Advanced MEA's for Enhanced Operating Conditions, Amenable to High Volume Manufacture

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3M Company

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Project ID # FC3

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start 1/1/02
- Project end 12/31/05
- 80% complete

Budget

- Total Project funding
  - $7 million DOE
  - $2 million contractor share
- Received in FY04: $2 million
- Projected funding for FY05: $1.8 million

Barriers

O. Stack Material & Mfg Cost

P. Durability

Q. Electrode Performance

R. Thermal & Water Mgmt

Targets

- Cost: $35/kW,
- Durability: > 5000 hrs,
- Precious metal loading: 0.2 g/ rated kW

For fuel cell stack system for 2010 from HFCIT Multi-Year Plan

Partners

- Case Western Reserve Univ.
- Colorado School of Mines
- Dalhousie University
- University of Illinois
- University of Miami
- University of Minnesota
- VAIREX Corporation
- Collaboration with LBNL and BNL

Objectives

Overall Contract Objective

Development of high performance, high durability, lower cost membrane electrode assemblies (MEA's) qualified to meet demanding system operating conditions of higher temperature, little or no humidification, while using less precious metal catalyst.

Past Year Objectives

a) **Tasks 1 & 3:** Demonstrate PFSA based MEA capability with: adequate membrane and catalyst performance to meet 0.2g Pt/kW , durability to potentially operate for 5000 hours in the range of $85 < T < \sim 120^{o}C$ under sub-saturated inlet conditions with start-stop cycling, and pilot-scale production levels.

b) **Task 2:** Development and characterization of new proton conducting electrolytes and incorporation into membranes for operation at $T > 120^{o}C$, based on non-aqueous proton conduction mechanisms.

Approach

Tasks 1 and 3: 85 < T < 120ºC MEA by roll-good processes

a) Develop 3M PFSA membranes for operation at 85 < T < ~ 120ºC, with enhanced durability operating on low humidification and pilot scale production capability.

b) Developed advanced 3M - NanoStructured Thin Film (NSTF) catalysts with high performance at ultra-low Pt loadings having enhanced durability for operation over 85 < T < 120ºC with start-stop cycling, using pilot scale production capability.

c) Match the 3M PEM and 3M NSTF catalyst for optimum performance, durability

d) Advance pilot scale process development for roll-good catalyst coated membrane (CCM) fabrication of the NSTF catalysts and 3M PEM from c).

e) Optimize the MEA GDL for dry operation with the CCM from d).

Task 2: High temperature electrolytes (T > 120ºC):

a) Develop membranes comprising polymers blended with stable non-volatile 3M superacids.

b) Investigate new heteropolyacid additives for proton transport under hotter, drier conditions and methods for stabilizing in presence of water.

Technical Accomplishments

Task 1, Task 3: 85 < T < 120^{o}C MEA by roll-good processes

- New 3M PEM shows greater than 15x increase in lifetime under 90/70/70^{o}C load-cycling accelerated tests, compared to standard PFSA membrane.
  - 3M PEM shown to have higher conductivity at lower water-per-sulfonate group.
  - New 3M PEM maintains 25-30 mS/cm conductivity at 120^{o}C and 80^{o}C dewpoint
- Over 1000 ft of 3M PEM coated at pilot scale.
- 3M NanoStructured Thin Film catalysts achieved 0.22 g-Pt/kW at 100kPA with 0.12mg-Pt/cm^2-MEA; and < 50 mV of mass transport overpotential at 2 A/cm^2.
- 3M NSTF/3M PEM MEA demonstrated over 1000 hour lifetime at 120^{o}C
  - 3M NSTF-ternary catalysts produce 75x less F^- than Pt/carbon dispersed catalysts at 120^{o}C with same PEM and GDL.
- 3M NSTF catalysts are ~ 80x more resistant to loss of ECSA via Pt dissolution by CV cycling between 0.6 – 1.2 volts, than Pt/carbon dispersed catalysts.

Task 2 : T > 120^{o}C electrolytes

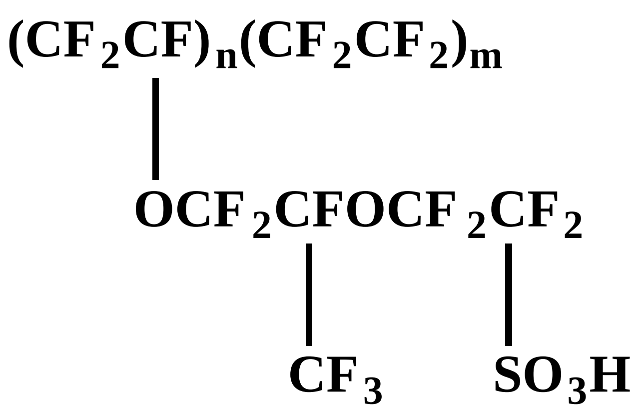
- Performance in fuel cell under H_2/air at 110^{o}C better than PBI/H3PO4 with catalyst loading of only 0.4/0.4 mg/cm^2 Pt/Pt (3M acid more ORR compatible).
- Pulse field gradient spin echo-diffusion measurements show lower activation barriers for H^+ transport of new heteropolyacids, and higher maximum Temps.

Technical Accomplishments – 3M PEM Definition

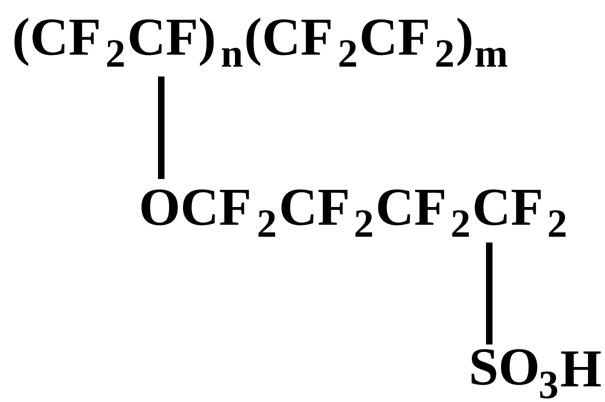
The new 3M ionomer has a slightly shorter side chain than standard PFSA membrane ionomer without the pendant -CF3 group:

Gives: - higher degree of crystallinity,
- higher modulus,
- higher Tg at a given equivalent weight (EW).

Allows: - lower EW membranes with higher conductivity,
- improved mechanical properties and durability under hot, dry conditions.
- enhanced oxidative stability in Fenton's test



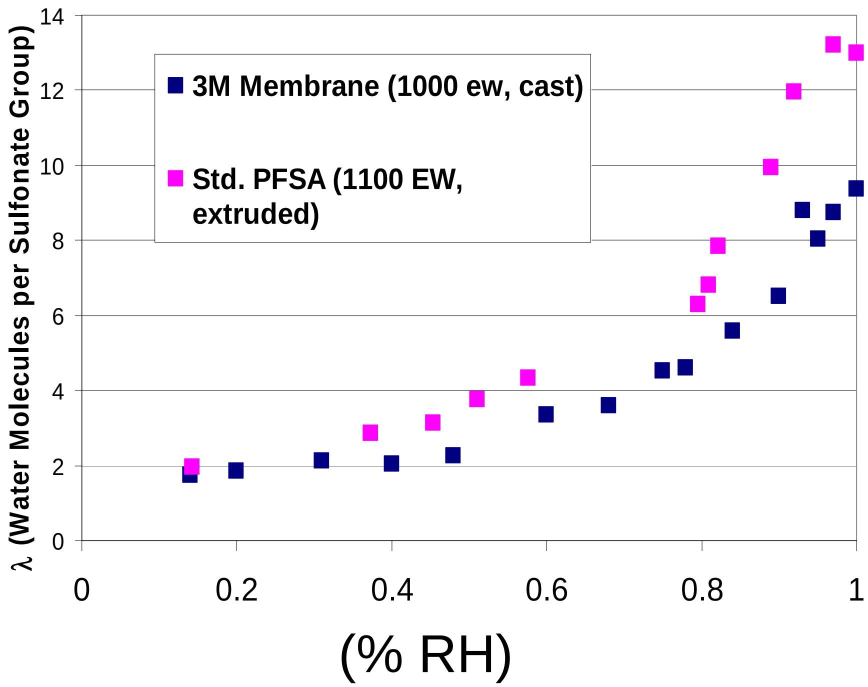
Standard PFSA

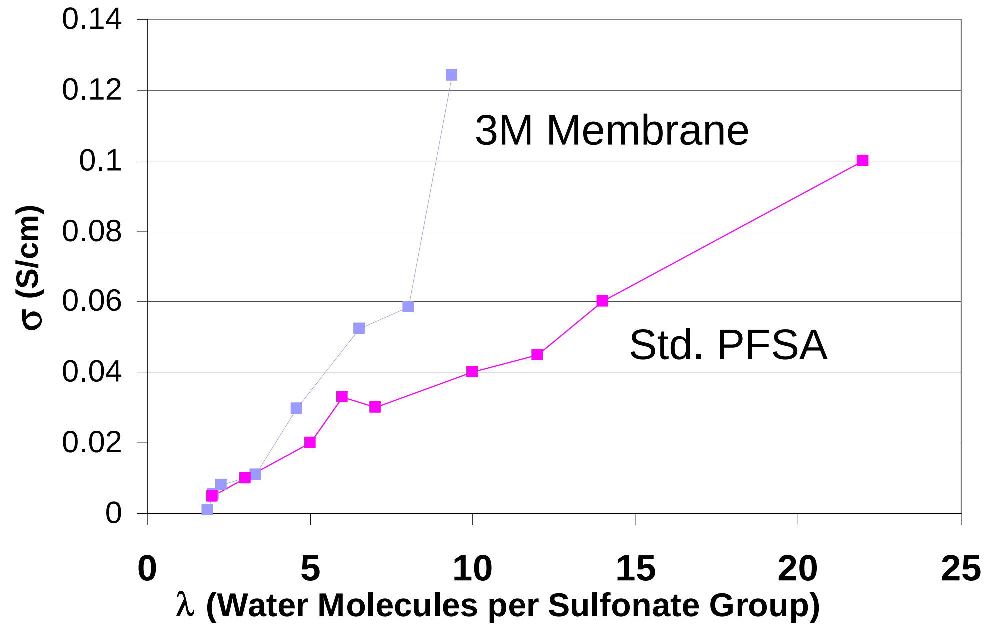


New 3M Polymer

Technical Accomplishments – 3M PEM Performance

Comparison of conductivity at 30°C vs. hydration state (λ) of 1000 EW 3M membrane and standard 1100 EW PFSA membrane





3M membrane exhibits lower water uptake for the same water activity compared to the standard PFSA membrane.

