Advanced Materials and Concepts for Portable Power Fuel Cells

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Project ID: FC091
Overview

Timeline

• Start date: September 2010
• End date: Four-year duration
• Completion: ca. 40%

Budget

• Total funding estimate:
  - DOE share: $3,825K
  - Contractor share: $342K
• FY11 funding received: $1,000K
• FY12 funding estimate: $975K

Barriers

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

Partners – Principal Investigators

Brookhaven National Laboratory
  – Radoslav Adzic

University of Delaware
  – Yushan Yan

Virginia Tech
  – James McGrath

Johnson Matthey Fuel Cells
  – Noelia Cabello-Moreno

SFC Energy
  – Christian Böhm

Oak Ridge National Laboratory
  – 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.

**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>

**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$-$0.7$ V

**The ultimate project goal!**
Approach: Focus Areas

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

<table>
<thead>
<tr>
<th>Date</th>
<th>Milestone or Go/No-Go Decision</th>
<th>Status</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dec 11</td>
<td>Complete equipment set-up for fuel cell testing with liquid feed of DME; improve the DDMEFC performance to reach $\geq 250$ mA/cm$^2$ at 0.40 V at 80°C. Go/no-go decision on DME research.</td>
<td>Complete</td>
<td>Set-up completed; a “go” decision for DME research based on anode activity and path forward for catalyst development.</td>
</tr>
<tr>
<td>Dec 11</td>
<td>Assess activity and stability in half-cell and fuel-cell testing of the PtRu benchmark HisPEC® 12000 and at least one developmental PtRu catalyst over the DMFC anode potential range 0.0-0.85 V.</td>
<td>Pending</td>
<td>HisPEC® 12100 and PtRu black testing completed; developmental catalysts to arrive soon at LANL for testing.</td>
</tr>
<tr>
<td>Jan 12</td>
<td>Go/no-go on PtSn catalysts development for methanol oxidation: PtSn catalyst exceeding half-cell mass activity of 200 mA/mg$_{Pt}$ at 0.35 V at 80°C (iR-corrected) and demonstrating durability at least matching that of the HisPEC 12100 benchmark catalyst.</td>
<td>Complete</td>
<td>“No-go” decision for PtSn development; a “go” for ternary PtRuSn catalyst; 200 mA/mg$_{Pt}$ milestone exceeded with ternary PtRuSn by at least 150%.</td>
</tr>
<tr>
<td>Jan 12</td>
<td>Demonstrate a ternary PtRhSnO$_2$ electrocatalyst capable of oxidizing ethanol to CO$_2$ with an efficiency of 50% at 0.4 V vs. RHE at 80°C.</td>
<td>Pending</td>
<td>Further catalyst optimization and DEMS set-up for CO$_2$ determination needed to complete task; expected in October 2012.</td>
</tr>
<tr>
<td>Mar 12</td>
<td>Synthesize at least one multiblock copolymer allowing for (i) current density $\geq 0.28$ A/cm$^2$ at 0.5 V, (ii) methanol utilization of $\geq 95$% at peak power, and (iii) less than 10% DMFC performance degradation for 100 h in a preliminary life-test at 80°C.</td>
<td>Complete</td>
<td>Current density greater than 0.28 A/cm$^2$ at 0.5 V; crossover reduced by 55% relative to Nafion® 212 and by 40% relative to the best earlier multiblock copolymers.</td>
</tr>
<tr>
<td>Mar 12</td>
<td>Complete kinetic study of DME adsorption and oxidation on PtRu catalysts to assess DDMEFC potential to deliver 1.25 kWh/L (conditional upon a “go” decision on DME research in Dec 11).</td>
<td>Complete</td>
<td>1.25 kWh/L (fuel) deliverable already at maximum power; 1.25 kWh/L (system) achievable at long operating times.</td>
</tr>
<tr>
<td>Aug 12</td>
<td>Complete equipment set-up for the evaluation of the stack with selected alternative membranes; adapt stack hardware to testing hydrocarbon membranes of different thickness.</td>
<td>Pending</td>
<td>Set-up for short-stack test stand ongoing at SFC ENERGY facility at Rockville, Maryland; timely completion planned.</td>
</tr>
<tr>
<td>Sep 12</td>
<td>Demonstrate improved methanol oxidation activity of a thrifted PtRu catalyst with durability at least matching that of the HisPEC® 12100 benchmark catalyst.</td>
<td>Pending</td>
<td>On track; durability of new JMFC’s thrifted PtRu catalysts under evaluation.</td>
</tr>
<tr>
<td>Sep 12</td>
<td>Scale up the synthesis of PtRu platelets for methanol oxidation to 0.5 g batch to allow MEA testing.</td>
<td>Pending</td>
<td>Scale-up synthesis underway.</td>
</tr>
<tr>
<td>Sep 12</td>
<td>Develop PtRu core-shell nanowires with methanol oxidation onset potential of $\leq 0.325$ V vs. RHE at room temperature and 5-fold improvement in mass activity relative to that of PtRu nanotubes in FY11.</td>
<td>Complete</td>
<td>Methanol oxidation onset potentials of 0.30 V and 0.31 V and 5-fold mass activity improvement demonstrated.</td>
</tr>
</tbody>
</table>
**Highlight**: PtRu “advanced anode catalyst” (AAC) exceeding the performance of benchmark HiSPEC® 12100 catalyst by ca. 40 mV

