

# 2005 DOE Hydrogen and Fuel Cells Program Review

**Development of a Low-cost, Durable Membrane and MEA for Stationary and Mobile Fuel Cell Applications**

Michel Fouré  
Arkema Inc.  
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**This presentation does not contain any proprietary or confidential information.**

# Project Overview

## Timeline

- Start Date: Jan. 2004
- End Date: Dec 2006
- 45% complete

## Barriers

- O. Stack Material & Manufacturing Cost
- P. Durability

## Targets

- Cost \$35/kW
- Durability 5000 hours

## Budget

- Total Funding
  - DOE: \$5,771,351
  - Partners: \$2,240,564
- FY 04 Funding: 1.90 M\$
- FY 05 Funding: 1.79 M\$

## Partners

- Arkema
  - Georgia Tech.
- Johnson Matthey Fuel Cells
- UTC Fuel Cells
  - University of Hawaii

# Project Objectives

## Global Objective:

- Development of a low cost and durable membrane to assist the DOE in driving the commercial reality of fuel cells by:
  - Developing a novel low cost membrane
  - Developing an optimized MEAs with this membrane
  - Validating in-cell performance with an optimized membrane/MEA

## Specific Objective Over Past Period:

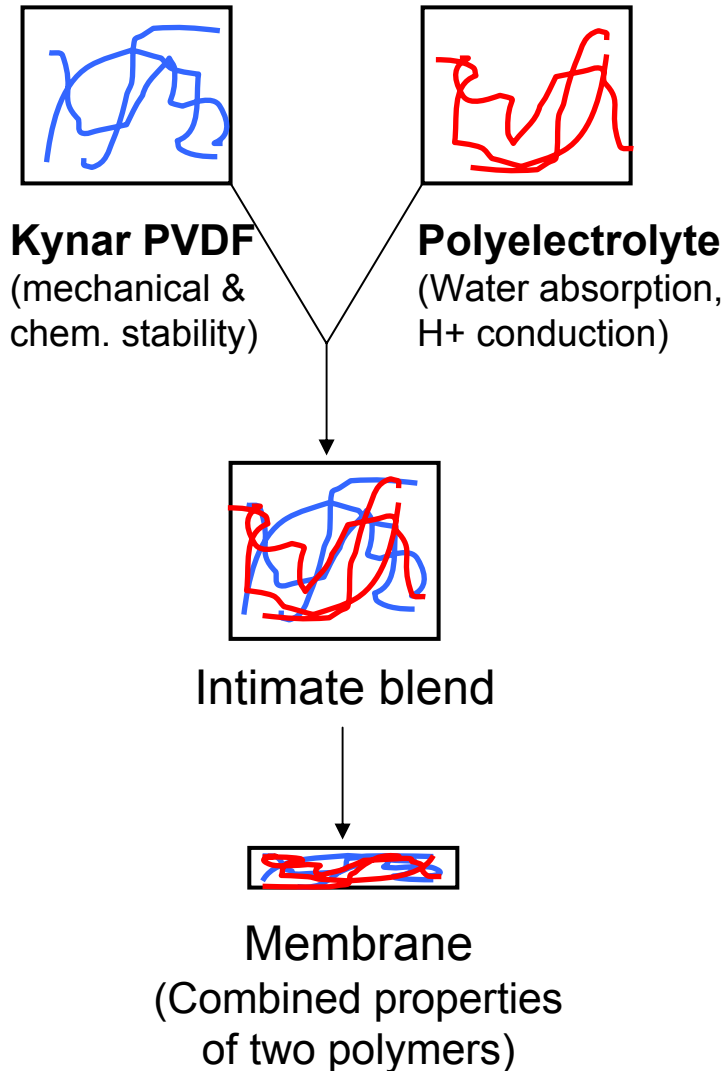
- While good initial electrochemical performance has been demonstrated, decay rates were too high. The project focus was to identify the reason for the high decay rate and begin work on making improvements.

# Reviewer's Comments

- Most comments pertained to developing an understanding of sulfur loss, decay rate and durability as a high priority
  - Several analytical methods have been developed to evaluate breakdown products during durability testing
  - The nature of the sulfur species evolved and the mechanism of loss has been determined
  - Cooperative work with Oakridge National Labs is starting to further assess atomic scale chemical and structural changes in membranes and MEAs

# Membrane Approach

- Use a blend of Kynar® PVDF and a proprietary polyelectrolyte to produce a novel low cost membrane
- Kynar® PVDF (Poly(vinylidene fluoride)):
  - Stable in acidic/oxidizing media (HF, HCl, HBr, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>...)
  - Electrochemically stable (Li ion batteries...)
  - No H<sup>+</sup> conduction
- Polyelectrolyte:
  - Novel composition to produce needed morphology when blended with PVDF
  - High H<sup>+</sup> conduction
- There are many variations possible in:
  - The type of Kynar used
  - The composition of the polyelectrolyte
  - The process to blend them



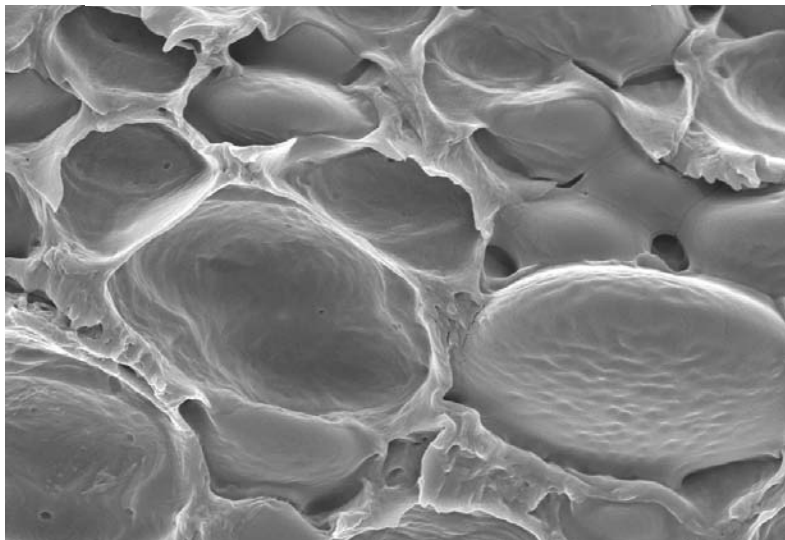
# Morphology Necessary for High Conductivity

