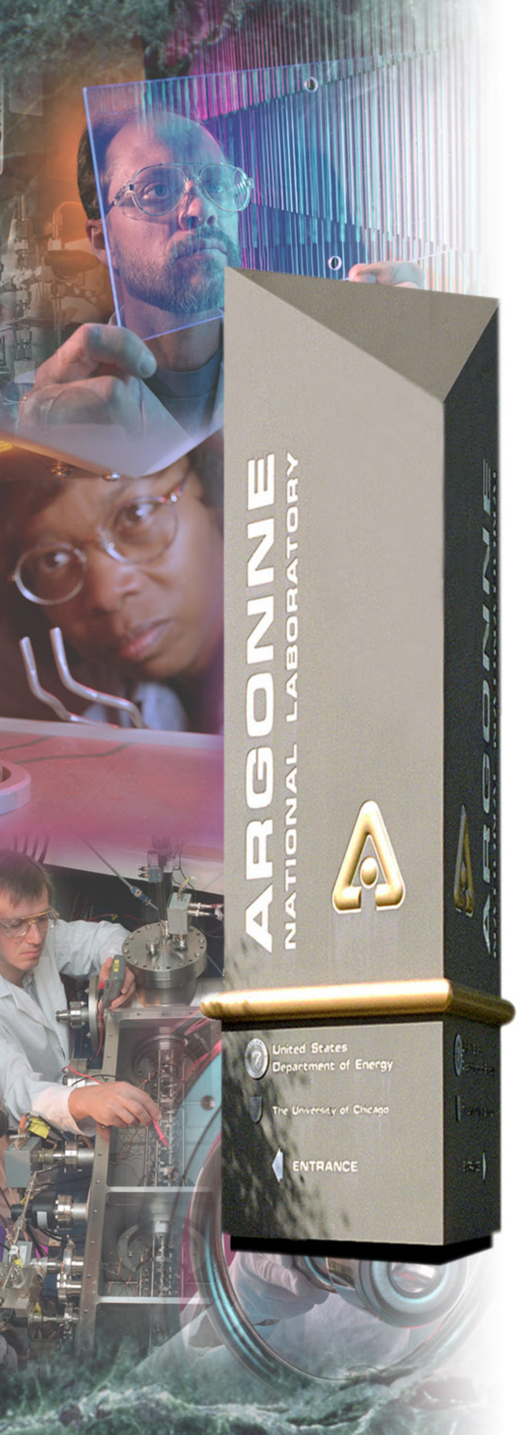

High-Temperature Polymer Electrolyte Membranes

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This presentation does not contain any proprietary or confidential information

Project ID: FC-7

Argonne National Laboratory

A U.S. Department of Energy Laboratory
Operated by The University of Chicago

Overview

Timeline

- **Start date: October 2001**
- **Project end date: Open**
- **Percent complete: 25%**

Budget

- **Total FY ’02 – FY ’05: $1285 K**
- **FY ’04: $250 K**
- **FY ’05: $335 K**

Barriers

- **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

Interactions

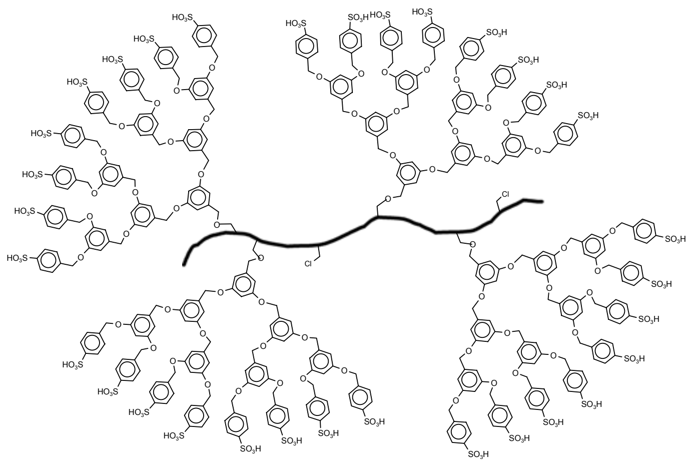
- **Provided samples to GM/Giner**

Project objectives

- **To develop a proton-conducting membrane electrolyte for operation at 120-150°C and low humidities to meet DOE's technical targets**
  - High, sustained proton conductivity (0.1 S/cm) at $\leq$120ºC and 25 kPa water vapor pressure (dew point 65°C)
  - Low oxygen and hydrogen cross-over (5 mA/cm²)
  - Low cost, $200/m²
  - Durability of 2,000 hours
  - Able to withstand temperatures as low as -30°C
- **Investigate use of dendritic macromolecules attached to polymer backbones, cross-linked dendrimers, and inorganic-organic hybrids**

