Argonne NATIONAL LABORATORY

High-Temperature Polymer Electrolyte Membranes

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Argonne National Laboratory

May 16-19, 2006

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Project ID: FC-1

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Work sponsored by U.S. Department of Energy, Hydrogen, Fuel Cells and Infrastructure Technologies Program

Overview

Timeline

- Start date: October 2001
- Project end date: Upon Tech Transfer
- Percent complete: n/a

Budget

- Total FY '02 – FY '06: $1635 K
- FY '05: $335 K
- FY '06: $350 K

Barriers

- This project addresses DOE's Technical Barriers for Fuel Cell Components:
  - A: Durability
  - B: Cost
  - C: Electrode Performance
  - D: Thermal and Water Management
  - I: Hydrogen Purification/Carbon Monoxide Cleanup

Interactions

- Collaboration with California Institute of Technology, W. A. Goddard III

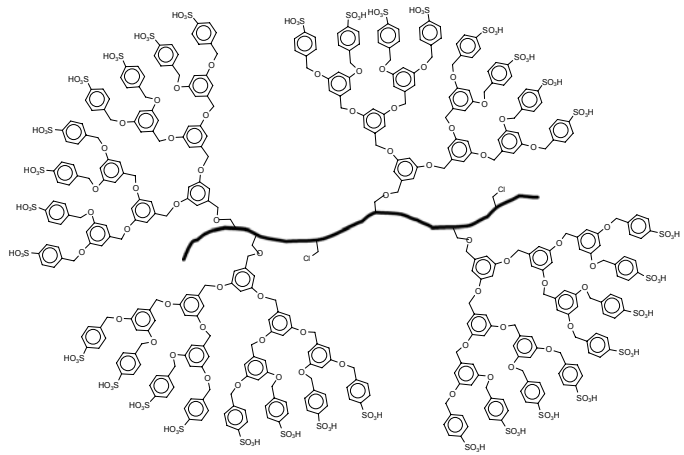
Objectives

- To develop a proton-conducting membrane electrolyte for operation up to 120°C or higher and low humidities to meet DOE's technical targets*
  - High, sustained proton conductivity (0.1 S/cm) at ≤120ºC and ≤ 1.5 kPa water vapor pressure
  - Proton conductivity (0.01 S/cm) at temperatures as low as –20°C
  - Low oxygen and hydrogen cross-over (2 mA/cm²)
  - Low cost, $40/m²
  - Durability of 2,000 operating hours (at >80°C)
  - Survivability to – 40°C

*2010 Targets

Approach: Dendronized Polymers

- Dendrons are highly branched macromolecules
  - High surface charge densities
    - *To facilitate high proton transfer with reduced water mediation*
    - *May improve water retention at high temperatures*



- Polymer backbone
  - Eliminates water solubility of highly-sulfonated dendrons
  - Allows control of mechanical/dimensional properties and phase separation
  - Can be used to control spacing between sulfonate groups

Molecular dynamics simulations show dendronized polymers have improved low RH properties

W.A. Goddard III, Boris Merinov, and Seung Soon Jang, California Institute of Technology

