Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes

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6/11/09

Project ID
FC039

Overview

Timeline

- April 1st 2006
- March 31st 2011
- 80% Complete

Budget

- Total project funding
  - DOE - $1,500K
  - Contractor - $375K
- Funding for FY09
  - $300K ($45K)
- Funding for FY10 to date
  - $300K ($45 K)

Barriers

- C **Performance**
- B **Cost**
- A **Durability**

Partners

- 3M - Industrial
- Project lead - CSM

Objectives/Relevance

• Overall	•Fabricate a hybrid HPA polymer (polyPOM) from HPA functionalized monomers with: – σ >0.1 S cm^{-1} at 120 C and <50% RH (Barrier C)
• 2010	•Optimize hybrid polymers in practical systems for proton conductivity and mechanical properties (Barrier C and A)
• 2011	•Optimize hybrid polymers for proton conductivity, mechanical properties, and oxidative stability/durability (Barrier A, B, and C)

Unique Approach

- Materials Synthesis based on HPA Monomers, Novel "High and Dry" proton conduction pathways mediated by organized HPA moieties – A NEW Ionomer System

- Task 3.1 – Optimization of proton conductivity and mechanical properties, through chemistry tuned for practical applications (eventual down selection) – 50% complete

- Task 3.2 – Optimization of proton conductivity, mechanical properties, and oxidative stability through chemistry tuned for practical applications and peroxide decomposition functionality of HPA – 10% complete

Approach - use Functional Inorganic Super Acids: Heteropoly acids

- +
  - High proton conduction, e.g. 0.2 S cm^{-1} at RT for 12-HPW
  - Thermally stable at the temperatures of interest, <200 C
  - Synthetically Versatile - even simple salts are interesting
- +/-
  - Water soluble – but easily immobilized by functionalization in polymers
  - Reduced form – electrically conductive, but fuel cell membrane environment generally oxidizing, however can be used to advantage on anode
  - Proton conductivity dependency on water content/interaction with polar/protonic components
  - Varied chemistry with peroxides

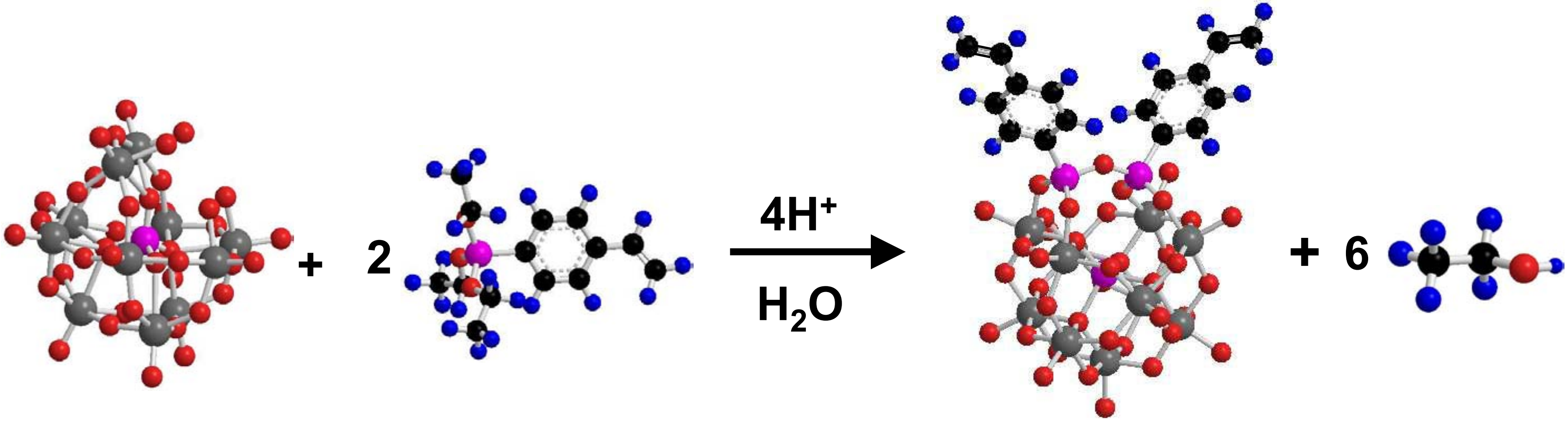
Approach - Generational Development

- Generation I films – Acrylate co-monomers, polymer system in a kit, but, ester linkages, methylene groups
- Generation II films – methylene groups
  - Could be good for cost reasons as HPA imparts strong oxidative stability
- Generation III films - no methylene groups

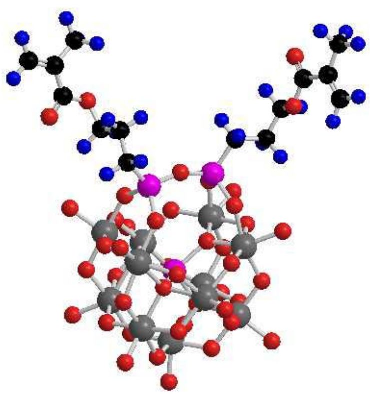
Technical Accomplishments

Month/Year	Milestone or Go/No-Go Decision
Jan 09	Demonstrate conductivity of 100 mS cm^{-1} at 50% RH and 120ºC – **30ºC 60% RH 120 mS cm^{-1}** **120ºC 46% RH >100 mS cm^{-1}** *Current automotive operating conditions* **>90ºC 50%RH >100 mS cm^{-1}** *Target automotive operating conditions*
Jan 10	Deliver membrane to topic 2 awardee Generation I film sent for MEA Development
March 10	Material Optimization 3 new material platforms under development, generation II and III films.

