Novel Materials for High Efficiency Direct Methanol Fuel Cells

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Arkema Inc.
May 13, 2011

Grant ID:
DE-EE0000474

Project ID# FC063

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Overview

Timeline
- Start: May 1st, 2010
- End: February 28th, 2013
- Percent Complete: 27% (as of March 1st)

Budget
- Total Project Funding: $3,472k
  - DOE: $2,612k
  - Contractor: $860k
- Funding Received for 2010: $700k
- Funding for 2011: $400k

Barriers
- Durability
- Cost
- Performance

Organization
- Project Lead
  - Arkema Inc.
- Partners (Subcontractors)
  - QuantumSphere Inc. (QSI)
  - Illinois Institute of Technology (IIT)
Relevance

● 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/cm² at 0.4 V and a cost of less than $0.80/W for the membrane and cathode catalyst

● Targets*

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Industry Benchmark</th>
<th>Project Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol Permeability</td>
<td>1-3·10⁻⁶ cm²/s</td>
<td>5·10⁻⁸ cm²/s</td>
</tr>
<tr>
<td>Areal resistance (Ωcm²), 70 ºC</td>
<td>0.120 (7 mil PFSA)</td>
<td>0.080 (2 mil thick film)</td>
</tr>
<tr>
<td>PGM Cathode Catalyst Specific Power (RDE) †</td>
<td>25 mW/mg PGM</td>
<td>≥50 mW/mg PGM</td>
</tr>
<tr>
<td>PGM Cathode Catalyst Loading</td>
<td>2.5 mg/cm² PGM</td>
<td>≤2 mg/cm²</td>
</tr>
<tr>
<td>MEA I-V Cell Characteristic</td>
<td>90 mW/cm² @ 0.4 V</td>
<td>150 mW/cm² @ 0.4 V</td>
</tr>
<tr>
<td>MEA Lifetime</td>
<td>&gt; 3,000 h</td>
<td>5,000 h</td>
</tr>
</tbody>
</table>

* Targets based on a methanol concentration of 1M
† conditions at 0.45 V & 70 ºC
## Approach/ Milestones

<table>
<thead>
<tr>
<th>Milestones &amp; Go/No-go Decisions for 2011</th>
<th>Date</th>
<th>Progress</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Membrane Milestone (Task 1)</strong>&lt;br&gt;Generation 1 membrane with areal resistance ≤ 0.080 Ωcm² and a methanol perm. coeff. ≤ 1·10⁻⁷ cm²/s</td>
<td>June 2011</td>
<td>11 high potential candidates identified with the required areal resistance and a permeation coefficient &lt; 3·10⁻⁷ cm²/s</td>
</tr>
<tr>
<td><strong>Catalyst Milestone (Task 2)</strong>&lt;br&gt;50 mW/mg&lt;sub&gt;PGM&lt;/sub&gt; RDE specific power in presence of 0.1M CH₃OH (0.45V, 70°C, 50% Pt reduction)</td>
<td>June 2011</td>
<td>115 mW/mg&lt;sub&gt;PGM&lt;/sub&gt;&lt;br&gt;RDE specific power in presence of 0.1M CH₃OH (0.45V, r.t, 50% Pt reduction)</td>
</tr>
<tr>
<td><strong>Go/No-go Decision:</strong>&lt;br&gt;MEA performance of 120 mW/cm² @ 0.4V (60°C, 1M methanol)</td>
<td>Dec 2011</td>
<td>120mW/cm² achieved with Arkema membrane and a <em>commercial GDE</em> <em>commercial GDE</em></td>
</tr>
</tbody>
</table>
Collaborations

PEM Development and testing
MEA diagnostics and durability

Catalyst development
MEA production and testing

Development of composite membranes
and characterization/diagnostics of MEAs
**Technical Approach:**

**Membrane Development (Task 1)**

- Polymer blend comprised of PVDF and polyelectrolyte to minimize methanol permeation
  - **Kynar® PVDF**
    - Chemical stability and mechanical strength
    - Excellent barrier against methanol
  - Polyelectrolyte
    - $\text{H}^+$ conduction
  - PVDF can be compatibilized with a range of polyelectrolytes
    - Latest generation taken to a pilot scale is M43 (baseline for this project)