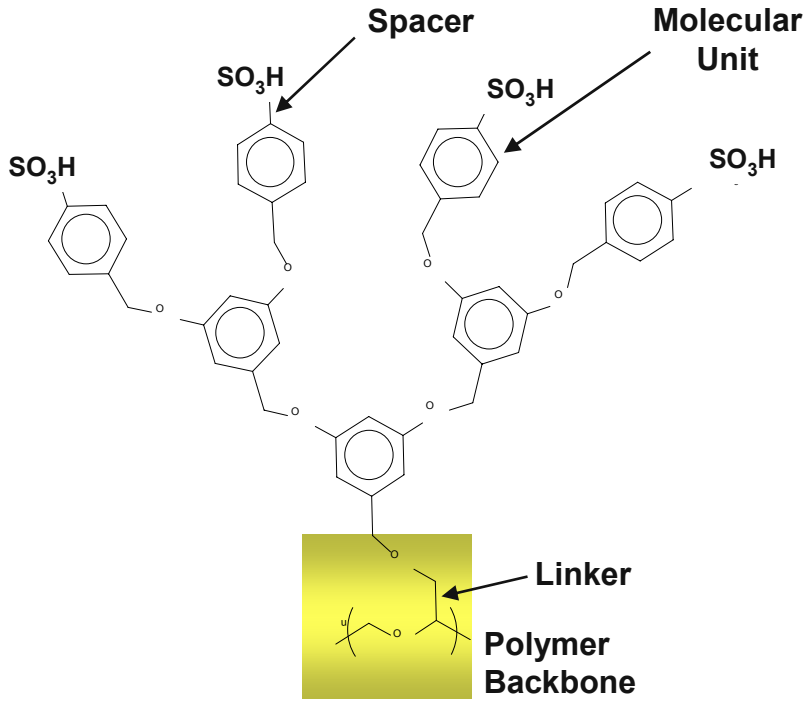
- Dendronized PTFE with 10 wt% water has water structure and transport properties equivalent to Nafion® with 20 wt% water
  - water forms connected bulk-water-like channels more efficiently
    - $D_{rotational}$ has a larger value at lower water content
    - $D_{hopping}$ has a comparable value at lower water content
  - water diffusion coefficient of dendronized PTFE is 4 to 7 times lower

Source: S.S. Jang et al., J. Phys. Chem. B, 109, 10154-10167 (2005).

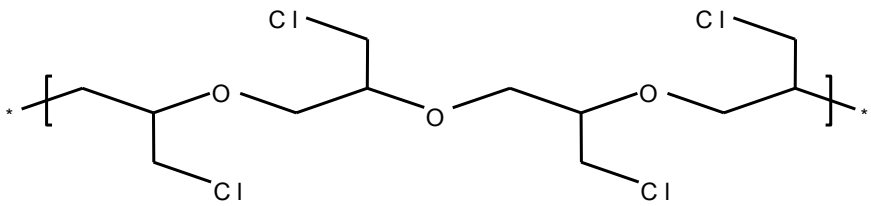
Membrane properties can be controlled by molecular design of polymer

Mechanical strength, conductivity, thermal and chemical stability can be controlled by choice of :

- Backbone Polymers
- Linkers (link between backbone and molecular units with proton-conducting groups)
- Molecular unit
- Spacers (linear chains between molecular units and proton conducting groups)
- Cross-linkers (for network formation between backbone polymer molecules)

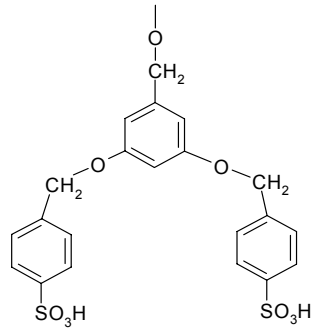


Polyaryl ether dendrons have been attached to a polyepichlorohydrin backbone

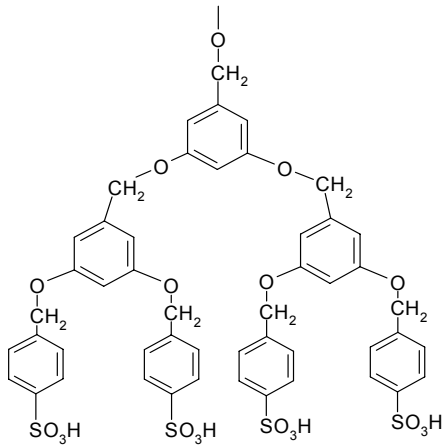


- Polyepichlorohydrin (PECH):
  - Flexible
  - regularly spaced functional groups

