Advanced Materials and Concepts for Portable Power Fuel Cells

Piotr Zelenay

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Project ID: FC091
Overview

Timeline

• Project start date: September 1, 2010
• Project end date: August 31, 2014

Budget

• FY13 DOE funding: $1,048K
• Planned FY14 funding: $810K
• Total DOE project value: $3,825K
• Cost share: 8.2%

Barriers

• A. Durability (catalyst; electrode)
• B. Cost (catalyst; membrane; MEA)
• C. Electrode Performance (fuel oxidation kinetics)

Partner Organization

– Principal Investigator

– Radoslav Adzic
– Yushan Yan
– James McGrath
– Alex Martinez Bonastre
– Christian Böhm
– Karren More
Relevance: Objective & Targets

**Objective:** Develop advanced materials (catalysts, membranes, electrode structures, membrane-electrode assemblies) 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.

### Original project technical targets (to be relaxed given modified targets above):

- **System cost target:** $3/W
- **Performance target:** Overall fuel conversion efficiency ($\eta_{\Sigma}$) of 2.0-2.5 kWh/L

For methanol fuel:

1. $2.0-2.5 \text{ kWh/L} \rightarrow \eta_{\Sigma} = 0.42-0.52$ (1.6-2.0× improvement over the state of the art, ~ 1.250 kWh/L)

2. If $\eta_{\text{fuel}} = 0.96$, $\eta_{\text{BOP}} = 0.90$, $V_{\text{th}} = 1.21$ (at 25°C)

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

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### Technical Targets: Portable Power Fuel Cell Systems (< 2 W; 10-50 W; 100-250 W)

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2011 Status</th>
<th>2013 Targets</th>
<th>2015 Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific power</td>
<td>W/kg</td>
<td>5; 15; 25</td>
<td>8; 30; 40</td>
<td>10; 45; 50</td>
</tr>
<tr>
<td>Power Density</td>
<td>W/L</td>
<td>7; 20; 30</td>
<td>10; 35; 50</td>
<td>13; 55; 70</td>
</tr>
<tr>
<td>Specific energy</td>
<td>Wh/kg</td>
<td>110; 150; 250</td>
<td>200; 430; 440</td>
<td>230; 650; 640</td>
</tr>
<tr>
<td>Energy density</td>
<td>Wh/L</td>
<td>150; 200; 300</td>
<td>250; 500; 550</td>
<td>300; 800; 900</td>
</tr>
<tr>
<td>Cost</td>
<td>$/W</td>
<td>150; 15; 15</td>
<td>130; 10; 10</td>
<td>70; 7; 5</td>
</tr>
<tr>
<td>Durability</td>
<td>Hours</td>
<td>1,500; 1,500; 2,000</td>
<td>3,000; 3,000; 3,000</td>
<td>5,000; 5,000; 5,000</td>
</tr>
<tr>
<td>Mean time between failures</td>
<td>Hours</td>
<td>500; 500; 500</td>
<td>1,500; 1,500; 1,500</td>
<td>5,000; 5,000; 5,000</td>
</tr>
</tbody>
</table>
Approach: Focus Areas & FY15 Milestones

- **DMFC anode research** (JMFC, LANL, BNL):
  (i) new catalysts with improved activity and reduced cost; (ii) durability improvements
- **Innovative electrode structures for better activity and durability** (UD)
- **Hydrocarbon membranes for lower MEA cost and enhanced fuel cell performance** (VT, LANL):
  (i) block copolymers; (ii) copolymers with cross-linkable end-groups
- **Alternative fuels for portable fuel cells:**
  (i) dimethyl ether research (LANL); (ii) ethanol oxidation electrocatalysis (BNL)
- **Advanced materials characterization** (ORNL, BNL, LANL); **MEA performance testing, including durability** (LANL, JMFC, SFC); **ten-cell stack** (SFC)

