

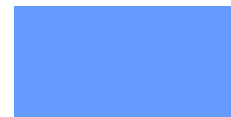
# Center for Intelligent Fuel Cell Materials Design Phase I

**2007 DOE Hydrogen Program  
Annual Merit Review  
No. DE-FG36-06GO86043**

**Denise M. Katona  
Chemsultants International  
May 16, 2007**

**Project ID # FC25**

**This presentation does not contain any proprietary, confidential or otherwise  
restricted information.**



# Phase I Project Overview

## Time Line

- Project start: **6/1/06**
- Revised Phase I completion: **11/30/07**
- Status: **65% complete**

## Budget

- Total Phase I project funding
  - DOE: \$1,485,000**
  - Cost Share: \$ 624,144**
  - 2006: \$ 767,199**
  - 2007 YTD: \$ 460,500**

## Technical Barriers

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

## Project Team

Chemsultants International  
Michigan Molecular Institute  
Case Western Reserve  
University



## Project Objectives

### **Develop novel polymer architectures capable of :**

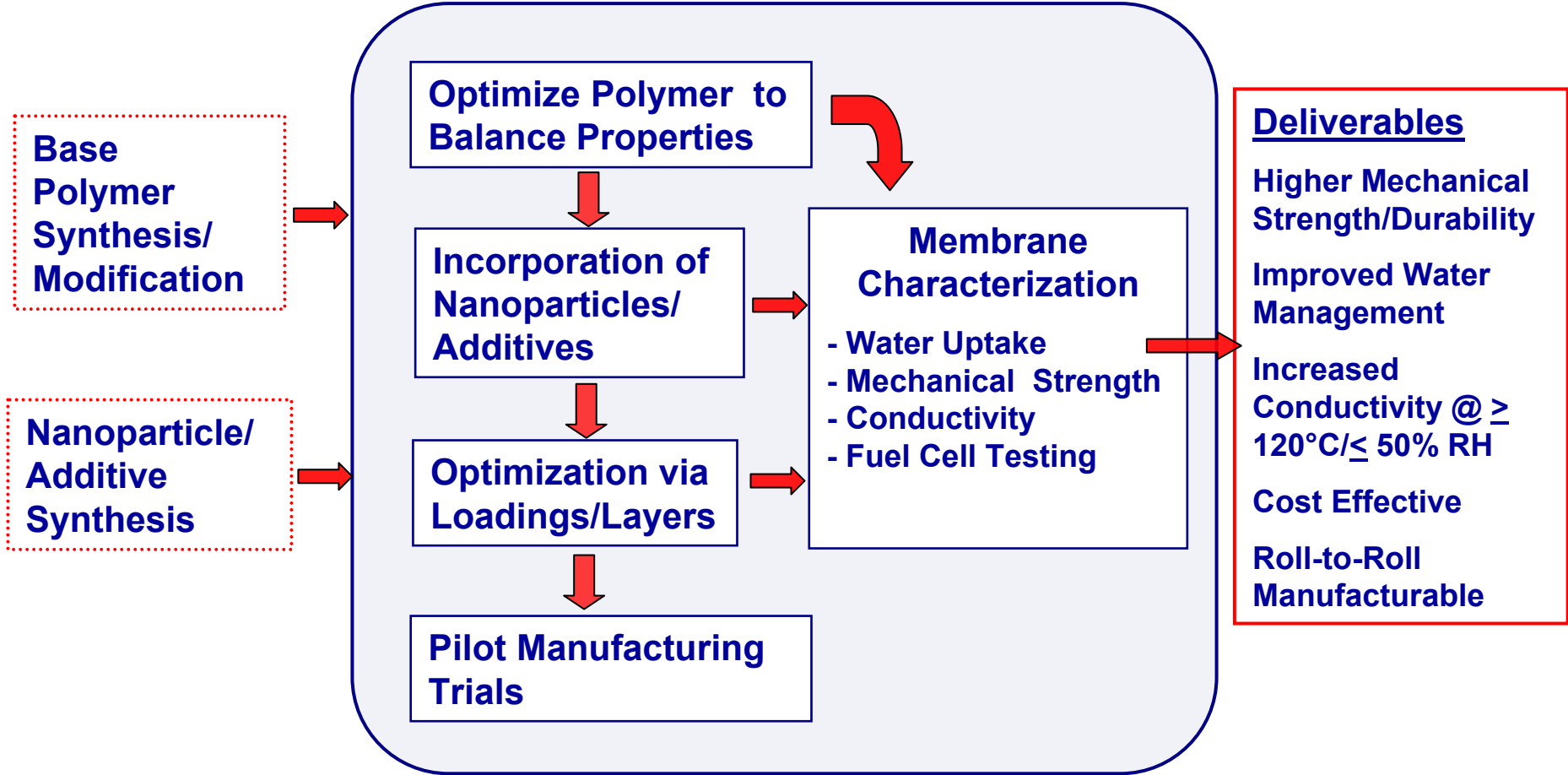
- improved mechanical stability vs. Nafion® (117) 212
- improved conductivity vs. Nafion® (117) 212
- $\geq 120^{\circ}\text{C}$  /  $\leq 50\%$  RH operational capability (4000 hours)

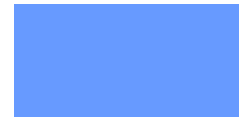
### **Identify new solution casting methodologies for thin, roll-to-roll membrane formation**

