Center for Intelligent Fuel Cell Materials Design:

Microstructural Design and Development of High Performance Polymer Electrolyte Membranes

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Project ID # FCP-12

Overview

Timeline

- Project start: 6/1/06
- Project end: 5/28/08
- Percent complete: 95%

Barriers

- O - Stack Material Cost
- P - Durability
- R - Thermal / Water mgmt.

Budget

- Total project funding
  - DOE $ 1,485,000
  - Contractor $ 624,144
- Funding received in FY07
  - $ 798,310
- Funding for FY08
  - $ 107,360

Partners

- Chemsultants International
- Michigan Molecular Institute
- Case Western Reserve University

Objectives

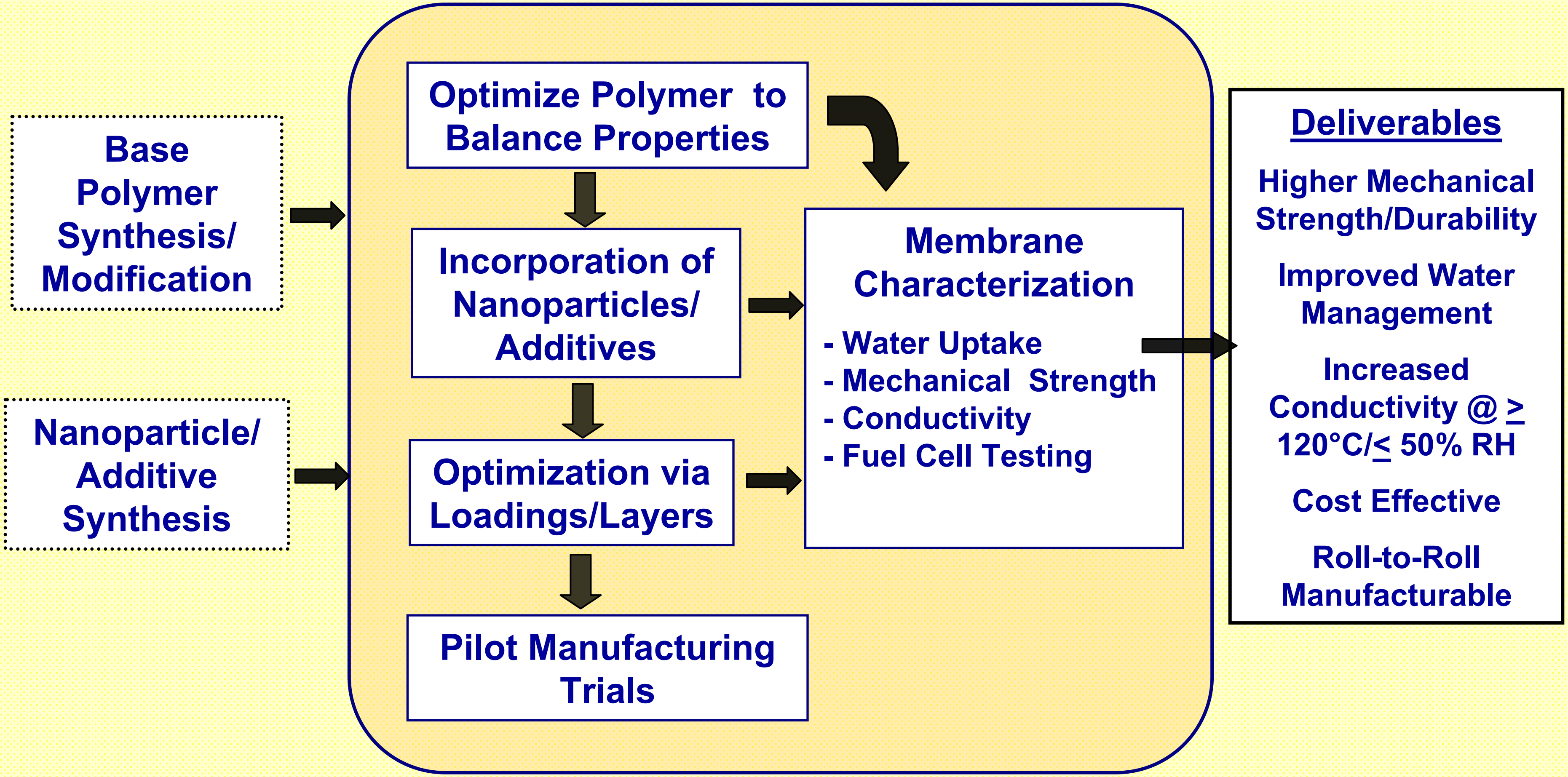
- **Develop novel polymer / nanoparticle multiple-layer membrane with**
  - **improved mechanical stability**
  - **improved conductivity**
  - **$\geq$ 120°C / $\leq$ 50% RH operational capability**

- **Identify a solution casting methodology suitable for roll-to-roll, multiple-layer membrane fabrication**

Requirements

High proton / Low electron conductivity
Low permeability to fuel
Low electro-osmotic drag coefficient
Good chemical stability
Ease of membrane fabrication

Objectives - Technical Approach



Milestones

Year	Milestone
2007	• Development of a procedure for the synthesis and characterization of Sulfonated Radel R-5000 with a target balance of physical, chemical and electrical properties. • Development of a procedure for the synthesis of an multi-sulfonated, Octa-Phenyl POSS nanoparticle
2008	• Development of a multilayer Proton Exchange Membrane with a balance of physical, chemical and electrical properties that combines the best fuel cell attributes of sulfonated Radel R-5000 and Sulfonated POSS • Development of a composite membrane with the optimal Sulfonated POSS loading and dispersion for high T / low RH conditions • Development of a solution casting application to produce thin, multilayer proton exchange membranes in a roll to roll form.