<table>
<thead>
<tr>
<th>Date</th>
<th>Milestones</th>
<th>Status</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dec 13</td>
<td>Synthesize multiblock copolymer based on tetramethyl bisphenol A capable of delivering &gt; 200 mA cm(^{-2}) at 0.50 V (DMFC, 75°C).</td>
<td>Complete</td>
<td>&gt; 200 mA cm(^{-2}) at 0.50 V achieved in a DMFC operating with TM-based multiblock copolymer at a cell temperature of 25°C</td>
</tr>
<tr>
<td>Mar 14</td>
<td>Improve mass activity of the precious metal catalyst of DME oxidation from the present-day 37 A g(^{-1}) to 50 A g(^{-1}) at 0.50 V (DDMEFC, 80°C).</td>
<td>Complete</td>
<td>Mass activity of 55 A g(^{-1}) (0.230 A cm(^{-2})) achieved with LANL-developed ternary Pt(<em>{55})Ru(</em>{35})Pd(_{10})/C catalyst at low Pt cathode loading (2.0 mg cm(^{-2})).</td>
</tr>
<tr>
<td>Jun 14</td>
<td>Achieve the DMFC performance goal of 150 mA cm(^{-2}) at 0.6 V with low Pt loadings (&lt; 1.0 mg cm(^{-2}) at anode).</td>
<td>Pending</td>
<td>Presently 40 mV away from target (150 mA cm(^{-2}) at 0.56 V, 90°C).</td>
</tr>
<tr>
<td>Sep 14</td>
<td>Complete testing of a short stack utilizing fully optimized new components developed in the project.</td>
<td>Complete</td>
<td>10-cell DMFC stack utilizing JMFC’s “advanced anode catalyst” (AAC) tested by SFC Energy for over 2,500 h; performance loss below that of a commercial stack with 2× higher PtRu loading.</td>
</tr>
</tbody>
</table>
MeOH Oxidation: Advanced Anode Catalyst (AAC) Development

**Main activities:** (i) further development of AAC (advanced anode catalyst) to meet the project milestone (0.15 A cm\(^{-2}\) at 0.60 V) and (ii) stack demonstration (in collaboration with SFC Energy)

**Strategy:** (i) increase AAC loading from 1.0 to 2.0 mg\(_{Pt}\) cm\(^{-2}\) (backup slide); (ii) lower carbon content to thin electrode layer; (iii) optimize Pt-to-Ru ratio to lower onset potential of MeOH oxidation; (iv) modify cell operating conditions (temperature, concentration)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt:Ru atomic ratio</th>
<th>Surface area by CO(_{ads}) (m(^{2}) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HiSPEC(^{\circledR}) 12100</td>
<td>1:1</td>
<td>37</td>
</tr>
<tr>
<td>PtRu/C advanced anode catalyst (AAC)</td>
<td>1:4</td>
<td>20</td>
</tr>
<tr>
<td>PtRuC (new catalyst)</td>
<td>1:6</td>
<td>29</td>
</tr>
</tbody>
</table>

- No significant gain in AAC performance brought about by catalyst loading increase (backup slide)
- A 33% increase in wt% of metal (Pt+Ru) in AAC having no effect on catalytic activity
- Pt-to-Ru 1:4 atomic ratio: Optimum combination of fast dehydrogenation, efficient CO removal and low Ru crossover to cathode
- **Highlight:** Ten 50 cm\(^{2}\) MEAs with optimized AAC prepared and supplied to SFC Energy for final stack testing
MeOH Oxidation: Testing Under Different Conditions

Anode: AAC, 1.0 mgPt cm$^{-2}$, 0.5 - 0.6 M MeOH; Cathode: Pt/C, 1.5 mgPt cm$^{-2}$, air (fuel cell), H$_2$ (anode polarization);
Membrane: Nafion® 115; Cell: 80 - 88°C

- An increase in cell temperature to 88°C bringing a gain of 20 mV at 150 mA cm$^{-2}$
- **Highlight**: Improvement in high current density observed without any additional methanol crossover loss with 0.6 M
- A decrease in $c_{MeOH}$ from 0.6 M at 80°C (0.5 M at 88°C) to 0.4 M resulting in mass transport limitations at a current density of 150 mA cm$^{-2}$