- thin single layer membranes
- discrete, multi-layer membranes
- reduction in stack component cost (membrane)



# Technical Approach





# Accomplishments

## Modified Polymer

- Completed modification of commercially available base polymer via sulfonation process
- Characterized and optimized sulfonated base polymer membrane
- Evaluated candidate casting sheet materials and chose suitable carrier for laboratory and manufacturing use
- Began pilot manufacturing membrane casting trials and identified process parameters

## Nano-Additives

- Synthesized two nanoparticle materials for use with modified polymer
- Developed dispersion methods for homogeneous suspension of nanoparticles in polymer casting solution
- Determined critical rheology parameters of casting solution including choice of appropriate solvent



# Accomplishments

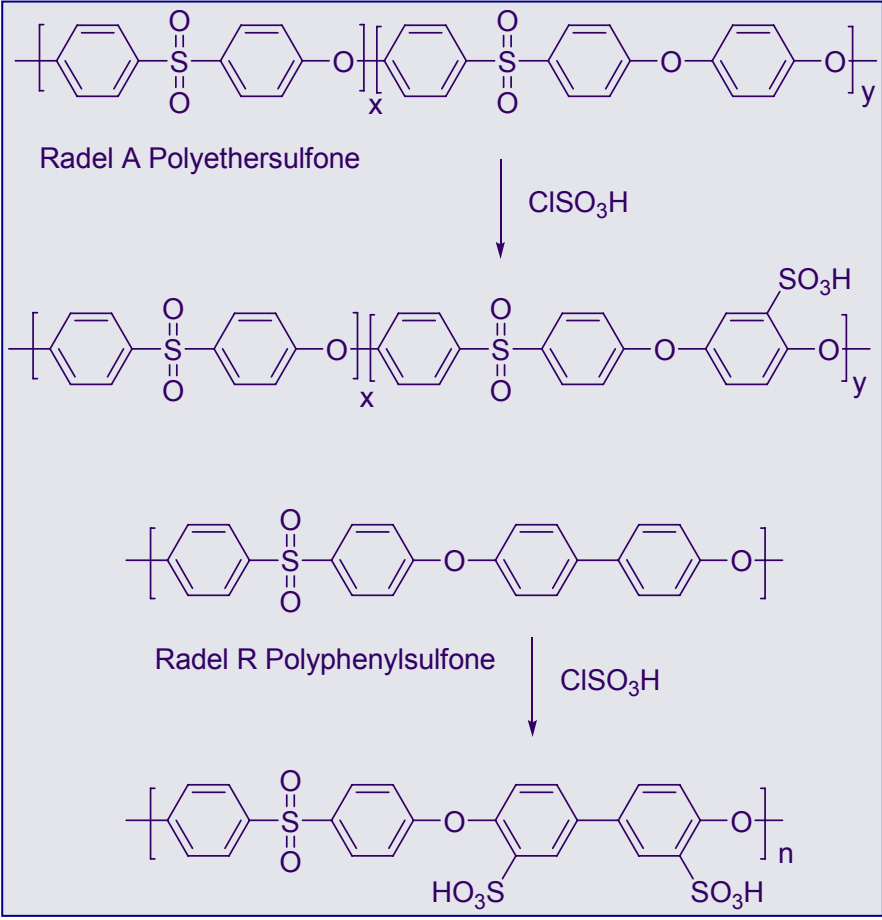
## Performance Testing

- Determined optimum degree of sulfonation of modified polymer based on conductivity, mechanical strength and water uptake data
- Ongoing optimization of particle loadings and layer development determined from performance test results
- Evaluating best membrane/composite membrane candidates using H<sub>2</sub>/Air fuel cell tests and PEM-LITE™ component evaluation test system

## Roll-to-Roll Product Casting Trials

- Scaled up initial laboratory casting and drying profiles to pilot casting line. Produced a defect-free membrane product successfully
- Beginning micro-layered membrane casting work on manufacturing equipment. Initial trials produced even thickness layers of unmodified base polymer

# Modification of Baseline Polymer

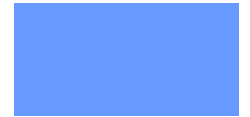


	Method	Sulfonation Level
Radel <sup>®</sup> A-100	SO <sub>3</sub> / NMP	3 wt.% SO <sub>3</sub> H
Radel <sup>®</sup> A-100	ClSO <sub>3</sub> H Ac <sub>2</sub> O	3 wt.% SO <sub>3</sub> H
Radel <sup>®</sup> R-5000	SO <sub>3</sub> / NMP	12 wt.% SO <sub>3</sub> H or below
Radel <sup>®</sup> R-5000	ClSO <sub>3</sub> H Ac <sub>2</sub> O	20 wt.% SO <sub>3</sub> H or below

**Chlorosulfonic acid sulfonation method best for higher wt.% SO<sub>3</sub>H**







# Solution Casting

## Solubility and Rheology

- N-Methyl-2-pyrrolidone (NMP) selected as best solvent for modified Radel<sup>®</sup> R-5000 polymer (limited solubility in other dipolar aprotic solvents)
- Solids level of 20% polymer in NMP produced good solution casting rheology with viscosity of 2800 cP (higher solids too viscous, lower solids produced films with maximum thickness limitations due to leveling effects)

