

V.J.1 Advanced Materials and Concepts for Portable Power Fuel Cells

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Project Start Date: September 2010

Project End Date: August 2014

- Synthesize multi-block copolymers capable of delivering $>200 \text{ mA cm}^{-2}$ at 0.5 V in a single-cell DMFC test at 75°C .
- Develop alternative oxides and intermetallic Pt supports for ethanol (EtOH) oxidation.
- Improve mass activity of the ternary PtRuPd/C dimethyl ether (DME) oxidation catalyst from the FY 2013 performance of 37 A/g to 50 A/g at 0.5 V in a single-cell direct DME fuel cell test at 80°C .
- Complete DMFC testing of a short stack, utilizing components developed in the project.

Technical Barriers

This project addresses the following technical barriers in the Fuel Cells section 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 the Fuel Cells 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 a guide with relevance to portable power systems, the following specific project targets have been devised:

- System cost target: \$5/W
- Performance target: Overall fuel conversion efficiency (η_{Σ}) 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_{Σ}) of 0.42-0.52, corresponding to a 1.6-2.0-fold improvement over state-of-the-art systems (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 numbers based on information obtained from DMFC systems developers), and using a theoretical voltage (V_{th}) of 1.21 V at 25°C , the cell voltage (V_{cell}) targeted in this project can be calculated as:

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

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 power fuel cell systems; assure path to large-scale fabrication of successful materials.

Fiscal Year (FY) 2014 Objectives

- Optimize thrifed "advanced anode catalyst" (AAC) to achieve key direct methanol (MeOH) fuel cell (DMFC) performance goal of 150 mA cm^{-2} at 0.6 V with low Pt loadings ($<1.0 \text{ mg cm}^{-2}$ at anode).
- Scale up the synthesis of PtRu/CuNWs to a 10-mg batch and test in MEAs.

TABLE 1. Project Technical Targets

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

Thus, the ultimate target of the material development efforts in the DMFC part of this project is to assure an operating single fuel cell voltage of ca. 0.60 V. Very similar voltage targets have been calculated for fuel cells operating on two other fuels, EtOH and DME.

FY 2014 Accomplishments

- Advanced anode catalysts that use much lower Pt loading compared to current state-of-the-art HiSPEC[®] 12100 PtRu/C catalyst (1.0 mg_{Pt} cm⁻² vs. 2.7 mg_{Pt} cm⁻²) were developed. Catalyst-coated membranes prepared by JMFC using the AAC were provided to SFC Energy for stack testing. In spite of much lower Pt loading, AAC exhibits better stability over 2,500 hours of stack operation than commercial catalyst without sacrificing performance.
- Tetramethyl bisphenol A (TM)-based multiblock copolymer systems with less than 30% water uptake and comparable proton conductivity to Nafion[®] were developed. MEAs using TM-based multiblock copolymers reached >200 mA/cm² at 0.5 V (75°C) with stable long-term performance without interfacial failure under DMFC accelerated stress test conditions.
- Direct DME fuel cell (DDMEFC) performance reached 0.220 A cm⁻² at 0.5 V (an anode catalyst mass-specific activity of 55 A g⁻¹) thanks to the development of a new ternary Pt₅₅Ru₃₅Pd₁₀/C catalyst and optimization of DDMEFC operating conditions. This not only exceeds the FY 2014 performance target, but also is the first time that performance of the DDMEFC matches and outperforms that of state-of-the-art DMFCs.



INTRODUCTION

This multitask, multi-partner project targets advancements to portable fuel cell technology through the development and implementation of novel materials and concepts for enhancing performance, lowering cost, minimizing size and improving durability of fuel cell power systems for consumer electronics and other mobile and off-grid applications. The primary focus areas of the materials research in this project are: (i) electrocatalysts for the oxidation of MeOH, EtOH, and DME; (ii) innovative nanostructures for fuel cell electrodes; and (iii) hydrocarbon membranes for reduced MEA costs and enhanced fuel cell performance (fuel crossover, proton conductivity). In parallel with new materials, this project targets the development of various operational and materials-treatment concepts, concentrating among others on the improvements to the long-term performance of individual components and the complete MEA.

