# Center for Intelligent Fuel Cell Materials Design Phase I

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

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Chemsultants International
May 16, 2007

Project ID # FC25

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# 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 Mgmnt.

## Project Team

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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
- ≥ 120°C / ≤ 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

Base Polymer Synthesis/ Modification

Nanoparticle/ Additive Synthesis

Optimize Polymer to Balance Properties

Incorporation of Nanoparticles/ Additives

Optimization via Loadings/Layers

Pilot Manufacturing Trials

**Membrane Characterization**

- Water Uptake
- Mechanical Strength
- Conductivity
- Fuel Cell Testing

**Deliverables**

Higher Mechanical Strength/Durability

Improved Water Management

Increased Conductivity @ $\geq$ 120°C/$\leq$ 50% RH

Cost Effective

Roll-to-Roll Manufacturable

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# 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

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MMI

GrafTech
Advanced Energy Technology Inc.
http://www.graftechaet.com

# Accomplishments

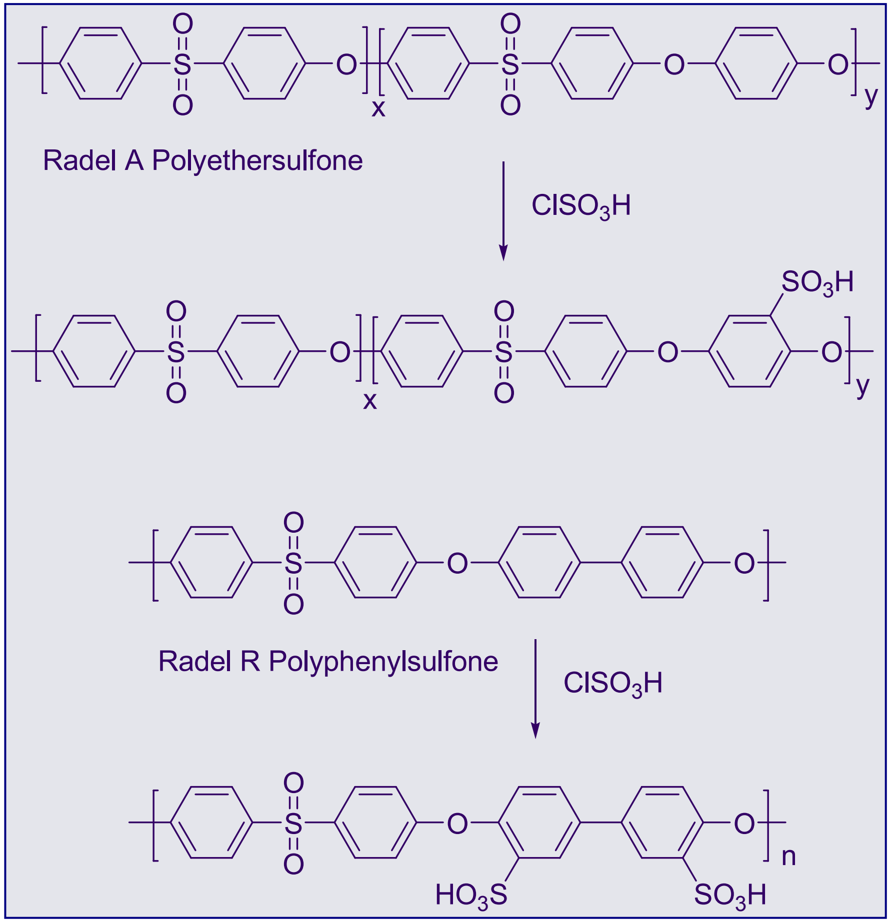
## Performance Testing

- 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 $H_2$/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