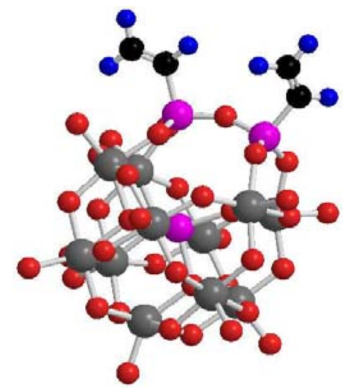
Synthesis of the Hybrid Monomer



HSiW11 **triethoxystyrylsilane** **HSiW11(styryl)2 monomer** **ethanol**



HSiW11(methacryl)2 monomer

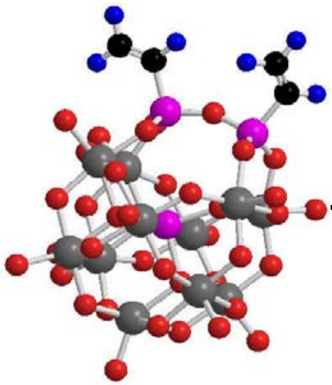


HSiW11(vinyl)2 monomer

Judeinstein, P. *Chem. Mater.* **1992**, *4*, 4-7
Mayer, C. R.; Thouvenot, R.; Lalot, T., *Chemistry of Materials* **2000,** 12, (2), 257-260
Weeks, M. S.; Hill, C. L.; Schinazi, R. F. *J. Med. Chem.* **1992**, *35*, 1216-1221

Generation I Film: PolyPOM-85v - HSiW11(vinyl)2/BA/HDDA Co-polymer

- 85 wt% $H_4SiW_{11}O_{39}(C_2H_3Si)_2O$ Proton Conducting Co-monomer [HSiW11(vinyl)2]
- 12.5 wt% Butyl Acrylate (BA)
- 2.5 wt% 1,6-Hexanediol diacrylate (HDDA)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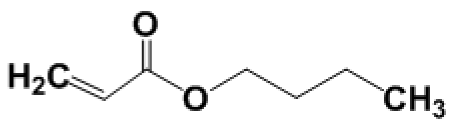
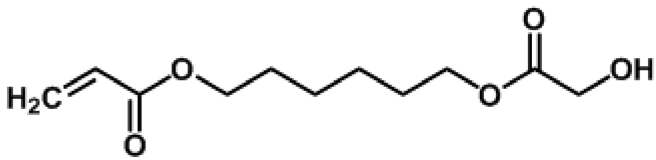