**Cell performance achieved:** $0.56 \text{ V at } 0.150 \text{ A cm}^{-2}$ (88°C)
(at present, only 0.04 V away from target)
Ten-Cell Direct Methanol Fuel Cell Stack

SFC EFOY Fuel Cell System 10-Cell DMFC Stack with JMFC AAC-Anode CCMs

- Maximum stack voltage reached 70 h of operation
- Pump failure after ca. 2,500 h apparently affecting performance at longer times
- **Highlight:** Decay rate of 19 μV/(h per cell), slightly lower than in commercial MEAs with much higher Pt loadings

**Stack milestone completed**

AAC – promises to enable DMFCs for higher power applications
MeOH Oxidation: PtRu Nanostructures (SEM, TEM, HADDF-STEM)

<table>
<thead>
<tr>
<th>PtRuNTs</th>
<th>PtRuCuNWs</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="SEM" /></td>
<td><img src="image2" alt="SEM" /></td>
</tr>
<tr>
<td><img src="image3" alt="TEM" /></td>
<td><img src="image4" alt="TEM" /></td>
</tr>
<tr>
<td><img src="image5" alt="HAADF-STEM" /></td>
<td><img src="image6" alt="HAADF-STEM" /></td>
</tr>
</tbody>
</table>

PtRuCuNWs: Cu-rich core, PtRu-rich shell
MeOH Oxidation: Innovative PtRu Nanostructure Catalysts

**Activity**

Solution: 1.0 M MeOH in 0.1 M HClO₄
PtRu/C: HiSPEC® 12100, Scan rate: 5 mV/s

- XPS Pt 4f and Ru 3p shifts attesting to facile removal of CO from PtRuCuNWs surface
- **Highlight:** Successful scale-up of PtRuCuNWs from 5 mg to 19 mg per batch
Decoration of Expanded Pt Monolayer with Ru for Improved MeOH Oxidation Activity

CO$_2$ the only observed product of methanol oxidation

- Ru deposition causing a shift in the onset potential of CO oxidation to ca. 0.30 V vs. RHE (25°C)

- Different Ru quantities allowing fine-tuning MeOH oxidation activity

<table>
<thead>
<tr>
<th>Ru Nanoclusters</th>
<th>Onset Potential at 0.05 mA (V)*</th>
<th>$i/i_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_{ML}$/Au</td>
<td>0.288</td>
<td>1.2</td>
</tr>
<tr>
<td>Ru$<em>{ML}$/Pt$</em>{ML}$/Au</td>
<td>0.185</td>
<td>3.1</td>
</tr>
<tr>
<td>Ru$<em>{2ML}$/Pt$</em>{ML}$/Au</td>
<td>0.133</td>
<td>2.9</td>
</tr>
<tr>
<td>(Pt$_3$Ru$<em>1$)$</em>{ML}$/Au</td>
<td>0.207</td>
<td>1.3</td>
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</table>

*Ag/AgCl potential scale
DMFC Hydrocarbon Membranes

<table>
<thead>
<tr>
<th>Technical Barrier</th>
<th>Related Property</th>
<th>Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>High cell resistance</td>
<td>Proton conductivity</td>
<td>Multi-block copolymer</td>
</tr>
<tr>
<td>Low fuel efficiency</td>
<td>Methanol permeability</td>
<td>Nitrile group</td>
</tr>
<tr>
<td>Durability</td>
<td>Water uptake</td>
<td>Tetra methyl (TM) bisphenol A</td>
</tr>
</tbody>
</table>

Importance of Low Water Uptake on Durability

* Kim et al., J. Electrochem. Soc. 2010, 157, B1616-B1623
DMFC Membranes: FY14 Multi-block Copolymers

Chemical Structure of FY14 Multi-block Copolymers

- Successfully synthesized high molecular weight BisA, DM and TM multi-block copolymers
- TM-based copolymer shows more ordered domain structure (SAXS), higher elongation (stress-strain curve), and lower methanol permeability (back-up slide)
- **Highlight:** Reached DMFC performance of > 200 mA cm⁻² at 0.50 V (75°C)

