



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

2006 Hydrogen Program Annual Review

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This presentation does not
contain any proprietary or
confidential information

Project ID#: FC 6

Project Overview

Timeline

- Start Date: Oct. 2003
- End Date: Mar. 2007
(with 6 mo. no-cost extension)

Barriers

- Cost
- Durability

Targets

- Cost \$30/kW
- Durability 5000 hours

Budget

- Total Funding
 - DOE: \$5,771K
 - Partners: \$2,241K
- FY2004 Funding
 - \$1,372K
- FY2005 Funding
 - \$1,284K

Partners

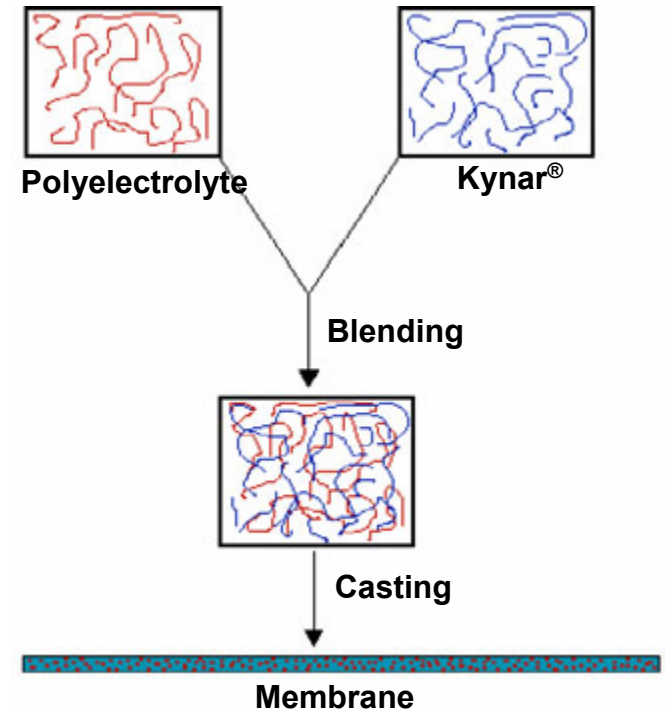
- Arkema:
 - Georgia Tech
- Johnson Matthey Fuel Cells
- UTC Fuel Cells
 - University of Hawaii

Project Objectives

- Overall
 - Develop low cost and durable membrane and MEA that can meet DOE targets and help drive the commercial reality of fuel cells
- 2005-2006
 - Optimize new polyelectrolytes
 - Confirm improved *ex-situ* durability
 - Characterize membranes *ex-situ* & *in-situ*
 - Begin MEA optimization of improved membrane
 - Characterize membrane/MEA microstructure
 - Optimize and validate high throughput methods

Arkema's Approach

- Use polymer blend system to decouple H⁺ conductivity from other requirements
 - Kynar® PVDF
 - Engineering thermoplastic
 - High chemical resistance
 - High electrochemical stability
 - No H⁺ conduction
 - Polyelectrolyte
 - Water absorption
 - H⁺ conduction
 - Physical properties unimportant
- A very flexible fabrication process
- Lower cost approach compared to PFSA
- M31 membrane demonstrated feasibility



M31 Summary of Major Findings

I. Membrane

- High conductivity achieved: 120-150 mS/cm (in water, at 70°C)
- Excellent mechanical properties in the dry state
- Excellent barrier to hydrogen and oxygen
- Process scaled up to pilot plant

II. MEA

- Beginning of Life performance comparable to PFSA MEA
- Demonstrated low cathode RH operation (despite limited ex-situ membrane conductivity at low RH)

● III. Durability

- Long-term durability is not sufficient
- Degradation mechanism positively identified
- Accelerated *ex-situ* test developed to mimic *in-situ* degradation

Blending of Kynar with Various Polyelectrolytes

Polyelectrolyte

Conductivity (mS/cm)

- Model materials

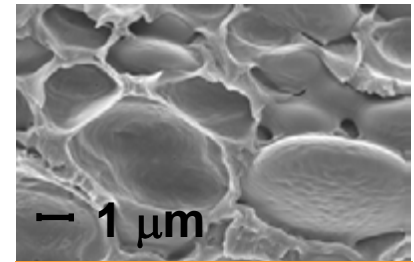
- P(AMPS) 90-120
- Sulfonated Polystyrene 50-90

Kynar® blending process is generally applicable for highly protogenic polymers

- Polymers developed for membrane evaluation

- Generation A (M31) 120-150
- Generation B 120-140
- Generation C 60-120
- Generation D 90-140

