Lead Research and Development Activity for DOE’s High Temperature, Low Relative Humidity Membrane Program

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University of Central Florida-FSEC
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Project ID # FC 15

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Overview

Timeline

- April 1, 2006
- March 31, 2011
- 40% Complete

Barriers

- Barriers addressed
  - D. High Conductivity at Low RH & High T
  - C. High MEA Performance at Low RH & High T
  - A. Membrane and MEA durability

- Targets
  - Conductivity = 0.07 S/cm @ 80% relative humidity (RH) at room temp using alternate material – 3Q Yr 2 milestone
  - Conductivity >0.1 S/cm @ 50% RH at 120 °C – 3Q Yr 3 Go/No Go

Budget

- Total project funding
  - DOE share - $2,500K
  - Contractor share - $625K

- Funding received in FY07 - $550K
- Funding for FY08 - $585K

Partners

- BekkTech LLC – In–plane conductivity protocols
- Scribner Associates – Through-plane conductivity protocols
- Project management
Objectives

- New polymeric electrolyte/phosphotungstic acid membranes
- Development of standardized characterization methodologies
  - Conductivity $f(RH, T, \text{Prep. Procedure})$ [Through- & In-Plane]
  - Characterize mechanical, mass transport and surface properties of membranes
  - Evaluate fuel cell performance and predict durability of membranes and MEAs fabricated from other eleven HT Low RH Membrane Programs
- Provide HTMWG members with standardized methodologies
- Organize HTMWG biannual meetings
<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone or Go/No-Go Decision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sept-07</td>
<td>Complete analysis of in-plane and through-plane conductivity of commercial membranes.</td>
</tr>
<tr>
<td>Dec-07</td>
<td>Milestone: Complete conductivity characterization of first three membranes from Topic 1 awardees.</td>
</tr>
<tr>
<td>Dec-07</td>
<td>Milestone: Demonstrate conductivity = 0.07 S/cm @ 80% relative humidity (RH) at room temp using alternate material</td>
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<tr>
<td>Jun-08</td>
<td>Milestone: Establish MEA test protocol</td>
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<tr>
<td>Sept-08</td>
<td>Milestone: Complete manufacturing of first MEA from working group members</td>
</tr>
<tr>
<td>Dec-08</td>
<td>Go/No-Go Decision: Demonstrate conductivity of 0.1 S/cm, 50% RH, 120 °C</td>
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Approach

**Improve Conductivity:**

**Task 1.** FSEC develops non-Nafion® based Poly[perfluorosulfonic acid] -phosphotungstic acid composite membrane and membrane electrode assembly (MEA) fabrication (PFSA-PTA)

**Task 2.** FSEC develops sulfonated poly(ether ketone ketone) or sulfonated poly(ether ether ketone) - Phosphotungstic Acid Composite Membrane and MEA Fabrication (SPEEK-PTA)

**Improve FC Performance:**

**Task 5.** Characterize performance of MEAs for Topic 1 members

**Task 6.** Characterize membrane and MEA durability for Topic 1 members

**Standardize Testing**

**Task 3.** In-Plane conductivity measurements by partner

**Task 4.** Through-Plane conductivity measurements by partner

**Task 7.** Meetings and Activities of HTMWG
Technical Accomplishments/Progress/Results

• Conductivity
• Performance
• Durability
  – Chemical
  – Mechanical
In-Plane Conductivity Measurements

Conductivity ≥0.1 S/cm @ 25 - 50% RH at 120 °C – 3Q Yr 3
Go/No Go

3QYr 2 Milestone - 0.07S/cm @ 80% RH at 30 °C

Current Status

Gap

Conductivity (mS/cm)

Relative Humidity (%RH)

- NRE-212 (3-20-07) 120C
- NRE-212 (3-20-07) 80C
- NRE-212 (3-20-07) 30C
• Samples tested at 30 °C, 80% RH ~100 kPa at BekkTech as of April 24, 2008
In-Plane vs. Through-Plane Conductivity
(milestone)

NRE 211 at 30, 80, & 120 °C
Also Tested NRE-212, NE-1135 & N 117

<table>
<thead>
<tr>
<th>Relative Humidity (%)</th>
<th>Conductivity (mS/cm)</th>
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</thead>
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<tr>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>40</td>
<td>1000</td>
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</table>

Graph showing the conductivity of NRE 211 at different temperatures and relative humidities.
FSEC-3 Meets Conductivity Milestone!
(PFSA-PTA)

Comparing to Nafion® at 30 °C 100 kPa

- FSEC-3 (2-26-08) 30°C
- NRE-212 (3-20-07) 30°C
- Sample Result at 80% RH, 30°C: 79.7 mS/cm
- DOE Milestone at 80% RH, 30°C: 70 mS/cm
FSEC-3 Tested at 30 °C, 80 °C, 120 °C (PFSA-PTA)
Conductivity of FSEC-SLR3 (SPEEK-PTA)

Comparing to Nafion® at 30 °C 100 kPa

- SLR-3 (4-10-08) 30C
- NRE-212 (3-20-07) 30C
- Sample Result at 80% RH, 30C: 35.7 mS/cm
- DOE Milestone at 80% RH, 30C: 70 mS/cm
Progress Toward 120 °C Go/No Go

Meet 30 °C, 80% RH Milestone

Status Toward 120 °C, 50% RH Go/No Go
Performance

Jun-08  Milestone: Establish MEA test protocol

Sept-08  Milestone: Complete manufacturing of first MEA from working group members
MEA Test Apparatus

