Hydrocarbon Membrane

Project: FCP5

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
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Sandia National Laboratories

Overview

Hydrocarbon PEMFC Membrane

Timeline

- Start Date: **3/15/05**
- End date: 9/30/05
- Project Completion: 30%

Budget

- Total project funding
  - DOE share: $150K
  - Contractor share: $0K
- Funding received in FY04: $0K
- Funding for FY05: $150K

Partners

- Interactions and Collaborations - None

Technical Barriers

Direct Methanol Fuel Cells

Barriers: B,C,D,F

High Temperature Membranes for Distributed Power Applications

Barriers: A,D,I

Advanced Membrane R&D

Barriers: A,C,D,I

MEA Materials, Components, and Processes

Barriers: A,B,C

Advanced MEA Meeting 2010 Targets

Barriers: A,B,C,D

Cold Start

Barriers: A,B,C,D,H,J

Barriers and Targets

PEMFC Membrane

Table 3.4.12. Technical Targets: Membranes for Transportation Applications

Characteristic	Units	2004 Status	2005	2010	2015
Membrane Conductivity at Operating Temperature Room temperature –20°C	 S/cm S/cm S/cm	 0.10 0.07 0.01	 0.10 0.07 0.01	 0.10 0.07 0.01	 0.10 0.07 0.01
Operating Temperature	°C	≤80	≤120	≤120	≤120
Inlet water vapor partial pressure	kPa (absolute)	50	25	1.5	1.5
Oxygen cross-over[a]	mA/cm²	5	5	2	2
Hydrogen cross-over[a]	mA/cm²	5	5	2	2
Cost	$/m²	65[b]	200	40	40
Durability with cycling At operating temp of ≤80°C At operating temp of >80°C	 hours hours	 ~1000[c] not available[e]	2000	 5000[d] 2000	 5000[d] 5000[d]
Survivability	°C	–20	–30	–40	–40
Thermal cyclability in presence of condensed water		Yes	Yes	Yes	Yes

[a] Tested in MEA at 1 atm O_2 or H_2 at nominal stack operating temperature.
[b] Based on 2004 TIAX Study and will be periodically updated.
[c] Durability is being evaluated. Steady-state durability is 9,000 hours.
[d] Includes typical driving cycles.
[e] High-temperature membranes are still in a development stage and durability data are not available.

Table 3.4.14. Technical Targets: MEAs

Characteristic	Units	2004 Status	2005	2010	2015
Operating Temperature	°C	≤80	≤120	≤120	≤120
Inlet water vapor partial pressure	kPa (absolute)	50	25	1.5	1.5
Cost[a]	$/kW	40[b]	50	15	10
Durability with cycling At operating temp of ≤80°C At operating temp of >80°C	 hours hours	 ~1000[c] not available[e]	2000	 5000[d] 2000	 5000[d] 5000[d]
Survivability Temperature	°C	–20	–30	–40	–40
Total Catalyst Loading (both electrodes)[f]	g/kW (rated)	1.1	2.7	0.33	0.20
Performance @ ¼ power (0.8V)	mA/cm² mW/cm²	200 160	250 200	400 320	400 320
Performance @ rated power	mW/cm²	600	800	1280	1280
Extent of performance degradation over lifetime[g]	%	10	10	10	10
Thermal cyclability in presence of condensed water		Yes	Yes	Yes	Yes

[a] Based on 2002$ and cost projected to high-volume (500,000 stacks per year).
[b] Based on 2004 TIAX Study and will be periodically updated.
[c] Durability is being evaluated. Steady-state durability is 9,000 hours.
[d] Includes typical driving cycles.
[e] High-temperature membranes are still in a development stage and durability data are not available.
[f] Equivalent total precious metal loading (anode + cathode): 0.1 mg/cm² by 2010 at rated power. Precious metal target based on cost target of <$3/kW precious metals in MEA [@$450/troy ounce ($15/g) and loading of < 0.2 g/kW$_e$].
[g] Degradation target includes factor for tolerance of the MEA to impurities in the fuel and air supply.

Barriers Addressed

- Membrane Areal Resistance
- Operating Temperature
- Survivability (-20°C to 120°C)
- Catalyst Loading
- Fuel Cell Performance

Project Objectives

Task and Milestone Schedule

Subtask 1.1 - Low Humidity Fuel Cell PEM						
		Target	Revised	Actual	% Complete	Progress
1.0	Funding Approval	10/1/04		3/1/05		Funding Receipt dictates schedule
1.1.1	Synthesize first generation SPEA materials and characterize physical properties (DSC, TGA, DMA, IR, water-uptake, IEC, Tensile Strength, and EA).	04/05	05/05			On-Track
1.1.2	Characterize SPEA ion conductivity from 10 - 100%RH at 0^{o}C to 100^{o}C as a function of IEC.	07/05	08/05			On-Track
1.1.3	Demonstrate that first generation SPEA has an ion conductivity at 80^{o}C and 75 %RH of 0.1 $\Omega^{-1}\cdot cm^{-1}$.	09/05				On-Track
1.1.4	Initiate development of novel SPEA materials based upon activity-structure relationships for this study.	10/05				On-Track

Subtask 1.2 - SPEA Catalyst Coating Membrane Studies						
		Target	Revised	Actual	% Complete	Progress
1.2.1	Establish electrochemical activity benchmark for Nafion-based electrodes and establish test protocol for SPEA-based electrodes	03/05	06/05			On-Track
1.2.1	Establish electrochemical activity benchmark for Nafion-based electrodes and establish test protocol for SPEA-based electrodes	03/05	06/05			On-Track
1.2.2	Demonstrate the SPEA performance of a CCM with Nafion and SPEA in the electrode structure at a total catalyst loading of 0.4 mg/cm^2	05/05				On-Track
1.2.3	Demonstrate that SPEA has a Hydrogen and Oxygen crossover current of < 7 mA/cm^2 at 80 ^{o}C and 25 %RH.	07/05	08/05			On-Track
1.2.4	Demonstrate a SPEA CCM with SPEA in the electrode with a membrane aerial resistance of 0.07 $\Omega^{-1}\cdot cm^{-2}$ at 80 ^{o}C and 25 %RH.	09/05				On-Track
1.2.5	Initiate development of SPEA CCM materials with reduced reactant crossover and increased fuel cell performance over initial materials and Nafion based upon an activity-structure relationship.	10/05				On-Track

Overview

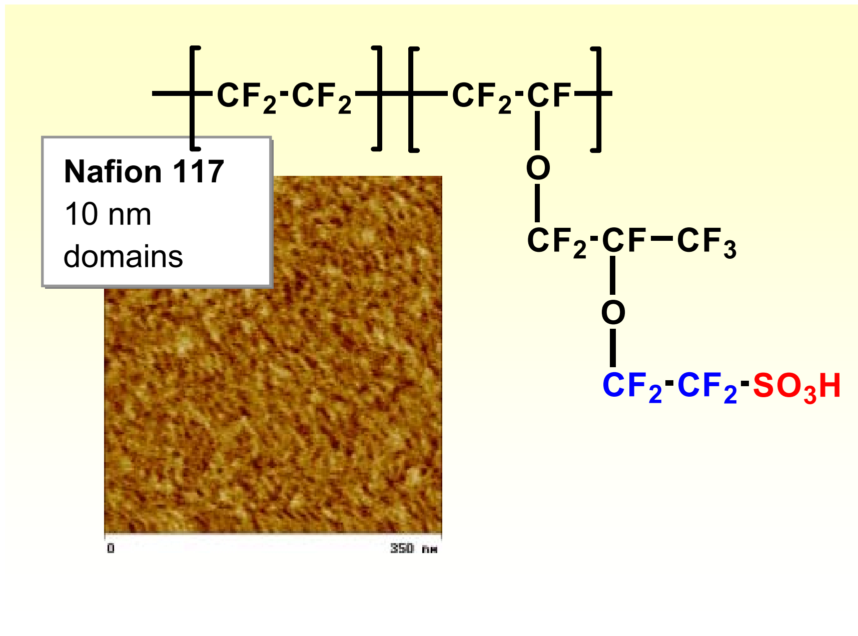
Improving Fuel Cell Membranes

Gas & Liquid Transport - *MEA*
- *Oxygen & Hydrogen*
- *Water (Cathode)*

Fuel Cross-Over - *PEM*
- *Oxygen & Hydrogen*
- *Methanol*

Stability – *PEM & MEA*
- *Temperature*
- *Chemical*
- *Dimensional & Mechanical*
- *Electrode Interface*