## Casting Sheet Material

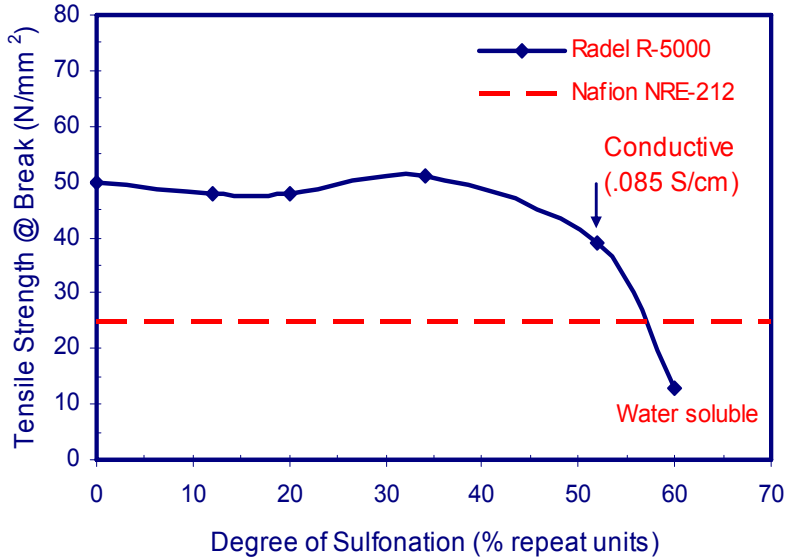
Materials obtained and evaluated:

- Fluorinated ethylenepropylene (FEP)
- Polymethylpentene (PMP)
- Ethylene-chlorotrifluoroethylene (E-CTFE)
- Ethylene-tetrafluoroethylene (ETFE)
- Silicone coated polyester (UV and fluorinated polysiloxane)
- Polyimide (Kapton<sup>®</sup>)
- **Polyester (Mylar<sup>®</sup>)**      **\*\*chosen as casting substrate**

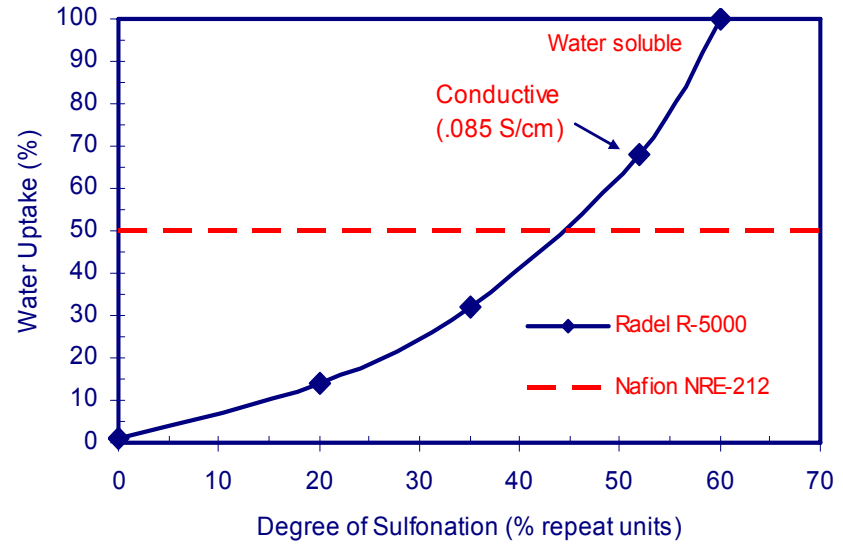


# Characterization of Modified Polymer and Composite Membranes

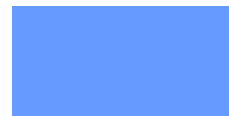
**Tensile Strength**



**Degree of Sulfonation vs Water Uptake**



**Trend shows Sulfonated Radel<sup>®</sup> R-5000 more mechanically stable than Nafion<sup>®</sup>**  
**Optimum degree of sulfonation most likely between 40% and 50%**



## Characterization of Modified Polymer and Composite Membranes

Sulfonated Radel<sup>®</sup> R-5000  
Degree of Sulfonation: 52%

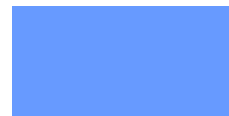
Membrane Description	Conductivity (S/cm)	Tensile @ Break (N/mm <sup>2</sup> )
Radel <sup>®</sup> R-5000 (D.S. 52%)	0.085	39
Radel <sup>®</sup> R-5000 + POSS (25%)	0.066	8
Radel <sup>®</sup> R-5000 + Phosphazene (20%)	0.105	15
<b>Nafion<sup>®</sup> NRE-212</b>	<b>0.099</b>	<b>25</b>

Sulfonated Radel<sup>®</sup> R-5000  
Degree of Sulfonation: 34%

Membrane Description	Conductivity (S/cm)	Tensile @ Break (N/mm <sup>2</sup> )
Radel <sup>®</sup> R-5000 (D.S. 34%)	0.002	51
Radel <sup>®</sup> R-5000 + POSS (10%)	0.005	23
Radel <sup>®</sup> R-5000 + Phosphazene (10%)	0.009	41

