guidance relevant to portable power systems, the following specific project targets have been devised:

- System cost target: $\$5/\text{W}$
- Performance target: Overall fuel conversion efficiency (η_c) of 2.0-2.5 kWh/L
- In the specific case of a DMFC, the above assumption translates into a total fuel conversion efficiency (η_c) of 0.42-0.52, corresponding to a 1.6 to 2.0-fold improvement over the state of the art (ca. 1.250 kWh/L). Assuming fuel utilization (η_{fuel}) and balance-of-plant efficiency (η_{BOP}) of 0.96 and 0.90, respectively (efficiency

TABLE 1. DOE Performance Targets for Portable Power Fuel Cell Systems in Three Power Ranges

| Technical Targets: Portable Power Fuel Cell Systems (< 2 W; 10-50 W; 100-250 W) | | | | |
|---|-------|---------------------|---------------------|---------------------|
| Characteristics | Units | 2011 Status | 2013 Targets | 2015 Targets |
| Specific power | W/kg | 5; 15; 25 | 8; 30; 40 | 10; 45; 50 |
| Power Density | W/L | 7; 20; 30 | 10; 35; 50 | 13; 55; 70 |
| Specific energy | Wh/kg | 110; 150; 250 | 200; 430; 440 | 230; 650; 640 |
| Energy density | Wh/L | 150; 200; 300 | 250; 500; 550 | 300; 800; 900 |
| Cost | \$/W | 150; 15; 15 | 130; 10; 10 | 70; 7; 5 |
| Durability | Hours | 1,500; 1,500; 2,000 | 3,000; 3,000; 3,000 | 5,000; 5,000; 5,000 |
| Mean time between failures | Hours | 500; 500; 500 | 1,500; 1,500; 1,500 | 5,000; 5,000; 5,000 |

numbers based on information obtained from DMFC systems developers), and using theoretical voltage (V_{th}) of 1.21 V at 25°C, the cell voltage (V_{cell}) targeted in this project can be calculated as:

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

- 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 0.60 V. Very similar voltage targets have been calculated for fuel cells operating on two other fuels, ethanol, and DME.

FY 2013 Accomplishments

- Ultra-thrifted catalysts (uTAAC and uT-PtRuSn) of methanol oxidation have been synthesized in 25 g batches; uT-PtRuSn meets the project anode activity target of 200 mA mg_{Pt}^{-1} at 0.25 V while ultra-thrifted Pt/Ru/C catalyst (uTAAC) is only 13 mV off that target.
- Thrifted PtRu/C catalyst (AAC) has come within 40 mV of the overall DMFC performance target of 0.15 A cm^{-2} at 0.60 V; AAC is ready for 50 cm^2 stack testing by SFC Energy.
- A very low onset potential target of methanol oxidation (0.288 V vs. RHE) has been achieved using PtRu/CuNW catalyst with optimized Pt-to-Ru ratio.
- Johnson Matthey Fuel Cells and Los Alamos National Laboratory data indicate that Ru crossover in MEAs with state-of-the-art carbon-supported PtRu catalysts, though detectable, is much reduced and does not impact oxygen reduction reaction (ORR) activity of the cathode.
- Cracking of metal-black or carbon-supported catalyst layers has little, if any, effect on performance; cracks may facilitate anode operation at high currents.
- Structural changes to the bisphenol unit are very effective in controlling the membrane water uptake and

reducing methanol crossover (by as much as 54% with a tetramethyl bisphenol A-based multi-block copolymer).

