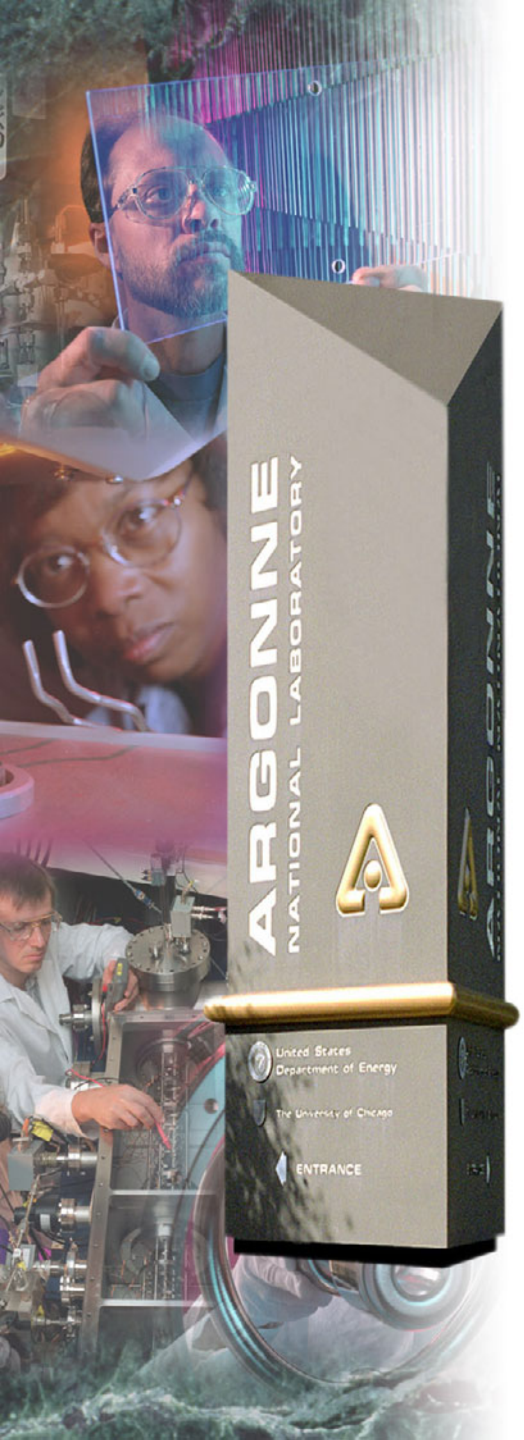

High-Temperature Polymer Membranes

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Argonne National Laboratory

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Project Objectives

- **To develop a proton-conducting membrane electrolyte for operation at 120-150°C and low humidities to meet DOE's technical targets**

- **Investigate use of dendritic macromolecules attached to polymer backbones, cross-linked dendrimers, and inorganic-organic hybrids**
  - Measure thermal stabilities and conductivities of samples 11/03✓
  - Prepare and characterize inorganic-organic hybrids 02/04✓
  - Fabricate and test MEAs using high-temperature membranes 09/04

Budget

- Total Project Funding, FY’02-FY’04: $700 K
- FY’04 Funding: $250 K

Technical Barriers and Targets

- **This project addresses DOE’s Technical Barriers for Fuel Cell Components**
  - E: Distributed Generation Durability
  - O: Stack Material and Manufacturing Cost
  - P: Component Durability
  - Q: Electrode Performance
  - R: Thermal and Water Management

- **DOE’s Technical Targets:**
  - High, sustained proton conductivity (>0.1 S/cm) at 120ºC and 25% RH (automotive)
  - Low oxygen and hydrogen cross-over (2 mA/cm^2)
  - Low cost, <$5/kW
  - Durability of >5,000 hours
  - Able to withstand temperatures as low as -40°C

Approach: Dendritic macromolecules and Organic/inorganic hybrids

- **Dendritic Macromolecules**
  - ✓ Highly branched spherical macromolecules
  - ✓ High surface charge densities
    - *May facilitate high proton transfer with reduced water mediation*
    - *May improve water retention at high temperatures*