**Highlight**: ACC (variation 4) successfully scaled-up to 100 g without performance loss (in spite of a slightly lower specific surface area)

Anode research on track to reach the target of improved activity of thrifted PtRu catalysts without a durability loss and to reach the project goal of 150 mA cm\(^{-2}\) at 0.60 V (DMFC)
Methanol Oxidation: Binary PtSn/C Catalysts

Cat prep 1 $\rightarrow$ base hydrolysis  Cat prep 1.1 $\rightarrow$ base hydrolysis, modified firing step
Cat prep 2 $\rightarrow$ complex route   Cat prep 3 $\rightarrow$ new preparation route

- Methanol-oxidation activity advantage of PtSn/C catalysts, Pt(3:1) in particular, relative to PtRu/C in the kinetic region (at low current densities, up to 150 mA cm$^{-2}$)
- PtSn/C performance limited at potentials higher than 0.2 V due to SnO$_2$ formation and resulting decrease in the OH availability*

No-go for the binary PtSn catalyst research

- Could PtSn/C be combined with a third metal to reduce methanol oxidation overpotential in the high current-density region?

* The effect of Sn content on MeOH oxidation activity in a Technical Backup Slide
MeOH Oxidation: Ternary PtRuSn/C Catalysts

- Highlight: JMFC’s ternary PtRuSn/C catalyst combining unique activity of PtSn/C at low overpotentials with superior performance of PtRu/C at high overpotentials
- Highlight: Significantly higher MeOH oxidation activity of PtRuSn/C catalyst than most active thrifted PtRu/C catalysts

Mass-activity milestone for Sn-containing catalysts exceeded by approximately 150%

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt at%</th>
<th>Ru at%</th>
<th>Sn at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtRu/C - HiSPEC® 12100</td>
<td>50</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>PtRu/C - advanced binary</td>
<td>20</td>
<td>80</td>
<td>-</td>
</tr>
<tr>
<td>PtSn/C - binary</td>
<td>77</td>
<td>-</td>
<td>23</td>
</tr>
<tr>
<td>PtRuSn/C - new ternary</td>
<td>19</td>
<td>71</td>
<td>10</td>
</tr>
</tbody>
</table>

Catalyst Deposition:

1st approach: Deposition of different amounts of Sn on a PtRu alloy
2nd approach: Deposition of different amounts of Ru on a PtSn alloy
3rd approach: Synthesis of catalyst with different PtRuSn at% at the surface
4th approach: Alternative synthesis to tailor a ternary catalyst

Anode Polarization (2.0 M MeOH, 80°C)

- > 500 mA/mgPt at 0.35 V

Graphical representation of the electrochemical performance of different catalysts at varying potentials.
MeOH Oxidation: PtRu and PtRu/C Anode Stability

Anode: PtRu (5 mg cm⁻²) or PtRu/C (3 mg cm⁻²), 0.5 M MeOH; Cathode: Pt (3 mg cm⁻²) or Pt/C (5 mg cm⁻²); Membrane: Nafion® 117 or 2×Nafion® 212; Cell: 80°C

- Performance losses with both systems attributed to Ru cathode contamination; only small anode losses observed
- Data after humidification and 2 h polarization: Ru contamination less severe and more difficult to induce with carbon-supported catalysts (PtRu/C - Pt/C) than with the blacks (PtRu - Pt) due to (i) the larger amount of unalloyed Ru phase in PtRu black at higher catalyst loading in the PtRu - Pt system (alloyed fraction similar based on XRD, cf. a Reviewer-Only Slide) and, though less likely, (ii) contribution of the carbon surface area in Pt/C (PtRu/C - Pt/C)
Methanol Oxidation: Innovative PtRu Nanostructure Catalysts