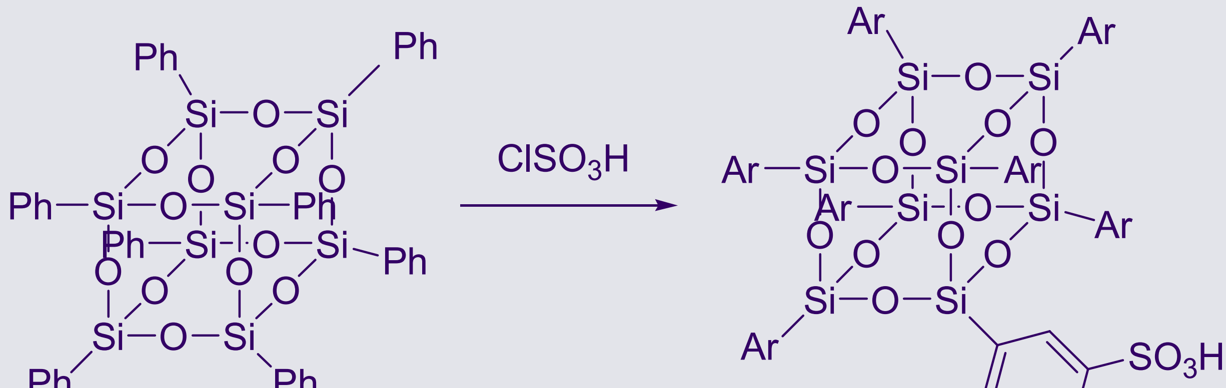
# Modification of Baseline Polymer



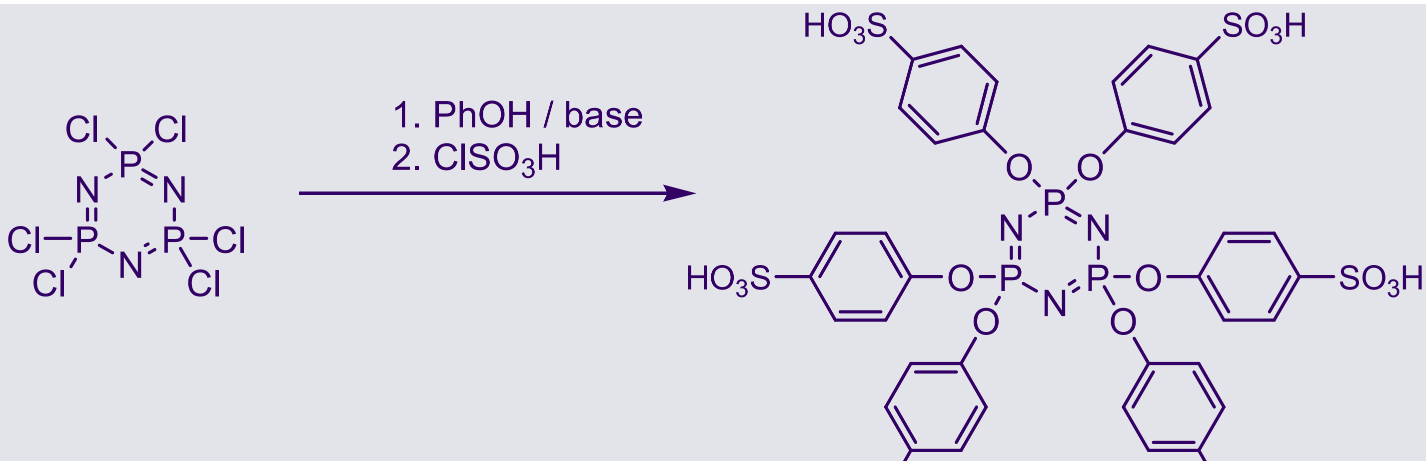

| | Method | Sulfonation Level |
|---|---|---|
| Radel® A-100 | $SO_3$ / NMP | 3 wt.% $SO_3H$ |
| Radel® A-100 | $ClSO_3H$<br>$Ac_2O$ | 3 wt.% $SO_3H$ |
| Radel® R-5000 | $SO_3$ / NMP | 12 wt.% $SO_3H$ or below |
| Radel® R-5000 | $ClSO_3H$<br>$Ac_2O$ | 20 wt.% $SO_3H$ or below |