- Striking structure/property correlation
- Scanning electron micrographs for similar formulations:

Range of morphologies possible

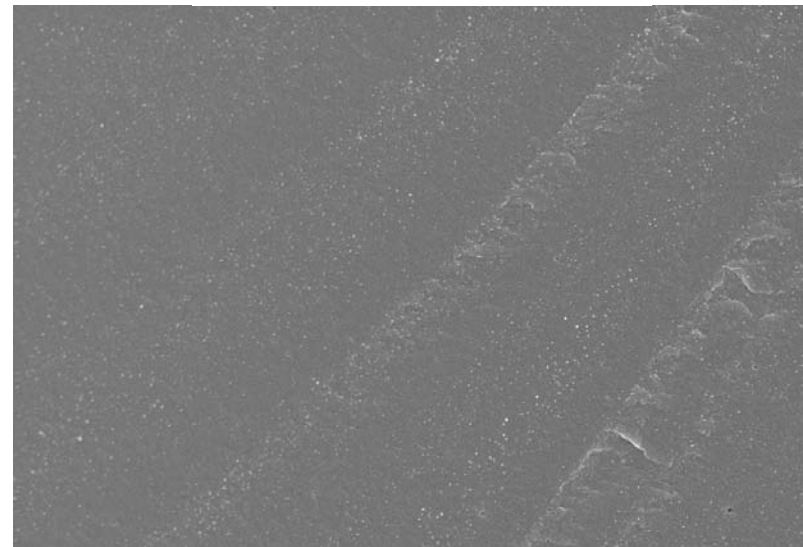


Phase Separated



20-40 mS/cm

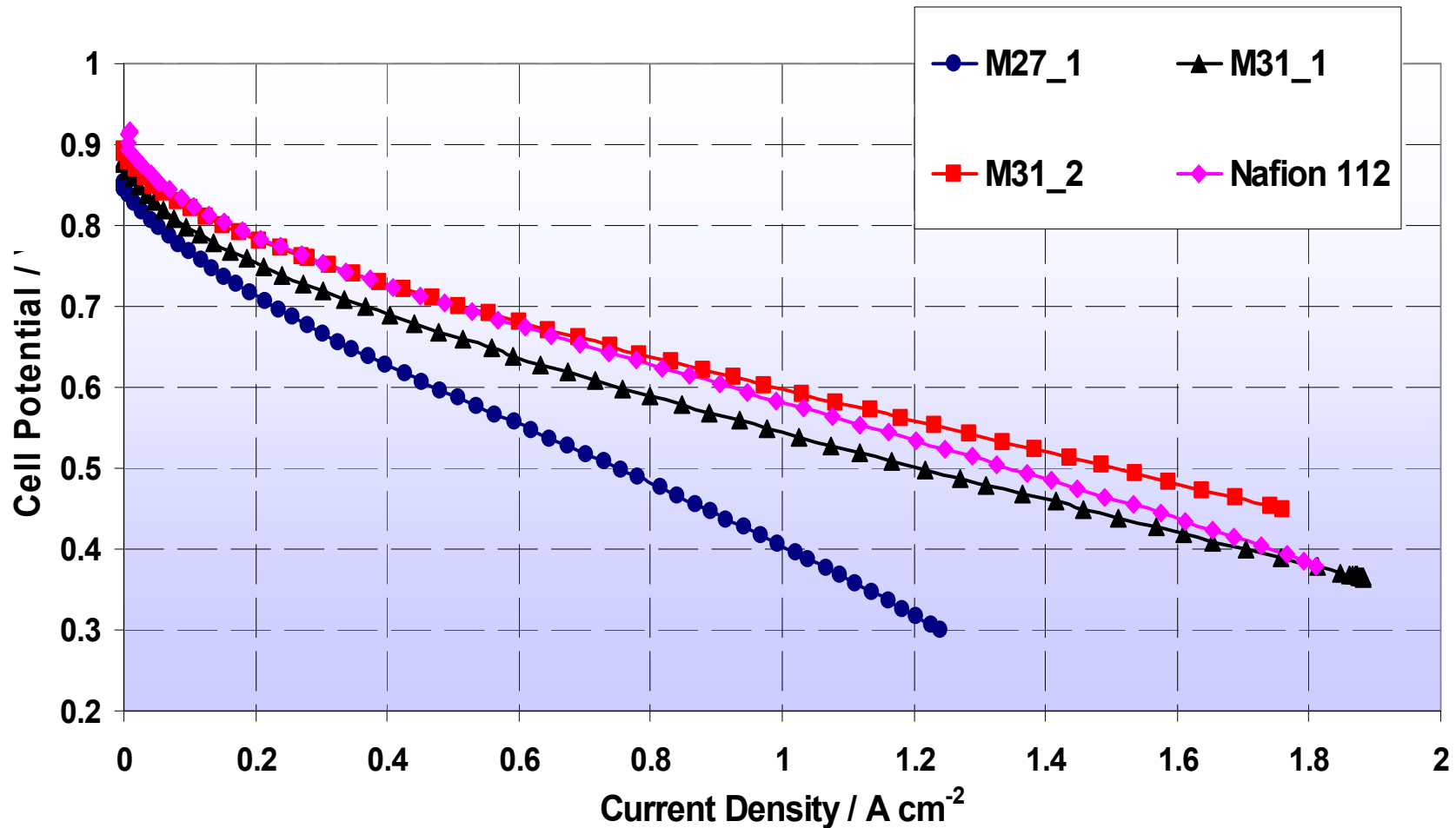
Compatibilized



1  $\mu$ m

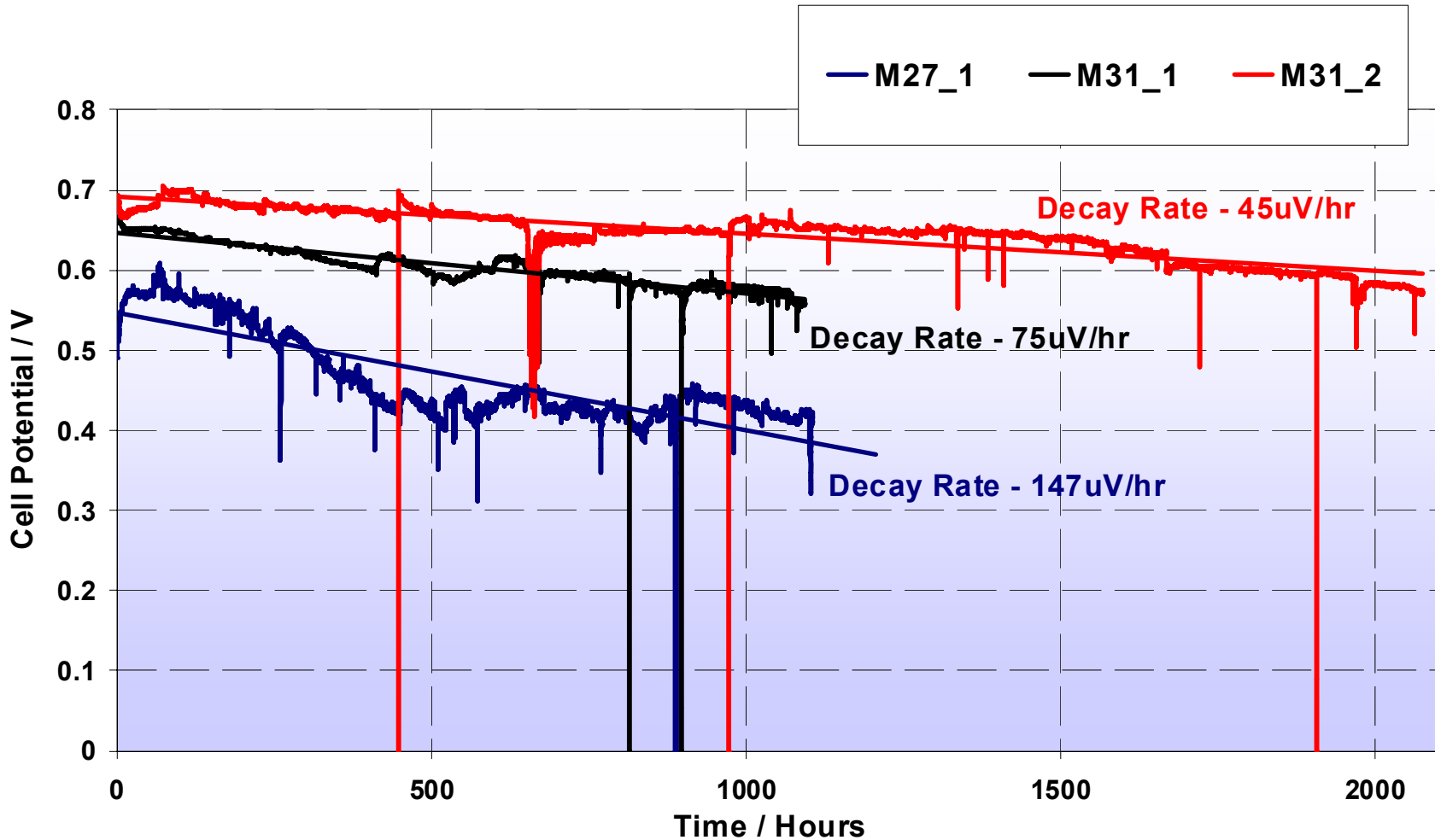
90-230 mS/cm