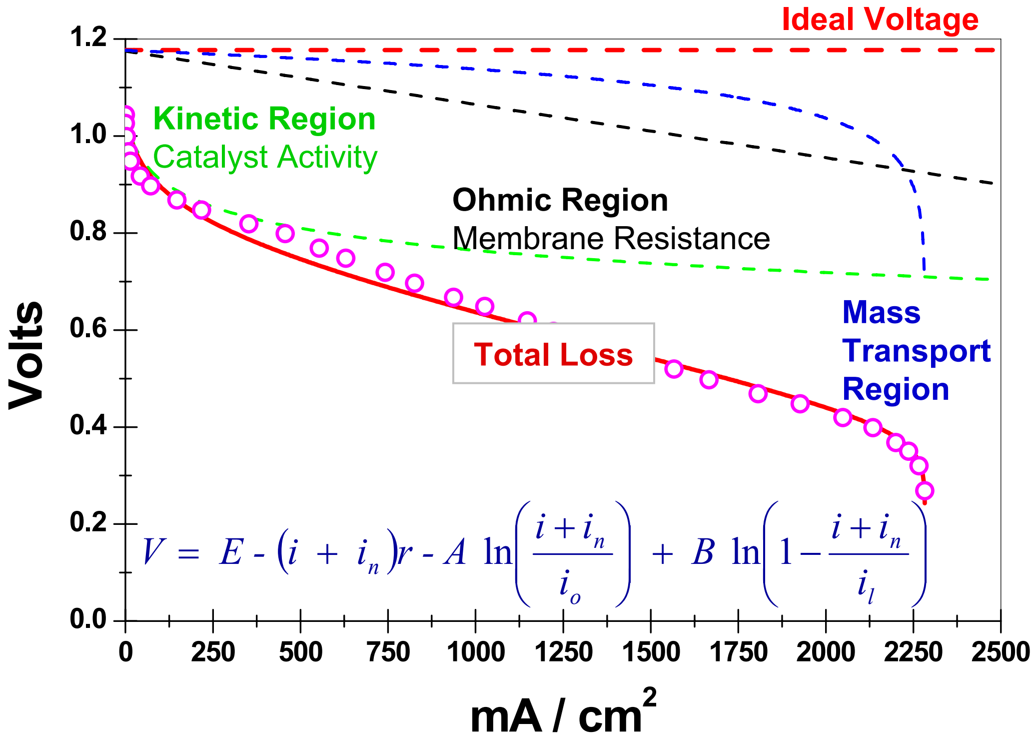
Conductivity – *PEM & MEA*
- *Low Humidity*
- *High Temperature (>120 °C)*

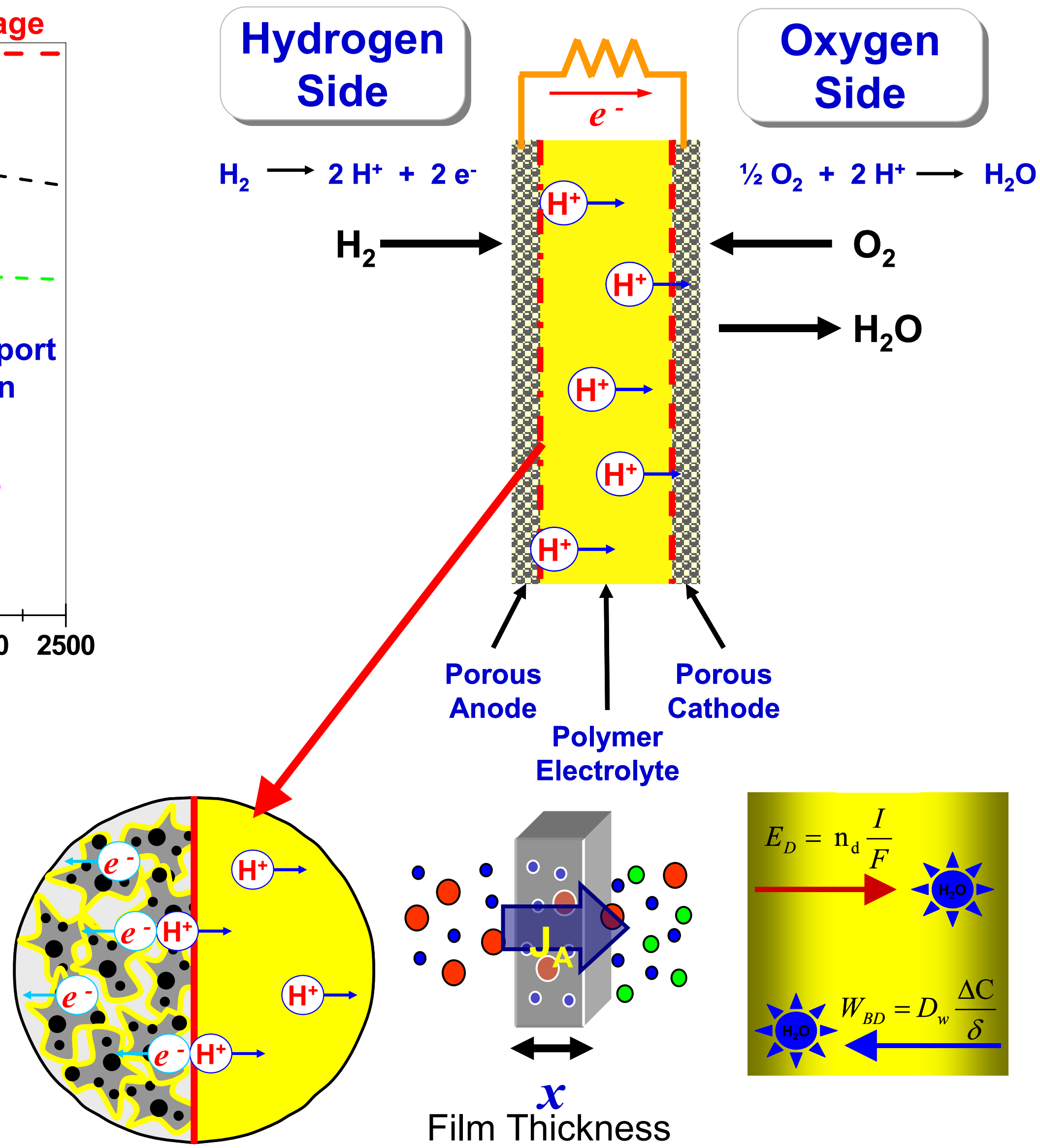


Need: Development of a *PEM that requires little to no water for proton conduction!*

PEM and MEA Challenge

Minimizing Losses





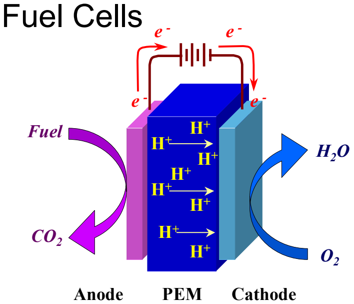
Improving Power

– Lowering iR
(PEM & Electrode *Interface*)
– Controlling Transport
(PEM, MEA, GDL)
– *Catalyst Activity*

