Advanced Materials and Concepts for Portable Power Fuel Cells

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Los Alamos, New Mexico 87545

Project ID: FC091
Overview

Timeline
• Start date: September 2010
• End date: Four-year duration
• Completion: ca. 70%

Budget
• Total funding estimate:
  – DOE share: $3,948K
  – Contractor share: $342K
• FY12 funding received: $975K
• FY13 funding received: $1,048K

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
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 (may 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. $2.0-2.5$ kWh/L $\rightarrow \eta_\Sigma = 0.42-0.52$ (1.6-2.0× improvement over the state of the art, $\sim 1.250$ kWh/L)
2. If $\eta_{\text{fuel}} = 0.96$, $\eta_{\text{BOP}} = 0.90$, $V_{\text{th}} = 1.21$ (at 25°C)

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

The ultimate project goal!
Approach: Focus Areas

• **DMFC anode research:**
  – new catalysts with improved activity and reduced cost (JMFC, LANL, BNL)
  – improved catalyst durability (JMFC, LANL, BNL)

• **Innovative electrode structures for better activity and durability** (UD)

• **Hydrocarbon membranes for lower MEA cost and enhanced fuel cell performance** (VT, LANL):
  – block copolymers
  – copolymers with cross-linkable end-groups

• **Alternative fuels for portable fuel cells:**
  – ethanol oxidation electrocatalysis (BNL, LANL)
  – dimethyl ether research (LANL)

• **Characterization; performance and durability testing; multi-cell device:**
  – advanced materials characterization (ORNL, BNL, LANL)
  – MEA performance testing (LANL, JMFC, SFC)
  – durability evaluation (LANL, JMFC, SFC)
  – five-cell stack (SFC)
<table>
<thead>
<tr>
<th>Date</th>
<th>Milestones</th>
<th>Status</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan 13</td>
<td>Complete construction of the DEMS instrument.</td>
<td>Complete</td>
<td>DEMS instrument has been constructed.</td>
</tr>
<tr>
<td>Feb 13</td>
<td>Improve the ternary PtRhSnO₂ electrocatalyst to oxidize ethanol to CO₂ with an efficiency of 30-50% at ( E = 0.4 \text{ V} ) at 60-80°C.</td>
<td>Delayed</td>
<td>More time required to verify and, if needed, resolve possible SnO₂ stability problem in ternary catalysts.</td>
</tr>
<tr>
<td>Mar 13</td>
<td>Demonstrate 150 mA cm(^{-2}) at 0.50 V in a DDMEFC operating with a new-generation PtRuPd/C anode catalyst at a loading of (&lt; 3.0 \text{ mg}_\text{Pt} \text{ cm}^{-2}) (80°C).</td>
<td>Complete</td>
<td>0.15 A cm(^{-2}) at 0.50 V achieved with new high-metal content ( \text{Pt}<em>{45}\text{Ru}</em>{45}\text{Pd}_{10} )/C catalyst; catalysts outperforming PtRu/C reference by catalyst by ca. 50 mV at 0.15 A cm(^{-2}).</td>
</tr>
<tr>
<td>Apr 13</td>
<td>Demonstrate PtRu or PtRuSn methanol oxidation catalyst that exceeds final project anode mass activity-target of 200 mA \text{mg}_\text{Pt}^{-1} \text{ cm}^{-2} \leq 0.25 \text{ V} ) at 80°C (iR-corrected), with durability at least matching that of the state of the art (HiSPEC© 12100).</td>
<td>Mass-activity target complete Durability target pending</td>
<td>Mass-activity target of 200 mA \text{mg}_\text{Pt}^{-1} \text{ at } \leq 0.25 \text{ V} ) (80°C) achieved with ultra-thrifted PtRuSn/C catalyst (uT-PtRuSn); durability of uT-PtRuSn in need of improvement; several other advanced anode catalysts showing better durability than the benchmark HiSPEC© 12100 catalyst.</td>
</tr>
<tr>
<td>May 13</td>
<td>Synthesize multi-block copolymer with methanol permeability reduced by at least 50% relative to Nafion® and maintained ionic conductivity and water uptake.</td>
<td>Complete</td>
<td>MeOH crossover in tetramethylbisphenol A (TM) copolymer reduced by more than 50% without ionic-conductivity or water-uptake penalties.</td>
</tr>
<tr>
<td>Aug 13</td>
<td>Characterize the most promising new DMFC anode catalyst and/or membrane developed in the project in a short stack under conditions simulating SFC's commercial products.</td>
<td>On schedule</td>
<td>Testing of JMFC’s AAC catalyst in a 50-cm(^2) five-cell stack planned by SFC Energy for the summer of 2013.</td>
</tr>
<tr>
<td>Sep 13</td>
<td>Develop PtRu/CuNWs based methanol oxidation catalysts with the onset potential &lt; 0.3 V vs. RHE and mass activity at 0.40 V vs. RHE at least matching that of the benchmark PtRu catalyst (HiSPEC©12100).</td>
<td>Complete</td>
<td>Onset potential of methanol oxidation of 0.288 V vs. RHE has been achieved by tuning Pt-to-Ru ratio in PtRu/CuNWs catalyst; mass activity is comparable to that of the benchmark catalyst.</td>
</tr>
</tbody>
</table>
Methanol Oxidation: New Ultra-Thrifted Anode Catalysts