T. Zawodzinski et al., CWRU

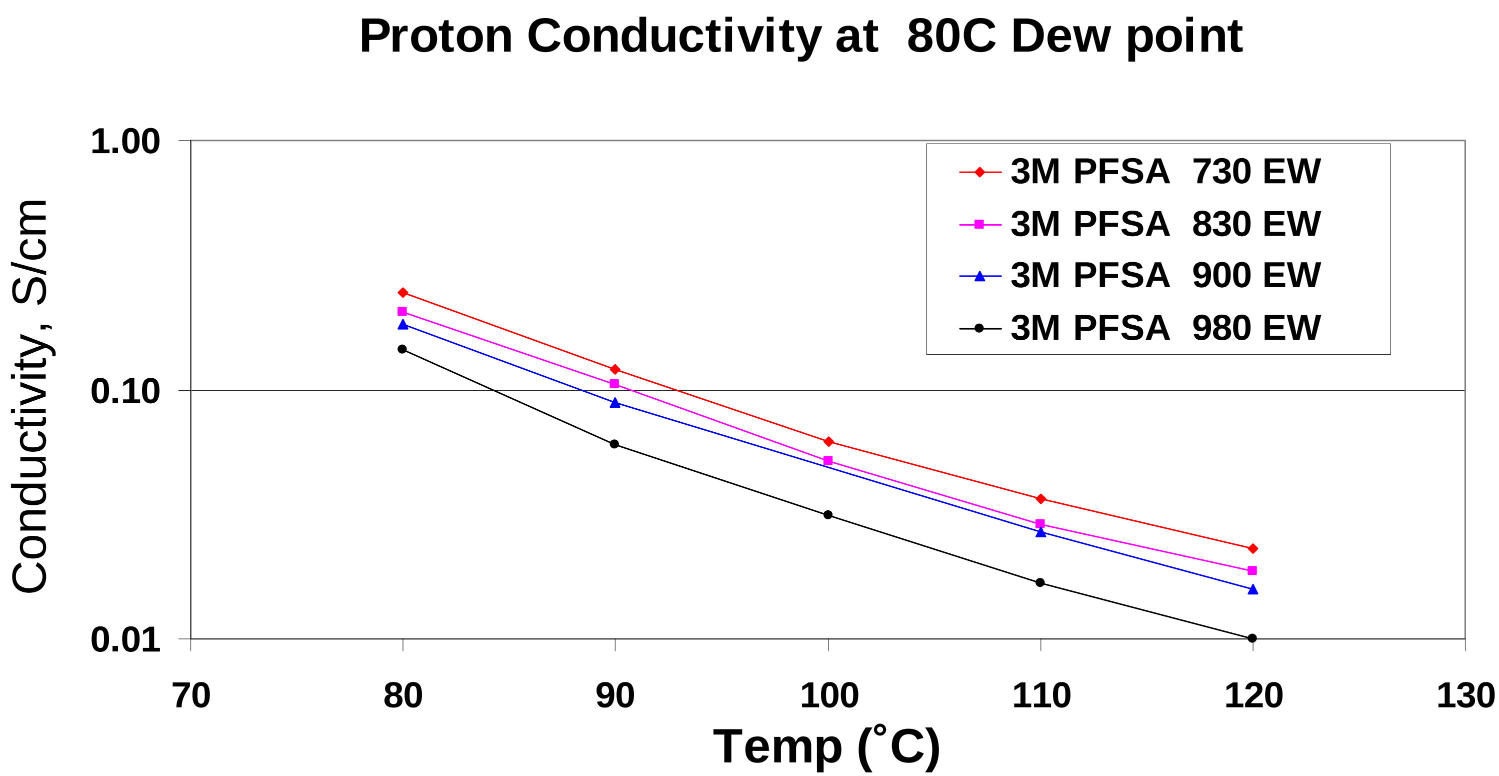
Conductivity of the 3M membrane increases more rapidly with number of water molecules per sulfonate group than standard membrane. This should allow drier operation of the MEA.

Technical Accomplishments – 3M PEM Performance

3M membranes with multiple EW's have been fabricated and evaluated.

- Conductivity vs. temperature for EW ionomers in 730 – 980 EW range.
- The lowest EW ionomer tested so far, 730 EW, shows a conductivity of about 25-30 mS/cm at 120˚ C, 80˚ C DP, very dry conditions.

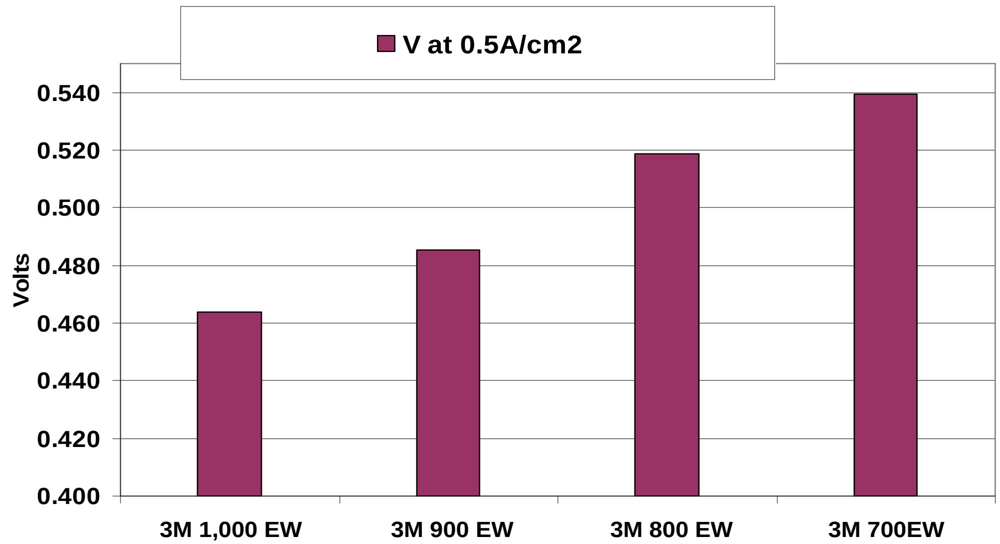
AC 4-point probe measurement, at ambient pressure.

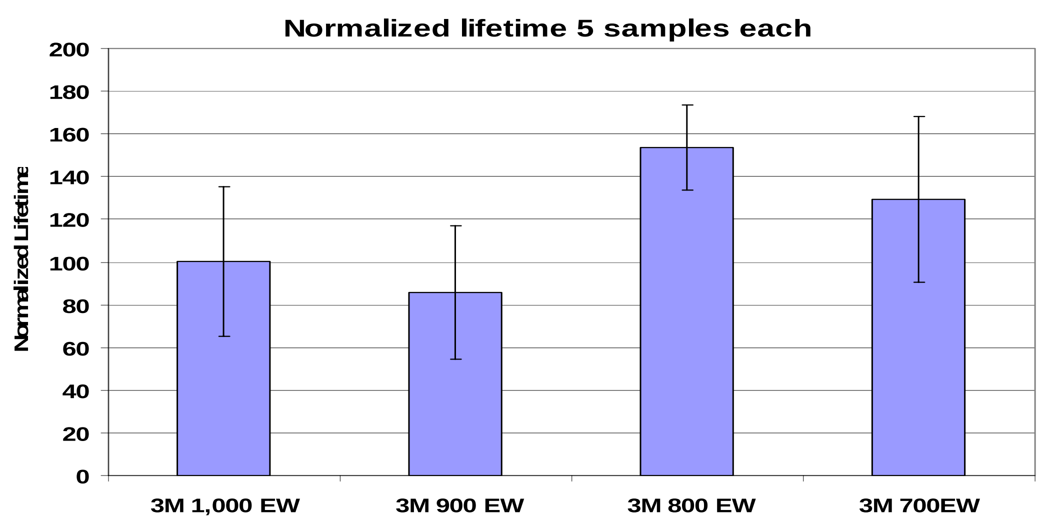


Technical Accomplishments – 3M PEM Durability

Lifetime and performance vs. EW under load cycling.

- Test run at 90˚C, 28% RH, load cycles between OCV and 0.5 A/cm^2.
- Performance increases with lower EW under hot, dry conditions.
- Lifetime defined as when OCV drops below 800mV.
- No statistically significant lifetime difference between 700 to 1,000 EW membranes in this test.
- All MEA's tested with dispersed Pt/C ink electrodes with 0.4/0.4 mg Pt / cm^2.





Technical Accomplishments – 3M PEM Durability

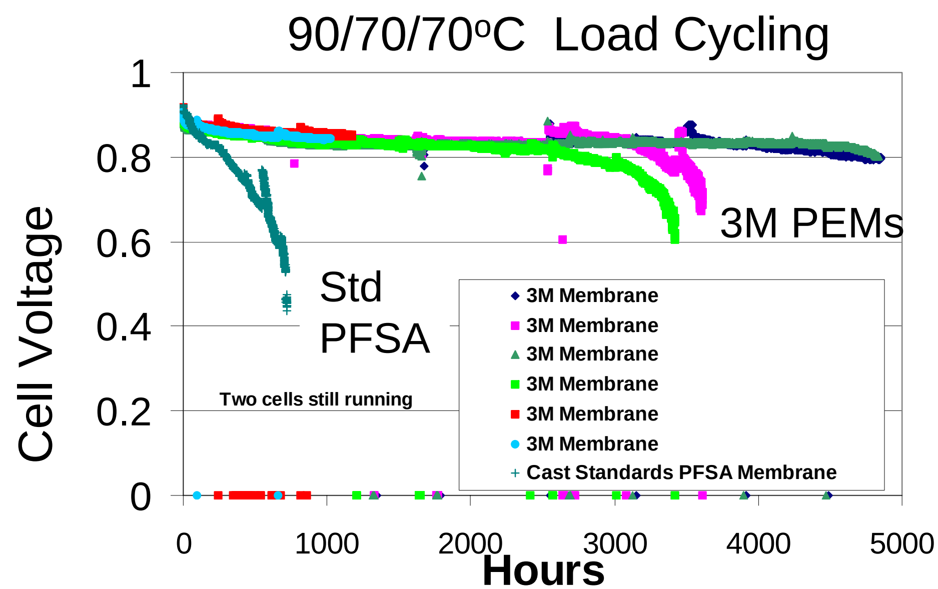
Performance and lifetime during accelerated durability testing

- 3M membrane with additives shows >15 X increase in lifetime (4 cell average ~ 4100 hrs) vs. 50 micron extruded standard PFSA membrane under load cycling tests at 90ºC, w/70ºC dewpoints.
- Accelerated durability testing was stopped periodically and sample was tested at 70˚C 100%RH.