Morphology & Mechanical Properties

- Anode: 2.7 mg cm⁻² Pt₅₀Ru₂₅/C, 1.0 M MeOH, 1.8 mL/min;
  Cathode: 2.0 mg cm⁻² Pt/C; Cell: 75°C

- December 2013 milestone achieved
DMFC Membranes: Progress in Multi-block Copolymer Research

- Extensive research performed towards reducing methanol crossover and water uptake
- **Highlight:** Much better performance with 60 µm TM-based copolymer MEA than with Nafion® 115 MEA (the industry standard); lower HFR, methanol crossover, and water uptake demonstrated at the same time

Thickness of all membranes - 60 µm; best performing PEM -

1. Nafion 115 (150 µm thick)
2. 6FBPSH0-BPSH (7K-7K)
3. 6FBPSH0-BPSH (11K-11K)
4. 6FBPSH0-BPSH (15K-15K)
5. 6FK-BPSH (7K-7K)
6. 6FK-BPSH (11K-11K)
7. 6FK-BPSH (15K-15K)
8. 6FPAEB-BPSH (7K-7K)
9. 6FPAEB-BPSH (11K-11K)
10. 6FPAEB-BPSH (15K-15K)
11. 6F100BPPAEB-BPSH (10K-10K)
12. 6F75BPPAEB-BPSH (10K-10K)
13. 6F50BPPAEB-BPSH (10K-10K)
14. 6F25BPPAEB-BPSH (10K-10K)
15. 6F50BisA50PAEB-BPS (10K-10K)
16. 6F50DM50PAEB-BPS (10K-10K)
17. 6F50TM50PAEB-BPS (10K-10K)
Ethanol Oxidation: Improved Synthesis of Ternary Catalysts

Reactive Spray Deposition for Ternary Catalysts and Oxide Supports
(with Radenka Maric, University of Connecticut)

- Combustion synthesis capable of forming multi-component catalysts in one-step, directly on gas diffusion layer (GDL)
- Possible issues: Cleaning remaining organics and preventing particles agglomeration
- **Highlight:** Resulting ternary catalysts show excellent activity and stability at 25°C and 60°C
Ethanol Oxidation: Alternative Oxide Catalysts & Intermetallic PtML Support

- **Highlight:** Several oxides, IrOx in particular, identified as promising replacement for insufficiently stable SnO2 in ternary catalysts of EtOH oxidation
- CeO2 considerately enhances activity of PtML/Pd/C in ethanol oxidation (also methanol oxidation, not shown)
- PtML/PdAuCo shows high ethanol oxidation activity relative to Pt; intermetallic PdAuCo exhibiting better performance as a PtML support than core-shell PdAuCo
DME Oxidation: MEA and Fuel Delivery System Optimization

- **Anode**: 4.0 or 3.0 mg\textsubscript{PGM} cm\textsuperscript{-2}, PtRu/C (HiSPEC\textsuperscript{®} 12100), 40 sccm DME gas, 26 psig; **Cathode**: 4.0 mg cm\textsuperscript{-2} Pt black, 500 sccm air, 20 psig; **Membrane**: Nafion\textsuperscript{®} 212; **Cell**: 80ºC

- **Highlight**: FY13 to FY14 DDMEFC performance increase from 0.095 A cm\textsuperscript{-2} to 0.215 A cm\textsuperscript{-2} at 0.5 V, in spite of lowering the PGM anode loading by 25% in FY14
### DME Oxidation: Development of Ternary PtRuPd/C Catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Crystallite size (nm)</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt₈₀Pd₂₀/C</td>
<td>1.9</td>
<td>3.93</td>
</tr>
<tr>
<td>Pt₈₀Ru₂₀/C</td>
<td>2.7</td>
<td>3.87</td>
</tr>
<tr>
<td>Pt/C (HiSPEC® 9100)</td>
<td>3.7</td>
<td>3.92</td>
</tr>
</tbody>
</table>