- **Inorganic/Organic Hybrids**
  - ✓ Variable charge density and distribution
  - ✓ High thermal and dimensional stabilities
  - ✓ Inorganic component improves water retention at high temperatures

Safety

- **Internal safety reviews have been performed for all aspects of this project to address ESH issues**
  - Membrane synthesis
    - *All synthesis is performed in a hood to exhaust vapors of organic solvents (e.g., DMF)*
    - *Used organic solvents are collected and disposed of through the laboratory's Waste Management Operations*
  - Membrane testing
    - *Thermal gravimetric analysis – purge gas exhausted into hood*
    - *Conductivity apparatus – "safe" hydrogen (<4% H_2 in He) is used as a purge gas*
- **Safety reviews are updated and renewed annually**

Project Timeline

FY'02			FY'03			FY'04			FY'05		
1	2	3	4	5	6	7	8	9	10	11	12

- 1, 2, 3: Evaluated 3 classes of dendrimers, established capability to measure ionic conductivity, down-selected to one class of dendrimer

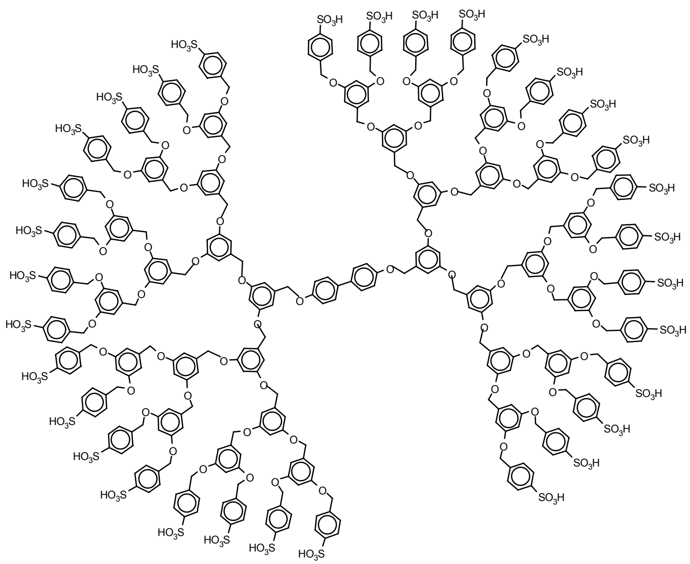
- 4, 5, 6: Characterized and measured ionic conductivity of polyarylether hyperbranched membrane, prepared membranes from modified commercial systems (PEO), improved membrane properties

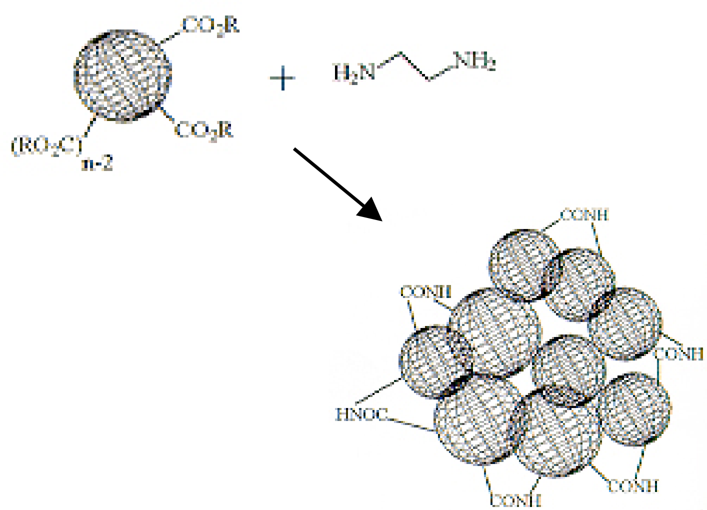
- 7, 8, 9: Measured thermal stabilities and proton conductivities of membranes, improved membrane-forming characteristics of materials, fabricate membrane-electrode assembly from most promising material

- 10, 11, 12: Down-select membrane materials, determine durability under fuel cell operating conditions, modify materials to improve performance

