Facilitated Direct Liquid Fuel Cells with High Temperature Membrane Electrode Assemblies

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Advent Technologies, Inc.
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Overview - Program

**Timeline**
- Project Start Date: Oct 1, 2015
- Project End Date: Sep 30, 2017

**Budget**
- Total Funding: $1,251,000
- Advent Cost Share: $252,000 (20%)
- DOE Funds Spent FY16*: $292,000
  *(Includes $225,000 to LANL)*

**Funded Partners**
- LANL (P. Zelenay): catalyst synthesis and fuel cell testing

**Barriers** (FCTO-MYRDDP, 2014)
- A. Durability: new membrane approach
- B. Cost: elimination of reformer, lower PGM
- C. Performance: highly active anode catalyst

Incubator program to explore new, high impact areas
**Objective:** Demonstrate direct dimethyl ether (DME) oxidation at high temperature MEA significantly better than direct methanol fuel cells (DMFC)

**Program Targets**

<table>
<thead>
<tr>
<th>Key Performance Indicator</th>
<th>Current DMFC</th>
<th>Target Hi T Direct DME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum power (&gt; )</td>
<td>0.180 W/cm²</td>
<td>0.270 W/cm²</td>
</tr>
<tr>
<td>Total precious metal loading</td>
<td>5 mg_{PGM}/cm²</td>
<td>3 mg_{PGM}/cm²</td>
</tr>
<tr>
<td>Degradation rate</td>
<td>19 $\mu$V/h at a 0.2 A/cm²</td>
<td>10 $\mu$V/h at a 0.2 A/cm²</td>
</tr>
<tr>
<td>Loss in start/stop cycling</td>
<td>1.5 mV/cycle; cycle</td>
<td>0.75 mV/cycle; cycle</td>
</tr>
<tr>
<td>Anode mass-specific activity</td>
<td>50 A/g at 0.5 V</td>
<td>75 A/g at 0.5V</td>
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</table>

**Benefit:** carbon neutral auxiliary power for trucks and transport; extended run backup power
1. Benchmark
   - Run high temperature MEAs at LANL
   - Compare Pt anode w MeOH, DME (160 °C – 180 °C)
   - Use both PBI and TPS HT MEAs

2. GDE at 5 cm²
   - Make gas diffusion electrode (GDE) with PtRu, run with DME
   - Compare to LANL ternary anode catalyst
   - Evaluate PBI and TPS DME cross-over and performance

3. Scale to 50 cm²
   - Optimize anode GDE for mass transport
   - Refine cathode, if needed
   - Adjust reaction conditions

This period

6 mo.

6-12 mo.
Go/No Go

12-24 mo.
Approach – Milestones – Phase 1

M1
- Benchmark lab performance

M2
- Power with Pt and DME
- Define reaction envelope (T, H₂O stoich, flow)

M3
- Demonstrate 1.5x (75 A/g at 0.5 V) improvement over DMFC anode activity

M4
- Select best PBI or TPS for scale-up

Go/No Go
- 5 cm² cell exceeds best DMFC
- Total PM <4.5 mg/cm²
- Anode mass-specific activity 75 A/g @0.5V
Approach – Milestones – Phase 2

M5
• Scale to 50 cm²
• Mass transport < DMFC using H₂ gain as reference

M6
• Improve mass transport
• <50% vs. DMFC

M7
• If DME cross-over impacts cathode, select alternative cathode catalyst

M8
• DME Hi-T MEA > DMFC per Slide 3 targets
DME vs. methanol fuel cell performance.
**Anode:** 4.0 mg_{metal} cm^{-2} PtRuPd/C (HiSPEC® 12100); DME 40 sccm, bp 26 psig; 1.8 mL/min 0.5 M or 1.0 M MeOH.
**Cathode:** 2.0 mg cm^{-2} Pt/C (HiSPEC® 9100); air 100 sccm, bp 20 psig. Membrane: Nafion® 212 (DME), Nafion® 115 (MeOH); cell: 80 °C.