# MEAs Tested for Durability



60°C, 100% RH, 1 atm., H<sub>2</sub>/O<sub>2</sub>

# Long-term Endurance Test



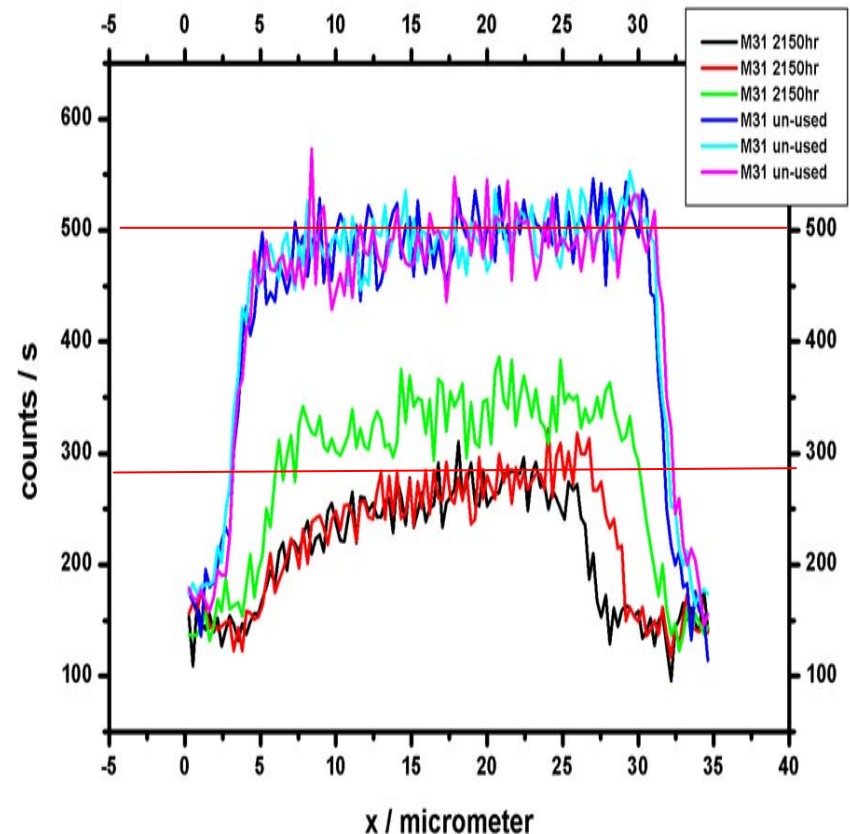
60°C, 100% RH, 1 atm., H<sub>2</sub>/O<sub>2</sub> (1.3/1.4), 0.5 A/cm<sup>2</sup>  
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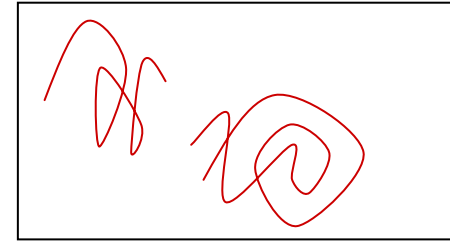
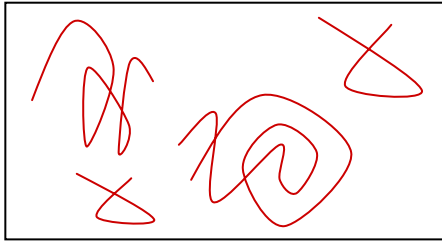
# Long Term Endurance Test