APPROACH

The two primary research goals of this project are: (i) 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 characterization efforts 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 contents, maximize mass activity and enhance durability. The electrode-structure component of the efforts 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 are also being tackled through collaboration between partners in this project.

RESULTS

DMFC Catalysts—Further development of the AAC, thrifed binary PtRu/C catalyst first synthesized in FY 2012, continued in FY 2014 to meet the project milestone of 0.15 A cm^{-2} at 0.60 V through: (i) optimizing the Pt-to-Ru ratio to lower the onset potential of MeOH oxidation, (ii) using a lower carbon content to thin the electrode

layer, and (iii) modifying the cell operation conditions (temperature, MeOH concentration). Among several Pt-to-Ru ratios, a 1:4 atomic ratio represented the optimum catalyst composition for fast dehydrogenation, efficient CO removal and low Ru crossover to the cathode. Additionally, increasing the Pt+Ru loading by 33% in AAC to thin the electrode had no effect on catalytic activity. When the cell temperature was increased to 88°C from 80°C , a gain of 20 mV at 150 mA cm^{-2} was obtained. With an increase in MeOH concentration from 0.5 M to 0.6 M , improvements in the current density at potentials lower than ca. 0.55 V were observed without any additional MeOH crossover loss. With these optimizations, a high performance of 0.56 V at 0.150 A cm^{-2} was achieved at 88°C , only 0.04 V away from the project target (Figure 1). Ten 50-cm^2 MEAs with optimized AAC were provided by JMFC to SFC Energy for stack testing. Noticeably, a decay rate of only $19 \mu\text{V/h}$ (per cell) was obtained, slightly lower than in commercial MEAs with much higher Pt loadings (Figure 2). This attests to AAC as a very promising catalyst with potential to enable DMFCs for higher power applications (such as kW-level power generators). A maximum stack voltage was reached after 70 hours of operation, and the