<table>
<thead>
<tr>
<th>Catalyst Code</th>
<th>Atomic Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>HiSPEC® 12100 PtRu/C – JMFC benchmark</td>
<td>50 50 -</td>
</tr>
<tr>
<td>PtRu/C (Advanced Anode Catalyst, AAC) – FY12</td>
<td>20 80 -</td>
</tr>
<tr>
<td>Ultra-thrifted PtRu/C (uTAAC) – FY13</td>
<td>10 90 -</td>
</tr>
<tr>
<td>PtRuSn/C – FY12</td>
<td>20 73 7</td>
</tr>
<tr>
<td>Ultra-thrifted PtRuSn/C (uT-PtRuSn) – FY13</td>
<td>10 85 5</td>
</tr>
</tbody>
</table>

**Highlight:** New ultra-thrifted PtRu/C catalyst (uTAAC) outperforming the HiSPEC® 12100 benchmark and ACC in terms of MeOH oxidation onset potential and mass activity; matching AAC in DMFC testing at a loading of only 0.3 mgPt cm⁻²

Mass-activity target of 200 mA mg⁻¹ at ≤ 0.25 V (80°C) achieved with uT-PtRuSn catalyst

**Highlight:** PtRuSn/C catalyst performing by far the best in DMFC testing at current densities <150 mA cm⁻² (Sn effect at low MeOH oxidation overpotentials)
**Methanol Oxidation: In-Situ Accelerated Anode Stability Testing (2.0 M MeOH)**

**Cell performance:** H₂-air fuel cell polarization and DMFC anode polarization plots. **Catalyst surface probing:** Stripping of MeOH-generated CO from anode and cathode.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loss after 300 Cycles / mV</th>
<th>E Increase after 300 Cycles, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HISPEC 12100 1.0 mgPt cm⁻²</td>
<td>24</td>
<td>8</td>
</tr>
<tr>
<td>Advanced Anode Catalyst (AAC) 1.0 mgPt cm⁻²</td>
<td>13</td>
<td>5</td>
</tr>
<tr>
<td>Ultra-thrifted PtRu (uTAAC), 0.3 mgPt cm⁻²</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>PtRuSn 1.0 mgPt cm⁻²</td>
<td>16</td>
<td>6</td>
</tr>
<tr>
<td>Ultra-thrifted PtRuSn (uT-PtRuSn), 0.3 mgPt cm⁻²</td>
<td>26</td>
<td>10</td>
</tr>
</tbody>
</table>