- Key to the target properties: control of composition, architecture, and processing of the membrane components.
  - PVDF matrix optimization
  - Tailor the polyelectrolyte composition (minimize methanol permeation)
  - Morphology
  - Acidic inorganic additives
# Technical Progress:
**Membrane Development (Task 1)**

## Progress versus Objectives

<table>
<thead>
<tr>
<th>Objectives of Task 1</th>
<th>Progress Notes</th>
<th>% Complete (3/1/11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane Milestone #1 Generation 1 membrane: areal resistance ≤ 0.080 Ω cm² and a methanol perm. coeff. ≤ 1·10⁻⁷ cm²/s</td>
<td>11 high potential candidates identified with the required areal resistance and a permeation coefficient &lt; 3·10⁻⁷ cm²/s</td>
<td>67%</td>
</tr>
<tr>
<td>Deliverable: Scaleup of composition from milestone #1 for MEA development work</td>
<td>M43 produced on a pilot scale several times; process recently extended to lower temperatures</td>
<td>50%</td>
</tr>
<tr>
<td>Membrane Milestone #2 Generation 2 membrane: areal resistance ≤ 0.080Ω cm² and a methanol perm. Coeff. ≤ 5·10⁻⁸ cm²/s</td>
<td>Work will build off of milestone #1. One composition displays the target perm. coefficient but resistance is 50% too high.</td>
<td>22%</td>
</tr>
</tbody>
</table>
Technical Accomplishments:
Membrane Screening

- Ex-situ properties of over 75 compositions tested → 11 of them identified as high potential candidates to reach the milestone

- Most of the testing has focused on PVDF grade, polyelectrolyte compositions, and polyelectrolyte loading

*Areal resistance was normalized to a membrane thickness of 1.5 mils. Sample thickness was typically 1.4-1.6 mils.*
Technical Accomplishments:
Lower Electro-osmotic Drag Coefficient

- 50% lower EOD coefficients for Arkema membranes than PFSA
- Lower EOD coefficient is advantageous for DMFC applications
  - Less cathode flooding, and easier water management
  - Reduced methanol crossover

*A is one of the most promising candidates identified from the screening study

Technical Accomplishments:
Lower Methanol Crossover & Membrane Resistance

- Arkema membranes showed substantially lower methanol crossover lower membrane resistance than 7mil PFSA
- Membrane Candidate A showed 60% lower crossover and 10% lower resistance than a 7mil PFSA membrane

Technical Accomplishments:
DMFC Performance

- Arkema membranes outperform 7mil PFSA membrane in both 3M and 10M methanol tests, especially in 10M.
- Candidate A (1.4mil) achieved the better performance in 10M methanol testing, due to lower crossover rate.
Technical Accomplishments:
Sulfonic Acid Functionalized Silica Additive

- No large scale phase separation observed from forming the composite
- Permeability and conductivity lowered as the silica is added. Selectivity increases with higher silica contents
- Conductivity may be improved by using a higher sulfonation level in silica

<table>
<thead>
<tr>
<th>Membrane + silica with 30% sulfonation</th>
<th>Conductivity @70°C, mS/cm</th>
<th>Permeability @ R.T., x10^{-7} cm^2/s</th>
<th>Conductivity/Perm Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arkema membrane</td>
<td>125 ± 7</td>
<td>6.7 ± 0.2</td>
<td>18.6</td>
</tr>
<tr>
<td>With 15 wt% silica</td>
<td>75 ± 4</td>
<td>5.7 ± 0.4</td>
<td>13.1</td>
</tr>
<tr>
<td>With 20 wt% silica</td>
<td>49 ± 1</td>
<td>3.4 ± 0.1</td>
<td>14.4</td>
</tr>
<tr>
<td>With 25 wt% silica</td>
<td>58 ± 9</td>
<td>3.2 ± 0.2</td>
<td>18.1</td>
</tr>
</tbody>
</table>
**Technical Approach:**

