Novel Materials for High Efficiency Direct Methanol Fuel Cells

2009 Fuel Cell Projects Kickoff Meeting

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Announcement Number: DE-PS36-08GO98009
Application Number: Arkema Inc. (1281)

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Project Objectives

- Develop ultra-thin membranes having extremely low methanol crossover, high conductivity, durability, and low cost.

- Develop cathode catalysts that can operate with considerably reduced platinum loading and improved methanol tolerance.

- Produce an MEA combining these two innovations and having a performance of at least 150 mW/cm$^2$ at 0.4 V and a cost of less than $0.80/W for the membrane and cathode catalyst.
Organization

PEM Development and testing
MEA diagnostics and durability

Catalyst development
MEA production and testing

Cutting-edge characterization of MEAs and development of composite membranes
Technical Barriers and Targets

- Barriers Addressed in DOE Fuel Cell Technical Plan:
  - Durability
  - Cost
  - Performance

- Targets

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Industry Benchmark</th>
<th>Project Target</th>
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<tbody>
<tr>
<td>Methanol Permeability</td>
<td>1-3·10^{-6} cm²/s</td>
<td>5·10^{-8} cm²/s</td>
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<tr>
<td>Areal resistance (Ωcm²), 70 °C</td>
<td>0.120 (Nafion® 117)</td>
<td>0.080 (2 mil thick film)</td>
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<td>Catalyst Mass Activity (RDE)†</td>
<td>22.5 mW/mg Pt</td>
<td>&gt; 100 mW/mg Pt</td>
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<td>MEA Cathode Catalyst Loading</td>
<td>4 mg/cm²</td>
<td>1.5 mg/cm²</td>
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<td>MEA I-V Cell Characteristic</td>
<td>90 mW/cm² @ 0.4 V</td>
<td>150 mW/cm² @ 0.4 V</td>
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<tr>
<td>MEA Lifetime</td>
<td>&gt; 3,000 h</td>
<td>5,000 h</td>
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† conditions at 0.45 V & 70 °C
Technical Approach: Membrane Development

- **Polymer blend**
  - Decouples conductivity from other requirements
  - Kynar® PVDF
    - Chemical and electrochemical stability
    - Mechanical strength
    - Excellent barrier against methanol
  - Polyelectrolyte
    - H⁺ conduction and water uptake

- **Robust blending process**
  - PVDF can be compatibilized with a large range of polyelectrolytes
  - Morphology and physical property control
  - Phase separation on a scale of 10-100s of nm

- **Lower cost approach compared to PFSA**
  - Kynar® PVDF - commercial product
  - Polyelectrolyte – hydrocarbon based
Technical Approach: Membrane Development

The key to the desired properties resides in careful control of composition, architecture, and morphology of the membrane components.

- Phase separation on the order of 10s of nm
  - Polymer architecture, composition, and type of compatibilizer

- PVDF matrix optimization
  - Degree of crystallinity

- Tailor the polyelectrolyte composition to minimize methanol permeation in this phase
  - Different acid and ion-containing groups

- Acidic inorganic additives
  - Reduce swelling in the membrane while maintaining conductivity
Preliminary Data: M43 Methanol Crossover

Conductivity: 140 mS/cm (1 mil) @ 70 °C (in DI Water)

- M43 was developed for hydrogen applications
- Without any optimization, M43 is already a good methanol barrier
Technical Approach: Methanol Tolerant Cathode Catalyst

- Pd based alloy nanocatalyst mixed with Pt/C
  - Improved mass activity by suppressing methanol oxidation
  - Significant cost reduction by lower Pt content
  - Particle size = 3-10nm
- Pd-based nanocatalysts prepared using gas phase condensation
  - Control of particle size, alloy ratio, and core-shell structure
- Catalysts screening by rotating disk voltammetry, in presence and absence of methanol
Technical Approach: MEA Testing

- **MEA development and characterization (QSI)**
  - Optimize catalyst layer composition/construction
    - Ionomer content
    - GDE vs CCM

- **MEA diagnostics (IIT, Arkema, QSI)**
  - Single cell polarization with 1-10M methanol/air
  - Anode and cathode half-cell polarization measurement using reference electrode
  - Linear sweep voltammetry and CO$_2$ sensor to monitor methanol crossover
  - Cyclic voltammetry for catalyst active area
  - In-situ AC impedance for MEA resistance and transport resistances.

- **MEA durability testing (Arkema, IIT, QSI)**
  - Constant current mode, monitoring voltage loss over time.
Preliminary Results: MEA Performance

Arkema M43 Low Crossover Membrane, QSI-Nano® Methanol Tolerant Cathode Catalyst (10M Methanol, 60 °C)
Proposed Project Timeline

Project start: January, 2010

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<thead>
<tr>
<th>Task Name</th>
<th>1Q01</th>
<th>2Q01</th>
<th>3Q01</th>
<th>4Q01</th>
<th>1Q02</th>
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<tbody>
<tr>
<td>Membrane</td>
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<td></td>
<td></td>
<td>G1</td>
<td>D1</td>
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<td>G2</td>
<td>D2</td>
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<td>D4</td>
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**G1:** Membrane w/ areal resistance $\leq 0.080 \, \Omega \, \text{cm}^2$ and a diffusion coefficient $\leq 1 \cdot 10^{-7} \, \text{cm}^2/\text{s}$

**G2:** Catalyst w/mass activity $> 70 \, \text{mW/mg}$

**D1:** Membrane scale-up for MEA development

**D2:** Catalyst scale-up for MEA development

**D3:** MEA w/ 50% Pt reduction and mass activity $> 100 \, \text{mW/mg}$

**M1:** MEA w/ ohmic resistance $< 0.12 \, \Omega \, \text{cm}^2$ (determined from impedance)

**D4:** MEA performance of 150 mW/cm² @ 0.4 V (60 °C, 1 M methanol)

**D5:** Membrane w/ areal resistance $\leq 0.080 \, \Omega \, \text{cm}^2$ and a diffusion coefficient $\leq 5 \cdot 10^{-8} \, \text{cm}^2/\text{s}$

**D6:** MEA passes 5,000 h durability testing
**Proposed Project Budget**

- Assuming start-up date Jan. 2010

- **Total Project Cost: $3,501,264**
  - Non-federal: $867,530
  - Federal: $2,633,734

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<th>FY2010</th>
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<td><strong>Total project</strong></td>
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