Approach

Systematic design - from theory to experiments

$$\sigma = F^2 \sum Zi^2 \mu_i C_i \qquad (1)$$

$$D_i = \mu_i RT \qquad (2)$$

$$\Rightarrow \quad \sigma = \frac{D_i Z_i^{\,2} C_i}{kT} \qquad (3)$$

σ : Conductivity
F : Faraday constant
Z_i : charge
μ : mobility
C_i : proton density
D_i : diffusion coefficient

C_i = f (proton density, acidity)

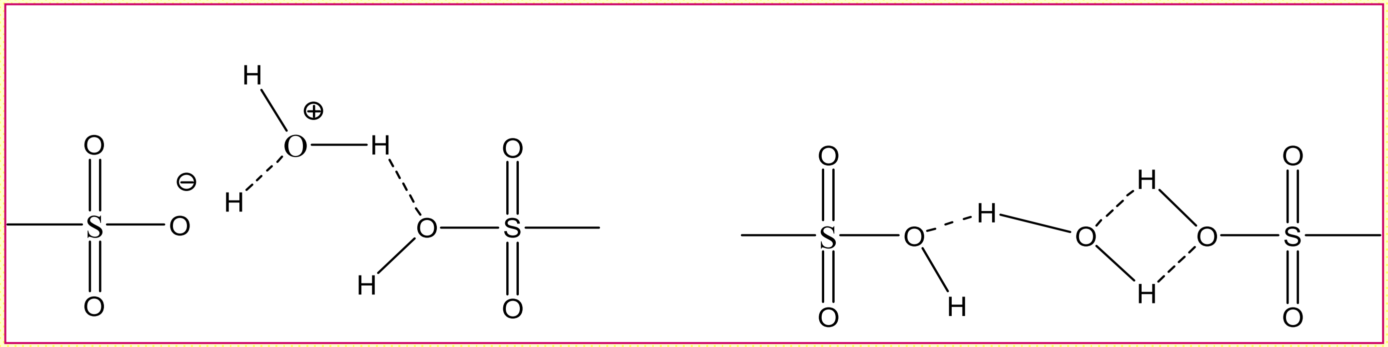
↑ Parameter 1 ↑ Parameter 2

D_i = f (local friction, tortuosity)

↑ Parameter 3 ↑ Parameter 4

Parameter control for experiments

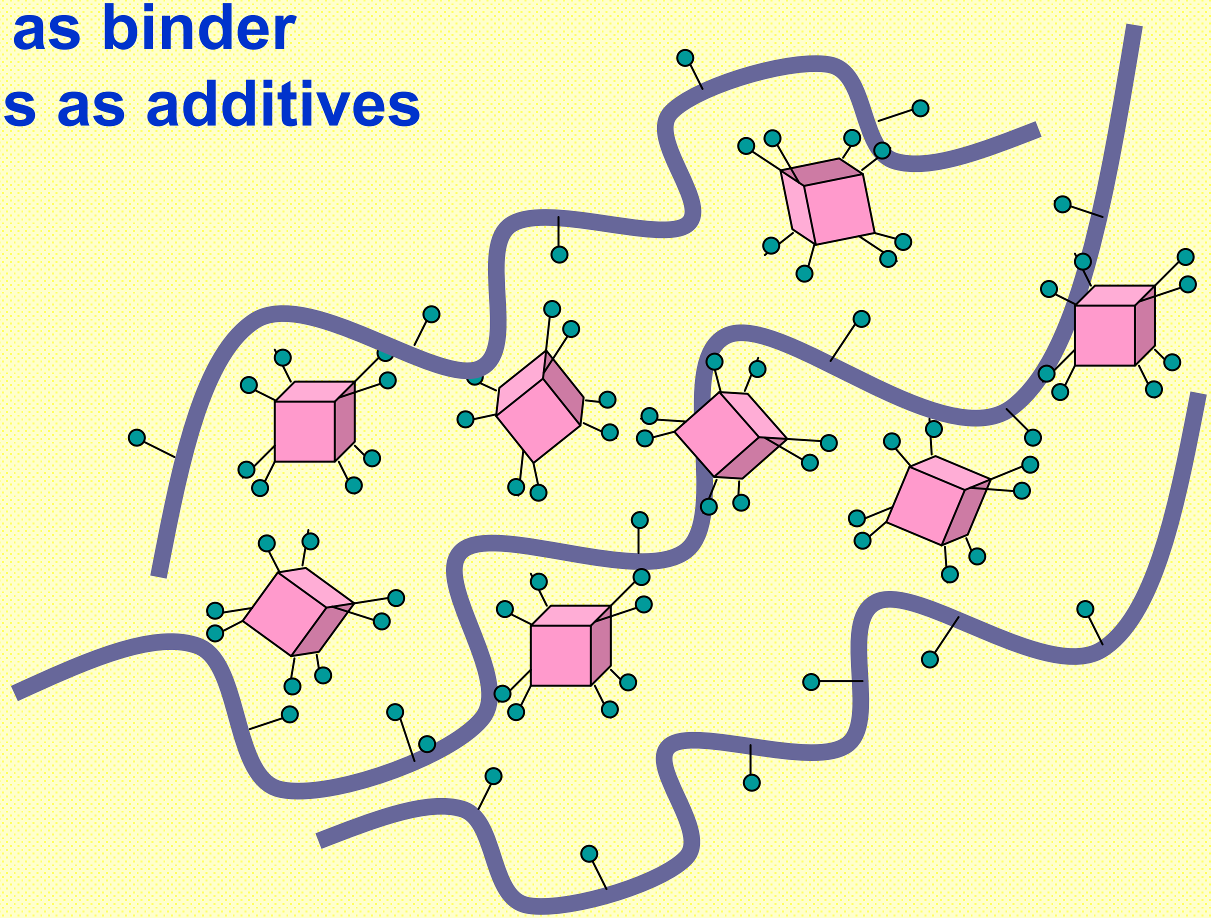
1. **Proton density:**
   SPOSS has an IEC of 3.5 mmol/g , higher than Nafion at 0.92 mmol/g
2. **Acidity:**
   Proton acidity from SPOSS is slightly lower than proton acidity from Nafion, but the synthesis is simplified.
3. **Local friction:**
   Water may form tight bonding to –SO_3H from SPOSS or SRadel at lower RH.