**DMFC Cathode Catalyst Development (Task 2)**

Utilize Pd-based nanoscale catalysts with Pt/C to:
- Increase $\text{mW/mg}_{\text{PGM}}$ by suppressing methanol oxidation
- Reduce Pt content $\rightarrow$ decrease $\$/W

**SYNTHESIS**
- Gas-phase condensation (GPC) synthesis of unsupported Pd-based metal nanoparticles

**DESIGN**
- Integration of Pt/C, alloys, core-shell structure, other co-catalysts, and processing methods

**SCREENING**
- TEM, XRD, BET, TGA. CV and RDE w, w/o CH$_3$OH. Down-select based on activity, cost, durability

**MEA Tasks**
## Technical Progress:
DMFC Cathode Catalyst Development (Task 2)

### Progress versus Objectives

<table>
<thead>
<tr>
<th>Objectives of Task 2</th>
<th>Progress</th>
<th>% Complete (3/1/11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milestone: 50 mW/mg&lt;sub&gt;PGM&lt;/sub&gt; RDE specific power in presence of 0.1M CH&lt;sub&gt;3&lt;/sub&gt;OH (0.45V, 70°C, 50% Pt reduction)</td>
<td>115 mW/mg&lt;sub&gt;PGM&lt;/sub&gt; RDE specific power in presence of 0.1M CH&lt;sub&gt;3&lt;/sub&gt;OH (0.45V, r.t, 50% Pt reduction)</td>
<td>67%</td>
</tr>
<tr>
<td>Deliverable: Catalyst scale up for MEA development work, 1.2 kg/month, 60% Pd recycling efficiency</td>
<td>Nano-Pd production rate @ 1kg/month, 85% Pd recycling efficiency</td>
<td>53%</td>
</tr>
<tr>
<td>Deliverable: MEA specific power of 40 mW/mg&lt;sub&gt;PGM&lt;/sub&gt;, 50% Pt reduction</td>
<td>MEA testing initiated</td>
<td>41%</td>
</tr>
</tbody>
</table>
Technical Accomplishments:
Demonstration of Methanol Tolerance

CV - Effect of Methanol QSI Pd Black
N₂ Sat., 0.1M HClO₄, r.t., 50mV/sec

CV - Effect of Methanol - 60% Pt/C
N₂ sat , 0.1M HClO₄, r.t. 50mV/sec

QSI nano-Pd only
Commercial Pt/C

- Cyclic Voltammetry: Methanol is not oxidized on nano-Pd, regardless of concentration
**Technical Accomplishments:**

**Increased Specific Power (RDE Measurement)**

- **Pt/C only**
  - >2x mass activity increase in presence of 0.1M Methanol @ 0.65V
  - 10% mass activity increase in presence of 0.1M Methanol @ 0.45V

- **Pt/C and nano-Pd**
  - 50% of Pt substituted with Pd

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**Graphs:**

1. Effect of Methanol on ORR - 60% Pt/C
   - 0.1M HClO₄, r.t. 5mV/sec

2. Effect of Methanol on ORR - QSI Nano-Pd Pt/C
   - 0.1M HClO₄, r.t. 5mV/sec
Technical Accomplishments:
Reduced Cost of Power

- 60% cost reduction at 0.65V (Cathode catalyst = $1.08_{PGM/W}, low volume)
- 33% cost reduction at 0.45V (Cathode catalyst = $0.88_{PGM/W}, low volume)
**Technical Accomplishments:**