**Highlight:** In agreement with proposed mechanism,
(i) Pd addition results in higher current density with the same onset potential as observed with Pt; (ii) Ru leads to lower onset potential of DME oxidation.
DME Oxidation: Development of Ternary PtRuPd/C Catalyst

Fuel Cell Test Conditions

**Anode**: 4.0 mg\( \text{PGM cm}^{-2} \) PtRuPd/C, HiSPEC® 12100, 40 sccm DME gas, 26 psig; **Cathode**: 2.0 mg cm\(^{-2}\) Pt/C HiSPEC® 9100, 100 sccm air, 20 psig; **Membrane**: Nafion® 212; **Cell**: 80ºC

**Highlight**: 220 mA cm\(^{-2}\) or 55 A g\(^{-1}\) at 0.50 V reached with ternary Pt\(_{55}\)Ru\(_{35}\)Pd\(_{10}\)/C and cathode loading of 2.0 mg\( \text{Pt cm}^{-2}\) (100 sccm air flow)*

DME Project Target and March 2014 milestone of 50 A g\(^{-1}\) achieved and exceeded

* 67 A g\(^{-1}\) reached with Pt\(_{50}\)Ru\(_{50}\)/C anode, 4.0 mg\( \text{Pt cm}^{-2}\) cathode and 500 sccm air flow (backup slide)
DME Oxidation: Progress at LANL FY11 - FY14

<table>
<thead>
<tr>
<th>FY</th>
<th>How Progress Has Been Made</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>Pt-to-Ru ratios screened and Pt$<em>{50}$Ru$</em>{50}$ selected</td>
</tr>
<tr>
<td>2012</td>
<td>DME-to-water stoichiometry ratio and membrane optimized</td>
</tr>
<tr>
<td>2013</td>
<td>New ternary Pt$<em>{45}$Ru$</em>{45}$Pd$<em>{10}$/C catalyst developed replacing the Pt$</em>{50}$Ru$_{50}$ black anode catalyst</td>
</tr>
<tr>
<td>2014</td>
<td>Ternary catalyst further optimized to Pt$<em>{55}$Ru$</em>{35}$Pd$_{10}$/C; MEA and fuel cell operating conditions improved</td>
</tr>
</tbody>
</table>

**Highlight:** DDMEFC performance improved by a factor of at least 2.5× over the project duration with concurrent significant reduction in precious metal loading.
DME Oxidation: DDMEFC and DMFC Performance Comparison

Anode: 4.0 mg$_{\text{metal}}$ 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 cm$^{-2}$ Pt/C HiSPEC® 9100, 100 sccm air, 20 psig; Membrane: Nafion® 212 (DME), Nafion® 115 (MeOH); Cell: 80ºC

Performance of the latest-generation DDMEFC slightly exceeding that of the state-of-the-art DMFC

(Both systems operating under their respective optimum conditions)
Collaborations

- Seven organizations with complementary skills and capabilities in catalyst development, electrode-structure design, materials characterization, MEA fabrication, and portable fuel cell development and commercialization:
  - Los Alamos National Laboratory (LANL) – *direct DOE EERE contract*
  - Brookhaven National Laboratory (BNL) – *direct DOE EERE contract*
  - University of Delaware – *subcontract to LANL*
  - Virginia Tech – *subcontract to LANL*
  - Johnson Matthey Fuel Cells – *subcontract to BNL*
  - SFC Energy – *subcontract to BNL*
  - Oak Ridge National Laboratory – *no cost partner*

- Collaborations outside Fuel Cell Technologies Program:
  - Oorja Fuel Cells, Fremont, California, USA – reduction in DMFC cost for applications in excess of 1.0 kW in power; two LANL DMFC patents licensed by Oorja in April 2014
  - University of Warsaw, Warsaw, Poland – development of components for direct dimethyl ether fuel cell (common program development phase)
  - Danish Technical University (DTU) – direct dimethyl fuel cell electrocatalysis (joint research proposal to be submitted in summer 2014)
Responses to Previous Year Reviewers’ Comments

“Very good progress was made in anode catalyst research. On the membrane research, it would be very useful to check how the TM membrane/electrode interface changes in durability test, to validate the hypothesis that matching water uptake to Nafion® can improve interface durability. Also, it is perhaps more useful to have the membrane swelling ratio data.”

