Hydrocarbon Membrane

Project: FC7

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy under contract DE-AC04-94AL85000.

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Overview

Hydrocarbon Membrane

Timeline

- Start Date: **3/15/05**
- End date: 9/30/06
- **Project Completion (FY06): 50%**

Budget

- Total project funding
  - DOE share: $300K
  - Contractor share: $0K
- Funding received in FY05: $150K
- **Funding for FY06: $150K**

Partners

- Interactions and Collaborations

  Automotive & FC Stack Producer (Independent Testing & DOE Call Partners)

  Academia (Virginia Tech, CWRU, Clemson, UK - Jun Jin)

Technical Barriers

Barriers: A, B, C, D, F, I

- High Temperature Membranes for Distributed Power Applications
- Advanced Membrane R&D
- Membrane Materials, Components, Processes
- Advanced MEA Meeting 2010 Targets
- Direct Methanol Fuel Cells
- Auxiliary/Portable Power

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Objectives

Research Program Goals – DOE 2010 Targets

Overall	• Membrane Conductivity (0.1, 0.7, & 0.01 S/cm @ Target, RT, -20^{o}C) • Operating Temperature (<= 120^{o}C & 1.5 kPa abs) • Catalyst Loading (0.3 g/kW) • Fuel Cell Performance (400 mA/cm^2 and 320 mW/cm^2 @ 0.8V) • Membrane cost (\$40/m^2) • Hydrogen and Oxygen Crossover (2 mA/cm^2) • Survivability (-40^{o}C to 120^{o}C) • Durability (5000 hrs @ <= 80^{o}C & 2000 hrs @ >= 80^{o}C)
2006	• Synthesize and Characterize SDAPP physical properties. • Demonstrate SDAPP (Sulfonated Diels-Alder Polyphenylene) PEM fuel cell performance (1st Generation). • Continue developing structure-property performance PEM and fuel cell relationships to create improvements in PEM materials.
2007	• Membrane Conductivity and Fuel Cell Performance • Survivability (-40 ^{o}C to 120 ^{o}C), Degradation, and Durability Studies • Catalyst Loading and Membrane Cost

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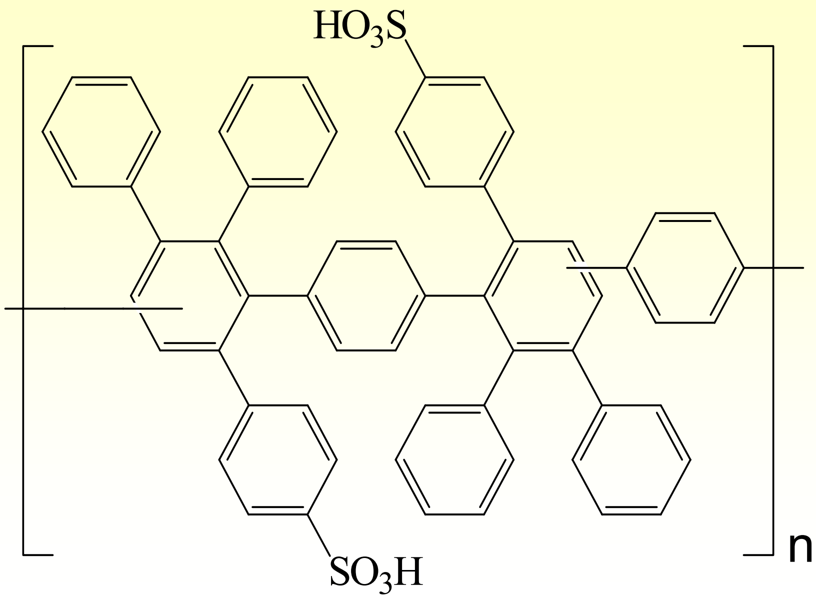
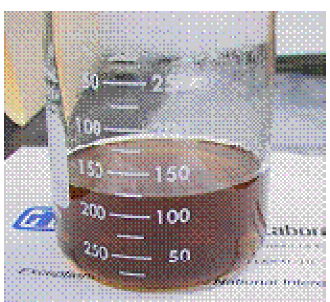
Approach

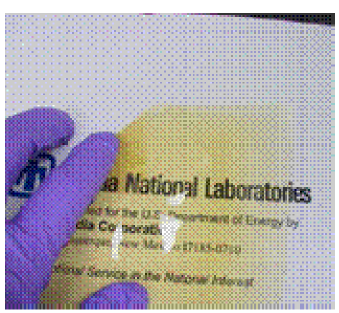
Hydrocarbon Membrane - SDAPP

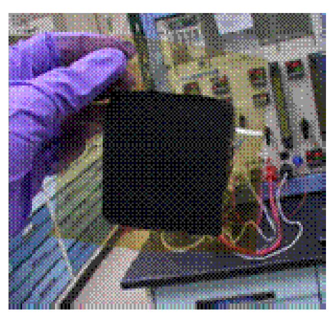


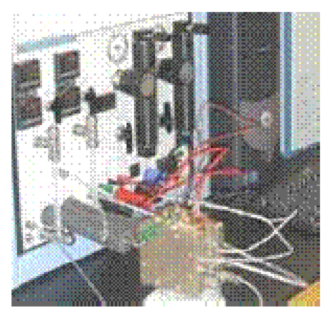
1st Generation Sulfonated Diels-Alder Polyphenylene (SDAPP)

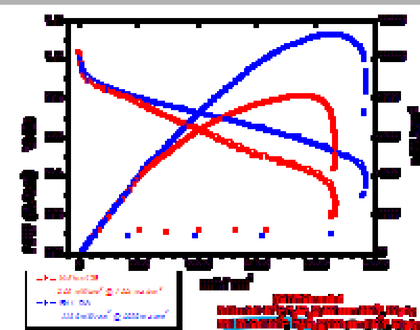
- Thermal & Chemical Stability
  - (*Thermal, Chemical, Processing)*
- Low Fuel Cross-Over
  - *(Low O2 & H2 - Tunable)*
- Gas Transport
  - *(Electrode & PEM)*
- Low Interfacial Resistance
  - (*MEA – Electrodes*)
- Chemical Diversity and High MW
- Proton Conductivity & Morphology