- **Highlight**: Onset potential of methanol oxidation improved by 30 mV and 20 mV with PtRu/CuNWs and PtSn/CuNWs relative to the benchmark PtRu/C catalyst (HiSPEC® 12100)

  Oxidation onset potential target of < 0.325 V and improvement in PGM mass activity at low overpotentials achieved with two catalysts

- **Performance stability demonstrated to be on par with the benchmark catalyst** (data included in a Technical Backup Slide)

**Solution**: 1.0 M MeOH in 0.5 M H₂SO₄; **Scan rate**: 5 mV s⁻¹

**Benchmark PtRu/C catalyst**: HiSPEC® 12100

(a) - (b) TEM images and (c) SAED pattern of Pt/CuNWs.
DMFC Multiblock Copolymers: Properties and Performance

**Multiblock Copolymers: Structure and Properties**

![Chemical structures of 6FBPS-BPSH100, 6FK-BPSH100, and 6FPAEB-BPSH100](image)

### DMFC Performance with 0.5 M MeOH

- **Anode:** 6.0 mg cm⁻² Pt₅₀Ru₅₀ black, 0.5 M 1.8 mL/min MeOH solution; **Cathode:** 4.0 mg cm⁻² Pt black; 500 sccm air; **Membrane:** multiblock copolymers and Nafion® 212; **Cell:** 80°C

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>6FBPS-BPSH100</th>
<th>6FK-BPSH100</th>
<th>6FPAEB-BPSH100</th>
<th>Nafion® 212</th>
</tr>
</thead>
<tbody>
<tr>
<td>Block size (g)</td>
<td>15,000</td>
<td>7,000</td>
<td>11,000</td>
<td>-</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>44</td>
<td>31</td>
<td>34</td>
<td>50</td>
</tr>
<tr>
<td>HFR (W cm²)</td>
<td>0.073</td>
<td>0.070</td>
<td>0.063</td>
<td>0.066</td>
</tr>
<tr>
<td>Crossover (A cm⁻²) with 0.5 M MeOH</td>
<td>0.150</td>
<td>0.149</td>
<td>0.173</td>
<td>0.181</td>
</tr>
<tr>
<td>i at 0.5 V (A cm⁻²)</td>
<td>0.272</td>
<td>0.292</td>
<td>0.252</td>
<td>0.240</td>
</tr>
</tbody>
</table>

**Highlights:**
- Highly conductive multiblock copolymers prepared using telechelic BPSH-100 oligomers *
- **Highlight:** Multiblock copolymer membranes outperforming Nafion® 212 in DMFC testing (0.5 M MeOH)
  
  DMFC milestone performance (> 0.28 A/cm² at 0.5 V) achieved with 3 out of 11 multiblock copolymers
- **Next:** Further reduction in methanol crossover

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* Synthesis details and spectroscopic data in a Technical Backup Slide
**DMFC Multiblock Copolymers: MeOH Crossover Reduction**

<table>
<thead>
<tr>
<th>6F&lt;sub&gt;x&lt;/sub&gt;BP&lt;sub&gt;100-x&lt;/sub&gt;PAEB-BPSH100 Multiblock copolymers</th>
</tr>
</thead>
</table>

- Methanol permeability controlled by introducing BP and varying BP-to-6F ratio
- SAXS profile indicating highly ordered structure of multiblock copolymers with decreasing interdomain distance (anisotropic behavior confirmed by NMR)
- Highlight: 55% reduction in methanol crossover compared to Nafion® 212

**SAXS Profiles**

Interdomain distance increasing with the 6F-BPA moiety decrease

6F<sub>x</sub>BP<sub>100-x</sub>PAEB-BPSH100 showing 2nd order peaks → lamellar structure

**1H NMR of Multiblock Copolymers (10K-10K)**

**Methanol Crossover with Various Membranes**

- 50 µm membranes
- cMeOH 0.5 M
- Temperature 80°C
- 6F<sub>75</sub>BP<sub>25</sub>PAEB-BPSH100
- 6F<sub>50</sub>BP<sub>50</sub>PAEB-BPSH100
- 6F<sub>25</sub>BP<sub>75</sub>PAEB-BPSH100
- Nafion® 212
**DMFC Multiblock Copolymers: Performance and Fuel Utilization (0.5 M MeOH)**