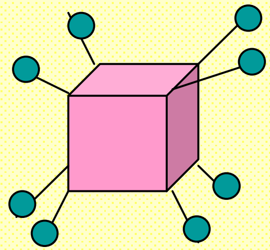
4. **Proton transfer path (Tortuosity)**
   Polymer matrix and nanoparticles need to be compatible.
   A suitable casting solution solvent helps the particles disperse well inside the polymer matrix.

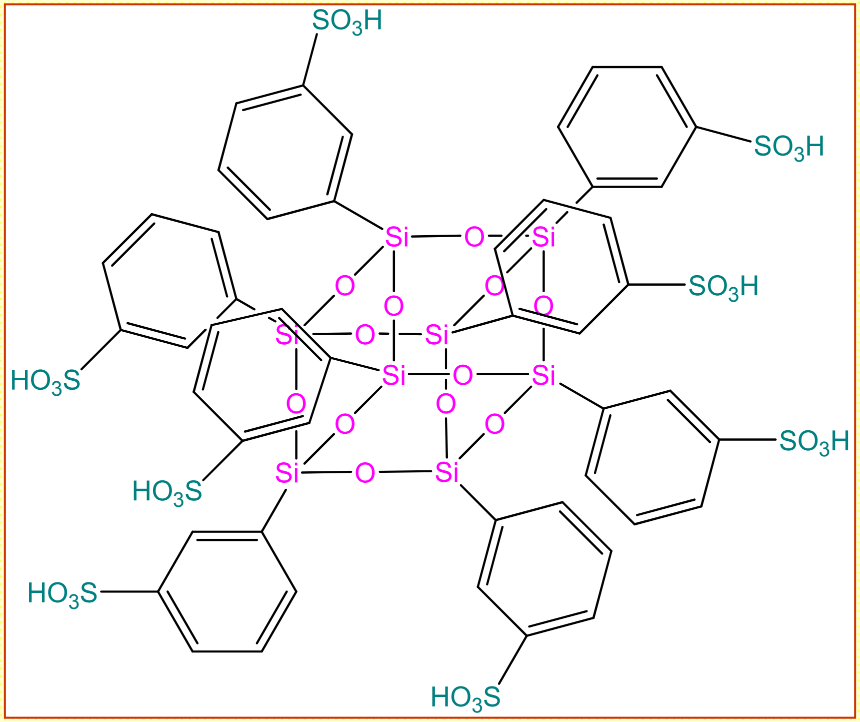
Material concept

Polymer as binder
Nanoparticles as additives

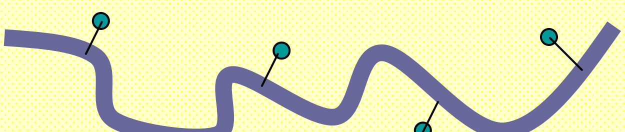


