

# Dimensionally Stable High Performance Membranes

**Giner, Inc.**

Cortney Mittelsteadt (P.I.)

Jason Willey

Zachary Green

**Rensselaer Polytechnic Institute**

Chulsung Bae

June 7, 2016

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# Overview

## Timeline

- Project Start Date 2/21/2016
- Project End Date 11/21/2016

## Budget

- Total Project Funding to Date: \$1.3k (2/29/2016)
- Total Project Value: \$150k
- Cost Share %: N/A

## Barriers addressed

- A. Durability
- B. Cost
- C. Performance

### Technical Targets (DOE 2017 Targets)

- $0.02 \Omega \cdot \text{cm}^2$  at 1.5 kPa H<sub>2</sub>O Air inlet
- $< \$20/\text{m}^2$
- $> 5000$  h lifetime,  $> 20,000$  RH Cycles

## Partners

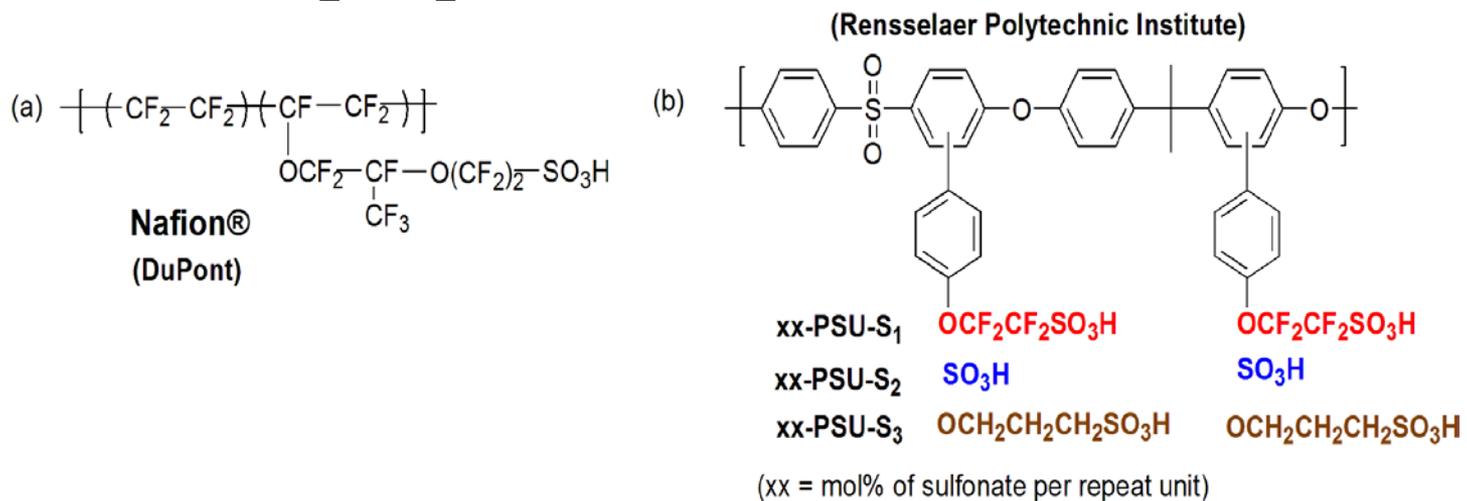
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# Relevance: Why New PEM?

- State of the Art
  - PSFA membranes like Nafion exhibit:
    - Poor mechanical properties at high temperature
    - Poor performance at low RH
  - Increasing conductivity of PFSA membranes by increasing charge density:
    - Makes the membranes much weaker
    - Only increases performance incrementally
- Hydrocarbon-based membranes can be tailored to low RH, high temperature operation