**Anode:** PtRu black (4.0 mg cm\(^{-2}\)); **Cathode:** Pt black (3.0 mg cm\(^{-2}\)); **Cell:** 80°C

**DMFC Polarization (0.5 M MeOH)**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Multiblock</th>
<th>Nafion®</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6F75 (50 µm)</td>
<td>6F25 (47 µm)</td>
</tr>
<tr>
<td>η(_{\text{fuel at 0.5 V, %}})</td>
<td>69</td>
<td>77</td>
</tr>
<tr>
<td>η(_{\text{fuel at peak power, %}})</td>
<td>92</td>
<td>95</td>
</tr>
</tbody>
</table>

- MEAs with multiblock-copolymer membranes showing superior performance to Nafion® 212 at DMFC voltages higher than ca. 0.55 V while maintaining similar resistance
- **Highlight:** Better fuel utilization obtained with multiblock copolymers MEAs than Nafion®
  
  **DMFC fuel utilization milestone of ≥ 95% at peak power achieved**
  with 6F25BP75PAEB-BPS100 copolymer

- **Next:** Further reduction of methanol crossover by replacing 6F and BP with hydroquinone

* Performance with 2.0 M MeOH feed in a Technical Backup Slide
DMFC Performance Degradation: 100-Hour Life Test

- Unrecoverable performance loss significantly increasing with methanol concentration; recoverable performance decreasing*
- Post-life-test HFR increasing with methanol concentration; loss of ionomer possible
- Highlight: 3% unrecoverable performance measured with 0.5 M MeOH at 0.4 V after 100 hours
- Next: Perform detailed degradation study

* Current and HFR changes during the life test in a Technical Backup Slide
DMFC Performance Degradation: Crack Formation in 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>Before test</td>
<td><img src="image1" alt="Anode Image" /></td>
<td><img src="image2" alt="Cathode Image" /></td>
</tr>
<tr>
<td>0.5 M 100 h</td>
<td><img src="image3" alt="Anode Image" /></td>
<td><img src="image4" alt="Cathode Image" /></td>
</tr>
<tr>
<td>1.0 M 100 h</td>
<td><img src="image5" alt="Anode Image" /></td>
<td><img src="image6" alt="Cathode Image" /></td>
</tr>
<tr>
<td>4.0 M 100 h</td>
<td><img src="image7" alt="Anode Image" /></td>
<td><img src="image8" alt="Cathode Image" /></td>
</tr>
</tbody>
</table>

Anode: 6.0 mg cm$^{-2}$ Pt$_{50}$Ru$_{50}$ black, 1.8 mL/min MeOH solution; Cathode: 4.0 mg cm$^{-2}$ Pt black; 500 sccm air; Membrane: Nafion® 212; Cell: 80ºC; Life test: constant voltage at 0.45 V

- Anode and cathode cracking increasing with MeOH concentration;* cathode more vulnerable
- Highlight: Potentially important factor for DMFC performance degradation determined
- Next: Develop mitigation strategy for cracking

* Effect of other life-test conditions in a Reviewer-Only Slide
Ethanol Oxidation: Monolayer Catalysts for Alcohols Oxidation (Approaches)

**Geometric and Ligand Effects: Pt$_{ML}$ on Substrates**
1. Decrease in Pt content to a single monolayer
2. Tuning of the catalytic properties of Pt monolayer
3. Establishment of predictive base for oxidation reactions

**Combination of Bifunctional and Electronic Effects**
1. Further modification of Pt$_{ML}$/Au(111) via bi-functional mechanism to tune catalytic properties of Pt monolayer
2. Incorporation of oxophilic elements (e.g., Ru, Ir) and hydroxides species (e.g., Sn(OH)$_x$) into Pt$_{ML}$

Sn(OH)$_x$/(Pt$_3$Ir$_1$)$_{ML}$/Au(111)  
Sn(OH)$_x$/(Pt$_3$Ru$_1$)$_{ML}$/Au(111)

Sn(OH)$_x$/Ir$_{1/2ML}$/Pt$_{ML}$/Au(111)