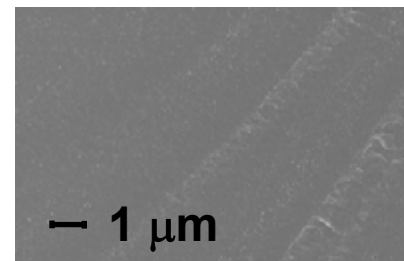
Phase Separated



20 - 40 mS/cm

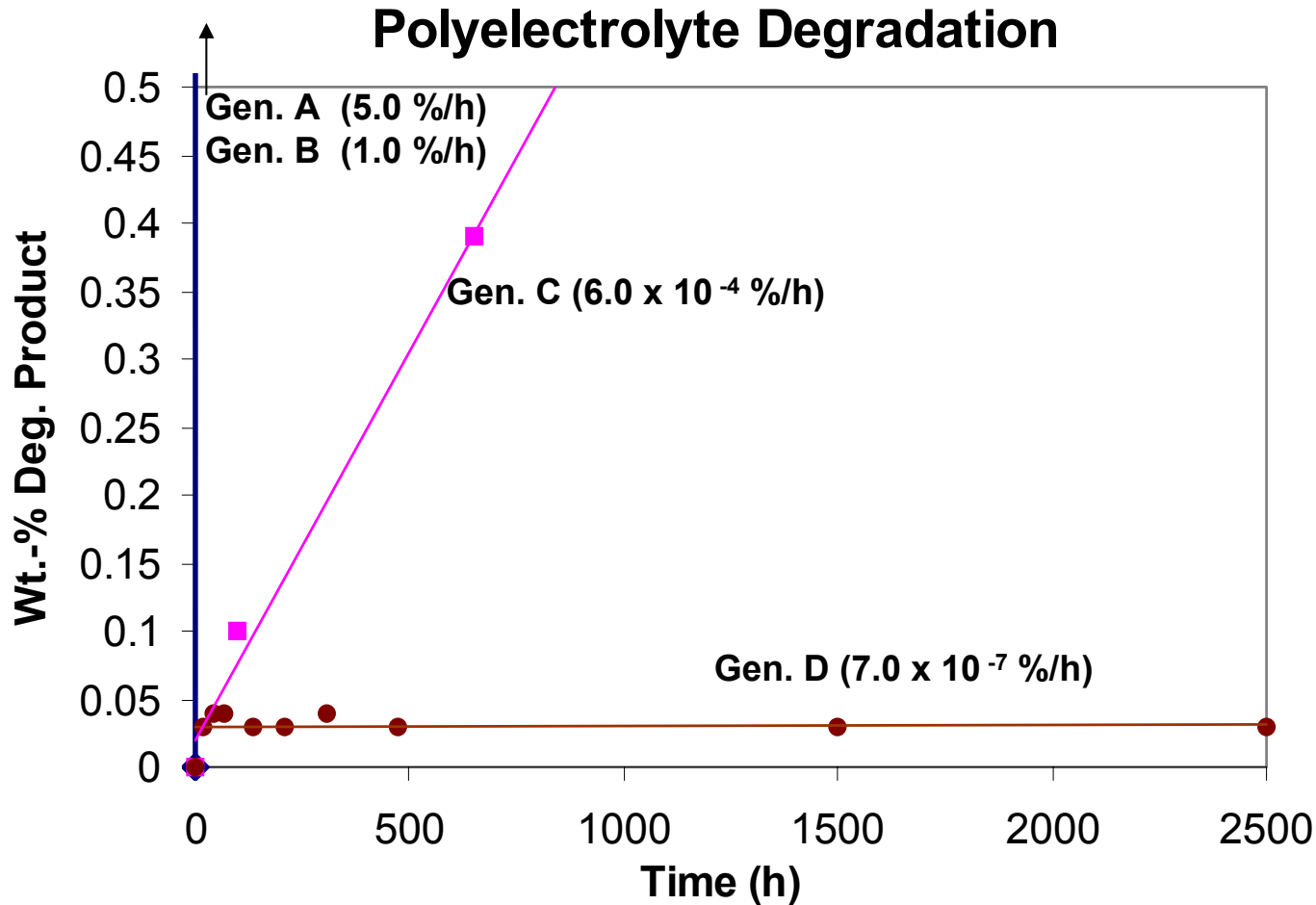


Compatibilized



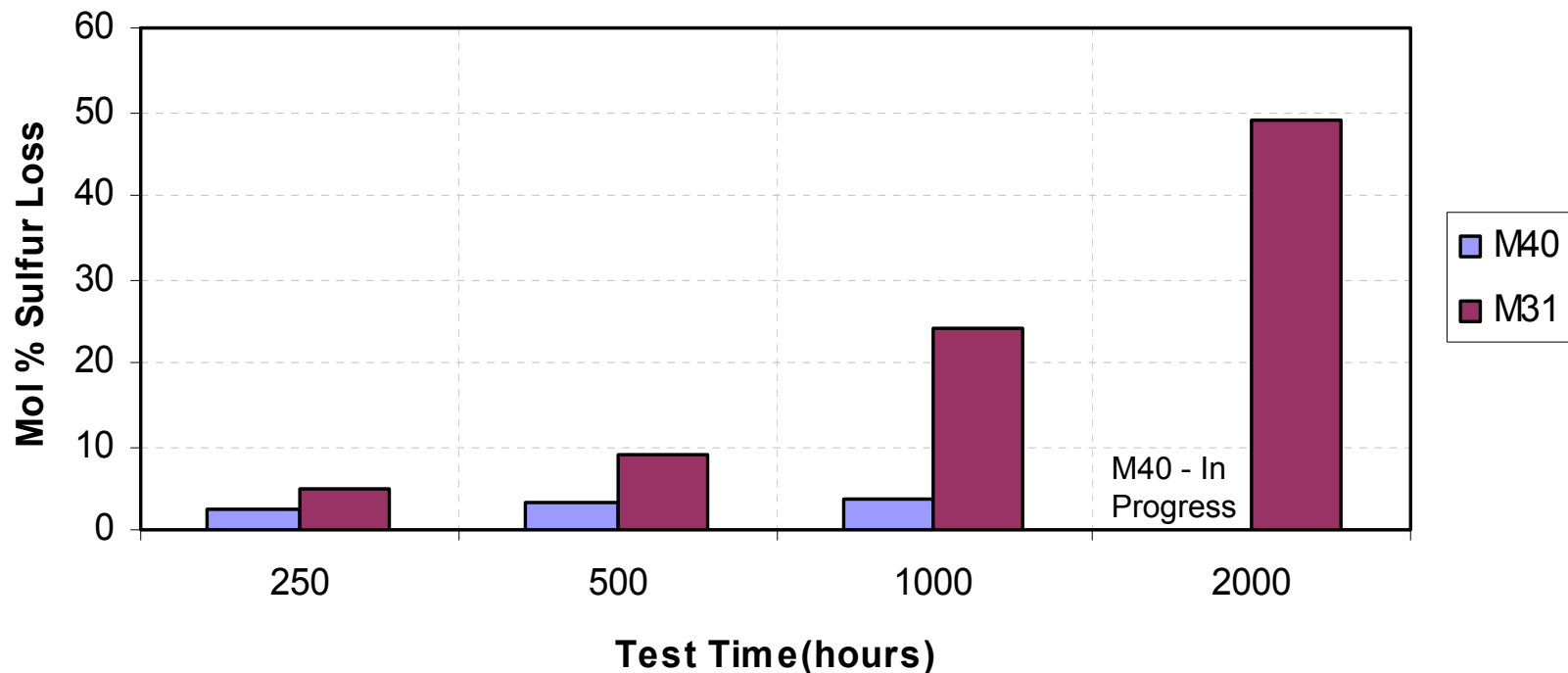
>100 mS/cm

Accelerated *Ex-Situ* Polyelectrolyte Testing



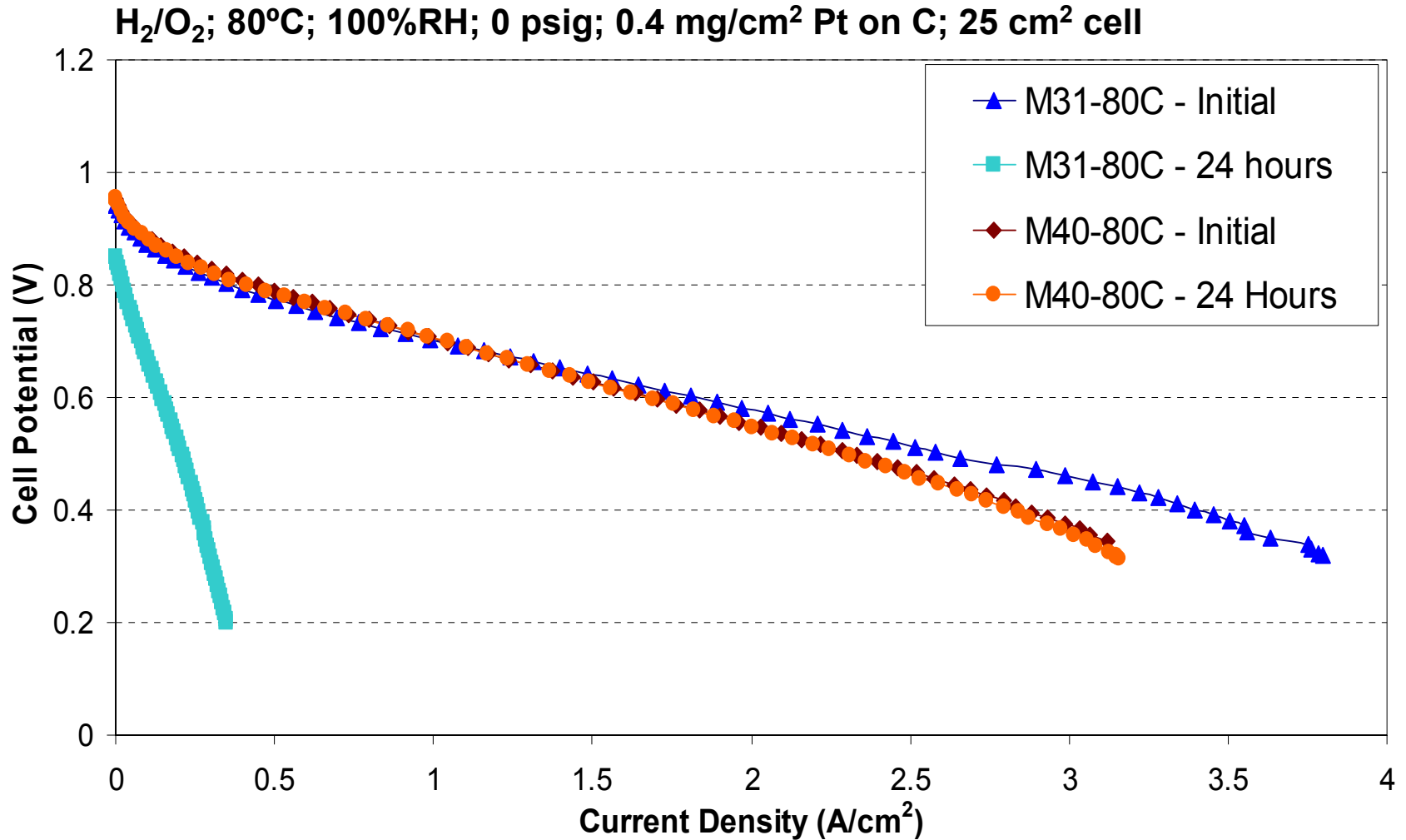
- Generation D polyelectrolyte shows no measurable degradation in our *ex-situ* accelerated testing