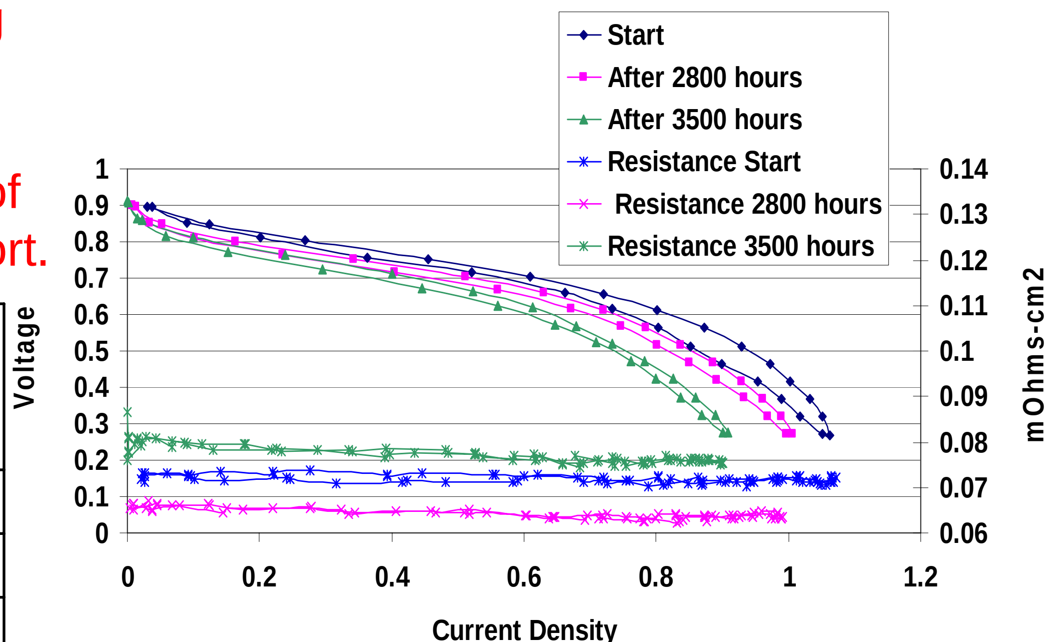
- No increase in crossover or shorting was detected before 3500 hours.

-IR change of PEM was minimal.

- Most performance loss due to loss of catalyst surface area or mass transport.



Pt/Carbon SEF (M^2/M^2)	H_2 Crossover (mA/cm^2)	Short Resistance ($OHM\text{-}CM^2$)	Testing Time
178.3	4.2	>500	0
102.9	3.4	>500	2800
78.1	17.0	>500	3500

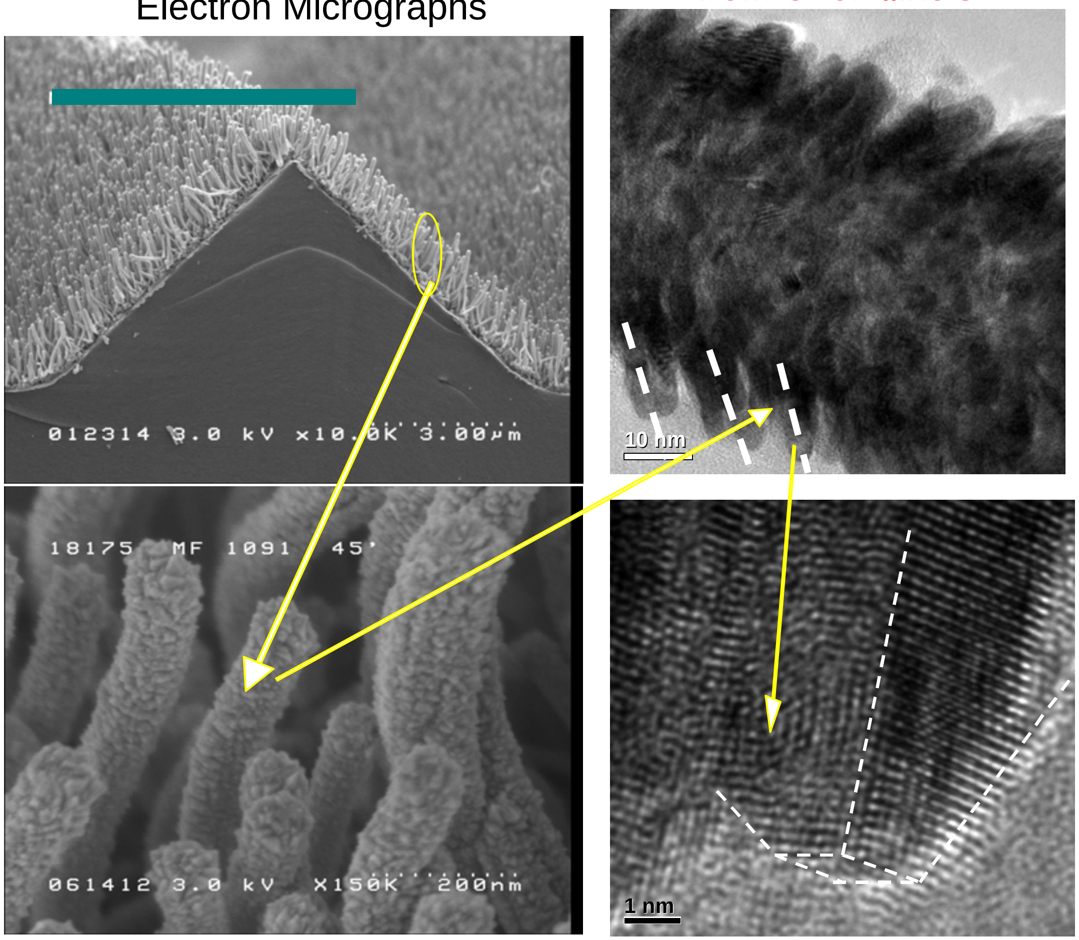


Technical Accomplishments – NSTF Fundamentals

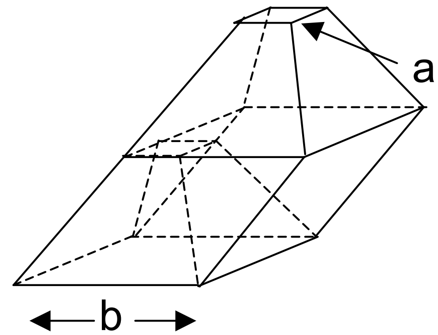
Relating fundamental catalyst morphology to enhanced properties.

3M Scanning
Electron Micrographs

Scanning Transmission
Electron Microscopy images
from U. of Illinois



Surface free energy of crystallites are minimized by truncating a [111] faceted pyramid with a [100] top.



Experimentally measured values of a ~ 2nm, b~ 6nm or a/b=1/3.

Calculated energy minimized when r = a/b ~ 0.33.

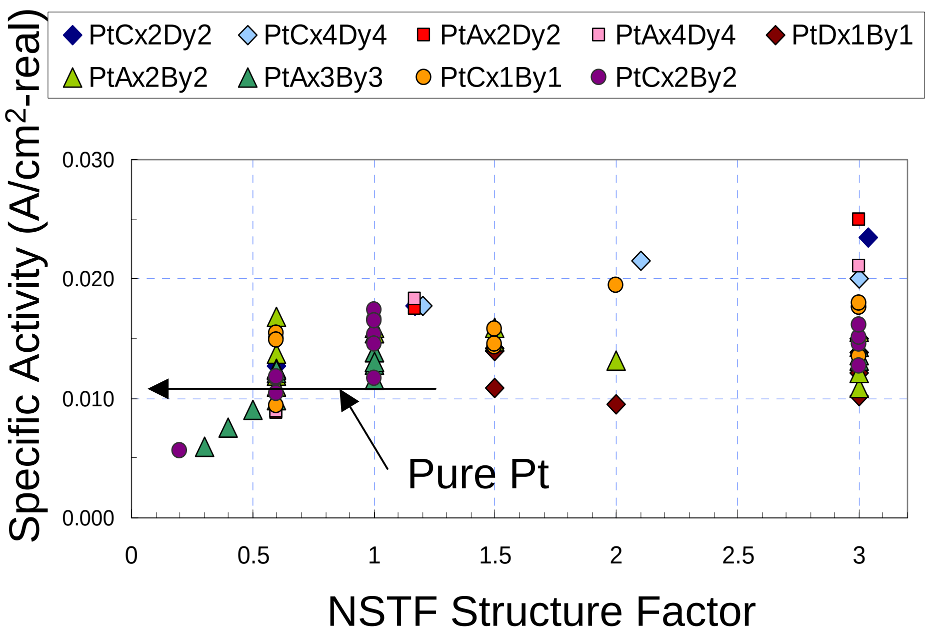
"Whiskerettes" growing on the sides of the larger whiskers as pyramidal crystallites with fcc(111) side facets and fcc(100) truncated top.
(L. Gancs, A. Wieckowski)

Technical Accomplishments – NSTF Catalyst Devel.