<table>
<thead>
<tr>
<th>$T_{cell}$</th>
<th>$T_{cathode humidifier}$</th>
<th>R. H.</th>
<th>$P_{total}$</th>
<th>Inlet $P_{H2O}$</th>
<th>Inlet $P_{O2}$ in Air</th>
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</thead>
<tbody>
<tr>
<td>°C</td>
<td>°C</td>
<td>%</td>
<td>kPa</td>
<td>kPa</td>
<td>kPa</td>
</tr>
<tr>
<td>80</td>
<td>73</td>
<td>75</td>
<td>101</td>
<td>35</td>
<td>13.86</td>
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<tr>
<td>100</td>
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<td>70</td>
<td>101</td>
<td>70</td>
<td>6.51</td>
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<tr>
<td>100</td>
<td>65</td>
<td>25</td>
<td>150</td>
<td>25</td>
<td>26.25</td>
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<tr>
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<tr>
<td>120</td>
<td>82</td>
<td>25</td>
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<td>20.79</td>
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<tr>
<td>120</td>
<td>100</td>
<td>50</td>
<td>150</td>
<td>101</td>
<td>10.29</td>
</tr>
</tbody>
</table>
Electrochemical Testing

Cell Performance with FSEC-3

80 °C Air and O₂ Performance FSEC-3

- Voltage, Oxygen
- Voltage, Air
- Resistance, Oxygen
- Resistance, Air

Cell Performance with Nafion® 112

80 °C Air and O₂ Performance Nafion 112

- Voltage, Oxygen
- Voltage, Air
- Resistance, Oxygen
- Resistance, Air

**LSV → H₂ Crossover**

**CV → ECA**

\[
ECA = \frac{(\text{Area under peak})}{(\text{scan rate}) \times (210 \mu C/cm² - \text{Pt}) \times (\text{Pt loading})}
\]
**In Situ Investigation of MEA Degradation**

- **MEAs investigated:**
  - Nafion® and FSEC-1 and FSEC-3

- **Tested MEAs under different degradation conditions:**
  - 90 °C; 35% RH; OCV; 100 hr

- **Degradation evaluated in several ways:**
  - Electrochemical Pre- and Post-testing
    - $\text{H}_2$ crossover, ECA, polarization, resistance
  - Material testing before and after degradation test
    - mechanical strength, materials science
  - During the test
    - fluoride emission rate, voltage monitored
Fluoride Emission Rate

90 °C; 35% RH; OCV; 100 hr

FER (μmol/cm² h)

N112 Anode
N112 Cathode
FSEC1 Anode
FSEC1 Cathode
FSEC3 Anode
FSEC3 Cathode

90°C 30% RH, OCV

Time (hr)
Rationale for the Investigation of Membrane/MEA Mechanical Degradation

• Mechanical properties degradation: phenomena and relevance
  – The beginning-of-life (BOL) mechanical properties of membranes are adequate, typically
  – Mechanical properties rapidly decay as a result of accumulated chemical (e.g., load cycling + OCV) and mechanical effects (e.g., RH cycling)
  – Fracture of mechanically weakened membrane can be the life-limiting failure mode for PEM devices

• It is important to
  – quantify the membrane mechanical robustness while optimizing other properties of high temperature membrane
  – further understand the underlying mechanisms that are responsible for the mechanical decay
Membrane/MEA mechanical degradation: modulus of toughness

Modulus of toughness = Energy per unit volume necessary to rupture the material, Joule/m³ or milli-Joule/mm³

N112 control | N112 after OCV | FSEC1 control | FSEC1 after OCV
---|---|---|---
Modulus of Toughness (mJ/mm³) | 21.757 | 16.446 | 26.554 | 23.159

X. Huang, W. Yoon, M. Rodgers
Future Work

• Complete characterization of HTMWG membranes
• Establish MEA test protocol (milestone)
• Manufacture first MEA from HTMWG membrane (milestone)
• Demonstrate conductivity of 0.1 S/cm, 50% RH, 120 °C (Go/No Go)
8-Cell MEA Durability Test System

- Simultaneous, independent operation of 8 cells
- Fully automatic – 24/7 operation
- Common RH system
- Adjustable cell temperature and reactant flow
- Individual cell diagnostics
- Manual over ride
- Individual cell replacement
Summary

• **Relevance** - A new membrane material for PEM Fuel Cells with sufficiently improved conductivity at high temperature (120 °C) and low RH is required for the transportation F/C market. A new method for measuring membrane conductivities with sufficient accuracy and reliability is required for DOE program decisions.

• **Approach** - Develop and demonstrate new materials for membranes, and define and apply new tools and procedures for membrane conductivity testing.

• **Tech. Accomplishments /Progress**
  – FSEC-3 exceeds conductivity goal, demonstrating conductivity >0.07 mS/cm at 80% RH and 30 °C.
  – Manufactured MEAs from Nafion® and FSEC membranes
  – Performance and durability testing of Nafion® and FSEC MEAs
  – Much reduced FER with FSEC membranes
  – Provided independent conductivity measurements for HTMWG members

• **Collaborations**
  – Active partnership with BekkTech LLC and Scribner Associates
  – Working closely with HTMWG members to provide accurate data under standardized conditions
  – Provided protocol to HTMWG members
  – Demonstrated Agreement between through-plane and in-plane conductivity measurements