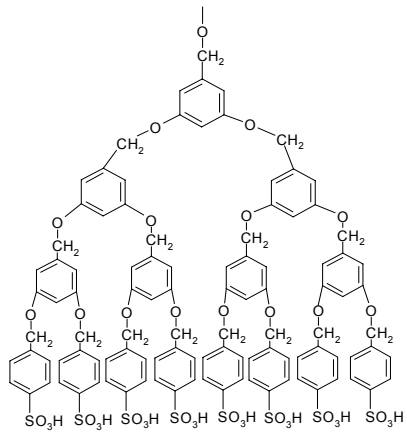
- Polyaryl ether dendrons, chosen for:
  - oxidative stability
  - water retention
  - established synthetic procedure



Generation 1 (G1)

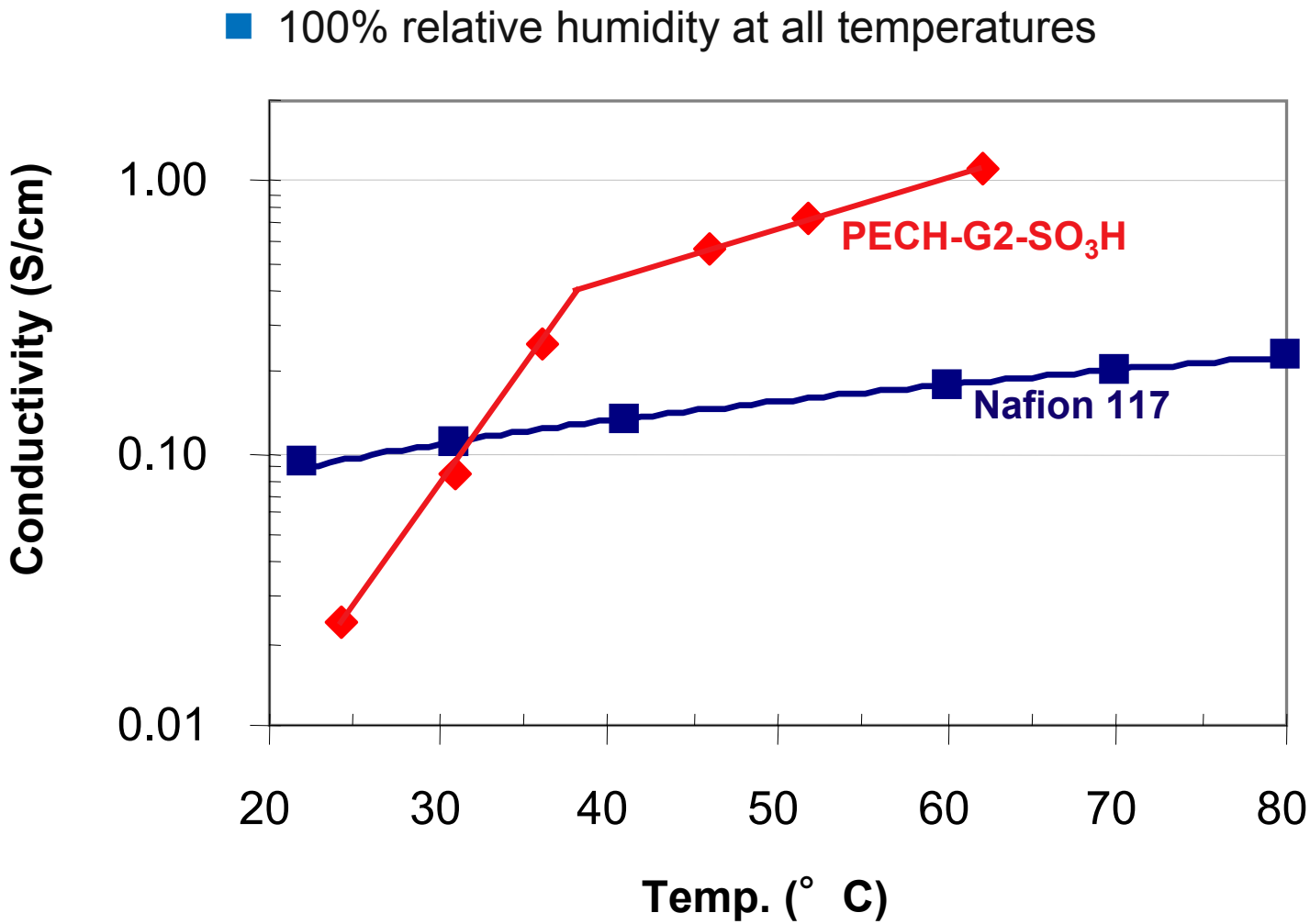


Generation 2 (G2)