Ex-situ Membrane Sulfur Loss Test

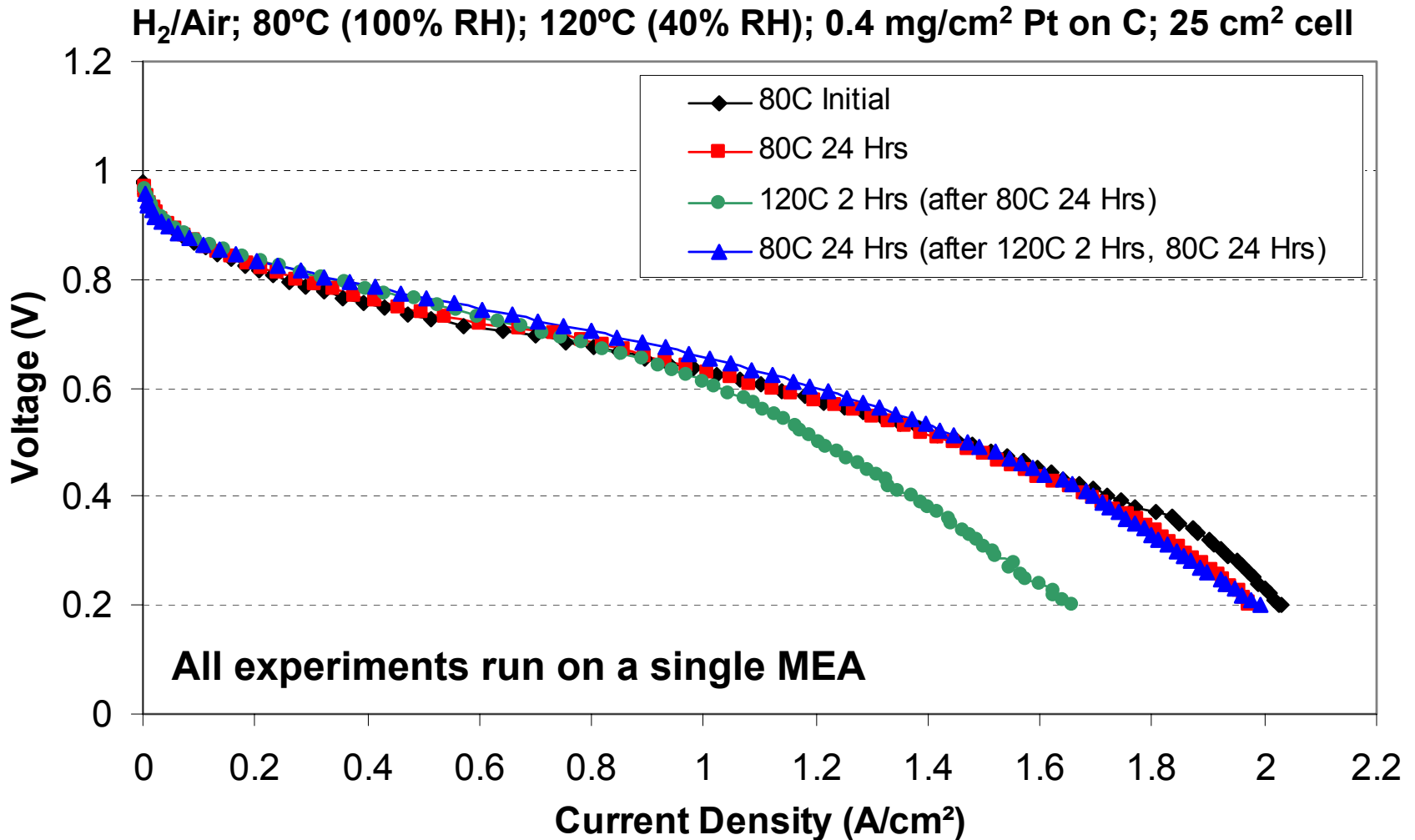


- M31 showed continual evolution of small molecule degradation product
- M40 (Gen. D) shows no continual evolution of small molecule sulfur loss over 1000 hours

M40 and M31 at 80°C Cell Temperature



M40 High Temperature

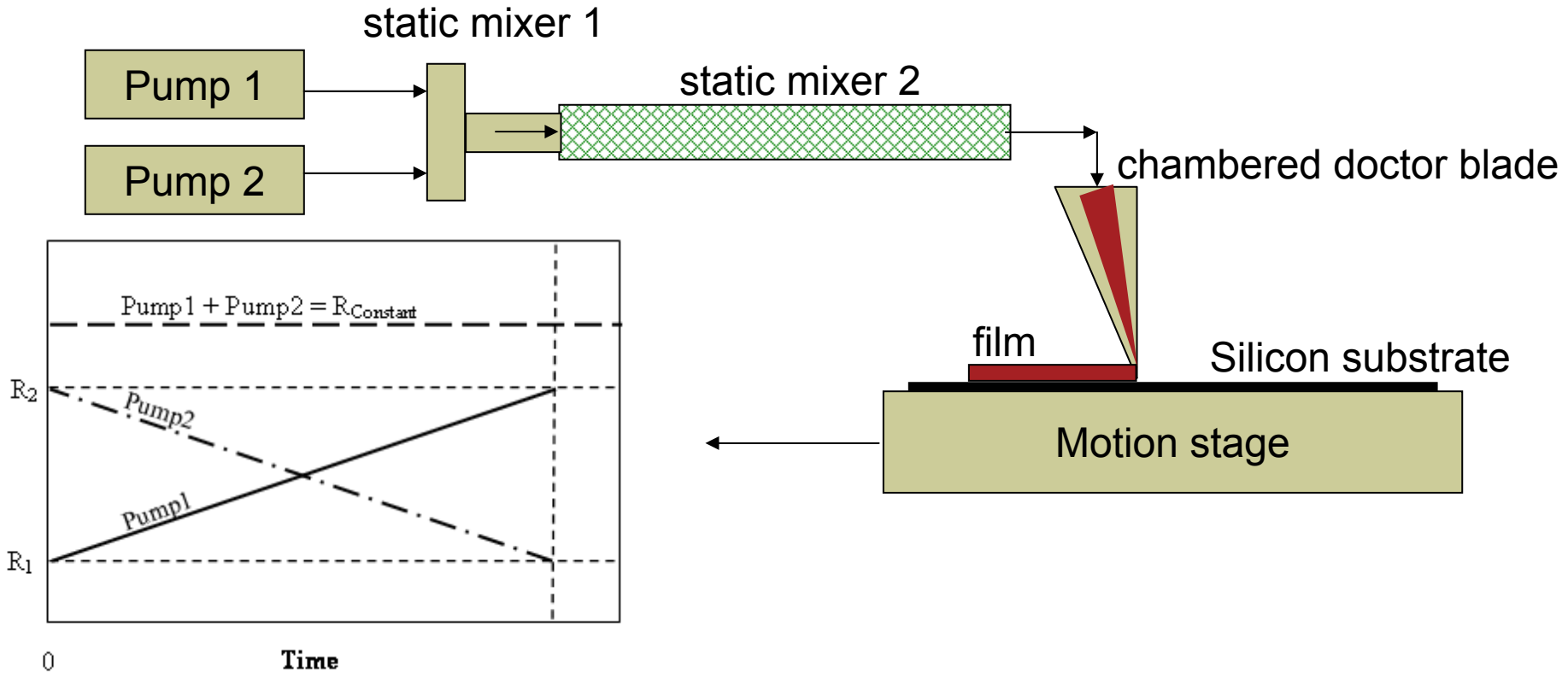


High Throughput Methodology – GA Tech

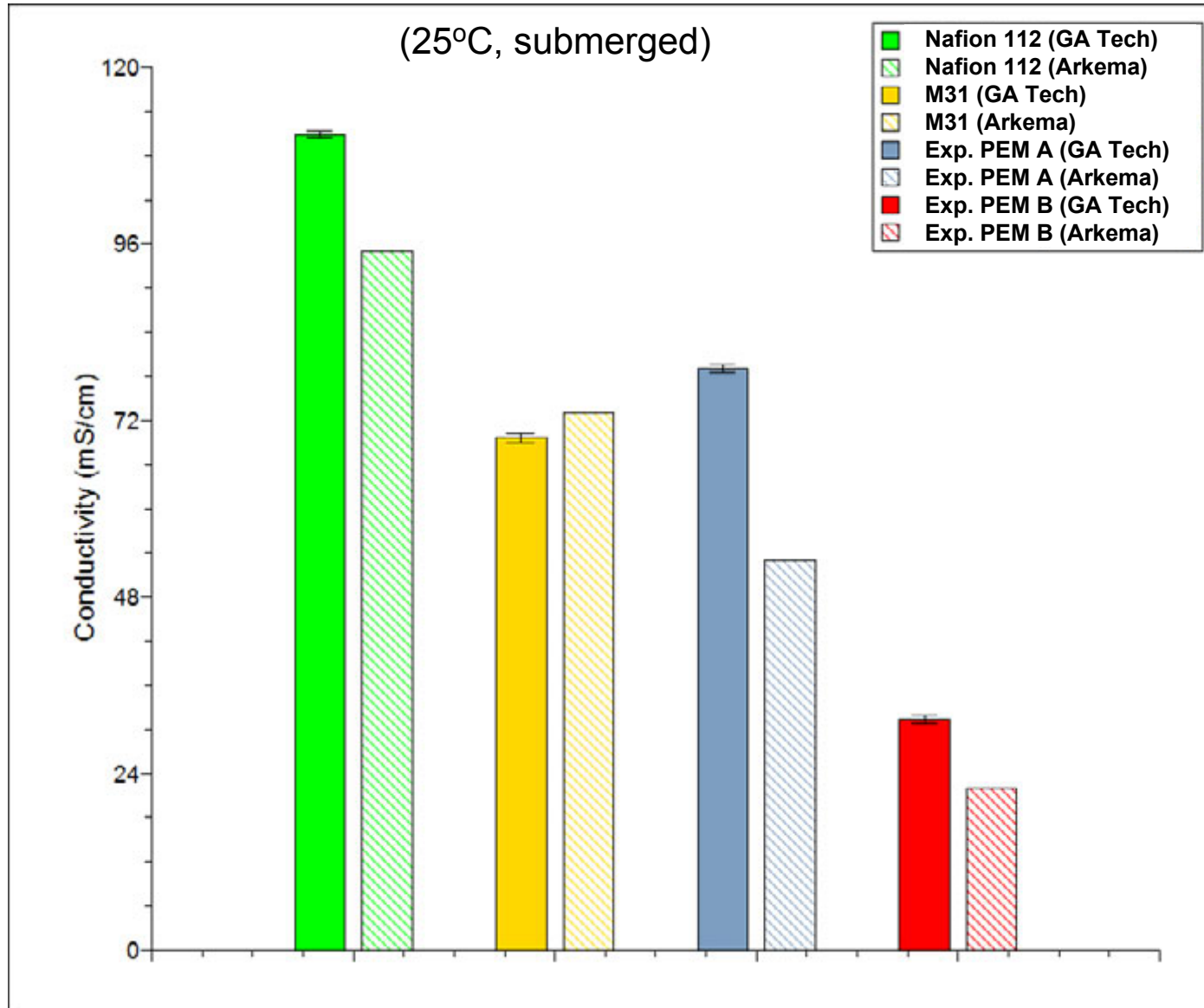
- Development of novel high-throughput screening technologies for fuel cell membranes.
 - Conductivity
 - Mechanical properties
 - Water sorption
- Apply screening techniques to search a large number of parameters for promising PEM materials.
 - Composition
 - Processing
- Data from the screening is passed on to Arkema to support efforts in optimizing membrane formulations

Composition Gradients – Direct Gradient Infusion

Mixture pumped through static or dynamic mixer and directly into a chambered doctor blade.