- Pt_{ML}/Au/C catalysts of ethanol oxidation have been synthesized by displacing the Cu underpotential deposition (UPD) layer on Au/C and by the microemulsion approach; catalysts have been further altered with various modifiers to enhance activity via the bifunctional approach; Pt_{ML} supported on such nanocores as PdAuFe and PdAuCo shows interesting potential as lower-cost ethanol catalysts.
- RhSnO₂/Pt_{ML}/Au/C catalyst exhibits high ethanol oxidation selectivity; CO₂ is the only product in the potential range of 0.3-0.7 V; non-CO₂ byproducts are observed at very high, and not necessarily direct ethanol fuel cell-relevant electrode potentials (above 0.7 V).
- Current density of 0.15 A cm^{-2} at a DDMEFC voltage of 0.50 V has been reached with a high metal content ternary catalyst of DME oxidation (Pt₄₅Ru₄₅Pd₁₀/C); density functional theory (DFT) calculations confirm the effect of Pd addition on the kinetics of both the C-O and C-H bond scission.



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 methanol, ethanol, and dimethyl ether; on innovative nanostructures for fuel cell electrodes; and on advanced polyaromatic membranes for lower cost MEAs 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 methanol, ethanol, and DME; and (ii) synthesis of polyaromatic multiblock copolymers 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 characterization effort including X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, nuclear magnetic resonance, and transmission electron microscopy.

Development of new catalysts and polymers is closely tied to 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 supports for metal catalysts.

In addition to the short-term testing and initial performance assessment, the catalysts, membranes, supports, electrode structures, and MEAs 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—Development of new methanol oxidation catalysts continued in FY 2013 through “thrifting” of Pt in the advanced anode catalyst (AAC, thrifted binary PtRu/C catalyst developed in FY 2012). The newly developed ultra-thrifted PtRu/C catalyst (uTAAC) has been found to outperform the HiSPEC[®] 12100 benchmark and AAC in terms of methanol oxidation onset potential and mass activity. uTAAC nearly matches AAC in DMFC testing at a loading of only 0.3 mg_{Pt}/cm², compared to the 1.0 mg_{Pt}/cm² catalyst loading of AAC (Figure 1). Furthermore, uTAAC maintains excellent mass activity (only 13 mV off the final project target) throughout the in situ accelerated anode stability test. The highest cycling durability (merely ca. 1% overall performance loss after 300 cycles) has been

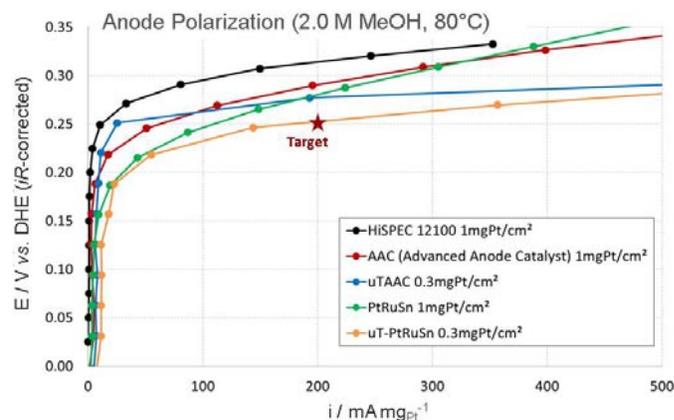


FIGURE 1. DMFC anode polarization plots recorded with new ultra-thrifted uTAAC and uT-PtRuSn catalysts with catalyst loading of 0.3 mg_{Pt}/cm². Polarization plots for AAC, PtRuSn/C and benchmark HiSPEC[®] 12100 PtRu catalysts with catalyst loading of 1.0 mg_{Pt}/cm² shown for reference.

demonstrated with the AAC in accelerated MEA stability testing (Figure 2, bottom). Fuel cell performance has been found not to be affected by limited Ru migration to the cathode, as revealed by post-mortem X-ray tomography of MEAs (Figure 2, top). Anode catalysts are on track to reaching the activity required for meeting the overall DMFC performance target of 150 mA cm⁻² at 0.60 V. This target is expected to be reached with AAC and/or uTAAC without a durability loss.