**Carbon-Supported Nanoparticle Catalysts: Pt$_{ML}$/Au**

1. **Pt$_{ML}$/Au/C**: Pt$_{ML}$ supported on Au nanoparticles
2. **Au-Pt/C**: Au-rich core and Pt-rich shell
3. **Pt$_{ML}$/AuNi$_{0.5}$Fe/C**: Pt$_{ML}$ supported on nanoparticles containing Au-rich shells and NiFe-rich cores to reduce noble metal loading

**Carbon-Supported Nanoparticle Catalysts: Pt$_{ML}$/Pd**

1. **Pt$_{ML}$/Pd/C**: Pt$_{ML}$ supported on Pd nanoparticles
2. **Pt$_{ML}$/Pd$_x$Au$_y$/C**: Pt$_{ML}$ supported on Pd$_x$Au$_y$ alloy nanoparticles

2. **SnO$_2$/Pt$_{ML}$/Pd$_9$Au$_1$/C**: SnO$_2$-modified Pt$_{ML}$ supported on Pd$_9$Au$_1$ alloy nanoparticles

Los Alamos National Laboratory

2012 Hydrogen and Fuel Cells Program Annual Merit Review
Ethanol Oxidation: Expanded/Compressed and “Engineered” Surfaces

- Lattice expansion in Pt_{ML} supported on Au(111) leading to significantly enhanced EtOH oxidation current relative to Pt(111) and to likely improved selectivity in CO2 generation

- Highlight: Further “engineering” of Pt_{ML}/Au(111) surface resulting in additional shift in the onset EtOH oxidation potential to below 0.2 V vs. RHE at the Sn(OH)_{x}/(Pt_{3}Ir_{1})_{ML}/Au(111) catalyst

- Cost-effective core materials needed
**Ethanol Oxidation: Carbon-Supported Nanoparticle Pt\textsubscript{ML} Catalysts**

- **Highlight:** Very promising activity demonstrated using Pt\textsubscript{ML}/AuNi\textsubscript{0.5}Fe/C catalyst with reduced noble metal loading in the nanoparticle core

- **Highlight:** SnO\textsubscript{2}/Pt\textsubscript{ML}/Pd\textsubscript{9}Au\textsubscript{1}/C catalyst exhibiting the lowest onset potential among carbon-supported catalysts, comparable to that measured with the most active single-crystal catalysts; high CO\textsubscript{2} yields possible

- In-situ infrared reflection-absorption spectroscopy (IRRAS) and on-line differential electrochemical mass spectroscopy (DEMS) being set up to study the substrate-induced change in Pt\textsubscript{ML}’s selectivity for the oxidation of ethanol
**Ethanol Oxidation: The Effect of Nanocatalyst Morphology**

- **Highlight:** A pronounced morphology effect in EtOH and CO$_{ads}$ oxidation on Pt nanowires and nanoparticles.
- **Higher activity of nanowires caused by a weaker bonding of CO$_{ads}$ and its more facile removal from the catalyst surface.
- **Effect potentially important for catalyst design.**

**Graphs and Images:**
- Comparison of Pt nanowires (NW) and Pt nanoparticles (NP) for ethanol oxidation.
- CO stripping curves showing distinct peaks for NW and NP.
- Electrocatalytic current density ($j / mA cm^{-2}$) versus potential (E/V vs. RHE) for different conditions.
- Time (s) vs. current density ($j / mA cm^{-2}$) for CO stripping.

**Notes:**
- 0.2M EtOH + 0.1M HClO$_4$.
- 10mV/s scan rate.
- 0.65V potential limit.
Ethanol Oxidation: Anode and DEFC Performance

**Anode:** 1 mg cm$^{-2}_\text{metal}$ 12 wt% PtIrSnO$_2$/C or 13% PtRhSnO$_2$/C, 0.5 M ethanol, 1.8 ml/min; **Cathode:** 4 mg cm$^{-2}$ Pt black, 200 sccm H$_2$; **Membrane:** Triple Nafion® 212 sandwich; **Cell:** 80°C

- **Anode:** 1 mg cm$^{-2}_\text{metal}$ 12 wt% PtIrSnO$_2$/C or 13% PtRhSnO$_2$/C, 0.5 M ethanol, 1.8 ml/min; **Cathode:** 4 mg cm$^{-2}$ Pt black, 500 sccm air; **Membrane:** Triple Nafion® 212 sandwich; **Cell:** 80°C