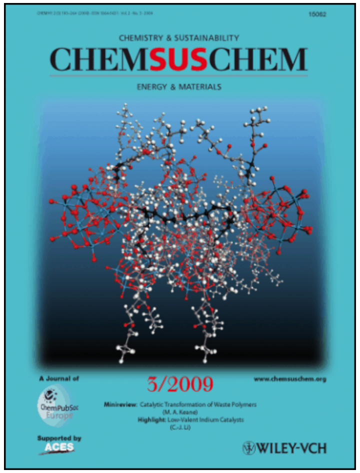
BA

+


HDDA

HSiW11(vinyl)2

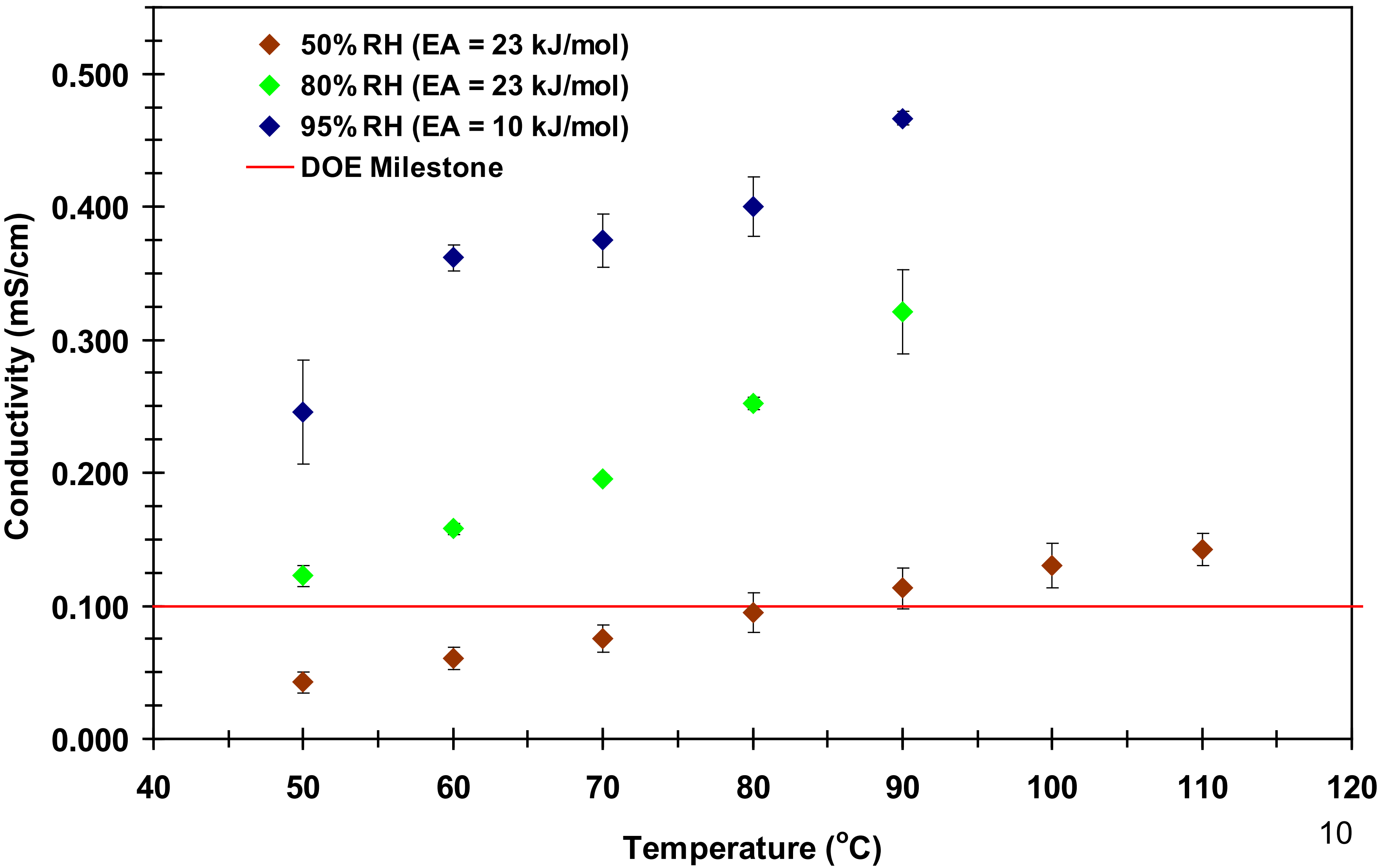
R•
→
μv or heat



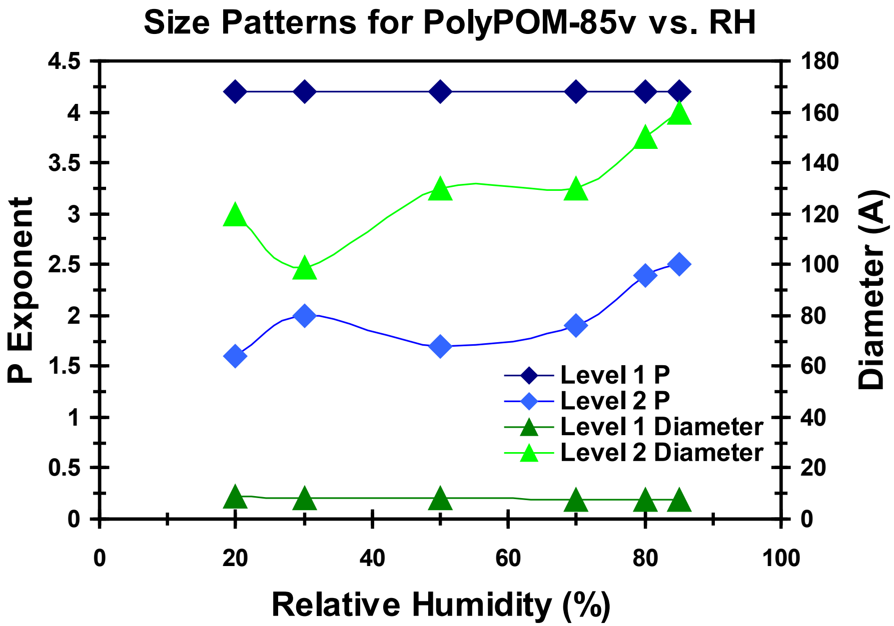
- PolyPOM85v/ BA
- ρ= 2.58 g cm^{-3}
- <100 μm

