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

Andrew M. Herring
Colorado School of Mines
Mathew H Frey
3M Corporate Research Materials Laboratory

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Overview

Timeline

• Project Start: April 1<sup>st</sup> 2006
• Project end: September 30<sup>th</sup> 2011 (6 month NCE)
• 100% Complete

Barriers

– C Performance
– B Cost
– A Durability

Budget

• Total project funding
  – DOE - $1,500K
  – Cost Share - $376K
  – FY11 Funding - $100K
  – Planned FY12 Funding - $0

Partners

• 3M - Industrial
• Project lead - CSM
Objectives/Relevance

| Overall | • Demonstrated a hybrid HPA polymer (polyPOM) from HPA functionalized monomers with:  
|         | – \( \sigma > 0.1 \text{ S cm}^{-1} \) at 120°C and <50% RH  
|         | (Barrier C) |
| 2010    | • Optimize hybrid polymers in practical systems for proton conductivity and mechanical properties - achieved  
|         | (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 and attachment to commercially viable polymers, Novel “High and Dry” proton conduction pathways mediated by organized HPA moieties – A NEW Ionomer System

- Generation I films – Acrylate co-monomers, polymer system in a kit,

- Generation II films – TFVE co-monomers

- Generation III films – Attachment to 3M Dyneon™ Fluoroelastomers
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
- Known to decompose peroxides
Previous Accomplishments

Generation I Films – PolyPOM85v/BA

Films Generally thick but ASR <0.02 Ω cm²
Progress - Generation II Films

TFVE-HPA copolymers

- Trifluorovinyl ethers (TFVE) functionalized HPA monomers synthesized on <100g scale
- Trifluorovinyl ethers polymerize thermally
- Large number of co-monomers available
Proton Conductivity - Variable

Conductivity vs. Temperature for MCK-VII-83A at 50% RH

- 3M Control 825
- MCK-VII-83A, Sample 2
- MCK-VII-35A - EA=No Data
- MCK-VII-89A1 (Ea=20.79 kJ/mol)
- MCK-VII-90A (Ea=15.96 kJ/mol)
- MCK-VII-97A - EA=15.9 kJ/mol
- MCK-VII-83A, Sample 1
- MCK-VII-26A - EA=6.7 kJ/mol
- MCK-VII-35B - EA=No Data
- MCK-VII-89A-2 (Ea=18.41 kJ/mol)
- MCK-VII-96A - EA=14.9 kJ/mol
- MCK-VII-100A

- Appears to synergistically vary based on film forming, chemistry, and morphology – complex design space
Conductivity Dependence on Morphology at 80 °C, RH 80%

For hybrid TFVE membranes

Wt% based on HSiW$_{11}$O$_{39}$(TFVE-Si)$_2$O monomer present

• 1st Approximation co-monomer chemistry important
95% RH Script Conductivity
Results

Conductivity (S/cm) vs. Temperature (°C)

Lines and symbols represent different materials:
- 3M 825 EW
- "MCK-VII-91A - 74% Hyb, 12% PVDF, 14% C8"
- "MCK-VII-113A - 80% Hyb, 6% PVDF, 14% C10"
- "MCK-VII-70A60% Hyb, 15% PVDF, 25% C8"
State of the art film same ASR as 3M 825EW but 7 x as thick
Crystalline Phases observed at low RH

SAXS, 25%, 50%, 75% and 95% RH and 80 °C

- Bragg peaks observed at low RH in SAXS,
- Phase changes observed at low RH in DVS
- Amorphous phase is the highly conducting phase
- Water content decreases on RH cycling
  (implies hard to measure equilibrium properties and increasing brittleness on cycling)
$^1$H NMR spectrum for 4-[(Trifluorovinyl)oxy]bromobenzene

Compound II
$^1$H NMR spectrum for pure 4-[(Trifluorovinyl)oxy]phenyltriethoxysilane

TFVE-Si(OEt)$_3$
Digital vapor sorption – total over 2 relative humidity cycles, based on initial mass ($M_o$)

- HPA containing membranes have considerably less water uptake than PFSAs
Progress, Generation III Polymer – Synthesis

\[
\text{OH} \quad \xrightarrow{\text{dehydrofluorination}} \quad \text{ONa}
\]

\[
\begin{align*}
\text{Concentration:} & \quad \text{mole\% of Br: 5-20\% of monomer units} \\
\text{Yield:} & \quad 47\%
\end{align*}
\]

\[
\begin{align*}
\text{Hydrolysis:} & \quad \text{Yield: 90\%}
\end{align*}
\]

\[
\text{HPA attachment} \quad \xrightarrow{\text{Yield: 50\%}}
\]

\[
\text{Yield: 20-40wt\%}
\]

\[
K_8[\text{SiW}_{11}\text{O}_{39}]\cdot13\text{H}_2\text{O}
\]
Membrane Processing

HPA attached, acidified hybrid fluoropolymer (crumb) was dissolved in DMSO at 4% concentration. Solution was then cast on ClearSIL® T10 silicone coated liner (or Kapton® polyimide (PI) liner in some cases). The resulting membrane below was first heated at 120ºC for 10min; Temp was then increased to 180ºC, membrane was heated at 180ºC for 10min.