**Chlorosulfonic acid sulfonation method best for higher wt.% $SO_3H$**

# Synthesis of Nano-Additives: $SO_3H$ Form




Sulfonated Octaphenyl POSS




Sulfonated Phosphazene

# Solution Casting

## Solubility and Rheology

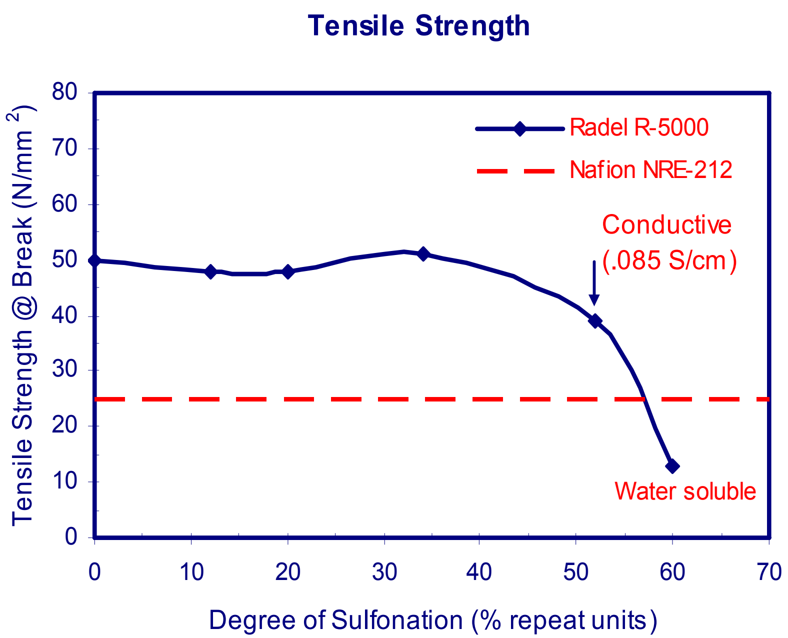
- N-Methyl-2-pyrrolidone (NMP) selected as best solvent for modified Radel® R-5000 polymer (limited solubility in other dipolar aprotic solvents)
- Solids level of 20% polymer in NMP produced good solution casting rheology with viscosity of 2800 cP (higher solids too viscous, lower solids produced films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

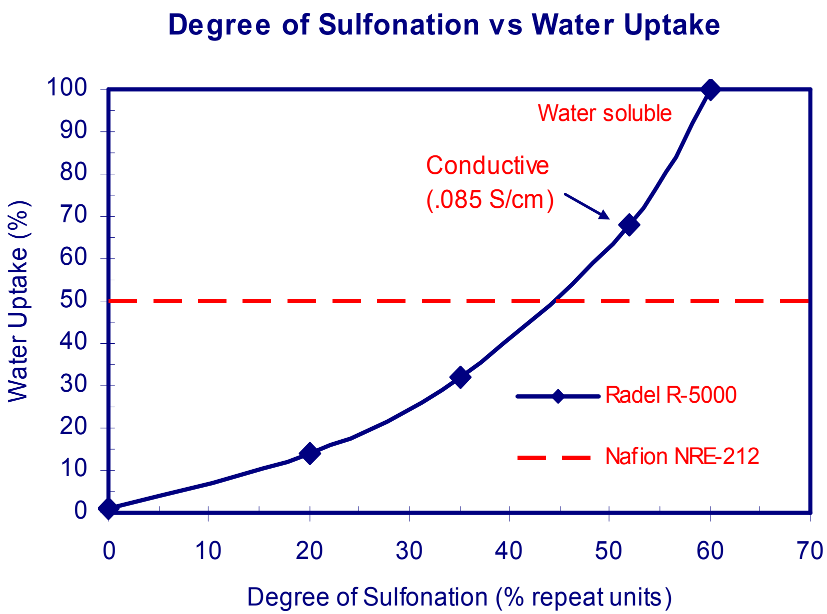
## Casting Sheet Material

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®)
- **Polyester (Mylar®)** ****chosen as casting substrate**