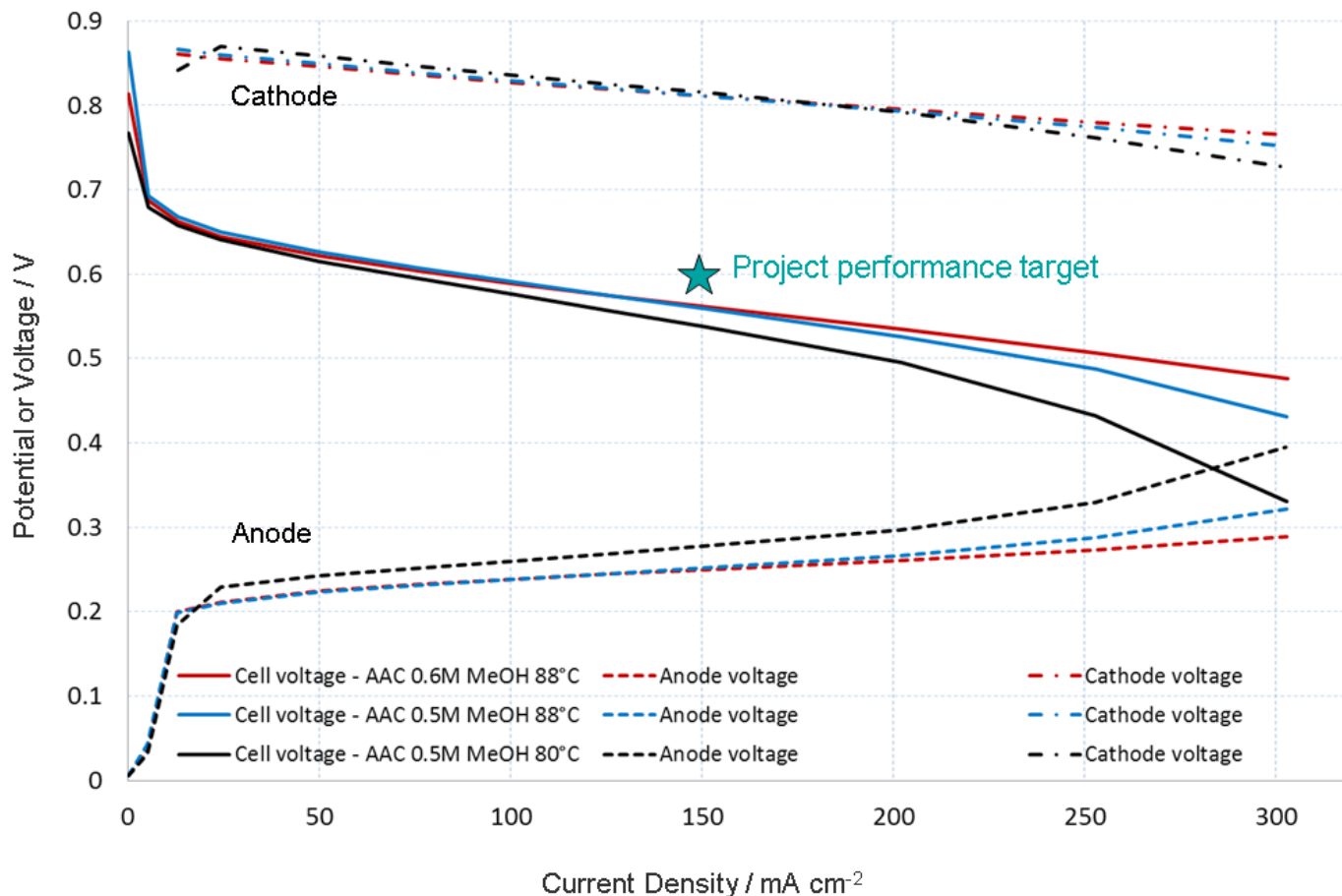


FIGURE 1. Polarization plots for AAC with catalyst loading $1.0 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$, 0.5-0.6 M MeOH. Cathode - Pt/C catalyst loading $1.5 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$, air (fuel cell), H_2 (anode polarization); Nafion[®] 115 membrane; cell temperature 80-88°C.