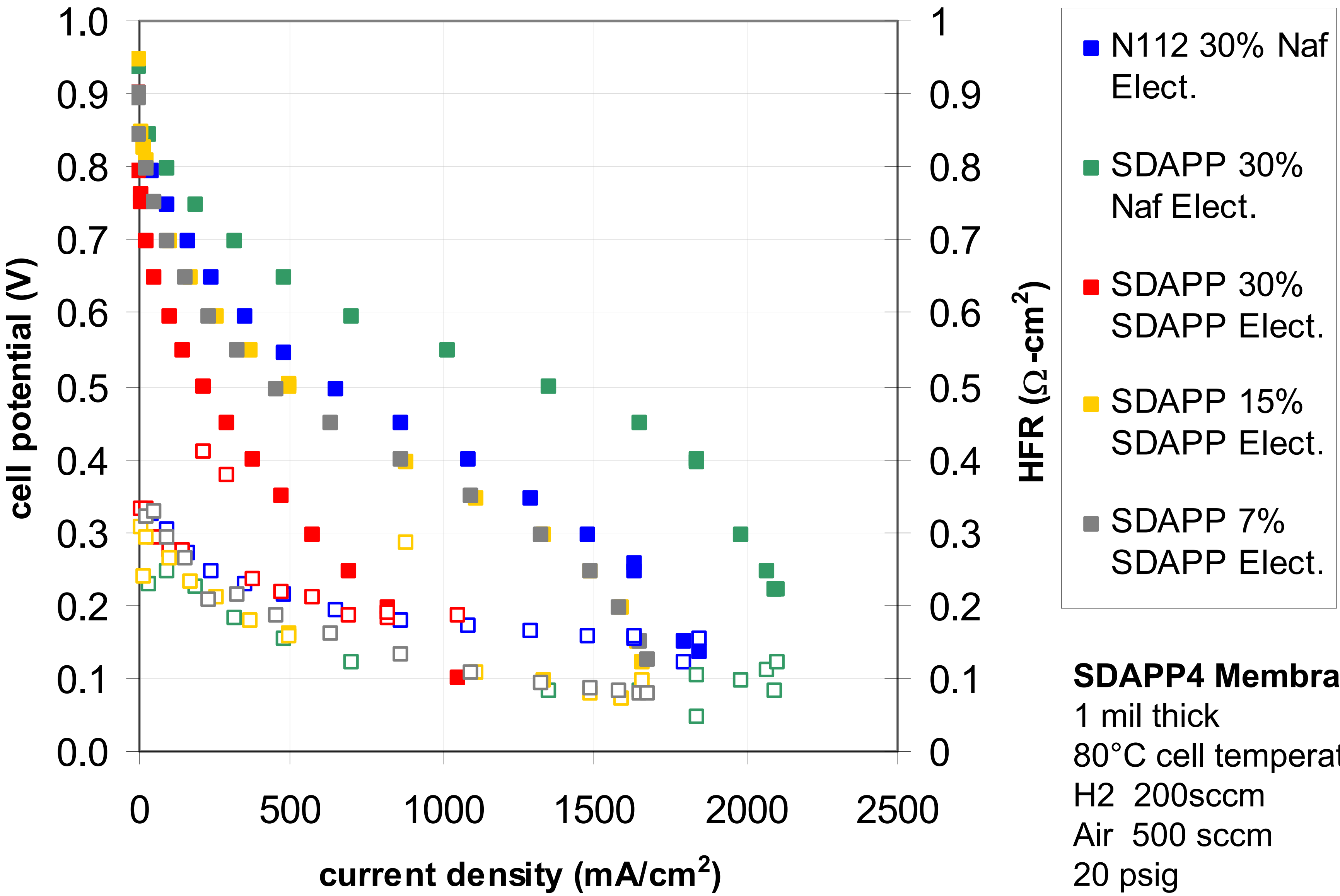






Fuel Cell Performance

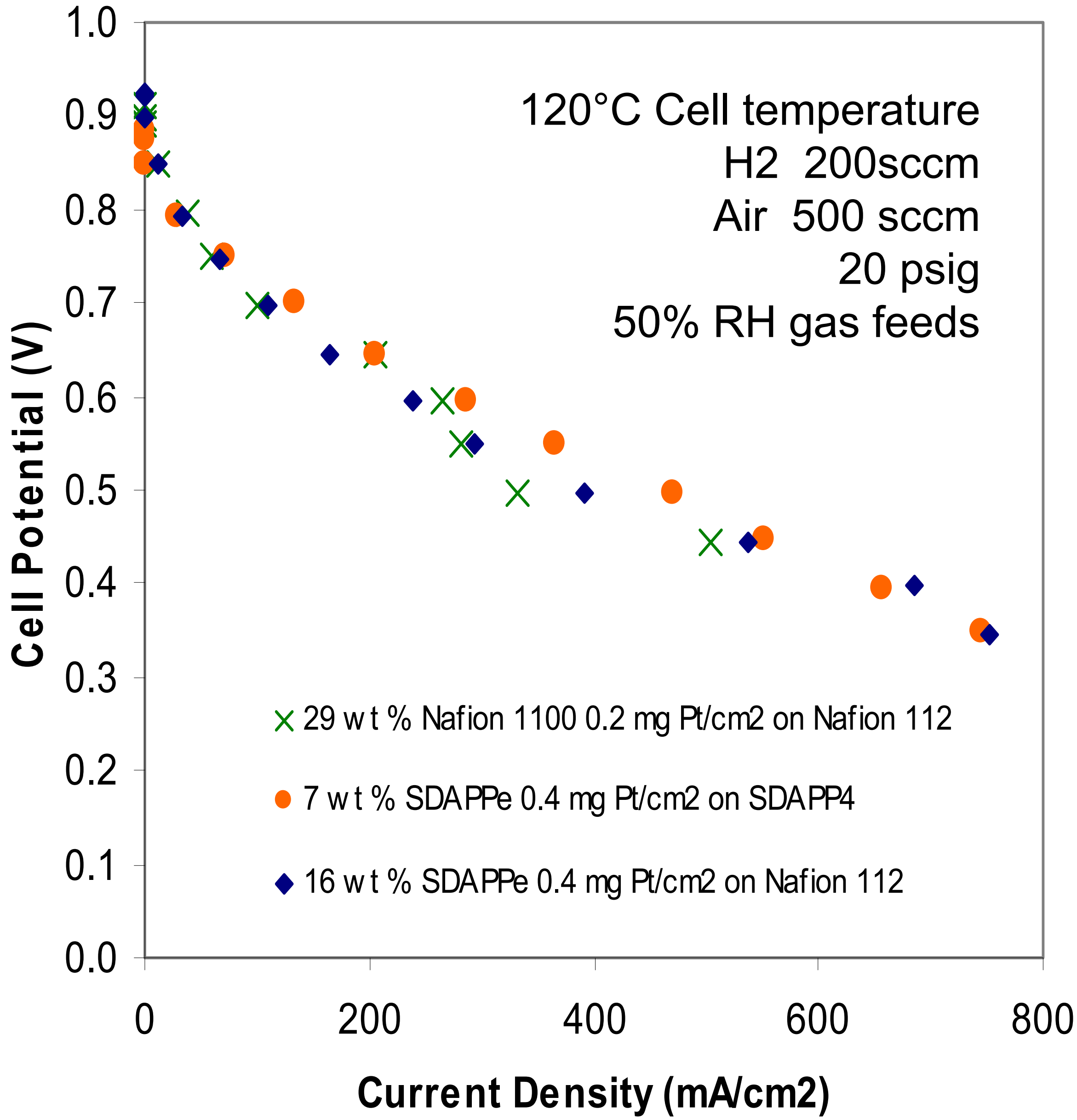
Development of Non-Nafion MEAs

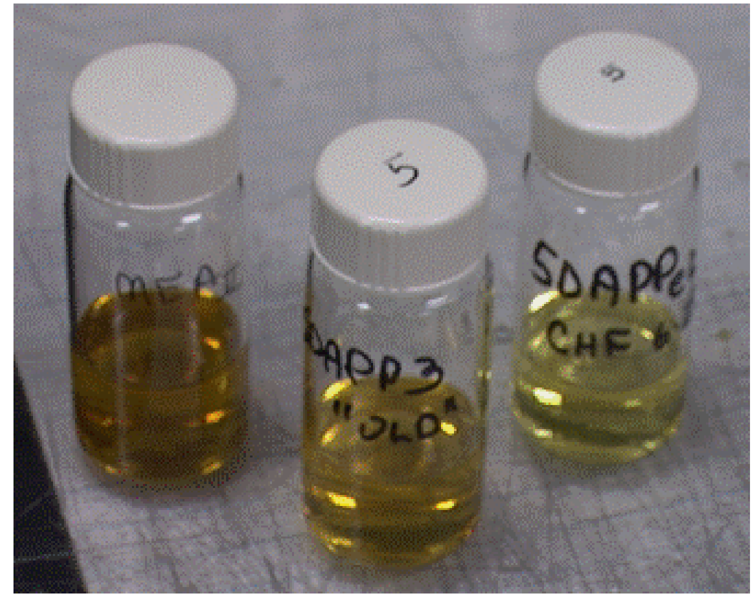


SDAPP4 Membrane
1 mil thick
80°C cell temperature
H2 200sccm
Air 500 sccm
20 psig
50% RH gas feeds

Fuel Cell Performance

Development of Non-Nafion MEAs





- Highly sulfonated samples do show good high temperature & low RH fuel cell performance.
- Enhanced performance due in part to our new alternative binders.