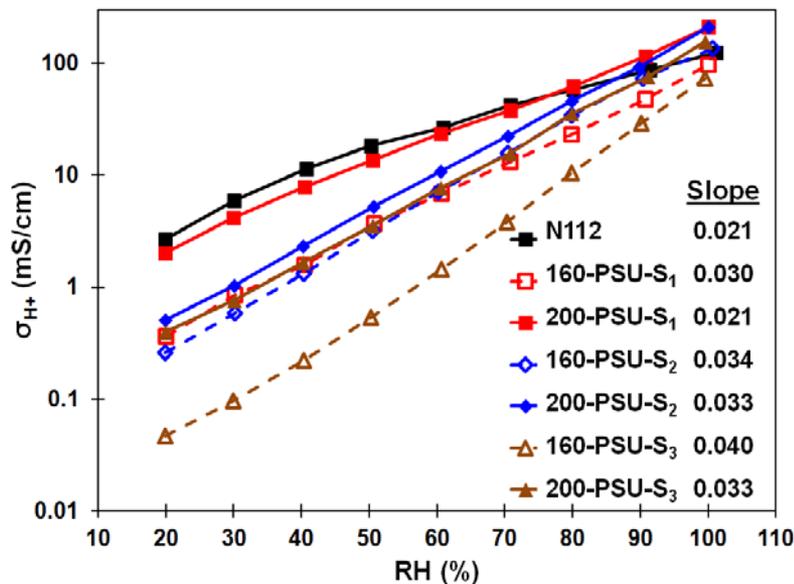
# Design of HC Membrane

- The new advanced ionomer will have:
  - Large segregated domains
  - High localized charge density
- Chulsung Bae has already developed membranes with these properties



# PSU-S<sub>x</sub> Series

- The sulfonated polysulfones developed by Prof. Bae were tested for conductivity at 100°C and varying RH

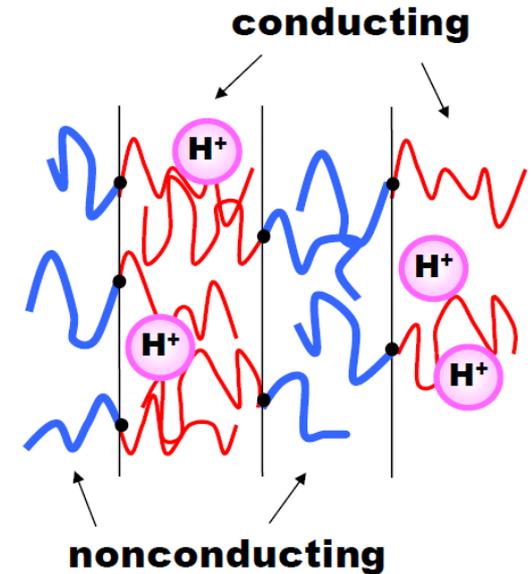


The 200-PSU-S<sub>1</sub> ionomer (IEC=1.94 meq/g) compared favorably with Nafion under decreasing RH conditions.

# Block / Graft polymer

## ADVANTAGES

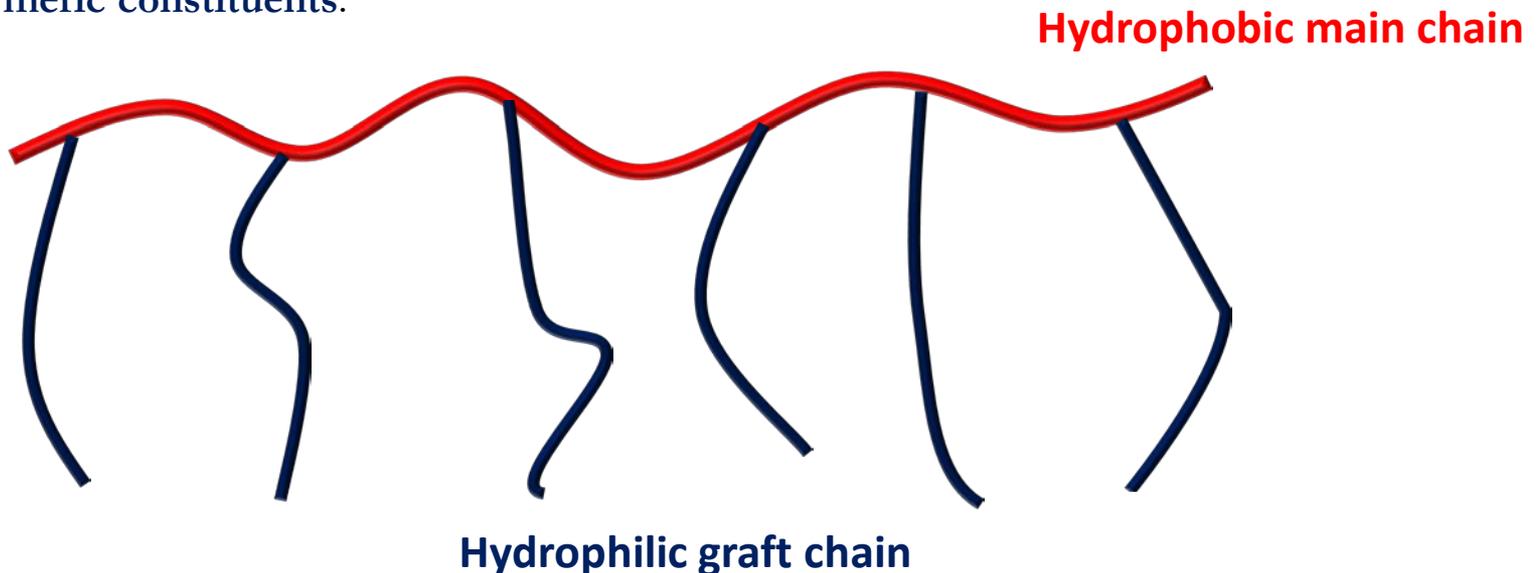
- Formation of ion conducting channels by microphase separation
- Hindering of swelling by surrounding non-sulfonated phase
- Lowering of MeOH permeability
- High mechanical stability