- **Highlight:** Ultra-thrifted PtRu catalyst (uTAAC) maintaining excellent mass activity (only 13 mV off the project target) throughout the stability testing
- **Ultra-thrifted PtRuSn catalyst (uT-PtRuSn) in need of stability improvement at high operating anode potentials encountered during stability testing**
Methanol Oxidation: In-Situ MEA Accelerated Stability Testing (2.0 M MeOH)

**Anode:** Thrifted PtRu/C advanced anode catalyst (AAC), $H_2O$; **Cathode:** $H_2$; **Anode Cycling:** 0.05 – 0.85 V, 300 cycles total

**Plots After Cycling**

- **Highlight:** Thrifted PtRu/C catalyst (AAC) showing excellent cycling durability at ca. 1% overall performance loss after 300 cycles (no cathode loss in spite of small Ru migration)
- **Ultra-thrifted PtRuSn catalyst (uT-PtRuSn)** in need of stability improvement at high potentials; Ru migration to the cathode detected in cathode CO stripping (see Technical Backup Slides) with a clear impact on cathode performance

**Stability increase**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Performance Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode loss</td>
<td></td>
</tr>
<tr>
<td>Anode loss</td>
<td></td>
</tr>
</tbody>
</table>

![MEA before cycling](image1)
![MEA after 300 cycles](image2)
Methanol Oxidation: DMFC Polarization Plots with 0.5 M MeOH

Anode: PtRu/C or PtRuSn/C, 0.5 M MeOH; Cathode: Pt/C (1.5 mgPt cm\(^{-2}\)), dry air; Membrane: Nafion\(^{\circledR}\) 115; Cell: 80°C

- **Highlight:** PtRu/C catalyst (AAC) at only 1.0 mgPt cm\(^{-2}\) 0.54 V at 150 mA cm\(^{-2}\), close to the project target of 0.6 V at 150 mA cm\(^{-2}\); further optimization of anode expected to lead to further performance gains

- At 0.5 M MeOH, PtRuSn catalysts not offering a performance advantage over Pt/Ru

  **AAC performance within 60 mV of the overall project DMFC target!**
Methanol Oxidation: Innovative PtRu Nanostructure Catalysts (Synthesis)

Synthesis of PtRuNTs

CuNWs → PtRuNTs

Simultaneous complete displacement of Cu in CuNWs with Pt and Ru to form PtRuNT

Synthesis of PtRu/CuNWs

CuNWs → PtRu/CuNWs

Simultaneous partial displacement of Cu in CuNWs with Pt and Ru to form PtRu coated on CuNWs structure

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
</tr>
<tr>
<td>PtRu/C (HiSPEC® 12100)</td>
<td>50</td>
</tr>
<tr>
<td>PtRu/CuNWs</td>
<td>23</td>
</tr>
<tr>
<td>Pt3Ru/CuNWs</td>
<td>23</td>
</tr>
<tr>
<td>Pt6Ru/CuNWs</td>
<td>28</td>
</tr>
</tbody>
</table>

SEM images: (a) CuNWs, (c) PtRuNTs, (e) PtRu/CuNWs. TEM images: (b) CuNWs, (d) PtRuNTs, (f) PtRu/CuNWs
Methanol Oxidation: Innovative PtRu Nanostructure Catalysts (Highlights)

Solution: 1.0 M MeOH in 0.1 M HClO₄; Scan rate: 5 mV s⁻¹; PtRu/C: HiSPEC® 12100

Solution: 1.0 M MeOH in 0.1 M HClO₄; Scan rate: 5 mV s⁻¹; PtRu/C: HiSPEC® 12100

Highlight: Very low onset potential of methanol oxidation of 0.288 V vs. RHE achieved by tuning the Pt-to-Ru ratio in PtRu/CuNW catalysts

Onset potential target of ≤ 0.3 V vs. RHE achieved with a PtRu/CuNW catalyst

Mass activity of PtRu/CuNWs based on total precious metal content higher than that of PtRu/C benchmark catalyst (HiSPEC® 12100)
DMFC Durability: 100-Hour Life Test with Metal Black Catalysts