- **Highlight:** Excellent activity demonstrated with two ternary catalysts; onset potential of EtOH oxidation very close to the thermodynamic value of ca. 0.04 V at 80°C
- **While exceeding the best DEFC performance published, the fuel cell performance of both catalysts greatly impacted by possible cathode contamination; reduction in non-noble metal migration from the anode likely needed**
DME Fuel Cell Research: Liquid Feed

- ** Liquid feed DME fuel cell milestone achieved **

**Anode:** 6 mg cm\(^{-2}\) Pt\(_{50}\)Ru\(_{50}\), 40 sccm DME gas, 30 psig, anode humidifier at 85°C or DME-saturated solution (1.65 M)*, 2.5 ml/min; **Cathode:** 4 mg cm\(^{-2}\) Pt, 500 sccm air, 20 psig; **Membrane:** Nafion® 117; **Cell:** 80°C


<table>
<thead>
<tr>
<th>Performance</th>
<th>Liquid Feed</th>
<th>Gas Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCV (V)</td>
<td>0.877</td>
<td>0.852</td>
</tr>
<tr>
<td>DME-crossover peak current (mA cm(^{-2}))</td>
<td>50</td>
<td>48</td>
</tr>
</tbody>
</table>

**Highlight:** Liquid-feed DME fuel cell showing higher OCV and slightly improved performance in the kinetic region compared with the fuel cell operating on gaseous DME

- **DME-to-H\(_2\)O ratio of 1.4:1 in FY11 DME fuel cell with anode humidifier at 85°C larger than stoichiometric (1:3), possibly resulting in water deficiency at the anode**
DME Fuel Cell: Effects of Anode Humidification and Membrane Thickness

Anode: 6 mg cm⁻² Pt₅₀Ru₅₀ black, 40 sccm DME gas, 30 psig; Cathode: 4 mg cm⁻² Pt black, 500 sccm air, 20 psig; Membrane: Nafion® 117; Cell: 80°C

- Highlight: DDMEFC performing better with the molar ratio of DME to H₂O closer to stoichiometric.
- Gas-feed DDMEFC with anode humidifier at 110°C outperforming liquid-feed DME fuel cell.
- Unlike DMFC performance, the iR-corrected DDMEFC performance shown to be independent of the membrane thickness, indicating relatively low fuel crossover and/or lower activity of the Pt cathode towards DMFE than MeOH at high potentials.

<table>
<thead>
<tr>
<th>Humidifier temperature (°C)</th>
<th>Total pressure (kPa)</th>
<th>H₂O vapor pressure (kPa)</th>
<th>DME partial pressure (kPa)</th>
<th>DME-to-H₂O ratio (molar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>143</td>
<td>58</td>
<td>85</td>
<td>1.4 : 1</td>
</tr>
<tr>
<td>95</td>
<td>177</td>
<td>84</td>
<td>93</td>
<td>1.1 : 1</td>
</tr>
<tr>
<td>110</td>
<td>191</td>
<td>143</td>
<td>48</td>
<td>1: 3</td>
</tr>
</tbody>
</table>
DME Fuel Cell: Performance Comparisons

- **Anode:** 6 mg cm\(^{-2}\) Pt\(_{50}\)Ru\(_{50}\) black, 40 sccm DME gas, 30 psig, anode humidifier at 85°C (FY11) or 110°C (FY12); **Cathode:** 4 mg cm\(^{-2}\) Pt black, 500 sccm air, 20 psig; **Membrane:** Nafion® 117 (FY11) or Nafion® 212 (FY12); **Cell:** 80°C

- **Anode:** 6 mg cm\(^{-2}\) Pt\(_{50}\)Ru\(_{50}\) black, 1.8 mL/min 1 M MeOH or 40 sccm DME, 30 psig, anode humidifier at 110°C; **Cathode:** 4 mg cm\(^{-2}\) Pt black, 20 psig (with DME) or 0 psig (with MeOH), 500 sccm air; **Membrane:** Nafion® 212; **Cell:** 80°C

**DME Fuel Cell: FY12 vs. FY11**

- **LANL DDMEFC FY12**
- **LANL DDMEFC FY11**

**DME Fuel Cell vs. DMFC**

- **LANL DDMEFC FY12**
- **DMFC with 1.0 M MeOH**

- **Highlight:** FY12 performance of the DME fuel cell reaching more than 250 mA cm\(^{-2}\) at 0.40 V and exceeding the FY11 performance at 0.50 V by ca. 65%

