High-Temperature Polymer Electrolyte Membranes Based on Dendritic Macromolecules and Organic/Inorganic Hybrids

Suhas Niyogi, Deborah J. Myers, and Romesh Kumar

Electrochemical Technology Program, Chemical Engineering Division, Argonne National Laboratory

Introduction: The state-of-the-art electrolyte for the polymer electrolyte fuel cell, being developed for vehicle traction and residential power, requires humidification to conduct protons and thus its operating temperature is limited to <100°C (typically 80°C). This requirement adds complexity, size, weight, and cost to the fuel cell power system. Argonne's approach to developing membrane electrolytes with high proton conductivity at low relative humidity and temperatures above 100°C is to utilize sulfonated polyaryl ether dendrimers (highly branched macromolecules). The polyaryl ether dendrimers were chosen as the membrane building blocks because they have a high density of proton-conducting functional groups, are thermally stable, and are expected to be stable in the fuel cell environment.

Limitations of Current Membrane Electrolytes

- Perfluorosulfonic acid membranes (e.g., Nafion®)
  - Rely on water to conduct protons through hygroscopic, sulfonate-lined pores
  - Lose conductivity at temperatures >100 °C due to loss of water
  - Typical operating conditions are 80 °C and 100% relative humidity
- Phosphoric acid-doped polybenzimidazole membranes
  - Require high phosphoric acid content to achieve high proton conductivity
  - Have durability problems due to leaching of phosphoric acid into product water

Motivation for a High-Temperature Membrane

- Higher operating temperatures would provide
  - Easier heat rejection from fuel cell stacks
  - Faster kinetics on cathode electrocatalyst
    - *Lower platinum loading
    - *May allow use of non-Pt electrocatalyst
  - Better CO tolerance on anode electrocatalyst
- Membranes not requiring external humidification would greatly simplify the fuel cell system

Desired Properties of a Proton-Conducting Membrane for Polymer Electrolyte Fuel Cells

- High, sustained proton conductivity at 80 to 150°C and low relative humidity (e.g., 0.1 S/cm @ 120°C)
  - Automotive: 120°C, low humidity (~25% RH)
  - Stationary: >150°C, very low humidity
- Low oxygen and hydrogen cross-over (<5 mA/cm²)
- Low cost
- Durability of >5,000 hours
- Able to withstand temperatures as low as -40°C

Organic/Inorganic Hybrid Membranes

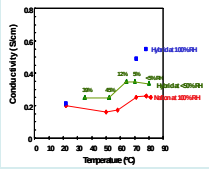
Organic/inorganic hybrid membranes have variable charge density and distribution and high thermal and dimensional stabilities. Their inorganic component improves water retention at high temperatures. They are low-cost and easy to prepare.

Status of Organic/Inorganic Hybrid Membranes Development

- Hybrid materials have been prepared from sulfonated organic macromolecules and silica
- Materials are thermally stable at temperatures exceeding 300°C
- Films have been formed by blending hybrid with Nafion solution
- Conductivity has been measured up to 80°C at 100% and lower relative humidity
- Other techniques of film formation, not relying on Nafion, are being developed
- Four more thermally stable hybrid materials have been prepared without Nafion and characterized

Initial Conductivity Results

- Organic/inorganic hybrid has higher conductivity than Nafion in testing up to 80°C
- Hybrid conductivity was stable in limited testing (4 days)

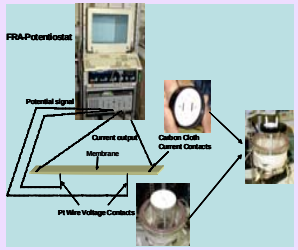


Membrane Characterization Techniques

Material evaluation techniques

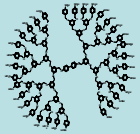
- Thermal gravimetric analysis (TGA)
  - Thermal stability of materials and membranes
  - Strength of water bond
- Nuclear magnetic resonance
  - Degree of functionalization of polymer backbone
- pH Titration
  - Acid sites per gram of material to determine equivalent weight (molecular weight per acid site)
- AC impedance - electrochemical characterization
  - Proton conductivity
    - Temperatures from RT to 150°C
    - Relative humidities up to 100%
- MEA fabrication - electrochemical characterization
  - Fuel cell performance
  - Stability in electrochemical environment

Conductivity Apparatus
Four-Point Probe AC Impedance



Dendritic Macromolecular Membranes

Dendritic macromolecules are highly branched and have high surface charge densities. The high density of proton-conducting groups is expected to improve water retention at high temperatures, and to facilitate high proton transfer with reduced water mediation.

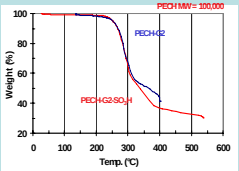


Approach to Fabricating Electrolyte Membranes

- Aryl ether dendrites chosen due to high thermal stability and stability in fuel cell environment
- High density of sulfonate groups imparts water solubility
  - Cross-linking eliminates solubility, controls swelling and enhances thermal stability
  - Identity of cross-linking molecules determines pore size and film-forming characteristics
  - Attaching dendrons to a polymer backbone is an alternative strategy to eliminate water solubility

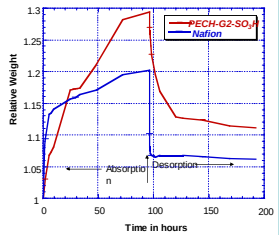
Dendronized PECH Is Stable up to 180°C

- Solvent removal up to 150°C
- Sulfonate group decomposes at temperatures >180°C
- Material decomposes at temperatures >230°C

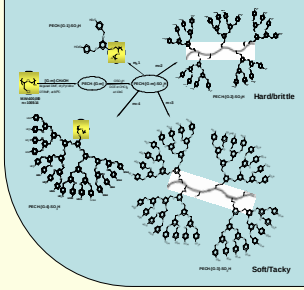


Sulfonated Dendronized PECH Retains More Water than Nafion®

- Polymers of comparable equivalent weight
- Moisture absorption at 25°C and 97% RH followed by desorption at 25°C and 40% RH

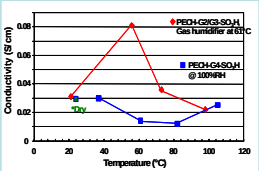


Dendrons Have Been Attached to Polyepichlorohydrin (PECH) for Water Insolubility and Film Formation



Initial Conductivity Results are Promising

- PECH-G2-SO_3H and PECH-G3-SO_3H have been blended (20/80) to enable film formation
  - PECH-G2-SO_3H has 215 G2 units per backbone
  - PECH-G3-SO_3H has 130 G3 units per backbone
- PECH-G4-SO_3H acid functionality has not yet been determined



Status of Dendritic Macromolecular Membrane Development

- Sulfonated dendritic blocks conduct protons without external humidification
- Sulfonated dendritic blocks were attached to polyepichlorohydrin to obtain water insoluble proton conducting membranes
- Dendronized polymers are thermally and oxidatively stable up to 150°C and retain more moisture than Nafion® under low RH
- Encouraging conductivity data have been obtained for dendronized polymers at low humidity levels

Research funded by U.S. Department of Energy, Hydrogen, Fuel Cells & Infrastructure Technologies Program (Nancy Garland, Technology Development Manager)

Argonne National Laboratory is operated by The University of Chicago for the U.S. Department of Energy Office of Science