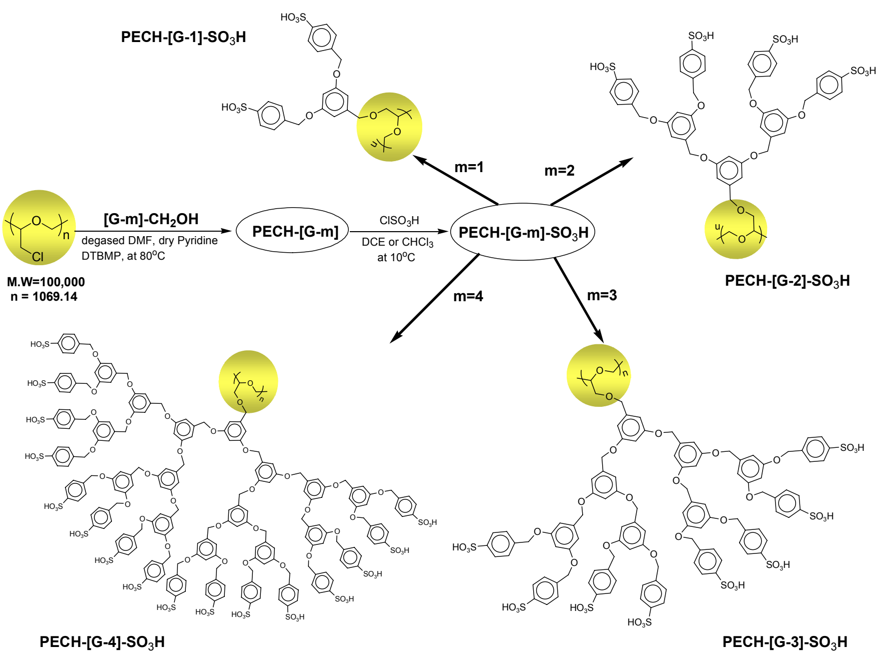
Dendritic macromolecular membranes

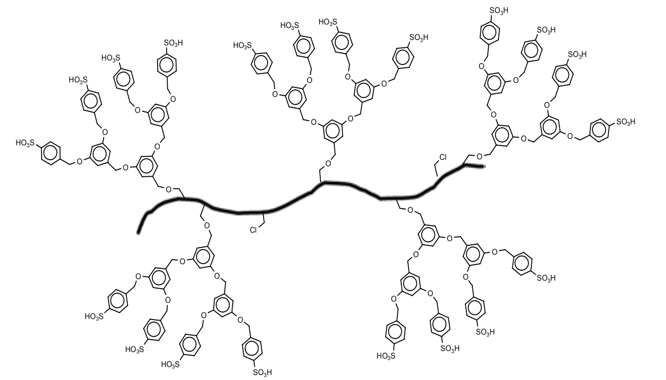
- **Aryl ether dendrimers chosen due to high thermal stability**
- **High density of sulfonate groups imparts water solubility**
  - cross-linking eliminates water solubility and controls swelling
  - identity of cross-linker determines pore size and film-forming characteristics
  - attaching dendrimer to polymer backbone is an alternative strategy to eliminate water solubility and allow film formation





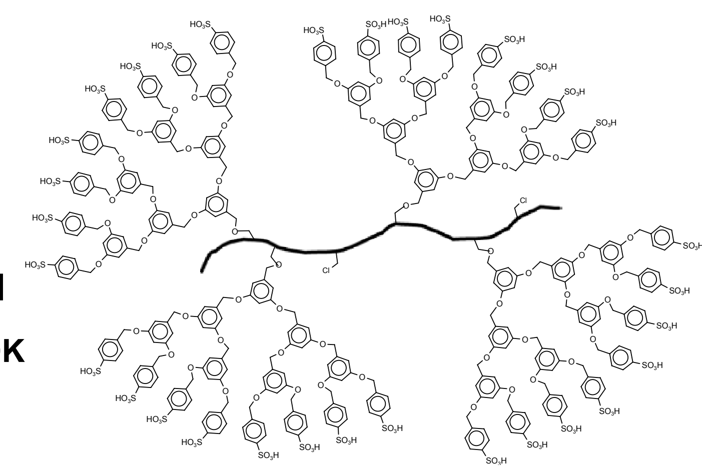
Dendrimers have been attached to polyepichlorohydrin to form water-insoluble films