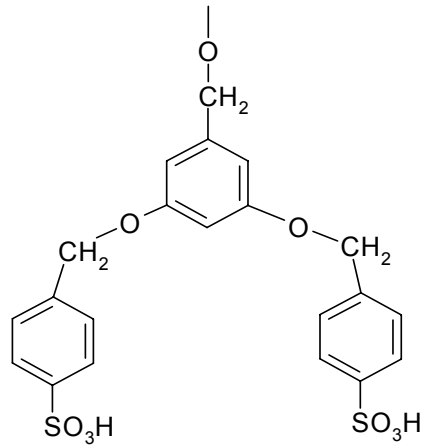
Generation 3 (G3)

High proton conductivities have been measured for PECH-G2-SO_3H



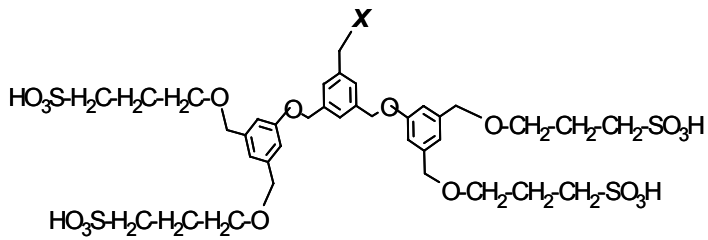
The shortcomings of polyaryl ether dendrons have been addressed

- Issues with polyaryl ether dendron:
  - Lack of control over the sulfonation of aromatic rings leading to inconsistent conductivity data
  - De-sulfonation of aromatic rings in humid environments, elevated temperatures