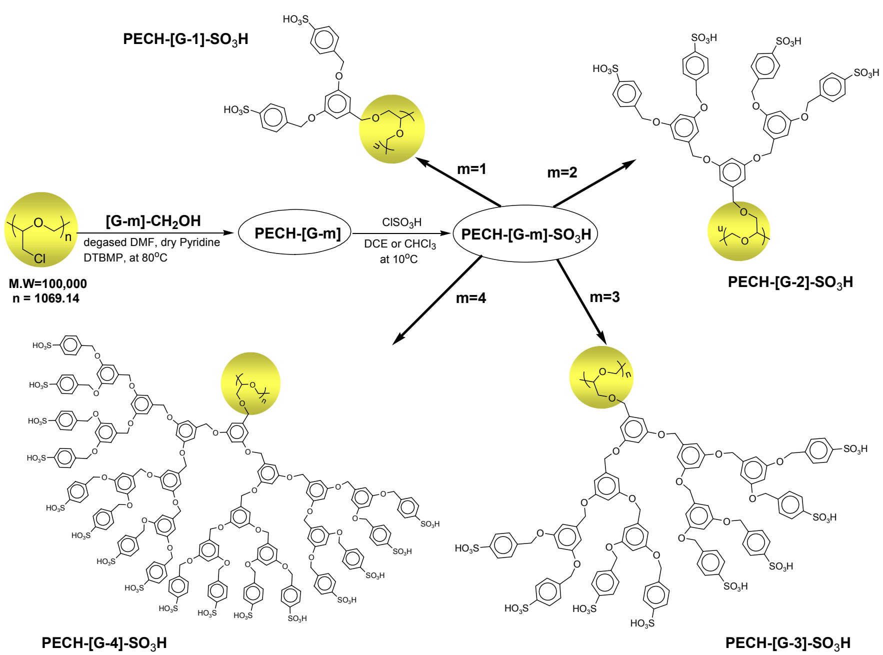
Approach: Dendritic macromolecules and Inorganic/organic hybrids

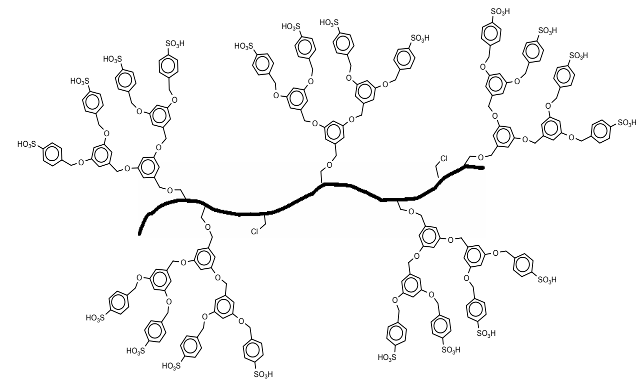
- **Dendritic Macromolecules**
  - ✓ Highly branched macromolecules
  - ✓ High surface charge densities
    - – *May facilitate high proton transfer with reduced water mediation*
    - – *May improve water retention at high temperatures*



- **Inorganic/Organic Hybrids**
  - ✓ Inorganic component improves water retention at high temperatures (e.g., colloidal silica)
  - ✓ Organic component chosen to have high density of functional groups and high thermal and dimensional stability

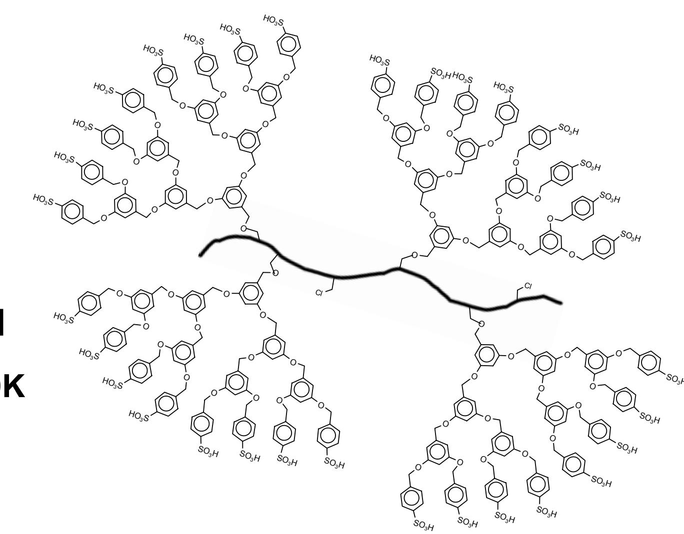
Dendrimers have been attached to polyepichlorohydrin to form water-insoluble films