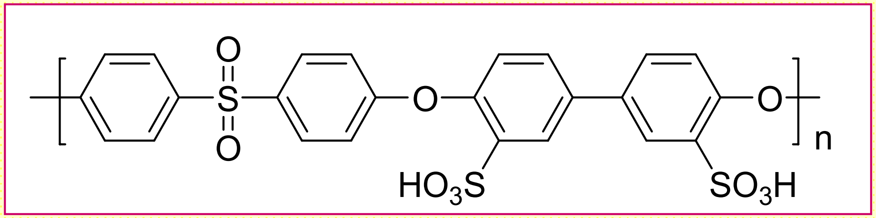
Materials selection





IEC = 3.5 mmol/g

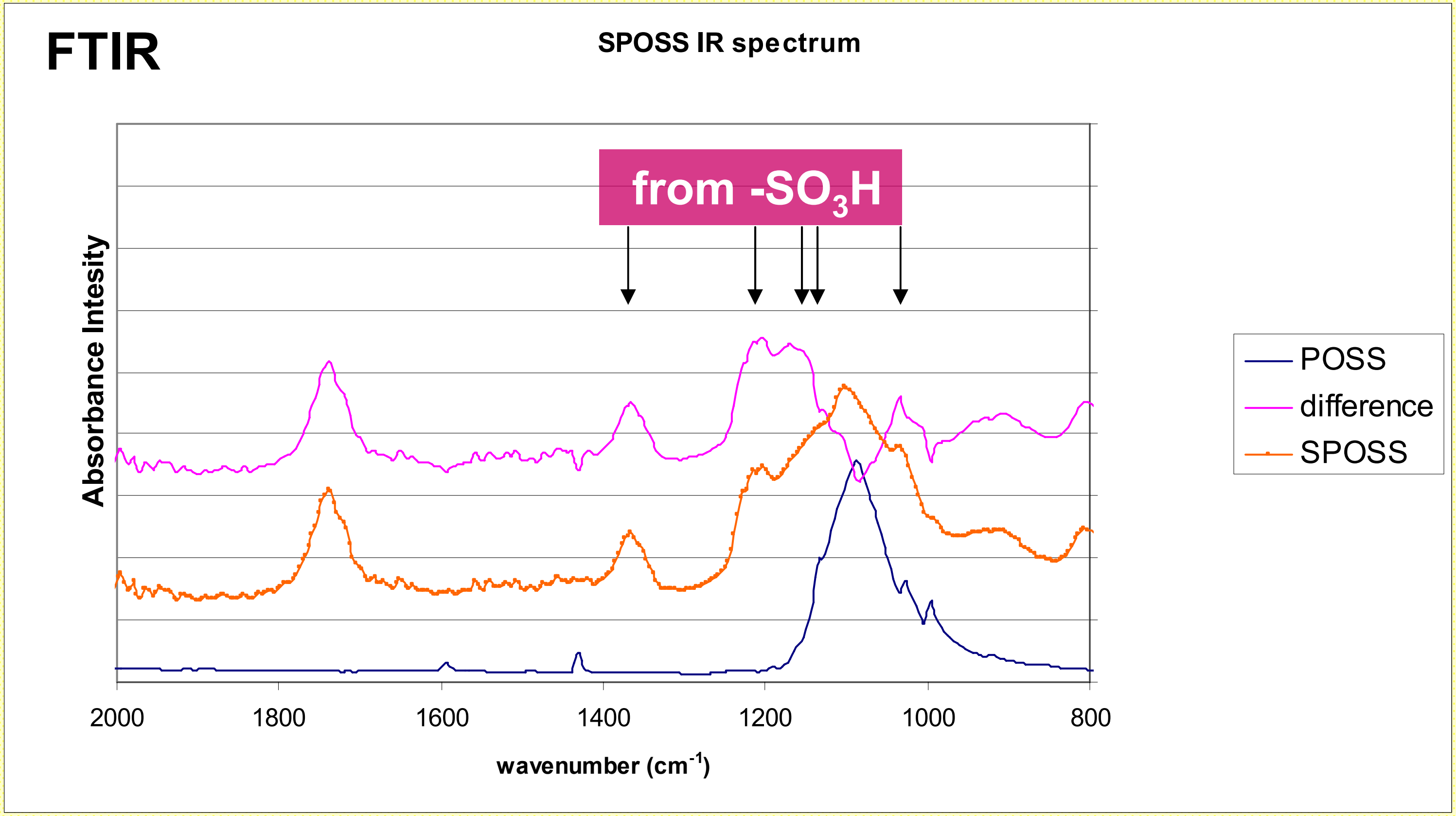




IEC = ~1.5 mmol/g

Accomplishments

Material characterization

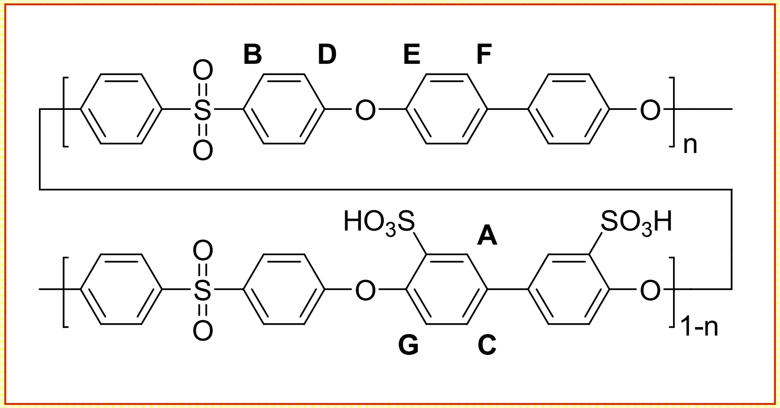


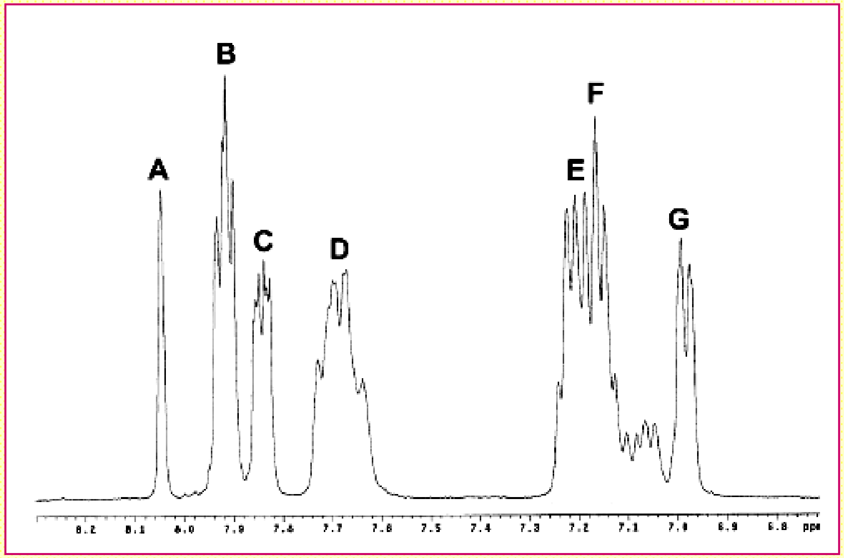
POSS nanoparticles successfully sulfonated.

Accomplishments

Material characterization

^{1}H NMR





Radel R-5000 polymer successfully sulfonated.