**Anode:** 6 mg cm⁻² Pt₅₀Ru₅₀ black, 1.8 mL/min MeOH; **Cathode:** 4 mg cm⁻² Pt black, 500 sccm air;  
**Membrane:** 3 × Nafion® 212; **Cell:** 75°C; **Life test:** 0.45 V, 100 hours

- **0.5 M MeOH**
- **1.0 M MeOH**
- **4.0 M MeOH**

- Most Ru crossover taking place during 2-hour H₂-air break-in; potential of CO stripping from the cathode virtually independent of methanol concentration
- Surface composition of the anode not affected by the concentration of MeOH in the 100-hour test
DMFC Durability: 100-Hour Life Test with Carbon-Supported Catalysts

Anode: 4 mg_{metal} cm^{-2} HiSPEC® 12100, 1.8 mL/min MeOH; Cathode: 2 mgPt/cm^{2} HiSPEC® 9100; 500 sccm air; Membrane: 3 × Nafion® 212; Cell: 75°C; Life test: 0.45 V, 100 hours

- High-frequency resistance gain at the highest MeOH concentration also observed with carbon-supported catalysts
- Very small Ru contamination of the cathode (in agreement with JMFC results)
DMFC Durability: Electrode X-Ray Tomography

**JMFC carbon-supported electrodes:** Significant presence of cracks in as-prepared and tested MEAs (16-19% anode, 8-12% cathode); possible benefit to mass transport

**LANL metal-black electrodes:** Virtually crack-free initially; crack formation during life test not causing any significant performance loss of metal-black electrodes

### X-Ray Tomography after 100-Hour Test (1x1 mm)

<table>
<thead>
<tr>
<th>MEA</th>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon-Supported 0 h</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>Carbon-Supported 100 h 4.0 M MeOH</td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td>Metal Blacks 0 h</td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
<tr>
<td>Metal Blacks 100 h 4.0 M MeOH</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
</tr>
</tbody>
</table>

### Crack Area (%)

- **Carbon-Supported Catalysts**
  - 0 hr: [Data Point]
  - 100 hr: [Data Point]
  - 4.0 M MeOH: [Data Point]

- **Metal-Black Catalysts**
  - Anode: [Data Point]
  - Cathode: [Data Point]
Ethanol Oxidation: Pt-Monolayer Catalysts Enhanced by Au Nanocore

**Approach:** Theoretical Prediction → Pt$_{\text{ML}}$/Au(111) Model Catalyst → Pt$_{\text{ML}}$/Au/C Nanocatalyst → (RhSnO$_2$, Ru)-Modified Pt$_{\text{ML}}$/Au/C

- Model catalyst study confirming DFT prediction of the expansive strain effect of underlying Au on the Pt$_{\text{ML}}$ activity
- **Highlight:** Pt$_{\text{ML}}$/Au/C nanocatalyst synthesized by displacing Cu UPD layer pre-deposited on Au/C; Pt$_{\text{ML}}$/Au/C further modified with SnO$_2$ to achieve high ethanol oxidation activity of bifunctional catalyst

**DFT Simulation (MeOH Oxidation)**

**Single-Crystal Model Catalysts**

**Pt$_{\text{ML}}$ Catalysts with MeOH and EtOH Oxidation Activity Enhanced by Au Nanocore**
- **Highlight:** CO$_2$ is the only product observed by IR in the potential range of 0.30 - 0.70 V
- CH$_3$COOH and CH$_3$CHO showing at potentials higher than 0.70 V
Microemulsion Synthesis of Au@Pt Core-Shell Nanoparticles

