Fuel Cells for Portable Power

Thanks to generally less stringent cost constraints, portable power fuel cells, the direct methanol fuel cell (DMFC) in particular, promise earlier market penetration than higher power polymer electrolyte fuel cells (PEFCs) for the automotive and stationary applications. However, a large-scale commercialization of DMFC-based power systems beyond niche applications already targeted by developers will depend on improvements to fuel cell performance and performance durability as well as on the reduction in cost, especially of the portable systems on the higher end of the power spectrum (100-250 W).

In this part of the webinar, we will focus on the development of advanced materials (catalysts, membranes, electrode structures, and membrane electrode assemblies) and fuel cell operating concepts capable of fulfilling two key targets for portable power systems: the system cost of $5/W and overall fuel conversion efficiency of 2.0–2.5 kWh/L. Presented research will concentrate on the development of new methanol oxidation catalysts, hydrocarbon membranes with reduced methanol crossover, and improvements to component durability. Time permitted, we will also present a few highlights from the development of electrocatalysts for the oxidation of two alternative fuels for the direct-feed fuel cells: ethanol and dimethyl ether.
Introduction to DMFCs

Advanced Materials and Concepts for Portable Power Fuel Cells

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### Fuels for direct-feed polymer-electrolyte fuel cells

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Fuel-cell reaction</th>
<th>Specific energy (Wh/g)</th>
<th>Energy density (Wh/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>H₂ + 0.5 O₂ → H₂O</td>
<td>33.0</td>
<td>2.7*</td>
</tr>
<tr>
<td>Carbon</td>
<td>C + O₂ → CO₂</td>
<td>9.1</td>
<td>19.2</td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄ + 2 O₂ → CO₂ + 2 H₂O</td>
<td>14.2</td>
<td>6.0*</td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈ + 5 O₂ → 3 CO₂ + 4 H₂O</td>
<td>13.3</td>
<td>6.6*</td>
</tr>
<tr>
<td>Decane</td>
<td>C₁₀H₂₂ + 15.5 O₂ → 10 CO₂ + 11 H₂O</td>
<td>12.9</td>
<td>9.4</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH + 1.5 O₂ → CO₂ + 2 H₂O</td>
<td>6.1</td>
<td>4.8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH + 3 O₂ → 2 CO₂ + 3 H₂O</td>
<td>8.0</td>
<td>6.3</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>C₂H₂O₆ + 2.5 O₂ → 2 CO₂ + 3 H₂O</td>
<td>5.3</td>
<td>5.9</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>CH₂O + O₂ → CO₂ + 2 H₂O</td>
<td>4.8</td>
<td>3.9*</td>
</tr>
<tr>
<td>Formic acid</td>
<td>HC₂O₄H + 0.5 O₂ → CO₂ + H₂O</td>
<td>1.7</td>
<td>2.1</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>C₂O₄H₂ + 0.5 O₂ → 2 CO₂ + H₂O</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH₃ + 0.75 O₂ → 0.5 N₂ + 1.5 H₂O</td>
<td>5.5</td>
<td>3.9*</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>N₂H₄ + O₂ → N₂ + 2 H₂O</td>
<td>5.2</td>
<td>5.3</td>
</tr>
</tbody>
</table>

* Based on the density of liquefied gas

Direct Methanol Fuel Cell

**Anode:** Pt-Ru  
**Cathode:** Pt  
**Membrane:** e.g. Nafion® 115

\[ \text{CH}_3\text{OH}_{(l)} + 1.5 \text{O}_2 \rightarrow 2 \text{H}_2\text{O}_{(l)} + \text{CO}_2^\uparrow \quad V = 1.21 \text{ V}; \quad \Delta G^\circ = 6.1 \text{ kWh kg}^{-1} = 4.8 \text{ kWh L}^{-1} \]
**DMFC vs. H₂-Air PEMFC: Rates of Electrode Processes**

### H₂-air fuel cell (PEMFC)

**Anode:** \( \text{H}_2 \rightarrow 2 \text{H}^+ + 2 \text{e}^- \)
- fast, low \( \eta \)

**Cathode:** \( 0.5 \text{O}_2 + 2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{O} \)
- slow, high \( \eta \)

---

**Overall:** \( 2 \text{H}_2 + 0.5 \text{O}_2 \rightarrow \text{H}_2\text{O}_{(l)} \)

### Direct methanol fuel cell (DMFC):

**Anode:** \( \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6 \text{H}^+ + 6 \text{e}^- \)
- slow, high \( \eta \)

**Cathode:** \( 1.5 \text{O}_2 + 6 \text{e}^- + 6 \text{H}^+ \rightarrow 3 \text{H}_2\text{O} \)
- slow, high \( \eta \)

---

**Overall:** \( \text{CH}_3\text{OH}_{(l)} + 1.5 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}_{(l)} \)
DMFC vs. H₂-Air PEMFC: Fuel Cell Polarization Plots

Additional DMFC cathode loss due to methanol crossover

Primary ORR kinetics loss at PEMFC cathode

Kinetic loss at DMFC anode

Kinetic loss at PEMFC anode

**Fundamental Research**

- Anode catalysts with improved methanol oxidation activity
- Methanol-tolerant cathode catalysts
- Membranes with reduced methanol permeability relative to perfluorosulfonic acid polymers
- MEA assembly design and structure
- Performance durability

**Stack and System Development**

- Novel stack materials research
- Hardware modeling and design
- MEA fabrication and production scale-up
- Balance-of-plant efficiency
- Stack components durability
- Cost reduction
### 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>
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<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>
Advanced Materials and Concepts for Portable Power Fuel Cells: The Team

- 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
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.