- Post mortem analysis of the MEA revealed:
  - Sulfur loss
  - Membrane thinning
  - MEA electrical shorting
- Cross-sectional XRF sulfur mapping
  - Sulfur concentration decreases
  - Sulfur loss occurs across the entire membrane thickness



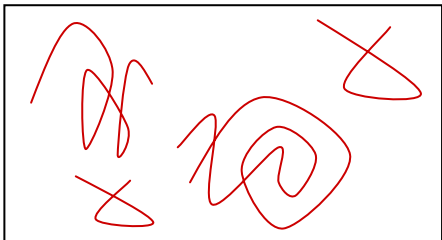
# How Could Sulfur Be Lost?

- 1) Leaching of low-molecular weight species



*Solution: increase molecular weight*

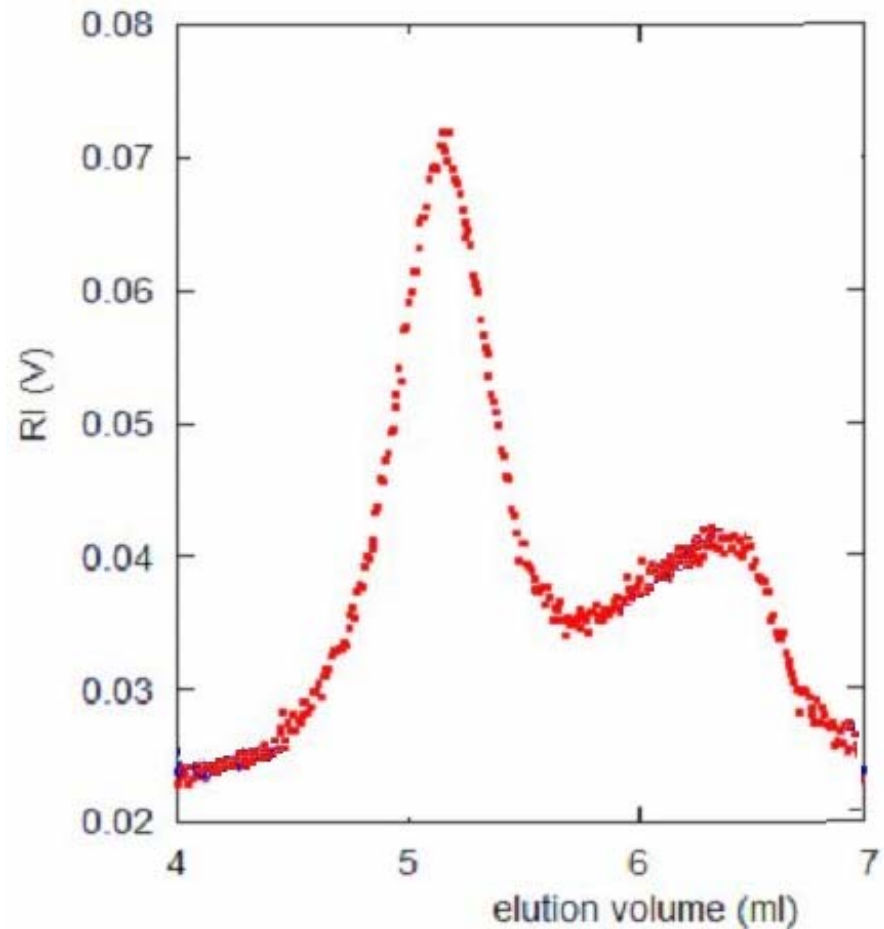
- 2) Chemical degradation



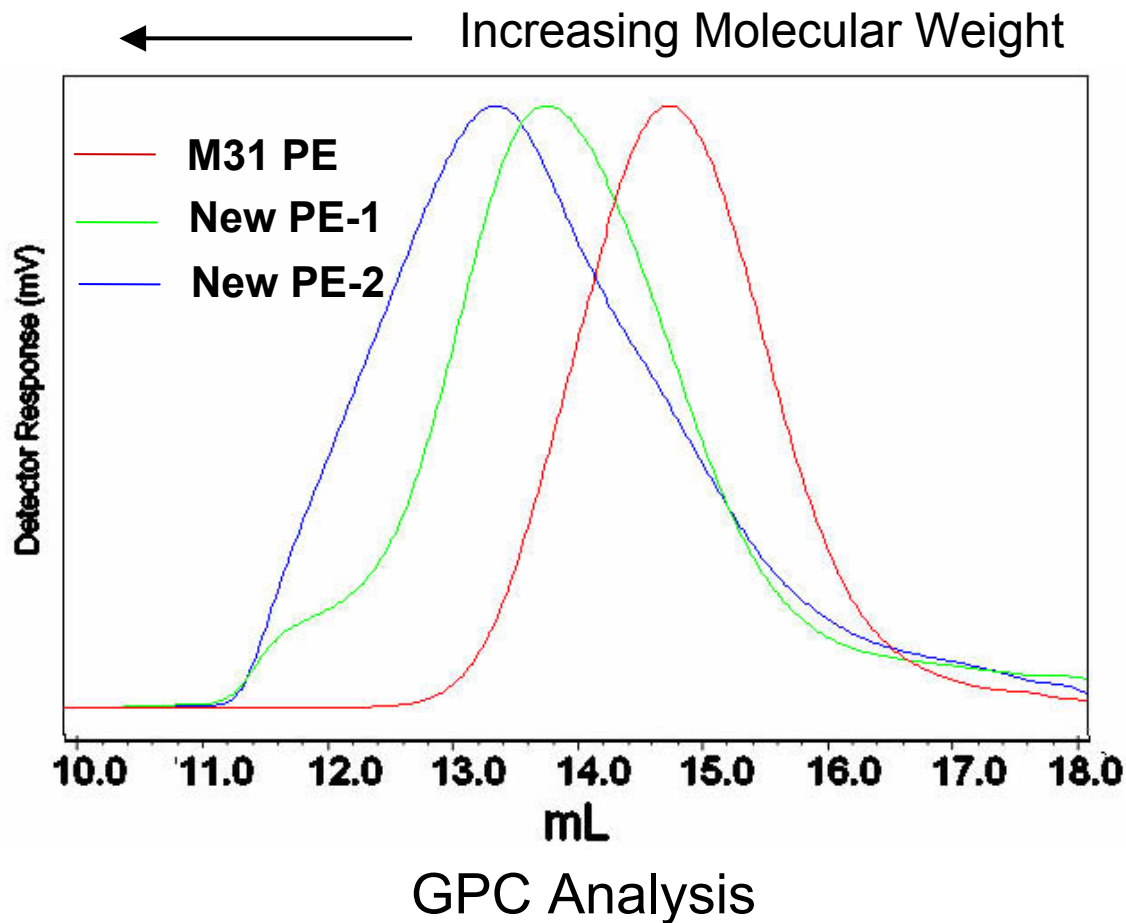
*Solution: modified chemistry*

# GPC Analysis of Fuel Cell Effluent

- Two primary peaks noted in GPC