**Ethanol Oxidation**

- **Highlight:** One-pot, easily scalable synthesis, less complex than the Cu UPD method; effective control of the core-shell architecture achieved
- **Au@Pt nanoparticles obtained, ~ 4 nm in average particle size; SnO₂-modified bifunctional catalyst performing similarly to the catalyst obtained using the Cu UPD approach**
Ethanol Oxidation: Pt$_{ML}$/Pd$_4$Au$_1$M$_5$/C Nanocatalysts (M = Ni, Fe, Co)

**Methanol Oxidation**

- Solution: 0.5 M MeOH/EtOH in 0.1 M HClO$_4$; Scan rate: 5 mV s$^{-1}$; Electrode: GC, 0.2 cm$^2$

- Highlight: Pt$_{ML}$/Pd$_4$Au$_1$Fe$_5$/C and Pt$_{ML}$/Pd$_4$Au$_1$Co$_5$/C demonstrating more than 8-fold increase in Pt and 2-fold increase in total PGM mass activity in ethanol oxidation at 0.70 V

**Ethanol Oxidation**

- Solution: 0.5 M MeOH/EtOH in 0.1 M HClO$_4$; Scan rate: 5 mV s$^{-1}$; Electrode: GC, 0.2 cm$^2$
DMFC Membranes: Barriers, Approach, Milestone

- **Technical Barriers**
  
  Low proton conductivity → addressed in FY11 with multi-block copolymers (> 0.1 S cm\(^{-1}\))
  
  High methanol permeability → addressed in FY12 with nitrile moiety (≥ fuel utilization 95% at peak power)
  
  Poor membrane-electrode interface → this year

- **Approach**
  
  Interfacial delamination between hydrocarbon membrane and Nafion\(^{\circledR}\)-bonded electrode typically caused by excessive membrane swelling.
  
  Approach used here to improve interfacial compatibility: Reduce water uptake by modifying chemical structure of hydrophobic blocks.

**Approach 1:** Control fluorination level

**Approach 2:** Control bisphenol structure

\[ 6F_{x} \text{ to BP ratio: } 6F100 \text{ BP0, 6F75 BP25, 6F50 BP50, 6F25 BP75} \]
DMFC Membranes: Nitrile Multi-Block Copolymers with Controlled Fluorination

6FₓBP₁₀₀₋ₓ PAEB-BPSH₁₀₀ Multi-Block Copolymers

- No significant effect of fluorination level on proton conductivity and water uptake
- **Highlight:** Higher conductivity (by 18%) and reduced MeOH permeability (by 55%) compared to Nafion® 212 achieved with 6F25BP75 thanks to an increase in biphenol (BP) moiety content

<table>
<thead>
<tr>
<th>6FₓBP₁₀₀₋ₓ (10K-10K)</th>
<th>IECᵃ (meq g⁻¹)</th>
<th>Proton conductivity (S cm⁻¹)</th>
<th>Methanol permeabilityᵇ (cm² s⁻¹)</th>
<th>Water uptake (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion®</td>
<td>0.91</td>
<td>0.11</td>
<td>3.14</td>
<td>22</td>
</tr>
<tr>
<td>6F100BP0</td>
<td>1.53</td>
<td>0.14</td>
<td>2.23</td>
<td>45</td>
</tr>
<tr>
<td>6F75BP25</td>
<td>1.55</td>
<td>0.14</td>
<td>2.18</td>
<td>44</td>
</tr>
<tr>
<td>6F50BP50</td>
<td>1.55</td>
<td>0.13</td>
<td>1.89</td>
<td>52</td>
</tr>
<tr>
<td>6F25BP75</td>
<td>1.50</td>
<td>0.13</td>
<td>1.41</td>
<td>54</td>
</tr>
</tbody>
</table>

ᵃ From ¹H NMR; ᵇ From limiting-current experiment (80°C)

**MeOH Crossover Current (0.5 M MeOH)**

Anode: 6.0 mg cm⁻² Pt₅₀Ru₅₀ black, 0.5 M MeOH, 1.8 mL/min; Cathode: 4.0 mg cm⁻² Pt black; 500 sccm N₂; Cell: 80°C, 5 cm² single cell hardware

