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

3M/DOE Cooperative Agreement No. DE-FC36-02AL67621

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May 24, 2004

This presentation does not contain any proprietary or confidential information.

Project Objectives : 5/03 – 5/04

Development of high performance, lower cost membrane electrode assemblies (MEA's) qualified to meet demanding system operating conditions of higher temperature and little or no humidification, with less precious metal catalysts, and higher durability membranes than current state-of-the-art constructions.

- Durable, lower cost MEA's for operation in the range of 85 < T < ~ 120ºC:
  - develop next generation, thin film, ultra-thin layer catalyst electrodes (NSTF)
  - optimize PFSA based ionomers modified for enhanced durability at low RH
  - match MEA components for enhanced performance under demanding cond.
  - utilize roll-good fabrication processes for lower cost
- Development of MEA's for operation in the range of 120 < T < 150ºC:
  - new PEM's that do not rely on standard modes of aqueous proton conduction
  - understanding relationships between materials, proton conductivity, T and RH
  - screening materials and fabrication processes

Budget FY04

Budget

3M/DOE Cooperative Agreement No. DE-FC36-02AL67621

($ million)

	Contractor	DOE	Total
Total project	2.03	6.99	9.03
FY04	**0.66**	**2.44**	**3.10**

Technical Barriers and Targets Addressed by This Project

Barriers for components

O. Stack Material and Manufacturing Cost
- Reduced catalyst costs: Reduced Pt with nanostructured thin film (**NSTF**) catalysts
- Simplified process: single step, high volume, dry, roll-good processing

P. Durability
- Enhanced catalyst support stability: 3M **NSTF** - whisker support particles ~ graphite
- Enhanced catalyst surface area stability at high T: Thin film nature of **NSTF** electrodes
- Enhanced oxidative stability of PEM: 3M PFSA ionomer with additives

Q. Electrode Performance
- Enhanced cathode performance: 5x gain in specific activity of 3M **NSTF** catalyst
- Reduced mass transport loss at high current density: Ultra-thin layer **NSTF** electrodes

R. Thermal and Water management
- Matched MEA components for sub-saturation operation

Relevant targets for fuel cell stack system for 2010 (Table 3.4.4 of MY RD&D Plan)

Cost : $35/kW
Durability : > 5000 hours
Precious metal loading : 0.2 g/rated kW

Approach

Task 1 is directed at advancing the state-of-the-art in cathode structures and modified PFSA based PEM's to stretch the limits of current MEA technology to 85 <T< 120 ^{o}C, drier operating conditions, with less Pt.

- Development of advanced cathode catalysts using combinatorial and other screening methods: Thin film Pt ternaries coated on novel nanostructured thin film support particles and incorporated as ultra-thin layer electrodes into new PFSA based PEM's, for high performance at high temperature
- Development of new membranes based on 3M's novel PFSA ionomer, with specific additives and chemistries to obtain enhanced oxidative stability under drier, hotter operating conditions
- Optimization of catalyst coated membrane assemblies and gas diffusion layers for high current density operation under low RH
- Use of pilot scale roll-good fabrication processes for catalysts, membranes and GDL's
- 3D, two phase modeling of MEA's and flow fields to optimize low RH operation
- Air management system modeling and prototype development to evaluate P vs flow rate constraints

Task 2 focuses on development of high temperature membranes that do not use water from humidified gases for H^+ transport and matching components to take the MEA into a new operating range of T >120°C.

- Synthesis and characterization of fluorinated conductivity-enhancing additives, and inorganic proton conductors as electrolyte replacements for water
- Incorporation of mixtures of those electrolytes into various polymer and microporous media
- Fuel cell performance characterization of catalyzed membranes

Safety

3M's established procedures regarding safety-related issues include:

- Hazard Reviews to ensure compliance with corporate environmental, health, and safety requirements:
  - New or modified facilities, equipment, & processes
  - Fabrication & testing equipment
  - Laboratory & Manufacturing
- New Product Introduction system
  - Risk assessment process in the design and production of products
  - Life Cycle Management process
  - Change Management

No unusual safety issues have been encountered to-date on this project.