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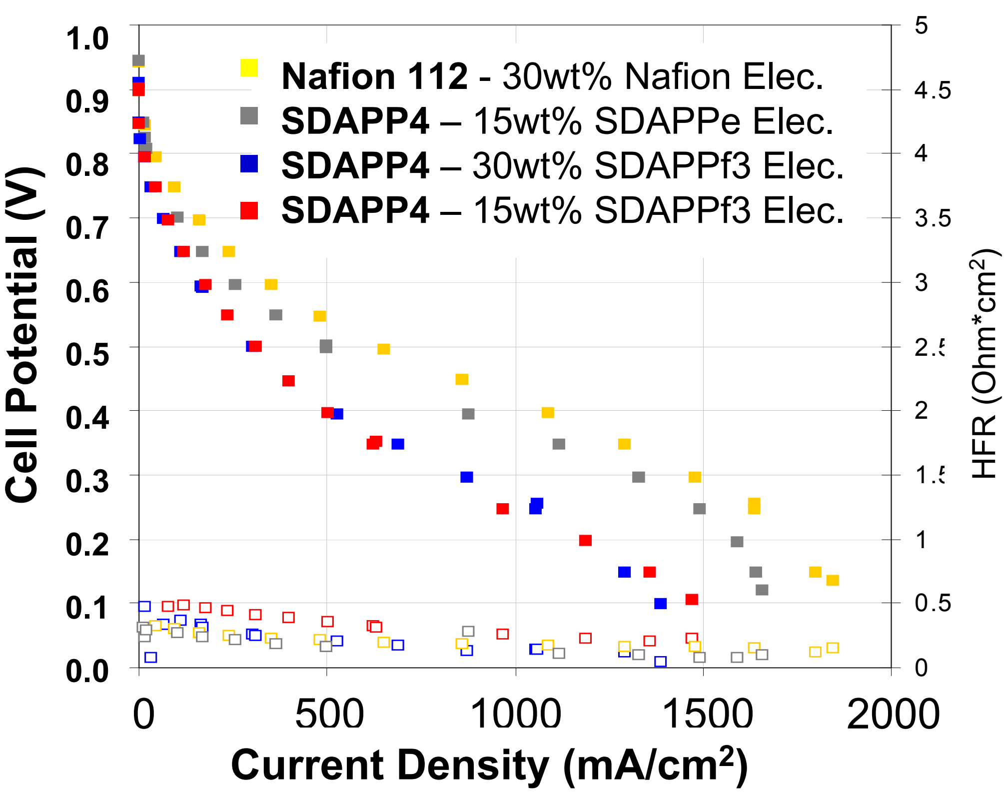
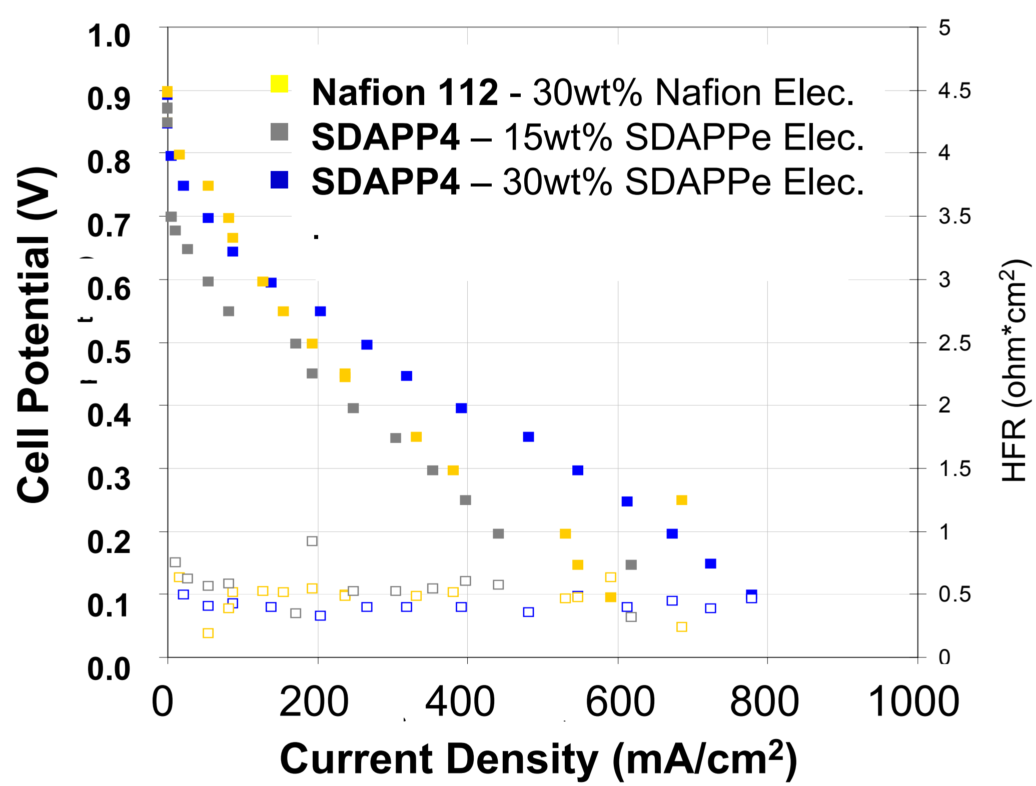
Fuel Cell Performance

50% RH @ 80 ^oC and 120 ^oC

80^{o}C



120^{o}C



Substituting SDAPPe and SDAPPf within the electrode layers can improve or approach same performance as a Nafion based MEA. However, fuel cell performance is dependent on electrolyte type, loading, and hydrogen fuel cell operating temperature.

