Development of Low-cost, Durable Membrane and MEA for Stationary and Mobile Fuel Cell Applications

2007 Hydrogen Program Annual Review

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Arkema, Inc.
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Project ID#: FC9

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Overview

Timeline
- Start Date: Oct. 2003
- End Date: June 2007 (with no-cost extension)

Budget
- Total Funding
  - DOE: $5,771K
  - Partners: $2,241K
- FY2006 Funding
  - $2,205K
- FY2007 Funding
  - $2,063K

Barriers
- B: Cost
  - $20/m² (Membrane Target)
  - $10/kW (MEA Target)
- A: Durability
  - 5000 hours (Target)

Partners
- Arkema:
  - Georgia Tech
- Johnson Matthey Fuel Cells
- UTC Fuel Cells
  - University of Hawaii
Objectives

● Overall
  ● Develop low-cost and durable membrane and MEA that can meet DOE targets and help drive the commercial reality of fuel cells

● 2006-2007
  ● Development and characterization of new-generation membranes
    ■ Morphology
    ■ Transport Properties
    ■ Mechanical Properties
    ■ Chemical Stability
  ● MEA optimization
  ● Durability testing of the membrane in fuel cells
Arkema’s Approach

- Polymer blend system to decouple H⁺ conductivity from other requirements
  - Kynar® PVDF
    - Engineering thermoplastic
    - High chemical resistance and electrochemical stability
    - Provide mechanical support
  - Polyelectrolyte
    - H⁺ conduction
    - Physical properties unimportant

- Robust blending process
  - Applicable for various polyelectrolytes
  - Capable of morphology and physical property control

- Lower cost approach compared to PFSA
  - Kynar® PVDF - commercial product
  - Polyelectrolyte – hydrocarbon based

- Feasibility demonstrated (M31)
**Approach: Project Progress**

**Development of Polyelectrolytes**
- Identified the requirements
- Down-selected a structure
- Synthesized sulfonated copolymer

**Formulation of Membranes**
- Validated blending versatility
- Demonstrated comparable properties
- Characterized morphology
- Developed high throughput methods
- Scaled up to pilot

**MEA & Fuel Cell Testing**
- MEA optimized
- Demonstrated comparable FC performance to PFSA
- High decay rate observed in long-term testing

**Large Cell Validation**
- Validation of BOL performance
- UEA fabrication
- UTC cell testing (400cm² active area)

**M31 Generation**
- Elucidated M31 failure mechanisms
- Developed ex-situ PE screening method
- Synthesized new generation chemically stable PE

**M41 Generation**
- Successful membrane formulation
- Property & morphology characterization
- Scale up to pilot

**Future Work**
- MEA fabrication
- UTC cell testing (400cm² active area)

**Completed**
- (Y06-Y07)**

**In Progress**
-
### M41 Physical Properties

<table>
<thead>
<tr>
<th></th>
<th>Nafion®111</th>
<th>M41</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Thickness (μm)</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Equivalent Weight</td>
<td>1100</td>
<td>800</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.8</td>
<td>1.5</td>
</tr>
<tr>
<td>Water Uptake (%)</td>
<td>37</td>
<td>60</td>
</tr>
<tr>
<td>X,Y Swell (%)</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Thickness Swell (%)</td>
<td>14</td>
<td>10-15</td>
</tr>
<tr>
<td>Tensile Stress Break (MPa)</td>
<td>19</td>
<td>27</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>103</td>
<td>95</td>
</tr>
<tr>
<td>Tear Strength(lbf/in)</td>
<td>404</td>
<td>934</td>
</tr>
<tr>
<td>Tear Propagation (lbf)</td>
<td>0.004</td>
<td>0.018</td>
</tr>
</tbody>
</table>

- **M41** shows equal/better mechanical properties than **Nafion® 111**
## M41 Transport Properties

- **Equivalent proton conductivity compared to Nafion**

<table>
<thead>
<tr>
<th>Material</th>
<th>Proton Conductivity (mS/cm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>M41</td>
<td>130</td>
</tr>
<tr>
<td>M41 (process optimized)</td>
<td>150</td>
</tr>
<tr>
<td>Nafion®</td>
<td>162</td>
</tr>
</tbody>
</table>

