

Low Cost, High Performance PPSA-based PEM Fuel Cell Membranes

DOE SBIR Phase I

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SBIR Phase I Project Overview



Timeline

- ❑ Started: 07/13/2004
- ❑ Ended: 04/13/2005
- ❑ Percent complete 100%

Budget

- ❑ Total project funding
 - ❑ DOE 100K
 - ❑ Contractor 31K
- ❑ Funding received in FY04: 60K
- ❑ Funding for FY05: 40K

Barriers

- ❑ **Barriers addressed:**
 - ❑ High cost of Current PFSA membranes;
 - ❑ Low proton conductivity of PFSA membranes at low R.H.
- ❑ **Targets:**
 - ❑ Develop new, lower-cost, longer-life materials
 - ❑ Develop MEAs that tolerate excursions to 120 °C and/or operate at RH 25-50%.

Partners

- ❑ [Case Western Reserve University](#)



Project Objectives

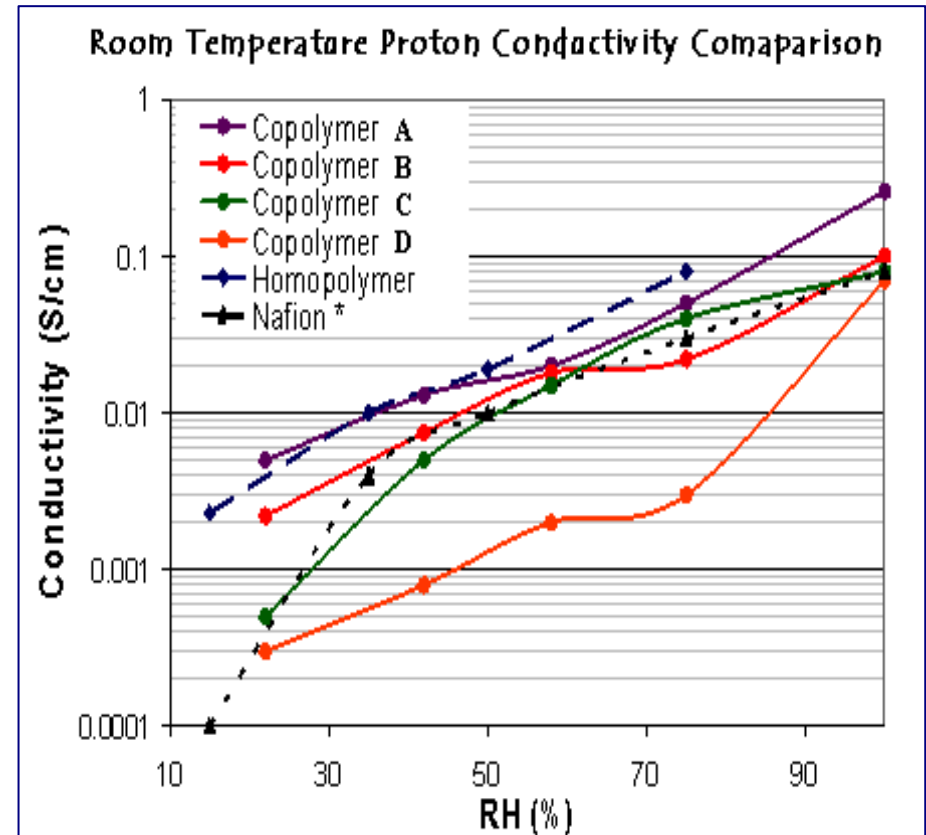
To develop a low-cost, high performance H_2/O_2 fuel cell polymer electrolyte membrane to replace state-of-the-art Nafion Perfluorinated membranes;

- ❑ To develop a low cost, thermally, chemically and electrochemically stable membrane material for applications in PEM fuel cell;
- ❑ To demonstrate a higher proton conductivity than PFSA membranes at any R.H.;
- ❑ To develop a molecular model for the new membrane material;
- ❑ Successful testing of the material in a H_2/O_2 fuel cell performance equal or better than PFSA membranes at similar operating conditions;

1. Development of a low cost, thermally and chemically stable, and mechanically robust membrane material:
 - ◇ Utilizing low cost precursors and easy fabrication;
 - ◇ Use highly stable Liquid Crystalline Polymers (LCPs) as base materials;
2. High proton conductivity at room Temperature and low R.H. (20-50%):
 - ◇ High degree of sulfonation;
 - ◇ Develop a unique LCP based rigid molecular channel structure that is capable of conducting Proton without larger amount of water.
3. Develop a working procedure for the fabrication membrane-electrode-assemblies and fuel cell demonstration:
 - ◇ Study the difference between the molecular structures and proton conduction mechanism between Nafion and PPSA;
 - ◇ Selection and development of a new catalyst binder system and fabrication procedure;

PPSA Membrane Proton Conductivity @ Room Temperature

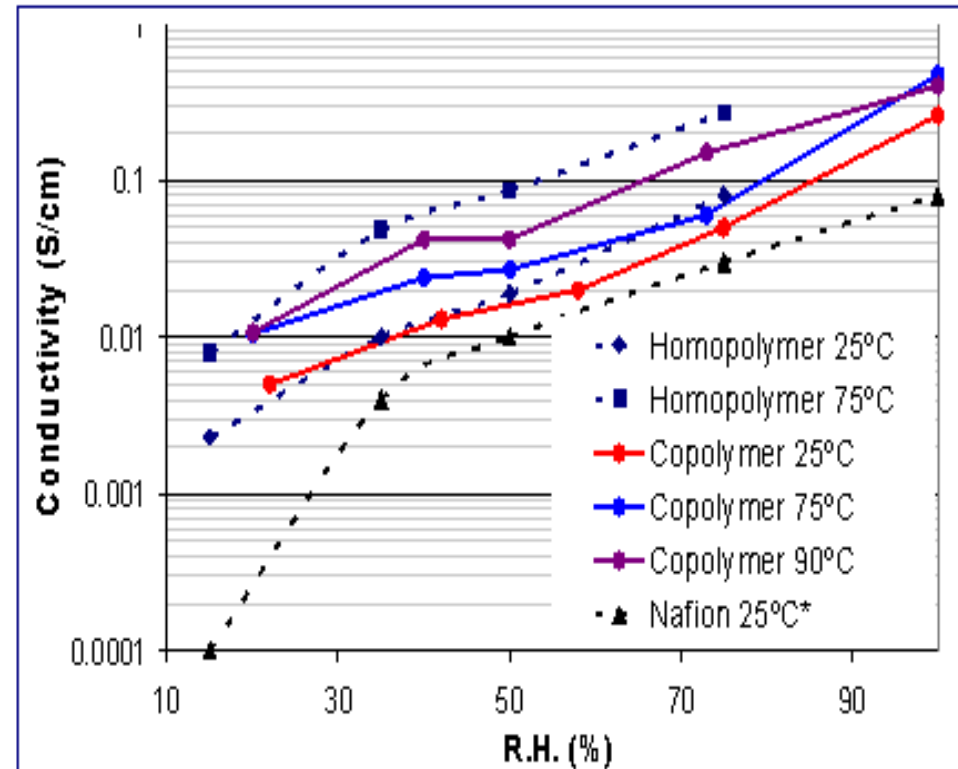
- ◇ Homopolymer is extremely soluble in water; Copolymers are insoluble in water;
- ◇ Copolymer A exhibited higher proton conductivity than Nafion at ~100R.H.
- ◇ The proton conductivity of copolymers A to D is **one** magnitude higher than Nafion at relative humidity of 20%;



PPSA Membrane Proton Conductivity @ elevated Temperature

- ◇ Copolymer A exhibited the best proton conductivity of all;
- ◇ The proton conductivity of copolymer A at 98% R.H. is ~ 0.15 S/cm.
- ◇ The proton conductivity of copolymers A is about **two-** magnitude higher than Nafion at relative humidity <20% ;

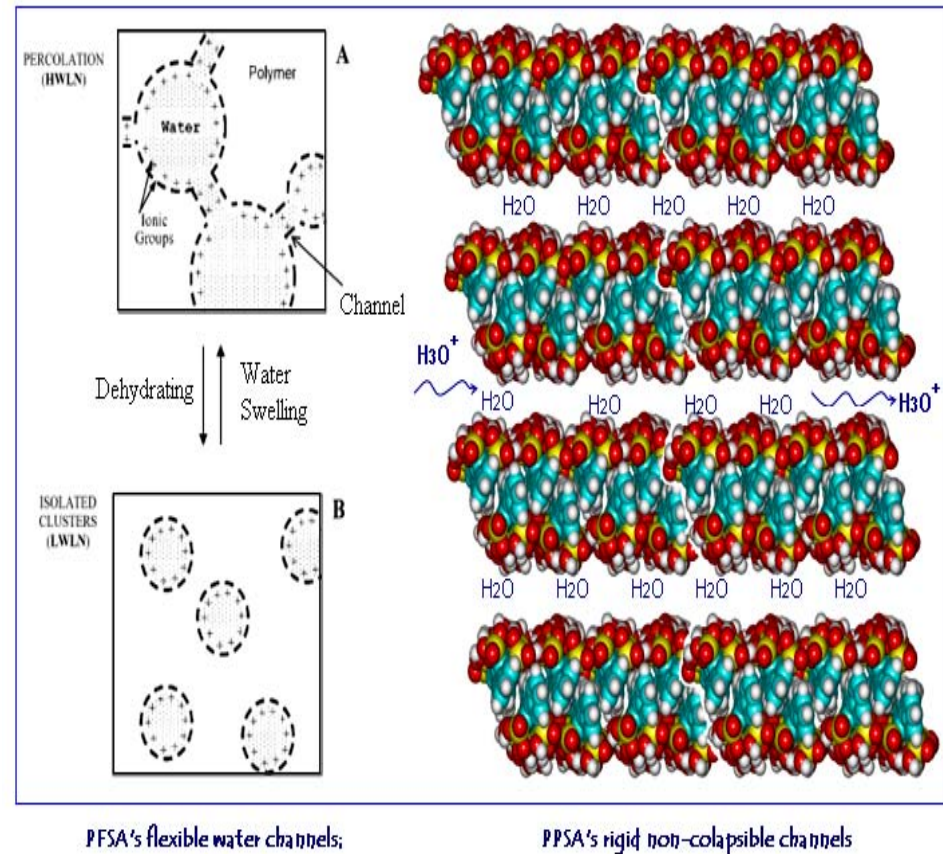
Proton Conductivity of Copolymer A
at different Temperature and Relative Humidity



Molecular Model and H⁺ conduction Mechanism of PPSA

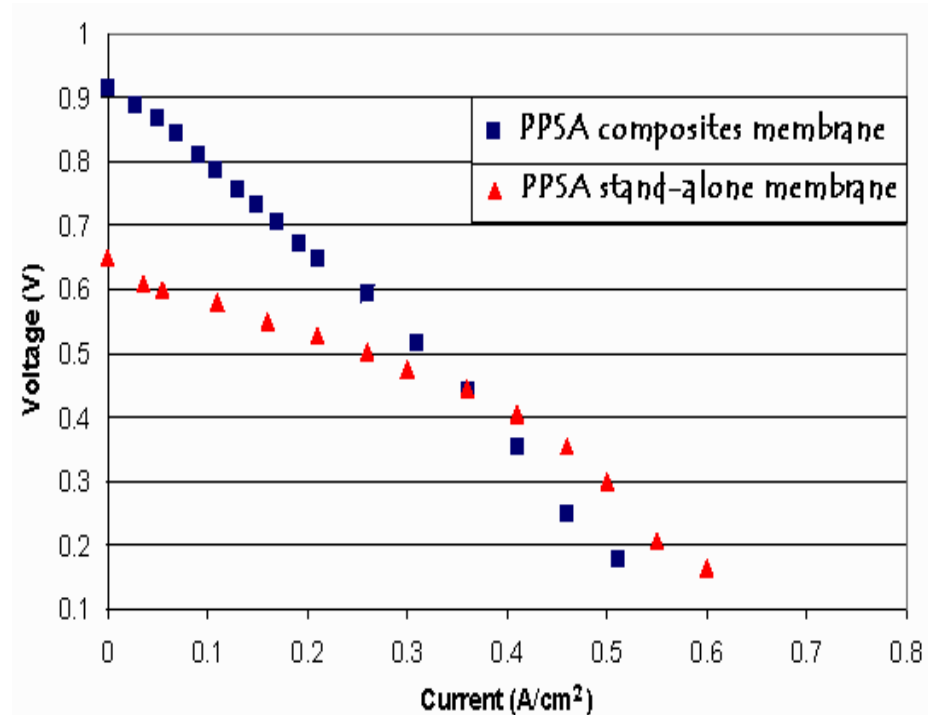
- ◇ Unlike PFSA, channels in PPSA are rigid and non-collapsible;
- ◇ High sulfonation degree of PPSA realizes the interconnection of sulfonation domains;
- ◇ Most of the water in PPSA is tightly bonded to sulfonic groups which can be removed only at high temperature;
- ◇ The PPSA channel gap is below 20Å;
- ◇ The permeability of PPSA is outstanding due to these rigid channels;

A Comparison of proton conduction mechanism between PPSA and PFSA



PPSA Membrane Fuel Cell Performance

- ◇ PPSA membrane-electrode-assemblies were fabricated under non-optimized conditions;
- ◇ Fuel cell performance was under totally non-optimized conditions;
- ◇ Significant IR loss due to high resistance at electrode and membrane interface;
- ◇ Due to the completely different structure of Nafion and PPSA - Nafion is not a good binder for PPSA MEAs;



Polarization curves of porous substrate supported PPSA and PPSA stand-alone membranes operating under totally non-optimized conditions in a 5 cm² H₂ / O₂ fuel cell; cell temperature 80°C; gas flow rate was 80 ml/min; Zero back pressure.

T/J's PPSA-PFSA Composite Membranes



- ◇ PPSA homo- and co- polymers stay in PFSA's channels and physically impossible to leach out !
- ◇ Permanently enlarge the water conduction channel of PFSA membranes therefore significantly increasing PFSA's proton conductivity at low R.H.;
- ◇ 10% PPSA in Nafion can increase its proton conductivity at 100 % R.H. by >30%;
- ◇ Enhance the mechanical properties and durability of PFSA therefore lengthen performance life;
- ◇ Rendering improved dimensional stability upon hydration and dehydration;
- ◇ Lower the cost of Nafion: if 10% PPSA is added into Nafion, 10% membrane cost will be saved, since PPSA can be made very cheap!

Demonstrate high proton conductivity at low R.H. for crosslinked PPSA materials:

- ◇ Instead of chemical crosslinking of PPSA, we found another way to make PPSA insoluble in water;
- ◇ High proton conductivity has been demonstrated for insoluble PPSA at low R.H.; $> 0.01\text{S/cm}$ at 20% RH.

Electrochemical stability of PPSA copolymer or composites in a fuel cell working environment:

- ◇ The PPSA copolymers has demonstrated to be extremely electrochemical stable;
- ◇ Performance life will be demonstrated in 2005;

Adequate Gas separation:

- ◇ Gas permeability data will be provided in 2005;



- ◇ Processing PPSA materials using optimized solution casting procedure or other new methods;
- ◇ New PPSA copolymer synthesis;
- ◇ Optimizing MEA with a completely new polymer – especially the catalyst and polymer interface;
- ◇ Demonstration of a H₂/air Fuel cell stack using PPSA as PEM;