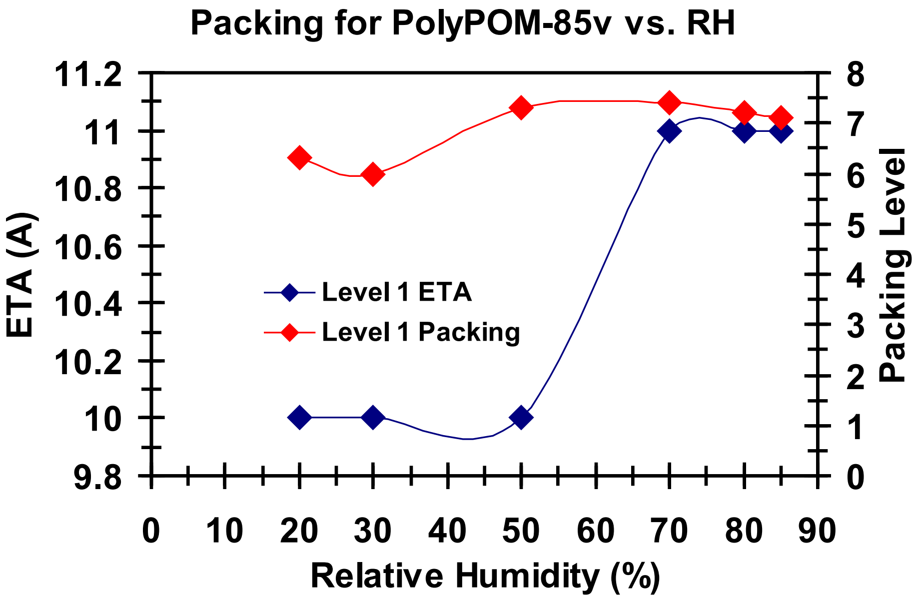
HSiW11(vinyl)2/BA/HDDA co-polymer

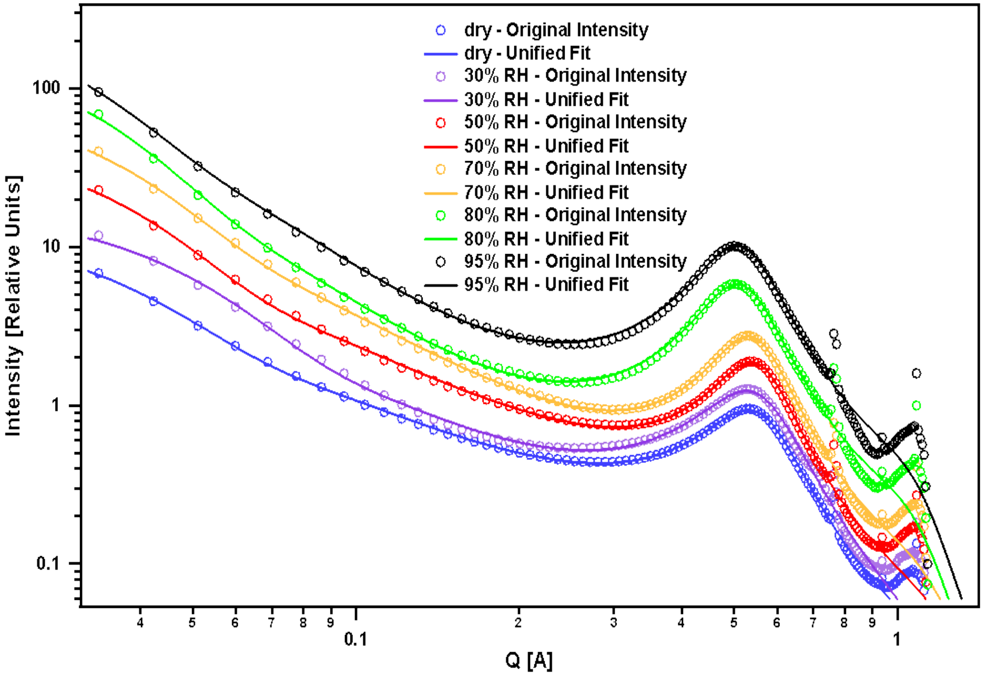
Technical Accomplishment I: Generation I PolyPOM-85v high conductivity