G1-SO_3H

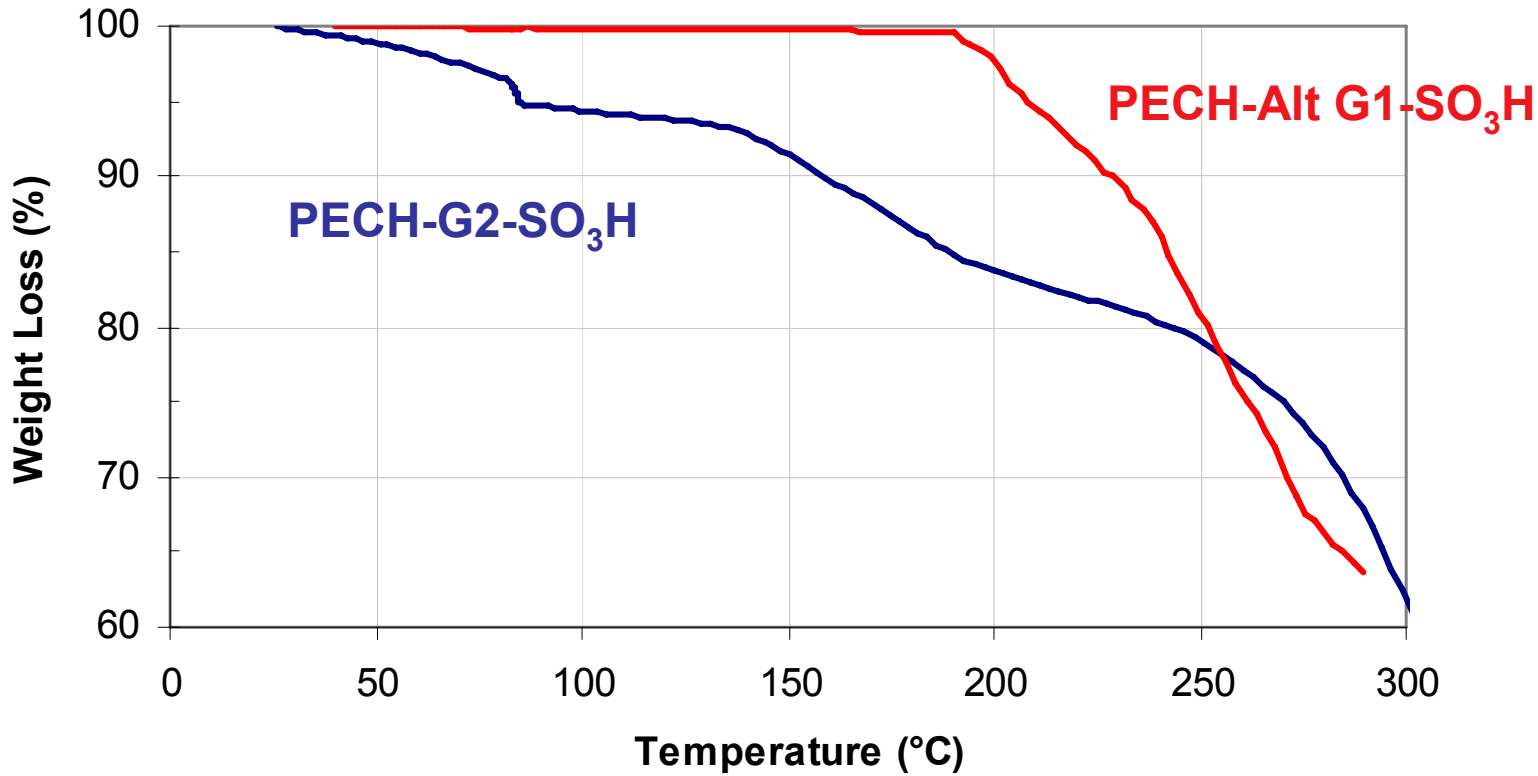
- Solution: Alternative dendron (Alt-G_n-SO_3H)
  - Sulfonate groups attached to aromatic ring through propyl or propyloxy groups
  - Sultone is used to alkylate methylol group on dendron, thus avoiding strong sulfonation conditions