**Membrane thickness = 50 microns**

***Polymer modification and additive loadings should be between the two extremes for a proper balance of properties***



## Characterization of Modified Polymer and Composite Membranes

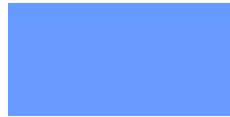
**Additive A:**  
SO<sub>3</sub>H-POSS

**Additive B:**  
SO<sub>3</sub>H  
Phosphazene

**ASTM  
D 1042  
Dimensional  
Stability Test**

	Nafion® 212	Sulfonated Radel® R-5000	75% Sulfonated Radel® R-5000/ 25% Additive A	80% Sulfonated Radel® R-5000/ 20% Additive B
Wt.% SO <sub>3</sub> H	8%	17%	22%	22%
In-plane $\sigma$	0.079 S cm <sup>-1</sup>	0.085 S cm <sup>-1</sup>	0.066 S cm <sup>-1</sup>	0.105 S cm <sup>-1</sup>
Through plane $\sigma$	0.099 S cm <sup>-1</sup>	0.110 S cm <sup>-1</sup>	0.061 S cm <sup>-1</sup>	0.089 S cm <sup>-1</sup>
L <sub>c</sub> (100% RH)	+10.4%	+2.3%	+3.2%	0%
L <sub>c</sub> (80°C)	-1.2%	-2.9%	0%	-4.5%
Water uptake (80°C / 24 hrs)	+50%	+68%	+444%	+58%
Water uptake (100% RH)	+17%	+15%	-2%	+1%
Tensile	25 N mm <sup>-2</sup>	39 N mm <sup>-2</sup>	8 N mm <sup>-2</sup>	15 N mm <sup>-2</sup>
Elongation	282%	11%	101%	112%

**Membranes have comparable conductivity to Nafion with superior dimensional stability**



# Characterization of Modified Polymer and Composite Membranes

## Parameters:

Single cell test station (Scribner Series 890B) with mass flow and temperature control

Catalyst loading - 0.4 mg/cm<sup>2</sup> (40%Pt/C)

Electrode area - 5 cm<sup>2</sup>

Membrane thickness = 50 μm

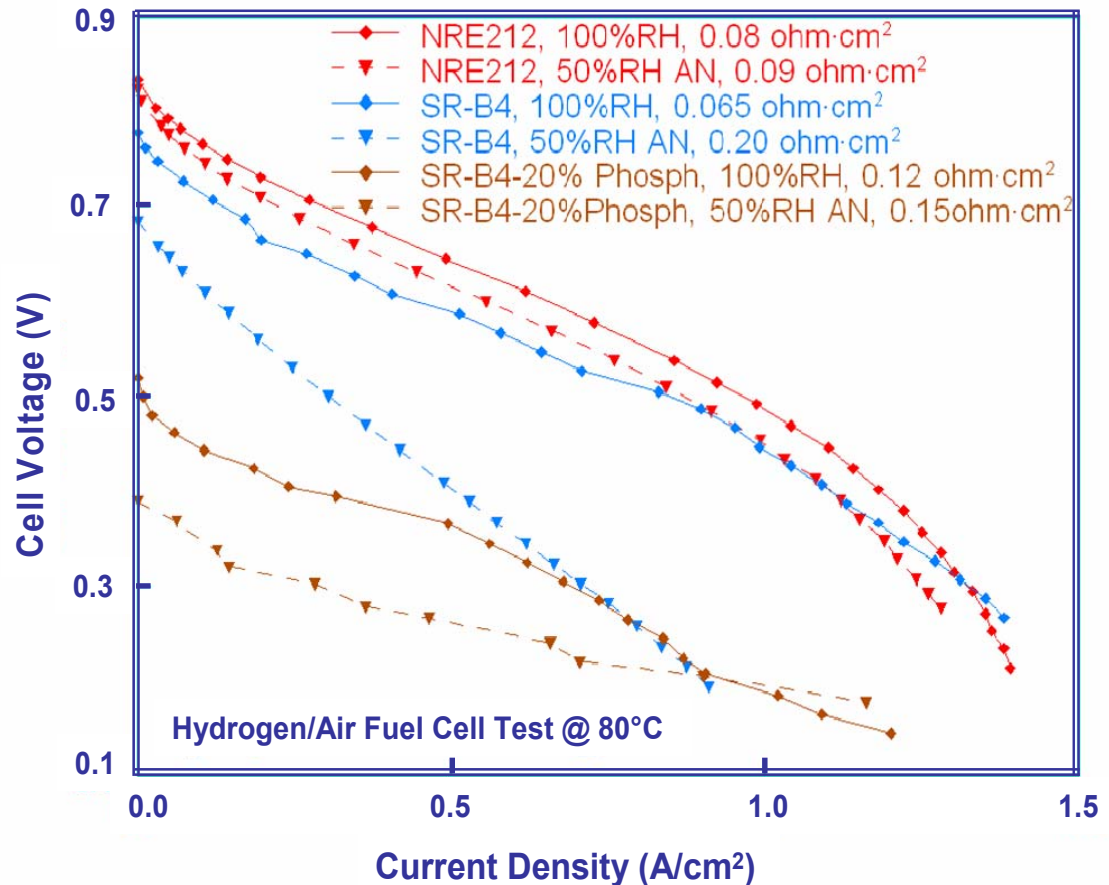
## Key:

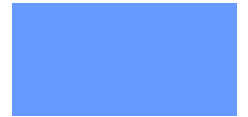
### SR-B4

Sulfonated Radel R-5000 (52%)