Project technical target:
• System cost target: $5/W
• Performance target: Overall fuel conversion efficiency ($\eta_\Sigma$) of 2.0 kWh/L
• Resulting DMFC operating voltage target DMFC (similar for other fuels):
  
  (1) $2.0 \text{ kWh/L} \rightarrow \eta_\Sigma = 0.42 \quad 1.6\times \text{improvement over the state of the art (1.25 kWh/L)}$

  (2) If $\eta_{\text{fuel}} = 0.96, \eta_{\text{BOP}} = 0.90, V_{\text{th}} = 1.21 \text{ (at 25°C)}$
    
    $V_{\text{cell}} = V_{\text{th}} \left[ \eta_\Sigma \left( \eta_{\text{fuel}} \eta_{\text{BOP}} \right)^{-1} \right] = 0.6 \text{ V} \quad \rightarrow \text{the ultimate project target}$
Advanced Materials and Concepts for Portable Power: Research Focus Areas

• **DMFC anode research:**
  - catalysts with improved activity and reduced cost
  - development of catalysts with improved durability

• **Innovative electrode structures for better activity and durability**

• **Hydrocarbon membranes for lower MEA cost and improved performance:**
  - block copolymers
  - copolymers with cross-linkable end-groups

• **Alternative fuels for portable fuel cells:**
  - ethanol oxidation electrocatalysis
  - dimethyl ether research

• **Characterization; performance and durability testing; multi-cell device:**
  - advanced materials characterization
  - MEA performance testing
  - durability evaluation
  - five-cell stack
The Slow Process of Methanol Oxidation

Bi-functional MeOH oxidation mechanism:

First step: \[ \text{CH}_3\text{OH} + n\text{Pt} \rightarrow [n\text{Pt-CH}_3\text{OH}] \rightarrow \text{CO-Pt} + 4\text{H}^+ + 4\text{e}^- + (n-1)\text{Pt} \]

Second step: \[ \text{CO-Pt} + \text{Ru-"O"}_m \rightarrow \text{CO}_2 + \text{Ru-"O"}_m\text{-1 + Pt} \]
\[ (\text{Ru-"O"}_m\text{-1 + H}_2\text{O} \rightarrow \text{Ru-"O"}_m + 2\text{H}^+ + 2\text{e}^-) \]

Anode catalysts:

- Binary: **PtRu** (10-40 at% surface Ru), PtSn, PtMo, PtOs, etc.
- Ternary (e.g., PtRuOs)
- Quaternary (e.g., PtRuOsIr, PtRuSnW)
Methanol Oxidation: Advanced Anode Catalyst Performance & Scale-Up

**Benchmark:** HiSPEC® 12100 (50% Pt), 1.0 mg Pt cm⁻²; **ACC variation 4:** PtRu/C (18% Pt), 1.0 mg Pt cm⁻²; **Scale-up:** 100 g ACC

- PtRu “advanced anode catalyst” (AAC) exceeding the performance of benchmark HiSPEC® 12100 catalyst by ca. 40 mV
- 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: Ternary PtRuSn/C Catalysts

1\textsuperscript{st} approach
• Deposition of different amounts of Sn on a PtRu alloy

2\textsuperscript{nd} approach
• Deposition of different amounts of Ru on a PtSn alloy

3\textsuperscript{rd} approach
• Synthesis of catalyst with different PtRuSn at\% at the surface

4\textsuperscript{th} approach
• Alternative synthesis to tailor a ternary catalyst

<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\textsuperscript{®} 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>

Anode Polarization (2.0 M MeOH, 80°C)

- > 500 mA/mg\textsubscript{Pt} at 0.35 V

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

**PtRu Nanotubes from Ag Template (Chemical)**

1. Displacement of Ag in AgNW with Pt to form PtNT;
2. Ru deposition from RuCl$_3$ (reduction with ethylene glycol in the presence of polyvinyl pyrrolidone for shape control);
3. Annealing to form PtRu alloy.

**PtRu Nanotubes from Ag Template (Electrochemical)**

1. Displacement of Ag in AgNW with Pt to form PtNT;
2. Electrochemical deposition of Ru from RuCl$_3$ in H$_2$SO$_4$ at 0.3 V for 2 minutes.