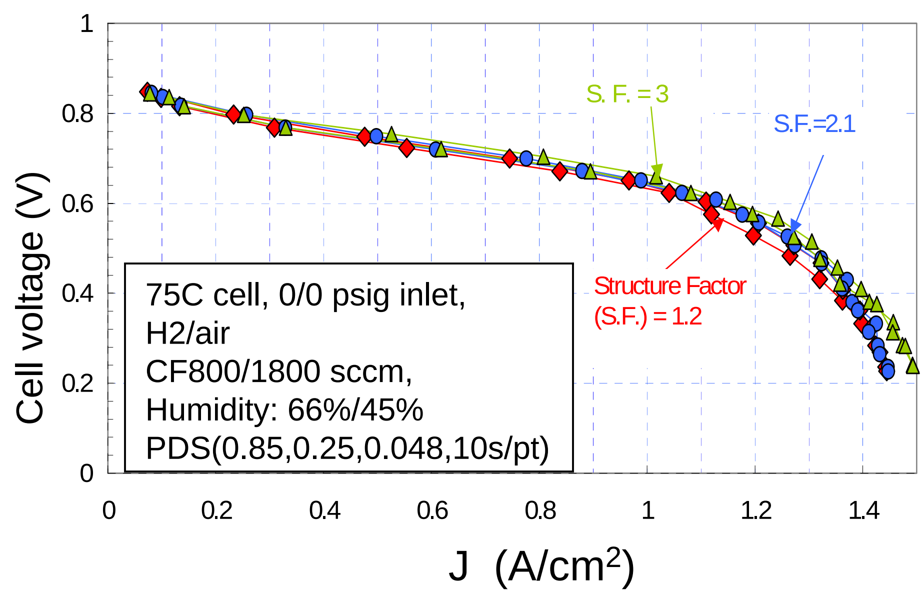
PtA_xB_y NSTF ternary catalyst development

- 113 different compositions/structures fabricated, all by roll-good process.
- Specific activities in 50 cm^2 cells depend on a structure factor, and composition
- Best performances obtained for most durable catalysts (see later slides) and their performance is insensitive to structure factor, implying a large process window

Summary of NSTF Ternary Catalyst Specific Activities



Best PtCD NSTF ternary
Cathode loading: 0.1 mg-Pt/cm^2
Anode loading: 0.15 mg/cm^2

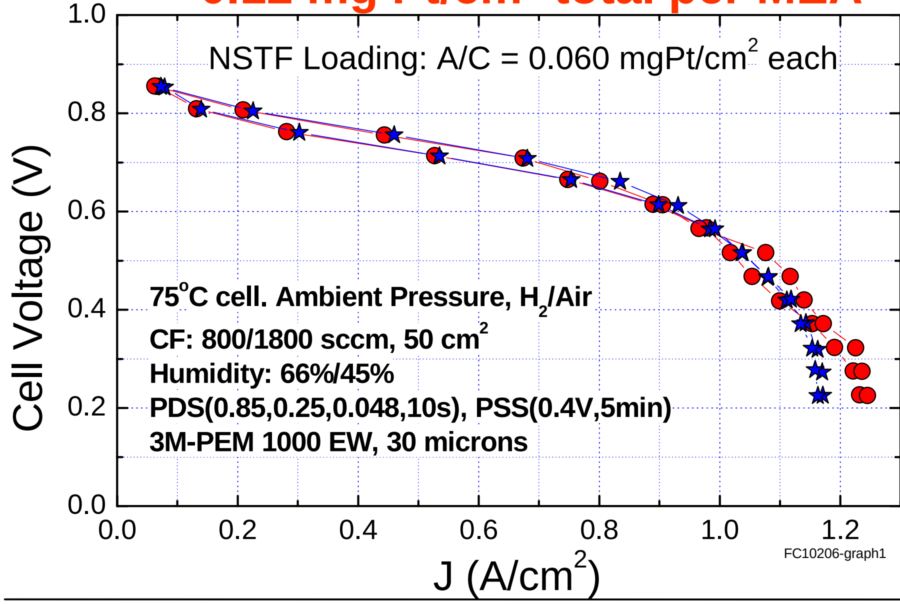


Technical Accomplishments – NSTF Catalyst Loadings

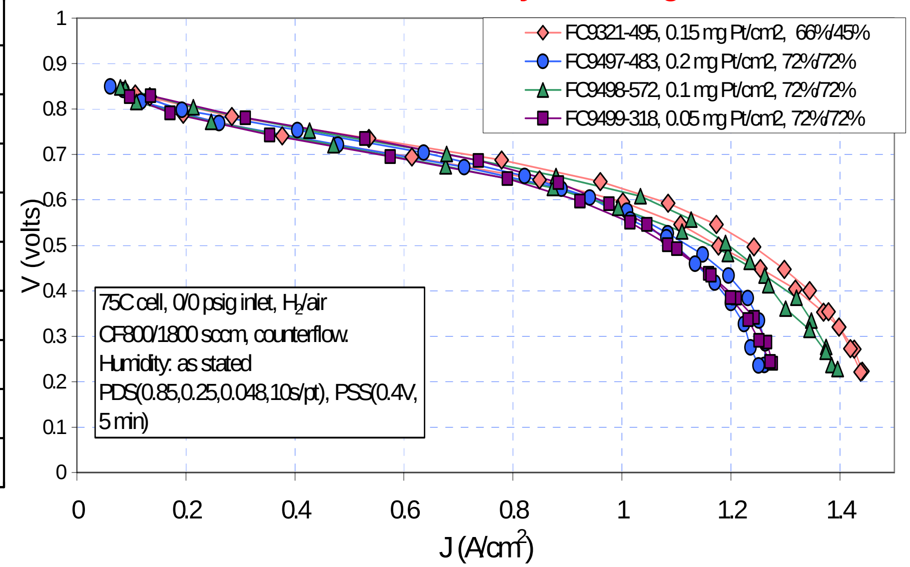
NSTF Catalysts with Ultra-low Pt Loading Continue to Improve

- Little effect of anode loading over range of 0.05 to 0.2 mg Pt/cm^2 above 0.6 V in MEA's having PtC_xD_y ternaries (0.1mg Pt/cm^2) on the cathode.
- 3M record performance achieved by better matching NSTF ternary catalyst and whisker support size and density, in MEA's having 0.060 mg-Pt/cm^2 on A/C.

0.12 mg Pt/cm^2 total per MEA

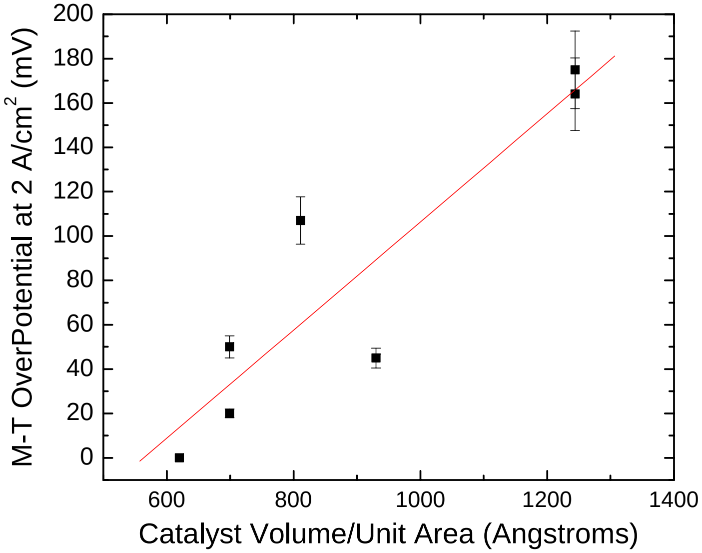


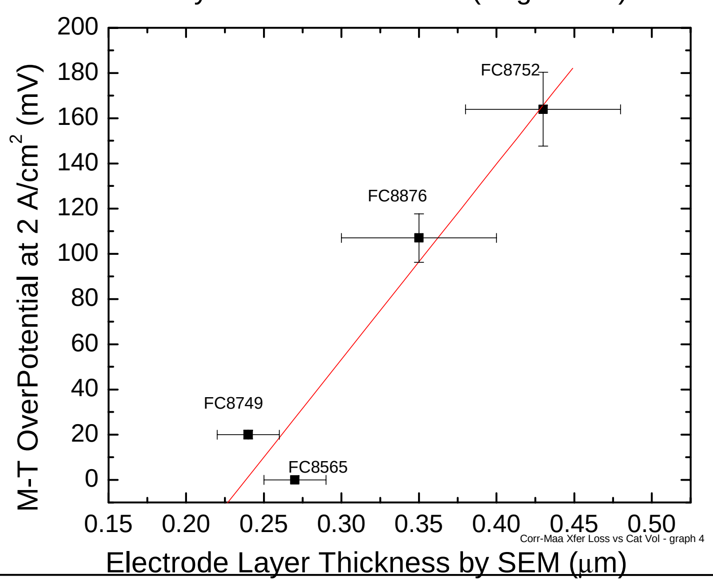
NSTF MEA (3M PEM and GDL) Performances with Different Anode Pt Loading (.05 to 0.2 mg Pt/cm^2) Cathode: PtAB ternary w/0.1 mg Pt/cm^2,



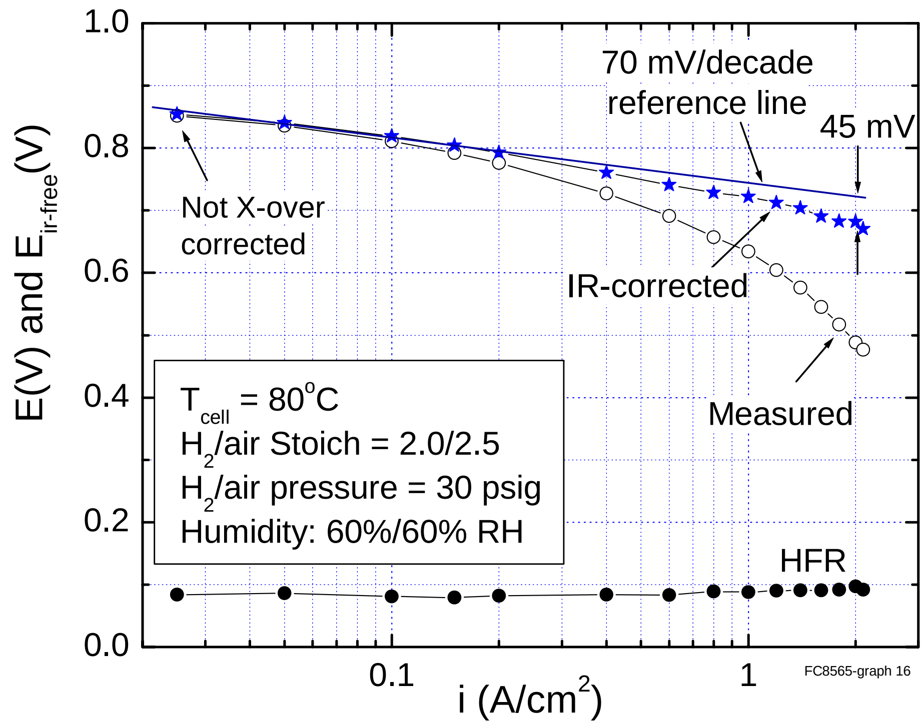
Technical Accomplishments – NSTF electrode

Mass transport overpotential (MTO) correlated to NSTF electrode thickness





- MTO < 50 mV at 2A/cm^2 possible for Pt ternary constructions w/ 0.1mg-Pt/cm^2 .
- SEM thicknesses agree with calculated thicknesses from known loadings
- Allows determination that electrode porosity is ~ 75%, filled with ionomer.