Project Timeline

CY2002				CY2003				CY2004				CY2005			
Q1	Q2	Q2	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	Q13	Q14	Q15	Q16

today

M1 M3 M6 M8 M10

M2 M4 M5 M7 M9 M11

Task 1.0 Medium Temperature MEA Development , 85 < T < 120 ^{o}C

M1. NSTF catalyst composition and support characteristics down-selected
M2. Modified 3M PEM and additives down-selected
M3. Electrode backing and GDL coating down-selected
M4. Pilot scale quantities of roll-goods fabricated for initial stack testing
M5. Short stack testing completed

Task 2.0 High Temperature MEA Development, T> 120^{o}C

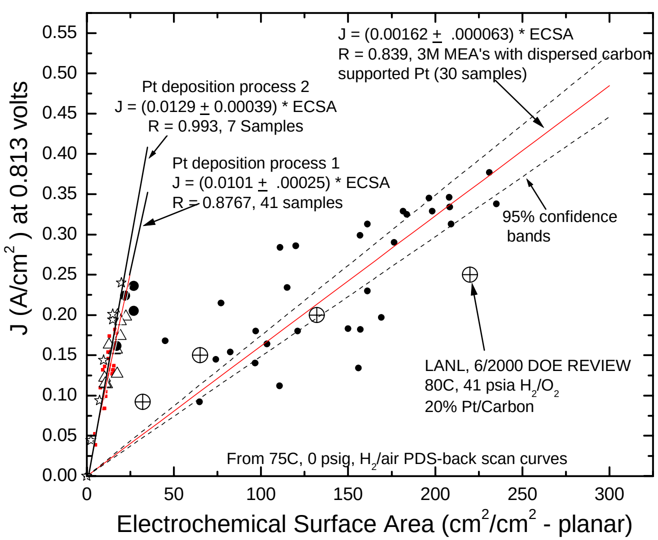
M6. Down-selection of electrolyte additives
M7. Down-selection of membrane matrix media and process
M8. Selection of anode and cathode catalysts for high temperature PEM
M9. Final high temperature testing completed of medium sized MEA’s

Task 3.0 Scale-up of optimized process for integrated MEA component fabrication

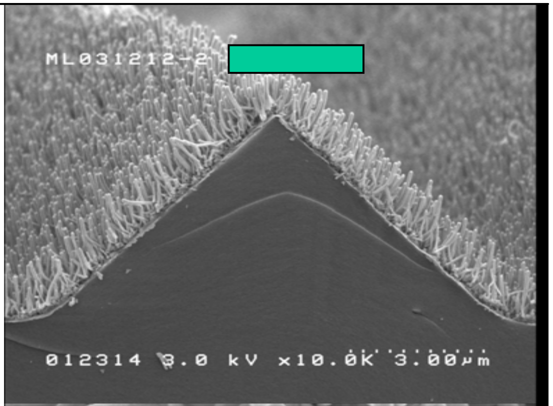
M10. Scale-up/optimization of fabrication processes for PEM, catalyst, CCM, GDL
M11. Completion of final MEA’s characterized in full-scale short stack

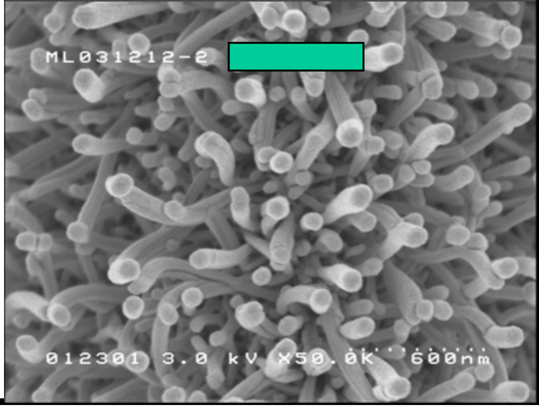
Selected Technical Accomplishments 5/03-5/04 : NSTF Catalysts

- 40 new NSTF PtA_xB_y ternary catalyst constructions fabricated and evaluated (~ 100 total)
- 17 large area combinatorial library arrays fabricated and evaluated on NSTF support films
- Documented 5x gain in specific activity of NSTF over Pt/Carbon by three methods:
  - – RRDE at LBNL and $50cm^2$ cells at 3M
- Eliminated mass transport losses under H_2/air at 2 A/cm^2 with ultra-thin NSTF electrodes
- Determined stable phases of PtM binary and PtAB ternaries in acid baths and fuel cells
- Demonstrated electrochemical and high temperature stability of NSTF catalyst surface areas
- Identified critical path for GDL/catalyst improvements to reach 2010 DOE performance targets



NanoStructured Thin Film (NSTF)Thin Layer Catalysts
- no carbon
- no ink layer
- organic crystalline whisker support particles
- thin film catalyst coating
- all dry roll-good processing
- 5x gain in specific activity
- <1µm electrode thickness





