Membranes and MEA's for Dry, Hot Operating Conditions

DE-FG36-07GO17006

Steve Hamrock
3M Company
February 13, 2007
Overview

Timeline
• Project start 1/1/07
• Project end 12/31/10
• 0% complete

Budget
• Total Project funding $11.4 million
  - $8.9 million - DOE
  - $2.5 million - contractor cost share (22%)
• Received in FY07: $ 0

Partners
• Case Western Reserve Univ.
• Colorado School of Mines
• University of Detroit Mercy
• University of Alabama Huntsville

Barriers
A. Durability
B. Performance

DOE Technical Targets
(2010)
• Durability w/cycling: > 5000 hrs,
• Conductivity 0.1 S/cm @120ºC
• Cost: $20/m²,

3M Contacts
• Principal Investigator Steven Hamrock
  Phone (651) 733-4254
  FAX (651) 737-5335
• Contract Administrator Steven L. Kays
  Phone (651) 737-0853
  FAX (651) 736-4777
Project Objectives

• The objective of this project is to develop a new proton exchange membrane with higher proton conductivity under hotter, dryer conditions and improved durability compared to state of the art membranes today.

• The target for this membrane is to operate and be stable under high and low humidification conditions and at temperatures ranging from -20°C to 120°C in order to meet DOE HFCIT 2010 commercialization targets for automotive fuel cells.

• Membranes developed in this project may also have improved durability and performance characteristics making them useful in stationary fuel cell applications.
## Technical Targets

### Material Targets

<table>
<thead>
<tr>
<th>Membrane Conductivity</th>
<th>Temperature</th>
<th>%RH</th>
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<tbody>
<tr>
<td>0.1 S/cm</td>
<td>120°C</td>
<td>≤ 25-50*</td>
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<tr>
<td>0.07 S/cm</td>
<td>20°C</td>
<td>≥ 100</td>
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<tr>
<td>0.01 S/cm</td>
<td>-20°C</td>
<td>≥ 100</td>
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O₂ Crossover: 2 mA/cm²  
H₂ Crossover: 2 mA/cm²  
Cost: $20/m²

### MEA/Stack Targets

- **Lifetime**: >5000 hours  
  (in DOE specified accelerated durability test)  
- **Membrane area specific resistance**: ≤0.02 ohms-cm²  
  (fuel cell w/ ≤ 1.5 kPa inlet water vapor pressure)  
- **Membrane must be stable to liquid water**

*Estimate for testing %RH which gives membrane humidification level equal to stack running w/ ≤ 1.5 kPa inlet water vapor pressure.*
Scope of Work

– New polymers, fluoropolymers, non-fluorinated polymers and composite/hybrid systems with increased proton conductivity and improved chemical and mechanical stability

– Developing new membrane additives for both increased conductivity and improved stability/durability under these dry conditions

– Experimental and theoretical studies of factors controlling proton transport both within the membrane and at the catalyst interface, mechanisms of polymer degradation and membrane durability in an MEA

– Focus on materials which can be made using processes which are scalable to commercial volumes using cost effective methods

– Integration of new membranes into MEA’s

– Testing performance and durability. Tests will be performed in conductivity cells, single fuel cells and short stacks using realistic automotive testing conditions and protocols.
Membranes and MEA's for Dry, Hot Operating Conditions – Kick off

Project Approach

- **Task 1** Membrane Subcomponent Development
  - **Subtask** Materials Development (Polymer development, conductivity enhancing additive development and stabilizing additive development)
  - **Subtask** Fundamental Studies for Downselection (conductivity, membrane physical properties, failure and degradation mechanisms)
  - **Subtask** Membrane Fabrication Process Development

- **Task 2** MEA Fabrication and Testing (MEA fabrication, performance and durability test method development, initial performance testing, accelerated durability testing)

- **Task 3** Final MEA Design and Integration (membrane fabrication, catalyst interface optimization and integration, final MEA optimization and fabrication)

- **Task 4** Final Fuel Cell Testing (stack fabrication and testing, durability and performance testing)

- **Task 5** Project Management, Deliverables and Reporting (building and testing short stack, reporting)
Relevant Prior Work

- 3M/DOE Cooperative Agreement No. DE-FC36-02AL67621
  - “Advanced MEA’s for Enhanced Operating Conditions”
- 3M/DOE Cooperative Agreement No. DE-FC36-03G013098
  - “MEA and Stack Durability for PEM Fuel cells”

Proton Conductivity as a function of pressure at 120°C, (water content = 80°C DP at 100 kPa)

90/70/70°C Load Cycling

Resistance and voltage at 97°C 70°C Dewpoint, 0.5 A/cm²
Membranes and MEA's for Dry, Hot Operating Conditions – Kick off

**Project Timeline**

- Tasks include Materials development, ex-situ testing, membrane and MEA fabrication, fuel cell testing, and reporting.
- One short stack will be provide for testing at a DOE designated entity.
- Two Go/No Go decisions
## Milestones and Go/ No Go points

**Year 1, Quarter 4:** Test method development and equipment modification complete.
New materials screening has begun.

**Year 2, Quarter 4:** New materials with improved conductivity and/or durability have been identified.

**Year 3, Quarter 2:** Go/no-go decision based on progress toward meeting DOE 2010 Membranes Technical Targets (this decision point coincides with the end of Budget Period 1). Membrane will have shown improvement over baseline material and measurable progress indicating a pathway to meeting DOE Membranes Technical Targets.

**Year 4, Quarter 2:** Catalyst/GDL/Process downselection, go/no-go decision for starting Subtask 4.1, Stack Fabrication and Testing.

**Year 4, Quarter 3:** Final short stack ready for independent testing at DOE designated entity.
Partner Goals/Responsibilities

3M (Task 1,2,3,4 and 5)
• Prepare of stable low EW perfluorinated polymers and composite fluorinated/hydrocarbon polymer membranes (with CWRU).
• Develop of new stabilizing / conductivity enhancing additives (with CSM).
• Develop of membrane fabrication techniques for improved properties.
• Test membrane properties including conductivity and physical/mechanical properties.
• Design, prepare and test MEA’s and final short stack.
• Fuel cell performance and durability testing.

Case Western Reserve University (Task 1.1, 1.2, 1.3)
• Prepare of polymers and membranes with high acidity based on aromatic.backbone polymers and composite fluorinated/hydrocarbon polymer membranes (with 3M).
• Characterize the water uptake and transport properties of these and other materials prepared in the project.
• Participate in work (with UAH) to explore the impact of high acid site density.
• Perform studies of the degradation products and relative rates of degradation of experimental membranes and small molecule model compounds.
Partner Goals/Responsibilities

University of Detroit Mercy (Task 1.3)
- Study the stability of new membrane materials when exposed to reactive oxygen radicals.
- Perform studies to determine the effect of various stabilizers on membrane stability.
- The major methods of study will be direct ESR and spin trapping.

University of Alabama in Huntsville (Task 1.3)
- Perform first principles based modeling of both the perfluoro and hydrocarbon ionomer systems and conductivity enhancing additives.
- Participate in the elucidation of failure and degradation mechanisms of the ionomers through first principles based calculation.

Colorado School of Mines (Task 1.1, 1.2, 1.3)
- Preparation and characterization of immobilized HPA and other inorganic super acids on nano-particles using SiO2, TiO2, etc. and tethered to a polymer backbone.
- Participate with team in the development of composite membranes incorporating these materials.
## Budget by Fiscal Year

**DE-FG36-07GO1706**

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