High ionic conductivity & good mechanical property

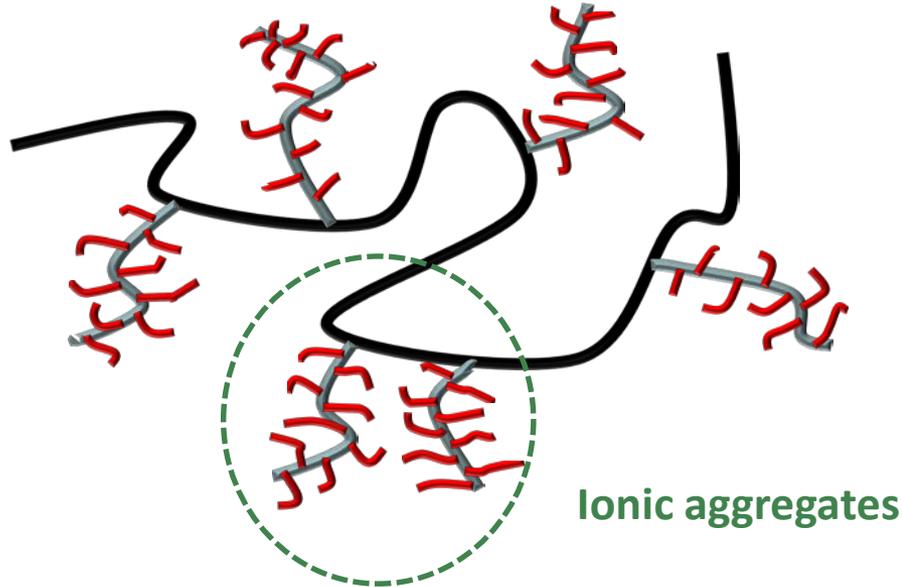
# Graft copolymer

- **Graft copolymers** are segmented copolymers with a linear backbone of one composite and have structurally different branches of another composite.
- Graft co-polymerization is an attractive method to impart a variety of functional groups to a polymer.
- Graft copolymers **allow the combination of properties of two highly incompatible polymeric constituents.**



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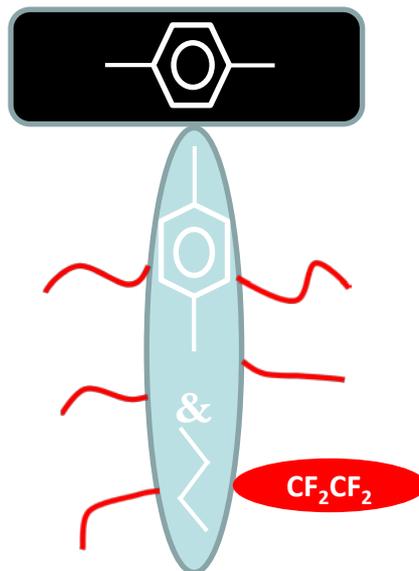
# Graft Copolymer PEM for Hydrogen Fuel Cells



- High molecular weight hydrophobic polymer backbone
- Oligomeric graft chain
- Superacidic fluoroalkyl sulfonate

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# General Structure of Target PEMs