# Characterization of Modified Polymer and Composite Membranes




***Trend shows Sulfonated Radel® R-5000 more mechanically stable than Nafion®***

***Optimum degree of sulfonation most likely between 40% and 50%***

# Characterization of Modified Polymer and Composite Membranes

## Sulfonated Radel® R-5000
## Degree of Sulfonation: 52%

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

## Sulfonated Radel® R-5000
## Degree of Sulfonation: 34%

| Membrane Description | Conductivity (S/cm) | Tensile @ Break ($N/mm^2$) |
|---|---|---|
| Radel® R-5000 (D.S. 34%) | 0.002 | 51 |
| Radel® R-5000 + POSS (10%) | 0.005 | 23 |
| Radel® 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***

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# Characterization of Modified Polymer and Composite Membranes

**Additive A:** $SO_3H$-POSS

**Additive B:** $SO_3H$ 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.% $SO_3H$ | 8% | 17% | 22% | 22% |
| In-plane σ | 0.079 S $cm^{-1}$ | 0.085 S $cm^{-1}$ | 0.066 S $cm^{-1}$ | 0.105 S $cm^{-1}$ |
| Through plane σ | 0.099 S $cm^{-1}$ | 0.110 S $cm^{-1}$ | 0.061 S $cm^{-1}$ | 0.089 S $cm^{-1}$ |
| $L_c$ (100% RH) | +10.4% | +2.3% | +3.2% | 0% |
| $L_c$ (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 $mm^{-2}$ | 39 N $mm^{-2}$ | 8 N $mm^{-2}$ | 15 N $mm^{-2}$ |
| 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$^2$ (40%Pt/C)