A highly active ternary PtRuSn/C catalyst was first introduced in FY 2012. Through Pt-thrifting and optimizing Sn content in this ternary catalyst, the new ultra-thrifted PtRuSn/C (uT-PtRuSn) catalyst has been developed in FY 2013. The new catalyst meets the mass-activity target of 200 mA mg_{Pt}⁻¹ at ≤ 0.25 V (80°C) with the Pt loading as low as 0.3 mg_{Pt}/cm² thanks to the effect of Sn at low methanol oxidation overpotentials (Figure 1). In order to become fully viable, the uT-PtRuSn catalyst needs stability improvements at higher operating potentials of the anode.

Future research will focus on further improvements in the DMFC performance and stability through optimization of AAC, uTAAC, and uT-PtRuSn-based anodes, and stabilizations of nano-particulate structures of the catalysts.

Innovative Electrode Structures—A very low onset potential of methanol oxidation of 0.288 V vs. RHE has been achieved by tuning the Pt-to-Ru ratio in the PtRu/CuNW catalyst. This result represents meeting (and exceeding) the onset potential target for the nanostructured PtRu catalysts of ≤ 0.3 V vs. RHE. The mass activity of the PtRu/CuNW catalyst based on the total precious metal content in the catalyst is higher than that of the PtRu/C benchmark catalyst (HiSPEC[®] 12100).

Multiblock Copolymers for Reduced Methanol Crossover—Poly(arylene ether benzonitrile) multiblock

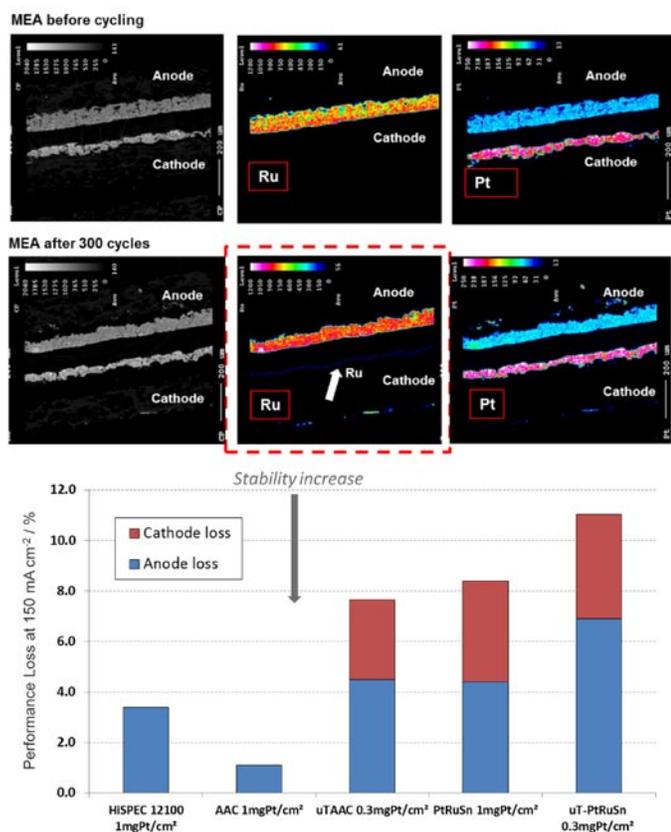


FIGURE 2. In situ accelerated MEA stability test. Post-mortem X-ray tomography of MEAs with an AAC anode revealing small amount of Ru at the cathode catalyst (top). Cathode/anode performance loss breakdown for MEAs after 300 cycles (0.05–0.85 V, 80°C) with different anode catalysts (bottom).