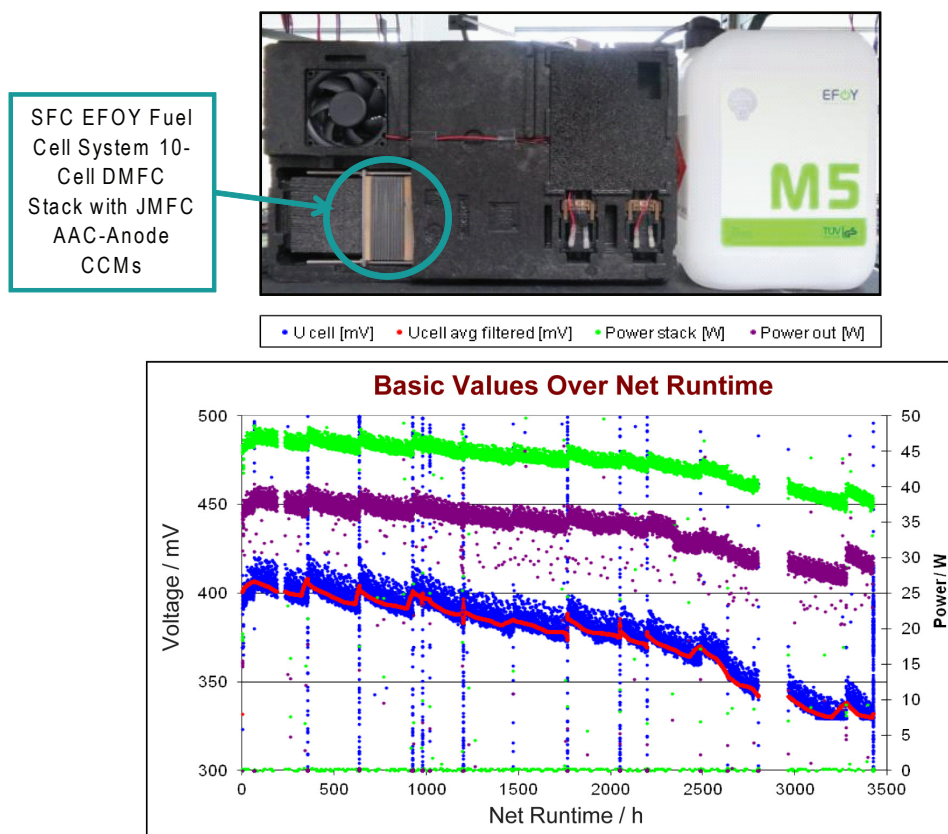


FIGURE 2. Durability Test of Ten-Cell DMFC Stack with JMFC AAC-Anode CCM

performance discontinuity observed around 2,800 hours of operation was due to pump failure.

Innovative Electrode Structures—In FY 2014, a successful scale up of PtRu/CuNWs from 5 mg to 19 mg per batch was achieved, accompanied by slightly higher MeOH oxidation activity. The cause of higher MeOH oxidation activity of PtRu/CuNWs compared to that of PtRu/C may be due to the facile removal of CO from the PtRu/CuNWs surface, as demonstrated by X-ray photoelectron spectroscopy Pt 4f and Ru 3p shifts.

Multiblock Copolymers for Better Interfacial Compatibility—We have focused this year on synthesizing multiblock copolymers with better interfacial compatibility with DMFC electrodes. It was achieved by reducing the membrane water uptake. Chemical modifications for this purpose included control of the fluorination level and of the bisphenol structure. We have successfully synthesized TM-based multiblock copolymers. This TM system had a water adsorption nearly half that of the dimethyl and bis A proton exchange membranes. MEAs using the highly hydrophobic TM system not only showed excellent DMFC performance, but met the FY 2014 performance milestone reaching $>200 \text{ mA/cm}^2$ at 0.5 V (75°C). In addition, the TM-based multiblock copolymers showed good interfacial compatibility

with Nafion[®]-bonded electrodes. Figure 3 shows the high-frequency resistance (HFR) of DMFC cells using three different membranes. The HFR of the cell using 6FPAEB-BPSH (water uptake = 57 vol%) constantly increases from 0.073 to 0.13 $\Omega \text{ cm}^2$ after 110 hours of the extended-term test. In contrast, the TM multi-block copolymer (water uptake = 23 vol%) shows stable HFR behavior during the entire 110 hour extended-term test. Nafion[®], which has a water uptake of 39 vol%, also shows a stable HFR behavior, likely due to the synergistic effect of low water uptake and a highly fluorinated structure. These results confirm our hypothesis regarding interfacial delamination and TM-based multi-block copolymers, and have the potential to be applied in practical liquid-fueled fuel cell applications.

Ethanol Oxidation Catalysts—In FY 2014, combustion catalyst synthesis was developed as a way of forming multi-component catalysts in a single-step that were successfully deposited on gas diffusion layers. The ternary catalyst (PtRhSnO₂/C) synthesized by this method exhibited excellent activity and stability at 25°C and 60°C.

To solve the SnO₂ instability issues, which were recognized in FY 2013, several oxides and intermetallic compounds were studied as supports that can replace SnO₂. Among several oxides investigated (CeO₂, Ti₄O₇, ITO,