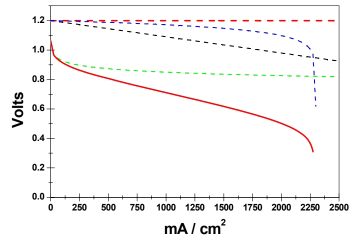
Research Approach

Sandia's PEM and MEA Research

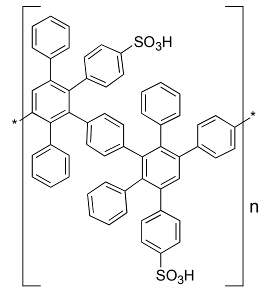
PEM Fuel Cells



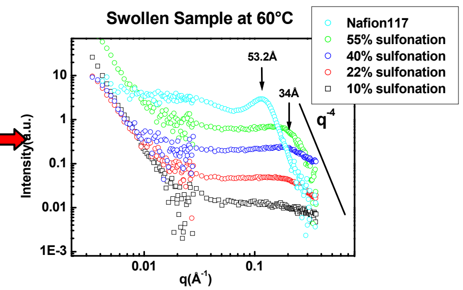
Challenges



New PEM materials



Characterization

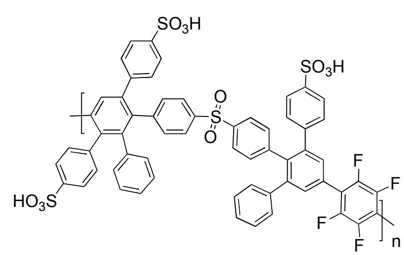


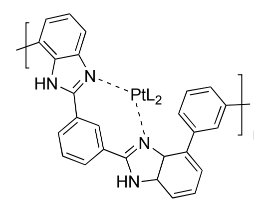
Making MEA's

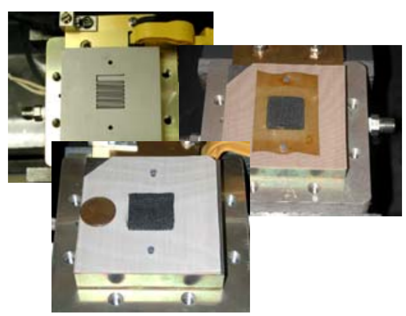
Building & Testing Fuel Cells

Next Generation Materials

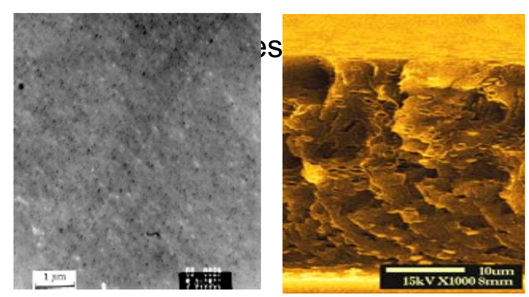
Tailored Electrode Materials







Supramolecular Templating



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Research Goal

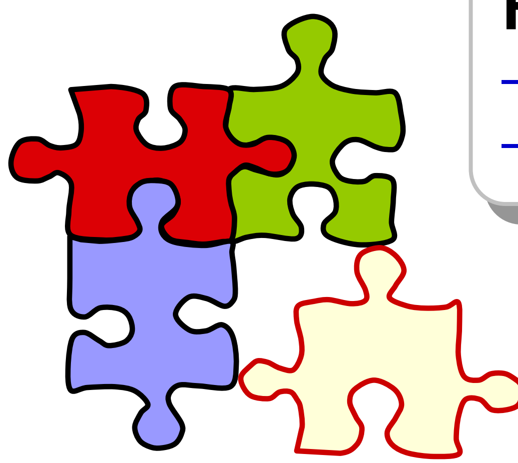
Hydrocarbon PEMFC Membrane

Research GOAL: ***Develop and Demonstrate a Low Relative Humidity PEM and MEA based upon alternative PEM technology***

– PEM & MEA Development
– Electrode Development
– Fuel Cell Testing

PEM Development
– Polymer
– Hybrid Composites

Fuel Cell Testing
– PEM & MEA Validation
– Lifetime & FC Stress Testing



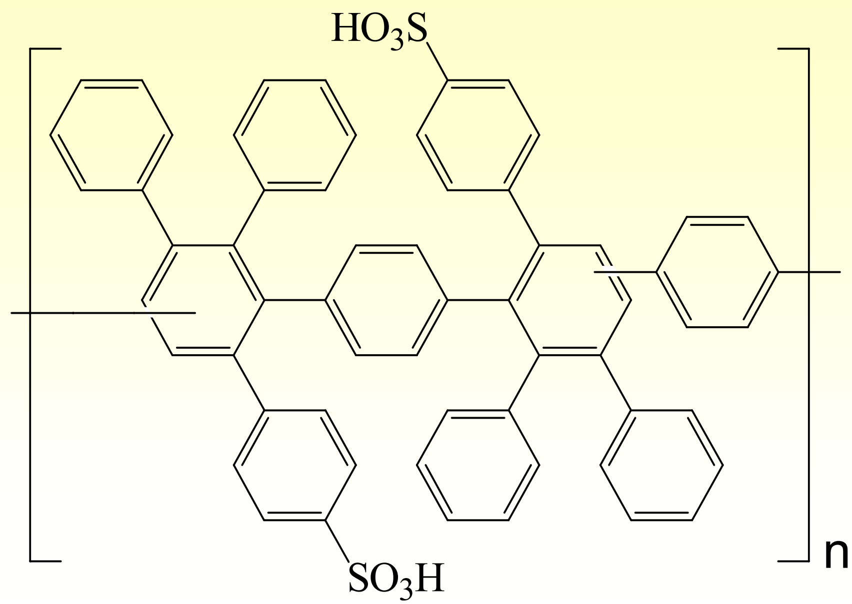
Collaborations
– Labs & Universities

Industry
– Real World Problems

Polyphenylenes

Sulfonated Diels-Alder Polymer (SDAPP)

- Thermal Stability
- Good Chemical Stability
- Low Fuel Cross-Over
- Gas Transport (*Tunable*)
- Low Interfacial Resistance (*MEA – Electrodes*)
- Chemical Diversity
- Proton Conductivity
- ***Morphology***



- Thermal Stability: 120 °C
- High Ionic Conductivity (0.1 S/cm)
- Improved Mechanical Properties (10x Stiffer)
- Cross-Over Resistance to MeOH (3x Lower)
- Membrane Electrode Assemblies (Nafion vs DA)
  - *40 % more Power at 80°C & O_2/H_2*
  - *20 % more Power at 80°C & O_2/MeOH (0.5 M)*

Thermochemical Stablility

Improving Fuel Cell Membranes

Thermal Stability

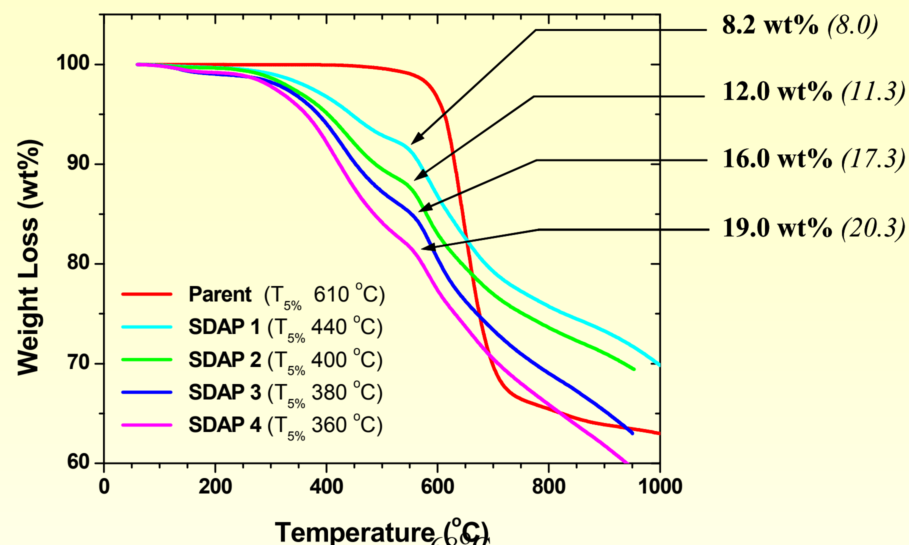
- SDAPP family demonstrates ability to retain SO3H groups and maintain its structure above 200°C as determined by TGA in air

Chemical Stability

- SDAPP survives Fenton's Test for > 2 hrs while other alternative PEM's dissolve at these conditions

IMPACT: PEM & MEA stability

Fuel Cell Stack Life!



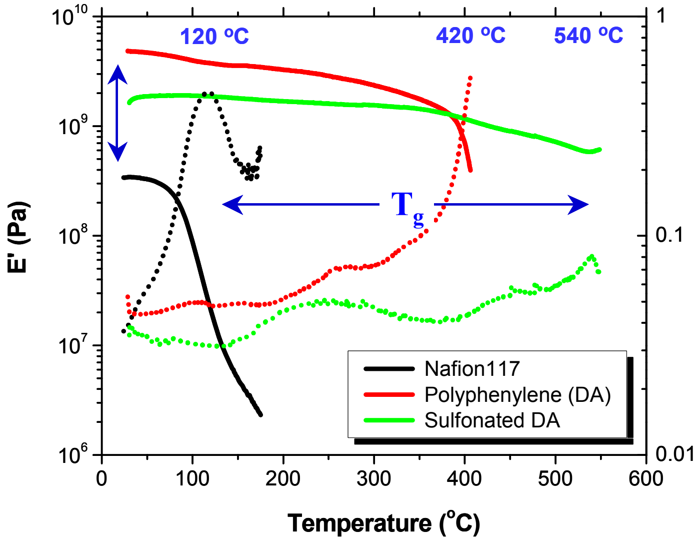
$$Fe^{+2}\ (4ppm) + HO{-}OH\ (3\%\ solution) \xrightarrow{68^{\circ}C} Fe^{+3} + \bullet OH + OH^{-}$$

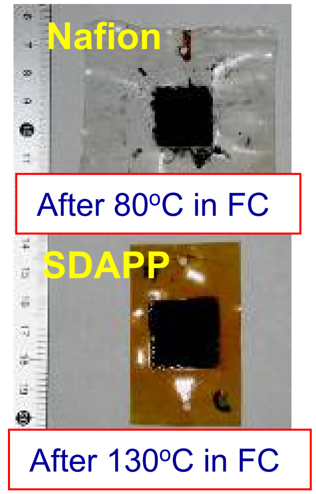
Time Hours	Weight Loss (%)	η_{int} (dL/g)
0	0	1.8
2	2	1.5
5	5	1.2
8	7	1.1
12	12	0.9

La Conti, A. B.; Hamdan, M.; McDonald, R. C. Handbook of Fuel Cells – Fundamentals, Technology and Applicatns, 2003, 647 - 662.