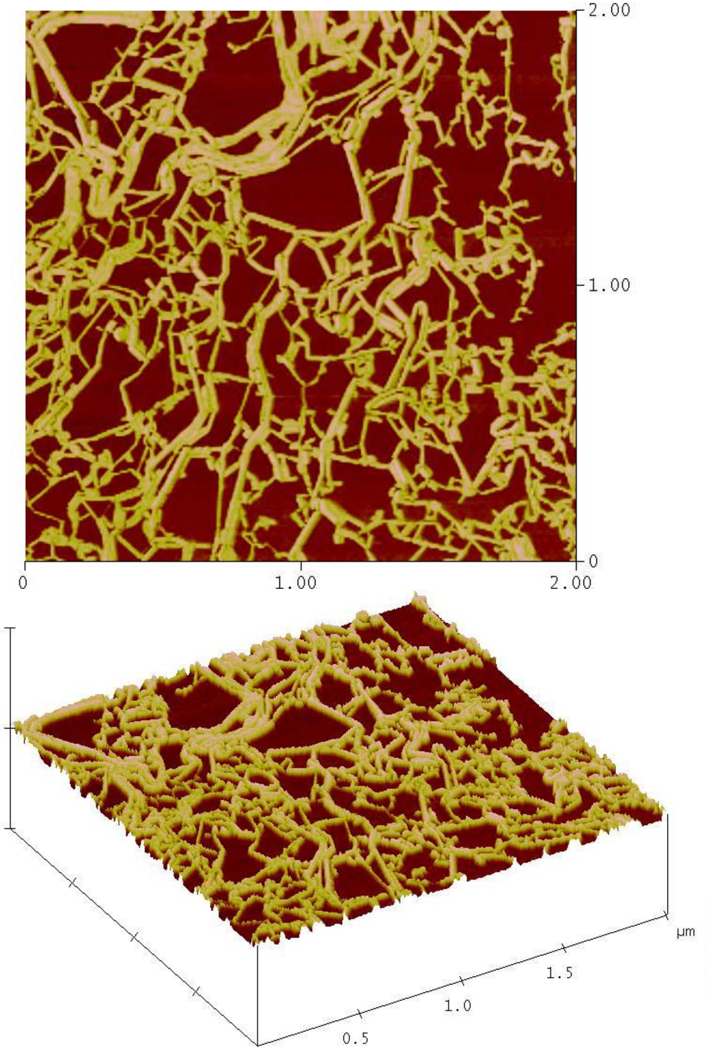
Morphological studies PolyPOM 85v, 80°C







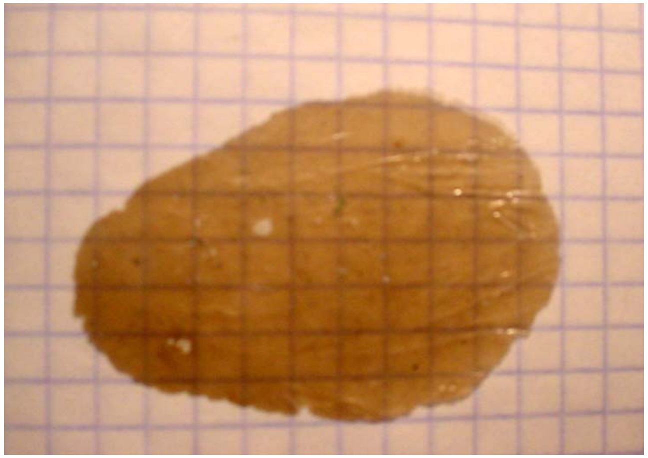
PolyPOM-85v – Morphologically unstable



Phase Image

- Generation I films developed to demonstrate High Conductivity
- Become brittle with time.
- New Film Chemistries developed to solve mechanical problems

Technical Accomplishment II: New Generation II Membrane Chemistry achieved



Membrane IIa Characteristics – simple approach; inexpensive co-monomers if oxidative stability proven

- ~0.1 to 0.2 mm thick
- Clear yellow color or dark opaque brown color
- Flexible, easy to manipulate
- High HPA Loading
- **Soluble in water**
  - Work is ongoing to solve this problem by investigating how to increase cross-linking and molecular weight.

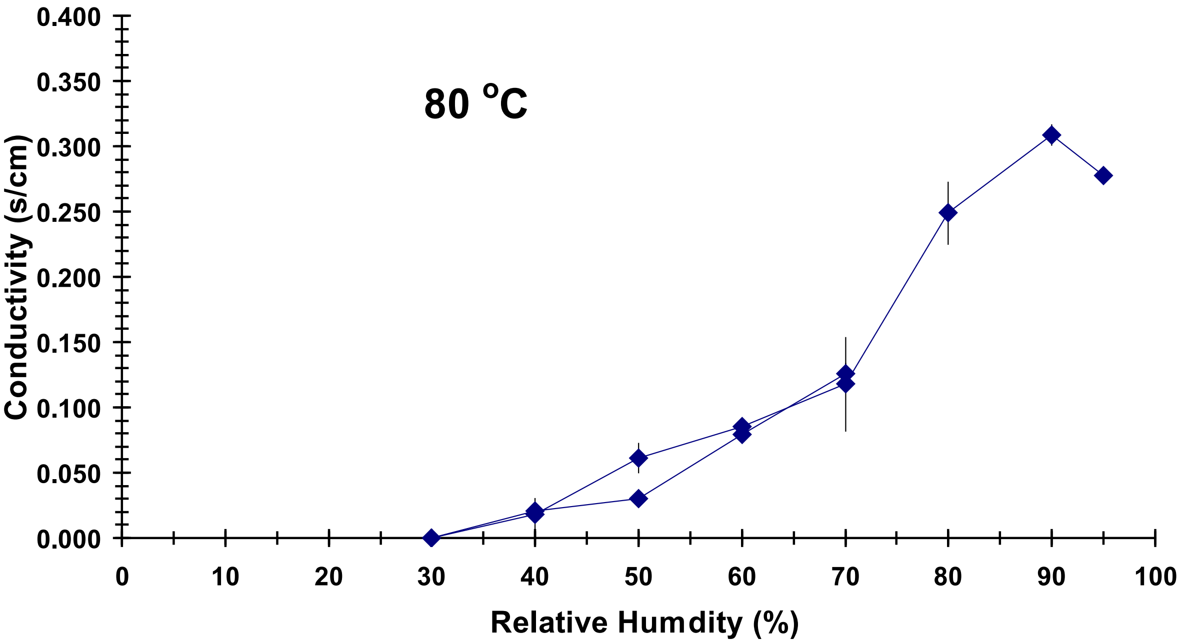
Membrane IIb Characteristics – more sophisticated robust chemistry

Insoluble in water, thin flexible films when supported (expanded PTFE, hydrocarbons) new co-monomers in development