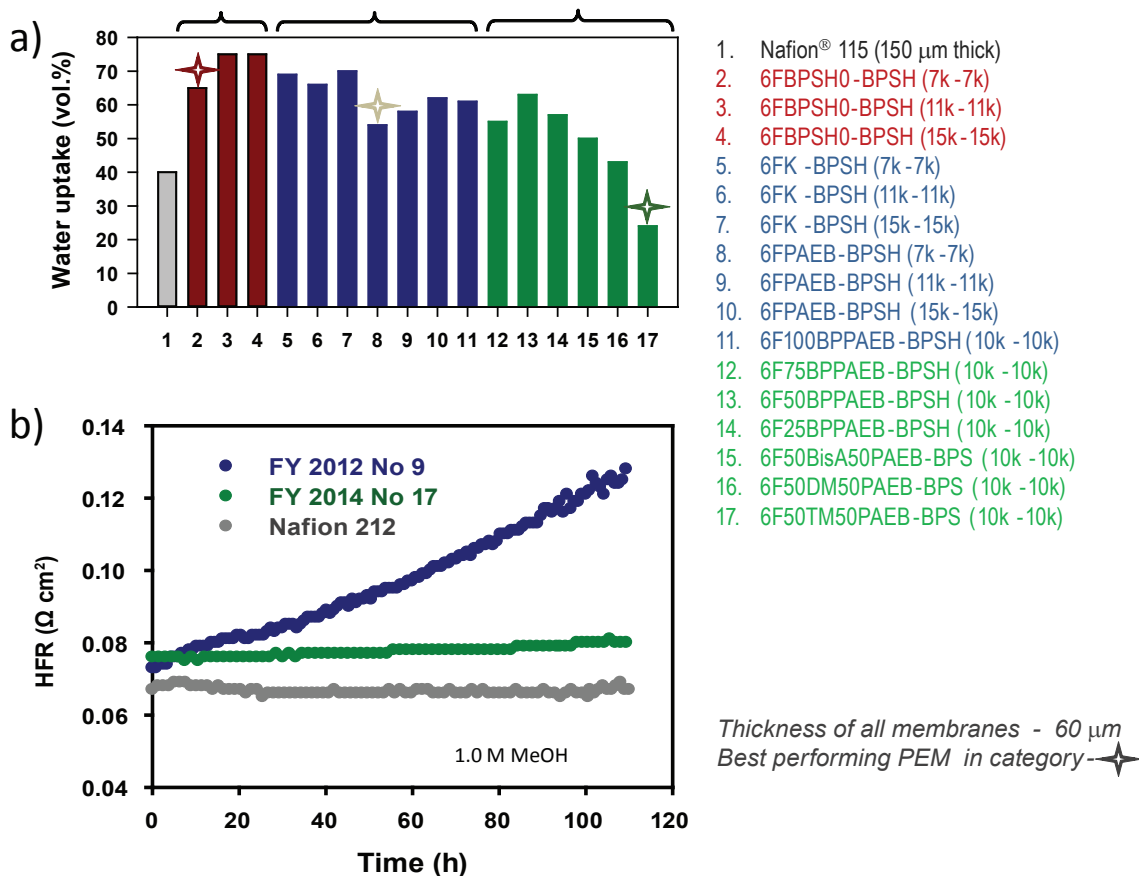


FIGURE 3. (a) Volumetric water uptake of multiblock copolymers (best performing membranes for each year denoted as \star), (b) its impact on DMFC durability. No. 9: FY 2012, membrane 6FPAEB-BPSH (11K-11K); No. 17: FY 2014 membrane 6F50TM50PAEB-BPS (10K-10k).

and IrO_x), IrO_x in particular was identified as a promising replacement for the SnO_2 in the ternary catalysts, and CeO_2 was also found to considerably enhance the activity of $\text{Pt}_{\text{ML}}/\text{Pd}/\text{C}$ catalysts for EtOH oxidation. The intermetallic compound, PdAuCo, also exhibits better performance as a Pt_{ML} support than core-shell PdAuCo.