Temperature dependence of DME fuel cell performance.
**Anode:** 4.0 mg_{metal} cm^{-2} PtRu/C (HiSPEC® 12100); DME 40 sccm, bp 26 psig.
**Cathode:** 4.0 mg cm^{-2} Pt black, air 500 sccm, bp 20 psig. Membrane: Nafion® 212; cell: 80 °C.

High DME activity with PtRuPd/C combined with temperature sensitivity
Accomplishments and Progress (1)

Milestone 1: “down-scaled” MEA at LANL within expected variation

- Good agreement between Advent (45 cm²) and LANL (5 cm²) testing
- Region of interest TPS = higher solids, lower acid, pyridine
- PBI = lower solids, higher acid, imidazole

HT PEM Membranes

Components of standard high temperature MEA including internal sub gasket, which was extended for testing 5 cm² MEAs in a 45 cm² test cell

E [V] vs. i [A/cm²] graph showing:
- Maximum curve (Advent-45)
- Average (Advent-45)
- LANL-TPS
- Minimum curve (Advent-45)
Accomplishments and Progress (2)

Milestone 2: Define reaction envelope (i.e., $\text{H}_2\text{O}$ range)

TPS MEAs with different water content in hydrogen fuel at 180 °C.

For the 40 °C and 60 °C humidifier case, anode backpressure 26 psig, cathode backpressure 20 psig. Air/$\text{H}_2$ stoich 2/1.2. MEAs at 5 cm$^2$.

Relatively robust performance to changing $\text{H}_2\text{O}$ content

General Guideline
$\text{H}_2\text{O} <20\%$ anode feed (reformate operation)

Use of humidifiers =
low control of water introduction
Accomplishments and Progress (2)

Milestone 2: baseline DME oxidation with Pt anode

TPS MEAs with different DME:water stoichiometry at 180 °C.
Anode: Pt/C, 1 mg/cm²; DME 500 sccm; backpressure 30 psig.
Cathode: Pt-alloy/C 1 mg/cm²; air 500 sccm; backpressure 30 psig.
MEAs: 5 cm²

Confirmed new set-up has precise H₂O control

Used HPLC pump to introduce H₂O
Sensitivity to DME:H₂O (1:3 chemical)
Feed dilution at DME:H₂O 1:3

Activity with methanol insignificant (results not shown)
Comparison of PBI and Nafion-based MEA in DME fuel cells.

**PBI MEA at 180 °C**: Anode: Pt/C, 1 mg/cm²; DME 500 sccm, backpressure 30 psig; DME:H₂O = 1:2.4. Cathode: Pt-alloy/C 1 mg/cm²; air 500 sccm, bp 30 psig.

**Nafion 212 MEA at 80 °C**: Anode: PtRu black 4 mg/cm², DME 40 sccm (saturated with H₂O), bp 26 psig. Cathode: Pt black 4 mg/cm²; air 500 sccm, backpressure 20 psig.

**Higher T operation confirms increase in fuel cell performance**
Accomplishments and Progress

Initial PtRu HT PEM DME oxidation

PtRu vs. Pt: PBI-based MEA DME fuel cell performance at 180 °C.
Pt/C: Anode: Pt/C, 1 mg/cm²; DME 500 sccm, backpressure 30 psig. Cathode: Pt-alloy/C 1 mg/cm²; air 500 sccm, backpressure 30 psig.
PtRu/C: Anode: HiSPEC® 12100 PtRu/C 1.9 mg/cm²; DME 500 sccm, backpressure 20 psig. Cathode: Pt-alloy/C 1 mg/cm²; air 300 sccm, backpressure 20 psig.