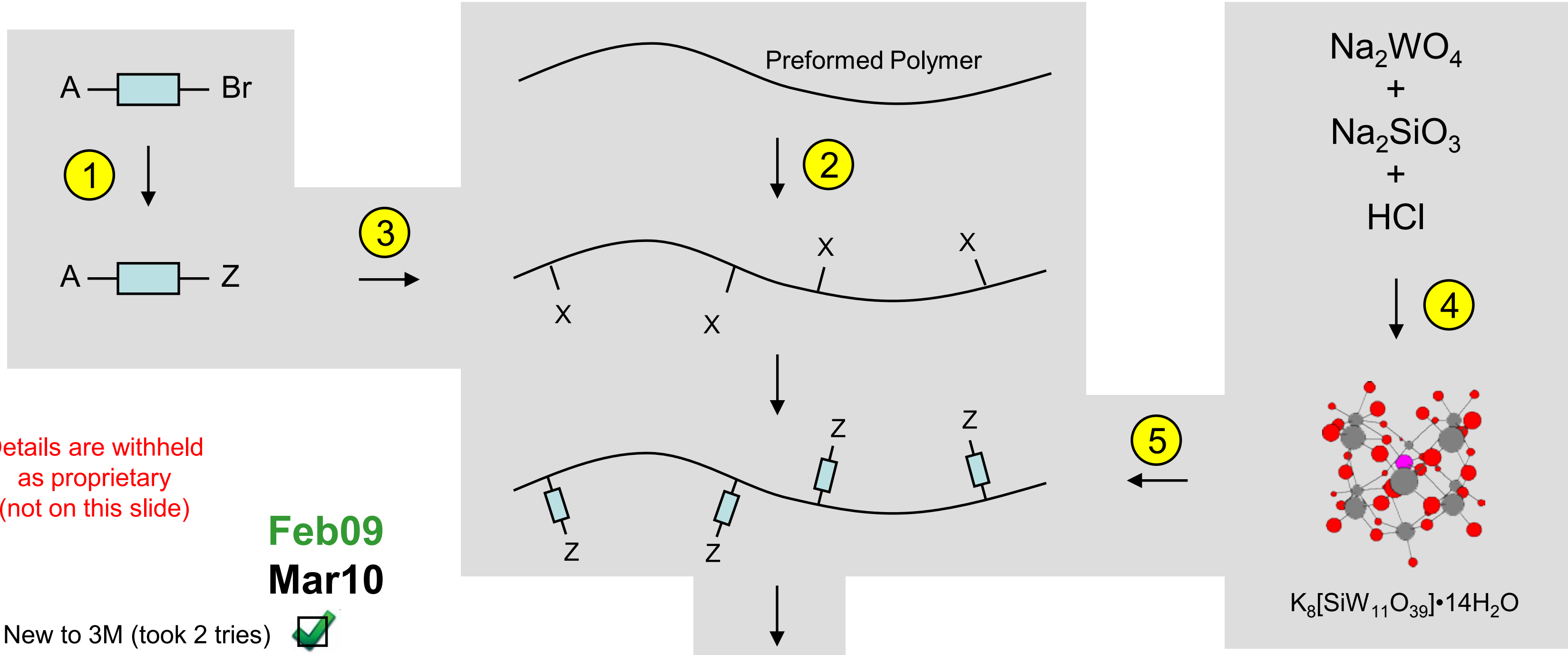
Conductivity Measurements at for first IIa Co-polymers Encouragingly high

Sample #	Conductivity (mS/cm)	Standard Deviation
1	56	0.291
2	50	0.283

95 ^{o}C and 50% RH



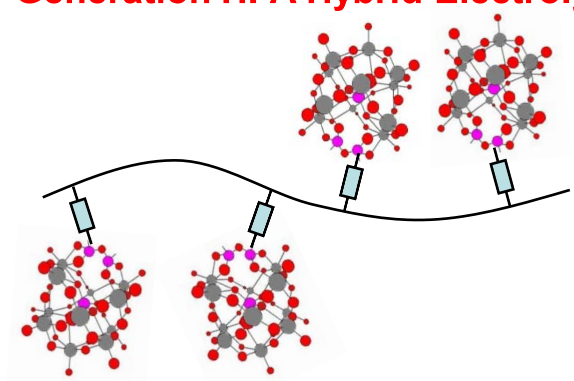
Technical Accomplishment III: Generation III films achieved via attachment to robust polymers



Details are withheld as proprietary (not on this slide)

	Feb09	Mar10
1 New to 3M (took 2 tries)	✓	
2 Core 3M chemistry	✓	
3 Extension of 3M chemistry		✓
4 Core CSM chemistry	✓	
5 Extension of CSM chemistry		✓

2nd Generation HPA Hybrid Electrolyte



Changes w.r.t. Phase I (ended Feb09)