PECH-G2-SO$_3$H

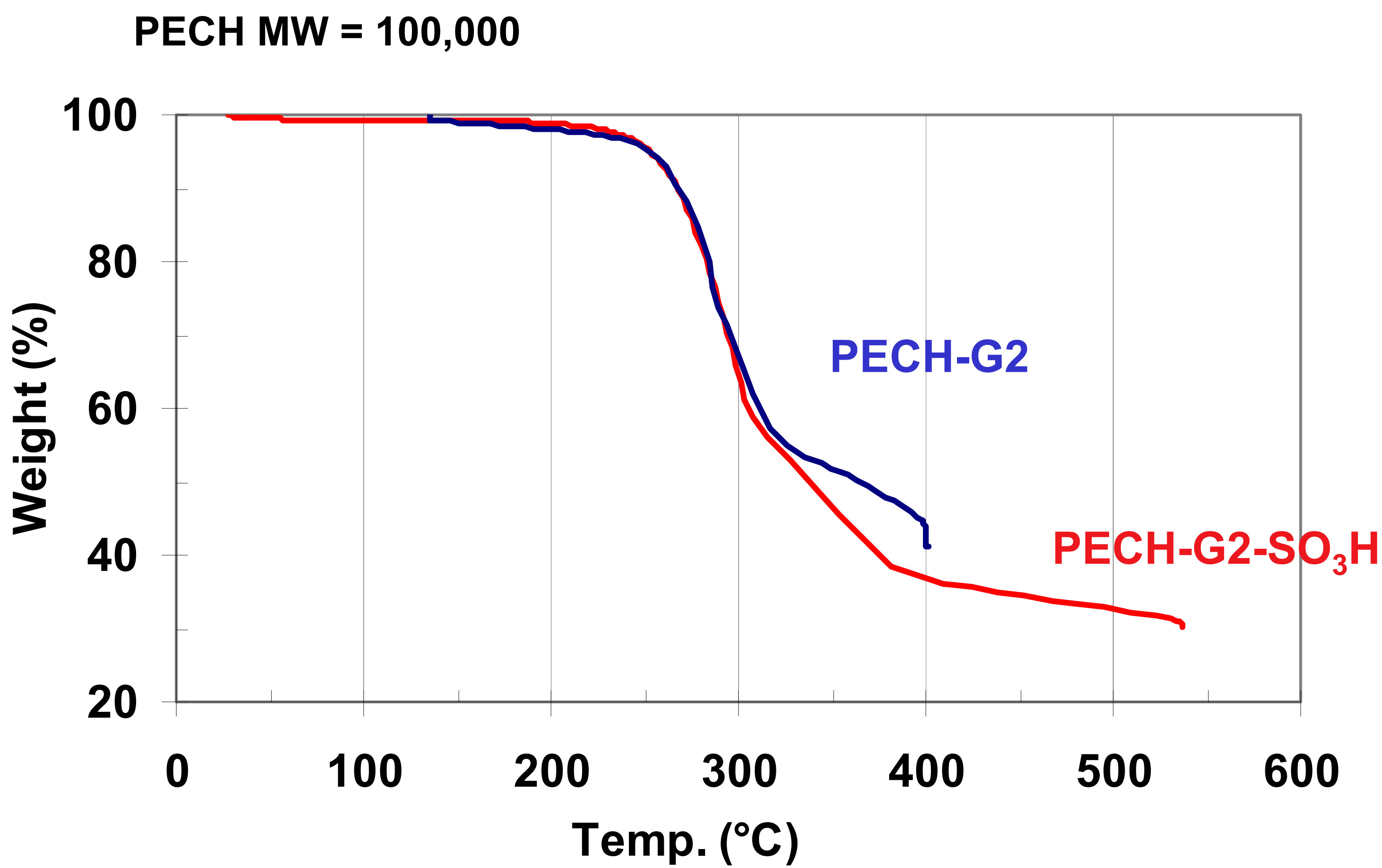
M.W of Polyepichlohydrin = 100K or 700K



PECH-G3-SO$_3$H

M.W of Polyepichlohydrin = 100K

TGA shows PECH-G2-SO_3H polymer is stable up to 190°C



Dendronized polyepichlorohydrin has a high density of proton-conducting groups, but is water insoluble