PECH-G2-SO$_3$H

M.W of Polyepichlohydrin = 100K or 700K

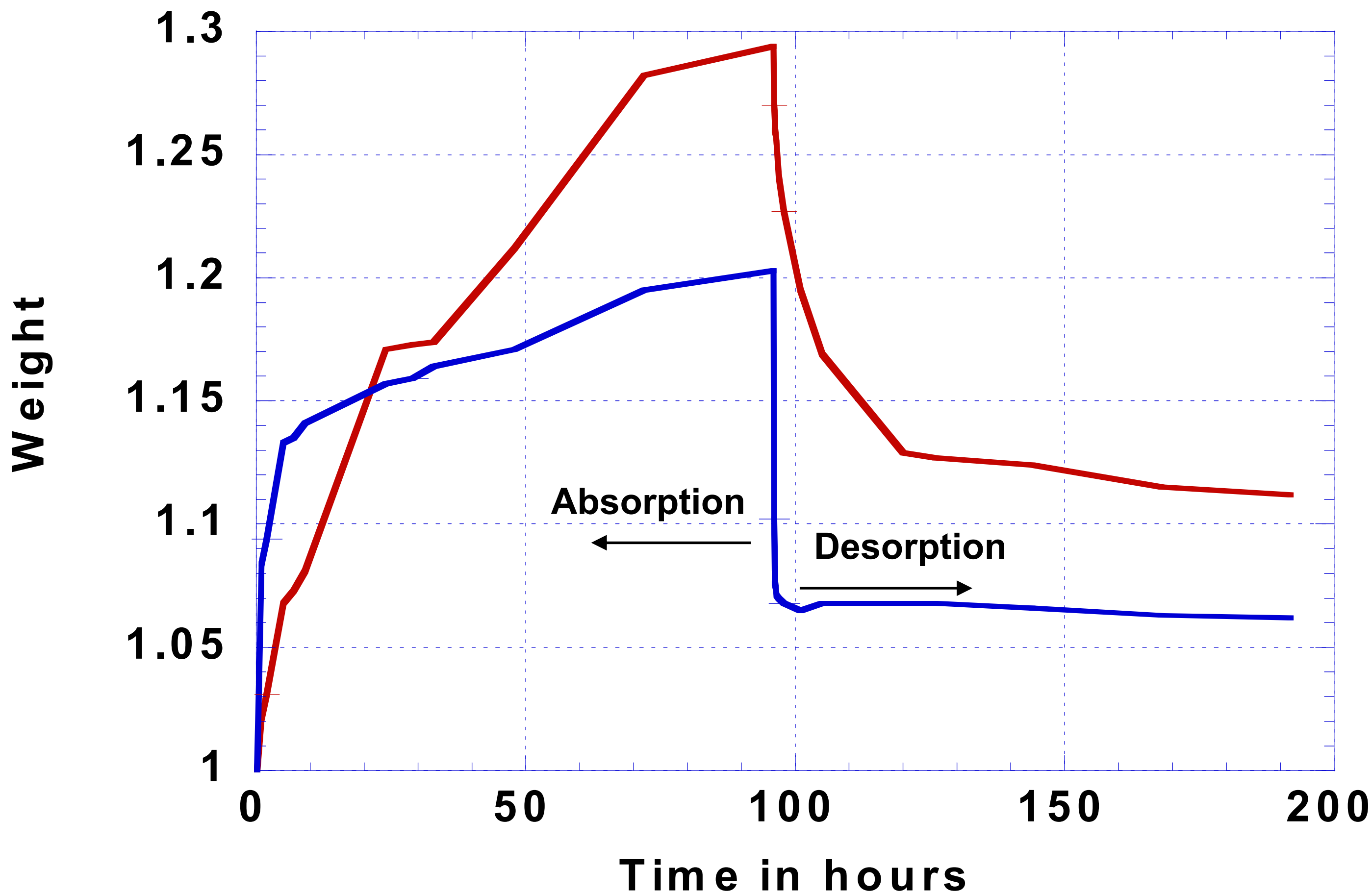


PECH-G3-SO$_3$H

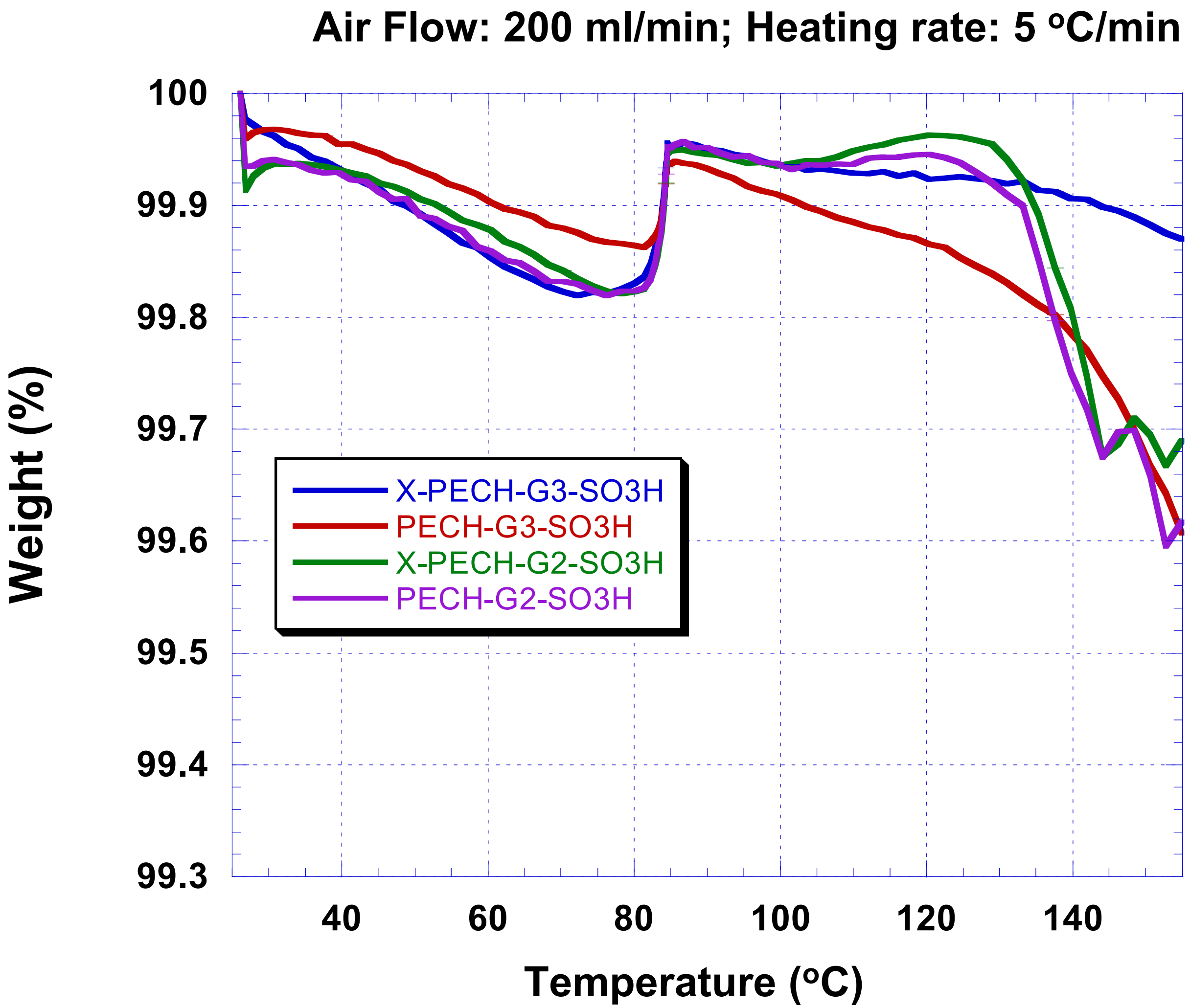
M.W of Polyepichlohydrin = 100K

Sulfonated dendronized PECH retains more water than Nafion

- Water absorption at 25°C and 97% RH, desorption at 25°C and 40% RH
- Polymers of comparable equivalent weights