Fuel Cell Research

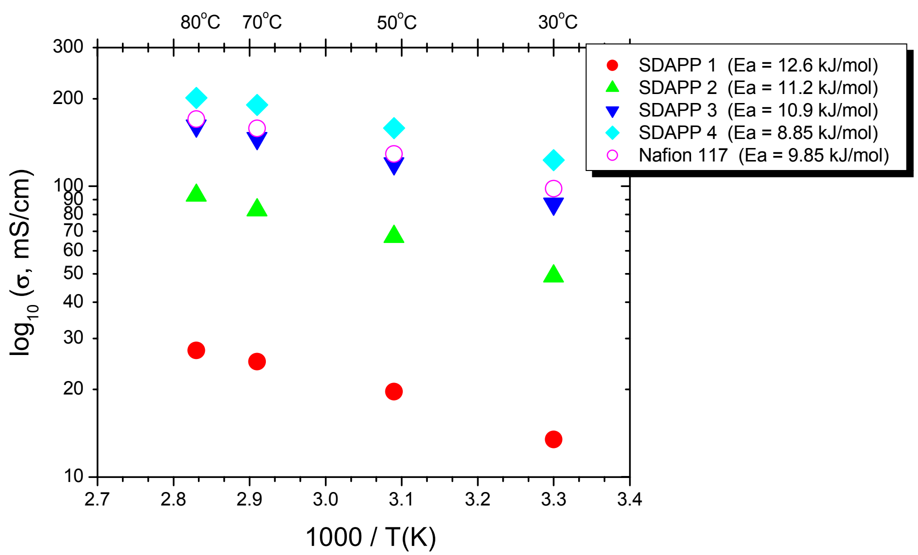
Improving Fuel Cell Membranes

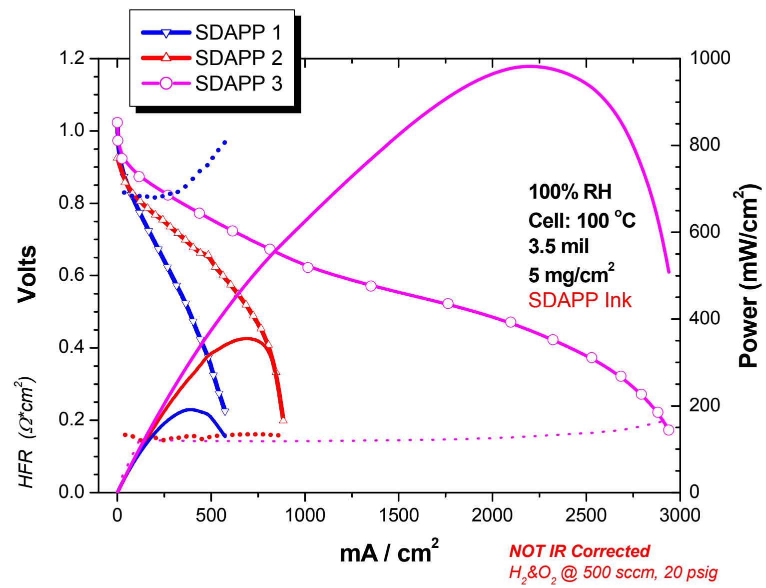




Thinner Films

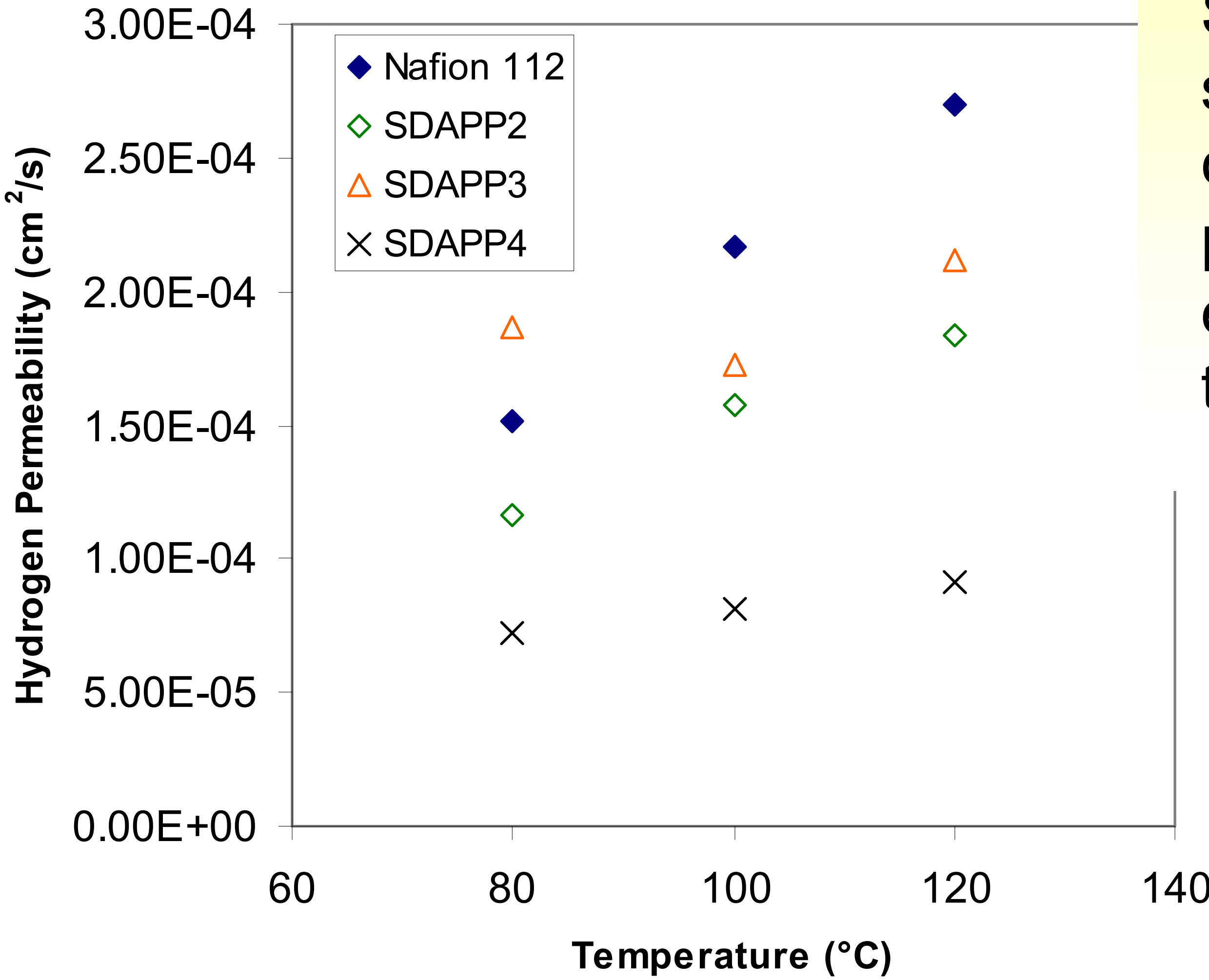
- Improved Performance
- Smaller Stacks
- Decreased $/kW