- Thickness - Normalized MeOH Crossover Current (mA cm⁻¹)
- Cell Voltage (V)
DMFC Membranes: Multi-Block Copolymers with Controlled Hydrophobicity

<table>
<thead>
<tr>
<th>6F_yX_{100-y} PAEB-BPSH100 Multi-Block Copolymers</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Chemical structure of 6F_yX_{100-y} PAEB-BPSH100" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>6F_{50-y}X_{50}</th>
<th>IEC (meq g^{-1})</th>
<th>Proton conductivity (S cm^{-1})</th>
<th>Methanol permeability (cm^{2} s^{-1})</th>
<th>Water uptake (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion®</td>
<td>0.91</td>
<td>0.11</td>
<td>2.36</td>
<td>22</td>
</tr>
<tr>
<td>BP*</td>
<td>1.50</td>
<td>0.13</td>
<td>1.47</td>
<td>54</td>
</tr>
<tr>
<td>Bis A</td>
<td>1.74</td>
<td>0.12</td>
<td>1.30</td>
<td>40</td>
</tr>
<tr>
<td>DM</td>
<td>1.65</td>
<td>0.15</td>
<td>1.42</td>
<td>35</td>
</tr>
<tr>
<td>TM</td>
<td>1.50</td>
<td>0.10</td>
<td>1.09</td>
<td>20</td>
</tr>
</tbody>
</table>

*6F25BP75, a From limiting-current experiment (75°C)

Preliminary DMFC Data (1.0 M MeOH)

- **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; 500 sccm, N\textsubscript{2}; **Cell**: 75°C, 5 cm\textsuperscript{2} single cell hardware

- **Significant performance improvement by reducing water uptake of multi-block copolymer**
- **Highlight**: Structural changes to bisphenol unit proven very effective in controlling membrane water uptake

MeOH crossover reduced in TM-based multi-block copolymer by 54% (membrane milestone achieved)
DME Oxidation: PtRuPd/C Catalysts with High Metal Content

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>PtRuPd/C</th>
<th>Pt50Ru50/C (JM HiSPEC® 12100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal loading by TGA in air (wt%)</td>
<td>65 ± 2</td>
<td>72</td>
</tr>
<tr>
<td>Pt:Ru:Pd atomic ratio by XRF</td>
<td>46:44:10</td>
<td>51:49:0</td>
</tr>
<tr>
<td>Crystalline size from XRD (nm)</td>
<td>3.2</td>
<td>3.6</td>
</tr>
<tr>
<td>Specific surface area (m²/g of metal)</td>
<td>60</td>
<td>49</td>
</tr>
</tbody>
</table>

- **Highlight**: PtRuPd/C catalysts with high metal content synthesized by a modified polyol method
- **Pt45Ru45Pd10/C** outperforming HiSPEC® 12100; 10 at% Pd assuring efficient C-O bond scission without inhibiting removal of surface CO by Ru hydroxide/oxides

Catalyst: PtRuPd/C or HiSPEC® 12100 on GCE (0.196 cm²); Loading: 60 µgPt/cm²; Electrolyte: 0.1 M HClO₄; Concentration of DME-saturated solution: 1.05 M

**Chronoamperometry**

**Steady-State Polarization Plots**

- **OCP, 100 s; 20 mV steps; 20 s/step**

Los Alamos National Laboratory

2013 Hydrogen and Fuel Cells Program Annual Merit Review
Highlight: Pd addition to PtRu resulting in significant lowering of the activation energy for C-H and C-O bond breaking during DME oxidation, by 0.19 eV and 0.25 eV, respectively.
**DME Oxidation: Pt\textsubscript{45}Ru\textsubscript{45}Pd\textsubscript{10}/C Catalyst Fuel Cell Performance**