Electrode area - 5 cm$^2$

Membrane thickness = 50 μm

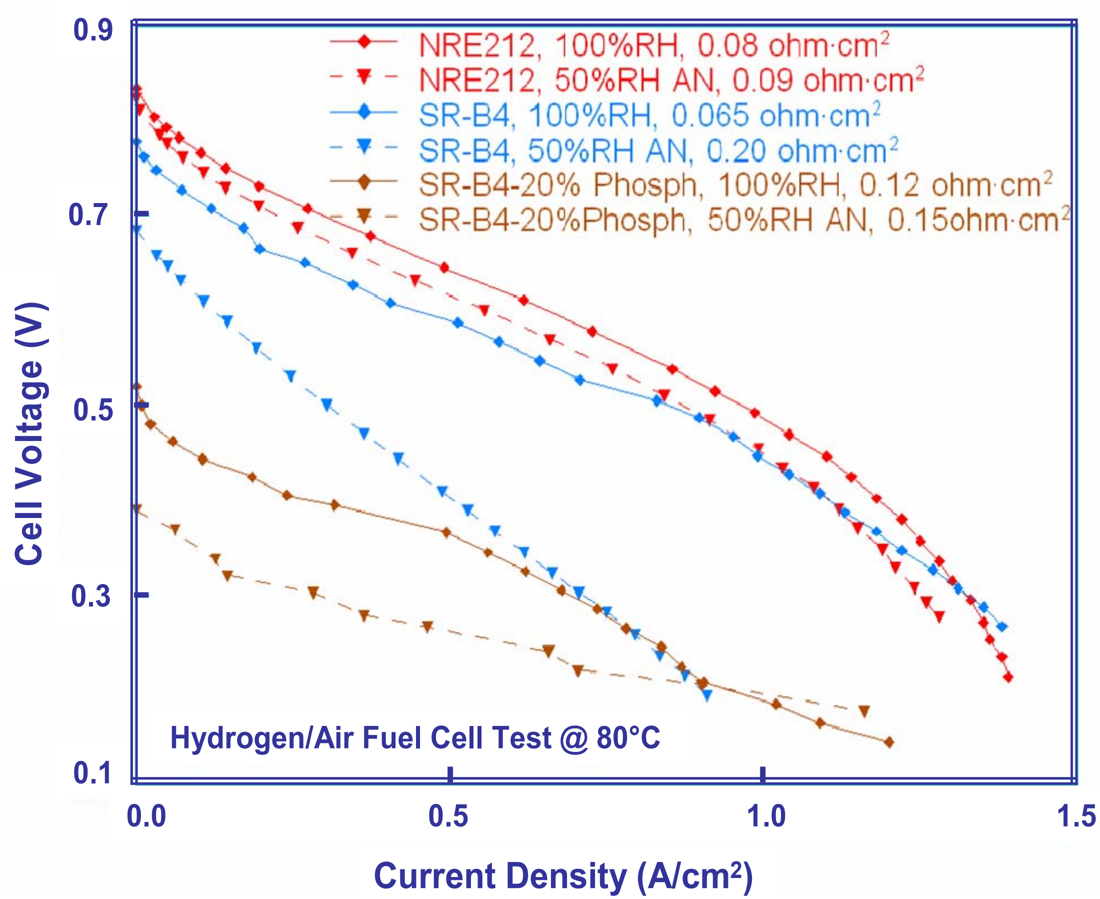
**Key:**

<u>SR-B4</u>

Sulfonated Radel R-5000 (52%)

<u>SR-B4-20%</u>

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



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# Characterization of Modified Polymer Using PEM-LITE™ System

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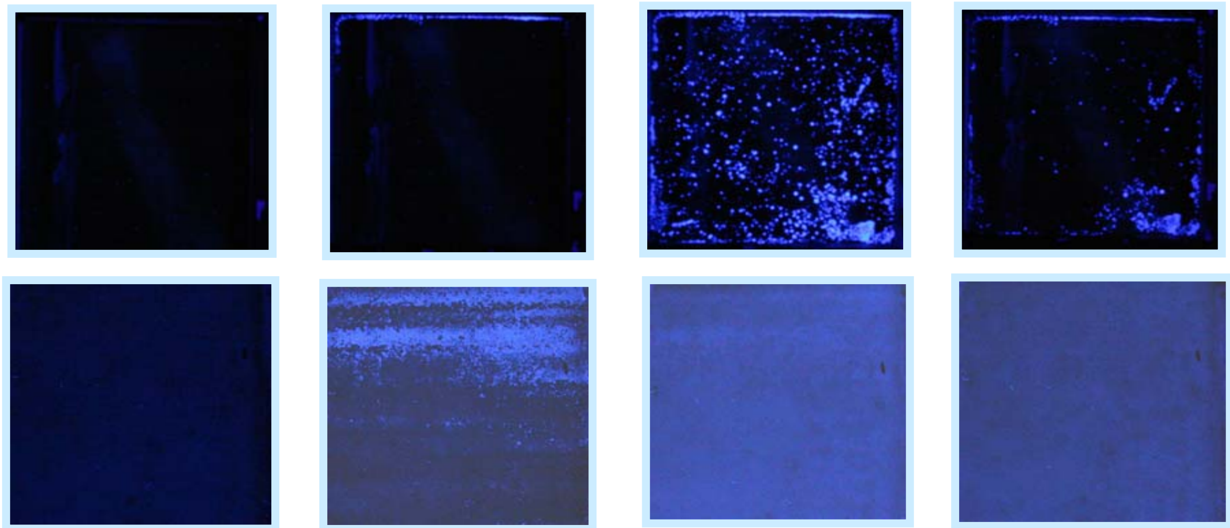
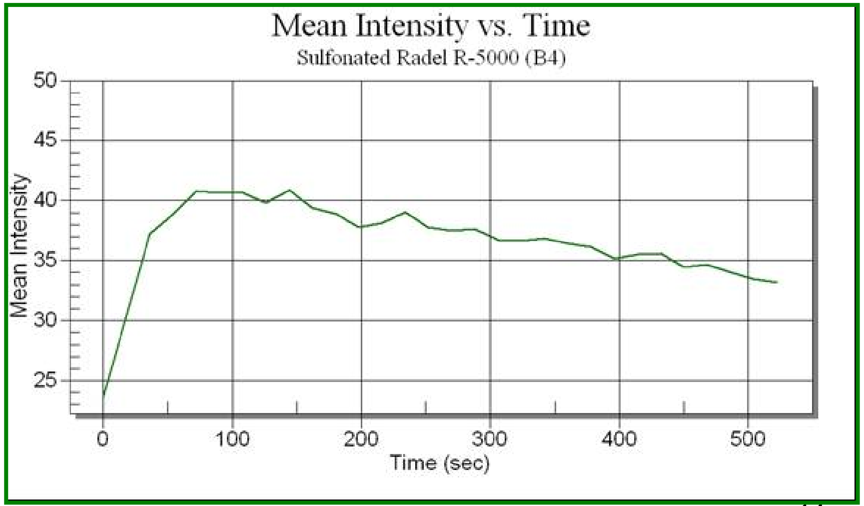
**Nafion® 212**