NSTF Cathode Specific Activity:

J(.813V)/ECSA = 10.1 ± .25 mA/cm²-Pt

Dispersed Cathode Specific Activity:

J(.813V)/ECSA =1.62 ± 0.06 mA/cm²-Pt

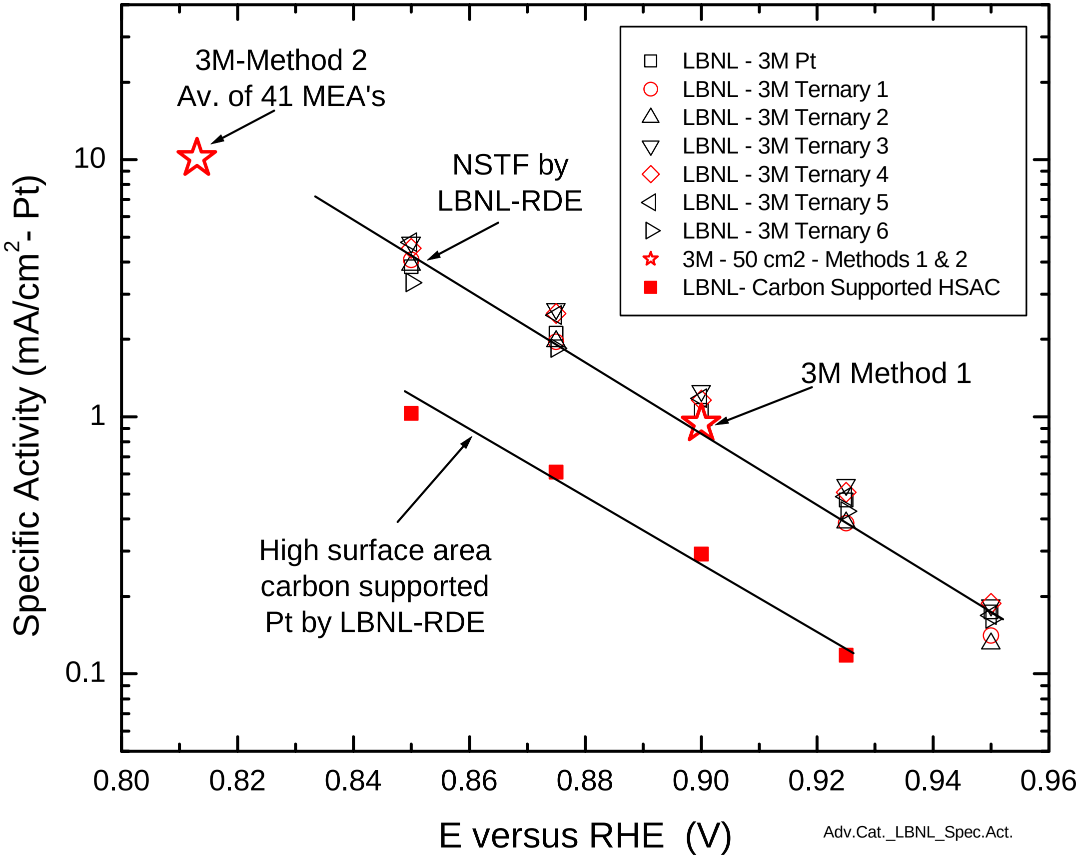
Method 2

Technical Accomplishments – NSTF Catalyst – Specific Activity

• Seven 3M nanostructured thin film catalyst samples were characterized by LBNL with their rotating ring disc electrode method - 1 baseline Pt and 6 PtAB ternaries:

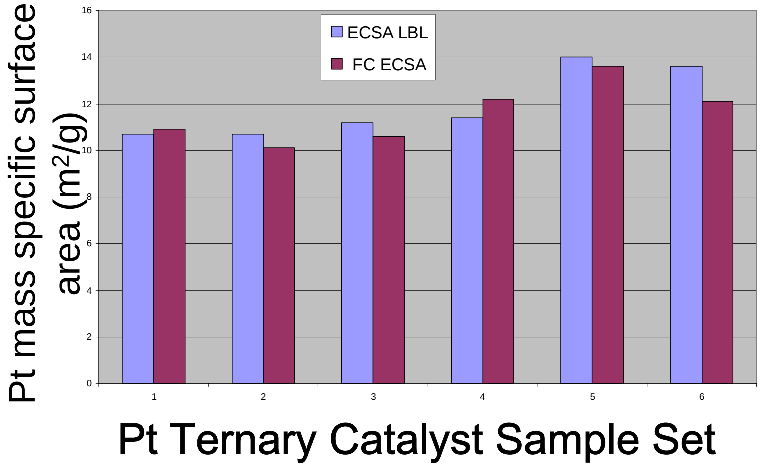
• LBNL's RRDE measurements agree well with 3M's two methods of specific activity measurement in 50 cm^2 cells: NSTF specific activity is ~ 5 x larger than Pt/Carbon catalysts.