Hydrogen Crossover

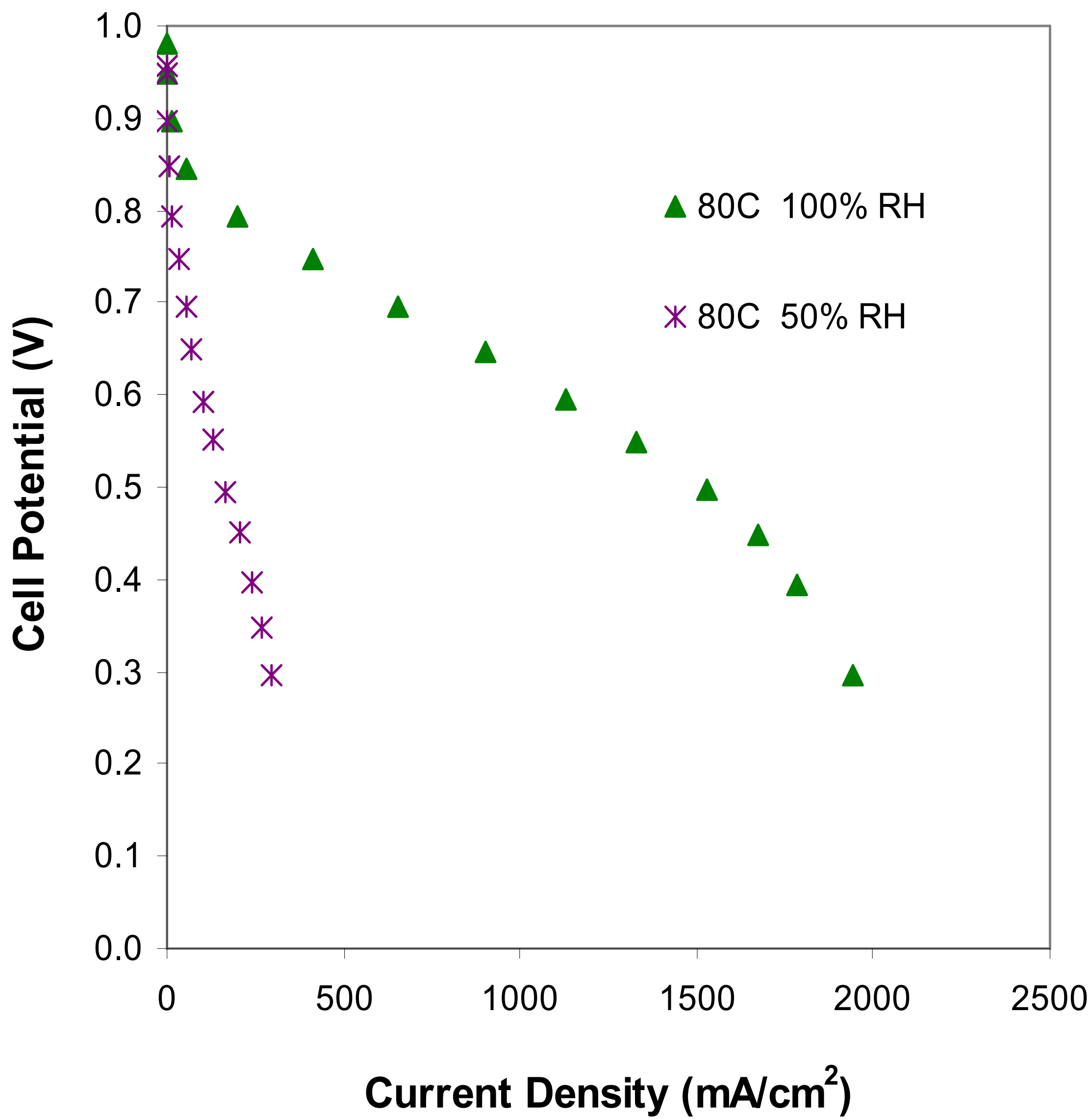
In-situ MEA Testing



SDAPP membranes show lower crossover currents and permeability than N112 especially at higher temperatures.

Fuel Cell Performance

30 wt% Nafion Binder



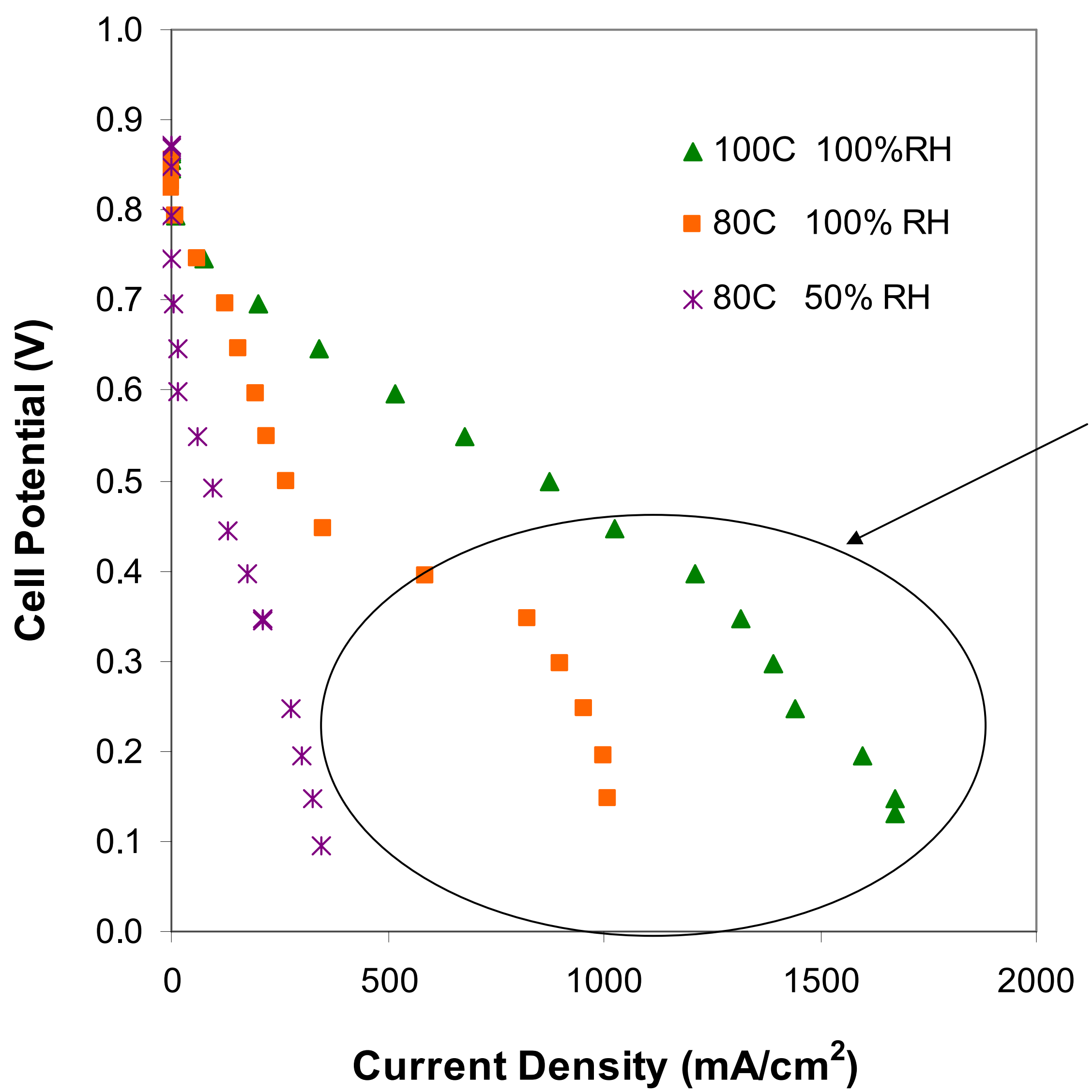
	HFR (Ω-cm^2)
80C 100% RH	0.11
80C 50% RH	0.60

Large losses in Nafion-based MEAs at low RH due to decreased membrane conductivity and proton transport resistance in electrodes.