Accomplishments

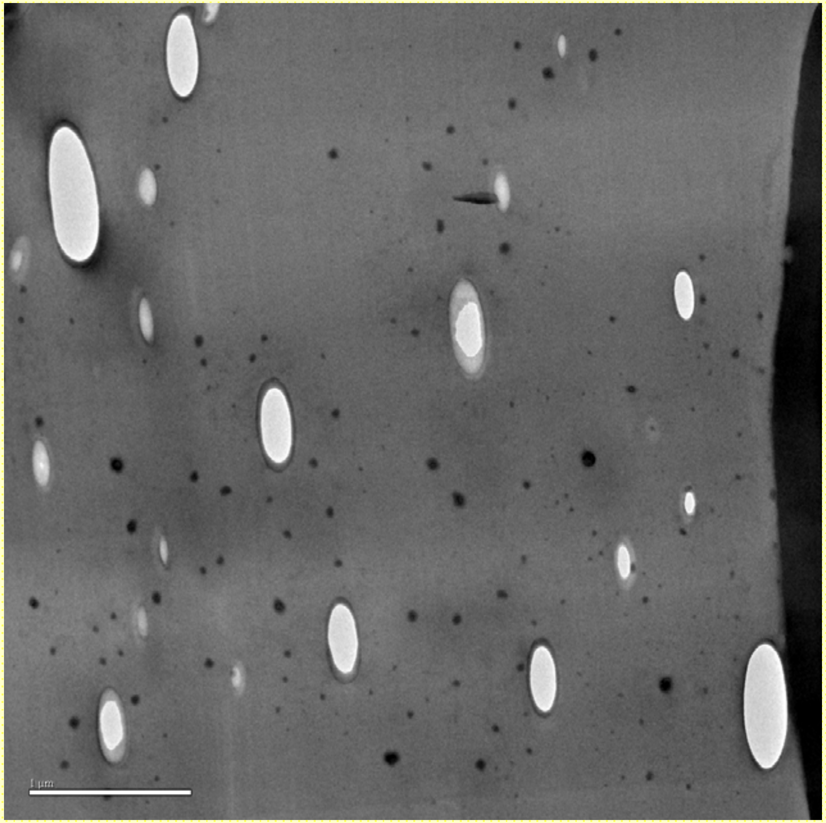
Optimal SPOSS loading

SPOSS loading (%)	Conductivity (mS/cm^{-1}) Room temperature, immersed in water
0	53
10	60
20	71
30	56
40	50

20% SPOSS is the optimum loading for maximum in-plane conductivity

Accomplishments

Nanoscale particle dispersion

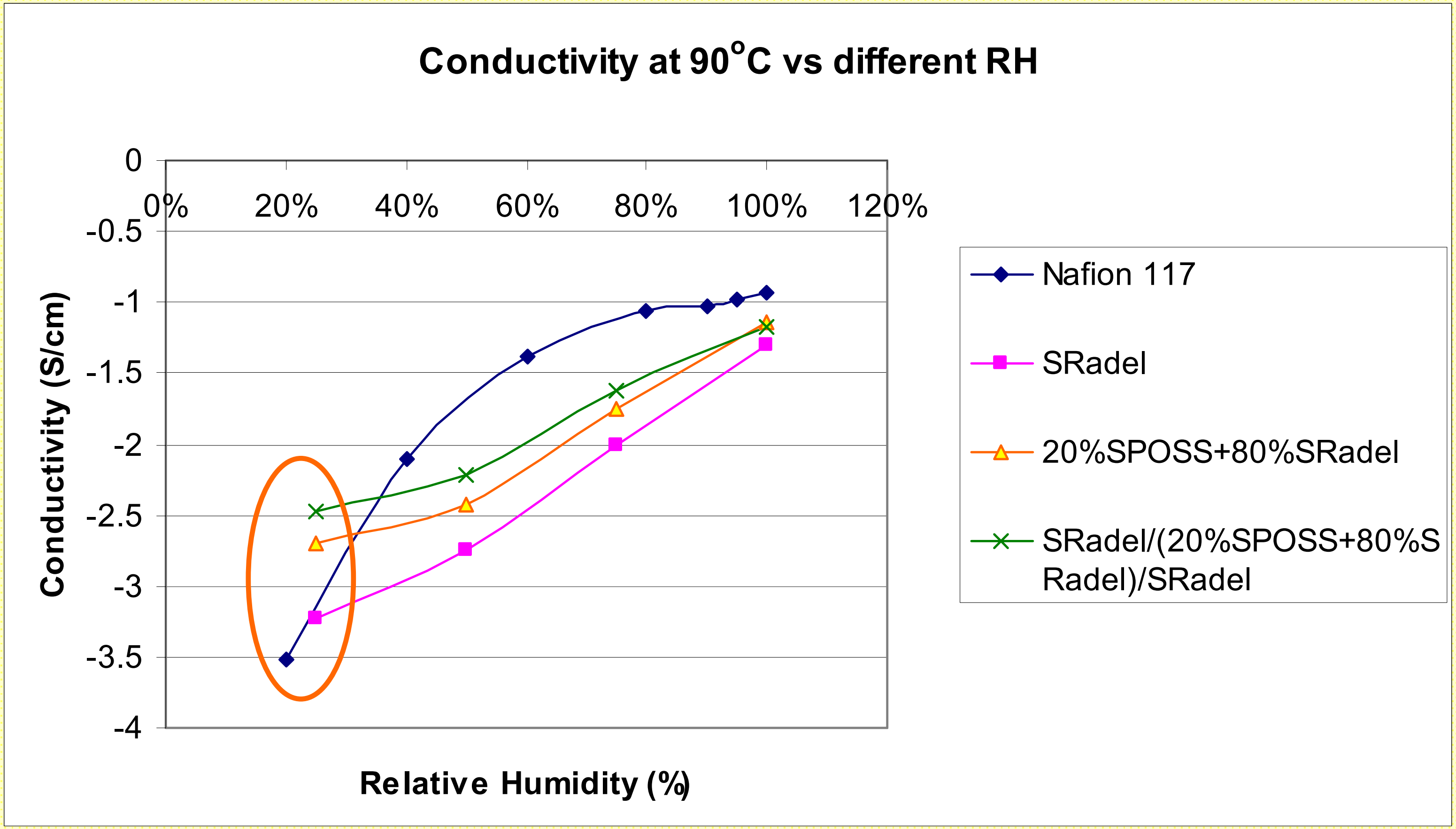


TEM image of a close-up of a cross section of 20% SPOSS / 80% sulfonated Radel R-5000 film cast from DMSO solvent, scale bar 1 micron, domain size in the 100 to 500 nm range.