Dimethyl Ether Fuel Cell Research—Significant progress was made in MEA and fuel delivery system optimization. Thanks to these advancements, from FY 2013 to FY 2014, DDMEFC performance increased from 0.095 A cm^{-2} to 0.215 A cm^{-2} at 0.5 V, in spite of lowering the Pt-group metal anode loading by 25%. Based on density functional theory calculations, in FY 2013 we proposed the individual role of each metal in the ternary PtRuPd/C catalysts as follows: Pt—primary DME adsorption and dehydrogenation; Ru—source of oxidant for CO removal; Pd—C-O and C-H bond scission catalyst. In FY 2014, using two binary PtPd/C and PtRu/C catalysts, we experimentally demonstrated that Pd addition indeed results in higher current densities with the same onset potential observed with Pt, and Ru leads to a lower onset potential of DME oxidation. This finding allowed

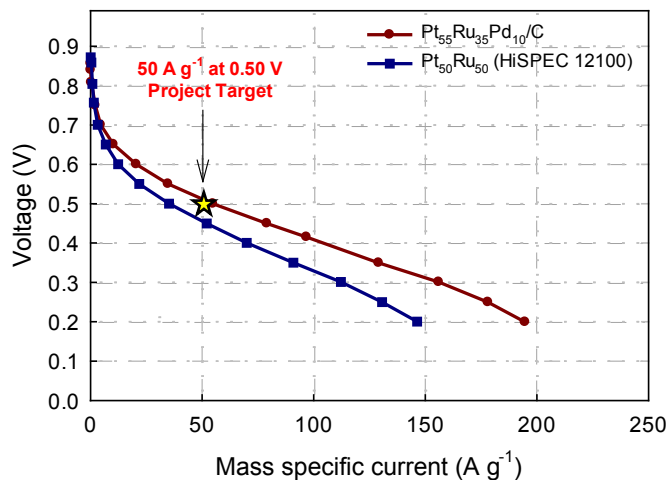


FIGURE 4. Polarization plots of DDMEFC. Anode: $4.0 \text{ mg}_{\text{PGM}} \text{ cm}^{-2}$ PtRuPd/C, HiSPEC[®] 12100, 40 sccm DME gas, 26 psig; cathode: $2.0 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ Pt/C HiSPEC[®] 9100, 100 sccm air, 20 psig; Nafion[®] 212 membrane; cell temperature 80°C.

us to develop an advanced ternary Pt₅₅Ru₃₅Pd₁₀/C catalyst, more advanced than the Pt₄₅Ru₄₅Pd₁₀/C catalyst developed in FY 2013. DDMEFC performance measured with this catalyst reached a high current density of 0.220 A cm⁻² (an anode catalyst mass-specific activity of 55 A g⁻¹) at 0.5 V, exceeding the FY 2014 performance target (Figure 4). Due to the new ternary Pt₅₅Ru₃₅Pd₁₀/C DME oxidation catalyst developments and optimization of the MEA and DDMEFC operation conditions over the project duration, DDMEFC performance has been improved by a factor of 2.5× in terms of current density at 0.5 V. This makes the performance of the latest-generation DDMEFC exceed that of the state-of-the-art DMFC (Figure 5).

CONCLUSIONS

- JMFC's AAC reached 0.150 A cm⁻² at 0.56 V with low anode loading of 1.0 mg_{Pt} cm⁻² (total 2.5 mg_{Pt} cm⁻²).
- AAC-based catalyst-coated membranes prepared by JMFC were used for a 10-cell SFC Energy stack test. In spite of much lower Pt loading (1.0 mg_{Pt} cm⁻² vs. 2.7 mg_{Pt} cm⁻² of HiSPEC[®] 12100), AAC showed better stability over 2,500 hours of stack operation than commercial catalysts.
- Progress in MeOH catalyst development is viewed by SFC Energy as an enabling factor for higher power DMFC applications (i.e., power generators) that are currently not feasible due to the prohibitive catalyst cost.
- A high current density of 0.200 A cm⁻² at 0.50 V (75°C) was achieved with TM-based multi-block copolymer. A 60-μm TM-based MEA showed lower resistance, MeOH crossover and water uptake than a Nafion[®] 115-based MEA—a DMFC industry standard.
- Significant progress in DME electrocatalysis with the development of ternary PtRuPd/C catalyst in conjunction with MEA and fuel delivery system optimization was demonstrated to result in a DDMEFC current density of 220 A cm⁻² at 0.5 V (an anode catalyst mass-specific activity of 55 A g⁻¹)—a 2.5-fold improvement in activity since project inception.
- The LANL DDMEFC was demonstrated to exceed state-of-the-art DMFCs across the entire range of current densities.
- Recent advancements in ethanol oxidation electrocatalysis at Brookhaven National Laboratory (Pt_{ML}/Au/C catalyst) led to a ca. 200 mV reduction in overpotential for EtOH oxidation relative to Pt/C.