**50 μm**

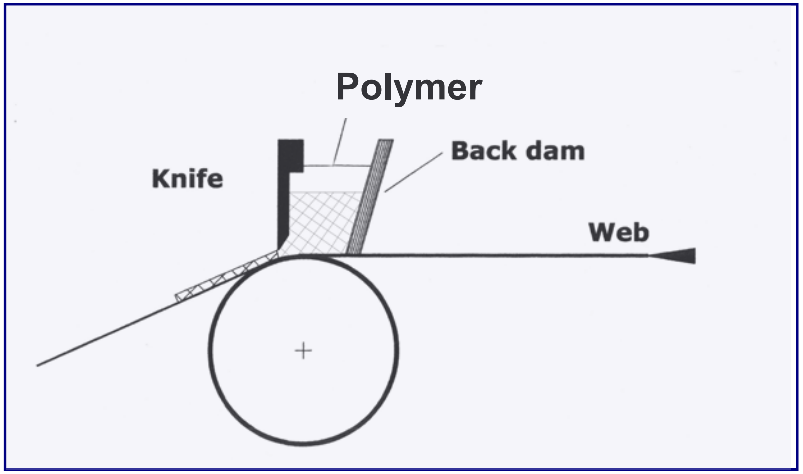
**Radel® R-5000 (52%) sulfonated**

**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

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

| 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 |

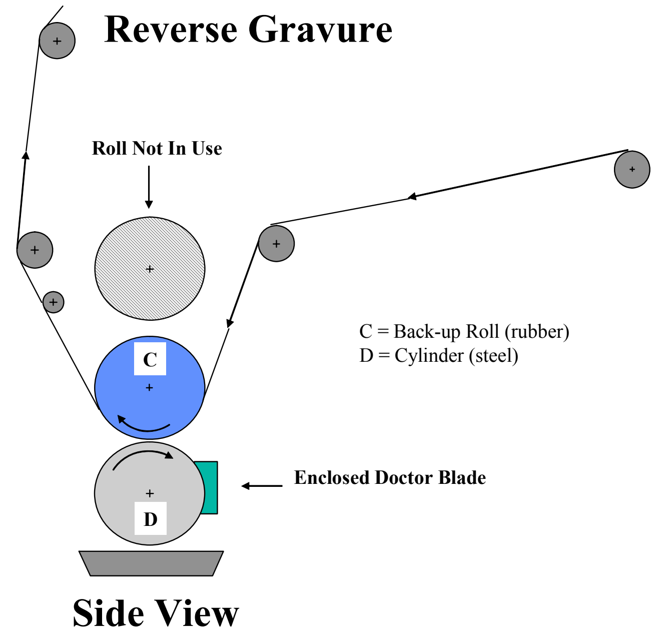
*Oven temperatures in degrees Fahrenheit