HPA attached hybrid fluoropolymer membrane cast on T10.

• Film processing critical to high performance
Morphology

AFM imaging --- Phase Image (recorded at CSM)
Proton Conductivity, 80°C

Conductivity vs Relative Humidity for 3M Generation III polymer (HPA-PVDF-HFP)

- **3M Ionomer Control - 825EW PFSA**
- **HP8/30min dissolution - 180°C/5min anneal - PI liner (4248-34B)**
- **HP9+/2hr dissolution - 180°C/8min anneal - PI liner (4248-32A)**
- **HP9+/2hr dissolution - 180°C/8min anneal - T10 liner (4248-32B)**
- **HP9+/2hr dissolution - 170°C/5min anneal - PI liner (4248-33A)**
- **HP9+/2hr dissolution - 170°C/5min anneal - T10 liner (4248-33B)**

**80°C Measured by Michael Emery, 3M TestEquity oven, atmospheric pressure Bekktech sample fixture**

- HP: Hot plate setting
- PI: Kapton® polyimide
- T10: ClearSIL®T10 silicone coated

*** Incompletely dissolved in DMSO (casting solvent); tested in November 2010; 37% HPA

- Film forming critical to high performance
Tensile Testing

- Functionalized Polymer gives stronger film could be tailored by Dyneon chemistry
Manufacturing Feasibility Assessment

Selected high-level comments:
• “This is a complex fine chemical synthesis.”… “Fine chemical processing is a lot like this.”
• “Chemically, there are no showstoppers.”…“No chemistry here that scares me.”
• “I wouldn’t be too discouraged.”
• “There are no exotic conditions…normal glassware.”

Selected detailed comments:
• “Process optimization is needed to improve volume utilization.”
• “% solids of each of these process steps will have a big impact on your reactor volume efficiency.”
• “A lot of dissolving and drying” … “Can you avoid drying to a solid every time?”…“Can you do any steps neat?”
• “Can you do solvent exchanges?”…”keep it soluble?”
• “Can you use a different PVDF-HFP?…some may be easier than others…different molecular weight?”
• “To use less solvent, could you carry some impurities along, and then clean up just once, at the end?”

If one were to pursue this material commercially at 3M, next steps:
• Initiate “New Materials Introduction” program within MRD.
• Review for entry into MRD lab.
• Carry out focused work against detailed comments above.

Overall Conclusions:
• The HPA-modified PVDF-HFP preparation appears likely to be feasible in manufacturing.
• Any additional development work on this type of material should include objectives related to solvent usage and process simplicity, as suggested above.
Collaborations

• Prime: Colorado School of Mines – STEM University
• Sub: 3M Corporate Material Research Laboratory
• Other Collaborators: the following have agreed to test membranes ex-situ or as MEAs from promising films.
  – 3M Fuel Cell Components Group
  – ProtonOnsite
  – GM (has offered to test promising materials)
  – Nissan Technical Center, North America (has offered to test promising materials)
Proposed Future Work (unfunded)

- New series of films with pure TFVE monomer, structured diblocks
- Improve Dyneon attachment chemistry with polymer designed for HPA attachment
- Incorporate work on Zr phosphonate hybrid films.
Summary

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

<table>
<thead>
<tr>
<th>Condition</th>
<th>DOE target 2017/ Ω cm²</th>
<th>CSM TFVE-HPA 2011/ Ω cm²</th>
<th>Thickness /µm</th>
<th>CSM TFVE-HPA if 10 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>120/40% RH</td>
<td>0.02</td>
<td>0.43</td>
<td>180</td>
<td>0.02</td>
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<tr>
<td>80/85% RH</td>
<td>0.02</td>
<td>0.13</td>
<td>130</td>
<td>0.01</td>
</tr>
<tr>
<td>30/90%RH</td>
<td>0.03</td>
<td>0.026</td>
<td>150</td>
<td>0.002</td>
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The data presented is for the best performing film at each condition. Further work is required to fully optimize one material for all conditions.