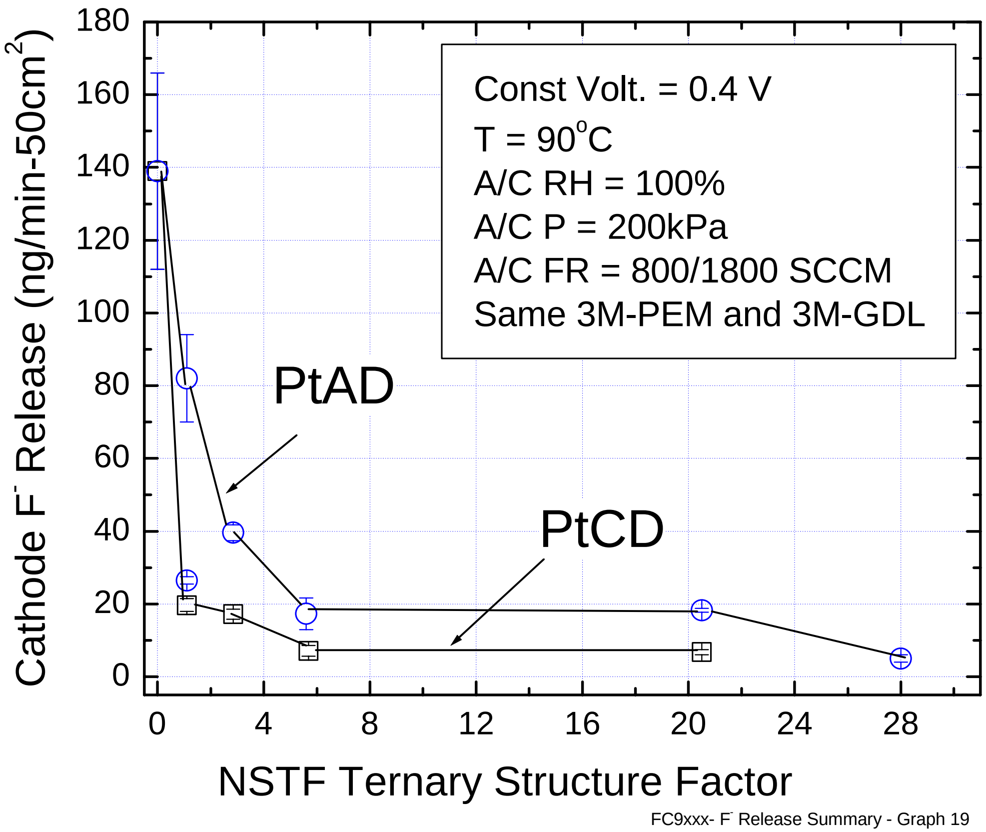


Technical Accomplishments – NSTF MEA Durability

NSTF catalysts and H_2O_2 production and F^- release rates

- F^- release rates (by IC) measured for a series of PtA_xD_y and PtC_xD_y NSTF ternary catalysts under a fixed protocol.

- F^- release(peroxide generation) rate is a function of NSTF construction.



- NSTF catalysts do not contain carbon, so any peroxides generated on carbon of carbon-supported dispersed Pt is eliminated.

- NSTF catalysts have 5x higher specific activity than Pt/Carbon, implying less H_2O_2 production

Technical Accomplishments – NSTF Durability

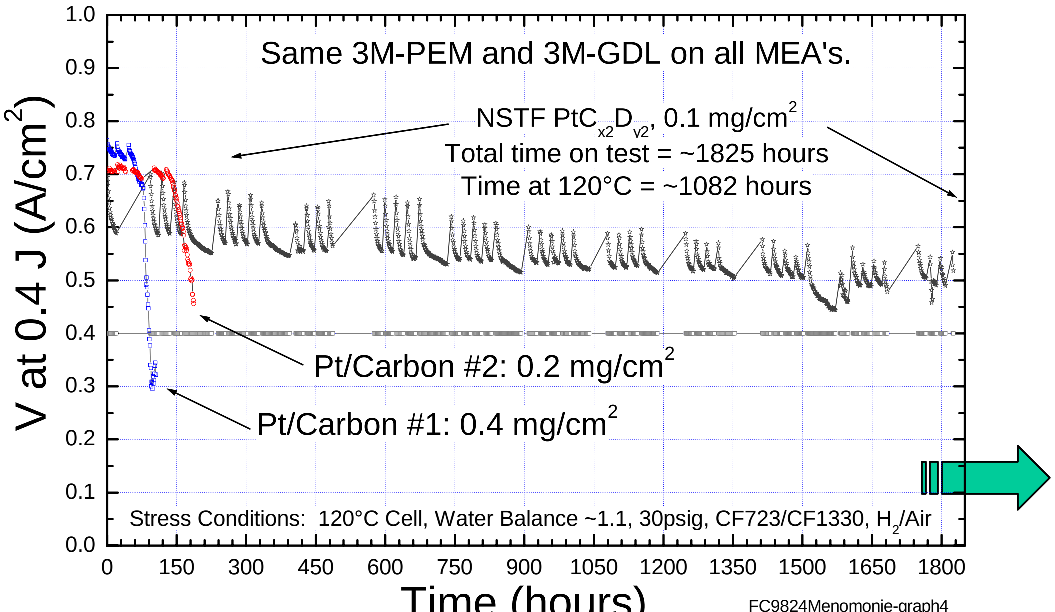
120^{o}C Stress tests of MEA and catalyst surface area durability

- CJ = 0.4 A/cm^2, 100 cm^2 cell, 300kPa H_2/air, A/C inlet % RH = 61%/84%
- 18 – 66 hrs at 120^{o}C, water collected for F^- release, then 6 hrs at 75^{o}C for ECSA, H_2 cross-over, short resistance measurements. Cycle repeated.

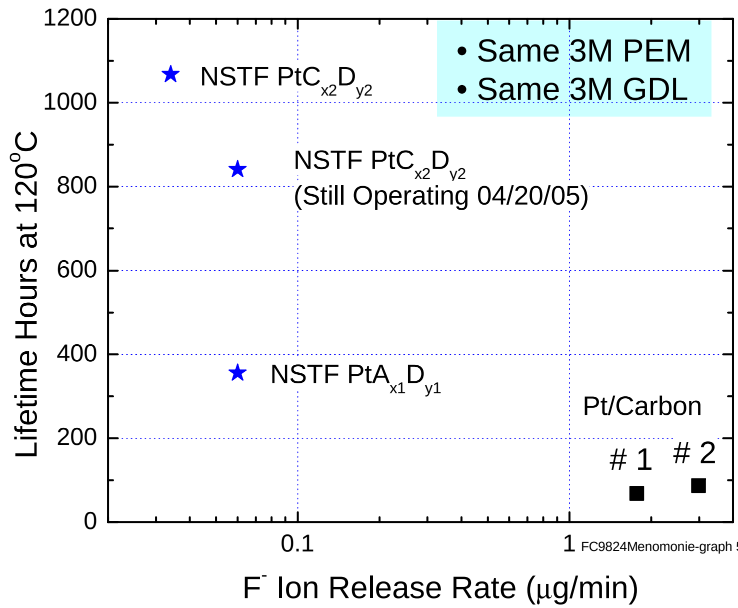
Recent results comparing NSTF and Dispersed Pt/Carbon (Neat 3M PEM)

- reversible impurity adsorption during each 18 hr cycle (cleans up during CV)
- **NSTF MEA lifetimes 15-20 x longer than dispersed Pt/Carbon catalyst MEA.**
- **MEA lifetime scales with F^- release. NSTF F^- release ~ 75 x less than Pt/C.**

Voltage vs time for NSTF and Pt/C MEA's at 120^{o}C



Lifetime versus F^- ion release rate for NSTF and Dispersed Pt/C MEA's



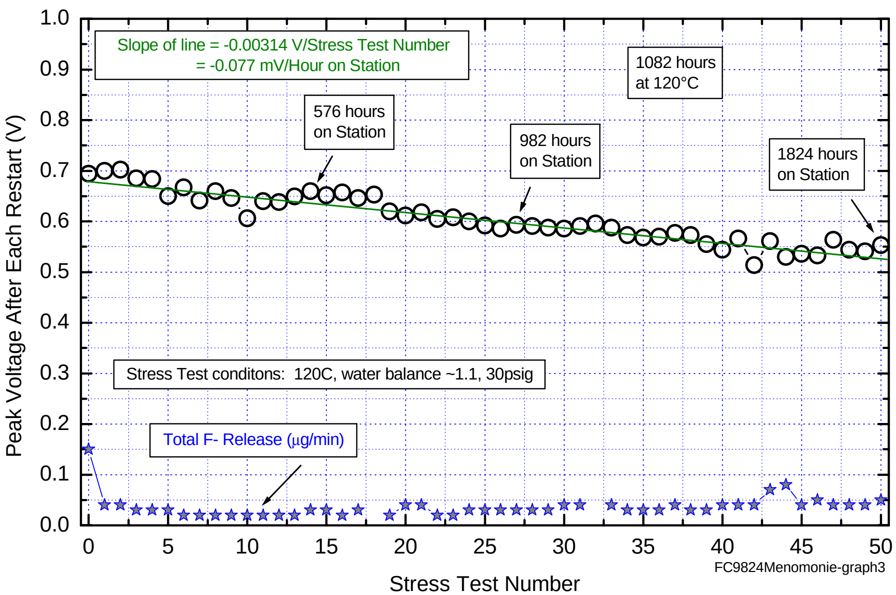
Technical Accomplishments – NSTF Durability