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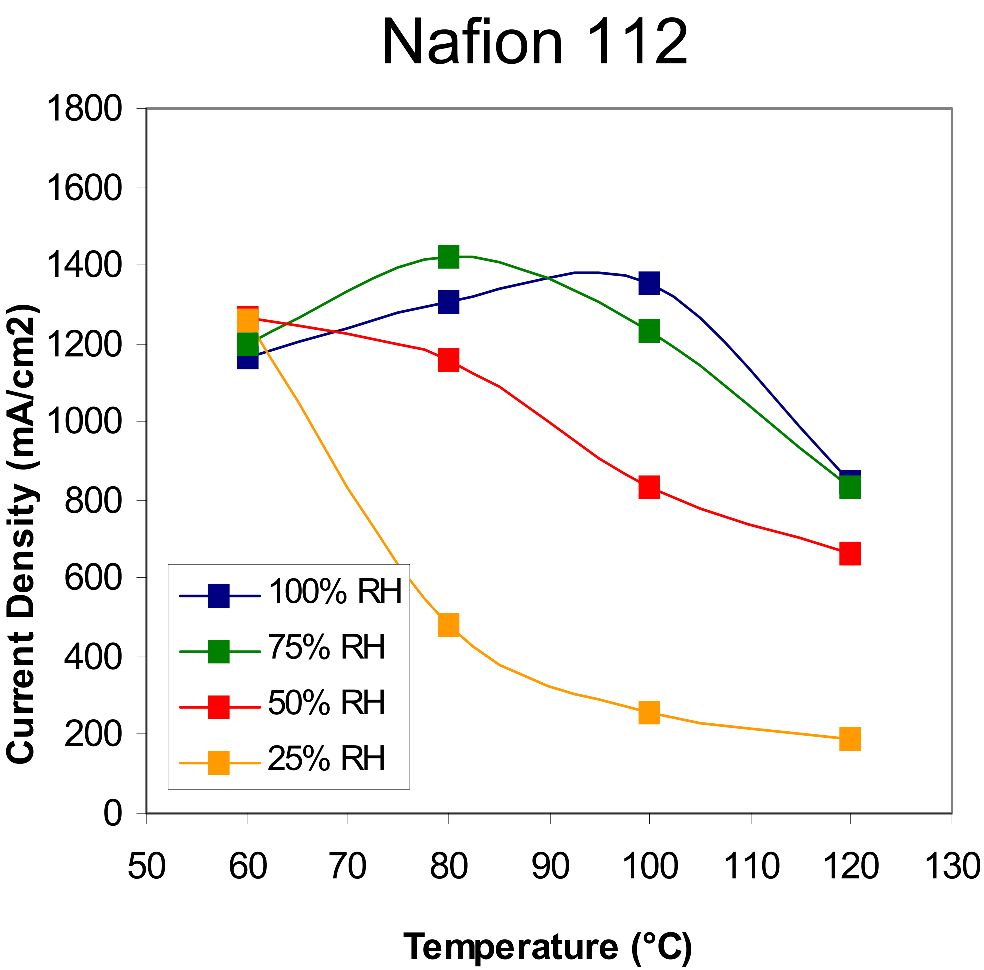
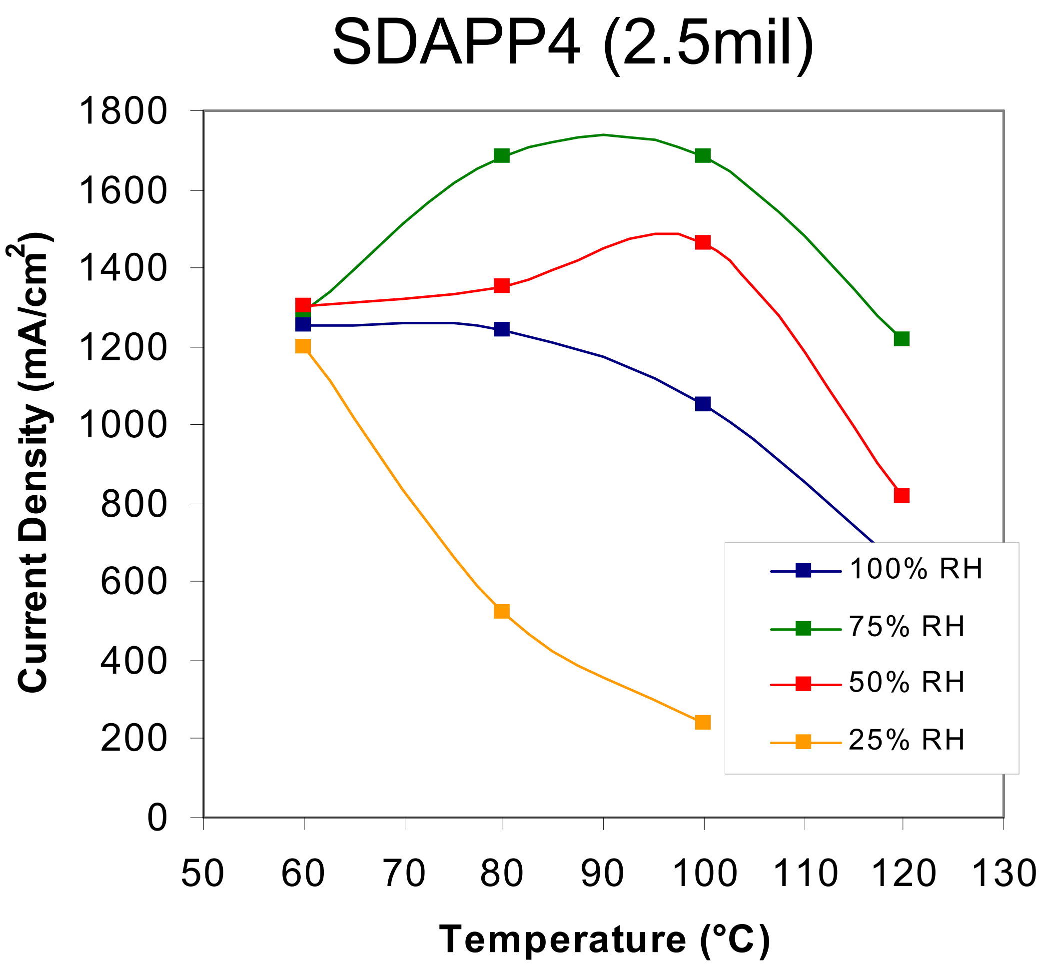
Fuel Cell Performance

O.5V with 30wt% Nafion Electrodes





0.4 mg Pt/cm^2
high stoic H_2/Air flow

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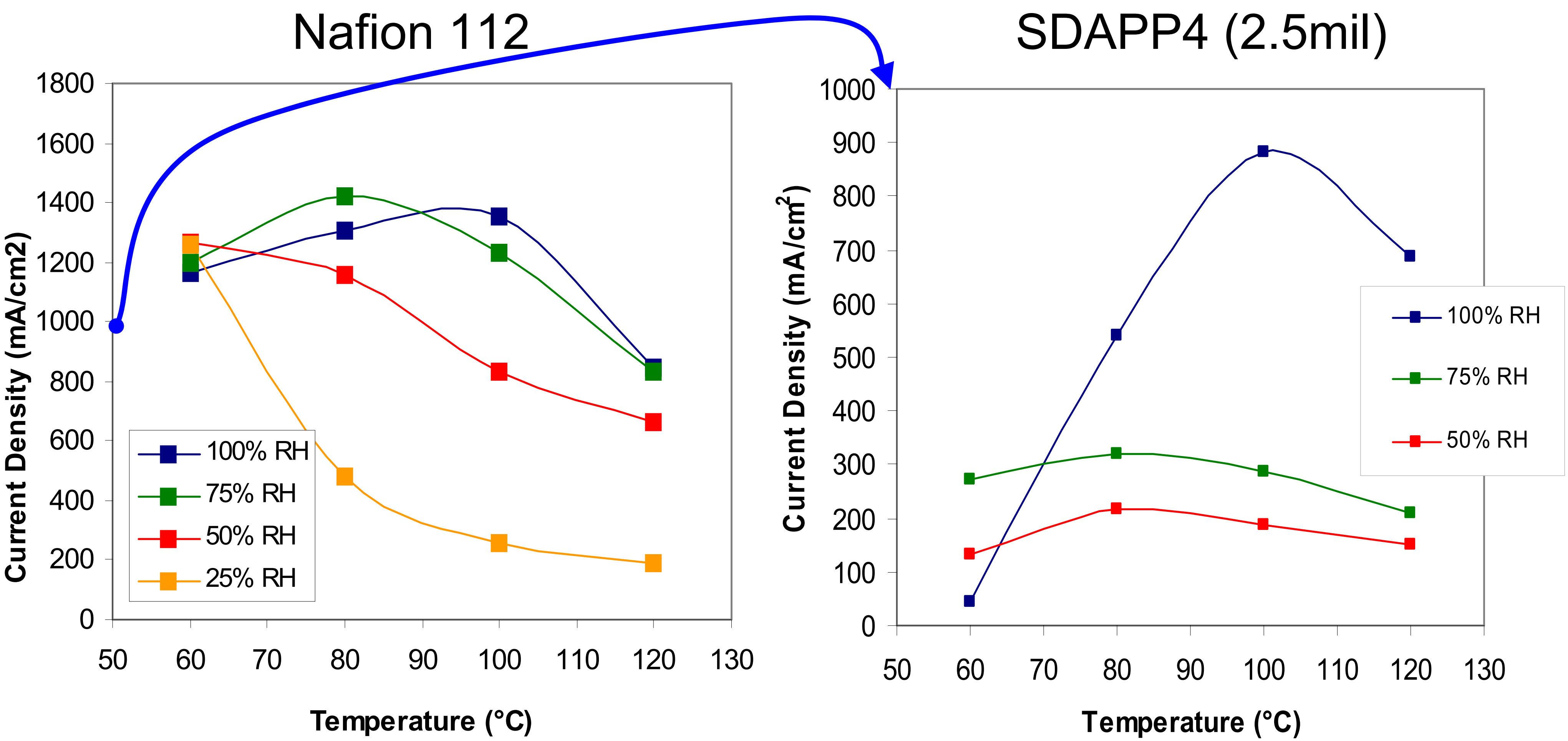
Fuel Cell Performance