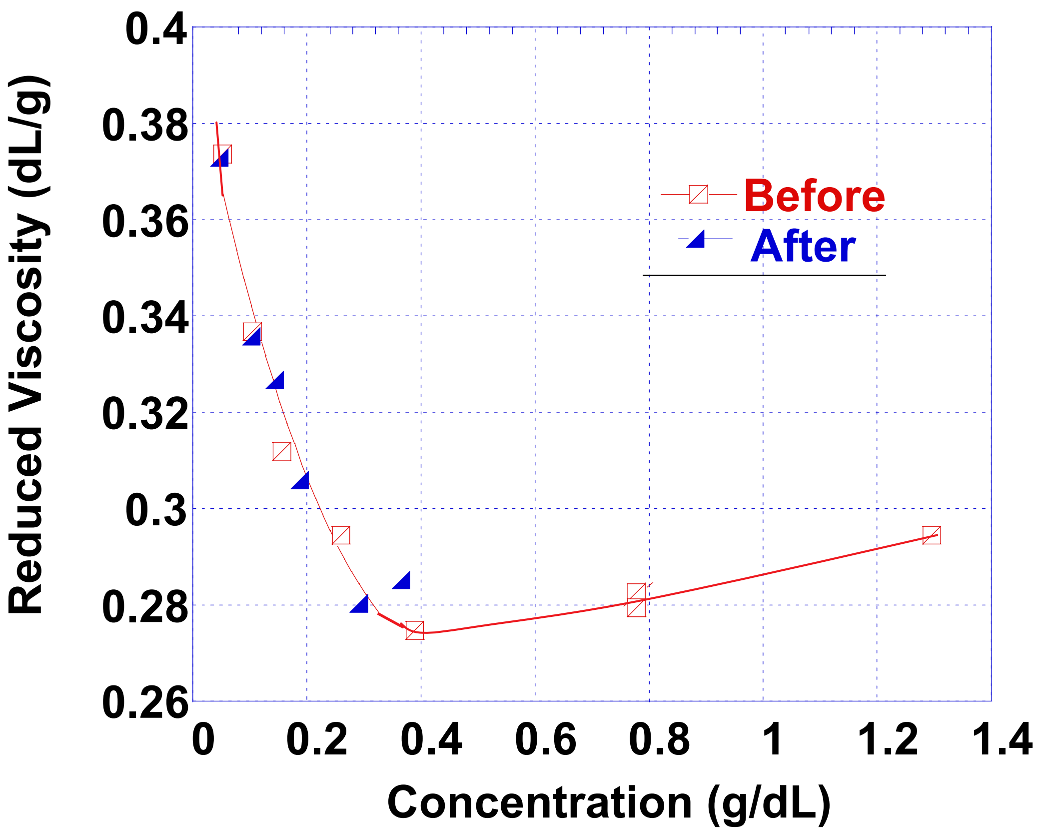


Thermal stability has been improved by cross-linking dendronized PECH



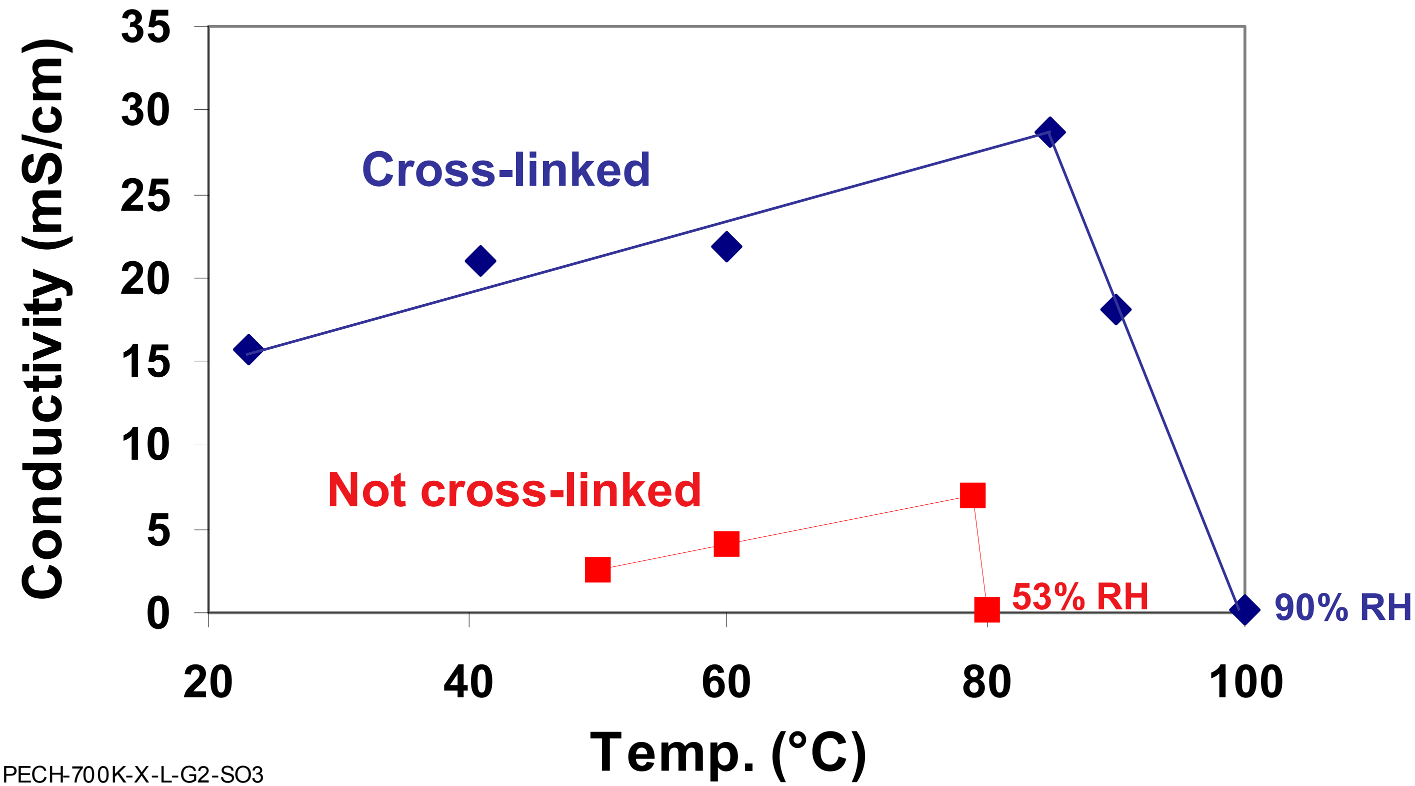
PECH-G2-SO_3H is stable under oxidizing conditions

- **Fenton's Test Conditions: Wt. Ratio $FeSO_4$:H_2O_2:Polymer = 25:165:254; pH 3.5, 32°C, 24 hours**
- **Viscosities of PECH-G2-SO_3H in DMF at 24.5°C**