To – date : Best NSTF MEA = NSTF ternary $PtC_{x2}D_{y2}$ (0.1 mg Pt/cm^2)

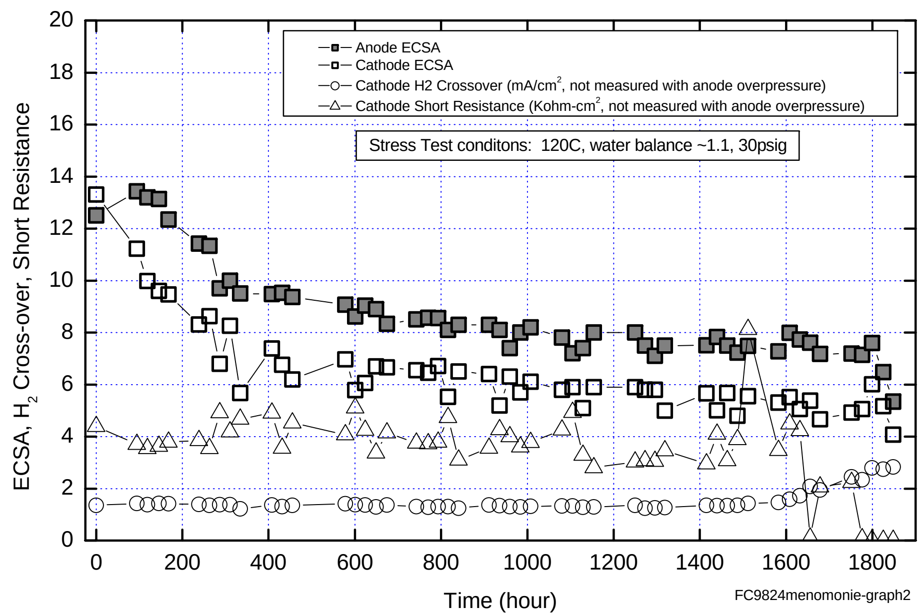
+ Neat 3M PEM (no additives, or edge protection tested yet)+ 3M GDL

- Cathode and anode surface area losses stabilize to ~ 40% and 50% of initial value.
- Shorting and H_2 cross-over values remain stable and low until end of life.
- F^- ion release rate at 120^{o}C remains < 24 nanogram / hr- cm^2 over 1800 hours.
- Decay rate of peak voltage is ~ 77 microvolts/hr over 1800 hr lifetime.

NSTF peak voltage and F^- ion release rate during 1825 hr test, 1080 hrs at 120^{o}C.



Surface areas, short resistances, and H_2-cross-over of NSTF PtCD MEA at 120^{o}C.

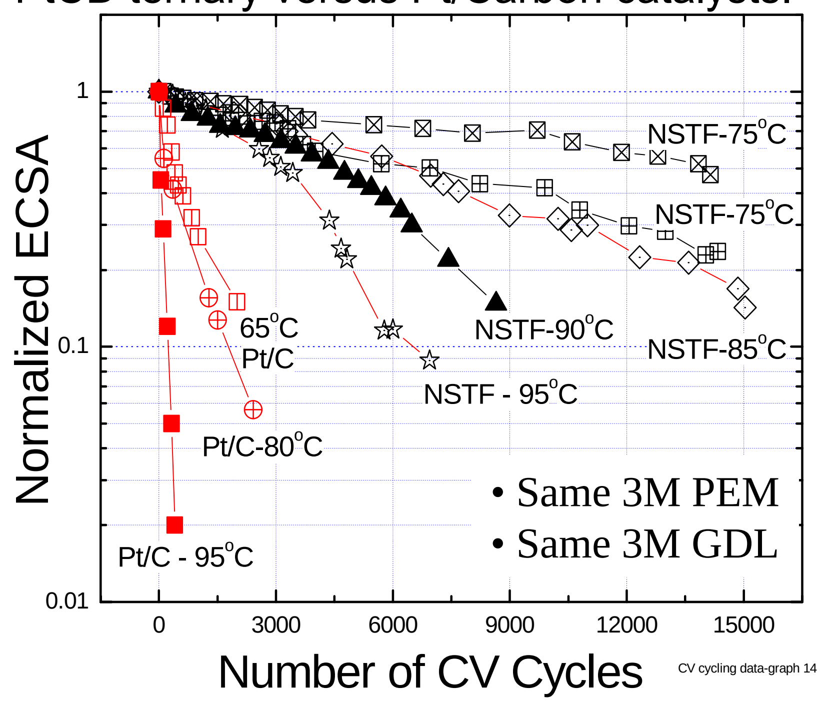


Technical Accomplishments – NSTF Durability

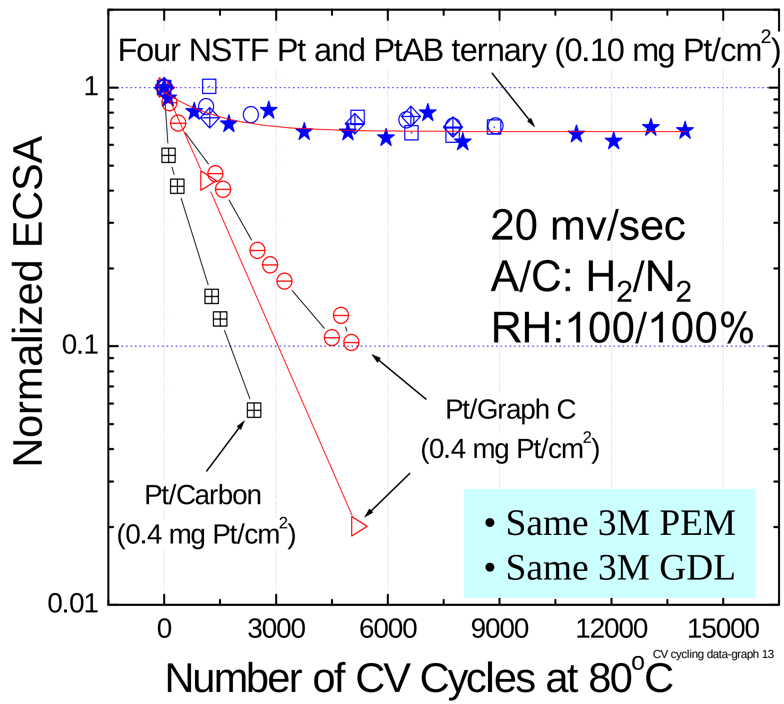
CV cycling measurements from 0.6 – 1.2 V test stability against Pt dissolution

- NSTF catalysts are much more resistant to loss of surface area from high voltage cycling than are dispersed Pt/Carbon or Pt/graphitic-carbon catalysts.
- NSTF catalysts should be more robust against shut down/start-up, and local H_2 starvation. 70% of NSTF ECSA remains after 12,000 cycles to 1.2 volts at 80°C.

CV cycling stability of catalyst surface area as a function of temperature for one NSTF PtCD ternary versus Pt/Carbon catalysts.



CV cycling stability of catalyst surface area at 80°C for NSTF Pt and best NSTF ternary versus Pt/C and Pt/graphitic carbon.

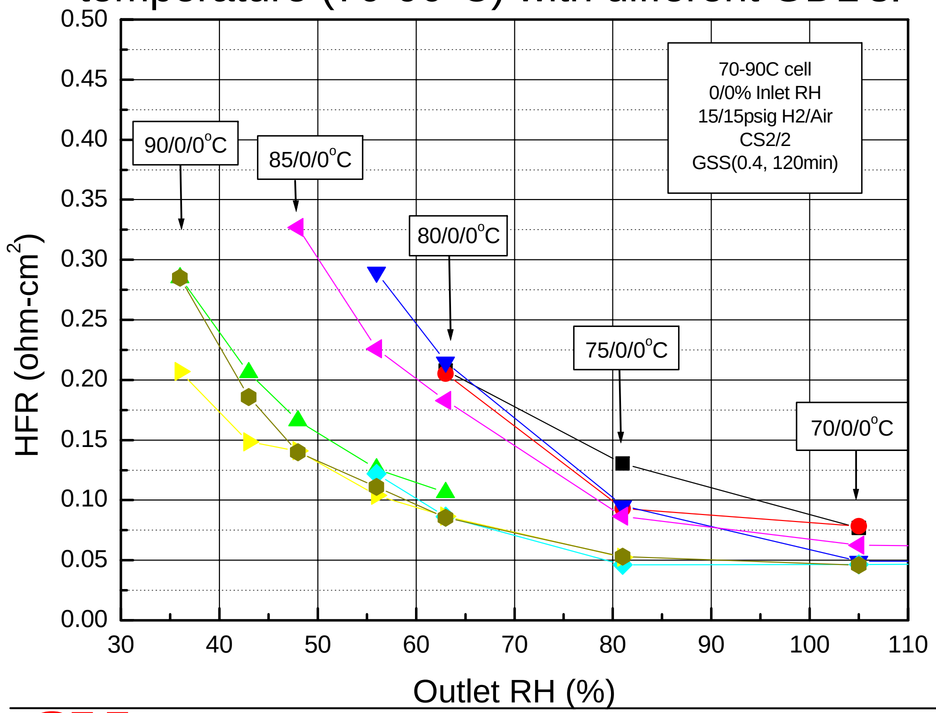


Technical Accomplishments – Thermal - Water Manag.