copolymers with high proton conductivity and low methanol permeability were developed in FY 2011 and FY 2012. However, those copolymers had relatively high water uptake often causing delamination with Nafion[®]-bonded catalyst layers. Membrane research in FY 2013 has thus focused on synthesizing multiblock copolymers with reduced water uptake. Chemical modifications for this purpose include (i) control of the fluorination level and (ii) control of the bisphenol structure. In the first approach, the ratio of hexafluoro bisphenol A (6F) to biphenyl (BP) has been varied in the hydrophobic segment in multiblock copolymers. The water uptake of the copolymers has decreased from 54% to 45% as the 6F/BP ratio increased from 0.25 to 1. However, the methanol permeability has also increased, from 1.4×10^{-6} to 2.2×10^{-6} cm² s⁻¹, due to the enhanced methanol solubility upon fluorination. In the second approach, modifications have been introduced to the biphenyl structure of the hydrophobic block segment. Multiblock copolymers having bisphenol A (Bis A), dimethyl bisphenol A (DM), tetramethyl bisphenol A (TM) have been synthesized. The bisphenol structural change turns out to be very effective in reducing both methanol permeability and water uptake. The TM-based multiblock copolymer shows very low methanol permeability

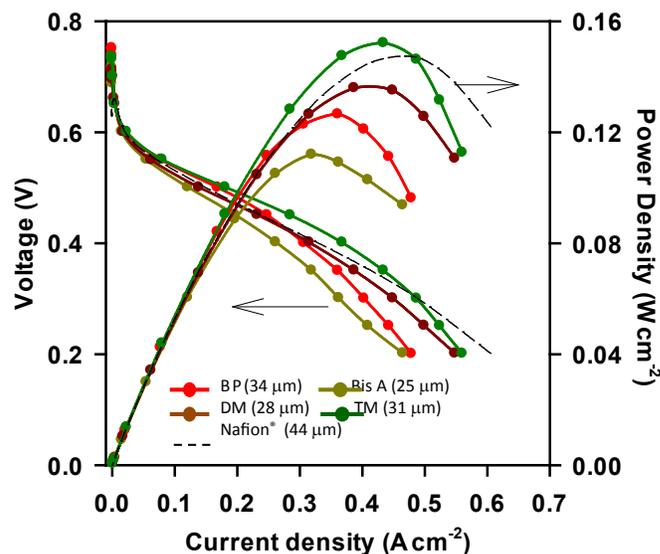
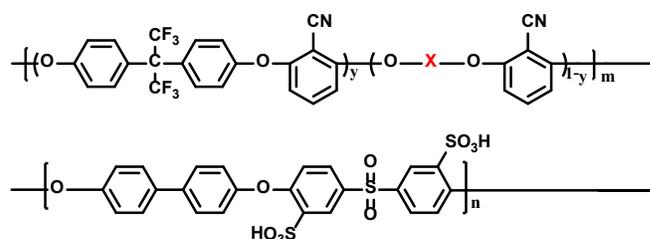


FIGURE 3. DMFC polarization plots recorded with four multiblock copolymer membrane and reference Nafion[®] 115 membrane; $c_{\text{methanol}} = 1.0$ M; cell temperature 75°C. BP: biphenyl; Bis A: bisphenol A; DM: dimethyl bisphenol A; TM: tetramethyl bisphenol A.

(ca. 1.09×10^{-6}) and water uptake (ca. 20%), with good proton conductivity (ca. 0.1 S cm⁻¹). The TM-based multiblock copolymer exhibits excellent performance as shown in Figure 3. Further structural optimization and DMFC durability test using TM-based multi-block copolymer are ongoing.

DMFC Performance Degradation—The rate of DMFC performance degradation with electrodes based on metal-black and carbon-supported catalysts has been studied at three methanol concentrations: 0.5 M, 1.0 M, and 4.0 M. Cathode CO stripping after 100-hour life tests indicates that most of the Ru crossover takes place during a two-hour H₂-air MEA break-in. CO stripping potential is independent of methanol concentration in the following 100 hours of DMFC operation, regardless of the catalyst type (unsupported or supported). In turn, CO stripping from the anode points to no significant change to the surface composition of both catalyst types during the 100-hour test. MEAs with metal black catalysts suffer from more severe Ru crossover than carbon-supported catalysts, which correlates with the performance loss observed with the two catalysts. A very small Ru contamination of the cathode is observed with carbon-supported catalysts, which does not impact the cathode

operation. This agrees with the durability test data involving AAC above.