Conductivity Screen Validation

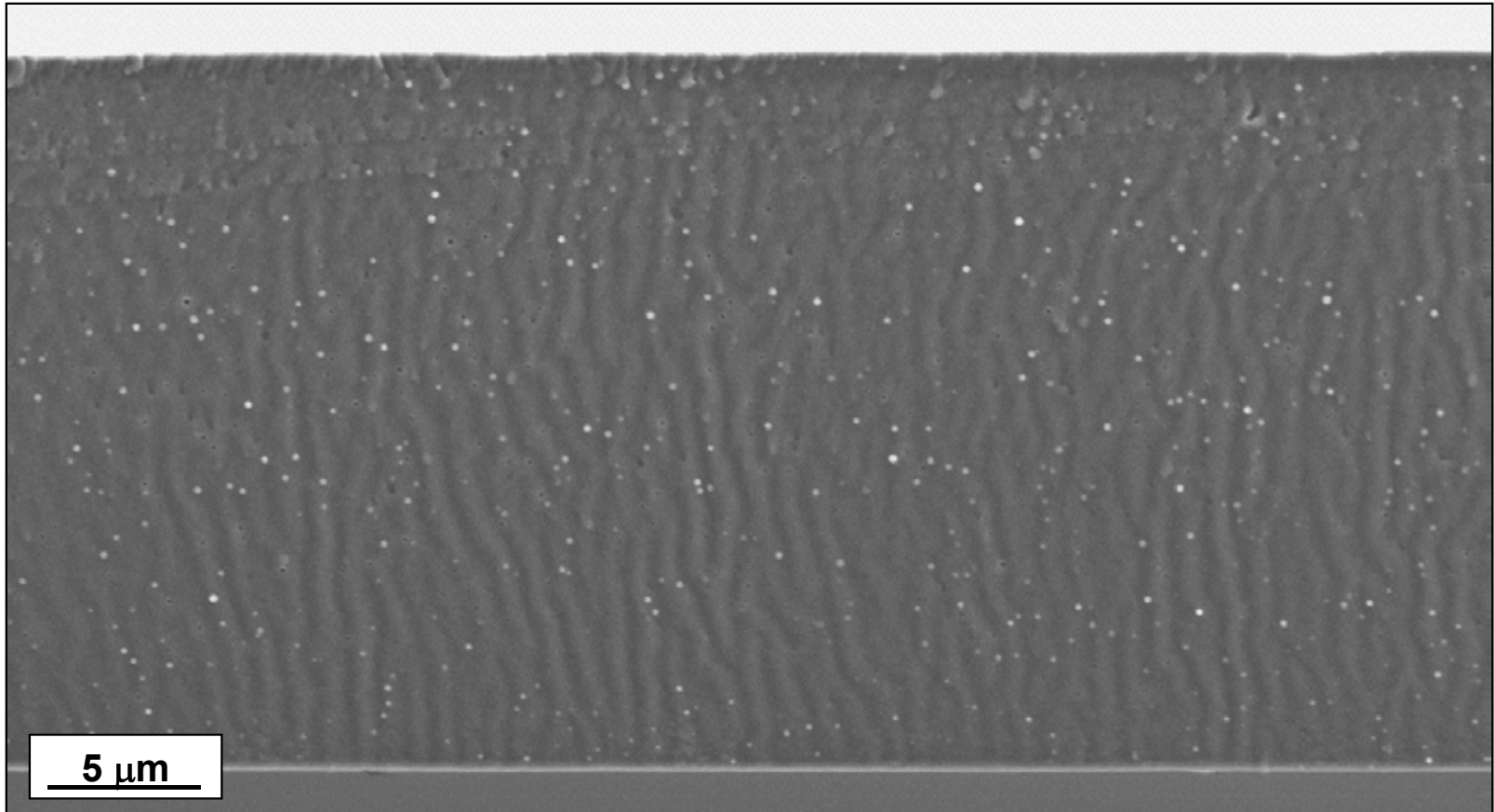


TEM Characterization – Oak Ridge Natl. Lab

- Collaboration with Karren More's TEM group
 - Started ~ May 2005
 - Characterization of blend morphologies in membranes
 - Structure change characterization in BOL and EOL MEAs
- Main features noted:
 - ~300 nm-wide “diffusion channels”
 - Formed during initial hydration
 - Perpendicular to plane of the membrane
 - Compressed and deformed during MEA prep.
 - 50 x 300 nm ‘ellipsoids’ of polyelectrolyte
 - Oriented parallel to the plane of the membrane
 - Morphology change observed for M31 EOL MEAs

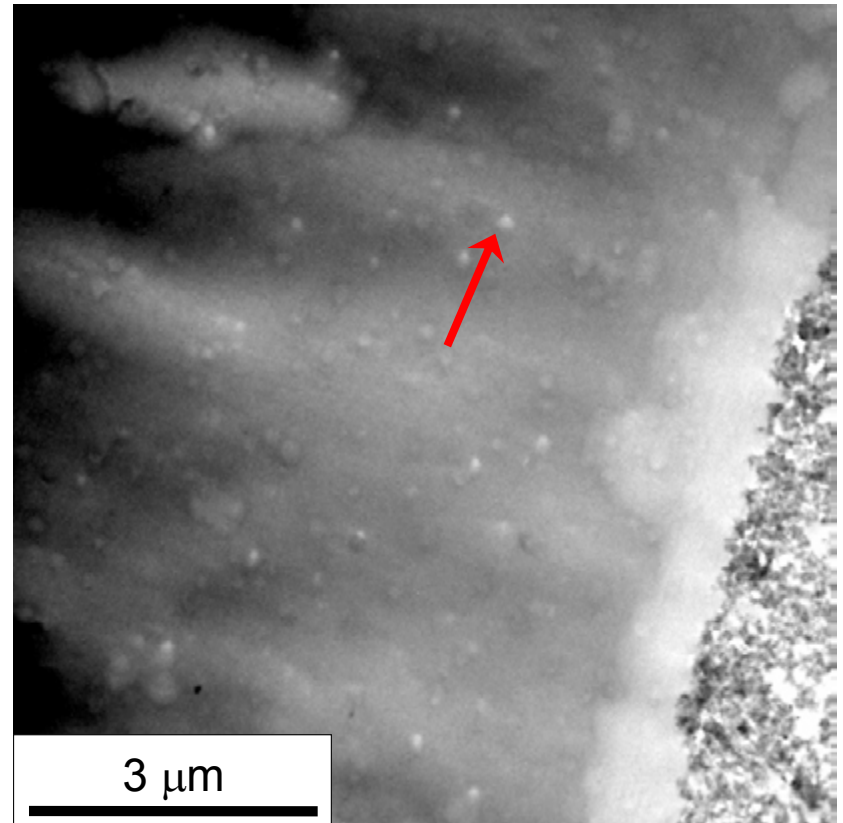
TEM Characterization – Diffusion Pathways

- ~300 nm-wide striations after protonation
 - Possible water diffusion pathways



M31 End-of-Life (EOL) MEA

- After 2000 hrs in-cell testing
 - Arrow shows domain of increased sulfur content not present in BOL MEA
 - Small-scale segregation of polyelectrolyte through membrane thickness