**PtRu Nanotubes from Cu Template**

1. Simultaneous displacement of Cu in CuNW with Pt and Ru to form PtRuNT;
2. Annealing to form PtRu alloy.

**SEM images:** (a) CuNW; (c) PtNT; (e) Pt$_{80}$Ru$_{20}$ (Cu); (g) Pt$_{50}$Ru$_{50}$ (Cu).

**TEM images:** (b) CuNW; (d) PtNT; (f) Pt$_{80}$Ru$_{20}$ (Cu); (h) Pt$_{50}$Ru$_{50}$ (Cu).
Onset potential of methanol oxidation improved by 30 and 20 mV relative to the benchmark PtRu/C catalyst (HiSPEC® 12100) with PtRu/CuNWs and PtSn/CuNWs, respectively.

Performance stability demonstrated to be on par with the benchmark catalyst.
DMFC Multiblock Copolymers: Properties and Performance

Multiblock Copolymers: Structure and Properties

**6FBPS-BPSH100**

**6FK-BPSH100**

**6FPAEB-BPSH100**

<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 cm⁻²)</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>

* Crossover limiting current density at zero DMFC current.

### DMFC Performance with 0.5 M MeOH

- **Anode**: 6.0 mg cm⁻² Pt₄₀Ru₆₀ 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

- **Highly conductive multiblock copolymers prepared using telechelic BPSH-100 oligomers**
- **Multiblock copolymer membranes outperforming Nafion® 212 in DMFC testing (0.5 M MeOH)**
  > **0.28 A/cm² at 0.5 V achieved with 3 out of 11 multiblock copolymers synthesized**
DMFC Multiblock Copolymers: MeOH Crossover Reduction

**6F<sub>x</sub>BP<sub>100-x</sub>-PAEB-BPSH100 Multiblock copolymers**

![Chemical structure of multiblock copolymers](image)

**SAXS Profiles**

Interdomain distance increasing with the 6F-BPA moiety decrease

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

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

![NMR spectra](image)

**Methanol Crossover with Various Membranes**

- 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)
- 55% reduction in methanol crossover compared to Nafion® 212
**DMFC Multiblock Copolymers: Performance and Fuel Utilization (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_{fuel} at 0.5 V, %</td>
<td>69</td>
<td>77</td>
</tr>
<tr>
<td>η_{fuel} at peak power, %</td>
<td>92</td>
<td>95</td>
</tr>
</tbody>
</table>

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

- MEAs with multiblock-copolymer membranes showing superior performance to Nafion\(^®\) 212 at DMFC voltages higher than ca. 0.55 V while maintaining similar resistance
- Better fuel utilization obtained with multiblock copolymers MEAs than Nafion\(^®\)

**DMFC fuel utilization of ≥ 95% at peak power achieved**
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
- 3% unrecoverable performance measured with 0.5 M MeOH at 0.4 V after 100 hours

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\(^{\text{R}}\) 212; Cell: 80ºC; Life test: constant voltage at 0.45 V
DMFC Performance Degradation: Crack Formation in Electrodes

X-Ray Tomography after 100-hour Test (1×1 mm)

<table>
<thead>
<tr>
<th>MEA</th>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before test</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>0.5 M 100 h</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>1.0 M 100 h</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>4.0 M 100 h</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

**Anode:** 6.0 mg cm⁻² Pt₅₀Ru₅₀ black, 1.8 mL/min MeOH solution; **Cathode:** 4.0 mg cm⁻² Pt black; 500 sccm air; **Membrane:** Nafion® 212; **Cell:** 80°C; **Life test:** constant voltage at 0.45 V

- Anode and cathode cracking increasing with MeOH concentration; cathode more vulnerable
- Potentially important factor for DMFC performance degradation determined

**Crack Area after 100-hour Life Test (%)**

<table>
<thead>
<tr>
<th>MeOH (M)</th>
<th>0.5 M</th>
<th>1.0 M</th>
<th>4.0 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>c&lt;sub&gt;MeOH&lt;/sub&gt; (M)</td>
<td>0.032</td>
<td>0.077</td>
<td>0.289</td>
</tr>
</tbody>
</table>

- Anode and cathode cracking increasing with MeOH concentration; cathode more vulnerable
- Potentially important factor for DMFC performance degradation determined
DMFC Performance Degradation: Crack Formation in Electrodes

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

<table>
<thead>
<tr>
<th>MEA</th>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 M MeOH, 0.85 V</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>1.0 M MeOH, 0.45 V</td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td>1.0 M MeOH, 0.60 A/cm²</td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
</tbody>
</table>

Anode: 6 mg cm⁻² Pt₅₀Ru₅₀ black, 1.8 mL/min 1 M MeOH solution; Cathode: 4 mg cm⁻² Pt black; 500 sccm air; Membrane: Nafion® 212; Cell: 80°C.

- Microcrack formation depending on DMFC operating conditions subjected to the test conditions, with the most severe damage induced at OCV
- Mitigation strategy for cracking needed
The latest PtRu “advanced anode catalyst” exceeds performance of the HiSPEC® 12100 benchmark methanol oxidation catalyst by 40 mV, a significant performance improvement.

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% near the peak-power point has been reached with 0.5 M MeOH feed.

While DMFC performance strongly depends on methanol concentration, the unrecoverable performance loss with 0.5 M MeOH feed is relatively small; durability improvements in the presence of higher methanol concentrations appear necessary.