

Development of Advanced High Temperature Fuel Cell Membranes

Andrew Chafin
Jennifer Irvin
Naval Air Warfare Center Weapons Division
China Lake, CA
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Objectives

- Develop a polymer electrolyte membrane (PEM) with stability at operating temperatures up to 150°C
 - Synthesize aromatic polymers bearing flexible perfluorinated side chains with sulfonic acid end groups
 - Confirm polymer stability by thermal analysis
 - Provide polymers to Case Western Reserve University (CWRU) for evaluation





Budget

• Total funding: \$85K

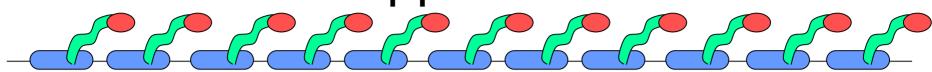


Technical Barriers and Targets

- DOE Technical Barriers for Fuel Cell Components
 - O. Stack Material and Manufacturing Cost
 - P. Durability
 - Q. Electrode Performance
 - R. Thermal and Water Management
- DOE Technical Target for Fuel Cell Stack System for 2010
 - Cost \$35/kW
 - Durability >5000 hours



Approach



- Synthesis of new monomers
 - Aromatic repeat for rigid, stable backbone
 - Flexible perfluorinated spacer for aggregation and chemical stability;
 initial modeling shows 4-6 repeats ideal
 - Perfluoroalkyl sulfonic acid end groups for conductivity
- Polymer synthesis
 - Polyethers, polyetherketones, polyethersulfones, polycarbonates, polysulfides, polybenzimidazoles, and/or polybenzoxazoles for chemical and thermal stability
- Membrane characterization
 - Membranes will be supplied to Prof. Tom Zawodzinski at CWRU for characterization

First Approach

- Nucleophilic Polymerization.
 - Would give a high concentration of sulfonic acid groups.

$$\begin{array}{c|c} & & & & \\ & & & \\ \text{SH} & & & \\ \text{SR}_{\text{f}} & & & \\ & & & \\ \text{SR}_{\text{f}} & & \\ \end{array} \begin{array}{c} & & & \\ & &$$

$$O_2N$$
 O_2
 O_2N
 O_2
 O_3
 O_4
 O_5
 O_5
 O_7
 $O_$





Next Approach

- Now concentrating on monomers for a Friedel-Crafts polymerization.
 - Gives a thermally stable polymer.
 - It is possible to modify either component.

$$COCF_3$$
 CF_3SO_3H CF_3

M. Zolotukhin, et al., Chem. Comm. 1030 (2004)





Technical Accomplishments/Progress

Monomer synthesized.

$$F_2$$
 F_2 F_2 F_2 F_2 F_2 F_2 F_2 F_2 F_3 F_4 F_5 F_5 F_6 F_7 F_8 F_9 F_9

 Polymerization with trifluoroacetophenone gives a water soluble polymer.

$$IR_{f}SO_{2}F \longrightarrow IR_{f}SO_{3}Na \xrightarrow{Ph} \underbrace{PhCOCF_{3}}_{NaO_{3}SR_{f}S} \underbrace{PhCOCF_{3}}_{SR_{f}SO_{3}Na} \underbrace{NaO_{3}SR_{f}S}_{NaO_{3}SR_{f}S} \underbrace{PhCOCF_{3}}_{SR_{f}SO_{3}Na}$$

Progress

 Next monomer and a precursor to a third monomer synthesized.

 $R_f = CF_2CF_2OCF_2CF_2$



Technical Accomplishments/Progress

 Successfully differentiated the ends of a dibromoperfluoroalkane.

 We will attempt to use it to synthesize a perfluorinated ketone.

$$\mathsf{Br} \overset{\mathsf{F_2}}{\overset{\mathsf{F_2}}{\overset{\mathsf{C}}{\overset{\mathsf{C}}{\overset{\mathsf{C}}{\overset{\mathsf{SiMe}_3}{\overset{\mathsf{COF}}{\overset{\mathsf{C}}{\overset{\mathsf{C}}{\overset{\mathsf{C}}{\overset{\mathsf{C}}}{\overset{\mathsf{C}}{\overset{\mathsf{C}}}{\overset{\mathsf{C}}{\overset{\mathsf{C}}}{\overset{\mathsf{C}}}{\overset{\mathsf{C}}{\overset{\mathsf{C}}}{\overset{\mathsf{C}}}{\overset{\mathsf{C}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}}{\overset{\mathsf{C}}}}{\overset{\mathsf{C}}}}}{\overset{\mathsf{C}}}}}{\overset{\mathsf{C}}}}{\overset{C}}}{\overset{C}}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}{\overset$$



Future Plans

- Optimize polymerization.
- Incorporate other sulfonic acids.



Synthetic Schemes

$$\begin{array}{c|c} \text{SH} & \text{SC} & \text{F}_2 & \text{F}_2 \\ \hline \\ \text{F}_2 & \text{F}_2 \\ \hline \end{array}$$



Interactions and Collaborations

- Membranes will be supplied to Prof. Tom Zawodzinski at CWRU for detailed characterization
- Researchers at China Lake will collaborate with the other program investigators whenever possible to maximize possibility for success



Future Work

- Monomer synthesis
- Polymer synthesis
- Membrane preparation
- Deliver membranes to CWRU for characterization





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Andrew Chafin
NAVAIR-1900 N. Knox Road, Stop 6306
Code 498220D, China Lake, CA 93555-6106
(760)939-1606 phone (760)939-1617 fax
andrew.chafin@navy.mil



Dr. Jennifer A. Irvin
NAVAIR-1900 N. Knox Road, Stop 6306
Code 498220D, China Lake, CA 93555-6106
(760)939-6655 phone (760)939-1617 fax
Jennifer.Irvin@navy.mil