### SR-B4-20%

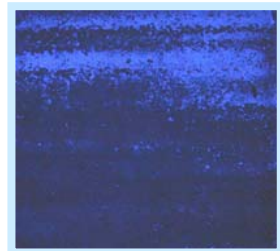
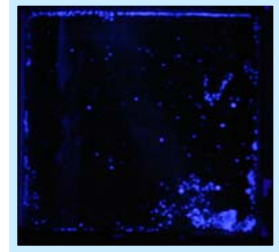
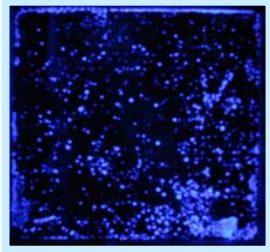
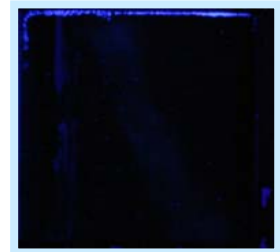
Sulfonated Radel R-5000 composite with 20% sulfonated phosphazene (solid composition)



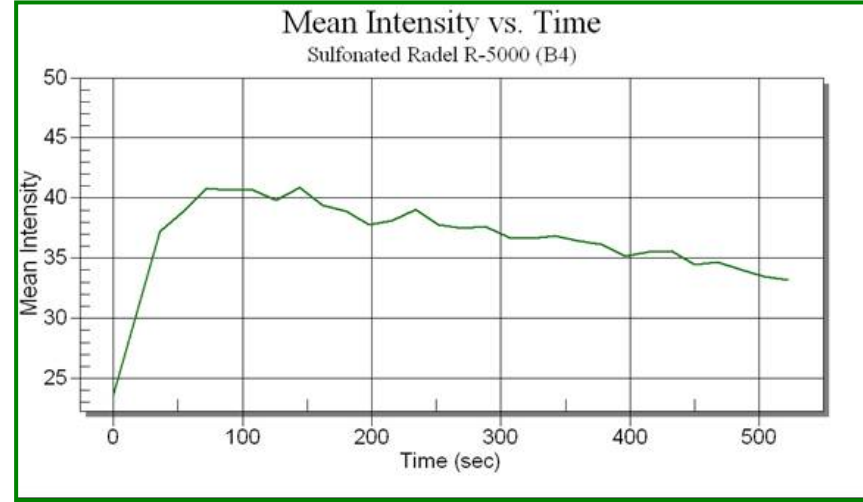
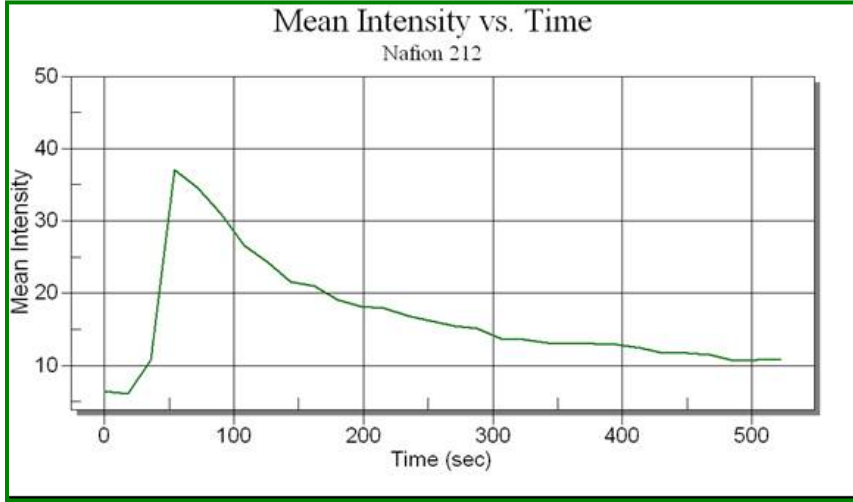


# Characterization of Modified Polymer Using PEM-LITE™ System

**Nafion® 212**  
50 µm



**Radel® R-5000**  
(52%) sulfonated  
45 µm



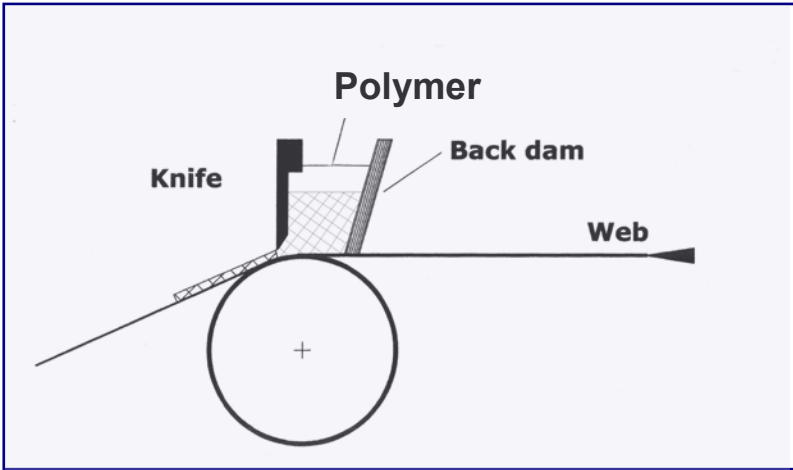


# Manufacturing Pilot Trials

## Knife over Roll (KOR)

The casting thickness is affected by

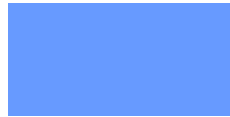
- 1) the gap between the knife and uncoated substrate
- 2) the blade configuration
- 3) the blade thickness
- 4) the viscosity of the liquid
- 5) the web speed
- 6) the porosity of the substrate
- 7) the rheology of the liquid