The data showed in our 2013 presentation was preliminary. Since then we have completed a thorough interfacial durability study of TM membrane/electrode, the results of which have been presented this year. While we plan to measure the swelling ratio of the multi-block copolymers, the relevance of the swelling ratio to interfacial durability may be questionable.

“Lack of long-term testing; 1000 hours is only a 2 month test; this is the fourth year of the program; this should have been done for all of their promising catalysts.”

Most durability testing in the project has been performed using potential/voltage cycling (accelerated stress testing) to avoid tying either electrochemical or fuel cell test equipment to one cell for prolonged times. However, the most promising DMFC anode catalyst, Johnson Matthey’s Fuel Cell’s advanced anode catalyst (ACC), underwent this year testing in a 10-cell SFC Energy stack for ca. 3,500 hours. In spite of a much lower catalyst loading (approximately half of that used in SFC’s commercial products), the catalyst showed lower rate of performance degradation than methanol oxidation catalysts used in commercial systems.

“As highlighted in this year’s presentation, advancements in DME research (both electrocatalysis and fuel delivery system) have been central to the project effort at Los Alamos. Test data shows that DME fuel cells can match, and in some cases outperform, the state-of-the-art DMFCs.
Remaining Needs, Barriers, and Challenges

Direct methanol and dimethyl ether fuel cells:

- Further improvements to mass activity of both anode and cathode catalysts by modifications to existing catalyst formulations or development of new catalysts
- Reduction in cost to allow application to high-power systems (for example, by lowering catalyst cost and improving performance durability)
- Increase in fuel conversion efficiency via progress in anode catalysis (new formulations), reduction in fuel and anode-component crossover and enhancements in cathode tolerance to fuel/anode-component crossover
- Development of alternative membranes with improved stability and reduced permeability of fuels and anode catalyst component(s)

Ethanol as alternative fuel for direct fuel cells:

- Development of active and chemically stable catalyst with high selectivity for 12-electron oxidation of ethanol to CO₂ (in fuel cell type electrodes)
- Forsaking anode catalyst formulations that rely on intrinsically unstable components (including some core-shell formulations)
- Leveraging of DMFC/DDMEFC experience in the development of membranes with reduced crossover and in addressing effects of crossover on cathode performance
Direct methanol fuel cells:
• Complete current catalyst development efforts to meet last remaining project milestone (0.15 A cm\(^{-2}\) at 0.60 V)
• Develop methanol oxidation catalysts free of intrinsically unstable components; possible formulations include two-dimensional platelets containing low-coordination atoms of precious metals and Au-core nanoparticles as supports
• Develop inks, GDL treatments, optimize and assure manufacturability by a scalable production process for advanced anode catalyst (AAC), targeting 50% Pt reduction in two years without performance/durability penalty (30% Pt reduction in FY15) and 500 W system

Direct DME fuel cells:
• 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

Ethanol oxidation catalysis:
• Develop new-generation catalysts of ethanol 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 and primary performance and selection criteria
• Perform assessment of DEFC viability at the present state of ethanol oxidation catalysis
• JMFC’s advanced anode catalyst (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 was used in CCMs prepared JMFC for a 10-cell SFC Energy stack; in spite of much lower loading, ACC showed better stability over 2500 hours of stack operation than commercial catalysts.

• Progress in methanol catalysis is viewed by SFC Energy as enabling for higher power DMFC applications, power generators in particular (presently off-limits due to the prohibitive catalyst cost).

• High current density of 0.200 A cm\(^{-2}\) at 0.50 (75°C) was achieved with TM-based multi-block copolymer; a 60-\(\mu\)m TM-based MEA showed lower resistance, methanol crossover and water uptake than a Nafion\textsuperscript{®} 115-based MEA – a DMFC industry standard.