FUTURE DIRECTIONS

- DMFCs: Complete current catalyst development efforts to meet the last remaining project milestone (0.15 A cm⁻² at 0.60 V); develop MeOH oxidation catalysts free of

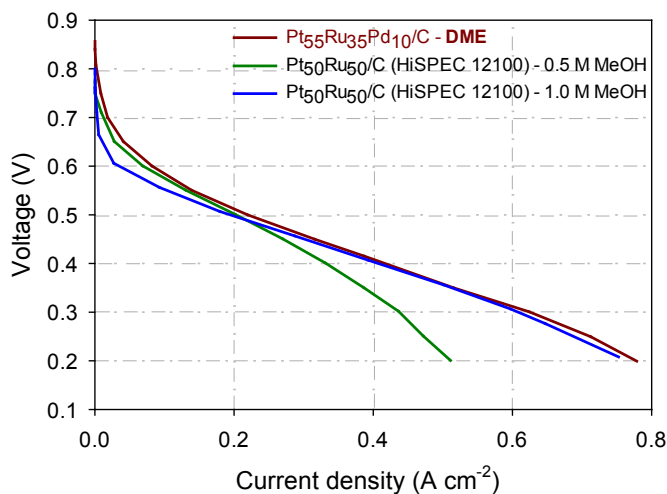


FIGURE 5. DDMEFC and DMFC performance comparison. Anode: 4.0 mg_{metal} cm⁻² PtRuPd/C, HiSPEC[®] 12100, 40 sccm DME gas, 26 psig, 1.8 mL/min 0.5 M or 1.0 M MeOH, 0 psig; cathode: 2.0 mg_{Pt} cm⁻² Pt/C HiSPEC[®] 9100, 100 sccm air, 20 psig; Nafion[®] 212 membrane (DME), Nafion[®] 115 membrane (MeOH); cell temperature 80°C.

intrinsically unstable components (possible formulations include two-dimensional platelets containing low-coordination atoms of precious metals and Au-core nanoparticles as supports); develop inks, gas diffusion layer treatments, optimize and assure manufacturability by a scalable production process for AAC targeting 50% Pt reduction in two years without performance/durability penalty (30% Pt reduction in FY 2015) and 500-W system.

- DDMEFCs: Complete development and optimization of the ternary PtRuPd catalyst for DME oxidation; implement multiblock copolymer membranes in DDMEFC-type MEAs; complete detailed study of DME crossover and its impact on DDMEFC performance.
- EtOH oxidation catalysis: Develop new-generation catalysts for EtOH oxidation, for example, catalysts on composites of stable oxides and lattice-expanded nanoparticles of precious metals; use in-fuel-cell stability and 12-electron selectivity as primary performance and selection criteria; perform assessment of direct EtOH fuel cell viability at the present state of ethanol oxidation catalysis.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Piotr Zelenay has been named a Fellow of The Electrochemical Society, 2014.