O.5V with 30wt% Nafion vs non-Nafion Electrodes



0.4 mg Pt/cm²
high stoic H_2/Air flow

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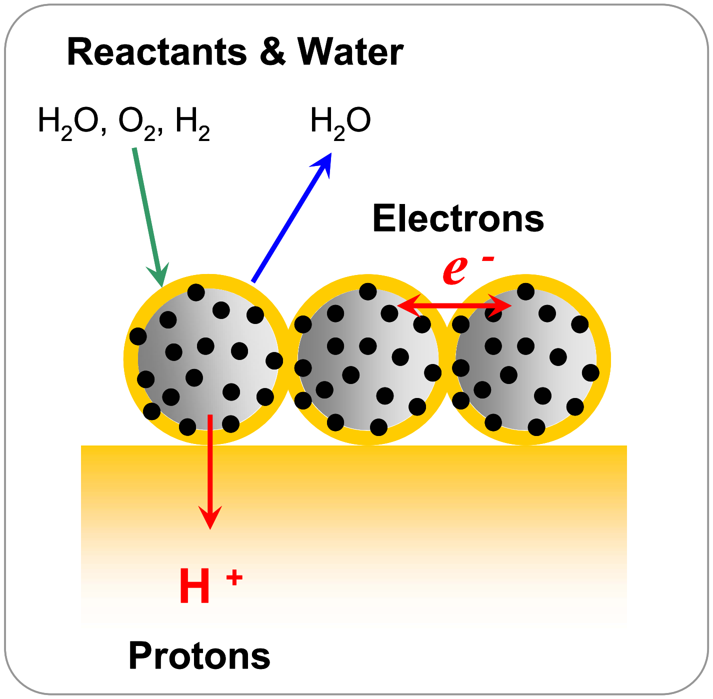
Fuel Cell Performance

Development of Non-Nafion MEAs



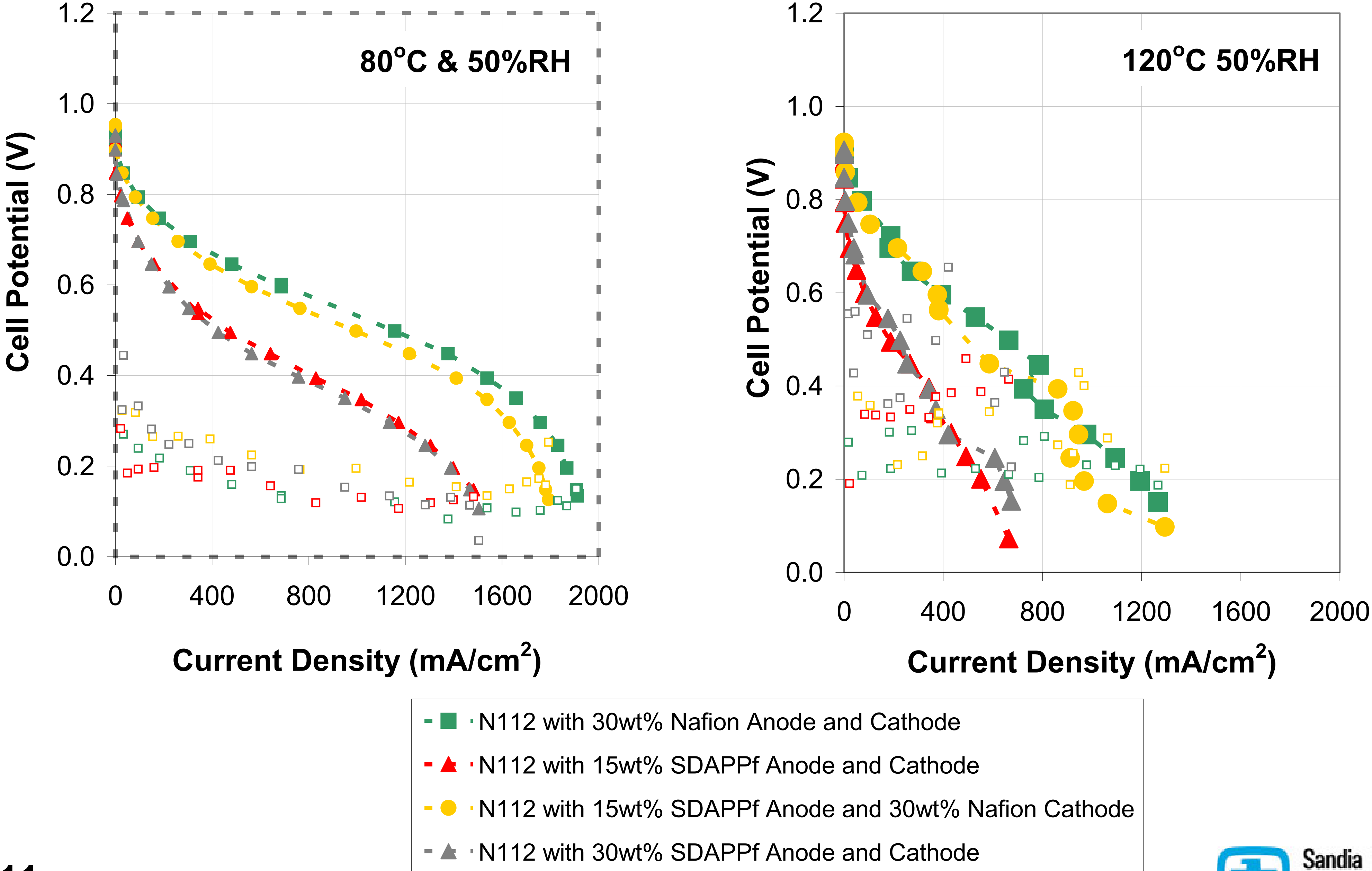
	BET Surface Area (m^2/g)
Nafion 30 wt %	70
SDAPPe 30 wt %	85
SDAPPe 15 wt %	131
SDAPPe 7 wt %	135

SDAPP electrodes provide good porosity and do not significantly impede electrochemistry within the electrode structures.