• Specific activity of these Pt ternaries is same as pure Pt coated whiskers.



• The LBNL RDE measured mass specific surface areas (m^2/g) agree well with the 3M measured values in 50 cm^2 cells.

• Mass specific area depends on NSTF support whisker geometry.



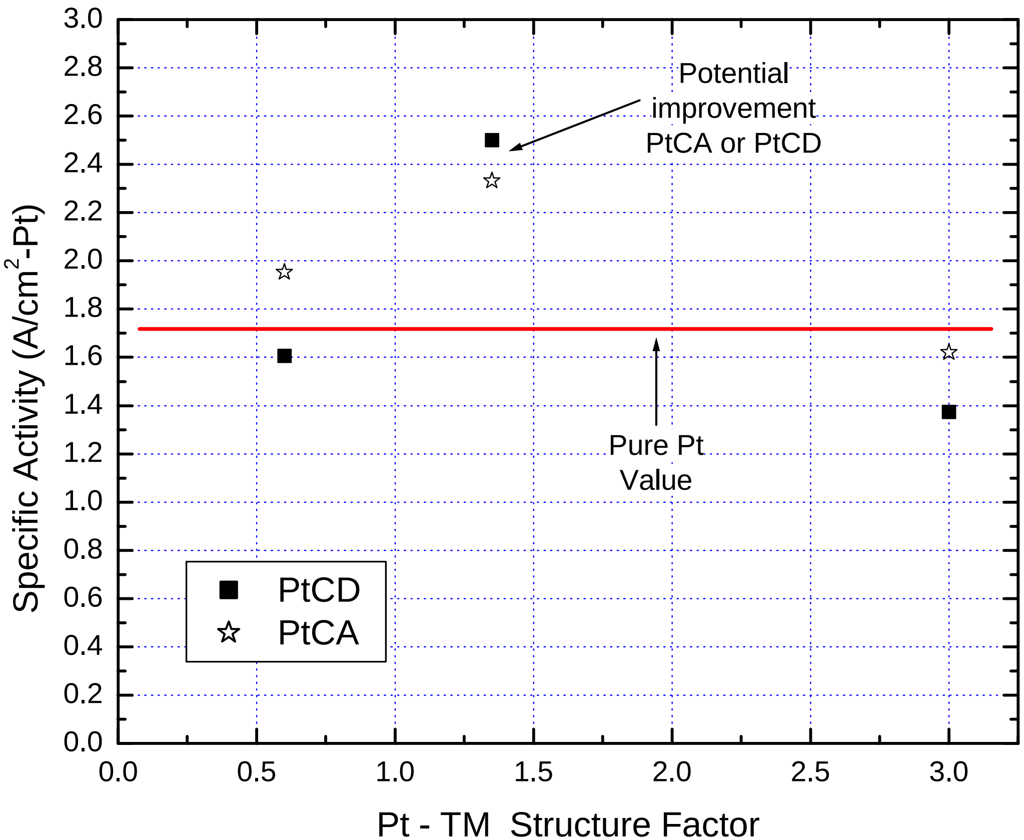
• **NSTF catalyst Specific Activities are similar to polycrystalline bulk platinum.**

Technical Accomplishments – NSTF Catalyst – Specific Activity

Combinatorial library coatings of Pt binary and ternary on NSTF support films at Dalhousie University using similar coating processes as 3M's:

Four commonly known transition metals in Pt ternary components tested thus far in variable discrete % compositions in 50 cm^2 cells, and as continuously variable combinatorial arrays tested in small area segmented cells: PtA, PtB, PtC, PtD, PtDB, PtAB, PtAD, PtCA, PtCD

Specific Activity of Segmented Cell Measurements of 50 cm^2 Combinatorial Library Arrays of PtCA and PtCD, Averaged over Segments.



* Segmented cell characterization of Dalhousie combinatorial catalyst library at 3M points to two ternaries , PtCA and PtCD , that should give a further gain in specific activity.