Summary

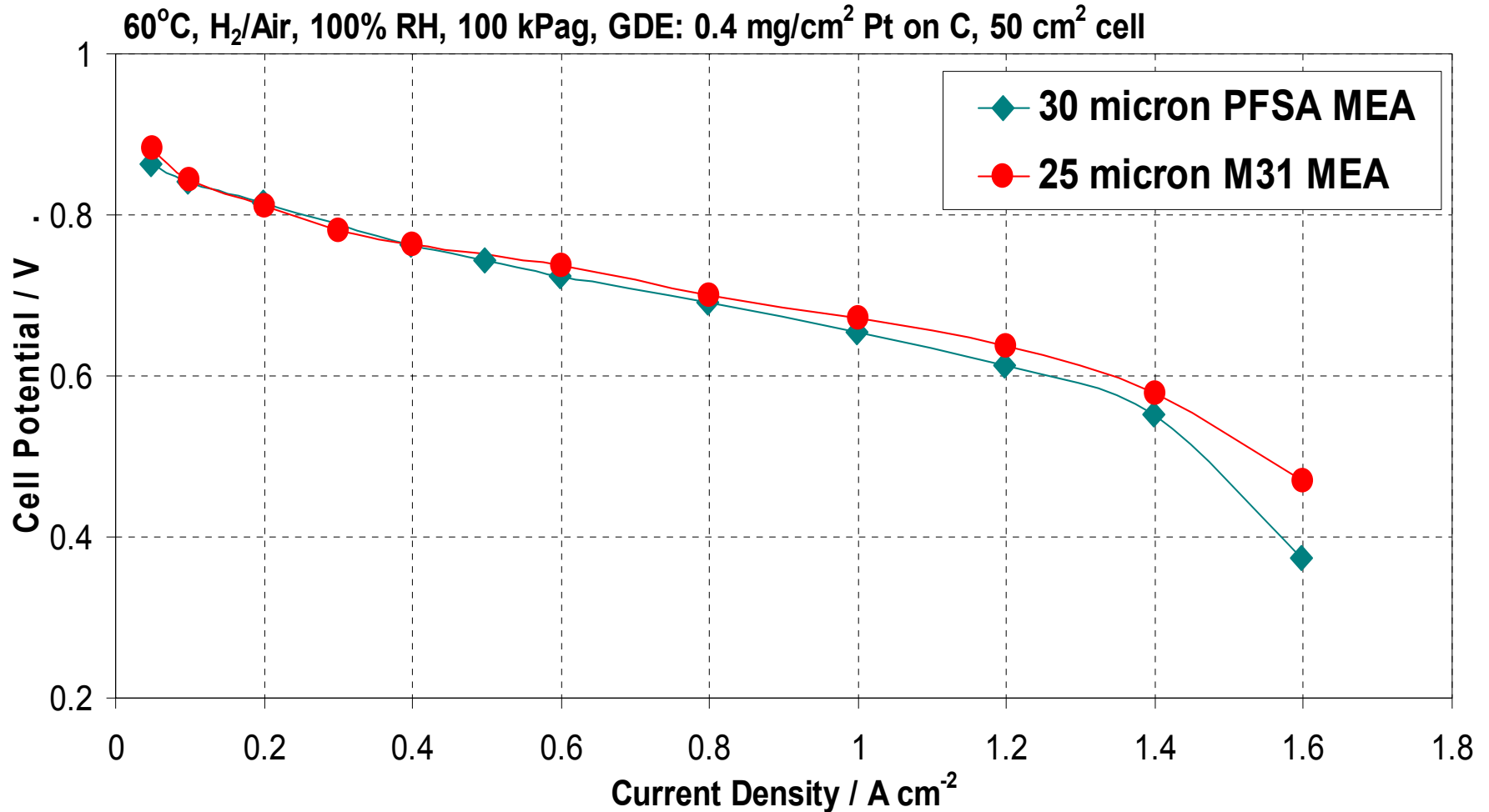
- Kynar/polyelectrolyte blend technology is generally applicable to highly protogenic polymers
- Gen. D polyelectrolyte shows outstanding *ex-situ* stability at 80°C
- M40 membranes based on Gen. D show far greater *ex-situ* and *in-situ* stability at 80°C
- Initial M40 electrochemical properties similar to M31
- GA Tech high throughput methods now producing Kynar/PE gradients
- ORNL TEM work has opened new avenue to understand membrane microstructure

Plan / Future Work

- Remainder FY 2006
 - M40 high-resolution morphology characterization (ORNL)
 - M40 scale up (Arkema)
 - Gen. D polyelectrolyte scale-up (complete)
 - Rolls of membrane for MEA testing to be prepared 2Q06
 - MEA optimization and testing (Arkema & JM)
 - Evaluate M40 MEA fabrication conditions
 - 80 °C and 120 °C in-cell testing
 - Accelerated in-cell testing (OCV hold, cycling, low RH)
 - Continue analysis of potential degradation mechanisms
- FY 2007
 - Continue small cell (< 100 cm²) testing (Arkema & JM)
 - Prepare 400 cm² MEAs (JM)
 - Testing of large MEAs in UTC hardware (UTC & Univ. of HI)