Post-mortem X-ray tomography of MEAs points to the presence of cracks in as-prepared and tested MEAs (16-19% anode, 8-12% cathode) in Johnson Matthey Fuel Cells carbon-supported catalysts used in gas diffusion electrodes. Los Alamos National Laboratory metal-black electrodes are initially crack-free, with cracks forming during life test (7-9%). The crack formation does not lead to any observable performance loss of metal-black electrodes.

Ethanol Oxidation Catalysts—The DFT prediction of the effect that lattice expansion has on the properties of a Pt monolayer (Pt_{ML}) supported on a single crystal of Au(111) vs. those of Pt(111) has been confirmed by single-crystal model catalyst studies. In agreement with the modeling, a considerable enhancement in the current density of ethanol oxidation is observed upon the Pt_{ML} lattice expansion. The $Pt_{ML}/Au/C$ nanoparticle catalysts have been synthesized by displacing a Cu UPD layer pre-deposited on Au/C nanoparticles. The most active catalyst, with ca. 200 mV lower onset potential of ethanol oxidation and ca. 14 times higher current density at 0.5 V vs. RHE has been developed by further modifying the expanded Pt_{ML} on an Au/C core with SnO_2 to induce bifunctionality.

A one-pot and easily scalable microemulsion synthesis method of $Au@Pt/C$, which is less complex than the Cu UPD method, has been developed (Figure 4, top). The obtained $Au@Pt$ nanoparticles are ca. 4 nm in average size. A SnO_2 -modified bifunctional $SnO_2/Au@Pt/C$ catalyst performs similarly to an analogous catalyst but obtained using the Cu UPD method (Figure 4, bottom). The microemulsion approach represents a new simple synthesis route for large-scale fabrication of Pt/Au core-shell catalysts.

In situ infrared reflection-absorption spectroscopy reveals that CO_2 is the only product of ethanol oxidation on $RhSnO_2/Pt_{ML}/Au/C$ in the potential range of 0.30-0.70 V vs. RHE. CH_3COOH and CH_3CHO are observed at potentials higher than 0.70 V vs. RHE.

Dimethyl Ether Fuel Cell Research—PtRuPd/C catalysts with high metal content (~65 wt%) have been successfully synthesized by a modified polyol method using ethylene glycol as a reducing agent. Transmission electron microscopy data point to a uniform distribution of ca. 2.7 nm PtRuPd nanoparticles on the carbon support. The formation of a $Pt_{45}Ru_{45}Pd_{10}/C$ alloy has been confirmed by the (111) peak shift relative to Pt in X-ray diffraction patterns. Electrochemical testing has shown that $Pt_{45}Ru_{45}Pd_{10}/C$ is more active in DME oxidation than $Pt_{40}Ru_{40}Pd_{20}/C$, $Pt_{34}Ru_{33}Pd_{33}/C$, and HiSPEC® 12100. 10 at% of Pd appears to effectively assist in the C-O bond scission without inhibiting the removal of surface CO by Ru hydroxide/oxides.

A DDMEFC operating with a $Pt_{45}Ru_{45}Pd_{10}/C$ anode can generate 0.15 A cm^{-2} at 0.50 V, by ca. 70 mV outperforming

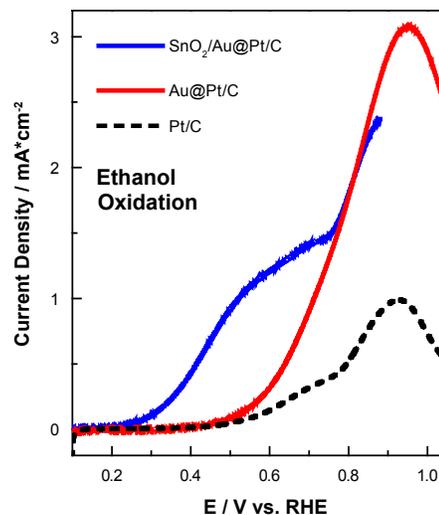
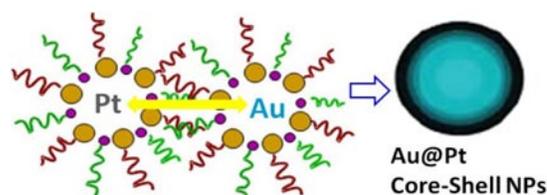