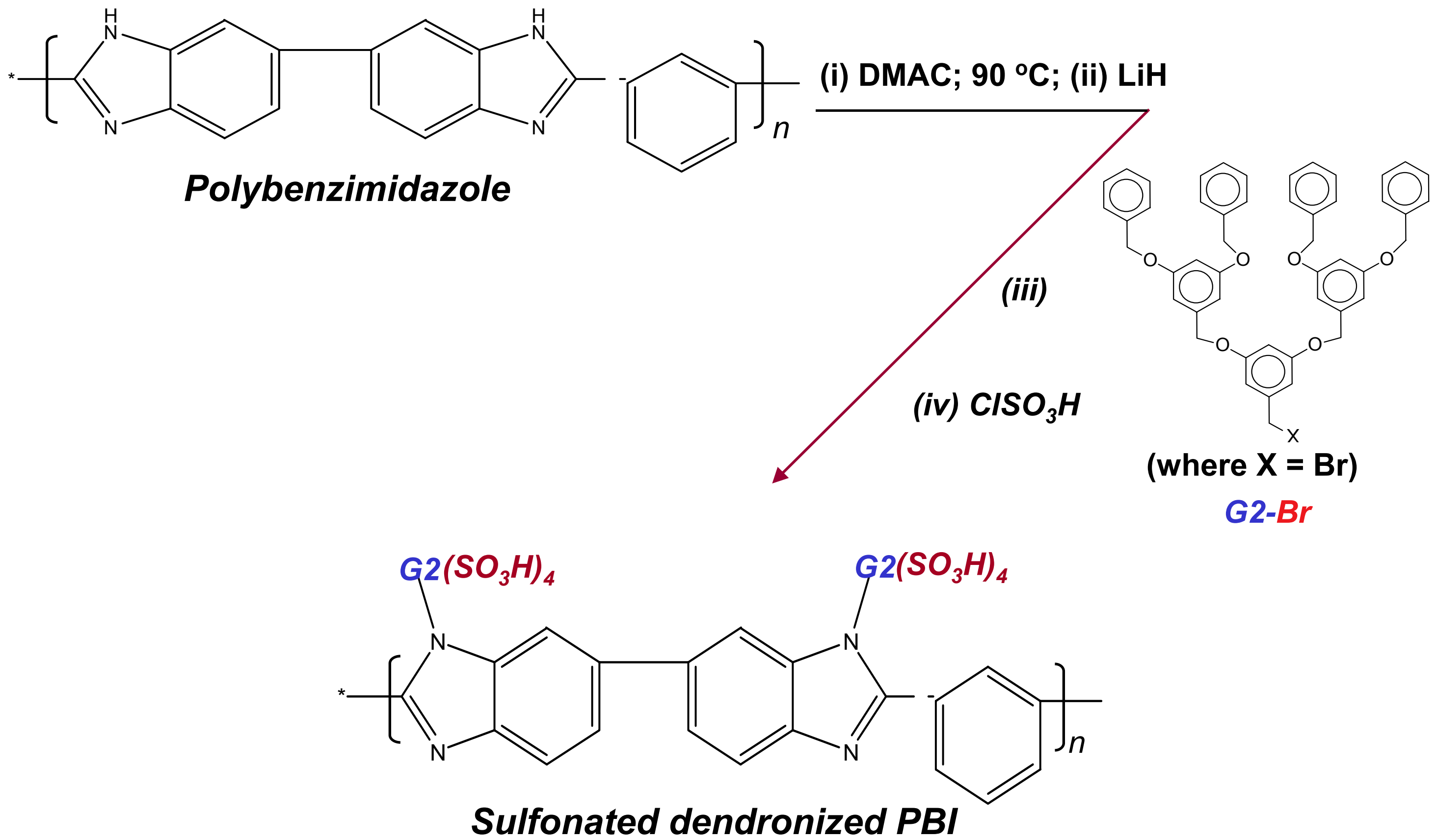
Dimensional stability and conductivity have been improved by cross-linking dendronized PECH

- PECH-G2-SO_3H (MW PECH = 700 K)
- 100% RH, except where noted
- Reference: Nafion 112, 80°C, 25 kPa steam (53% RH), ~35 mS/cm