- **Acid titration results:**
  - PECH-G2-SO_3H: 4.0 meq/g
  - PECH-G3-SO_3H: 4.05 meq/g
  - Nafion: 0.91 meq/g
- **Initial conductivity results for PECH-G2/G3-SO_3H: (20% G2/80% G3)**

Temperature (°C)	Relative Humidity (%)	Conductivity (S/cm)
21	100	0.031
56	100	0.081
73	59	0.036
98	22	0.022

- **Initial conductivity results for PECH-G2-SO_3H (MW PECH = 700K):**
  - 0.101 S/cm at 76°C and 6% relative humidity

Inorganic-organic hybrid membranes

- **Cyclic organic component**
  - high thermal stability (>300°C)
  - high density of sites for functionalization
  - low cost

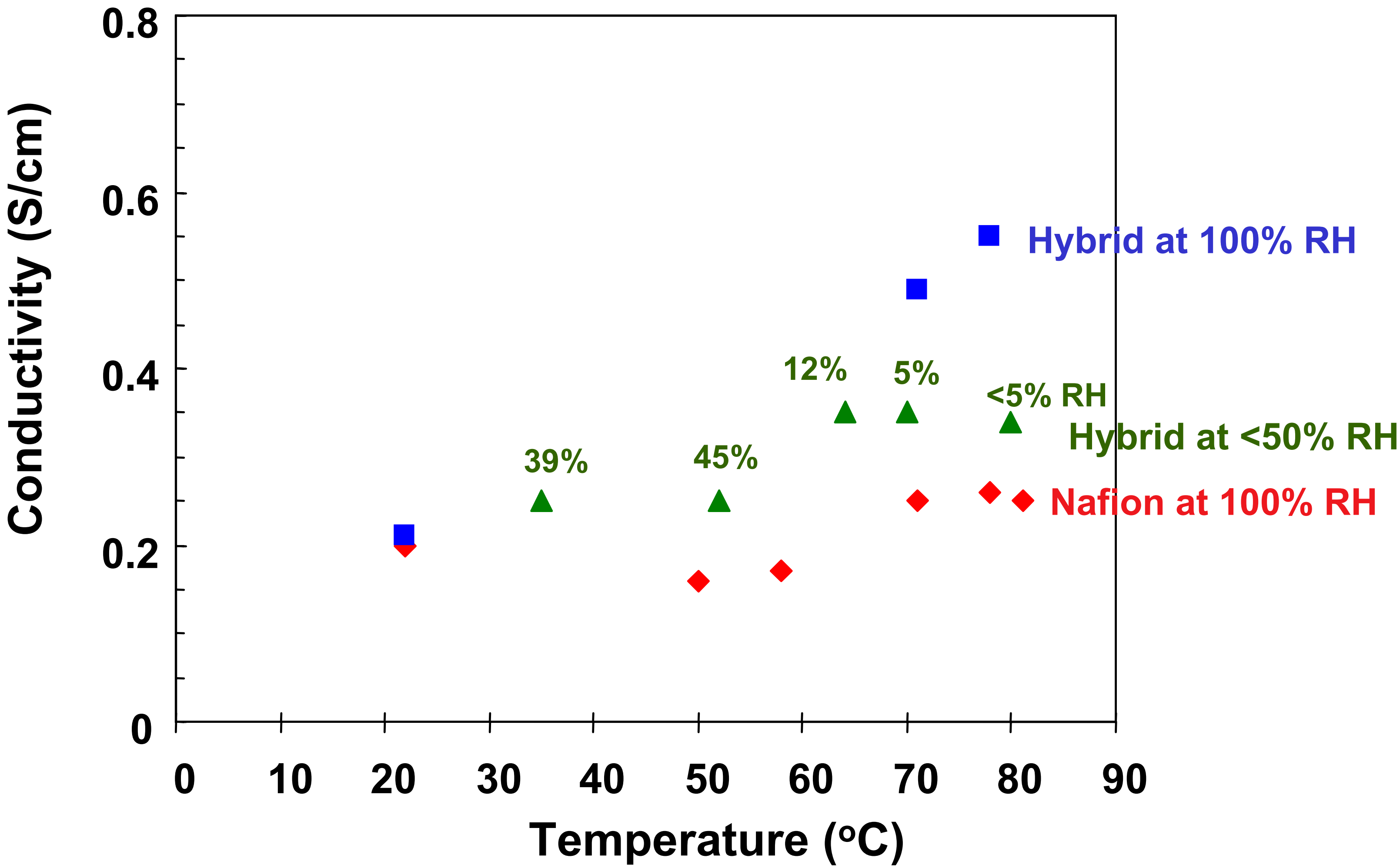
- **Sulfonated organic component blended with colloidal silica in formaldehyde to form a gel**