  - A larger peak at higher MW indicating possible oligomer presence
  - A smaller peak at lower MW indicating a possible degradation product



# Effect of Polyelectrolyte (PE) Molecular Weight Increase



- A process to increase PE molecular weight was developed
- Increasing PE molecular weight significantly decreased membrane sulfur loss

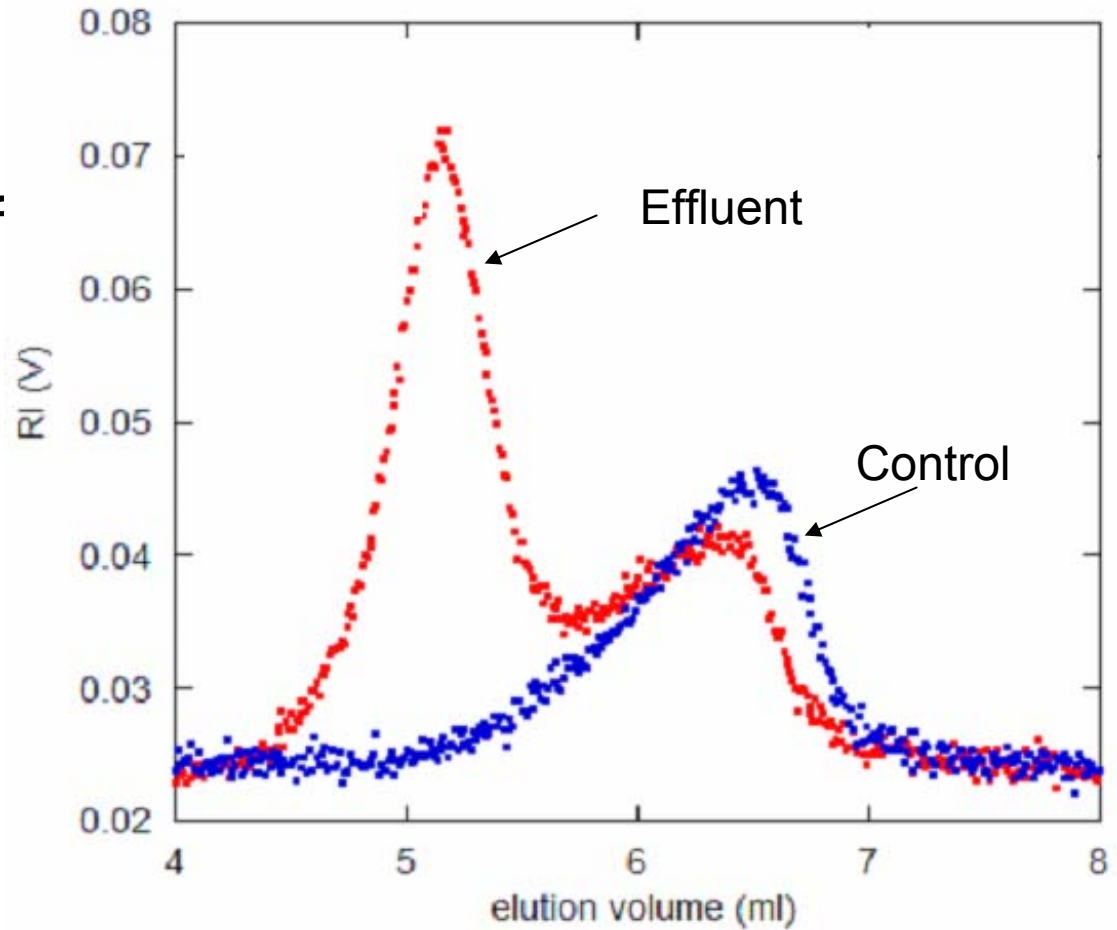
# Ion Chromatography of Water Effluents

Effluent	F	SO <sub>4</sub> <sup>2-</sup>	SO <sub>3</sub> <sup>2-</sup>
M31 80 °C (Johnson Matthey in-cell)	0.16	6.0	0.42
PFSA 80 °C (Johnson Matthey in-cell)	0.91	< 0.1	0
M31 80 °C (Arkema ex-situ)	0.10	0.02	3.52