PECH-700K-X-L-G2-SO3

Route for further improvements in dimensional stability of dendronized polymers



Inorganic/organic hybrids are thermally stable

Sample 2132-40

90% Binder, 10% sulfonated cyclic organic component

Sample 2132-41

91.9% Binder, 8.1% sulfonated cyclic organic component-colloidal silica

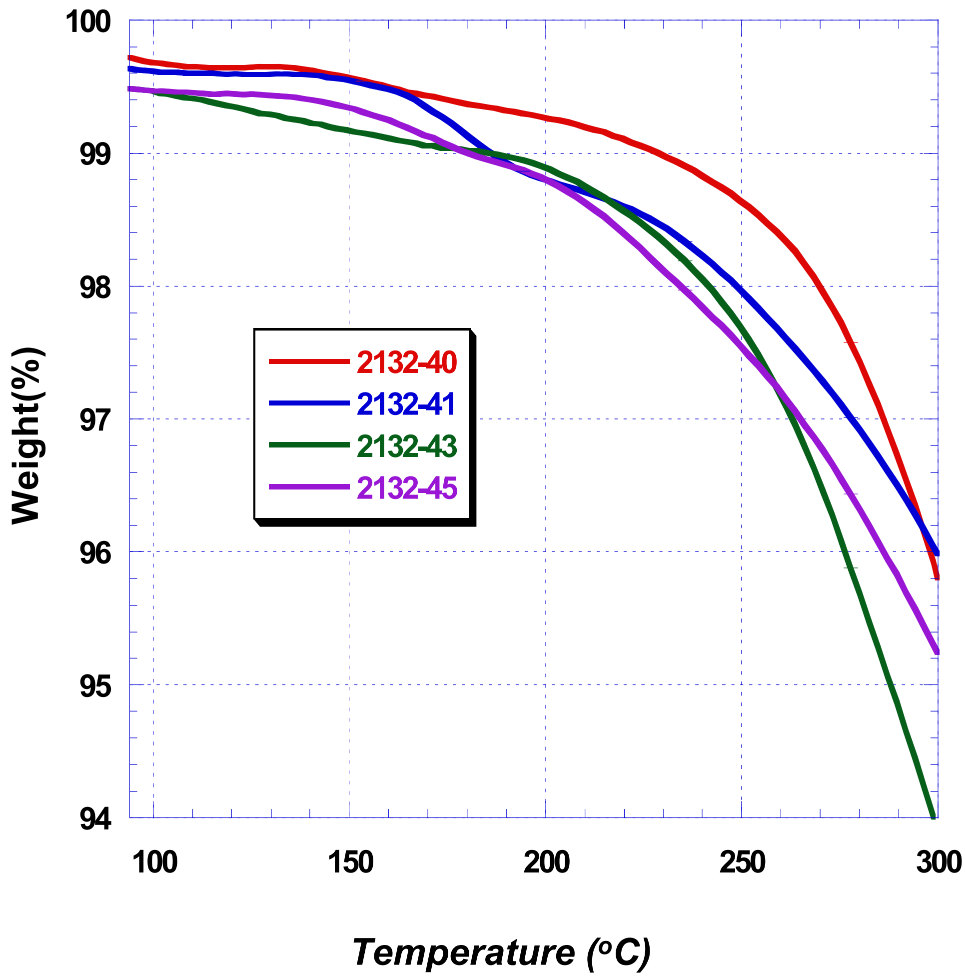
Sample 2132-43

84.1% Binder, 15% sulfonated cyclic organic component, 0.9% alumina fiber

Sample 2132-45

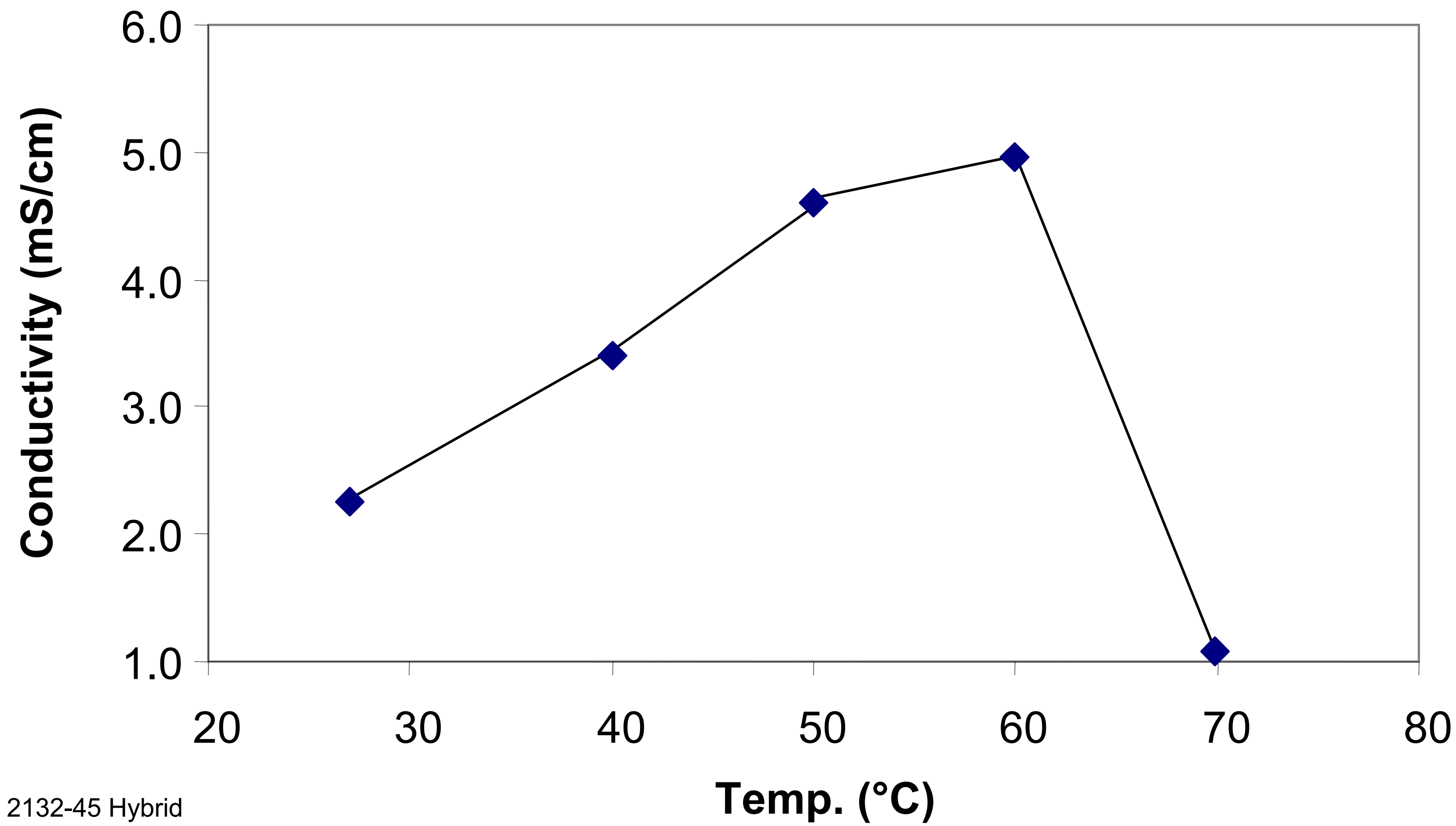
89.2% Binder, 8.8% sulfonated cyclic organic component, 2% alumina fiber