# 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 |

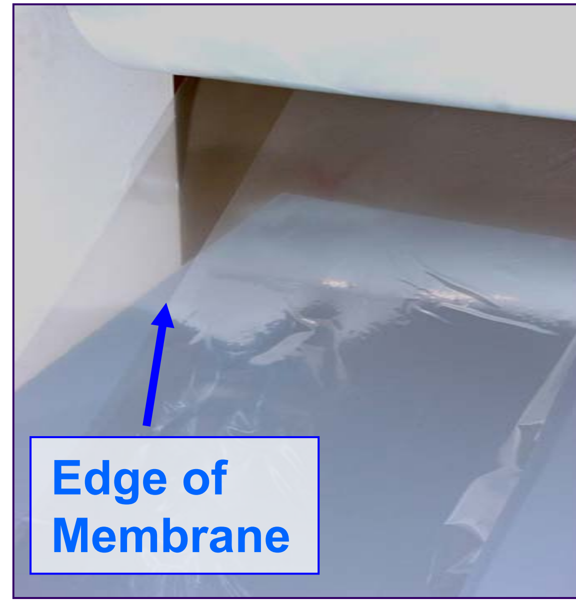
*Oven temperatures in degrees Fahrenheit

*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 $H_2$/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)*

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# 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

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

**Radel® retained a good modulus at elevated temperatures**

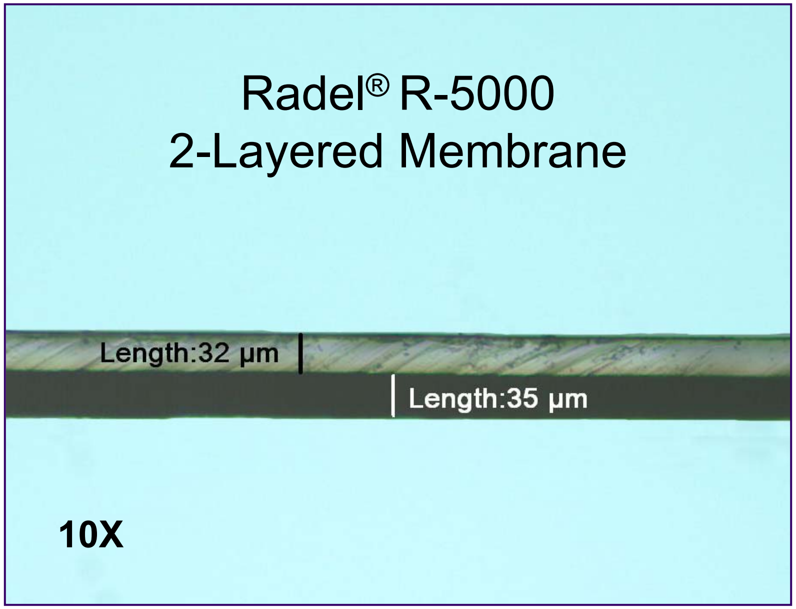
# Multi-Layered Membranes

Optical micrograph showing uniform thickness of layers

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

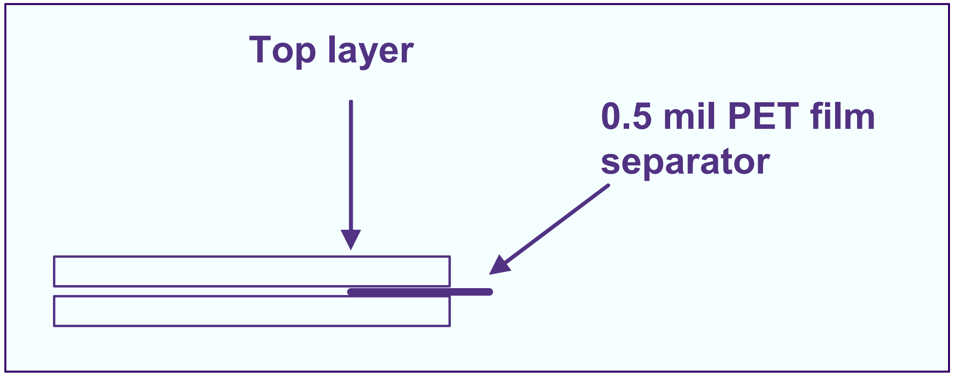
**Micrometer: Clear 32 µm Black: 34 µm**