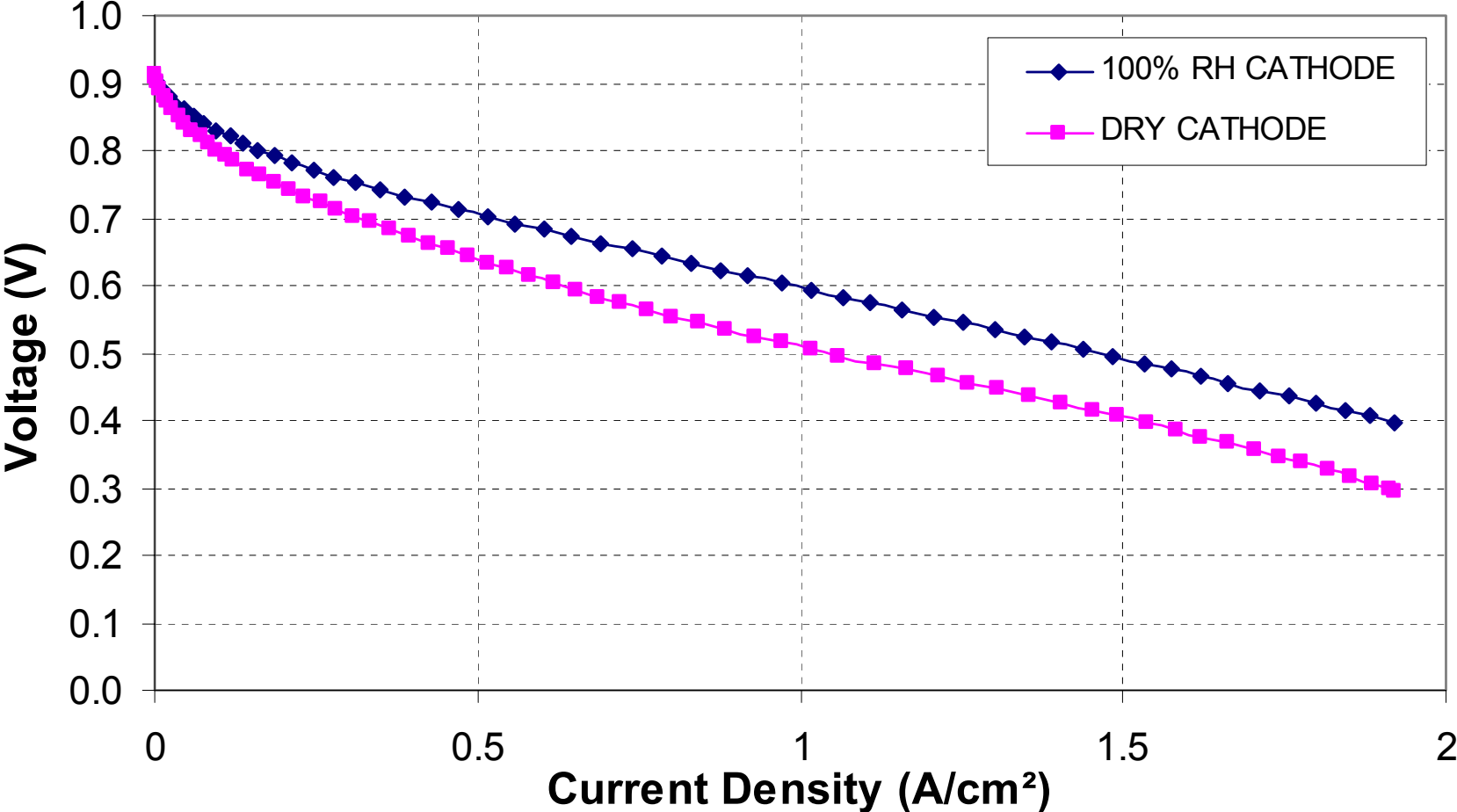
Backup Slides

BOL Performance of M31 & Standard PFSA MEAs

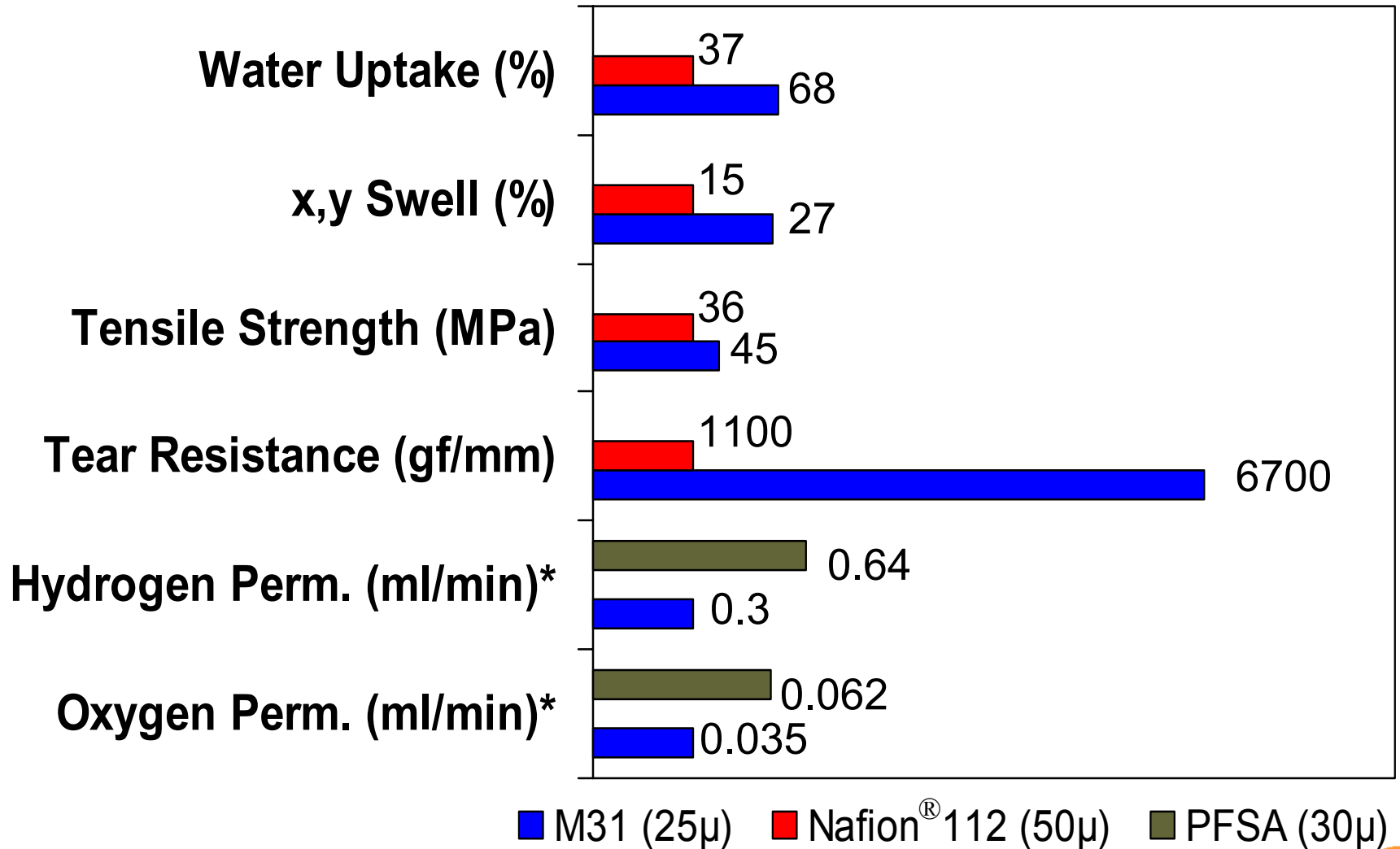


M31 Dry Cathode

H₂/O₂, 60 °C, 0 kPag GDE: E-TEK LT-120 (0.4 mg/cm² Pt on C); 25 cm² cell



Physical Properties



* 50 cm² cell

Gas Crossover vs. DOE Targets

Gas	2004 DOE Target	2010 DOE Target	Arkema M31 Membrane
Oxygen	5 mA/cm ²	2 mA/cm ²	0.8 mA/cm ²
Hydrogen	5 mA/cm ²	2 mA/cm ²	1.0 mA/cm ²

Arkema Membrane Performance vs. DOE Targets

Characteristic	2004 DOE Targets	Arkema 2006 Status	2010 DOE Targets
Operating Temperature	<80°C	80°C (w/120°C excursions)	<120°C
Inlet water vapor partial pressure	50 KPa _{abs}	50 KPa _{abs}	<1.5 KPa _{abs}
Membrane Conductivity at inlet water vapor partial pressure and: Operating Temperature	0.10 S/cm	0.10-0.14 S/cm ^(g,h)	0.10 S/cm
Room temperature	0.07 S/cm	0.07-0.085 S/cm ^(h)	0.07 S/cm
-20°C	0.01 S/cm	(not available)	0.01 S/cm
Oxygen cross-over ^(a)	5 mA/cm ²	0.8 mA/cm ² (w/ 25 μm membrane)	2 mA/cm ²
Hydrogen cross-over ^(a)	5 mA/cm ²	1.0 mA/cm ² (w/ 25 μm membrane)	2 mA/cm ²
Area Specific Resistance	0.03 ohm cm ²	0.022 ohm cm ²	0.02 ohm cm ²
Cost ^(b)	65 \$/m ² ^(c)	≤ 65 \$/m ²	40 \$/m ²
Durability with cycling At operating temp <80°C	~2000 hr ^(d)	2100 hr ⁽ⁱ⁾	5000 hr ^(e)
At operating temp >80°C	(not available) ^(f)	(not available)	2000 hr
Unassisted start from	-20°C	(not available)	-40°C

(a) Tested in MEA at 1 atm O₂ or H₂ at nominal stack operating temperature.

(b) Based on 2002 dollars and costs projected to high volume production (500,000 stacks per year).

(c) Based on 2004 TIAX Study that will be periodically updated.

(d) Durability is being evaluated. Steady-state durability is 9,000 hours.

(e) Includes typical drive cycles.

(f) High-temperature membranes are still in a development stage and durability data are not available.

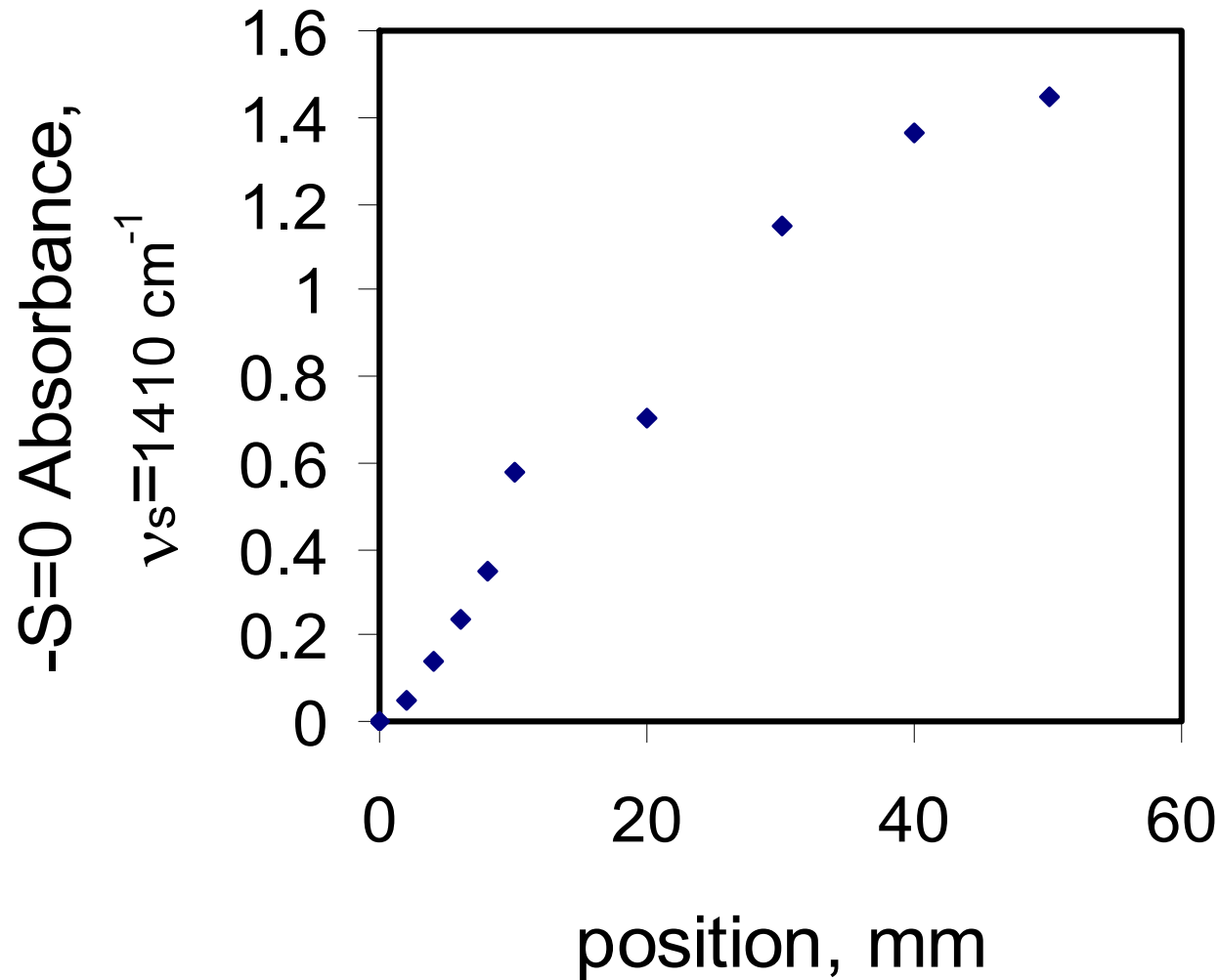
(g) At 70°C.