Air Flow: 250 ml/min; heating rate: 5 °C/min



Inorganic-organic hybrids are proton-conducting despite low organic component content

- **Water vapor partial pressure: 25 kPa (dew point of 65°C)**
- **8.8% cyclic organic component, 89.2% binder, 2% alumina fibers**



FY 2005 milestones and progress

- **Measure thermal stabilities and conductivities of dendronized PECH membranes (12/04)**
  - *Completed; measured stabilities and conductivities of G2, G3, and G4-containing materials*

- **Complete 100 h durability test on dendronized PECH membrane (06/05)**
  - *Re-designed cross-linking process for improved high-temperature properties*
  - *Synthesizing materials with PBI as film-forming backbone*

- **Fabricate and test MEAs using high temperature membranes (08/05)**
  - *Will begin once suitable membrane is identified*

Response to FY ’04 Reviewers’ Comments

- **“Only membrane work, not integrated with other MEA components”**
  - *Will include determination of oxygen reduction kinetics and MEA fabrication after obtaining a membrane with properties approaching targets*
- **“Initial samples being characterized for conductivity at temperatures <100°C even though target is >120°C”**
  - *Conductivity cell has been re-designed to allow operation up to 120°C, dimensional stability of membranes at high temperatures is being improved*
- **“It is not apparent that the epichlorohydrin polymers will have sufficient stability for the fuel cell operation”**
  - *Fenton’s test results showed polymer to be stable under oxidizing conditions*

Future work

- **Improve dimensional stability and conductivity of dendronized polymers at high temperatures**
  - *Improve film processing to ensure complete removal of plasticizing/conductivity masking solvent*
  - *Optimize dendrimeric network with better cross-linker for dendronized materials*
  - *Evaluate PBI and other film-forming polymers as backbones*
  - *Incorporate ionic liquids into membrane to improve conductivity and reduce dependence on water*
- **Improve dimensional stability and conductivity of inorganic/organic hybrid films**
  - *Increase content of sulfonated organic component*
  - *Improve homogeneity of dispersed, proton-conducting phase*
- **Fabricate and test MEAs using the most promising materials**

Acknowledgments

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- Nancy Garland, DOE Technology Development Manager

Publications and presentations

- "High-Temperature Polymer Electrolyte Fuel Cell Electrolytes Based on Dendronized Polymers", Seong-Woo Choi, Suhas Niyogi, Romesh Kumar, and Deborah Myers, presentation and extended abstract, 206th Fall Meeting of the Electrochemical Society, Honolulu, Hawaii, Oct. 3-8, 2004
- "High-Temperature Polymer Electrolyte Membranes Based on Dendritic Macromolecules and Organic/Inorganic Hybrids", Seong-Woo Choi, Suhas Niyogi, Deborah J. Myers, and Romesh Kumar, poster and extended abstract, 2004 Fuel Cell Seminar, San Antonio, Texas, Nov. 1-5, 2004
- "High-temperature polymer electrolyte development at ANL", International Energy Agency-Polymer Electrolyte Fuel Cell Annex, Fall, 2004 Workshop, Rome, Italy, Nov. 18-19, 2004

Hydrogen safety

- **Hydrogen is not used during the processing and fabrication of the polymer membranes**

- **“Safe” hydrogen (<4% H_2 in He) is used as a purge gas in the membrane conductivity apparatus to stay below the flammability limit of hydrogen in air**