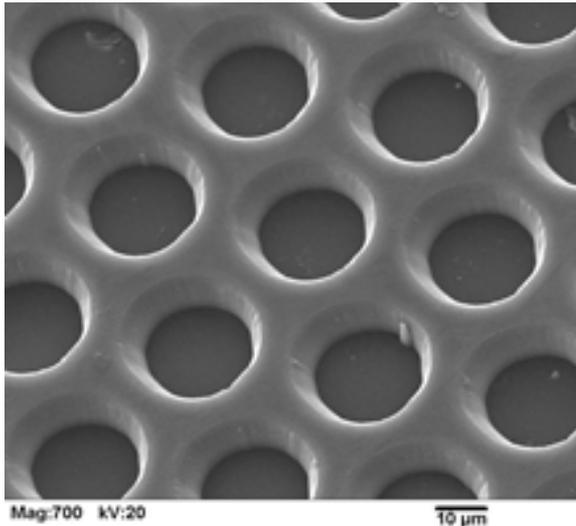


- **Fluorine-containing hydrophobic main chain:** good mechanical & chemical stabilities
  - Only C-C bond in the main chain
- **Rigid & flexible oligomeric graft chains:** high ion density
- **Superacidic fluoroalkyl sulfonate group for  $H^+$  conductivity**

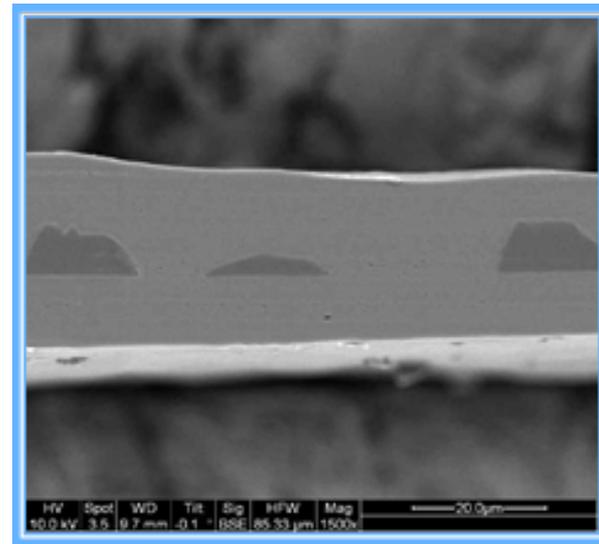
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# Mechanical Stability

- Giner will incorporate some of the membranes provided by Prof Bae into its DSM supporting structure to provide mechanical strength



DSM mechanical structure



Cross-section of a membrane  
with the incorporated structure

# Objective

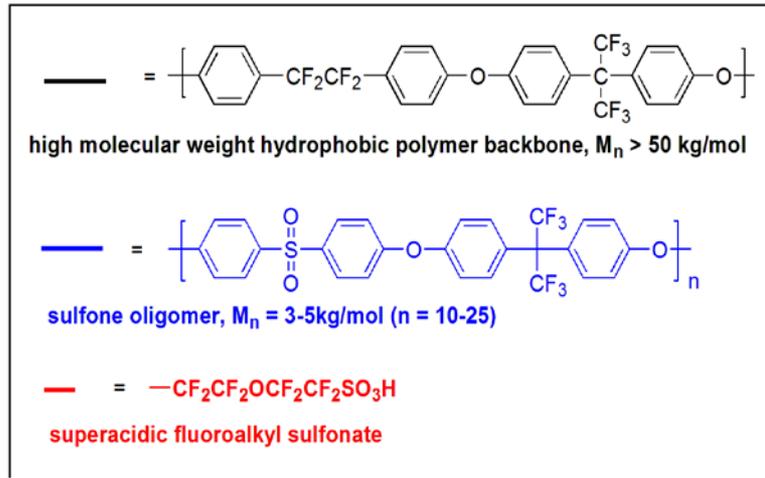
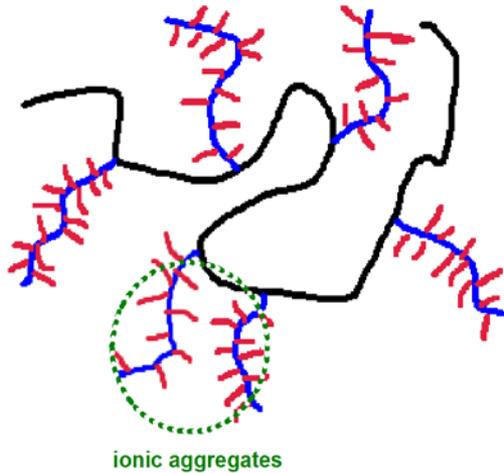
- The overall technical objective of this program is to develop a fuel cell PEM displaying
  - High conductivity
  - Good mechanical qualities
  - High chemical durability
- For use in low-RH, high temperature applications