- Presence of sulfate species from in-cell test was unexpected
- Ex-situ testing simulates loss, but as sulfonate, (as expected) not sulfate
- Difference due to oxidation of leached species
- Pure form of suspected sulfonate species tested and matched that found in ex-situ effluent test
- Fluoride emission from M31 membrane lower than commercial PFSA membrane

# GPC Analysis of Fuel Cell Effluent Plus Control

- Retention time of control matched low molecular weight peak of fuel cell effluent



# Summary of Sulfur Loss

- An accelerated ex-situ test, while not perfect, provides the same trends as those observed in a fuel cell.
- The analytical methodology to understand the fate of sulfur species has been developed.
- Sulfur loss for M31 has been traced back to:
  - Oligomer leaching (~50%)
  - Chemical degradation (~50%)
- Elimination of oligomer leaching was demonstrated via increasing molecular weight but chemical degradation necessitates further polyelectrolyte modification

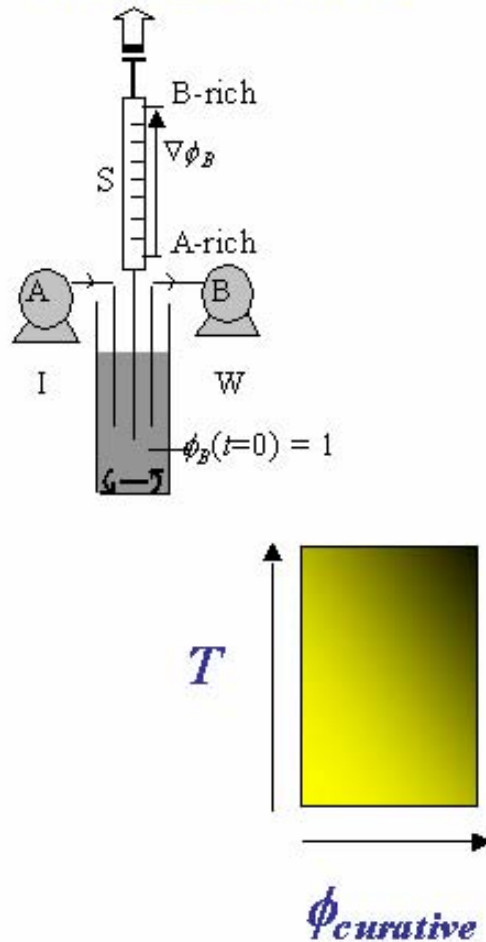
# Membrane Status

- Family “A” membranes (M31 Type)
  - Initial electrochemical performance in optimized MEAs similar to PFSA based MEA
  - Increased PE molecular weight yielded significant reduction in sulfur loss
  - Sulfur loss too high to ensure long term durability but mechanisms now clearly understood
- Family “B” membranes
  - Problematic chemistry in Family “A” identified and replaced
  - Molecular weight effect again confirmed
  - Initial electrochemical performance not significantly changed compared to Family “A”
  - Sulfur loss still believed to be too high for long term durability
- Family “C” membranes
  - Currently in development and will address both molecular weight and chemistry issues noted in Family “A”