	Average Tafel Slope (10-20 mA)			
	50RH		100RH	
	O2	Air	O2	Air
N112 Nafion 30% Nafion Electrodes	-87.5	-83.5	-59.1	-51.2
SDAPP 30% SDAPP Electrodes	-83.1	-79.3	-63.1	-67.6

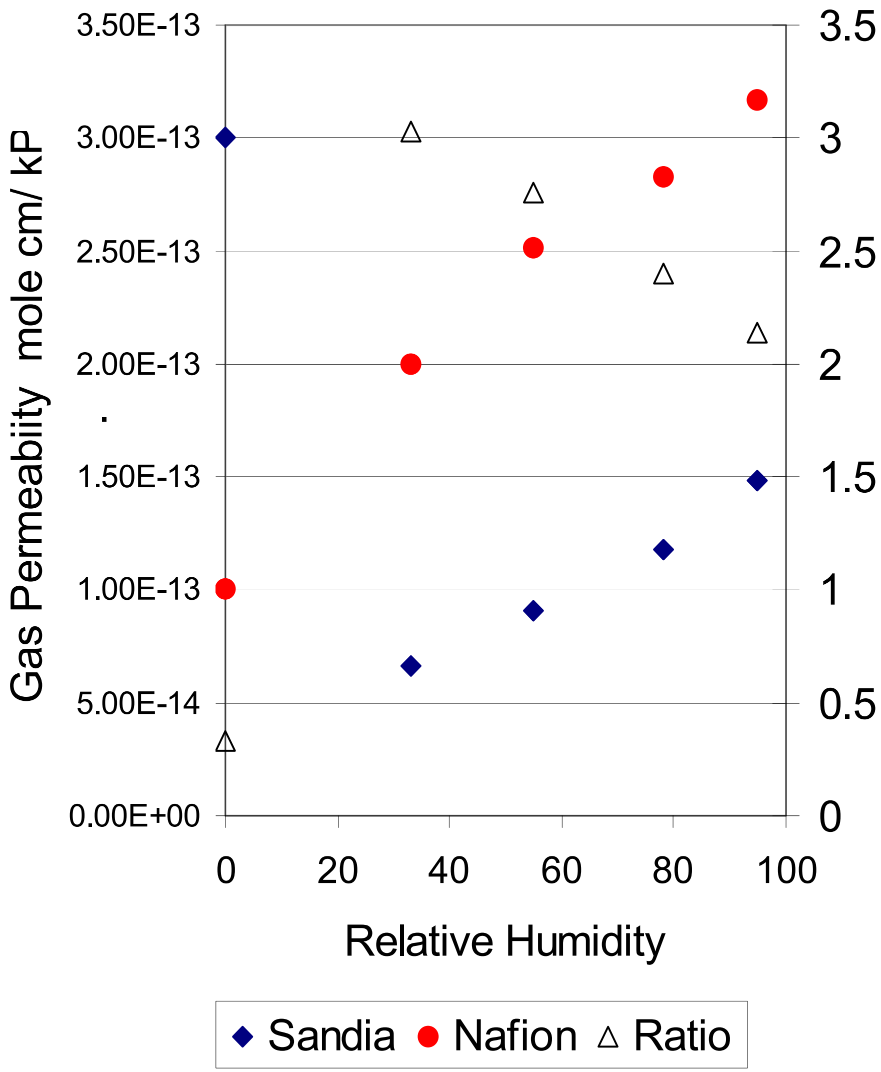
Fuel Cell Performance

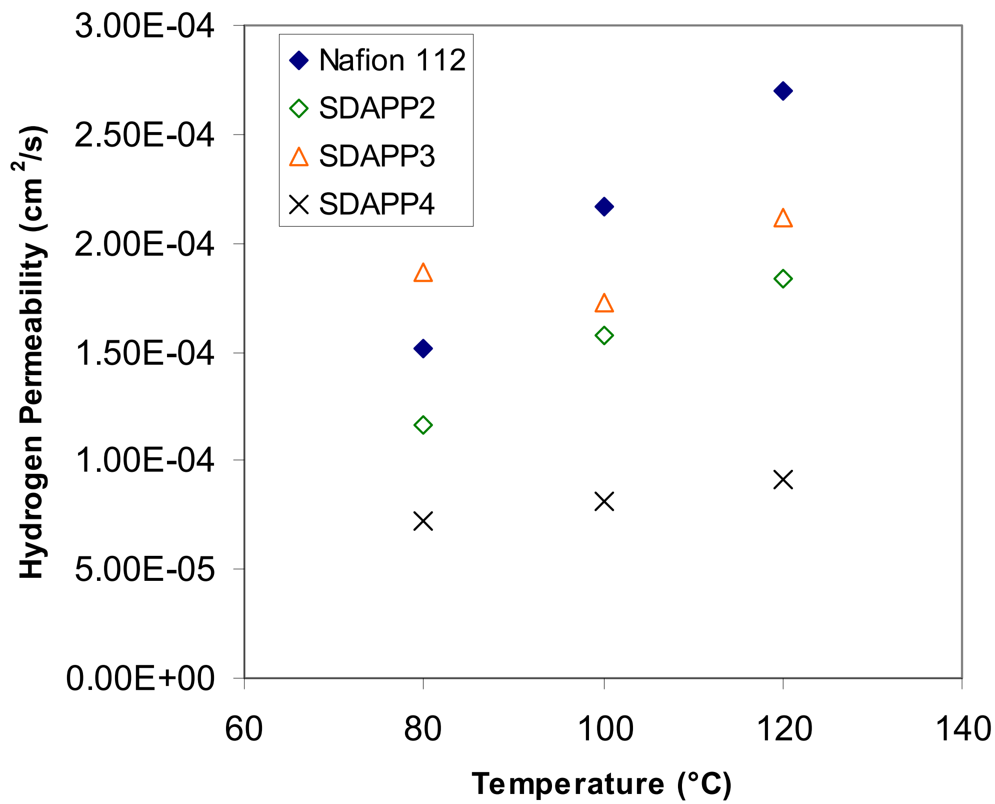
50%RH Nafion & Non-Nafion Electrodes on N112



Hydrogen Crossover

MEA & PEM Testing





Barriers Addressed

- O_2 and H_2 Crossover
- Fuel Cell Performance
- Thermochemical Stability

In collaboration/Contract with Giner Electrochemical Systems

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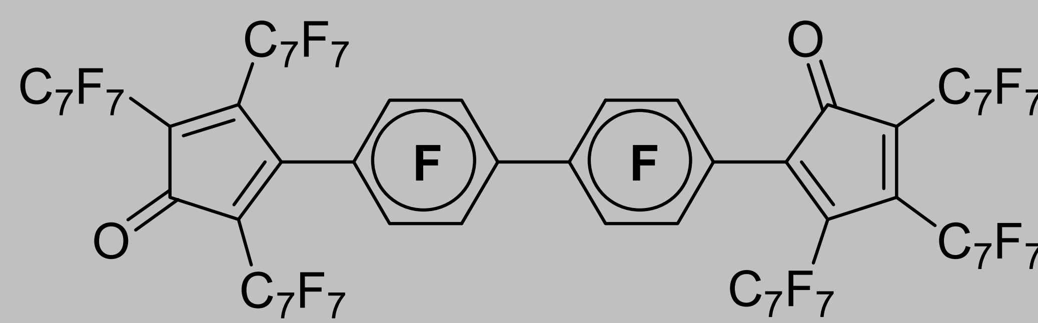
Fuel Cell Performance