PtRu/C increases fuel cell performance substantially

<table>
<thead>
<tr>
<th>MEA</th>
<th>Specific <a href="mailto:Power@0.2V">Power@0.2V</a> W/g PGM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion PtRu</td>
<td>14</td>
</tr>
<tr>
<td>PBI Pt</td>
<td>13</td>
</tr>
<tr>
<td>PBI PtRu</td>
<td>17</td>
</tr>
</tbody>
</table>
Response to Previous Year Reviewers

Project not reviewed last year
Collaborations

Next generation PBI membranes (later in project)
- University of South Carolina (B. Benicewicz)
- Independent of DOE H&FC Program
- Supplier of materials

Impact of high water in anode feed
- EHT-Zurich/PSI Switzerland (T. Schmidt)
- Independent of DOE H&FC Program
- Theoretical perspective on acid and water migration in HT PEM
Remaining Challenges and Barriers

- Is the optimum DME:H$_2$O ratio compatible with the membrane phosphoric acid?
- Does the phosphoric acid promote unwanted chemical reactions with DME?
- Identifying upper H$_2$O limit in DME/H$_2$O fed to the fuel cell anode
  - MEAs with PtRu/C as anode catalyst
  - MEAs with PtRuPd/C as anode catalyst
  - Scale-up from 5 cm$^2$ to 45 cm$^2$
## Proposed Future Work

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Target</th>
<th>Path</th>
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<tbody>
<tr>
<td>3</td>
<td>Demonstrate 1.5x (75 A/g at 0.5 V) improvement over DMFC anode activity</td>
<td>Incorporate PtRu and PtRuPd anode catalysts, vary electrode structure</td>
</tr>
<tr>
<td>4</td>
<td>5 cm² cell exceeds best DMFC Total PGM &lt; 4.5 mg/cm² Anode mass-specific activity 75 A/g @ 0.5 V</td>
<td>Select best of TPS or PBI MEAs; optimize reaction conditions and catalyst layer</td>
</tr>
<tr>
<td>5 &amp; 6</td>
<td>Scale to 50 cm² Mass transport &lt; DMFC using H₂ gain as reference; then improve mass transport 50%</td>
<td>Optimize GDL and electrode layer on GDL</td>
</tr>
<tr>
<td>7</td>
<td>If DME crossover impacts cathode, select alternative cathode catalyst</td>
<td>Consider the new PGM-free cathode catalysts</td>
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</table>
Advent will approach Hi T MEA customers that currently build systems based on reformed methanol

Advantage will be reduction in system cost (no reformer) and simplicity

UltraCell LLC can use 45 cm² scale in their current systems

SerEnergy (Denmark) has interest in auxiliary power for marine systems that use low emission, carbon-neutral fuels

- Advent will need to scale to at least 165 cm²
- SerEnergy has previously demonstrated battery range extenders for electric vehicles using reformed MeOH
- DME is “environmental diesel” and runs in slightly modified diesel engines
**Objective:** Demonstrate direct DME oxidation with high temperature MEA and LANL catalyst significantly outperforming state-of-the-art DMFC

**Relevance:** DME is a carbon-neutral hydrogen carrier that can be used both for internal combustion and as cost-effective fuel for auxiliary fuel cell power systems in automotive transportation

**Approach:** Incorporate new ternary anode catalyst in gas diffusion electrodes designed for high temperature MEAs. Evaluate with two different high temperature membranes (PBI and TPS). Optimize structures and reaction conditions

**Accomplishments:** 1) Developed system for precise control of DME to water ratios, 2) demonstrated baseline operation with platinum MEAs, 3) higher temperature operation facilitates performance, and 4) Initial PtRu performance at higher temperature confirms approach
Technical Back-Up Slides

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Zelenay@LANL.gov
HPLC pumps precise H₂O into DME stream
1. **Assumption:** Activation barrier to DME oxidation is from CO poisoning of catalyst, which is shifted with higher temperature.  
**Approach:** Although preliminary results support this hypothesis, we have latitude in being able to adjust the make-up of the ternary catalyst to optimize high T performance.

2. **Assumption:** DME crossover limited by its solubility in phosphoric acid.  
**Approach:** The TPS membrane has higher solids/lower acid content than PBI, so if our assumption is false, this platform should show an advantage. Furthermore, next-generation PBI membranes have higher solids.

3. **Assumption:** PtRu or PtRuPd will be stable at the higher T.  
**Consideration:** Thermodynamics predicts segregation of Ru from Pt; however, target markets have 5,000 hour life expectations, which should still be within the stability window of these catalysts.