- **Gel is freeze-dried to form an inorganic-organic hybrid material with an equivalent weight of ~600**

- **Initial film formed by blending with Nafion solution**
  (Nafion 70 wt%, Organics 14 wt%, Silica 16 wt%)

Inorganic-organic hybrid has higher conductivity than Nafion in testing up to 80ºC

- **Hybrid conductivity was stable through four days of testing**

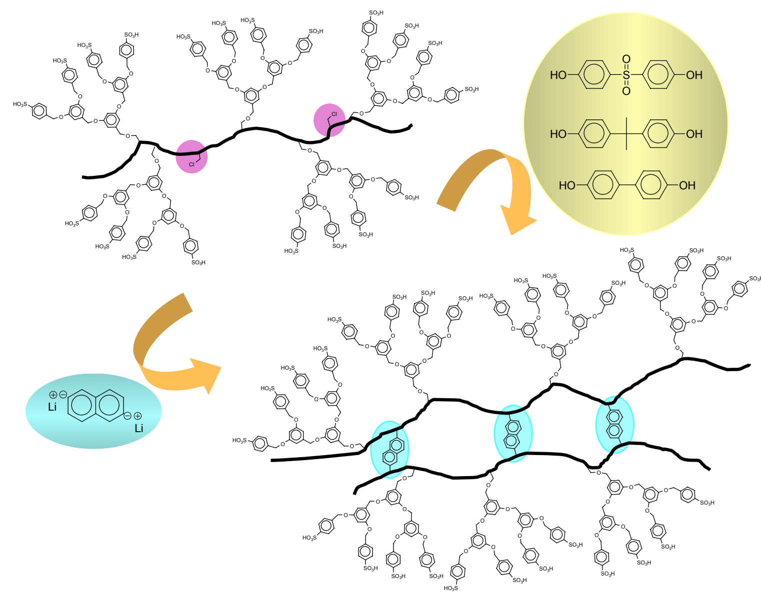


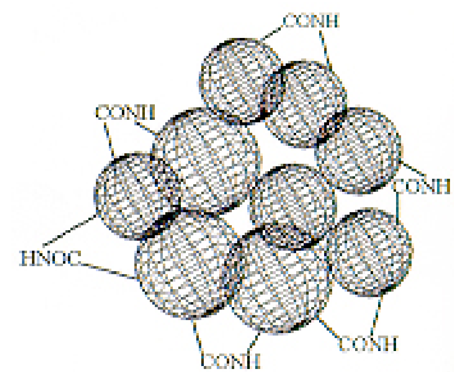
Interactions and Collaborations

- Sub-contract with Case Western Reserve University to prepare all-aromatic dendrimers was completed 12/03
- Presentations at International Energy Agency workshops
- U.S. Patent Application 20030035991
- Establishing collaboration with Toyota Motor Corporation

Future Work

- Complete characterization of G2, G3, and G4 dendritic polymers with PECH (MW = 100K and 700K)
- Cross-link PECH-dendritic polymers to improve mechanical properties
- Cross-link dendrimers to form dendrimeric network
- Develop film-forming techniques for inorganic-organic hybrids that do not rely on Nafion
- Fabricate and test a MEAs using high-temperature membranes





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