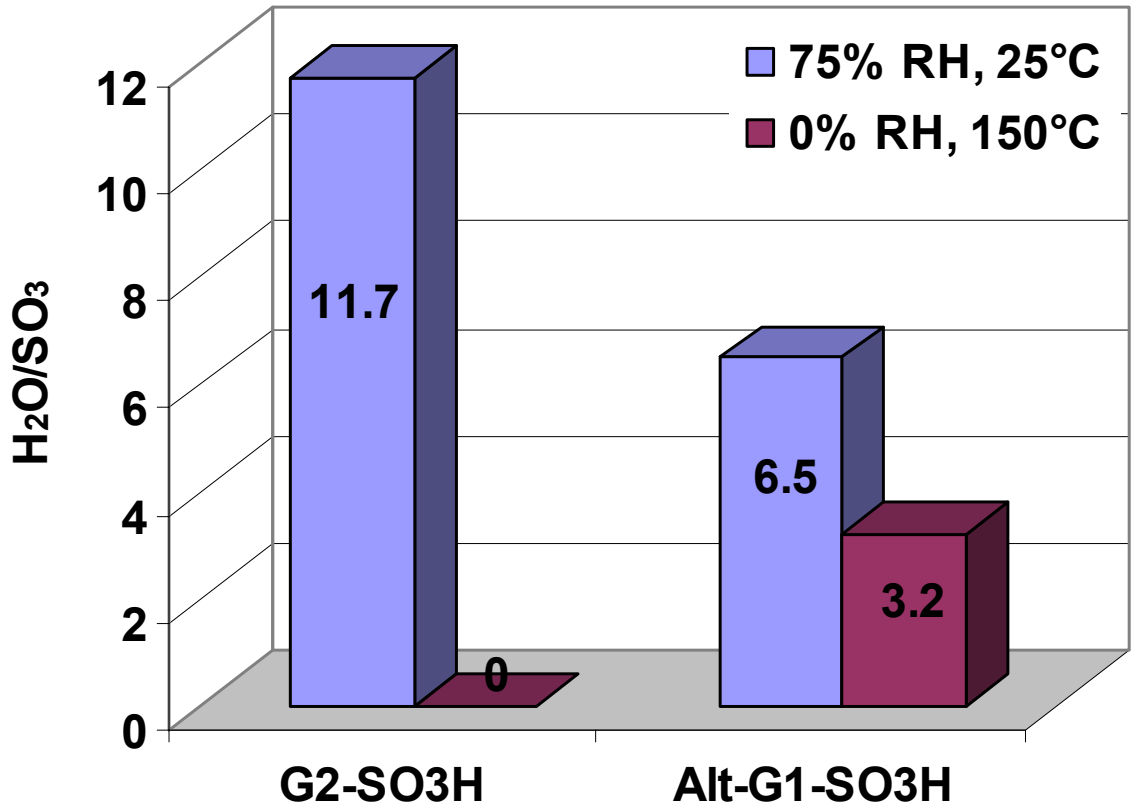
Alt-G1-SO_3H

PECH-Alt-G_1-SO_3H is more stable than PECH-G_2-SO_3H

- TGA, humid air, 6°C/min

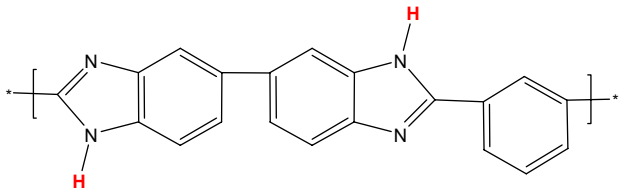


Alt-G1-SO_3H retains more water than G2-SO_3H at 150°C, 0%RH



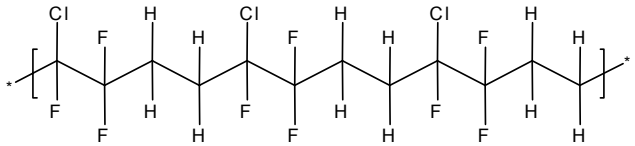
Alternative backbones are being investigated to improve mechanical and low RH properties

- Improve phase segregation and dimensional stability of dendronized polymers using thermally stable, hydrophobic backbones

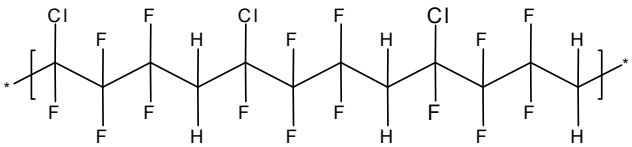


Polybenzimidazole

✓ 15 mol% of G1 dendron has been attached to a PBI backbone

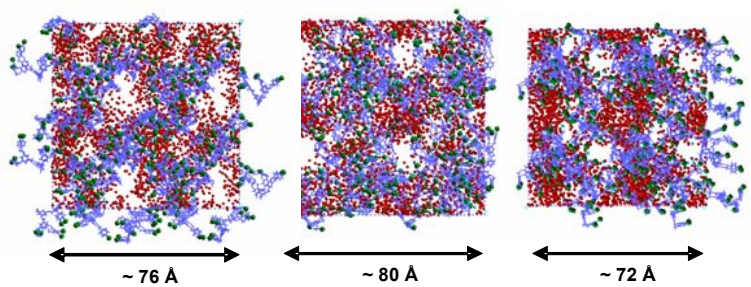


Poly(chlorotrifluoroethylene-alt-ethylene)



Poly(chlorotrifluoroethylene-co-vinylidene fluoride)