- Different backbone
- New linkage
- Different film-forming process

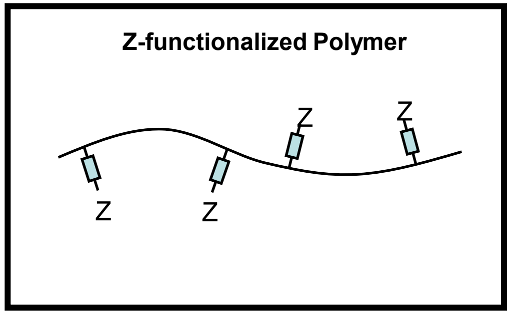
Features

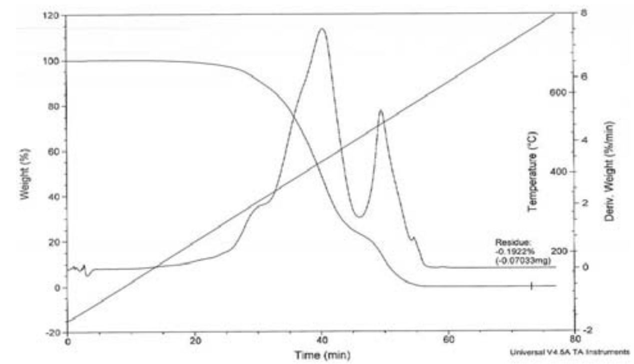
- More durable (chem & mech)
- Expected to be easier to mfr.
- Crosslinkable
- Expecting better reproducibility

3M Immobilization generation III, HPA immobilized

Thermogravimetric Analysis:

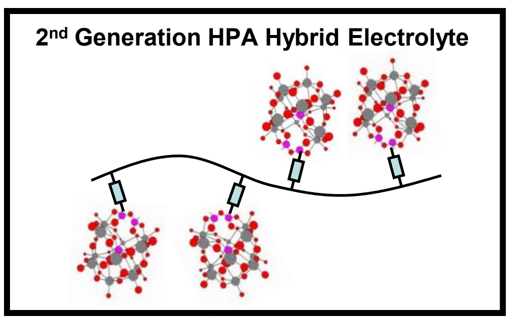
Indicator of heteropolyacid incorporation and immobilization