SDAPP 2.2 meq/g IEC membrane
5.8 mil thick
Nafion 1100 electrodes
29 wt % polymer in electrodes
H2 200sccm
Air 500 sccm
20 psig

Fuel Cell Performance

30 wt% SDAPPe Binder



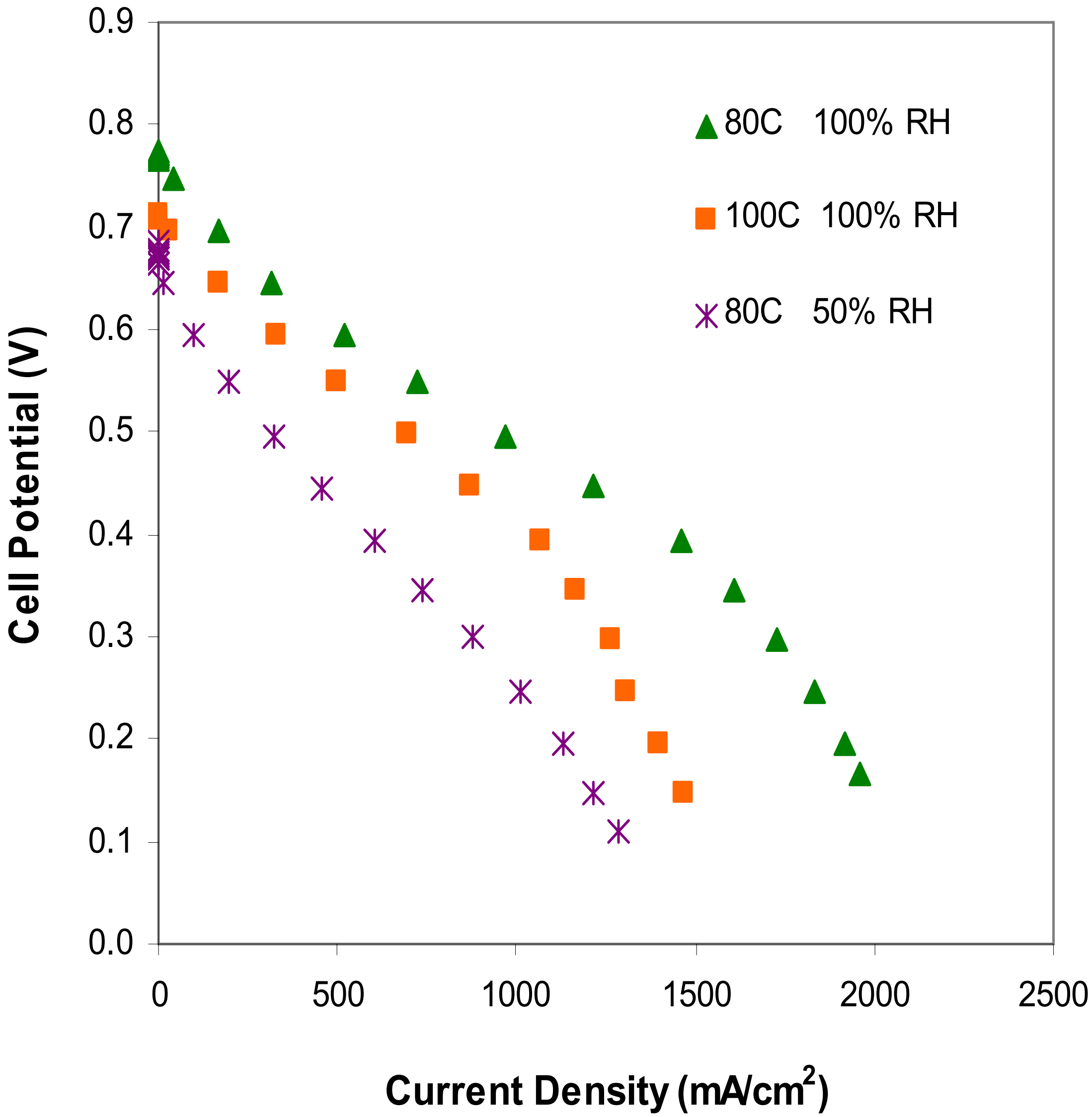
	HFR (Ω-cm^2)
80C 100% RH	0.08
100C 100% RH	0.05
80C 50% RH	0.75

30 wt % SDAPPe electrodes show two mass transport limiting steps. Increasing the operating temperature of the cell alleviates this problem. Still poor performance at 50% RH.

SDAPP 2.2 meq/g IEC membrane
1 mil thick
SDAPPe electrodes 120mS/cm
29 wt % polymer in electrodes
H2 200sccm
Air 500 sccm
20 psig

Fuel Cell Performance

15 wt% SDAPPe Electrode Binder



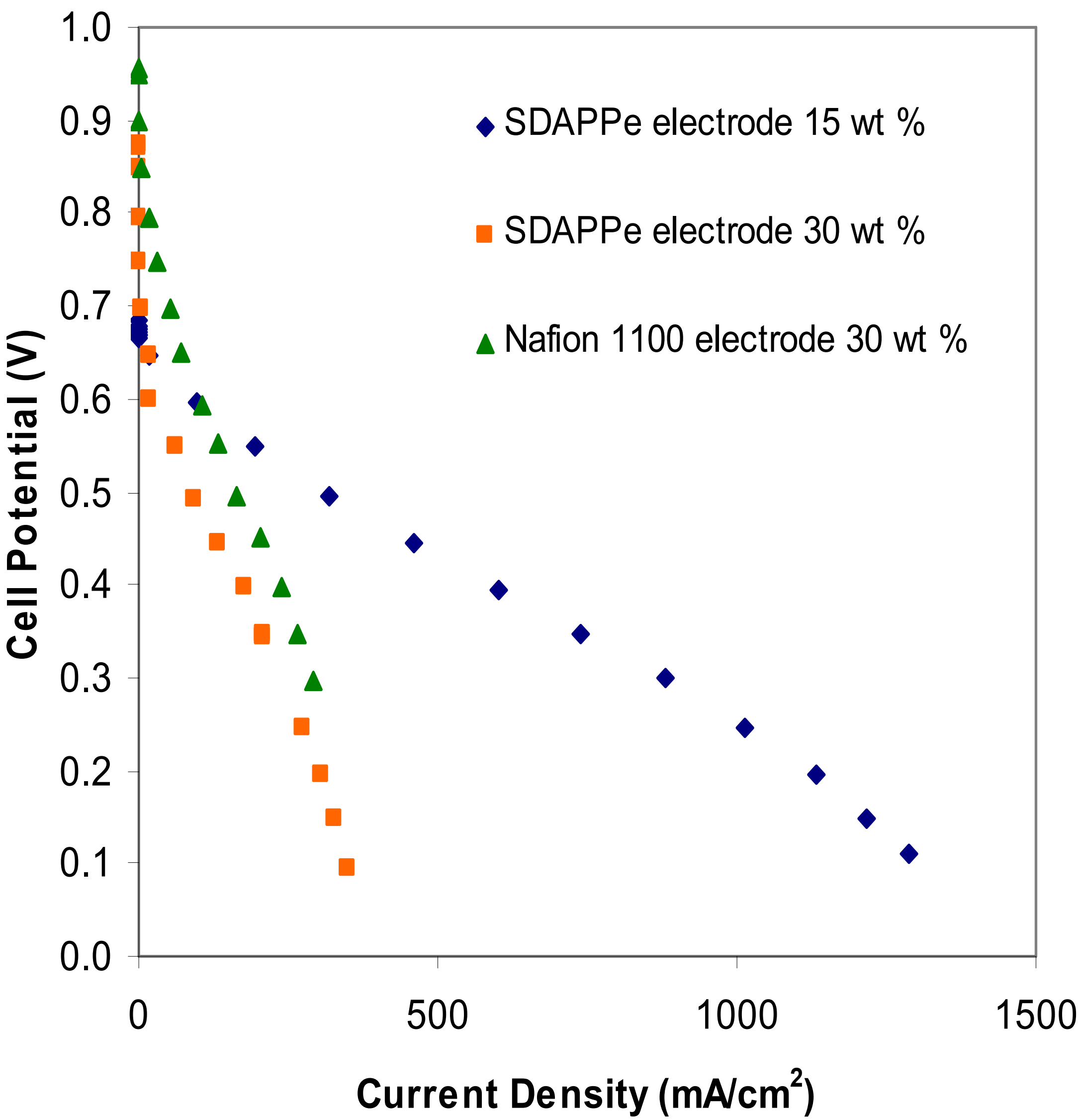
	HFR (Ω-cm^2)
80C 100% RH	0.06
100C 100% RH	0.10
80C 50% RH	0.21

No mass transport limiting behavior at intermediate current densities with 15 wt % SDAPPe in electrode. Also 50% RH performance is improved with lower wt % ionomer in electrode layer.

SDAPP4 Membrane
0.8 mil thick
SDAPPe electrodes 120mS/cm
15 wt % polymer in electrodes
H_2 200sccm
Air 500 sccm
20 psig

Fuel Cell Performance

Nafion vs. SDAPPe Electrodes: 80°C and 50% RH



Catalyst layers with greater ionomer binder contents show large activation and transport losses at low RH.