FY 2014 PUBLICATIONS

1. Yu Seung Kim, Kwan-Soo Lee, "Fuel Cell Membrane Characterizations", *Polym. Rev.*, in press.
2. Meng Li, Nebojsa S. Marinkovic, "In situ Infrared Spectroelectrochemistry: Principles and Applications", in *Infrared Spectroscopy: Theory, Developments and Applications*. Edited by Daniel Cozzolino. Nova Science Publishers, in press.
3. Qing Li, Gang Wu, Christina M. Johnston, Piotr Zelenay, "Direct Dimethyl Ether Fuel Cell with Much Improved Performance", *Electrocatalysis*, 2014, 10.1007/s12678-014-0196-z.
4. Jarret R. Rowlett, Yu Chen, Andrew T. Shaver, Gregory B. Fahs, Benjamin J. Sundell, Qing Li, Yu Seung Kim, Piotr Zelenay, Robert B. Moore, Sue Mecham, James E. McGrath, "Multiblock Copolymers Based Upon Increased Hydrophobicity Bisphenol A Moieties for Proton Exchange Membranes;" *J. Electrochem. Soc.* 161 (4) F535-F543 (2014).
5. Yijin Kang, Meng Li, Yun Cai, Matteo Cargnello, Rosa E. Diaz, Thomas R. Gordon, Noah L. Wieder, Radoslav R. Adzic, Raymond J. Gorte, Eric A. Stach, Christopher B. Murray, "Heterogeneous Catalysts Need Not Be so 'Heterogeneous': Monodisperse Pt Nanocrystals by Combining Shape-Controlled Synthesis and Purification by Colloidal Recrystallization", *J. Am. Chem. Soc.*, 135 (7), 2741-2747 (2013).
6. Qing Li, Yu Chen, Jarrett R. Rowlett, James E. McGrath, Nathan H. Mack, Yu Seung Kim, "Controlled Disulfonated Poly(Arylene Ether Sulfone) Multiblock Copolymers for Direct Methanol Fuel Cells", *ACS Appl. Mater. Interfaces*, 6, 5779-5788, 2014.
7. Meng Li, David A. Cullen, Kotaro Sasaki, Nebojsa S. Marinkovic, Karren L. More, Radoslav R. Adzic, "Ternary Electrocatalysts for Oxidizing Ethanol to Carbon Dioxide: Making Ir Capable of Splitting C-C bond", *J. Am. Chem. Soc.*, 135 (1), 132-141 (2013).
8. Hoon T. Chung, Joseph H. Dumont, Ulises Martinez, Piotr Zelenay, "Catalyst Development for Dimethyl Ether Electrooxidation", 225th Meeting of the Electrochemical Society, Orlando, Florida, May 11-16, 2014.
9. R.R. Adzic, "Platinum Monolayer Electrocatalysts: Tuning Their Properties by Core-shell Interactions", CEC 2014 Annual Workshop on Electrochemistry, University of Texas at Austin, Texas, February 8-9, 2014 (invited lecture).
10. R.R. Adzic, "Platinum Monolayer Electrocatalysts: Recent Improvements for the Oxygen Reduction Reaction and the Oxidation of Ethanol and Methanol", Electrochemical Conference on Energy and Environment, Shanghai, China, March 13-16, 2014 (invited keynote lecture).
11. Piotr Zelenay, "Development and Characterization of Catalysts for Fundamental Electrode Reactions in Polymer Electrolyte Fuel cells", Department of Chemistry, University of Warsaw, Warsaw, Poland, December 9, 2013 (invited lecture).
12. Jie Zheng, David Cullen, Yushan Yan, "PtRuCuNWs catalysts for methanol oxidation reaction in direct methanol fuel cells", 224th Meeting of the Electrochemical Society, San Francisco, California, October 27 – November 1, 2013.
13. Qing Li, Dusan Spornjak, Yu Seung Kim, Piotr Zelenay, Performance Stability of Carbon-Supported vs. Metal-Black DMFC Catalysts, 224th Meeting of the Electrochemical Society Meeting, San Francisco, California, October 27 – November 1, 2013.
14. Jie Zheng, Yushan Yan, "PtRu coated CuNWs as an efficient catalyst for methanol oxidation reaction", Center for Catalytic Science and Technology Annual Review, Newark, Delaware, October 10, 2013.
15. Jie Zheng, Yushan Yan, "PtRu coated CuNWs as an efficient catalyst for methanol oxidation reaction", SUNCAT Summer Institute 2013, Menlo Park, California, August 26, 2013 (poster).

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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