**Microscope: Clear 32 µm Black: 35 µm**




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

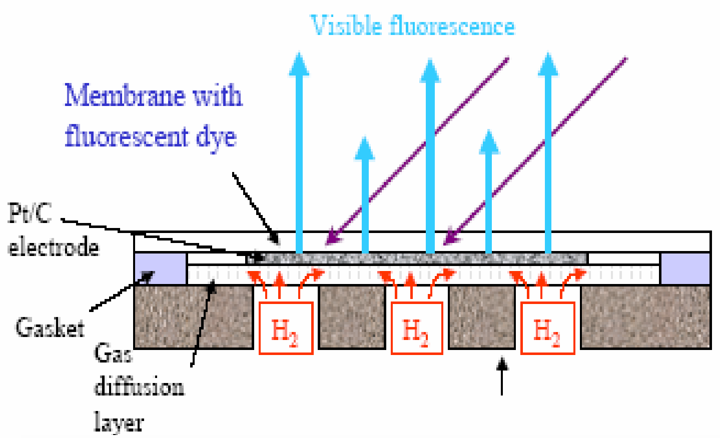
T-Peel Configuration

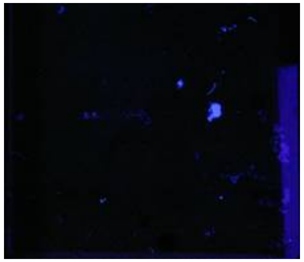



**Interlayer adhesion evaluated using ASTM T-peel and Tensile Test methods. Interlayer adhesion excellent for Radel® R-5000.**

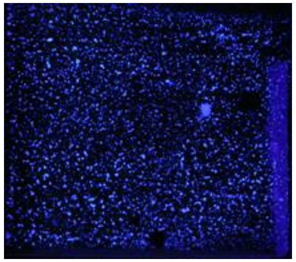
# Characterization of Modified Polymer and Composite Membranes

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

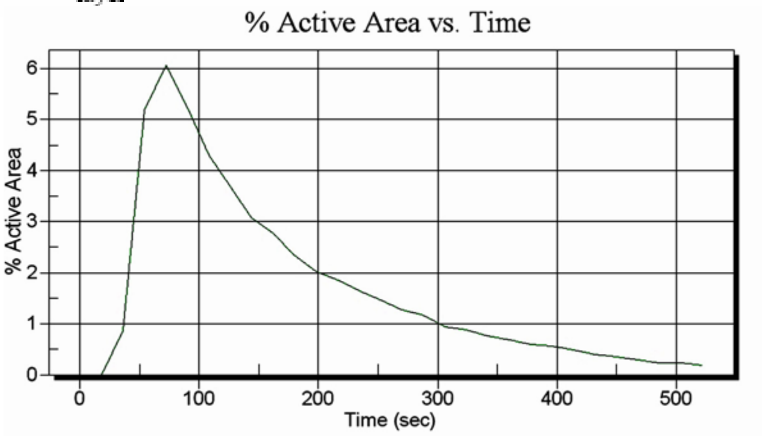


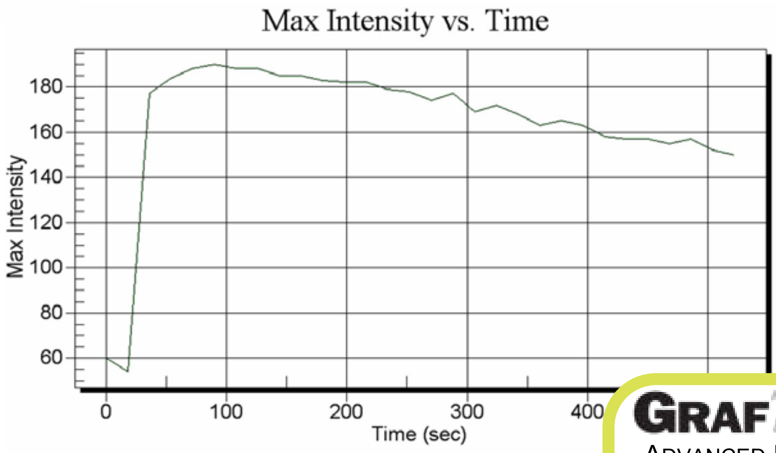



Nafion 112 0 sec



Nafion 112 60 sec




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