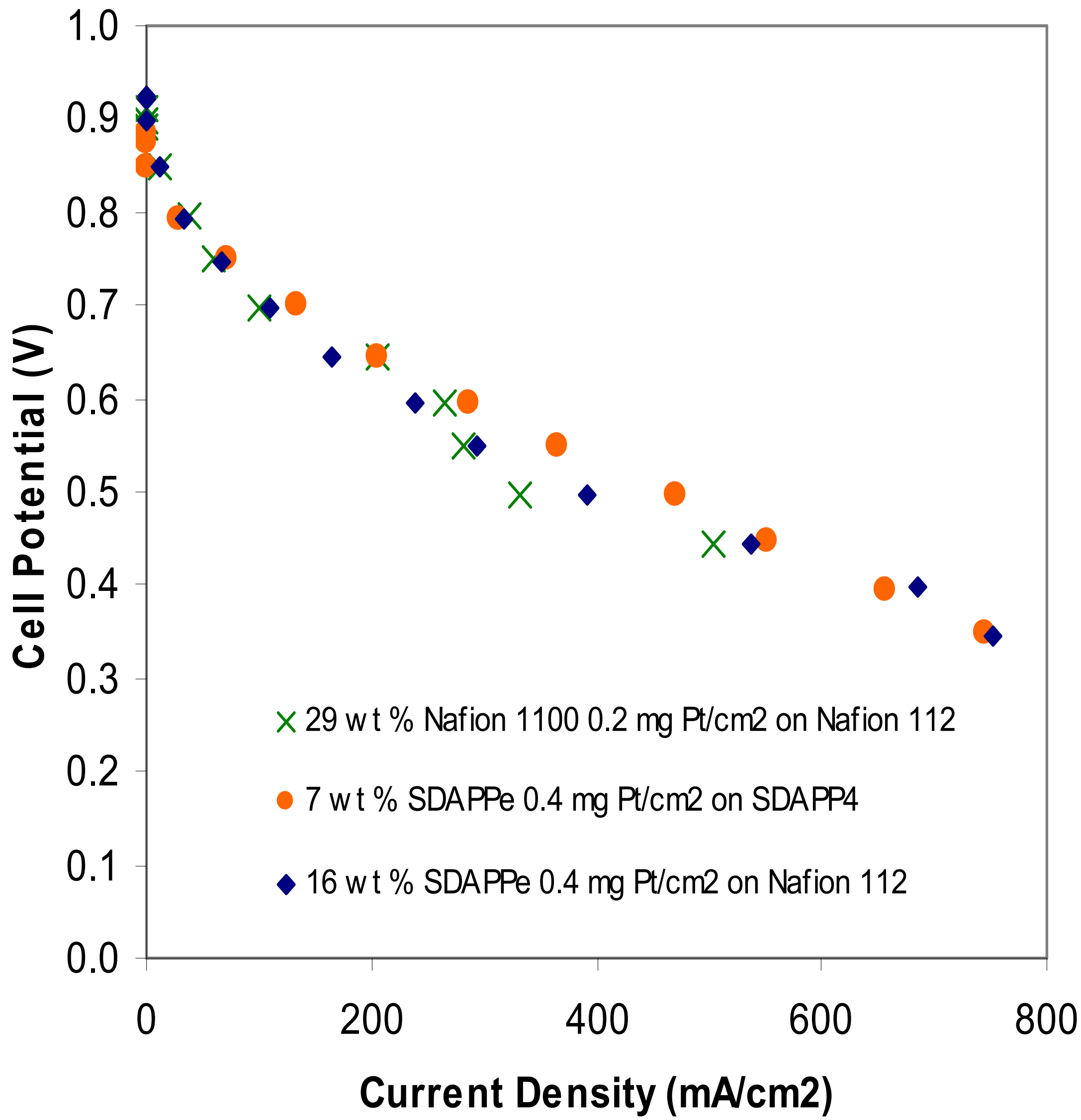
15 wt % ionomer binder in the electrode shows superior mass transfer performance, but there are problems in the activation region.

SDAPP4 Membrane

1 mil thick
80°C cell temperature
H2 200sccm
Air 500 sccm
20 psig
50% RH gas feeds

Fuel Cell Performance

SDAPPe Electrodes: 120°C and 50% RH



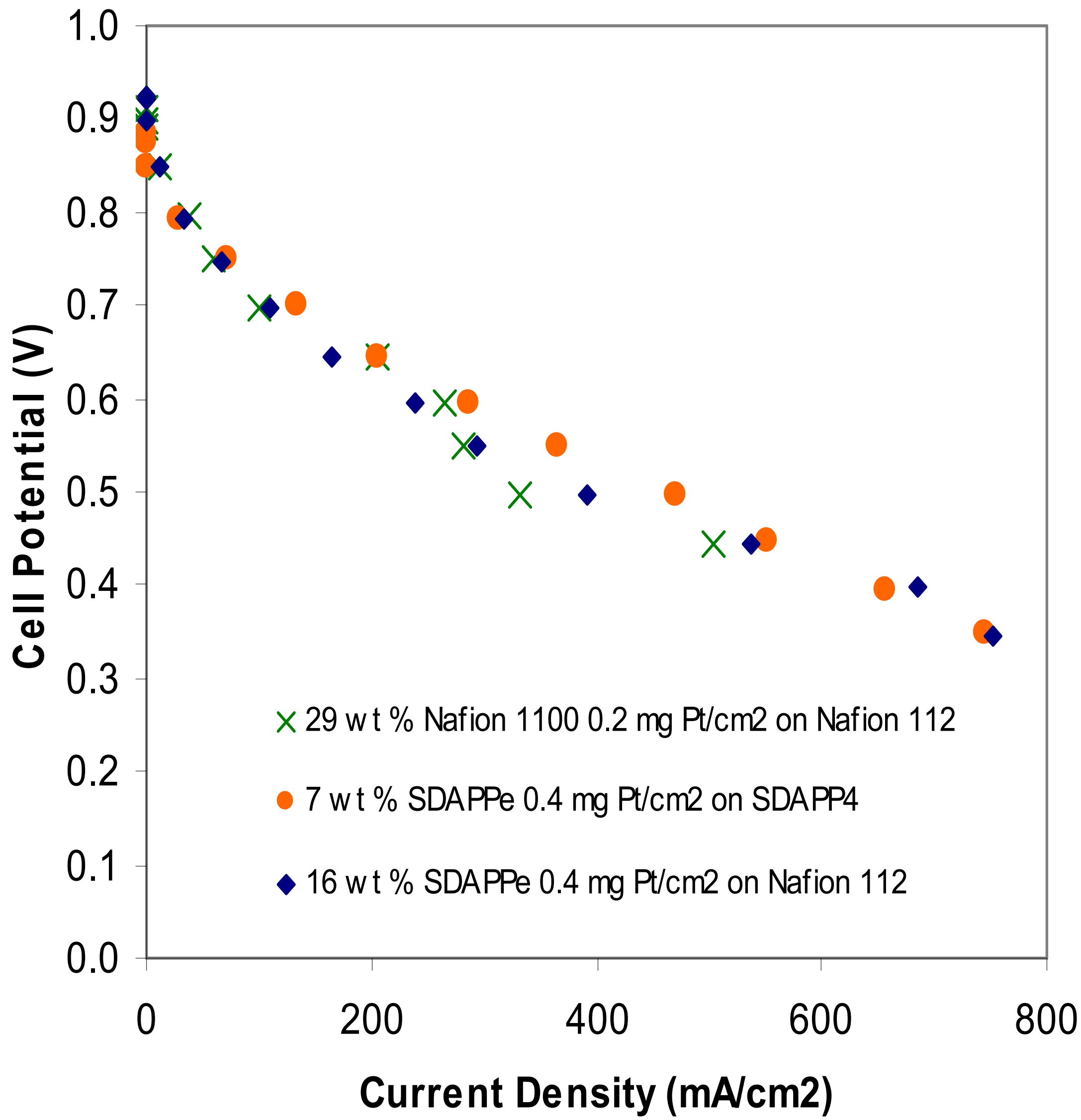
Low ionomer binder content in SDAPP-based electrodes may provide routes to high performance electrodes at low RH.

Can currently match Nafion performance with an MEA based entirely on SDAPP with slightly higher Pt loadings.

120°C Cell temperature
H2 200sccm
Air 500 sccm
20 psig
50% RH gas feeds

Fuel Cell Performance

SDAPPe Electrodes: 120°C and 50% RH



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Can currently match Nafion performance with an MEA based entirely on SDAPP with slightly higher Pt loadings.