Oven 1 Temp	Oven 2 Temp	Oven 3 Temp	Oven 4 Temp	Oven 5 Temp	Speed (ft/min)	Gap (mils)	Solids (%)	Caliper (mils)
160	206	208	228	229	7	20	25	3.5
173	201	203	225	222	7	12	25	1.5
174	201	203	225	222	7	14	25	2.1
174	201	203	225	222	7	14	25	2.0
112	203	207	225	222	7	14	25	2.0
107	123	131	231	232	7	14	25	1.8
96	112	122	217	214	7	15	25	2.1
93	111	122	218	216	7	18	25	2.8
92	109	120	210	207	7	18	25	2.8
91	106	114	183	180	7	18	25	2.7
81	91	100	193	192	7	21	25	2.9
80	93	103	204	203	7	22	25	3.7
82	96	106	212	210	7	22	25	4.0
83	99	112	229	228	7	23	25	3.9

**KOR method resulted in a wide thickness range of defect-free Radel® membranes**

\*Oven temperatures in degrees Fahrenheit



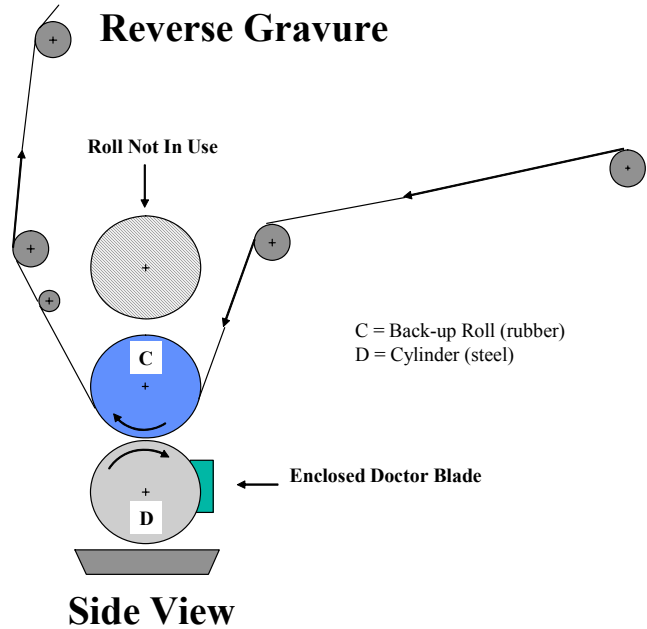
# Manufacturing Pilot Trials

## Reverse Gravure

Reverse gravure typically produces thinner, smooth, dry coatings with excellent precision and accuracy (between 0.1 mil and 2.5 mils dry)

Coating thickness is proportional to

- area & depth of cells
- line speed vs cylinder speed
- coating % solids & rheology



Run	Oven 1 Temp	Oven 2 Temp	Oven 3 Temp	Oven 4 Temp	Oven 5 Temp	Speed (ft/min)	Solids (%)	Cylinder	Caliper (mils)
1	79	91	100	194	193	7	25	TH 24	1.4
2	80	93	102	194	192	7	25	TH 24	2.1
3	81	94	103	194	192	7	25	TH 24	1.5
4	82	96	104	195	193	7	25	TH 24	1.9

\*Oven temperatures in degrees Fahrenheit

\*TH24 cylinder is mechanically engraved, triangular shaped groove cell configuration

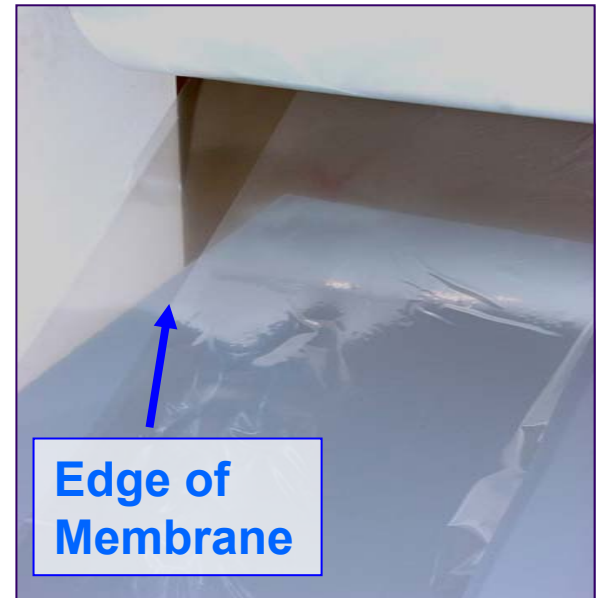
**Reverse gravure process produced smooth, defect-free Radel® membranes**



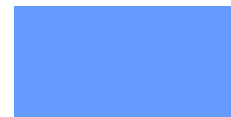


## Manufacturing Pilot Trials

Radel® R-5000 Membrane  
cast on PET Carrier



Membranes comprised of 5 consecutive layers with a total thickness of 50 microns have been successfully cast using the Knife over Roll method