Increasing Durability & Conductivity



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30%

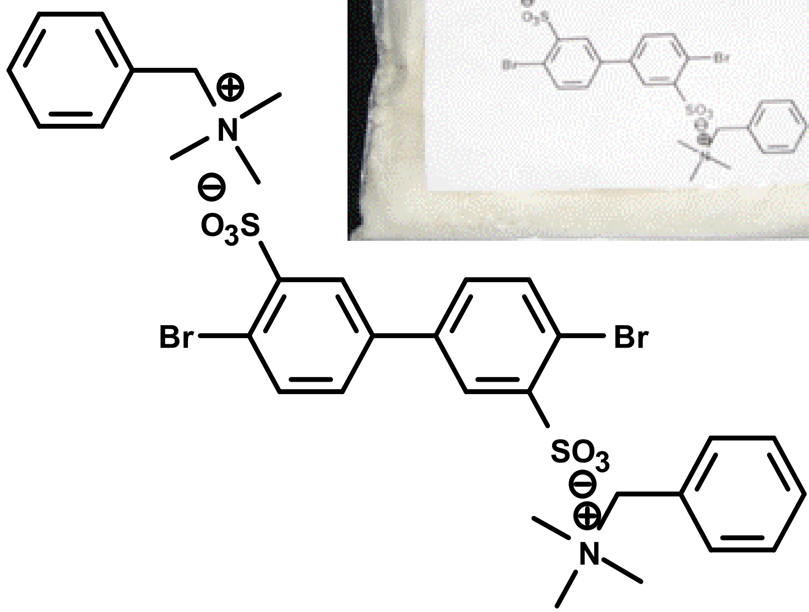
- Polymerization yielded solid polymer
- Incorporation into DA PEM - TBD
- Physical Properties - TBD

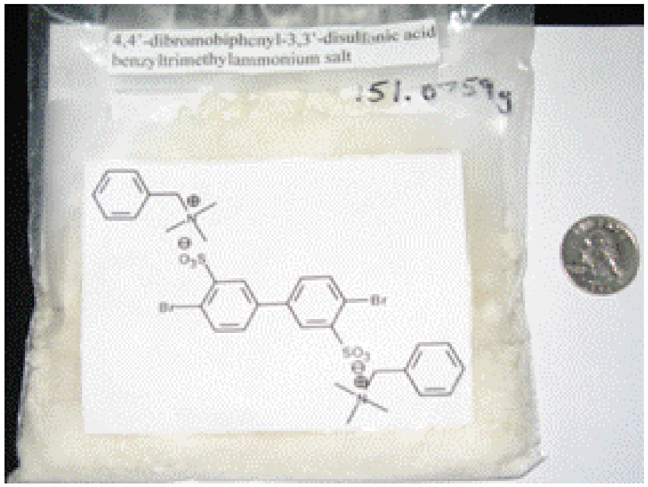
Barriers Addressed
- Conductivity
- Fuel Cell Performance
- Thermochemical Stability

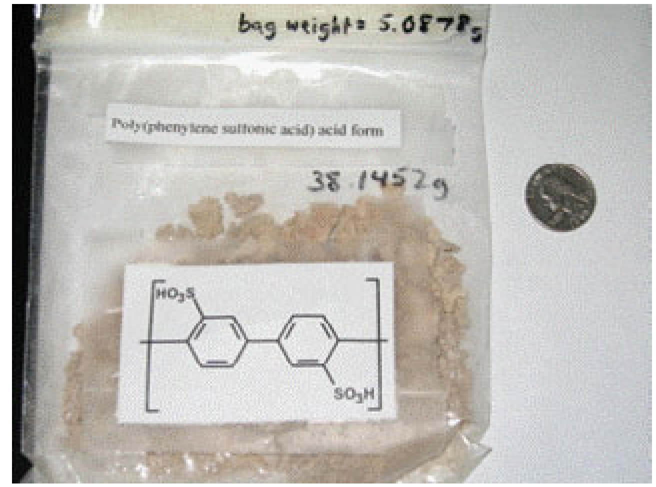
In collaboration/Contract with Dr. Deck – Virginia Tech

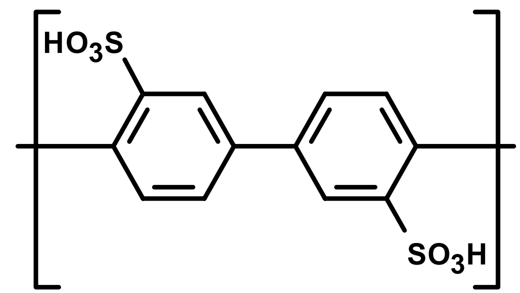
Fuel Cell Performance

Increasing Conductivity – Ullman Reaction









- Polymerization yielded solid polymer/ionomer
- MW - TBD
- IEC & Conductivity – TBD
- Physical Properties - TBD

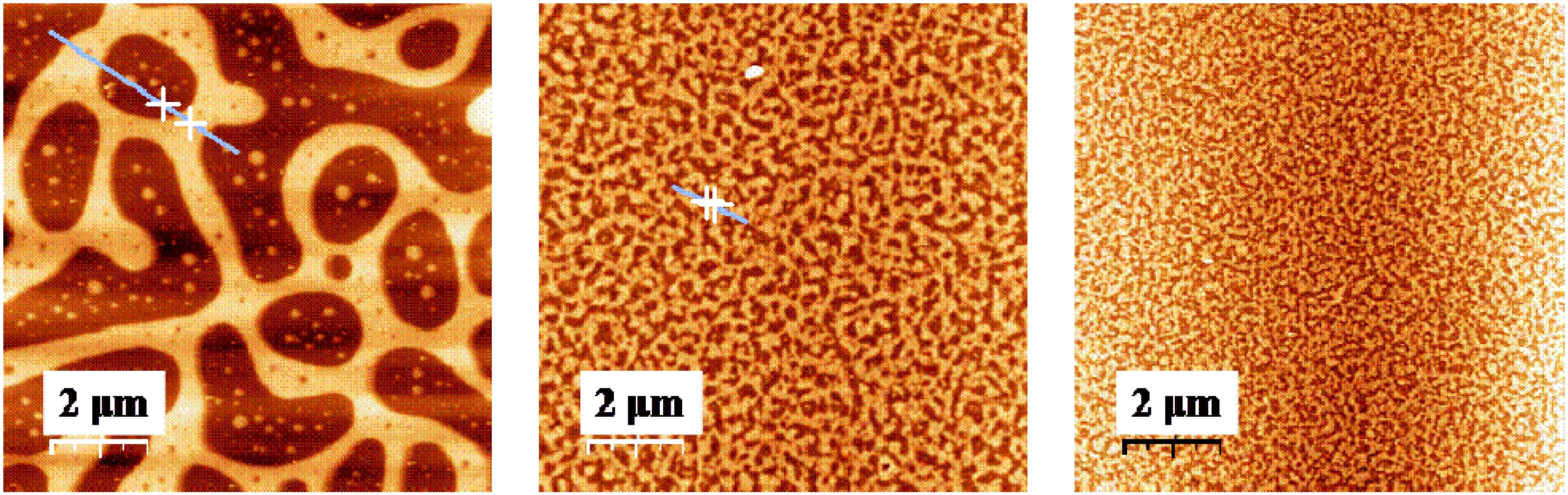
Barriers Addressed

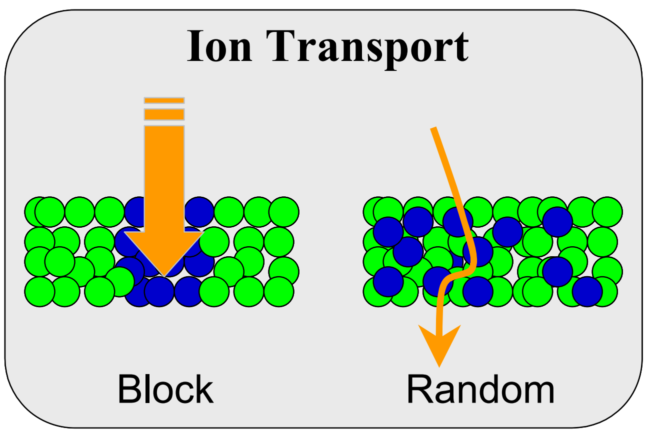
– Conductivity
– Fuel Cell Performance
– Membrane Cost