120°C Cell temperature
H2 200sccm
Air 500 sccm
20 psig
50% RH gas feeds

Fuel Cell Performance

Elevated Temperature: 120°C and 50% RH

Thermal Stability

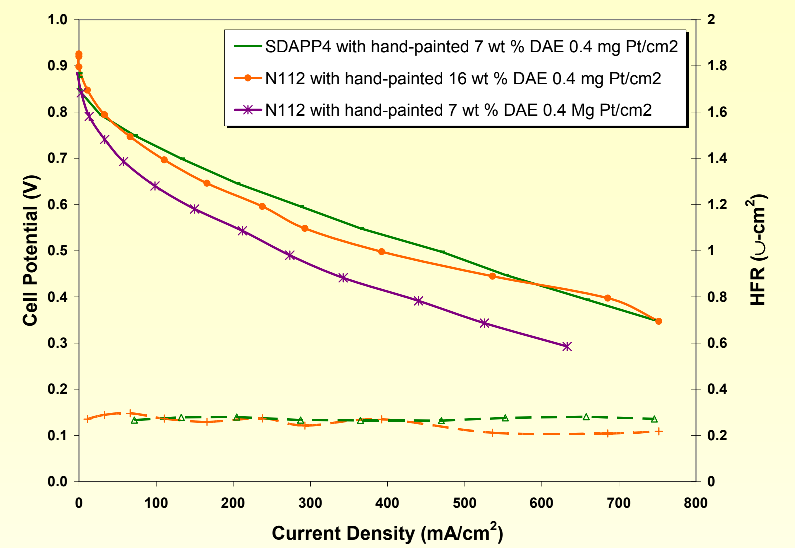
- SDAPP family demonstrates ability to retain SO3H groups and maintain its structure above 200°C as determined by TGA in air

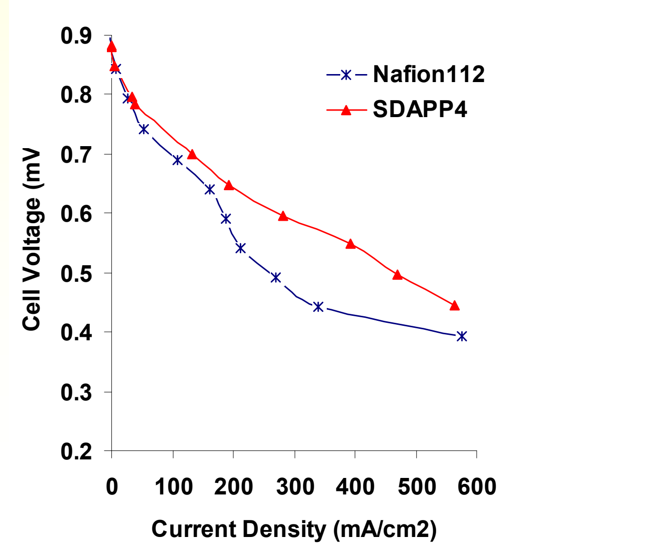
Chemical Stability

- SDAPP survives Fenton's Test for > 2 hrs while other alternative PEM's dissolve at these conditions

IMPACT: PEM & MEA stability

Fuel Cell Stack Life!





0.4 mg/cm2 (Pt Black)
A/C: H2 (200sccm) and Air (500sccm)

Future Work

Improving Fuel Cell Membranes

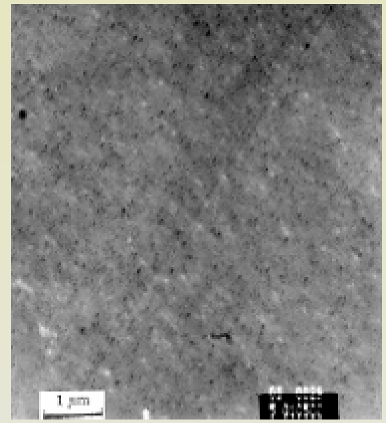
Enhanced Acidity
- *Acid Groups*

Enhaced Hydration Properties
- *Imidazole Functionalized SDAPP*
- *Inorganic Domain Type*

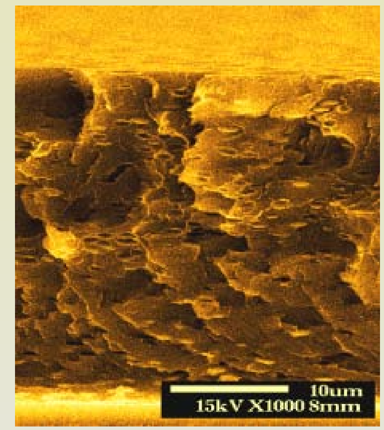
Inorganic Domain Conductivity
- *HPAs & HPA Sol-Gel Materials*

Polymer Structure-Property
- *Controlled Sulfonation*
- *Structured Materials*
- *Crosslinking*
- *Blends*

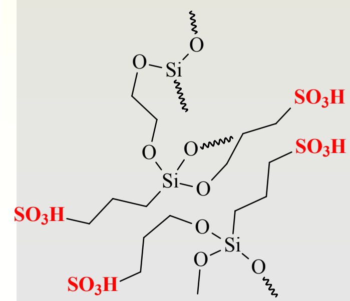
Polymer Hybrid Composites

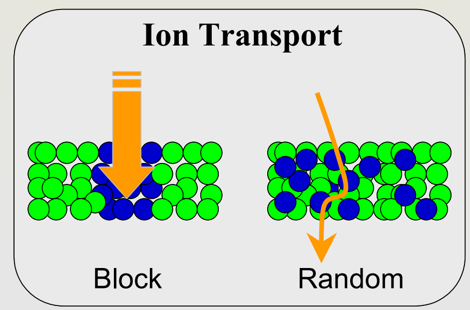


Inorganic



Polymer





Proton - Conductive Inorganic Domains

Future Work

Controlling Gas Transport

Gas Transport (*Tunable*)

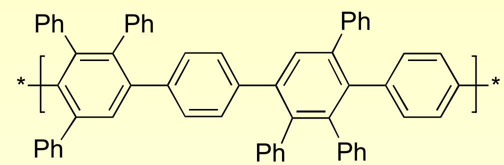
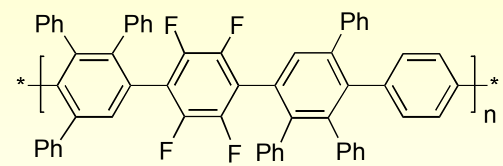
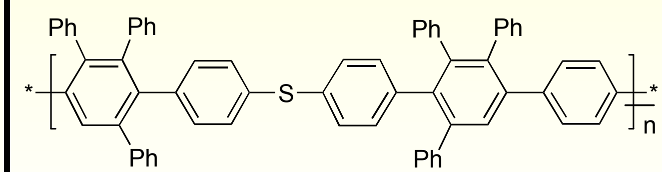
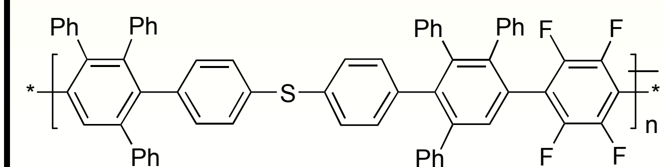
- SDAPP has diversity in chemistry to address unique PEM and MEA needs

Lower Interfacial Resistance

- SDAPP can be substituted into electrode structure

Stability

- SDAPP has good thermal and chemical stability, high Tg, and high modulus that will enable the formation of mechanically stable thin films

	H_2	O_2
	94	19
	99	24.5
	5.2	
		270

Barrer = $10^{-10} cm^3/cm^2$ s cm of Hg (at STP)

Fujimoto, C.; Loy, D.A.; Cornelius, C; Wheeler, D. R.; Jamison, G. M. Manuscript in Preparation, *J. Membrane Sci.*

Conclusions

Improving Fuel Cell Membranes

- Demonstrated Promising H_2 Fuel Cell Performance with 1st Generation SDAPP Family from RT to 120^{o}C and recognize need for improved systems.
- Post-Sulfonation Crude… Future work will utilize functionalized monomers that will lead to controlled PEM morphology
- Capabilities Established: Material design and synthesis, characterization, device testing, system performance measurements, and predictions
- Opportunity to arrive at improved materials through newer generation materials.

Project Safety

- Primary Hazard Screening in place for all labs and workers are experienced with the use of equipment and chemicals.

- Safeguards in place to minimize electric hazards. Hydrogen and oxygen are kept separate and vented into hoods.

- Training and standard operating procedure for all test equipment in all labs.

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

Hydrogen leaks from fuel cell and its combining with Oxygen or other oxidant sources.

Our approach to deal with this hazard is:

We have removed all oxidants from the lab. Our fuel cell lab is sole designated for fuel cell research. Pressure release valves and flow restriction valves are located on all gas cylinders and oxygen and hydrogen cylinders are located away from each other as prescribed by our ES&H staff. All exhausted gases from the fuel cell are vented separately into a ventilation hood to dilute hydrogen below its explosion limit.