- **Anode**: 2.7 mg\textsubscript{Pt} cm\textsuperscript{-2} PtRuPd/C or HiSPEC\textsuperscript{®} 12100, 40 sccm DME gas, 30 psig; **Cathode**: 4.0 mg cm\textsuperscript{-2} Pt black, 500 sccm air, 20 psig; **Membrane**: Nafion\textsuperscript{®} 212; **Cell**: 80\textdegree}C

- **Highlight**: Cell voltage value measured with Pt\textsubscript{45}Ru\textsubscript{45}Pd\textsubscript{10}/C at 0.15 A cm\textsuperscript{-2} by ca. 70 mV higher than voltage measured with PtRu/C reference catalyst

- **DME fuel cell performance milestone of 0.15 A cm\textsuperscript{-2} at 0.50 V achieved**

- **No significant performance loss observed for 100 hours**
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 and Brookhaven National Laboratory – *direct DOE EERE contracts*
  ✓ University of Delaware and Virginia Tech – *subcontracts to Los Alamos National Laboratory*
  ✓ Johnson Matthey Fuel Cells and SFC Energy – *subcontracts to Brookhaven National Laboratory*
  ✓ Oak Ridge National Laboratory – *no cost partner*

• Collaborations outside Fuel Cell Technologies Program:

  ✓ Oorja Protonics, Fremont, California, USA – reduction in cost of direct methanol fuel cell components and system for applications in excess of 1 kW in power (common program development phase)
  ✓ Warsaw University, Warsaw, Poland – dimethyl ether oxidation on platinum-free electrocatalysts
  ✓ University of Waterloo, Waterloo, Ontario, Canada – development of nanostructured methanol oxidation catalysts
Methanol oxidation catalysis:
- Improve anode mass activity of thriftyed (AAC) and ultra-thriftyed (TAAC) PtRu/C catalysts
- Stabilize nano-particulate structures of PtRu/C and PtRuSn/C to minimize Ru and Sn dissolution
- Optimize AAC-based anodes; complete 50 cm² five-cell stack testing by SFC Energy
- Scale-up and test in MEAs PtRu platelets and Pt monolayer catalysts

Innovative membranes and electrode structures:
- Optimize membrane thickness and MEA processing for better performance of membranes with controlled hydrophobicity
- Improve durability of alternative membranes in the presence of higher concentrations of MeOH
- Identify the mechanism of DMFC performance degradation in prolonged life tests, up to 500 h, and develop mitigation strategies
- Further improve mass activity of PtRu/CuNWs; scale up nanostructured catalyst synthesis

Ethanol oxidation catalysis:
- Develop catalysts based on expanded Pt monolayers decorated by SnO₂ and Rh islands and optimized 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 for efficiency and power at high and intermediate DDMEFC voltages, respectively
• Ultra-thrifted catalysts (uTAAC and uT-PtRuSn) of MeOH oxidation have been synthesized in 25 g batches; uT-PtRuSn meets the project anode activity target of 200 mA mg\textsubscript{Pt}\textsuperscript{-1} at 0.25 V while ultra-thrifted Pt/Ru/C catalyst (uTAAC) is only 13 mV away from that target

• Thrifted PtRu/C catalysts (AAC) has come within 40 mV of the overall DMFC performance target of 0.15 A cm\textsuperscript{-2} at 0.60 V; AAC is ready for 50 cm\textsuperscript{2} stack testing by SFC Energy in the summer of 2013

• A very low MeOH oxidation onset potential target of 0.288 V vs. RHE has been achieved with a PtRu/CuNW catalyst with optimized Pt-to-Ru ratio; catalysts synthesis scale-up is ongoing

• JMFC and LANL data indicate that Ru crossover in MEAs with state-of-the-art carbon-supported PtRu catalysts, though detectable, is much reduced and does impact ORR activity of the cathode

• Under conditions used, up to 4.0 M MeOH, 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 bisphenol unit are very effective in controlling membrane water uptake and reducing MeOH crossover (by as much as 54% in TM-based multi-block copolymer)