# Future Work – To End of Project

## Modified Polymer/Additives

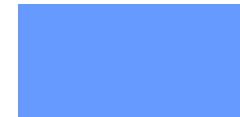
- Synthesis and evaluation of an additional “novel” polymer (*Chemsultants, MMI*)
- Synthesis and testing of two additional nanoparticle additives to increase water management (*MMI, Chemsultants*)
- Optimization of current nanoparticle/modified polymer composite system via particle loading and micro-layering (*Chemsultants*)
- Evaluate morphology of composite membranes with SEM, TEM and other microscopic techniques (*MMI*)

## Performance Testing

- Continue evaluation of developed membranes using H<sub>2</sub>/Air Fuel Cell testing and PEM-LITE™ System with goal to correlate performance data (*CWRU, Chemsultants*)

## Manufacturing Processes

- Continue to develop defect-free, roll-to-roll membrane product on manufacturing equipment incorporating new and optimized materials (*Chemsultants*)
- Strategically cast uniform multi-layered membranes using a more tightly controlled casting process (*Chemsultants*)



## Project Summary

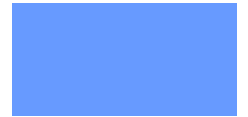
**Relevance:** Developing alternative polymer/nanoparticle membrane structure with capability of functioning in a high temperature/low humidity fuel cell operating environment with suitable ionic transport capabilities, improved water management functionality and mechanical integrity.

**Approach:** Two phase: (1) Polymer modification/nanoparticle synthesis and characterization and (2) Optimization of composite membranes including micro-layering and roll-to-roll solution casting methodologies.

**Technical Accomplishments and Progress:** Demonstrated improved mechanical strength and conducting ability via polymer modification and use of synthesized nanoparticle species. Initiated path towards enhanced water management by strategic use of nanoparticle additives in multiple layered structures.

**Technology Transfer/Collaborations:** Active partnership with Michigan Molecular Institute and Case Western Reserve University.

**Future Work:** Complete optimization of modified polymer/nanoparticle composite membrane and evaluate in extended fuel cell testing at high temperature/low humidity. Continue manufacturing scale-up of membrane casting process including production of a prototype material.



# Additional Slides



## Selection of Baseline Polymer

	T <sub>g</sub> (DSC) / °C	Inception of Major Weight Loss (TGA) / °C	Storage Modulus at RT (DMA) / MPa	Storage Modulus at 170°C (DMA) / MPa
Nafion <sup>®</sup> 117	~110	330 (1 <sup>st</sup> ) 400 (2 <sup>nd</sup> )	600	< 50
Solvay Udel <sup>®</sup> P3500 PSU	184	450	2250	250
Solvay Radel <sup>®</sup> A-100 PES	218	425	1700	1000
GE Ultem <sup>®</sup> PEI	216	450	2800	100
Parmax <sup>®</sup> 1200CK	155	406	8000	50

**Radel<sup>®</sup> retained a good modulus at elevated temperatures**



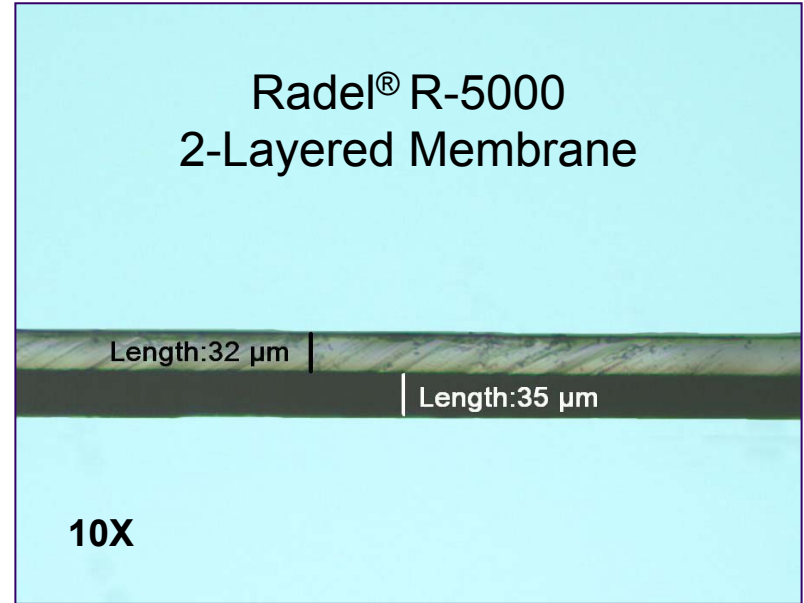
# Multi-Layered Membranes

Optical micrograph showing uniform thickness of layers

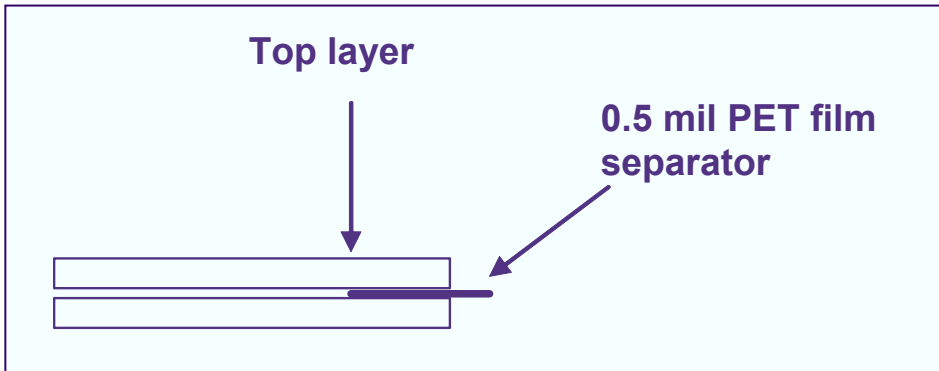
Actual micrometer measurements of individual layers correspond to those measured by the optical microscope:

Micrometer: Clear 32  $\mu\text{m}$     Black: 34  $\mu\text{m}$

Microscope: Clear 32  $\mu\text{m}$     Black: 35  $\mu\text{m}$

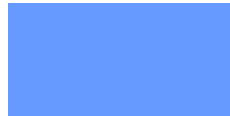


## T-Peel Configuration



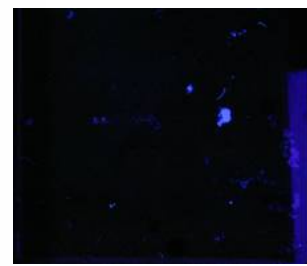
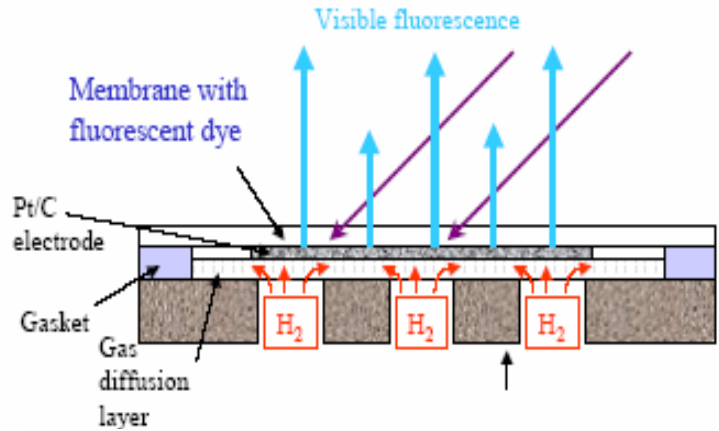
*Bottom layer dyed with masstone black pigment for viewing layer structure*

**Interlayer adhesion evaluated using ASTM T-peel and Tensile Test methods. Interlayer adhesion excellent for Radel® R-5000.**

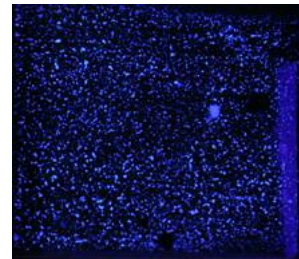


# Characterization of Modified Polymer and Composite Membranes

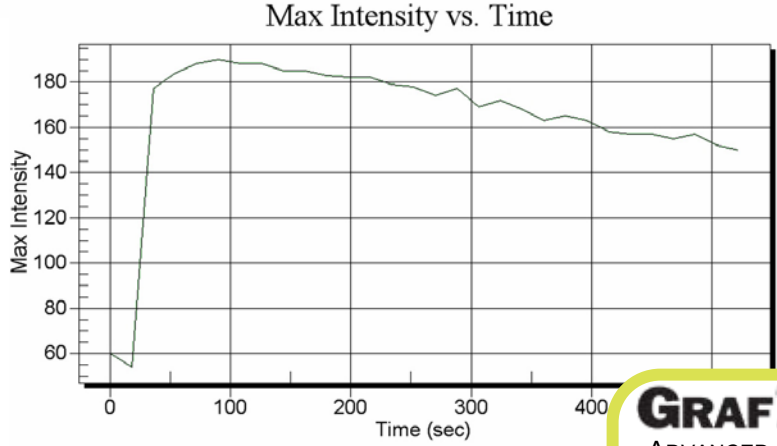
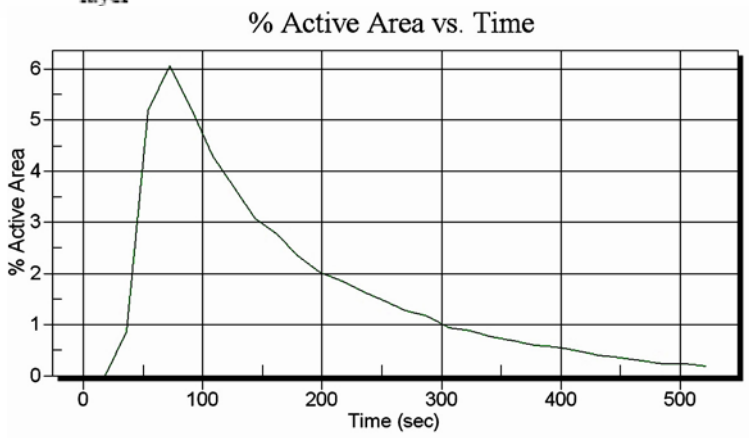
The PEM-LITE™ System allows for direct visualization of gas diffusion activity in half-cell assemblies via measurement of fluorescence intensity



Nafion 112 0 sec



Nafion 112 60 sec



Note: Schematic taken from PEM-LITE™ System Operating Manual