**DME fuel cell performance milestone achieved**

- At voltages higher than 0.49 V, DME fuel cell performance superior to that of the DMFC, mainly due to reduced effect of DME crossover compared to that of MeOH

**“Go” decision for further DME research**
DME Fuel Cell: New Ternary PtRuPd Catalyst for DME Oxidation

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>HiSPEC® 12100</th>
<th>LANL PtRuPd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal loading by TGA in air (wt%)</td>
<td>73</td>
<td>24</td>
</tr>
<tr>
<td>Pt:Ru:Pd mass ratio by XRF</td>
<td>67:33:0</td>
<td>74:10:16</td>
</tr>
<tr>
<td>(51:49:0 at%)</td>
<td></td>
<td>(60:15:25 at%)</td>
</tr>
<tr>
<td>ECSA by H₂ adsorption/desorption (m²/gmetal)</td>
<td>51</td>
<td>103</td>
</tr>
<tr>
<td>Onset potential of DME oxidation (V vs. RHE)</td>
<td>0.43</td>
<td>0.38</td>
</tr>
<tr>
<td>Particle size from XRD (nm)</td>
<td>3.6</td>
<td>4.3</td>
</tr>
</tbody>
</table>

*a Determined at a current exceeding the background current by 3δ (δ - the standard deviation of the background current)

- Pd aiding in the C-O bond cleavage
- Alloying verified by the right shift in the (111) XRD peak for PtRuPd vs. Pt
- Highlight: LANL PtRuPd ternary catalyst exhibiting significant catalytic activity in DME oxidation in half-cell testing
- **Next**: Ternary catalyst optimization for maximum activity and stability under DME fuel cell operating conditions
Collaborations

- Seven organizations with highly 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 – next-phase research and development aimed specifically at reducing cost of the direct methanol fuel cell components and system for applications in excess of 1 kW in power (early phase)
  - Warsaw University, Warsaw, Poland – dimethyl ether oxidation on platinum-free electrocatalysts
  - University of Waterloo, Waterloo, Ontario, Canada – development of nanostructured methanol oxidation catalysts (early phase)
Methanol oxidation catalysis:
• Further develop PtRuSn ternary catalysts to improve the kinetic performance at low Pt loadings
• Develop protocols for stack testing under SFC Energy conditions (75-80°C, 0.5 M MeOH)
• Evaluate stability and durability of new MeOH oxidation catalysts; meet durability milestone (durability of thrifted PtRu catalyst matching that of HiSPEC® 12100 w/o activity loss); carry out breakdown of performance losses in DMFCs and initiate development of mitigation strategies
• Optimize accelerated corrosion test to mimic decay mechanisms in long-term stack testing

Innovative membranes and electrode structures:
• Continue reducing methanol crossover by introducing hydroquinone into multiblock copolymers
• Improve durability of alternative membranes in the presence of higher concentrations of MeOH
• Develop PtSn/CuNW structure to achieve the onset potential of methanol oxidation of 0.29 V and 20% improvement in PGM mass activity of innovative nanostructure catalysts

Ethanol oxidation catalysis:
• Establish methodology for the synthesis of Pt_{ML} - nanoparticle catalysts with cost-effective core materials for deposition of Pt_{ML} and active promoters (SnO_x, SnO_2, Ru, etc.); scale-up the synthesis
• Implement in-situ IRRAS and on-line DEMS to determine substrate-induced selectivity of Pt_{ML}’s in EtOH (and MeOH) oxidation and EtOH oxidation at ternary PtRhSnO_2/C and PtIrSnO_2/C catalysts
• Determine the mechanism of cathode performance loss in DEFCs operating with ternary anode catalysts; develop a mitigation strategy

DME research:
• Develop a comprehensive model of the DME oxidation mechanism and catalyst requirements
• Optimize the ternary PtRuPd catalyst for maximum activity and stability at the DME fuel cell anode
Summary

