Design and Development of High-Performance Polymer Fuel Cell Membranes

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DOE Hydrogen Program Review
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Overview

Timeline

Project start date: 4/2006
Project end date: 4/2011
Percent complete: New Project

Barriers

Barriers addressed

• Membrane cost
• Membrane durability

Budget

Total project funding

• DOE share: $1.5M
• GE share: $0.5M

Funding for FY06

• DOE: $150K
• GE: $50K
GE Program Objective

Design and develop novel polymer electrolyte membrane materials for fuel cell operation at high temperature (up to 120 °C) and low relative humidity (25-50 %RH)

Goals for FY06

• Design and synthesize new high performance polymer structures
• Design and synthesize hydrophilic organic additives
• Evaluate membrane performance with and without additives
Approach

5-Year, $2 Million Program for the Development of High Temperature, Low Relative Humidity Polymer Membranes

Program Deliverables
- High performance, durable membrane films
  - Conductivity >0.1 S/cm at 120°C and 50% RH
  - Chemical and mechanical stability

Anticipated Program Benefits
- Increased scientific knowledge to improve future generation of PEMs
- U.S. leadership in automotive fuel cell development and manufacturing
- Reduced environmental pollution
- Lower reliance on petroleum imports

GE Global Research
World Leader in High Performance Polymers

Program Rationale
Current PEM materials do not meet the performance requirements necessary for high temperature, low relative humidity operation of fuel cells

Unique Polymer Architectures
- Random Graft Copolymer
- Blocky Graft Copolymer
- Long Graft Chains

Hydrophilic Organic Additives
- Design, synthesis, and characterization of novel ionomeric films with unique polymer architectures and hydrophilic fillers.
GE Progress in New Membrane Development

GE 1st Generation
Random copolymers

GE 2nd Generation
Block copolymers

New Concepts
Unique polymer architectures

Over 150 new materials and compositions

Proton conductivity (S/cm) vs. Relative humidity (%)

- Nafion (benchmark)
- GE polymer 1
- GE polymer 2
- GE polymer 3

Desired space

Conductivity @ 80°C/100%RH

- GE-1
- GE-2
- GE-3
- GE-4
- Nafion

Water Uptake @ 30°C

Relative humidity (%) vs. Proton conductivity (S/cm)
GE Membrane Characterization

All samples

- Proton conductivity (9-point)
  - 20°C, 100 %RH; 100°C, 75 %RH
  - Humidity scan from 25-100 %RH at 80°C
  - Temperature scan from 60-120°C at 50 %RH

- Vapor uptake (12-point)
  - Room temperature, 6-100 %RH

- Water uptake (4-point)
  - Weight and volume change in liquid water at room temperature, 60, 90, and 100°C

Select samples

- Microscopy (TEM, AFM)
  - Membrane morphology under dry and wet conditions

- Thermal-hydro-mechanical (TMA, DMA)
  - Dynamic, creep, and stress relaxation tests under dry and wet conditions

- Fuel cell performance
  - Gas crossover, polarization curves, durability at various temperature and RH conditions

- Accelerated durability testing
  - Mechanical and/or chemical stability under accelerated cycling conditions

- State of water (DSC, TGA)
  - Free, slightly bound, bound water, and their effect on polymers

- Small angle X-ray scattering (SAXS)
  - Membrane morphology under dry and wet conditions
GE Material Design

Thermally stable aromatic hydrocarbon polymers
• Build on GE’s strength and expertise in engineering polymers

No perfluorinated polymers
• Lower cost
• Benefit environment

Balance proton conductivity, water uptake, and mechanical properties via material design
• Direct polymer synthesis from monomer building blocks
• Functionalization with acidic/basic groups, additives
• Control of membrane morphology through polymer architecture

Polymer Architecture determines Membrane Morphology controls Balance of proton conductivity and water uptake
Increasing Proton Conductivity

More open, connected membrane morphology $\rightarrow$ higher proton conductivity

Random Copolymer
$\sigma \sim 10^{-3} \text{ S/cm (50 \%RH)}$

Block Copolymer
$\sigma \sim 10^{-2} \text{ S/cm (50 \%RH)}$
Improving Performance, Cost, and Durability

Optimize membrane morphology: new concepts in polymer chain design

- Promote phase separation and ionic aggregation
- Higher proton conductivity with good balance of water uptake properties

**Design: Graft copolymers**
- Higher concentration of acidic groups on pendant chains
- More efficient proton conductivity due to enhanced phase separation
- Neutral polymer backbone provides better mechanical support when hydrated

**Materials: Aromatic hydrocarbon polymers**
- Unprecedented architectures in aromatic hydrocarbon polymers
- Synthesis is non-trivial

**Current status:**
- Several synthetic approaches developed
- Explored two approaches
- Synthesis in progress
Improving High Temperature, Low RH Performance

Additives to maintain high T, low RH performance:
• Water retention at low RH
• Water supplement/replacement (with participation in proton conduction)

- **Design: Additives**
  - Hydrophilic/hygroscopic
  - Thermally, hydrolytically stable
  - May participate in proton conduction

- **Materials: Organic compounds**
  - Simple and versatile synthesis

- **Current status**
  - Designed and synthesized several additive candidates
Future Work
FY06/FY07

Materials synthesis
• Demonstrate feasibility of synthetic approaches to making new aromatic hydrocarbon polymer structures
• Design, synthesize, and characterize new monomers, polymers, and hydrophilic organic additives

Membrane evaluation
• Evaluate membrane properties (proton conductivity, water uptake, mechanical properties)
• Study membrane morphology to understand the effect of variations in polymer architecture on membrane performance
Project Summary

Relevance

Apply new concepts in polymer membrane design to resolve challenging technical issues related to membrane performance over a wide range of temperatures and humidities.

Approach

Design and synthesize new polymer architectures that promote membrane phase separation and ionic aggregation. Explore hydrophilic organic additives to improve performance at high temperature, low RH.

Progress

Developed synthetic approaches. Synthesis and evaluation in progress.

Future research

Continue design, synthesis, and evaluation of new materials. Develop further understanding of the effect of polymer architecture on membrane morphology and performance.