- **Superior gas barrier property than Nafion membranes**

<table>
<thead>
<tr>
<th>Material</th>
<th>H₂ permeation rate (mA/cm²)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>M41</td>
<td>0.5</td>
</tr>
<tr>
<td>Nafion®111</td>
<td>1.5</td>
</tr>
</tbody>
</table>

* by 4-point in-plane AC measurements in water at 70°C
** by electrochemical method at 80°C with 100% RH
Morphology Characterization and Control

- Range of morphologies possible
- High-resolution TEM characterization (collaboration with ORNL) to gain understanding of structure and property
M41 Chemical Stability

- In-house developed *ex-situ* sulfur loss test

- M41 shows less than 1% sulfur loss over 2000hr.
Fuel Cell Testing: BOL Performance

H₂/O₂, Fully Humidified, 80°C, 0 psig, 0.4 mg/cm² Pt on C, 25cm² cell

- Comparable in-cell performance to Nafion® 111 demonstrated
Fuel Cell Performance Diagnostics

- Ohmic resistance ($R_{ohm}$) by: (1) hydrogen pump and (2) current interruption
- Decouple the proton resistance ($R_{H+}$) and the electron resistance ($R_{e-}$) by

- Effect of temperature

\[ R_{ohm}(T) = \frac{t_m}{k_m(T)} + R_{e-} \]

- Effect of membrane resistance

- Good interfacial contact between M41 and electrodes demonstrated

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High Temperature Excursion Stability

- Stable membrane performance is shown after 8 hrs at 120°C
- Electrode degradation is shown by higher O₂ gain and 20% loss of ECA
**OCV Durability: Hydrogen Crossover**

- **Nafion® 111IP membrane** failed around 100 – 150 hrs
- **M41 membrane** exhibits superior chemical stability in fuel cells

Steady state OCV (H$_2$/O$_2$), 25cm$^2$ single cell (3-serpentine), 90°C cell temperature, 30%RH, 1 l/min dry gases, no back pressure
OCV Durability: Effect of Electrical Short

- Electrical short resistance is increased for both Nafion® 111IP and M41.
- OCV is dictated by the shorting resistance for both membranes.
  - Probably caused by the roughness of gas diffusion electrodes.
  - M41 showed no changes in H₂ crossover current density.
OCV Durability: Effluent Water Analysis

- M41 shows significantly lower F⁻ release rates
- M41 shows similar sulfate release rates to Nafion® 111IP
OCV Durability: Post-Mortem Analysis

- Nafion® 111IP failed due to chemical degradation leading to local pin-holes (no membrane thinning observed)
- M41 exhibited no sign of membrane failure due to chemical degradation after 400+hr OCV durability test
  - No change in gas crossover rates
  - No change in membrane thickness
  - No change in proton transport resistance
  - Identical performance after OCV test
Future Work

- Complete accelerated in-cell durability tests (Arkema, JM)
  - Continue OCV durability test
  - RH cycle durability test is in progress
  - Voltage cycle durability test is in progress

- High-resolution morphology characterization for structure-property understanding (ORNL, Arkema)

- Complete large-size fuel cell testing
  - Prepare 400cm$^2$ MEAs (JM)
  - Testing in UTC Fuel Cell hardware (U of Hawaii and UTC Fuel Cells)

- Develop new-generation polyelectrolytes (new grant award)
  - Optimized for Low RH operation
  - Higher temperature stability (up to 120$^\circ$C)
Summary

- Arkema developed Kynar®/Polyelectrolyte blending technology and produced membranes suitable for fuel cells (low cost and durability)
  - Equivalent fuel cell performance to Nafion membranes
  - Better mechanical properties
  - Lower gas permeability
  - Pilot scale production

- The new generation membrane (M41) demonstrated superior membrane durability in *in-situ* OCV test
  - At least 4x increase in OCV durability versus Nafion® 111
  - No increase in gas crossover rate after 400+ hrs
  - Significantly lower F- release rate compared to Nafion® 111
  - Humidity cycle and load cycle tests are underway

- Demonstrated morphology characterization and control capability
  - Further work is in progress to understand structure/property relationships