- The latest PtRu “advanced anode catalyst” exceeds performance of the HiSPEC® 12100 benchmark by 40 mV; the catalyst synthesis has been successfully scaled up to 100 g
- A “no-go” decision has been made for further PtSn catalyst research; effort redirected towards PtRuSn catalyst, already showing unprecedented MeOH oxidation activity
- Carbon-supported PtRu catalysts cause less cathode contamination by Ru than blacks
- PtRu/CuNW catalyst exhibits a 30 mV improvement in the onset potential of MeOH oxidation relative to the HiSPEC® 12100 benchmark, similar stability maintained
- Multiblock copolymers, e.g. 6F25BP75PAEB-BPS100, allow for up to 55% reduction in MeOH crossover relative to the Nafion® 212 benchmark; fuel utilization up to 95% has been reached with 0.5 M MeOH feed near the peak-power point
- While DMFC performance strongly depends on methanol concentration, the unrecoverable performance loss with 0.5 M MeOH feed is relatively small
- Several Pt_{ML} catalysts with expanded lattice and “engineered” catalysts have onset potential of EtOH oxidation near 0.2 V vs. RHE (20°C - 25°C); EtOH oxidation is very strongly dependent on catalyst morphology (e.g. nanowires vs. nanoparticles)
- Both PtIrSnO_{2}/C and PtRhSnO_{2}/C ternary catalysts allow to reach in MEA the onset potential of MeOH oxidation close to the thermodynamic value of 0.04 V at 80°C
- DME performance has been improved by 65% vs. FY11, resulting in a “go” decision for DME further research; new PtRuPd/C catalyst promises to aid in C-O bond cleavage
Co-Authors

- ethanol and methanol anode catalyst research
  R. R. Adzic (PI), S. Bliznakov, M. Li, P. Liu, K. Sasaki, W.-P. Zhou

- anode catalyst and membrane research; characterization

- nanostructure catalyst structures
  Y. Yan (PI), S. Alia, J. Zheng

- hydrocarbon membrane research
  J. McGrath (PI), Y. Chen, J. Rowlett

- methanol anode catalyst research; MEA integration
  N. Cabello-Moreno (PI), G. Hards, G. Spikes

- MEA integration and testing; final deliverable
  C. Böhm (PI), V. Graf, P. Hassell

- microscopic characterization (no-cost partner)
  K. More (PI), D. Cullen
Technical Backup Slides
A series of PtSn (3:1) catalysts with variable Sn content prepared by Cat prep 3 route

The plot of activity vs. Sn content revealing a volcano plot with a maximum at 6.5 wt% Sn
Methanol Oxidation: Innovative PtRu Nanostructure Catalysts

**CO Stripping**

<table>
<thead>
<tr>
<th>E/V vs. RHE</th>
<th>PtRu/CuNW</th>
<th>PtSn/CuNW</th>
<th>Pt/CuNW</th>
<th>PtNT(Cu)</th>
<th>PtRu/C</th>
<th>Pt/C</th>
</tr>
</thead>
</table>

**Performance Stability Testing**

<table>
<thead>
<tr>
<th>t/min</th>
<th>PtRu/CuNW</th>
<th>PtSn/CuNW</th>
<th>Pt/CuNW</th>
<th>PtNT(Cu)</th>
<th>PtRu/C</th>
<th>Pt/C</th>
</tr>
</thead>
</table>

**Solution:** 1.0 M MeOH in 0.5 M H₂SO₄; **Voltammetry:** scan rate 5 mV s⁻¹; **Benchmark PtRu/C catalyst:** HiSPEC® 12100
DMFC Multiblock Copolymers: Synthesis and Characterization

**19F NMR of 6F_{50}BP_{50}PAEB 10k Oligomer**

**Hydrophilic Telechelic BPSH-100 Oligomers**

Multiblock copolymer with reduced methanol permeability
DMFC Multiblock Copolymers: Performance and Fuel Utilization (2.0 M MeOH)

- MEAs with multiblock copolymer membranes showing better performance and lower methanol crossover with 2.0 M methanol feed than the control Nafion® MEA
- Low fuel utilization (no more than 80%) caused by high methanol feed concentration
DMFC Performance Degradation: Current Density and HFR Changes

- **Anode:** 6 mg cm\(^{-2}\) Pt\(_{50}\)Ru\(_{50}\) black, 1.8 mL/min MeOH solution; **Cathode:** 4 mg cm\(^{-2}\) Pt black; 500 sccm air; **Membrane:** Nafion\(^\circledR\) 212; **Cell:** 80\(^\circ\)C

### Current Density in 100-Hour Life Test at 0.40 V

- **HFR in 100-Hour Life Test at 0.40 V**

- Higher initial HFR value observed in more concentrated MeOH
- Little time-dependence of HFR with 0.5 M and 1.0 M MeOH feed concentrations
- Continuous HFR increase with 4.0 M MeOH feed, most likely due to structural MEA degradation