- Modeling effort at Caltech is guiding choice of polymers

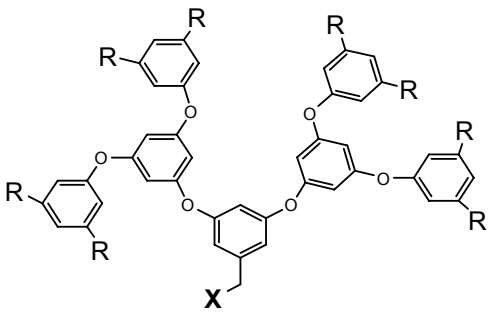


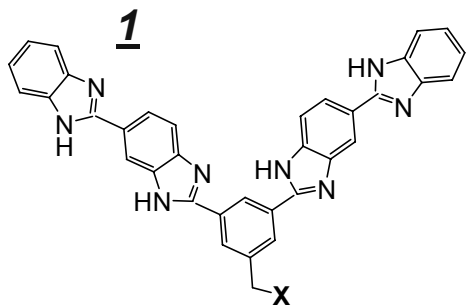
Technical Accomplishments

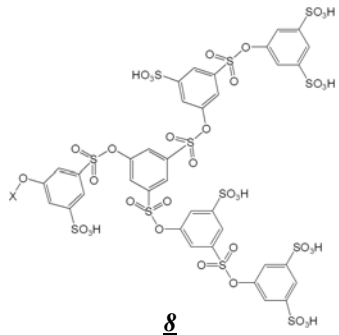
- Demonstrate proton conductivity of 0.03 S/cm for dendronized polymers and inorganic-organic hybrids 06/06
  - Demonstrated a conductivity of 1 S/cm at 60° C and 100% RH for dendronized PECH
- Improved stability and control over placement of sulfonate groups using alternative dendron
  - Alternative dendron is stable to >200°C
  - Alternative dendron retained 3 H_2O/SO_3 at 150°C
  - Devising ways to control water solubility of this material, cross-linking is being pursued
- Improved dimensional and thermal stability of polymer backbone by attaching dendrons to polybenzimidazole

Future work

- Molecular modeling of dendronized polymers with proposed fluorinated backbones
- Continue work on sulfonation of dendronized PBI, begin work on fluorinated backbones
- Further improve stability of dendrons:



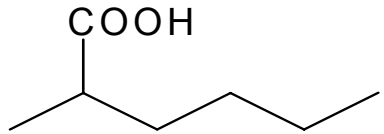




Dendrimeric sulfonate

- Enhance stability and acidity of sulfonate groups using spacers:

-O-CH_2-CH_2-CH_2- -O-CF_2-CF_2-CF_2-CF_2-



Summary

- Molecular modeling at Caltech has shown dendronized polymers are promising for achieving high proton conductivity at reduced relative humidity
- Multiple PECH-G2-SO_3H membranes have been characterized
  - Film is thermally stable up to 180°C
  - High proton conductivities have been achieved at 100%RH and <70°C, however reproducibility is difficult due to lack of control over sulfonation
  - Long-term hydrolytic stability is an issue
  - Film flows at approximately 75°C
- An alternative dendron has been synthesized to address these issues, and has been attached to PECH
  - 1 PECH/1 G1: 5 meq acid/g, water soluble
  - 3 PECH/1 G1: 1.2 meq acid/g, cross-linked, non-film-forming
  - 6 PECH/1 G!: 0.4 meq acid/g, cross-linked, non-film-forming
- To address dimensional stability, G1 dendron has been attached to a PBI backbone (15 mol%)
  - Film is thermally-stable, post-dendronization sulfonation removes dendrons

Publications

- D. Colombo, M. Krumpelt, D.J. Myers, and J.P. Kopasz, “Improved Proton Conducting Membranes for Fuel Cells”, U.S. Patent 6,977,122, Dec. 20, 2005.

Response to FY '05 Reviewers' Comments

- "Dimensional stability of materials"
  - *Dendrons are now being attached to alternative, high-temperature polymers, such as PBI*
- "Need to articulate quantitatively what leads researcher to believe the targets are ultimately achievable using the proposed approach"
  - *Molecular modeling results from Caltech have demonstrated that dendronized polymers can achieve better performance than Nafion at low relative humidity*
- "Address the subzero operation capacity"
  - *An environmental chamber has been purchased for subzero testing*