FIGURE 4. Schematic diagram of microemulsion synthesis of $Au@Pt$ core-shell nanoparticles (top). Ethanol oxidation plots on $Au@Pt/C$ and $SnO_2/Au@Pt/C$ catalysts in aqueous 0.1 M $HClO_4$ at room temperature; $c_{ethanol} = 0.5$ M (bottom).

PtRu/C reference catalyst (HiSPEC® 12100). No significant performance loss has been observed after 100 hours of the cell operation (Figure 5).

DFT calculation has confirmed that the addition of Pd to PtRu should result in a significant lowering of the activation energy for both C-H and C-O bond breaking during DME oxidation, by 0.19 eV and 0.25 eV, respectively.

CONCLUSIONS

- New ultra-thrifty catalysts (uTAAC and uT-PtRuSn) of methanol oxidation demonstrate high activity at a Pt loading of 0.3 $mg\ cm^{-2}$. uT-PtRuSn meets the project anode activity target of 200 $mA\ mg_{Pt}^{-1}$ at 0.25 V while uTAAC is only 13 mV off that target.
- AAC shows excellent cycling durability, losing only ca. 1% of its performance after 300 cycles; small Ru migration to the cathode appears to have no effect on durability.
- While Sn enhances methanol oxidation activity at low overpotentials, Sn dissolution from the ternary catalyst needs to be addressed.
- CuNW support benefits the mass activity of PtRu/CuNW without a performance penalty in electrochemical