• Pt\textsubscript{ML}/Au/C catalysts EtOH oxidation have been synthesized by displacing Cu UPD layer on Au/C and by microemulsion approach; catalysts have been further modified with various modifiers to enhance activity via bifunctional approach; Pt\textsubscript{ML} supported on such nanocores as PdAuFe and PdAuCo show interesting potential as lower-cost EtOH catalysts

• RhSnO\textsubscript{2}/Pt\textsubscript{ML}/Au/C catalyst exhibits high ethanol oxidation selectivity; CO\textsubscript{2} is the only product in the potential range of 0.3-0.7 V; non-CO\textsubscript{2} byproducts are observed at very high potentials (above 0.7 V)

• Current density of 0.15 A cm\textsuperscript{-2} at DDMEFC voltage of 0.50 V has been reached with a new high metal-content ternary catalyst of DME oxidation (Pt\textsubscript{45}Ru\textsubscript{45}Pd\textsubscript{10}/C); DFT calculations confirm the effect of Pd addition on the kinetics of both the C-O and C-H bond scission
– ethanol and methanol anode catalyst research
  Radoslav Adzic (PI), Meng Li, Miomir Vukmirovic

– anode catalyst and membrane research; characterization
  Piotr Zelenay (Project Lead), Hoon Chung, Yu Seung Kim, Qing Li, Gerie Purdy, Dusan Spernjak, Xiaodong Wen, Gang Wu

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

– hydrocarbon membrane research
  James McGrath (PI), Yu Chen, Jarrett Rowlett, Andy Shaver

– methanol anode catalyst research; MEA integration
  Alex Martinez Bonastre (PI), Noelia Cabello Moreno, 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
Methanol Oxidation: Loading Dependence (uTAAC and uT-PtRuSn)

- Loading studies performed in the range from 0.2 to 1.0 mg\textsubscript{Pt} cm\textsuperscript{-2} with uTAAC and from 0.2 to 0.5 mg\textsubscript{Pt} cm\textsuperscript{-2} with uT-PtRuSn; thinner layers benefiting from better catalyst utilization

- **Highlight:** At the optimum catalyst loading of 0.3 mg\textsubscript{Pt} cm\textsuperscript{-2}, the ultra-thrifted carbon-supported PtRuSn catalyst reaching the mass activity target of the project (200 mA mg\textsubscript{Pt}\textsuperscript{-1})

- Significant improvement on the benchmark DMFC anode catalyst (HiSPEC\textsuperscript{®} 12100) achieved with several new materials
Methanol Oxidation: Stripping of MeOH-Derived CO (PtRu Catalysts)

- Largest increase in Pt character observed with AAC anode
- Cathode in MEA with uTAAC indicating the largest Ru crossover
Methanol Oxidation: Stripping of MeOH-Derived CO (PtRuSn Catalysts)

- CO-stripping peak on Sn-containing anodes becoming much narrower after cycling (Sn loss?)
- Possible accumulation of Sn on cathodes in MEAs with Sn-containing anodes
Ethanol Oxidation: Pd$_4$Au$_1$M$_5$/C Particles as Nanocores (STEM and XAS)

**HRTEM, HAADF-STEM, and EELS**

- STEM and EELS studies confirming core-shell structure of Pd$_4$Au$_1$Co$_5$ nanoparticles, with Co-rich core and PdAu-rich shell
- In-situ XAS attesting to good protection of Co core by PdAu shell and stabilization of Pd
DME Oxidation: Pt$_{45}$Ru$_{45}$Pd$_{10}$/C Catalyst (Characterization)

- Uniform and narrow distribution of PtRuPd nanoparticles on carbon support (average size ~ 2.7 nm)
- Alloying verified by the positive shift of the (111) XRD peak for PtRuPd vs. Pt (atomic radii: $r_{\text{Pt}} = 1.39$ Å, $r_{\text{Ru}} = 1.34$ Å, $r_{\text{Pd}} = 1.37$ Å)