# Tasks

- Prepare hydrocarbon membranes (RPI)
- Fabricate DSM using hydrocarbon membranes (Giner)
- Characterize the hydrocarbon membranes (Giner)
- Downselect membranes for Phase II

# Approach: Task 1 – Prepare Hydrocarbon Membranes

- 20 graft and random copolymers will be prepared by RPI



Graphical illustration of proposed sulfonated graft polymers and representative structures of each unit

# Approach: Task 2

## Hydrocarbon DSM

- Each of the 20 films produced by RPI will be incorporated into the DSM substrate
  - Comparison of properties will be done for the HC DSMs against the neat ionomer
- Close consultation with RPI will be done to ensure proper hot-pressing parameters
- Giner's SEM will be used to validate membrane adherence after pressing

# Approach – Task 3 Membrane Characterization



- Conductivity
  - Giner will test membrane conductivity at varying temperatures and RH levels (to 95%)
  - Five membranes can be tested at a time up to 140°C
- Gas Permeability
  - H<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> permeability will be measured
  - Temperature up to 130°C
  - RH from 0 to 95%
- Water uptake
  - Using Giner's novel Sievert-type water uptake apparatus
  - RH levels from 0 to 100%
  - Temperatures from 25 to 95°C
- Physical Properties
  - Giner's DMAs will be used to measure stress-strain curves at various temperatures and RH levels

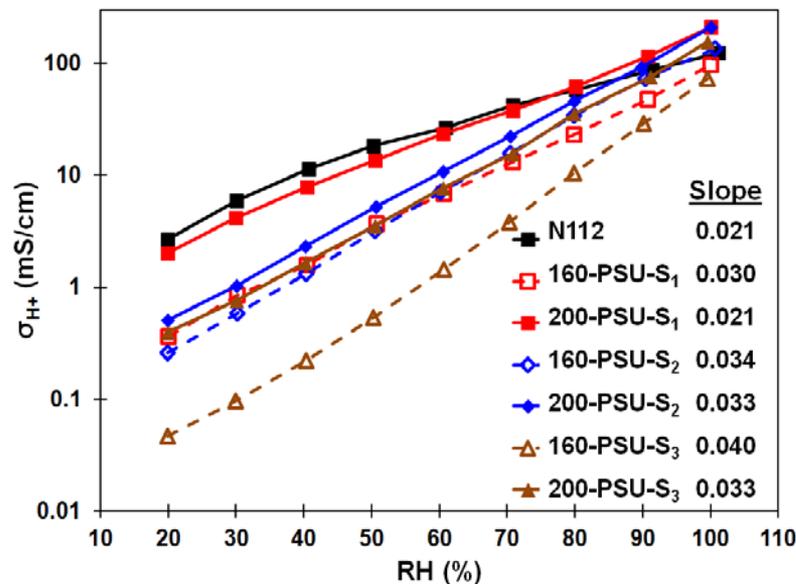
# Approach: Task 4

## Down select Membranes

- The membranes showing the best combination of properties will be selected for use in the Phase II
- The Phase II will consist of
  - Membrane optimization
  - MEA fabrication
  - Short- and long-term MEA operation in a high-temperature, low-RH fuel cell system

# Achievements: (\$1333 Spent to Date)

- Task 1: Baseline Hydrocarbons Prepared
- Task 3: Baseline Membrane Measured



# Future Work: Scheduling

| Task   | Month |   |   |   |   |   |   |   |   |
|--|-------|---|---|---|---|---|---|---|---|
|  | 1     | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 1. Prepare hydrocarbon membranes (RPI)               |       |   |   |   |   |   |   |   |   |
| 2. Fabricate DSM using hydrocarbon membranes (Giner) |       |   |   |   |   |   |   |   |   |
| 3. Characterize the hydrocarbon membranes (Giner)    |       |   |   |   |   |   |   |   |   |
| 4. Downselect membranes for Phase II                 |       |   |   |   |   |   |   |   |   |
| Report   |       |   |   |   | X |   |   |   | X |

| Milestones                    | Month |
|-------------------------------|-------|
| Mid-program Report            | 5     |
| Downselected membrane choices | 9     |
| Final Report                  | 9     |

# Collaborations

- Rensselaer Polytechnic Institute