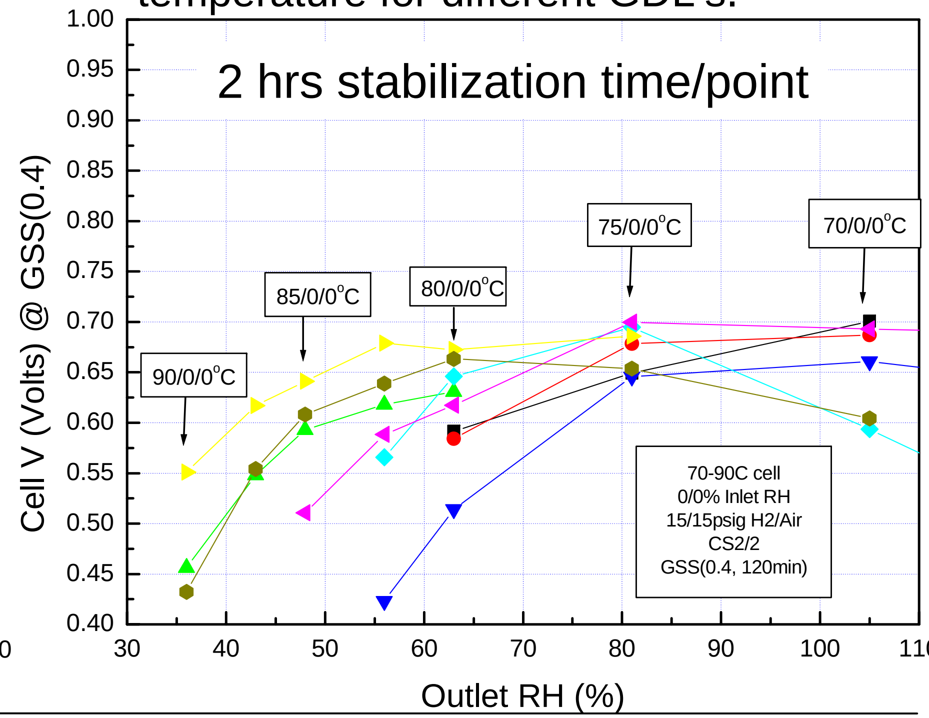
Dry operation –GDL Screening and Optimization

- Operation with totally dry inlet H_2/air is possible at 75°C and 200kPa with no loss of performance for some GDL/NSTF combinations. (1000 EW 3M PEM)
- Introducing some inlet RH allows operation at higher T°C.
- Further optimization necessary for both hot dry and cold start.
- All GDL's are roll-good fabricated, like NSTF and 3M-PEM.

High frequency impedance changes at 15 psig and 0%/0% RH inlet humidification for varying temperature (70-90°C) with different GDL's.



Cell voltage operation at 15 psig and 0%/0% RH inlet humidification with varying temperature for different GDL's.

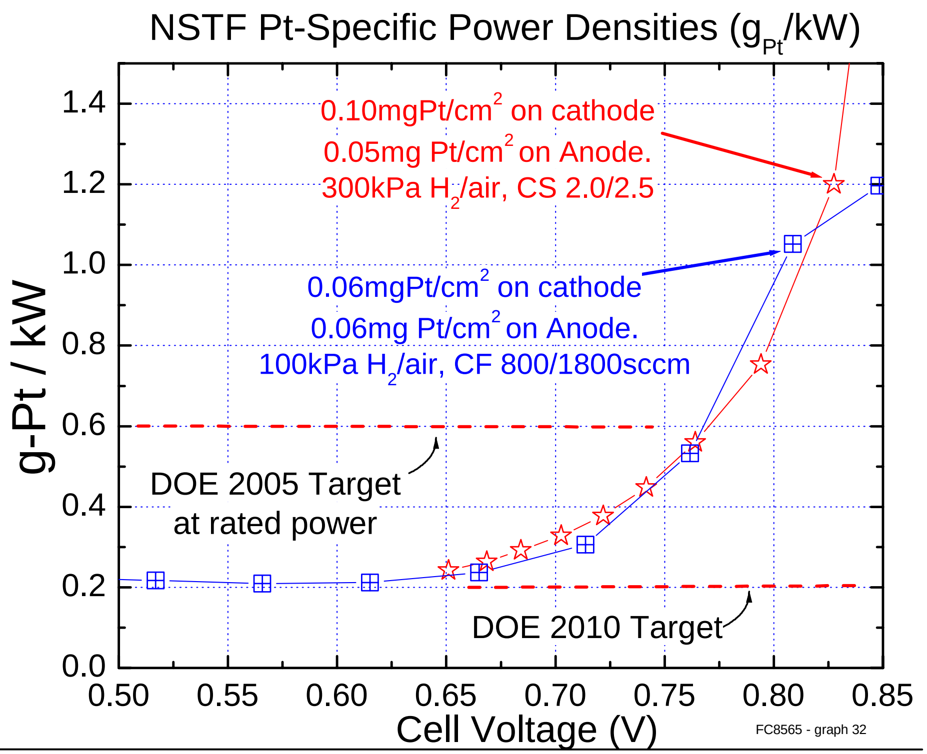


Technical Accomplishments – Performance Targets

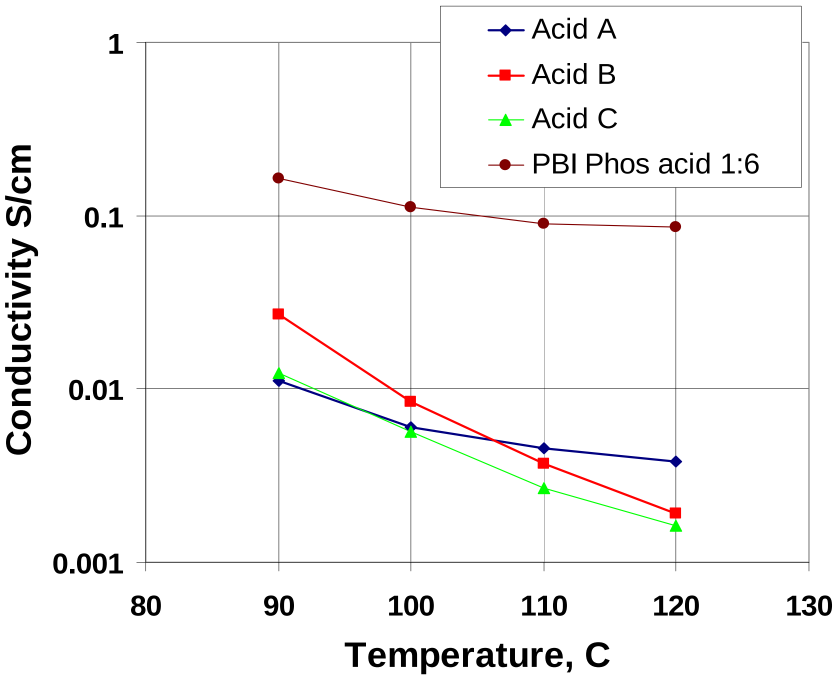
- NSTF Pt specific power density is < 0.3 gPt/kW for cell voltages < 0.70 V for conditions shown. Entitlement may be lower still due to:
  - Opportunity to increase mass activity by optimizing support whisker
  - Opportunity to further reduce impedance of electrode and GDL
- NSTF catalyst based MEA's with 3M PEM clearly show potential to reach 5000 hours of lifetime for 80ºC < T < 120ºC, due to:
  - Enhanced stability and lower F^- release rates of NSTF catalyst,
  - Enhanced stability, mechanical properties of 3M PEM

- Stable operation with totally dry input gases is possible under conditions near water balance – requires optimization of the GDL and further gains matching lower EW PEM to NSTF catalysts.

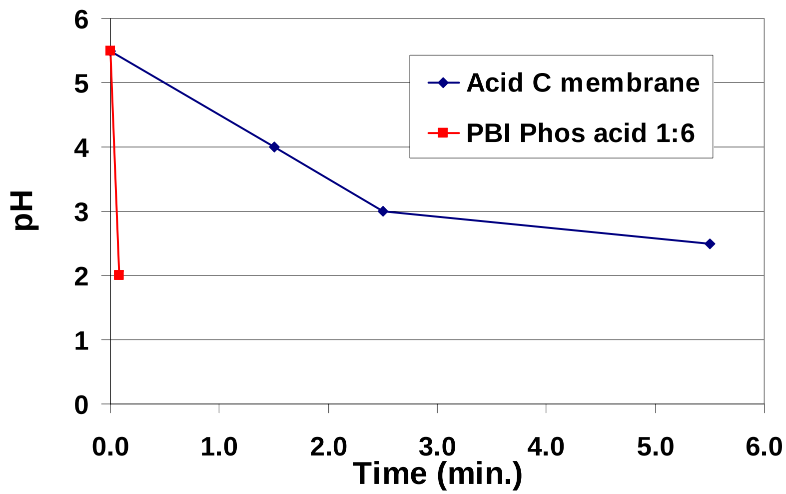
- All 3M PEM, NSTF catalyst, and GDL are currently fabricated using scalable, cost-effective, roll-good fabrication processes.

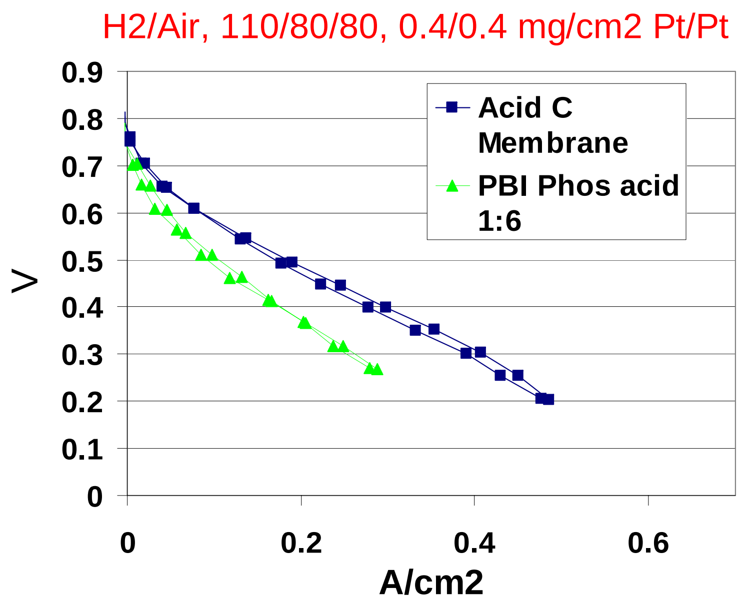


Technical Accomplishments – Electrolytes for T > 120°C



- Temp/RH dependence was significantly lower for polymer swollen with Acid A than with Acid B or C measured by AC impedance. Conductivity was measured with an 80˚C dew point.
- Polymer swollen with Acid C retained acid much better when immersed in water than PBI/H_3PO_4 as shown by pH versus time.
- Even though Acid C had lower conductivity, Fuel cell performance was higher, presumably due to better cathode kinetics.