Nanometer scale SPOSS was successfully dispersed inside the polymer matrix

Accomplishments

Improved conductivity at 25%RH and 90°C



Membrane with 20% SPOSS has improved conductivity vs. Nafion at 25%RH, 90°C.

Accomplishments

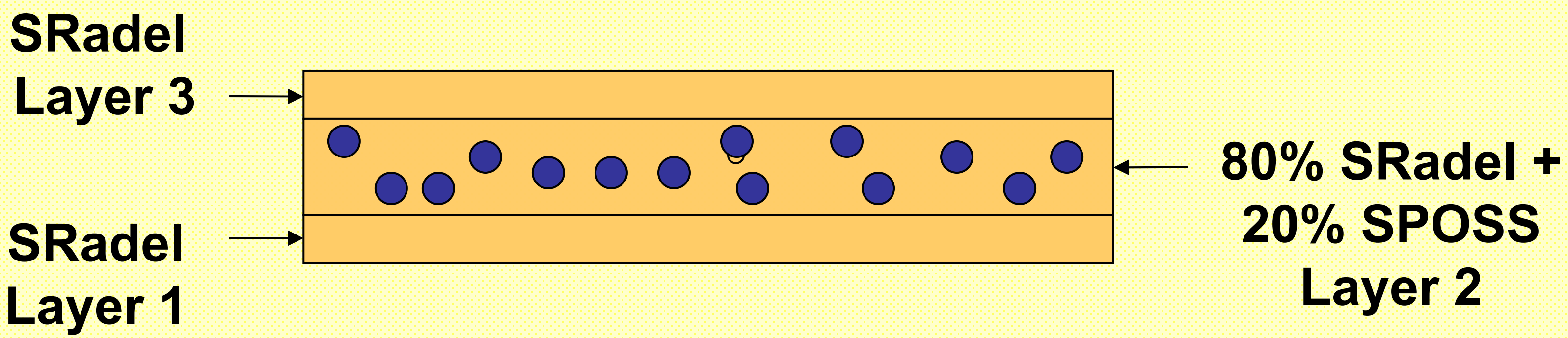
Water uptake at 25%RH and 90°C

	Water uptake (%)
Nafion 112	3.0
SRadel	4.4
20% SPOSS + 80% SRadel	**6.3**

Composite membrane provides better water uptake and leads to better conductivity. ASTM D1042 testing indicates membrane swelling is reduced by adding SPOSS particles

Accomplishments

Increasing mechanical strength by using a multiple layer structure



The 1st and 3rd unfilled polymer layers provide flexibility and mechanical strength.

Accomplishments

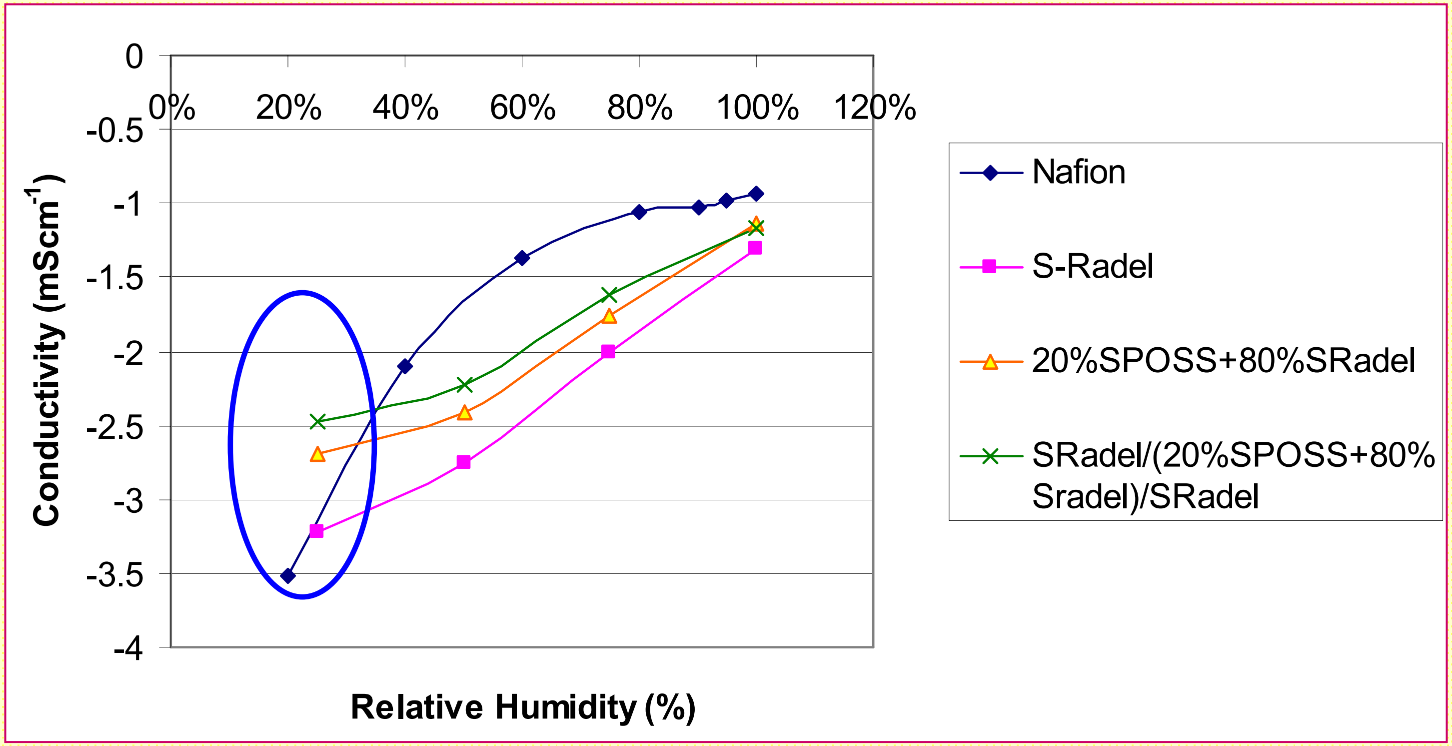
Increasing mechanical strength by using a multiple layer structure