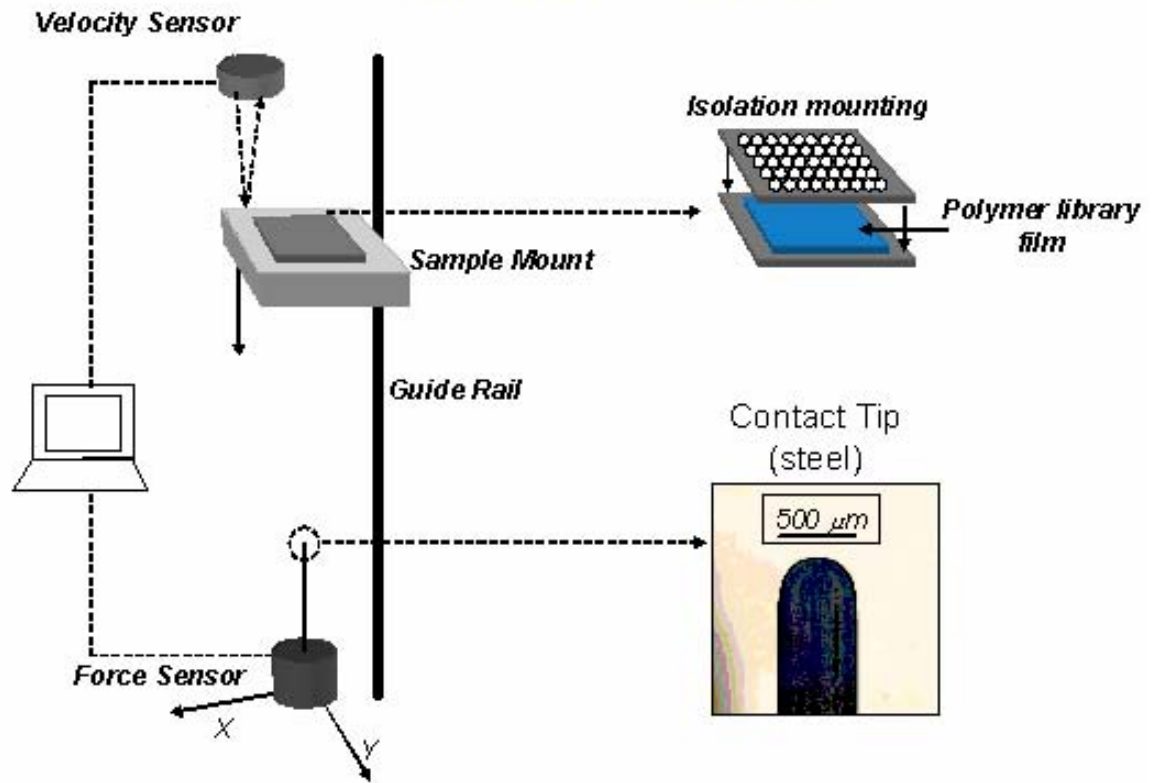


# Georgia Tech: High-Throughput Synthesis & Mechanics

## Gradient Libraries

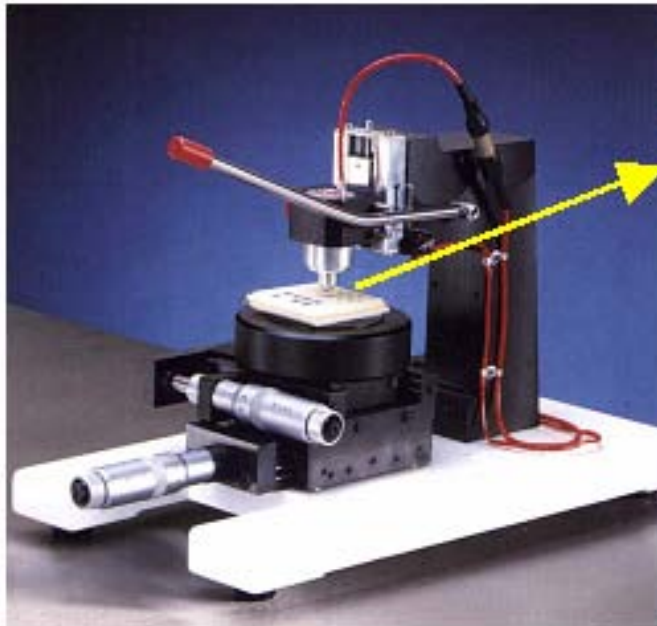


## Mechanical Screening



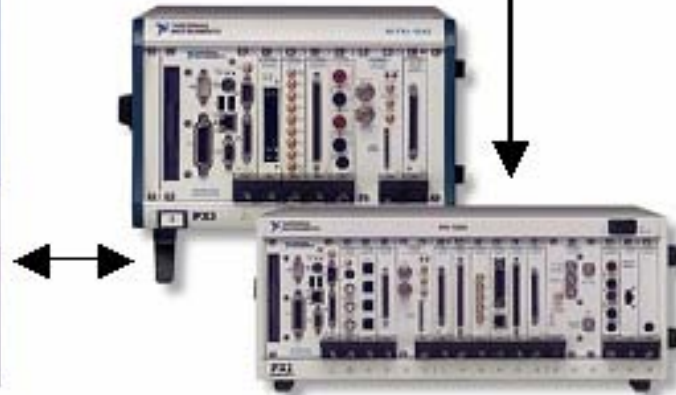
# Georgia Tech: High-Throughput Conductivity

Rapid point-to-point  
Jandel Scientific



4-point probe  
600  $\mu\text{m}$  spacing

Screw allows pressure to be user adjusted



PXI-Based AC Signal Generator and  
Measurement

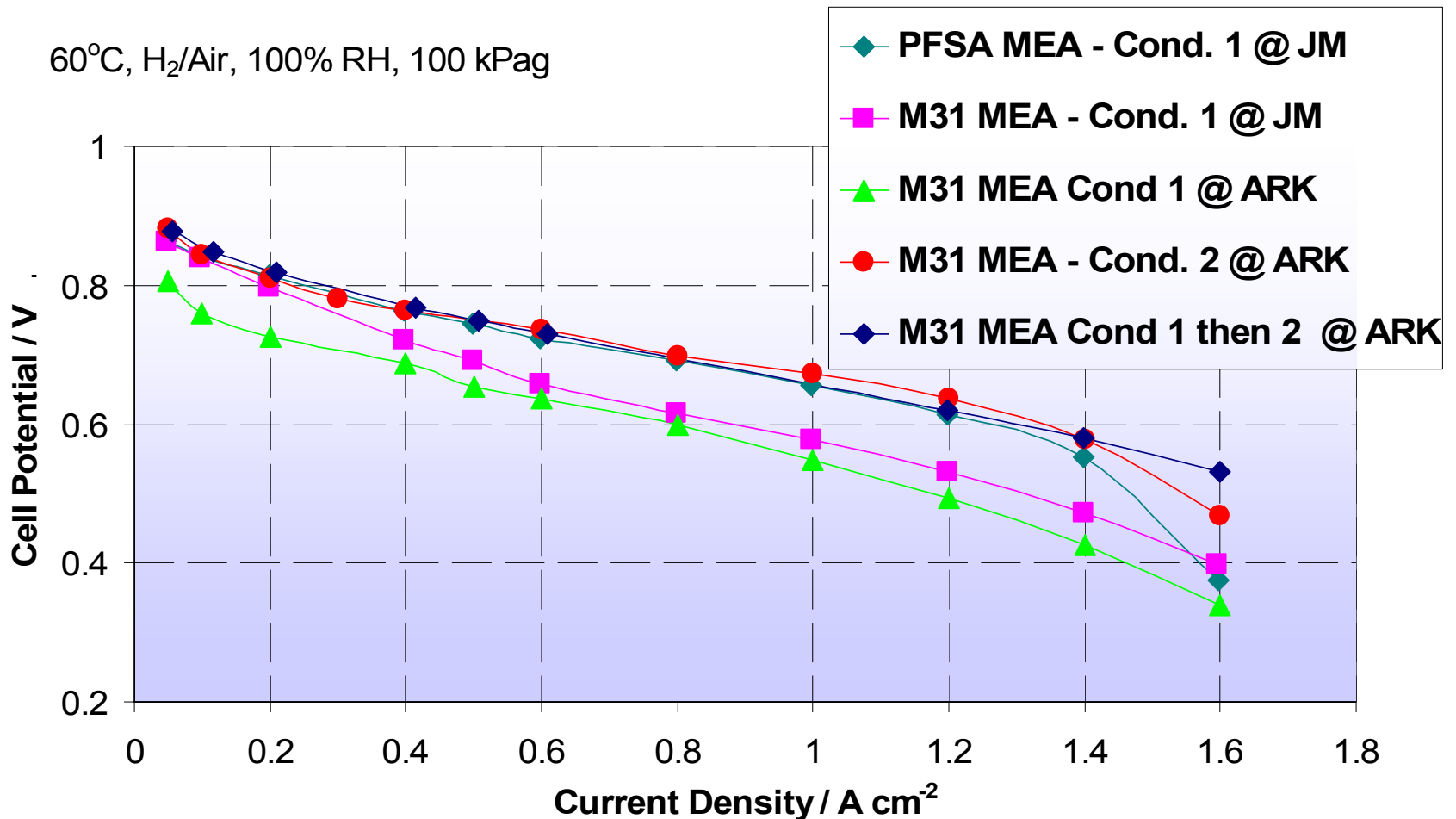
# Johnson Matthey Gas Permeability Testing