(h) In liquid water measured by EIS.

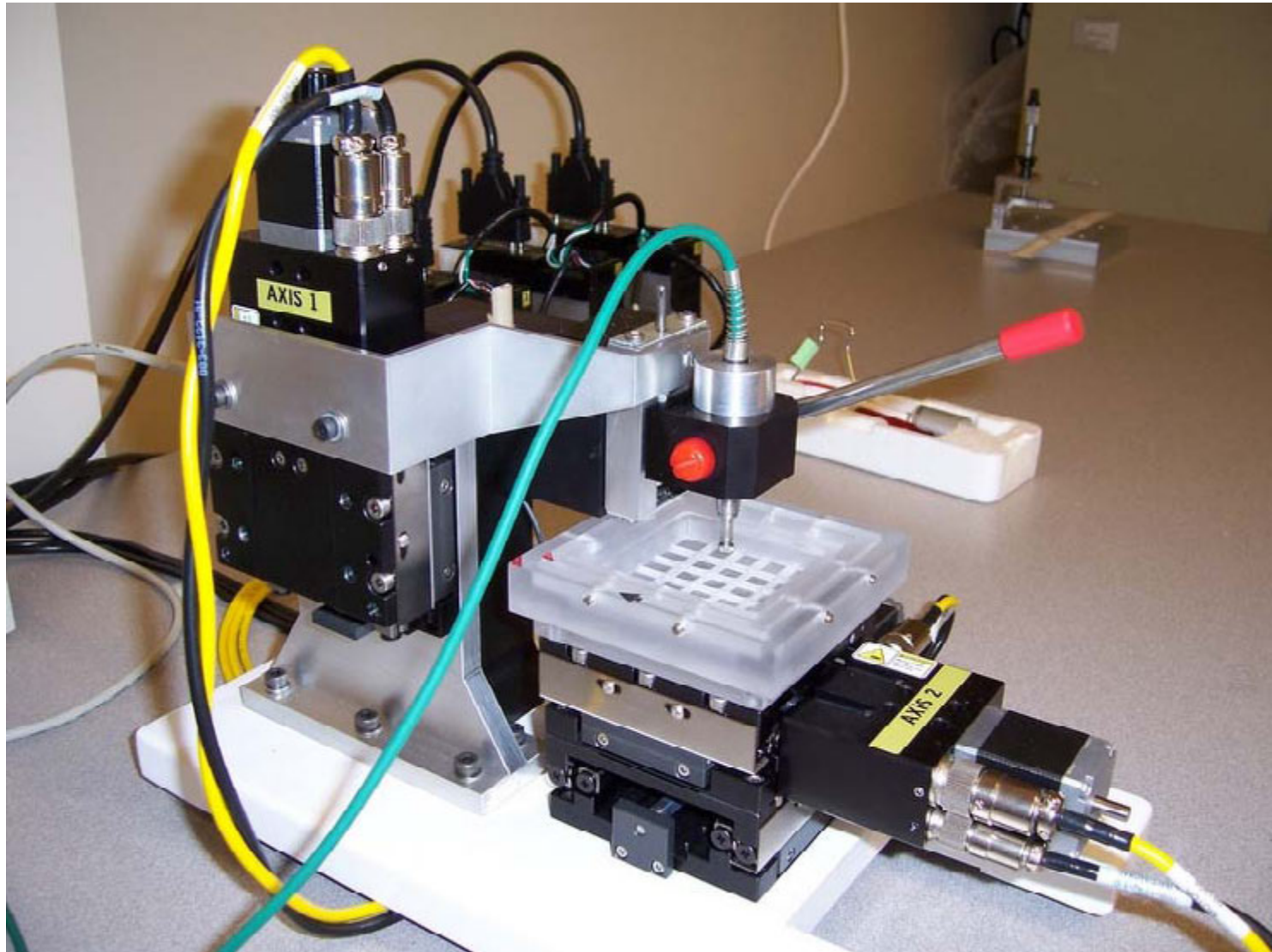
(i) Steady state at 0.5 A/cm²; 60°C; H₂/O₂, 100% RH, 0 KPag.

GA Tech Validation of Kynar/PE System

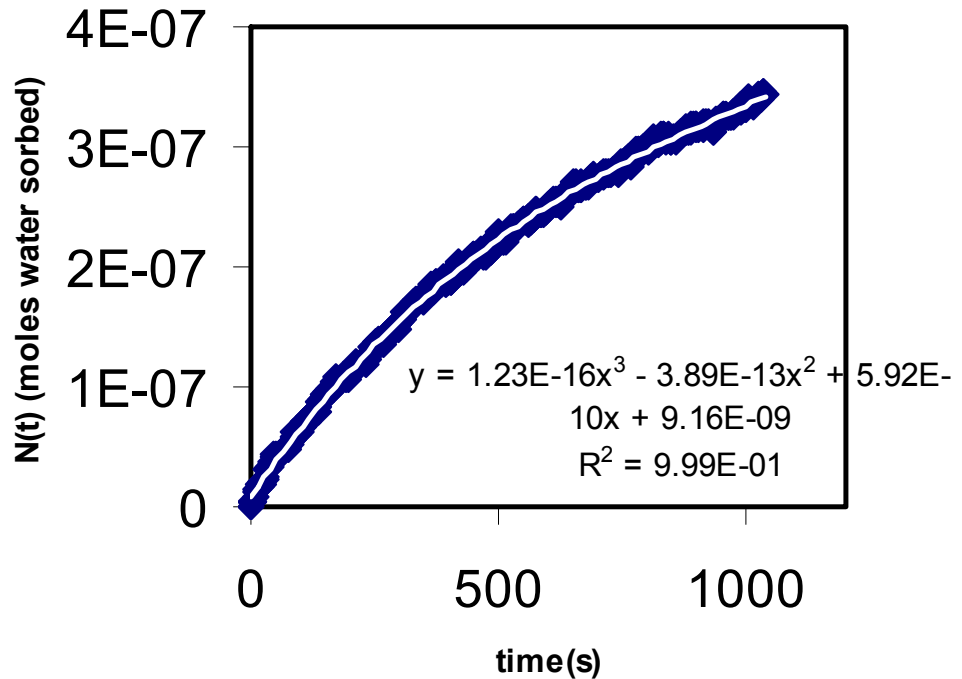
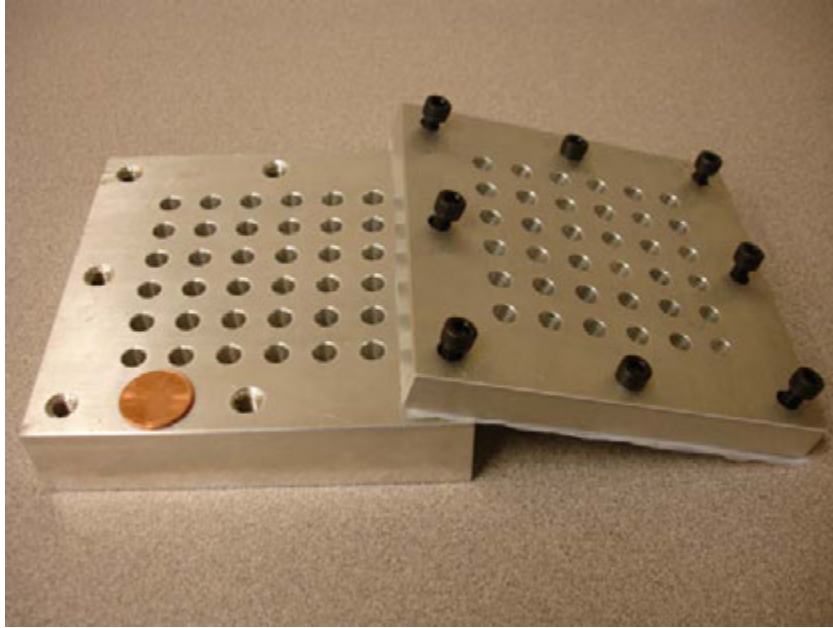
Gradient Composition