Membrane	Storage Modulus at 30°C (MPa)	Storage Modulus at 120°C (MPa)	Storage Modulus at 170°C (MPa)
Nafion 117	600	Low	Low
Single-layer Sulfonated Radel (SRadel)	1954	1750	884
Single-layer (20% SPOSS + 80% SRadel)	1426	1120	23
3-layer SRadel / (20% SPOSS + 80% SRadel / SRadel	1348	1320	**1202**

3 layer membrane maintains a high storage modulus at 170°C.

Accomplishments

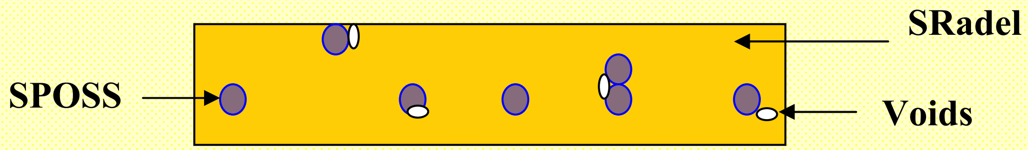
Conductivity improvement at 25%RH and 90°C



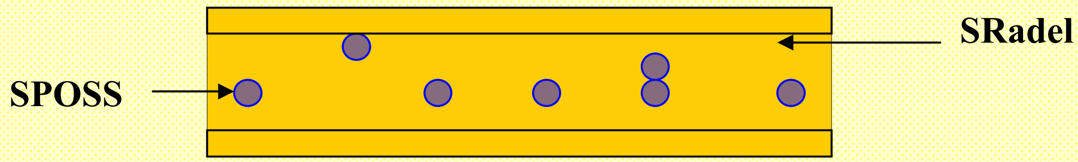
Multiple-layer structure improves proton conductivity at 25% RH and 90°C.

Accomplishments

Benefit of Multiple layer membrane



Voids may exist inside the single-layer membrane, especially near the particles.