**Pd-based Catalyst Synthesis**

<table>
<thead>
<tr>
<th>Catalyst Pd, Pd-”M”</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QSI-Nano Pd black (ref)</td>
<td>57.4</td>
</tr>
<tr>
<td>Other Commercial Pd black</td>
<td>7.3</td>
</tr>
<tr>
<td>QSI-Nano Pd-Cr</td>
<td>65.8</td>
</tr>
<tr>
<td>QSI-Nano Pd-Ag</td>
<td>38.3</td>
</tr>
<tr>
<td>QSI-Nano Pd-Mn</td>
<td>94.5</td>
</tr>
<tr>
<td>QSI-Nano Pd-Co</td>
<td>80.6</td>
</tr>
<tr>
<td>QSI-Nano Pd-Fe</td>
<td>134.2</td>
</tr>
<tr>
<td>QSI-Nano Pd-Ni</td>
<td>99.8</td>
</tr>
<tr>
<td>QSI-Nano Pd-Sn</td>
<td>65.4</td>
</tr>
<tr>
<td>QSI-Nano Pd-Se</td>
<td>82.9</td>
</tr>
</tbody>
</table>

- High surface area nanoscale metals successfully produced, currently been screened by *BET, TEM, elemental analysis, CV, RDE*

- Electrochemical impact of alloying (Pd-M) vs. bimetallic (Pd + M) is under investigation
Future Work

● Membrane Development (Task 1)
   ● Down-select membrane candidates that pass YR 1 milestone and begin refining their properties (Q2 2011)
   ● Produce pilot scale membrane quantities of best membrane candidate, perform cost analysis, and deliver material to QSI & IIT (Q3 2011)

● Catalyst Development (Task 2)
   ● Down-select cathode catalyst composition, perform ex-situ durability evaluation (Q2 2011)
   ● Increase reactor production rate, collect cost metrics, deliver catalyst to Arkema, IIT (Q3 2011)
   ● Evaluation of catalyst at MEA level (Q4 2011)
   ● Demonstrate 50% Pt reduction at MEA-level (Q1 2012)

● MEA Development (Task 3)
   ● Initiate development of MEAs with Arkema membrane and QSI catalyst (Q4 2011)

● MEA Testing and Durability (Task 4)
   ● Initiate testing of MEAs from Task 3 (Q1 2012)
Summary

Primary project objective is to develop new materials for DMFC that can be the basis for a device to meet the DOE’s technical targets for consumer electronics.

- 11 membrane compositions identified as high potential candidates to reach the year 1 milestone.

The Arkema membrane technology showed lower methanol permeation and electro-osmotic drag coefficients than 7 mil PFSA, while maintaining lower membrane areal resistance.

- Composite membranes with a sulfonated silica additive were prepared. Higher sulfonation level is needed to improve conductivity.

- Nano-Pd mixed with Pt/C catalyst showed 2x mass activity over Pt/C (on total PGM basis) at 0.65V, in presence of 0.1M methanol.
Technical Accomplishments:

DMFC Conditioning

- **Objective:** Achieve optimal and repeatable performance in minimal time

- **Challenge:**
  - Arkema M43-based MEAs condition slower than PFSA
  - Common conditioning methods were developed based on PFSA, and do not work effectively on Arkema membranes

- **Arkema conditioning method**
  - Quick voltage cycling between OCV/0.4/0.2V
  - Air starvation during part of OCV time
  - Runs on Methanol/air only, no hydrogen conditioning needed

- **Cell fully conditioned within 18 hours**

- **Consistent performance (<10% variation) from cell to cell**
Technical Accomplishments:
M43 Performance Improvement

- Heat treatment of M43 membranes at 135°C significantly increased the DMFC performances, especially at 10M methanol.
- No such effect was observed on PFSA 7mil membrane.
Technical Accomplishments:

M43 MEA Performance: 1M Methanol

At 0.4V, M43 reaches 300mA/cm², or 120mW/cm² power, with commercial Johnson Matthey gas diffusion electrodes.
Technical Approach:
Synthesis of Sulfonic Acid Functionalized Silica

Tetraethyl orthosilicate (TEOS) + HCl

Hydrolisis step

Si(OH)₄

+ Pluronic® 123 (template)

Condensation step

+ (3-mercaptopropyl) Trimethoxysilane (MPTMS) Functionalization precursor

+ H₂O₂

SiO₂-SO₃H (mesoporous silica)

Pluronic® is a registered trademark of the BASF Corp.