In collaboration/Contract with Dr. Litt - CWRU

Fuel Cell Performance

Improving PEM Morphology & Function - AFM





Barriers Addressed

– Conductivity
– Fuel Cell Performance
– Membrane Cost & Durability

In collaboration/Contract with Dr. Perahia - Clemson

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Future Work

Improving Fuel Cell Membranes

Enhanced Acidity & Hydration

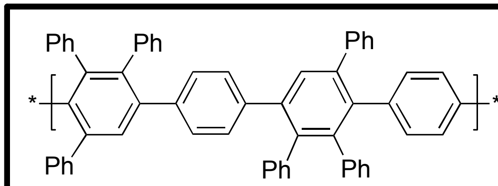
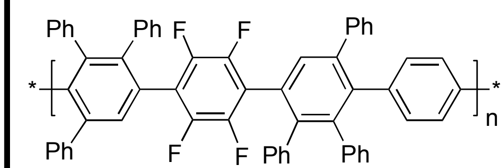
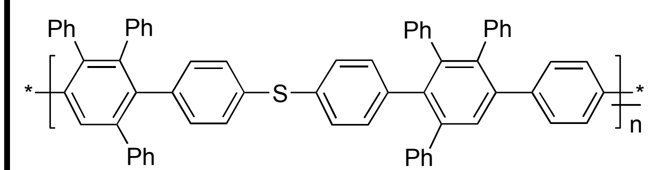
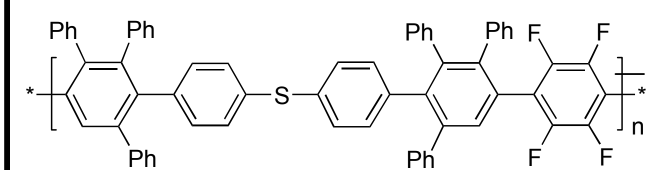
- *Acid Groups*
- *Organic-Inorganic Composites*

Gas Transport

- *Tailoring polymers for Electrode and PEM utilization*

Structure-Property-Function

- *Structured Materials (sulfonation)*
- *Improved Stability (Mechanical (cycling) and chemical)*
- *Minimize interfacial resistance and improve adhesion of PEM and catalyst layer*

	H_2	O_2
	94	19
	99	24.5
	5.2	
		270

H_2 and O_2 Permeability Units in Barrer
$10^{-10} cm^3/cm^2$ s cm of Hg (at STP)

Summary

Hydrocarbon Membrane

Relevance:

Identify and Answer fundamental issues with Nafion and alternative PEM and MEA fuel cell implementation

Approach:

Develop a Structure-Property-Performance relationship of alternative PEMs in order to mitigate poor fuel performance relative to DOE targets.

Technical Accomplishments and Progress:

Capabilities Established: Material design and synthesis, characterization, device testing, system performance measurements, and predictions

Technology Transfer & Collaborations:

Active involvement with industry and academia

$50K award by Lockheed Martin under a Shared Vision to initiate the understanding of hydrocarbon PEM scale-up.

Proposed Future Research:

Continue structure property function improvements to achieve DOE fuel cell goals

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Reviewer's Comments

Response to Previous Year Review

1.Relevance to overall DOE objectives – (*Weight - 20%*)

- Key technology that must be enhanced.

We have taken our first generation membrane and are adding functionalities to improve conductivity, durability, and performance.

2.Approach to performing the R&D – (*Weight - 20%*)

- Separate MEA interface from bulk PEM properties
- Improve Conductivity (low RH) then Electrode Interface

Research goals separate PEM from MEA interface. New Chemistry initiated during the next fiscal years is expected to address 2010 DOE performance targets.

3.Technical Accomplishments and Progress toward overall project and DOE goals – (*Weight - 35%*)

- Measure conductivity of new membranes as a function of T and RH in order to separate PEM versus MEA advances.

Research goals separate PEM from MEA interface. New Chemistry initiated during the next fiscal years is expected to address 2010 DOE performance targets.

Reviewer's Comments

Response to Previous Year Review

4.Technology Transfer / Collaborations with industry / universities / other laboratories – (*Weight - 10%*)

- Need to develop industrial contacts
- Develop collaboration on MEA durability and electrode integration

We have taken our first generation membrane and are adding functionalities to improve conductivity, durability, and performance.

5.Proposed Future Research approach and relevance – (*Weight - 15%*)

- Need more aggressive challenges
- Too Broad – optimize PEM then electrode

Research goals separate PEM from MEA interface. New Chemistry initiated during the next fiscal years is expected to address 2010 DOE performance targets of performance, durability, and cost).

Publications and Presentations

March 2005 - Present

Publications

Hickner, Michael A.; Fujimoto, Cy H.; Cornelius, Christopher J. "Transport in sulfonated poly(phenylene)s: Proton conductivity, permeability, and the state of water" *Polymer* (accepted April 18th, 2006).

Fujimoto, Cy H.; Hickner, Michael A.; Cornelius, Christopher J.; Loy, Douglas A. "Ionomeric Poly(phenylene) Prepared by Diels-Alder Polymerization: Synthesis and Physical Properties of a Novel Polyelectrolyte" *Macromolecules* (2005), 38(12), 5010-5016.

Presentations

Fall 2006: FuelCell 2000 (2), ECS (1) and ACS (1)

Technical Advances

(*pre-patents*)**:** 3

Critical Assumptions & Issues

Hydrocarbon Membrane

1. **Achieving Adequate Proton Conductivity**
   - **Proton Mobility and Acidity** – current synthetic method is amenable for inclusion of more acidic groups – current approaches are in the correct direction to achieve goal.
   - **Improved Morphology** – improvements in structure will enhance proton conduction via better utilization of proton carrying groups to improve low RH fuel cell function.
   - **Interface versus Bulk** - Separate MEA (*interface*) from PEM (*bulk*) to understand interrelationships. Improving proton conductivity and transport properties within the electrode (low RH & Durability).

2. **Mechanical and Chemical Durability**
   - **Mechanical** – Improving flexibility of PEM backbone to accommodate cyclic stress and asymmetric water induced stresses.
   - **Chemical** – Improving stability with more chemically stable monomers

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Acknowledgements

Hydrocarbon Membrane – Project: FCP5

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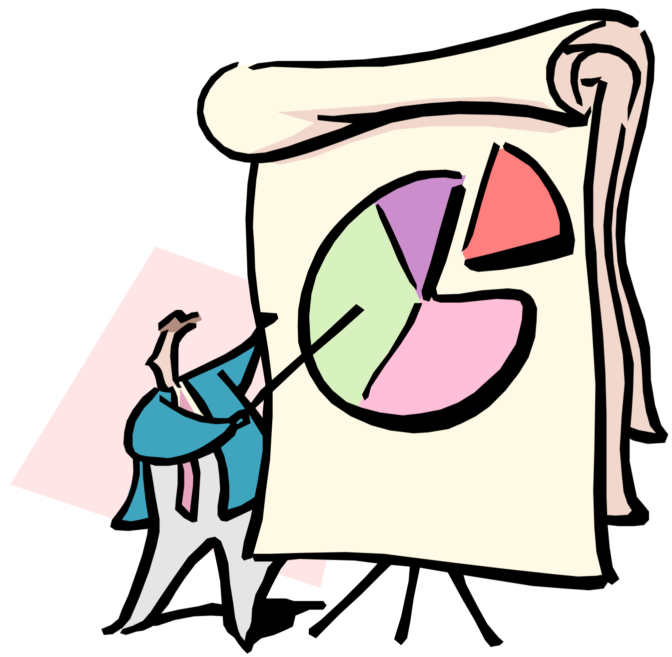
Jessica Price
Mariam Konate

Giner Electrochemical Systems, LLC
Cortney Mittelsteadt

Case Western Reserve University
Professor Morton Litt



Thank you for your attention

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