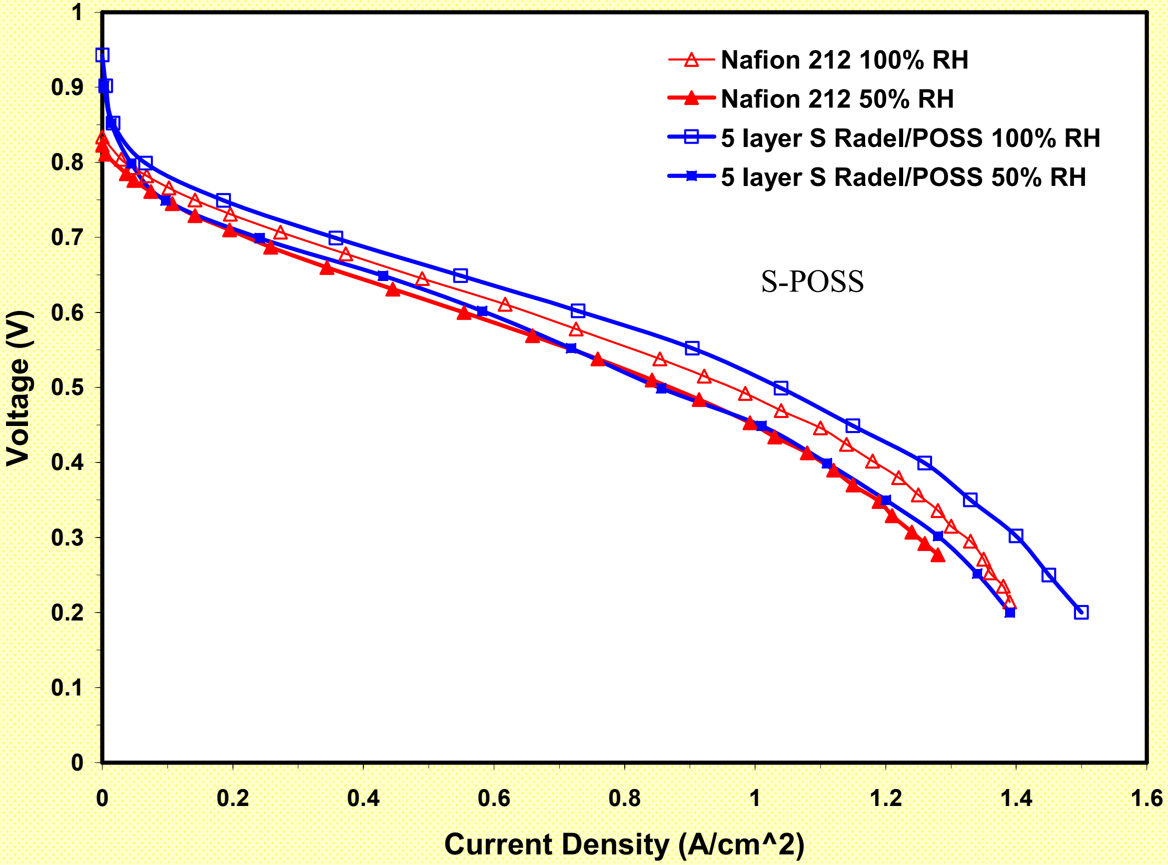


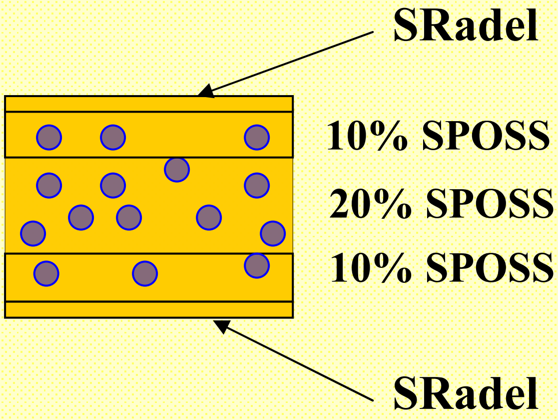
When the 3rd layer is coated on the "semi-wet" 2nd layer, the polymer solution settles down to the 2nd layer and fills the voids.

Multiple-layer structure increases mechanical strength and fills potential voids formed in composite layer

Accomplishments

Fuel cell testing at 50%RH, 80^{o}C



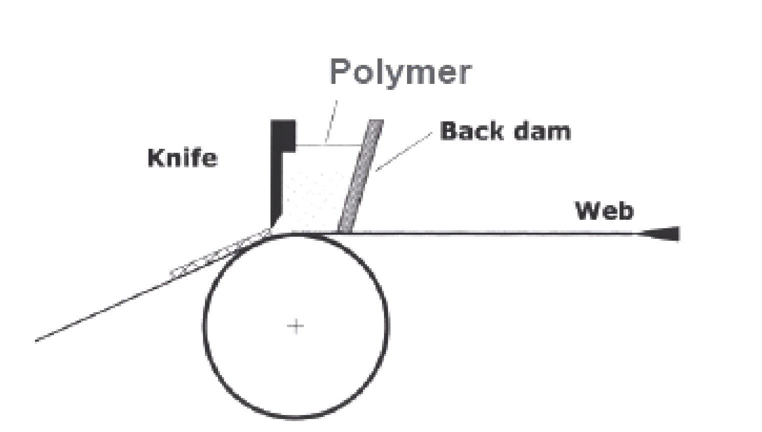


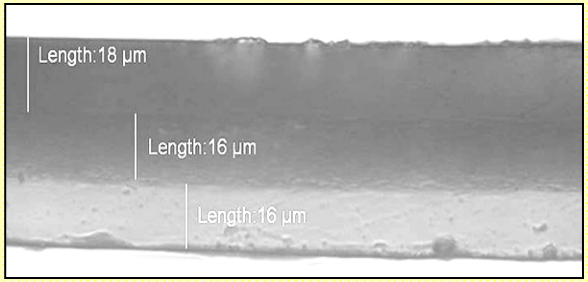
Multiple-layer composite membrane has similar performance to Nafion at 50%RH and 80^{o}C.

Accomplishments

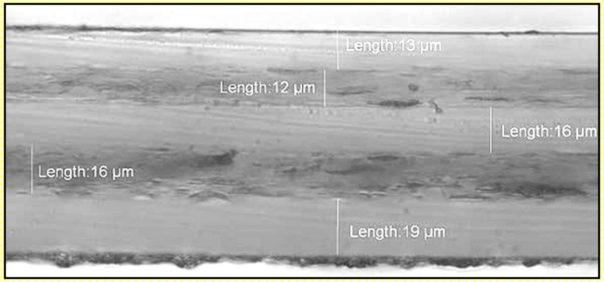
Solution casting multiple-layer membranes

Knife over roll process





3-layer membrane

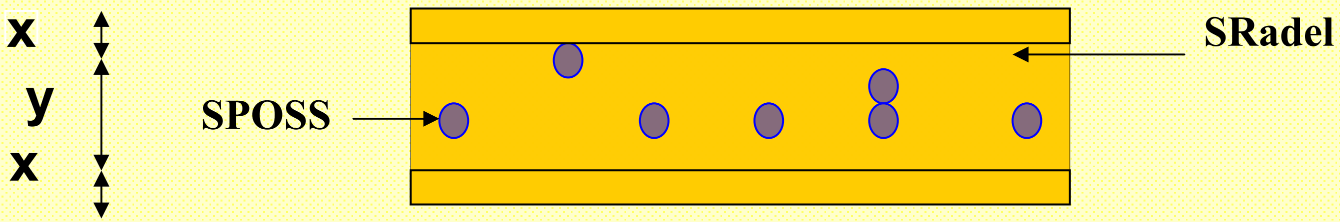


5-layer membrane

Future Work

- Optimize the caliper (thickness) of individual membrane layers and of the total multiple-layer membrane
- Expand membrane pilot casting trials for optimum multiple-layer formation development
- Complete additional fuel cell testing of multiple-layer membranes at 25% RH and 120^{o}C.

Future work – optimize layer & membrane thickness



Caliper "x" needs to be thin enough to prevent membrane drying, but conversely it must also be thick enough to provide sufficient mechanical strength.

Summary

- **A method to prepare high proton conducting SPOSS particles was developed. The ion exchange capacity achieves 3.5 mmol/g.**
- **Membranes produced with 20% sulfonated POSS particles and 80% sulfonated Radel R-5000 polymer have conductivity close to 10^{-2} Sc m^{-1} at 25% RH and $90^{o}C$.**
- **Pilot scale casting carried out using a commercial scale process produces uniform and pin-hole free multiple-layer membrane structures.**