<b>Hydrogen</b> Permeability measurements	Electrochemical	GC gas phase
	ml/min	ml/min
Commercial Perfluorinated (30 $\mu\text{m}$ )	~1.4 - 1.5	~ 0.64
M31 (25 $\mu\text{m}$ )	~0.16	~0.2 - 0.4

<b>Oxygen</b> Permeability measurements	Concentration	Rate
	ppm	ml/min
Commercial perfluorinated (30 $\mu\text{m}$ )	~107	~0.062
M31 (25 $\mu\text{m}$ )	~60	~0.035

- Arkema's 25 $\mu\text{m}$  membrane has significantly less hydrogen and oxygen permeation than a commercial 30 $\mu\text{m}$  PSFA membrane.
- Reduced permeation is expected to lessen peroxide formation and improve durability

# Coordination of Johnson Matthey & Arkema Conditioning



# Collaboration with Oak Ridge National Lab

## Objectives

- Evaluate degradation and material change of Arkema membrane and MEA structure.
- Evaluate MEA process variables to optimize performance.

## Technical Approach

- Quantitative characterization of atomic scale structural and chemical changes in both the membrane and the electrode using:
  - Ultramicrotomy (<50nm) of 5-layer MEAs
  - TEM + Analytical Electron Microscopy
  - SAXS

# Planned Testing at Hawaii National Energy Institute

- With the cooperation of UTC Fuel Cells, fuel cell testing will be conducted with Arkema membranes to assess the following.
  - Experience with UTC-FC Hardware
    - i. Unique cell design
    - ii. Gasketing
  - Scale up of MEAs
    - i. Feasibility
    - ii. Reliability
  - More in-depth studies of MEA under UTC conditions
    - i. Hel-Ox studies
    - ii. Water management
- The work will only focus on short-term electrochemical performance.

# Summary of Major Findings To-Date

- Membrane
  - High conductivity achieved: 130-200 mS/cm (in water).
  - Improved conductivities at low Relative Humidities.
  - Good mechanical properties in the dry state.
  - Process scaled up to pilot plant.
  - Developed high-throughput methodology for rapid screening (conductivity, water solubility and permeability, mechanical properties) (Georgia Tech).
- MEA
  - Initial performance comparable to commercial MEA (JM).
  - Initial OCV comparable to commercial MEA.
  - Demonstrated low RH operation (despite limited ex-situ membrane conductivity).
  - Excellent impermeability to hydrogen and oxygen.
  - Achieved 2100 hour endurance test.
  - Understood failure mechanism.
  - Developed road map to resolve.

# Future Work

- Remainder of FY 2005
  - Optimization of Family “C” polyelectrolyte (Arkema & GA Tech)
    - Confirm improved durability
    - Characterize membranes ex-situ & in-situ
    - Characterize membrane/MEA microstructure (ORNL)
  - Begin MEA optimization of Family “C” based membrane (Johnson Matthey & Arkema)
  - Generate fuel cell data under UTC protocol (Univ. HI & UTC)
- FY 2006
  - Optimize MEA with Family “C” based membrane
  - Conduct in-cell durability tests
  - Verify full size cell performance
  - Scale up membrane process



# Backup Slides

# Publications and Presentations

- Aug 2004: DOE quarterly review meeting to the and FreedomCAR Tech. Team; Detroit, MI
- Aug 2004: American Chemical Society meeting; Philadelphia, PA
- Nov 2004: 2004 Fuel Cell Seminar; San Antonio, TX
- Jan 2005: DOE quarterly review meetings; Washington DC

# Hydrogen Safety

- The most significant hazard associated with this project is the potential for hydrogen leaks and fires during unattended operation (primarily for extended durability testing).
- As example, during and extended durability test, a small fire ignited within the fuel cell test stand during attended operation. Because it was during attended operation, the fire was quickly extinguished and damage was minimal. Had this occurred during unattended operation, significant damage would have resulted.

# Hydrogen Safety (cont.)

- From the experience we had, several measures were taken to ensure safe operation during unattended and attended operation including:
  - All hydrogen tanks were relocated to a safer remote location (no tanks are present in the fuel cell test lab)
  - Additional hydrogen sensors were installed
  - An automatic CO<sub>2</sub> fire suppression system with integrated heat and smoke sensors was installed within each fuel cell test stand