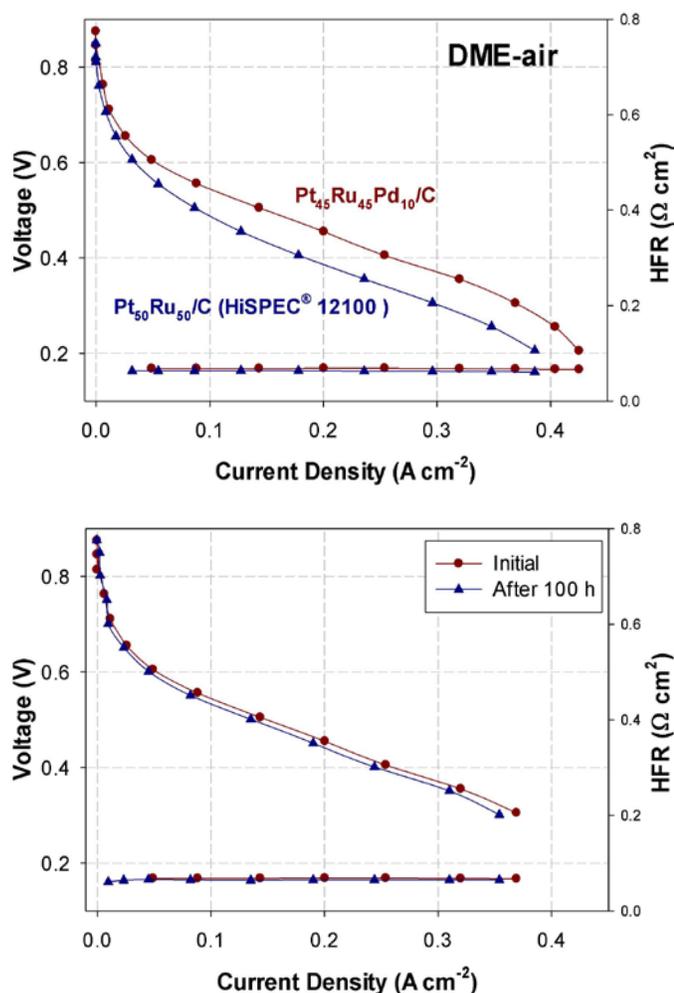


FIGURE 5. DDMEFC polarization plots measured with $\text{Pt}_{45}\text{Ru}_{45}\text{Pd}_{10}/\text{C}$ and HisPEC® 12100 catalysts (top); DDMEFC polarization plots measured with $\text{Pt}_{45}\text{Ru}_{45}\text{Pd}_{10}/\text{C}$ before and after 100-hour life time at 0.4 V (bottom). Anode: $2.7 \text{ mg}_{\text{Pt}} \text{ cm}^{-2} \text{Pt}_{45}\text{Ru}_{45}\text{Pd}_{10}/\text{C}$ or HisPEC® 12100, 40 sccm DME gas, 30 psig; cathode: 4.0 mg cm^{-2} Pt black, 500 sccm air, 20 psig; membrane: Nafion® 212; cell: 80°C .

testing; that result warrants catalyst scale-up for fuel cell testing.

- Structural changes to the bisphenol unit provide an effective method of controlling the membrane water uptake and reducing methanol crossover; the most significant performance improvement has been achieved with a TM-modified membrane.
- One-pot, scalable, and simple microemulsion method yields an $\text{Au}@\text{Pt}/\text{C}$ catalyst with the ethanol/methanol oxidation properties similar to those of an $\text{Au}@\text{Pt}/\text{C}$ catalyst obtained using much more complex Cu UPD method.

- CO_2 is the only product of ethanol oxidation on the ternary $\text{RhSnO}_2/\text{Pt}_{\text{ML}}/\text{Au}/\text{C}$ catalyst in the fuel cell-relevant potential range of 0.30-0.70 V vs. RHE.
- Ru crossover in DMFCs with carbon-supported PtRu anode catalysts is much reduced compared to fuel cells with metal-black anodes; the crossover in cells with carbon-supported PtRu catalysts has little effect on the ORR activity of the cathode over the operating times used in this research.
- A new, high metal-content ternary catalyst of DME oxidation ($\text{Pt}_{45}\text{Ru}_{45}\text{Pd}_{10}/\text{C}$) allows for 0.15 A cm^{-2} to be achieved in a DDMEFC at 0.50 V and shows no significant performance loss after 100 hours of operation.
- DFT calculation confirms the activation effect of Pd in both the C-O and C-H bond scission.

FUTURE DIRECTIONS

- Methanol oxidation catalysis and electrode structures: Improve mass activity of thrifed and ultra-thrifed AAC PtRu/C catalysts; stabilize the nano-particulate structures of PtRu/C and PtRuSn/C to minimize Ru and Sn dissolution; optimize AAC-based anodes; scale up and test in MEAs PtRu platelets and Pt monolayer catalysts; further improve mass activity of PtRu/CuNWs; scale up nanostructured catalyst synthesis; complete 50-cm^2 stack testing.
- Innovative membranes: Optimize membrane thickness and MEA processing with controlled hydrophobicity; improve durability of alternative membranes at higher methanol concentrations; identify the mechanism of DMFC performance degradation in prolonged life tests, up to 500 h; develop mitigation strategies.
- Ethanol oxidation catalysis: Develop catalysts based on expanded Pt monolayers decorated by SnO_2 and Rh islands and optimized such catalysts for ethanol oxidation; scale up ternary and Pt-monolayer catalysts for ethanol oxidation and test in MEAs.
- DME research: Optimize composition and morphology of ternary DME oxidation catalysts to improve mass activity.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Piotr Zelenay, The Electrochemical Society Energy Technology Division Research Award, The Electrochemical Society Meeting, Toronto, Canada, May 2013.
2. Piotr Zelenay, 2012 Los Alamos National Laboratory Patent & Licensing Award (August 2012; for year 2011).