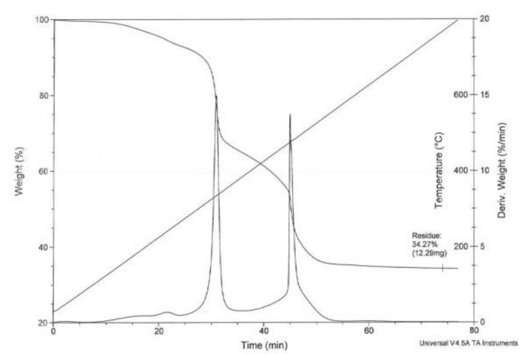


Z-functionalized polymer

0% Inorganic Residue @ 800°C

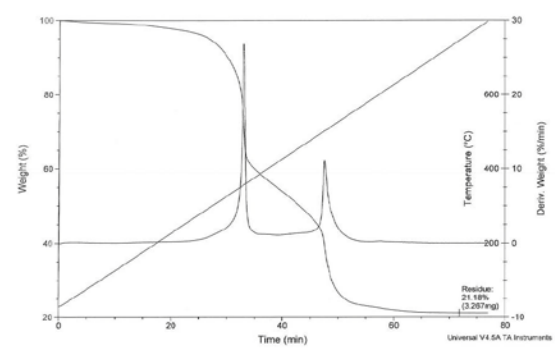


Acid Form



HPA-attached polymer

34% Inorganic Residue @ 800°C



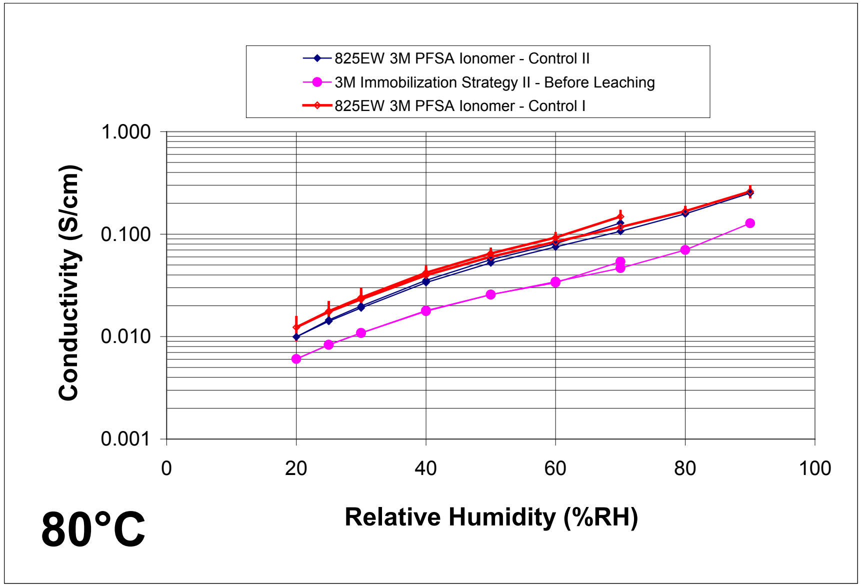
HPA-attached polymer

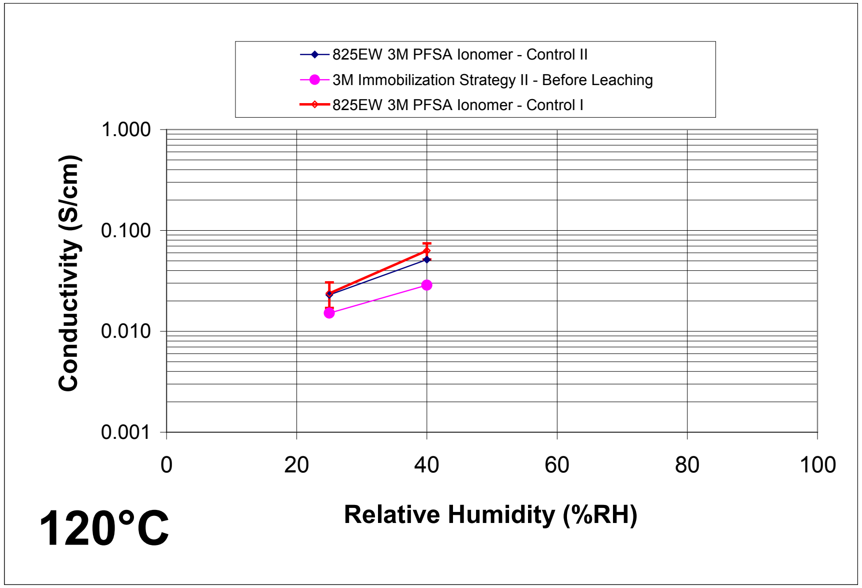
(after leaching – 10hrs boiling water)

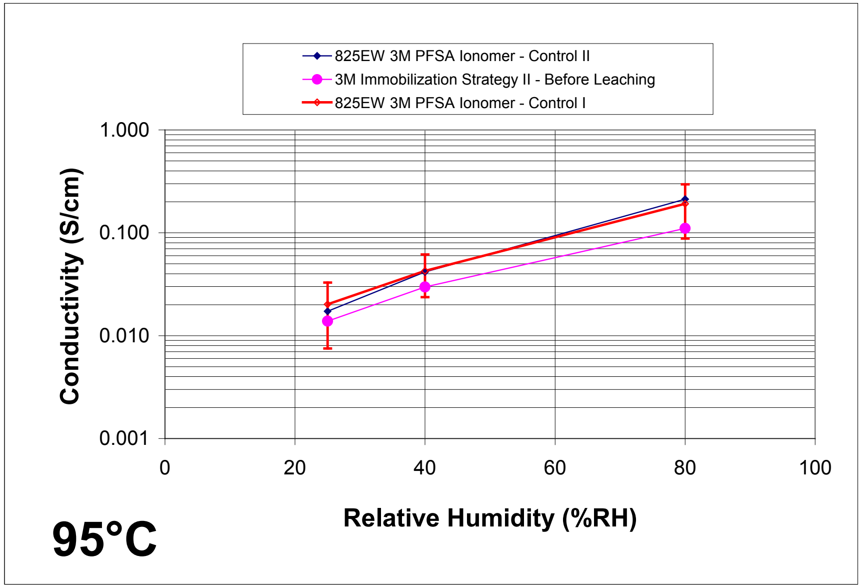
21% Inorganic Residue @ 800°C

All samples vacuum-dried 60-70°C/5hrs before TGA

3M Immobilization Generation III: Un-optimized conductivity high







- First result high conductivities for only 20wt% HPA
- Optimization for high conductivity on-going

Collaborations

- Prime: Colorado School of Mines – University
- Sub: 3M Corporate Material Research Laboratory
- Other Collaborators: the following have agreed to manufacture MEAs from promising films.
  - 3M Fuel Cell Components Group
  - FSEC
  - GM (has offered to test promising materials)

Proposed Future Work

Technical Advancement of 3M Generation III

Processing effects on conductivity
- Annealing conditions
- Solvent selection
- Membrane morphology

HPA incorporation
- Yield of z-functionalization
- Yield of HPA attachment
- Goal is to maximize both

Fuel cell demonstration
- Polarization curve
- Area-specific resistance
- Initial stability assessment vs. 1st generation (vinyl-HPA/co-acrylate)

Technical Advancement of CSM Generation II

Demonstrate Insolubility
- Optimal co-monomer to HPA ratio

Improve Film Properties
- Optimize HPA content – conductivity and oxidative stability
- Optimize Morphology
- Optimize mechanicals

Fuel cell demonstration
- Send samples to FSEC, 3M, GM

3M Manufacturing study

Chemical processing
- Large scale raw materials sourcing
- Equipment needs
- Handling issues

Membrane formation
- Suitability of existing film-forming equipment
- Chemical/materials handling issues
- Failure modes

MEA fabrication
- Status of program materials vs. mechanical requirements
- Compatibility with other materials in construction
- Storage and handling

Summary Slide

- Consistently High Proton Conductivity in Robust films
- 3 New Film Chemistries developed
  - High Oxidative stability
  - Excellent Mechanical properties

	DOE target 2010	FY09	FY10
H^+ conductivity At 20ºC	70 mS/cm	126 mS/cm 60%RH, 31ºC	50 mS/cm 50%RH, 50ºC
H^+ conductivity at 120ºC	100 mS/cm	100 mS/cm 47%RH	>100 mS/cm <50%RH