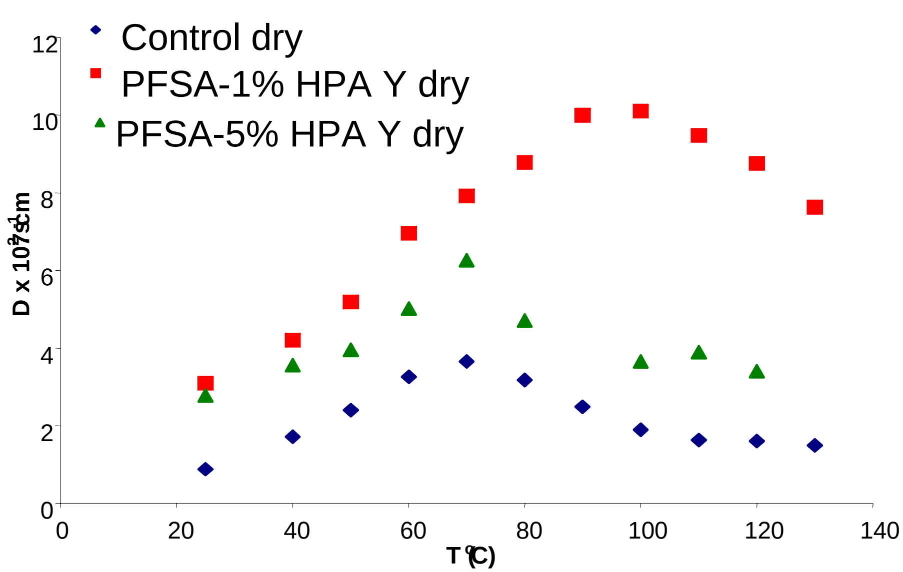


Technical Accomplishments – Electrolytes for T > 120°C

Pulse Field Gradient Spin Echo – Diffusion Measurements

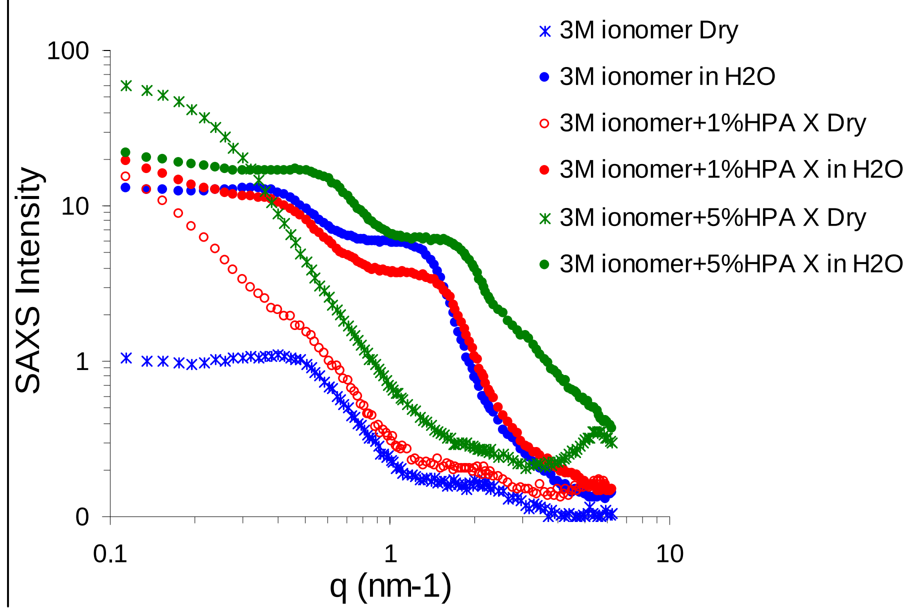
- Preliminary measurements on dry membranes
- Control Ea = 27.5 KJ mol^{-1}, Most HPA doped around 15 KJ mol^{-1}

A. Herring, Colorado School of Mines



SAXS

- Two scattering domains:
- hydrophilic <D> 1.7, d 3.1 nm – dry
<D> 3.8, d 5.1 nm – wet
- hydrophobic <D> 8, d 14 nm – wet or dry
- HPA – higher scattering intensity, larger distribution of scattering domains and a Bragg peak corresponding to HPA crystallites



Response to 2004 Reviewers' Comments

1. "I have mixed reactions to 3M's claims re: less fluoride generation by their new membranes. Are these results because of mismanufacturing of Nafion-based MEA's?"
   * F^- release rates from new 3M PEM are well documented and correlate with much longer lifetimes under accelerated testing.
   * 3M has sold over 200,000 MEA's using Nafion based ionomers and has optimized the manufacturing process.
   * 3M's NSTF catalysts can lower F^- rates even further with 3M PEM.

2. "Stay the course but do accelerate the outside collaborations with industry."
   * 3M will introduce the new 3M PEM to selected customers 2nd quarter 2005, and NSTF ternary MEA's to selected customers end of 2005.

3. "Conductivity and fuel cell polarization measurements should be extended down to 20°C, perhaps even down to –20°C."
   * Low temperature testing is outside the scope of the project and DOE targets for the contracted work.
   * However, cold start and freeze tolerance are very important and are being studied at 3M.

Future Work

Completion of Task 3: Advanced MEA Development for 85< T < 120°C:
- MEA pilot level scale-up and large area stack testing.

- M1 – down-selection of final x/y values for PtCxDy ternary and loading
- M2 – down-selection of final 3M-PEM properties for durability, ramp-up
- M3 – down-selection of final GDL for reduced IR loss and dry operation
- M4 – CCM process transfer to new pilot scale equipment
- M5 – Statistical validation of pilot scale roll-good fabricated CCM's
- M6 – MEA fabrication for designated stack testing (312 cm^2)
- M7 – Short stack testing (~ 3-5 kW)
- M8 – Testing customized Vairex air management systems w/NSTF MEA.

Completion of Task 2: High Temp. Electrolytes for T > 120°C.

- Further characterization of polymer/acid combinations focused on membrane conductivity and stability.
- Moving to <u>immobilized</u> heteropolyacids for fuel cell testing.

Publications & Presentations

1. "Dissolution of Fe and Ni in Combinatorially Sputtered $Pt_{1-x}Fe_x$ and $Pt_{1-x}Ni_x (0<x<1)$ Electrocatalysts," A. Bonakdarpour, J. Wenzel, D. A. Stevens, S. Sheng, T. L. Monchesky, R. T. Atanasoski, A. K. Schmoeckel, G. D. Vernstrom, M. K. Debe and J. R. Dahn, presented at the First International Conference on Fuel Cell development and Deployment, March 7-10, 2004, Connecticut Global Fuel Cell Center, Stores, CT.
2. "Studies of Transition Metal Dissolution from Combinatorially Sputtered, Nano-Structured $Pt_{1-x}M_x$ (M=Fe, Ni;$0<x<1$) Electrocatalysts for PEM Fuel Cells," A. Bonakdarpour, J. Wenzel, D. A. Stevens, S. Sheng, T. L. Monchesky, R. Lobel, R. T. Atanasoski, A. K. Schmoeckel, G. D. Vernstrom, M. K. Debe and J. R. Dahn, J. Electrochemical Society, Vol. 152 (1), 2005, A61-A72.
3. "In-situ Vibrational Spectroscopy with Fuel Cell Catalysts," Andrzej Wieckowski, Lajos Gancs, Matthew McGovern, Guo-Qiang Lu, Radoslav Atanasoski, and Mark K. Debe, presented at the American Chemical Society meeting, Anaheim, CA, March 29-April 2, 2004.
4. "Advanced MEA's for Enhanced Operating Conditions," 2004 DOE Hydrogen Fuel Cells and Infrastructure Technologies Annual Review, Philadelphia, PA, May 24-27,2004.
5. "Advanced MEA's for Enhanced Operating Conditions," submitted for 2004 Hydrogen Program Annual Report, July, 2004.
6. "NanoStructured Thin Film, Thin Layer Electrodes Optimized for PEM Fuel Cell Performance at High Current Density," 2005 Fuel Cell Seminar, San Antonio, TX, Nov. 1-5, 2004.
7. "Corrosion of Transition Metals in $Pt_{1-x}M_x$ (M=Fe, Ni, Mn) Proton Exchange Membrane Fuel Cell Electrocatalysts," A. Bonakdarpour et al., presented at the Fall 2004 Electrochemical Society Meeting, Honolulu, HI, USA.
8. "64-Channel Fuel Cell for Testing Sputtered Combinatorial Arrays of Oxygen Reduction Catalysts," D. A. Stevens et al., presented at the Fall 2004 Electrochemical Society Meeting, Honolulu, HI, USA.
9. "Combinatorial PEM Fuel Cell Studies of Binary Platinum Alloys," D. A. Stevens et al., presented at the Fall 2004 Electrochemical Society Meeting, Honolulu, HI, USA.
10. "The Search for Higher Temperature Proton Conductors for the PEM Fuel Cell," J. Woods Halley, Symposium on Fuel Cells, MRS Meeting, Boston, MA, December 1, 2004,
11. "The Development of New Membranes for PEM Fuel Cells", Steve Hamrock, Advances in Materials for Proton Exchange Membrane Fuel Cell Systems, Asilomar Conference Grounds, Pacific Grove, CA, February 21, 2005.

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- Accidental H_2 release in cylinder closet leading to ignition from:
  - H_2 line or manifold breach
  - Accident during replacement of cylinders

Hydrogen Safety

Our approach to deal with this hazard is:

- Design
  - Hydrogen cylinder closet and gas distribution system adhere to codes.
  - Reduction in number of cylinders in the closet
  - 2-step regulators (less susceptible to failure and designed to fail closed)
  - H_2 sensors in all labs and cylinder closet, alarm system
  - Automatic shut-off of H_2 gas supply if sensors detect H_2 release
- Procedures
  - SOP's for cylinder changing, alarm responses, test station operation
  - Cylinder changing restricted to highly trained personnel
  - Regular maintenance checks – sensors, leak check of valves etc.
- Installing H_2 Generator (in non-inhabited mechanical room) to significantly reduce total volume of H_2 in facility