• Significant progress in DME electrocatalysis with the ternary PtRuPd/C was demonstrated resulting in a DDMEFC current density of 220 A cm\(^{-2}\) (55 A g\(^{-1}\) mass-specific activity of the anode catalyst) – a 2.5-fold improvement in activity since project inception.

• LANL DDMEFC was demonstrated to match state-of-the-art DMFC across the entire range of current densities.

• Recent advancements in ethanol oxidation electrocatalysis at BNL (Pt\textsubscript{ML}/Au/C catalyst) led to ca. 200 mV reduction in overpotential of EtOH oxidation relative to Pt/C; LANL fuel cell testing is upcoming.
Co-Authors

- ethanol and methanol anode catalyst research
  Radoslav Adzic (PI), Meng Li, Miomir Vukmirovic, Kotaro Sasaki

- anode catalyst and membrane research; characterization
  Piotr Zelenay (Project Lead), Hoon Chung, Joseph Dumont, Qing Li, Yu Seung Kim, Ulises Martinez, Yun Xu, Gang Wu

- nanostructure catalyst structures
  Yushan Yan (PI), Jie Zheng

- hydrocarbon membrane research
  James McGrath (PI), Jarrett Rowlett, Andy Shaver

- methanol anode catalyst research; MEA integration
  Alex Martinez Bonastre (PI), Willie Hall, Graham Hards, Emily Price, Jonathan Sharman, Geoff Spikes

- MEA integration and testing; final deliverable
  Christian Böhm (PI)

- microscopic characterization (no-cost partner)
  Karren More (PI), David Cullen
Technical Backup Slides
MeOH Oxidation: AAC Anode; Effect of Annealing Temperature and Loading

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO metal area / m² g&lt;sub&gt;cat&lt;/sub&gt;&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAC</td>
<td>20</td>
</tr>
<tr>
<td>High metal content AAC @ T1</td>
<td>20</td>
</tr>
<tr>
<td>High metal content AAC @ T2</td>
<td>21</td>
</tr>
<tr>
<td>High metal content AAC @ T3</td>
<td>27</td>
</tr>
<tr>
<td>High metal content AAC @ T4</td>
<td>30</td>
</tr>
</tbody>
</table>

Anode: AAC, 1.0 mg<sub>Pt</sub> cm<sup>-2</sup>, 0.5 - 0.6 M MeOH; Cathode: Pt/C, 1.5 mg<sub>Pt</sub> cm<sup>-2</sup> air; Membrane: Nafion<sup>®</sup> 115; Cell: 80°C

- Increase in annealing temperature helps performance of high metal-content (low carbon-content) catalysts (via increase in surface area), but not beyond that of low metal-content AAC
- Only small performance gain achieved with 2.0 mg<sub>Pt</sub>/cm<sup>2</sup> (noticeably lower Pt mass activity)

Anode: AAC@T2, 2.0 mg<sub>Pt</sub> cm<sup>-2</sup>, 0.5 - 0.6 M MeOH; Cathode: Pt/C, 1.5 mg<sub>Pt</sub> cm<sup>-2</sup> air (fuel cell), H<sub>2</sub> (anode polarization); Membrane: Nafion<sup>®</sup> 115; Cell: 80°C

0.6 V; 150 mA cm<sup>-2</sup>
Synthetic Procedure of FY14 Multi-block Copolymers

Note: Methanol crossover data above are for novel MEAs highlighted earlier (Slide 12).

Methanol Crossover Limiting Current

Anode: 2.7 mg cm\(^{-2}\) Pt\(_{50}\)Ru\(_{25}\)/C, 1.0 M MeOH, 1.8 mL/min;
Cathode: 2.0 mg cm\(^{-2}\) Pt/C; Cell: 75°C
DME Oxidation: MEA and Fuel Delivery System Optimization

- MEA and fuel delivery system optimization carried out with commercial PtRu/C HiSPEC® 12100 catalyst
- **Highlight:** Mass-specific activity of **67 A g⁻¹** reached with PtRu/C – the highest ever recorded, but obtained with a relatively high cathode loading of 4.0 mgₚt cm⁻² and very high air flow (500 sccm)