FY 2013 PUBLICATIONS (UNTIL APRIL 2013)

1. M. Li, R.R. Adzic, "Low Platinum Content Electrocatalysts for Methanol and Ethanol Electrooxidation", *Electrocatalysis in Fuel Cells: A Non and Low Platinum Approach*, Edited by Minhua Shao, ISBN 978-1-4471-4911-8, Springer, 2013, Chapter 1, pp. 1-26.
2. M. Li, W.-P. Zhou, N.S. Marinkovic, K. Sasaki, R.R. Adzic, "The Role of Rhodium and Tin Oxide in the Platinum-based Electrocatalysts for Ethanol Oxidation to CO₂", *Electrochim. Acta*, in press.
3. K. Sasaki, M. Li, "Electrocatalysts for Anodic Reactions", *Encyclopedia of Applied Electrochemistry*, edited by Robert F. Savinell, Kenichiro Ota and Gerhard Kreysa. Springer, in press.
4. Q. Li, D. Spornjak, P. Zelenay, Y.S. Kim, "Electrode Degradation of Direct Methanol Fuel Cells Evidenced by X-ray Tomography," *ECS Trans.*, 50 (2), 2199-2205 (2012).
5. Q. Li, G. Wu, Z. Bi, C.M. Johnston, P. Zelenay, "A Ternary Catalyst for Dimethyl Ether Electrooxidation" *ECS Trans.*, 50 (2), 1933-1941 (2012).
6. M. Li, P. Liu, Radoslav R. Adzic, "Platinum Monolayer Electrocatalysts for Anodic Oxidation of Alcohols", *J. Phys. Chem. Lett.* 3, 3480–3485 (2012).
7. M. Li, N.S. Marinkovic, K. Sasaki, "In Situ Characterization of Ternary Pt–Rh–SnO₂/C Catalysts for Ethanol Electrooxidation", *Electrocatalysis* 3, 376-385 (2012).

FY 2013 PRESENTATIONS (UNTIL APRIL 2013)

1. Q. Li, D. Spornjak, P. Zelenay, Y.S. Kim, "Electrode Degradation of Direct Methanol Fuel Cells Evidenced by X-ray Tomography", 222nd Meeting of the Electrochemical Society, Honolulu, Hawaii, October 7–12, 2012.
2. Q. Li, G. Wu, C.M. Johnston, P. Zelenay, "A Ternary Catalyst for Dimethyl Ether Electrooxidation", 222nd Meeting of the Electrochemical Society, Honolulu, Hawaii, October 7–12, 2012.
3. Y. Chen, J.R. Rowlett, C.H. Lee, Y.S. Kim, Q. Li, P. Zelenay, J.E. McGrath, "Controlled Fluorination Level Poly(arylene ether benzonitrile) Hydrophobic-Disulfonated Poly(arylene ether sulfone) Hydrophilic Multiblock Copolymer for Direct Methanol Fuel Cells (DMFCs)", 244th Meeting of the American Chemical Society, August 19–23, 2012, Philadelphia, Pennsylvania.
4. M. Li, R.R. Adzic, "Electrocatalysts for Electrochemical Oxidation of Small Organic Molecules", DARPA Workshop "Low-temperature Electrochemical Oxidation of Hydrocarbon Fuels". Broomfield, CO, July 2012.
5. M. Li, K. Sasaki, M.B. Vukmirovic, R.R. Adzic, "In situ XAS and IRRAS of Platinum Monolayer Fuel Cell Electrocatalysts", 221st Electrochemical Society Meeting. Seattle, WA, May 2012.
6. Q. Li, G. Wu, Y.S. Kim, C.M. Johnston, P. Zelenay, "Direct Dimethyl Ether Fuel Cell with Much Improved Performance", 221st Meeting of the Electrochemical Society, Seattle, Washington, May 6-10, 2012.

REFERENCE

1. *Multi-Year Research, Development and Demonstration Plan: Section 3.4 Fuel Cells*, Fuel Cell Technologies Program, 2011. http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf