High Temperature and Low Humidity Membranes

Cy Fujimoto
(chfujim@sandia.gov)
Sandia National Laboratories

June 8th, 2015

FC124

Overview

Timeline and Budget

- Project Start Date: 09/18/14
- Project End Date: 09/18/15
- Total Project Budget: $250k
  - Project lead: SNL $200k [synthesis and basic characterization of membranes]
  - Collaborator: ORNL $50k [proton conductivity and MEA testing]
  - Total Funds Spent $150k [60% spent as of April 7th, 2015]

Barriers Addressed

- Membrane cost in PEMFCs
- Performance/conductivity at 120°C at 35-50% RH
- Membrane durability

Partners

- Project lead: Sandia National Laboratories
- Sub contractor: Oak Ridge National Laboratories
- Industrial partner: Automotive Fuel Cell Cooperation (in kind)

Relevance

Objectives

To develop a 1) hydrocarbon membrane that can operate with minimal resistance losses (0.05 ohm-cm^2) at 120^{o}C and humidity ranges between 30-50%. 2) fabricate and test MEAs at 120^{o}C and humidity ranges between 30-50%. 3. durability testing of MEAs at 120^{o}C at 50%RH

Technical Barriers

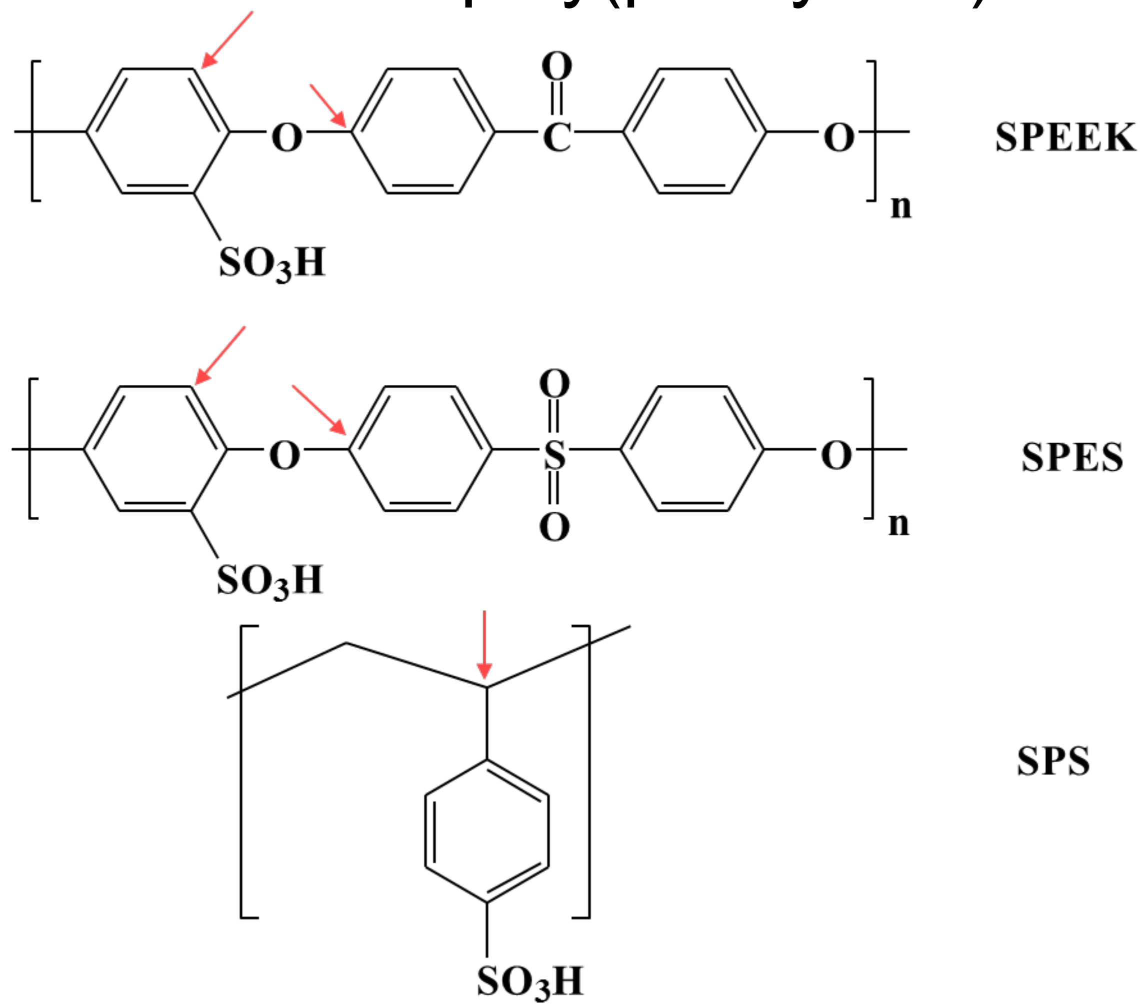
Perfluorinated ionomers, such as Nafion®, cannot operate effectively at 120^{o}C due to its relatively low Tg (120-150^{o}C). Although, hydrocarbon ionomers can have much higher Tgs (>150^{o}C), typically their conductivity/fuel cell performance lag from Nafion at low RH (<50%). At SNL, we have developed hydrocarbon ionomers that not only have very high Tgs (>250^{o}C) but show fuel cell performance comparable to perfluorinated ionomers.

- Demonstrate ASR 0.05 ohm-cm^2 at 120^{o}C and 50%RH (or 25 mm film 50mS/cm)
- Demonstrate 100 hrs of fuel cell performance under load at 120^{o}C

Approach

Why focus on Diels Alder poly(phenylene)?

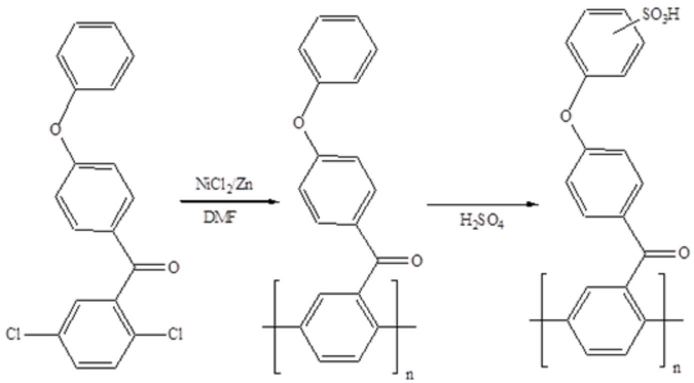
- Shown are some common polymer backbones that have been investigated
- Polymers have long term stability issues
- Red arrows indicate "weak points"

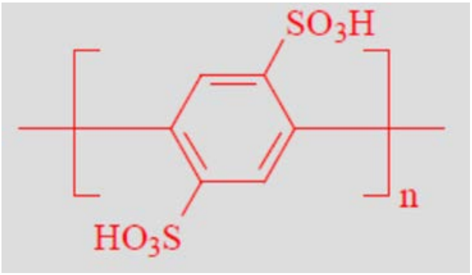


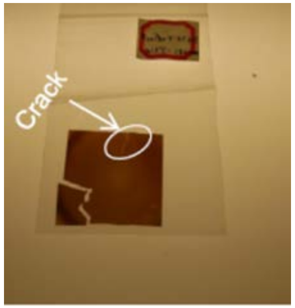
Hubner, G.; Roduner, E. *J. Mater. Chem.,* **1999**, 9, 409-418

Approach

Poly(phenylene)s offer higher chemical-thermal stability







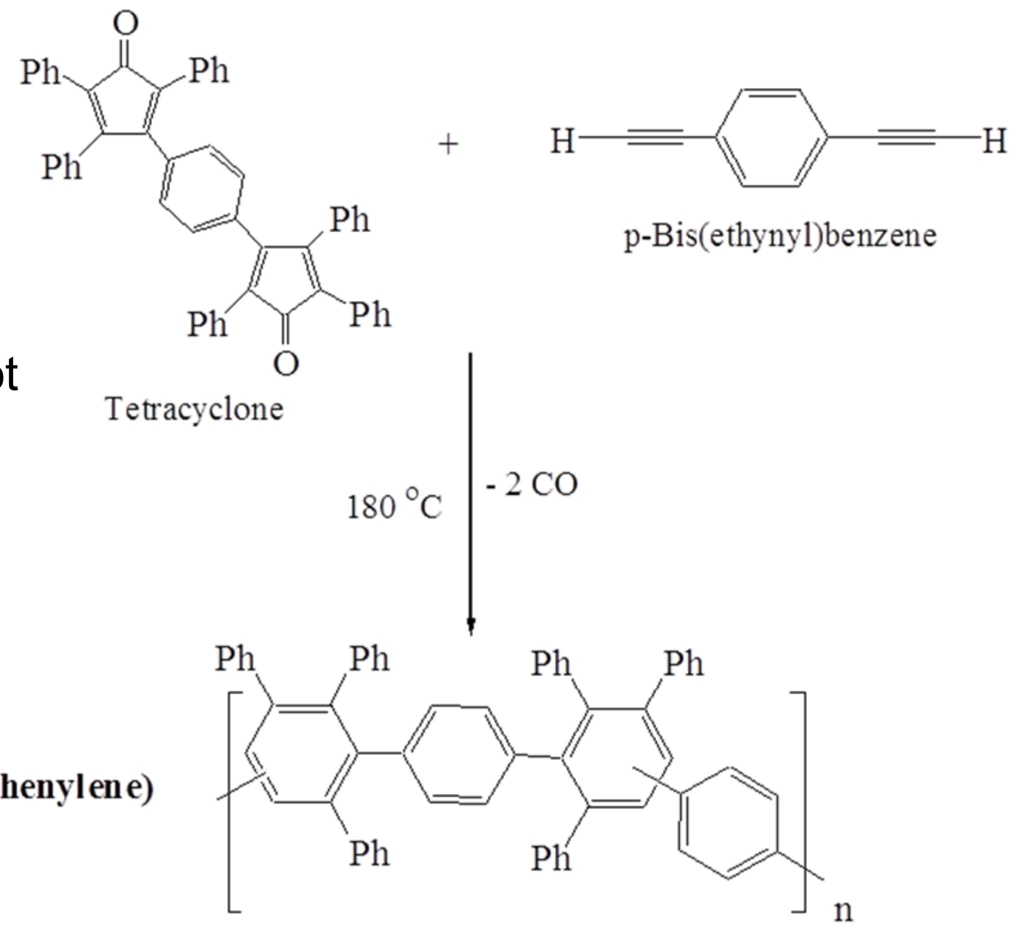
Disadvantages

1. Require use of metal catalysis: Reaction moisture sensitive and must remove catalysts after polymerization [increase costs]

2. Resultant polymers are ridged rods (PPP), very difficult for chain entanglements = brittle mechanical properties even with high Mn

Approach

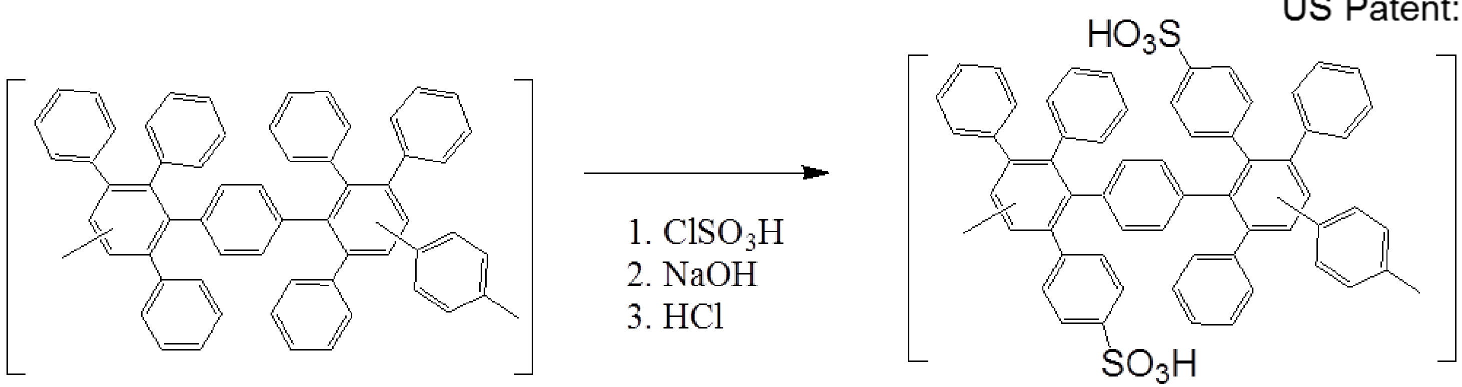
- Diels Alder reaction: no metal catalyst required, not moisture sensitive
- The loss of CO drives the reaction – not reversible, can generate very high Mn
- In reaction intermediate, two possible approaches the ethynyl group can occur; polymer not ridged rod



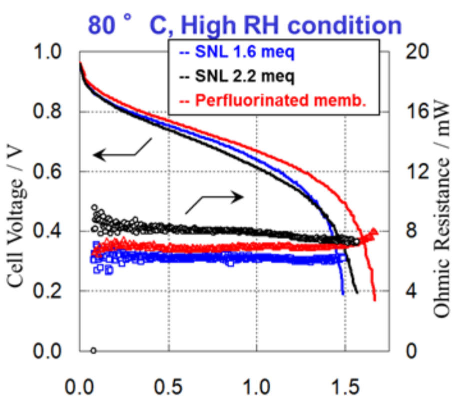
Poly(phenylene)

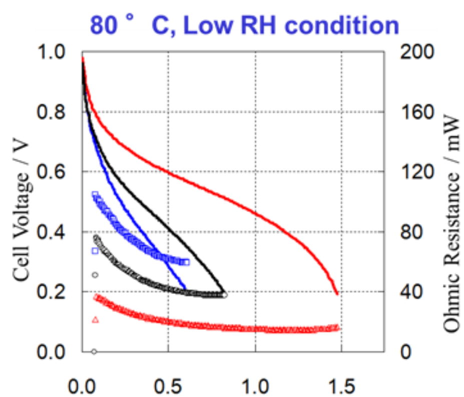
Approach

US Patent: 7,301,002



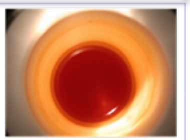
SDAPP = Sulfonated Diels Alder PolyPhenylene





- Condition : 60 ° C, 2 Hrs (for HC membranes)
- Solution : 3 wt% H_2O_2, 4 ppm Fe^{2+}
- Result : 99 % remained (1.6 meq), 97 % remaind (2.2 meq)

- Membrane : 2.2 meq
- Solution : 1 wt% H_2O_2, 10 ppm $FeCl_2$
- Condition : 100 ° C, 2 Hrs
- Result : Completely destroyed
  A little amount of precipitations was remained in the solution.



- Commercially available Nafion shows 2 ~ 4 % decrease in weight with standard condition for 8 Hrs.

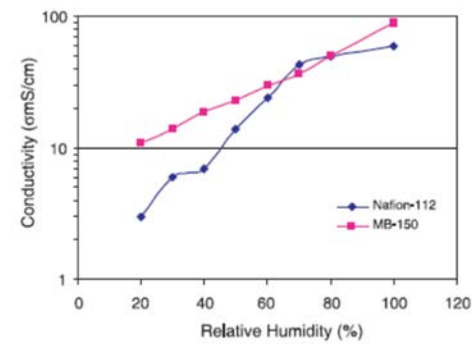
Highly durable as a HC membrane, but desired to improve durability

Very good humidified performance and good durability

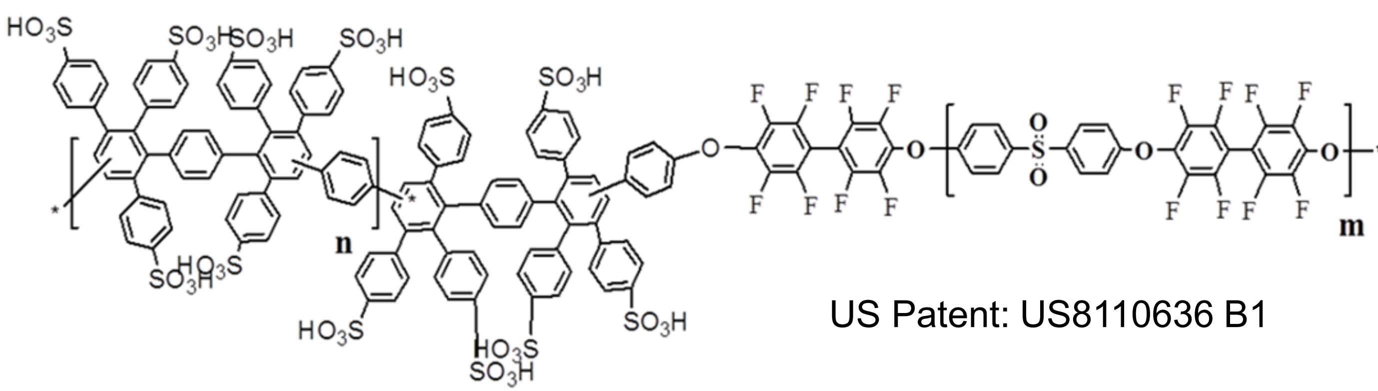
Poor low RH performance and not as durable as PSFAs

Approach

- Random sulfonated polymers FC performance severally lagged behind PFSAs especially under low RH
- Seminal by McGrath, Zawodzinski and Ghassemi proved hydrocarbon multi-block co polymers could compete with PFSAs at low RH [DOE EERE funded]
- Work began on developing multi blocks employing the Sandia poly(phenylene) unit



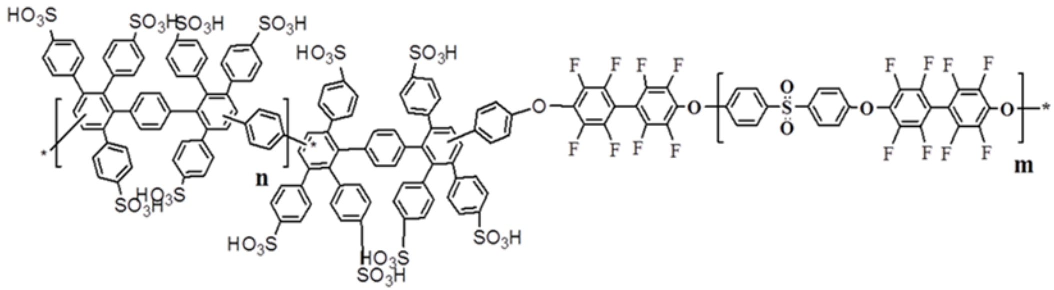
Ghassemi, H.; McGrath, J.E.; Zawodzinski, T. Polymer, 47, 2006, 4132-4139



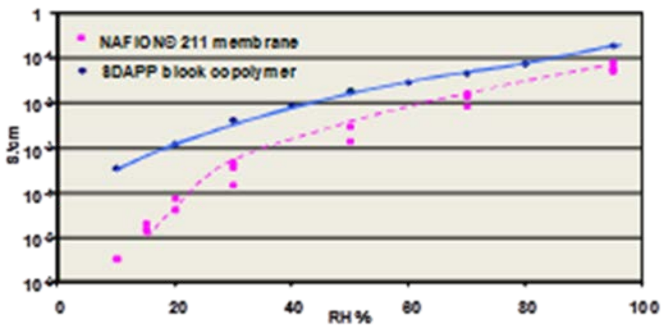
US Patent: US8110636 B1

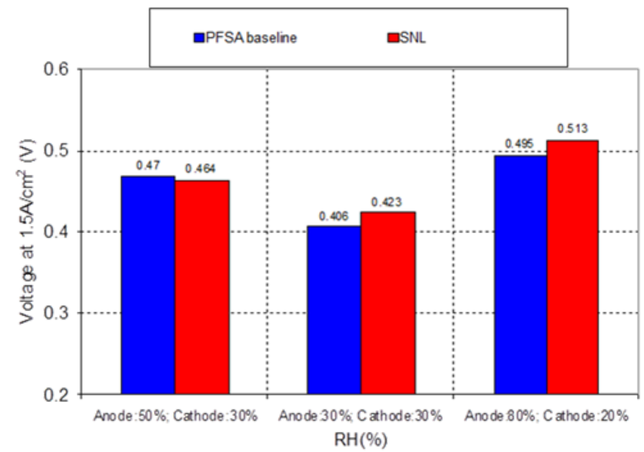
Advantage of the DAPP - Unlike BPSH type polymers, in the hydrophilic domain there is a "break" in acid content, the DAPP unit can be fully sulfonated with a much higher acid content

Approach

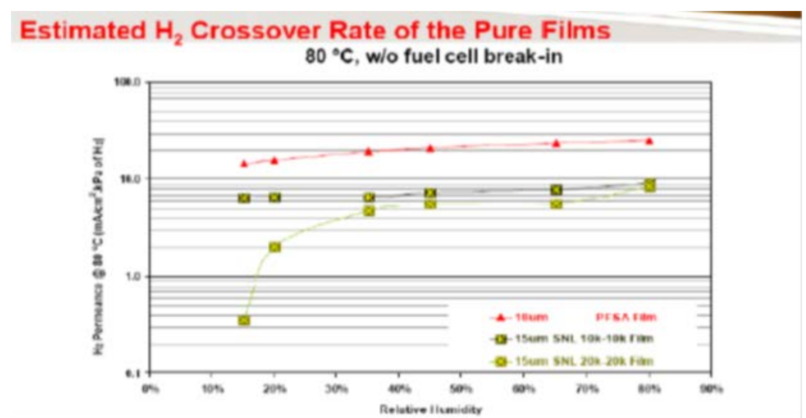


m = 11 n = 27
IEC = 2.7 meq/g

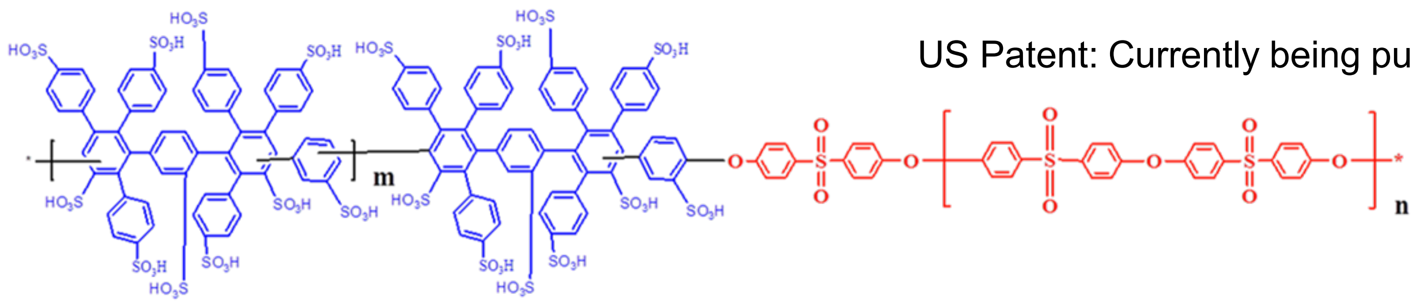




- This material has shown good conductivity at low RH but also have shown comparable fuel cell performance compared to PFSAs
- This material has also shown lower H_2 permeability than PFSAs
- Unfortunately, due to the relatively high water uptake (150%) the films showed low cyclic durability



Approach



US Patent: Currently being pursued

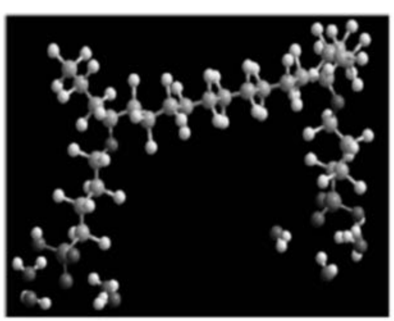
1. From separate program on flow batteries, we discovered that the backbone aryl groups could also be sulfonated. This almost doubles the acid content from our previous work. More importantly, the hydrophilic domain can be smaller in segment length, but still offer high conductivity and better mechanical strength

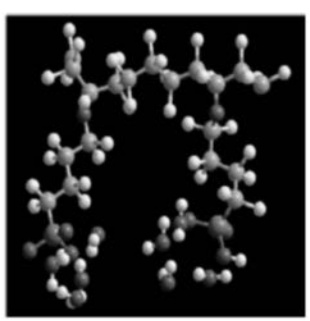
Visual concept

previous | current

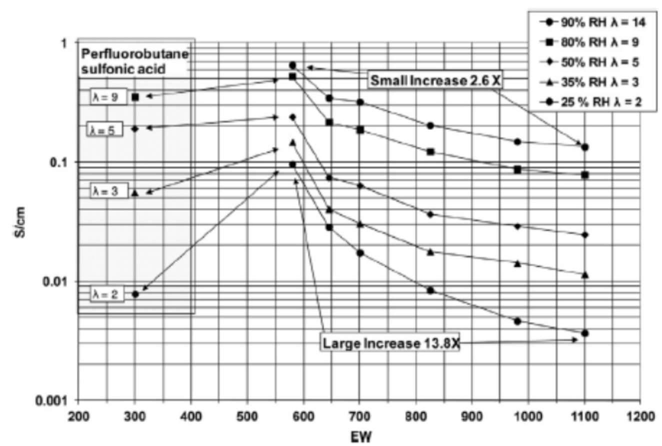
m = 11 | n = 27 | m = 15 | n = > 40

2. Impact on Short acid-acid distances



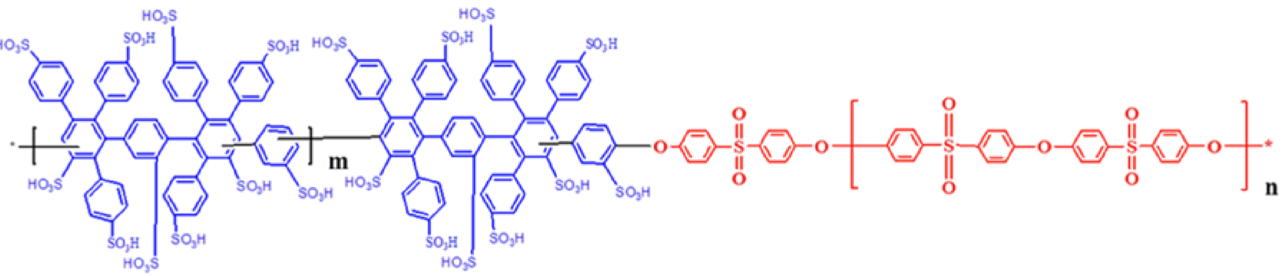


EW 825 → EW 585



Maalouf, M.; Sun, C.; Pyle, B.; Emery, M.; Haugen, G.; Hamrock, S.; Zawodzinski, T. Int. J. Hydrogen Energy, 39, 2014, 2795-2800

Accomplishments



- Synthesized samples with m = 15 (3.0, 2.5, 2.0 meq/g)
- Since time limited full characterization on promising samples only
- Synthesized 10 films of SDAPP so ORNL could develop MEA protocols for the hydrocarbon membranes

Temperature (°C)	RH%	N211 Conductivity (mS/cm)	2nd Gen Block Conductivity (mS/cm)
85	30%	9.14x10-3	$1.80x10^{-4}$
85	95%	1.10x10-1	$1.42x10^{-1}$
120	No RH control		$1.18x10^{-5}$

Table 1. Proton conductivity of 2nd Gen Block vs Nafion 211

Shipped films to AFCC for conductivity testing, AFCC 1st tested the 3.0 meq/g sample, conductivity lower than Nafion (water uptake >150%)

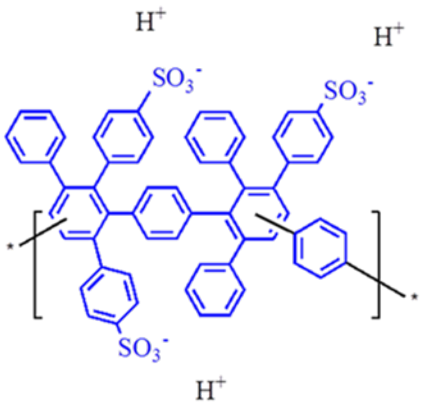
Accomplishments

- However, AFCC just measured m= 15, IEC 2.5 meq/g and it shows promising data (as of Feb. 23, 2015)
- Note, at 120°C has no RH because AFCC ran test without back pressure
- The theoretical RH limit at 120°C without backpressure is around 33%
- Tom's group is building a system to run at 120°C with RH control

		NRE211		SNL	
Temperature	RH	Conditioning Time (hours)	Conductivity (S/cm)	Conditioning Time (hours)	Conductivity (S/cm)
85 C	30	24	9.59E-03	114	9.95E-03
	50	4	3.65E-02	4	5.13E-02
	95	3.25	1.79E-01	3.25	5.80E-01
120C	-	7.5	2.56E-02	7.5	4.79E-02

This membrane has nearly 2x the conductivity of NRE211 at 120°C at approximately 30% RH
Membrane is 30 micrometers ∴ ASR = 0.06 ohm•cm² at 120°C and 30%RH! Accomplished Go-No Go!

Accomplishments



ORNL has made MEA's with SDAPP

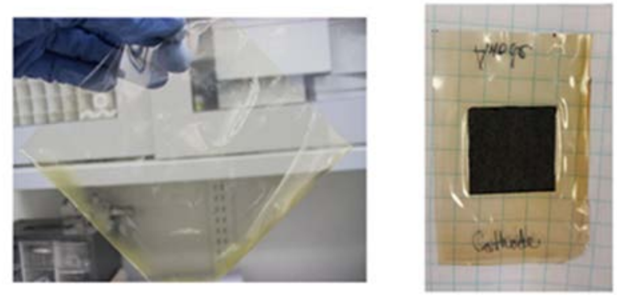
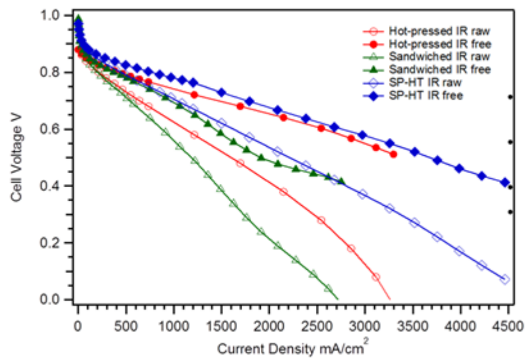


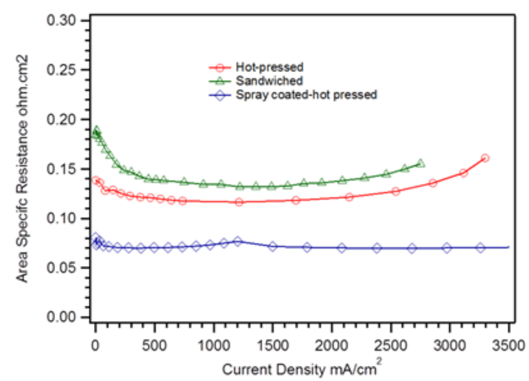
Figure 4a. Post sulfonated Diels Alder poly(phenylene) film and structure

Figure 4b. MEA fabricated by ORNL of the post sulfonated Diels Alder poly(phenylene) film



- Cathode 0.4 mg Pt/cm2; Anode 0.2 mg Pt/cm2;
- Cell/Cathode/Anode: 80/80/80˚C ; RH=100%;
- H2 and O2 flow rate: 200sccm;
- Backpressure 30 psi.

Figure 5a. Polarization curves of Sandwiched (green), Hot Pressed (red) and Spray painted hot press (blue) MEAs of SDAPP



- Cathode 0.4 mg Pt/cm2; Anode 0.2 mg Pt/cm2;
- Cell/Cathode/Anode: 80/80/80˚C ; RH=100%;
- H2 and O2 flow rate: 200sccm;
- Backpressure 30 psi.

Figure 5b. Area specific resistance of Sandwiched (green), Hot Pressed (red) and Spray painted hot press (blue) MEAs of SDAPP

ORNL have begun fabricating MEAs of the block co-polymers and will begin testing soon

Collaborations

Institutions	Type	Extent	Role and Importance
Sandia National Laboratory	Federal Laboratory	Major	▪ *DOE Hydrogen and Fuel Cell Program (Prime)* ▪ Synthesis and preparation of membranes
Oak Ridge National Laboratory	Federal Laboratory	Major	▪ *DOE Hydrogen and Fuel Cell Program (Sub)* ▪ Proton conductivity ▪ MEA fabrication and testing
Automotive Fuel Cell Cooperation	Industry	Major	▪ Proton conductivity ▪ MEA fabrication and testing ▪ Industry interest

Remaining Challenges and Barriers

- Synthesized block co-polymer that has shown good conductivity (ASR = 0.06 ohm cm^2) at high temperature (120^oC) and low RH (approx. 30%). Although MEAs have been fabricated, actual running performance at 120^oC still needs to be completed and compared to Nafion.

- Durability testing will be performed by running cell constantly at 120^oC and 30% RH for 100hrs; will MEA be durable enough to produce constant power output under these conditions?

Proposed Future Work

1. Testing of block co-polymer MEAs at high T and low RH

2. Depending on results from 1 we will either scale the chemistry so AFCC can do larger testing (25 cm^2 or possibly stack testing), further optimize MEA fabrication for high temperature (120^{o}C) or modify hydrophobic domain so more compatible with PFSA binder.

3. Although this program was focused on 120^{o}C and 30% RH, for practical application a larger range in temperature and humidity also needs to be examined. Therefore, in addition to the "focused targets" we will also synthesize materials aimed for broader use.

Technology Transfer Activities

- SNL is currently pursing a patent on the disclosed materials
- The materials described in this work has also found use in VRFB and we are working with undisclosed industrial partners to get testing done at their facilities
- Working with DOE contractor, Sanjiv Malhotra, for tech transfer opportunities

Summary Slide

Objectives: To develop hydrocarbon membranes that can operate with minimal resistance losses at 120°C , fabricate and test MEAs using the hydrocarbon membrane at 120°C .

Relevance: Perfluorinated ionomers, such as Nafion, cannot operate effectively at 120°C due to its relatively low Tg (120-150°C). At SNL, we have developed hydrocarbon ionomers that not only have very high Tgs (>250°C) but show fuel cell performance comparable to perfluorinated ionomers.

Approach: Unique approach; employing polymers that may have architecture that may facilitate ion transport at high temperature and low RH

Accomplishments: Synthesized membranes that meet the go-no go milestone of 0.06 ohm cm^2 at 120°C and 30%RH.

Fabricated MEAs of both post sulfonated polymers and block co-polymers; tested post sulfonated polymers.

Collaborations: Oak Ridge National Laboratories and Automotive Fuel Cell Cooperation