GA Tech Conductivity / Thickness Screening

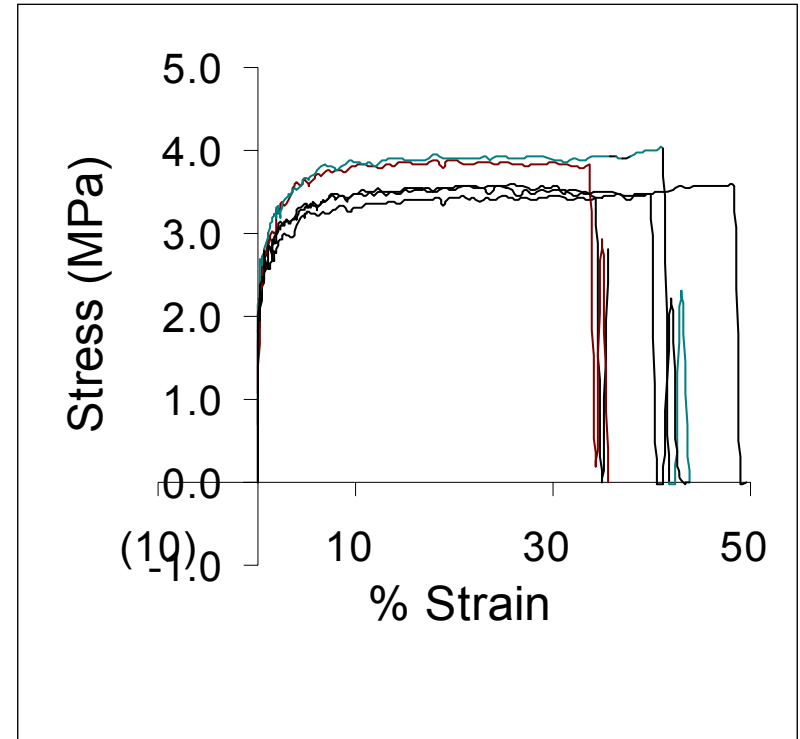
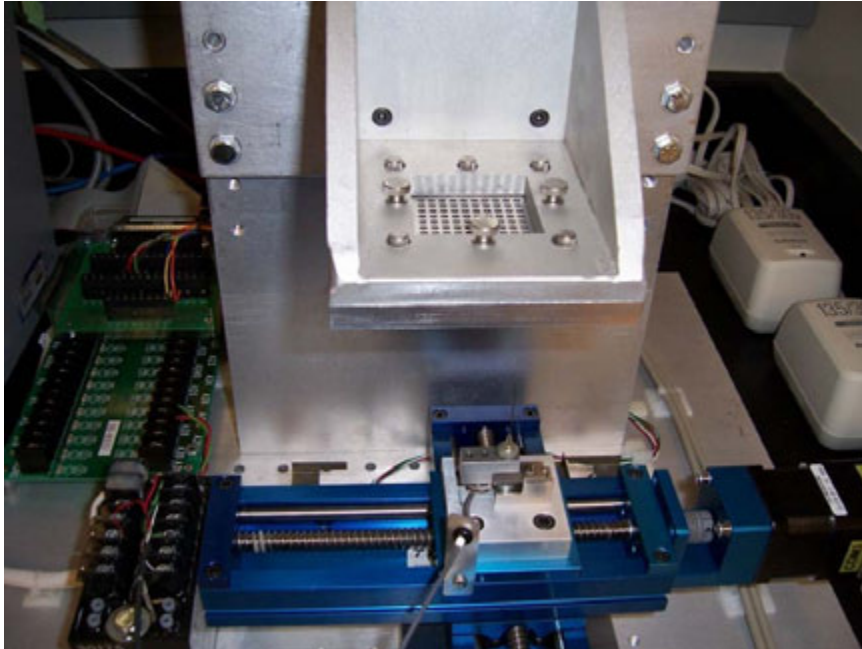


GA Tech Permeation Screening



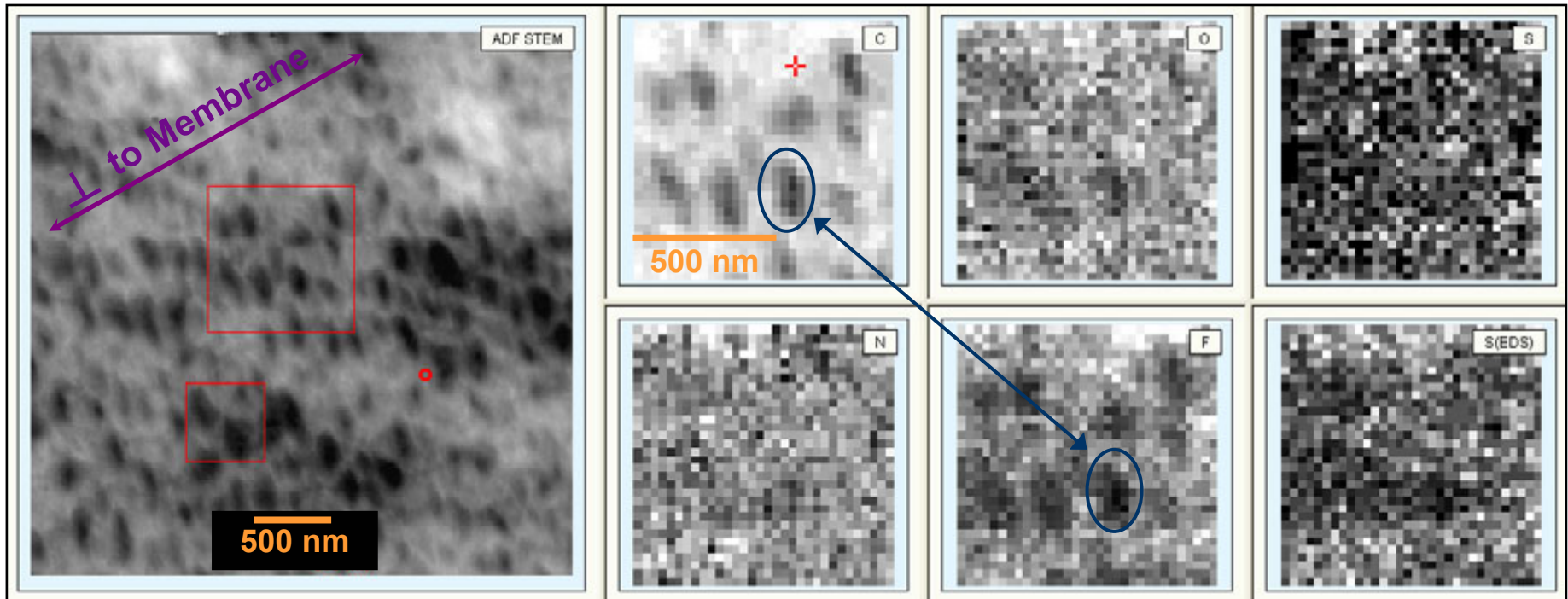
- One side of membrane/library exposed to superheated steam at $t = 0$
- Close feed valve and monitor pressure drop
- Moles sorbed = $(P_i - P_f) V/RT$
- Experiment time for a library is ~ 18 minutes

GA Tech Mechanical Properties Screening



- High throughput device to measure mechanical properties of libraries (HTMECH)
- Collects stress vs. strain data on an entire library within ~30 minutes
- Currently being modified to be run inside a controlled humidity chamber and use a temperature-controlled stage

ORNL - High Resolution TEM & Atomic Mapping



- Morphology with atomic density information
 - Readily observed for 50-100 nm sized structures

Response to Reviewer Comments

- Have not provided data to show sulfur loss can be decreased.
 - Data generated this past year (and shown in this presentation) demonstrate that *ex-situ* sulfur loss and *in-situ* short-term durability have been greatly improved by first identifying the degradation mechanism and second modifying the PE chemistry to eliminate the mechanism.
- No discussion of membrane morphology
 - Via assistance from the DOE, a collaboration between Arkema and ORNL was established in 2005. The high-res TEM work conducted by Karren More has clearly shown a dense non-porous membrane with discrete 50-100 nm domains. In addition, atomic mapping of these domain was accomplished to positively identify the chemical species, and entire MEA cross-sections have been imaged. This tool is being used to understand morphology and changes as a results of cell testing.
- Membrane costs have not been discussed
 - Arkema believes that its membrane technology can meet the 2010 DOE target of \$40 m². While we are not ready to publicly disclose cost figures, Arkema has provided confidential information to the DOE to demonstrate this feasibility.

Publications and Presentations

- Aug 2005: DOE quarterly review meeting and FreedomCAR Tech. Team; Detroit, MI
- Nov 2004: 2005 Fuel Cell Seminar; Palm Springs, CA
- March 2006: DOE quarterly review meetings; Washington, DC
- April 2006: AIChE National Meeting; Orlando, FL

Critical Assumptions and Issues

- Membrane Durability
 - The primary degradation mechanism for M31 was identified and eliminated in the M40 chemistry. Early cell testing on M40 has confirmed the improved short-term durability but longer-term testing is just beginning. If M40 membrane durability were to need further improvement, the same cycle of mechanism identification and chemistry improvement would be used. The use of a Kynar blended membrane would still be used to speed development.
- Catalyst Ionomer Choice
 - MEAs fabricated with Arkema membranes have typically used PFSA ionomer in the catalyst layer. Good bonding and initial performance has been observed and we will continue this strategy in the near term. As the M40 allows high temperature operation, it is not clear whether the PFSA ionomer will have sufficient performance or not. Regardless of the results with PFSA ionomer, plans are in place to evaluate Arkema developed polyelectrolytes in the catalyst layer.