* Initial 50cm^2 cell tests confirm an improvement in specific activity.

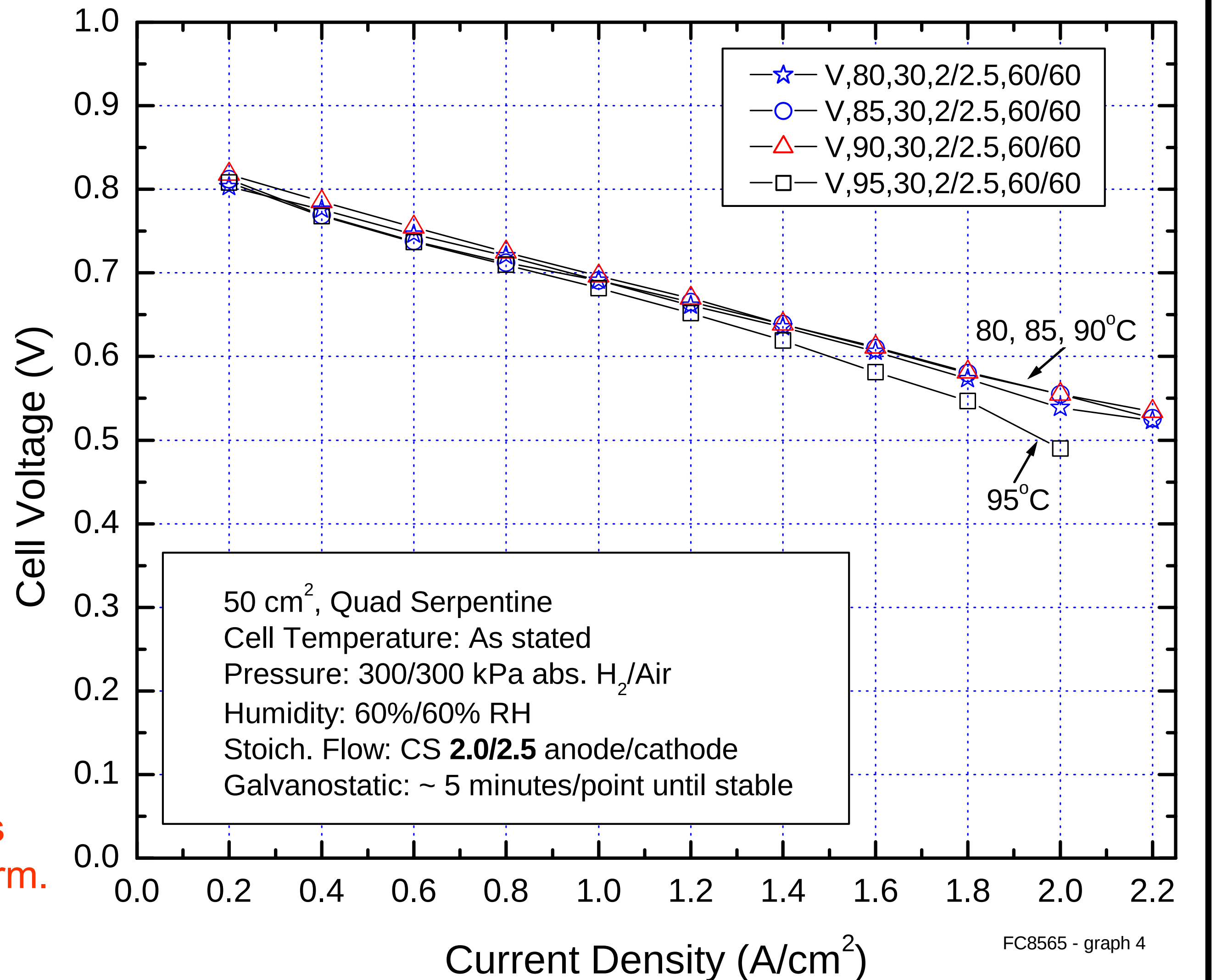
Technical Accomplishments – NSTF Catalyst – Low mass transport loss

Achieving high current density for high power density stacks requires minimal mass transport losses. The NSTF ultra-thin layer electrode thickness minimizes loss.

MEA

- Cathode Catalyst: 0.10 mg-Pt/cm² in PtAB ternary
- Anode Catalyst: 0.15 mg-Pt/cm²
- PEM: 3M-Cast Nafion 36 micron thick
- GDL/EB: 3M GDL on carbon cloth backing:

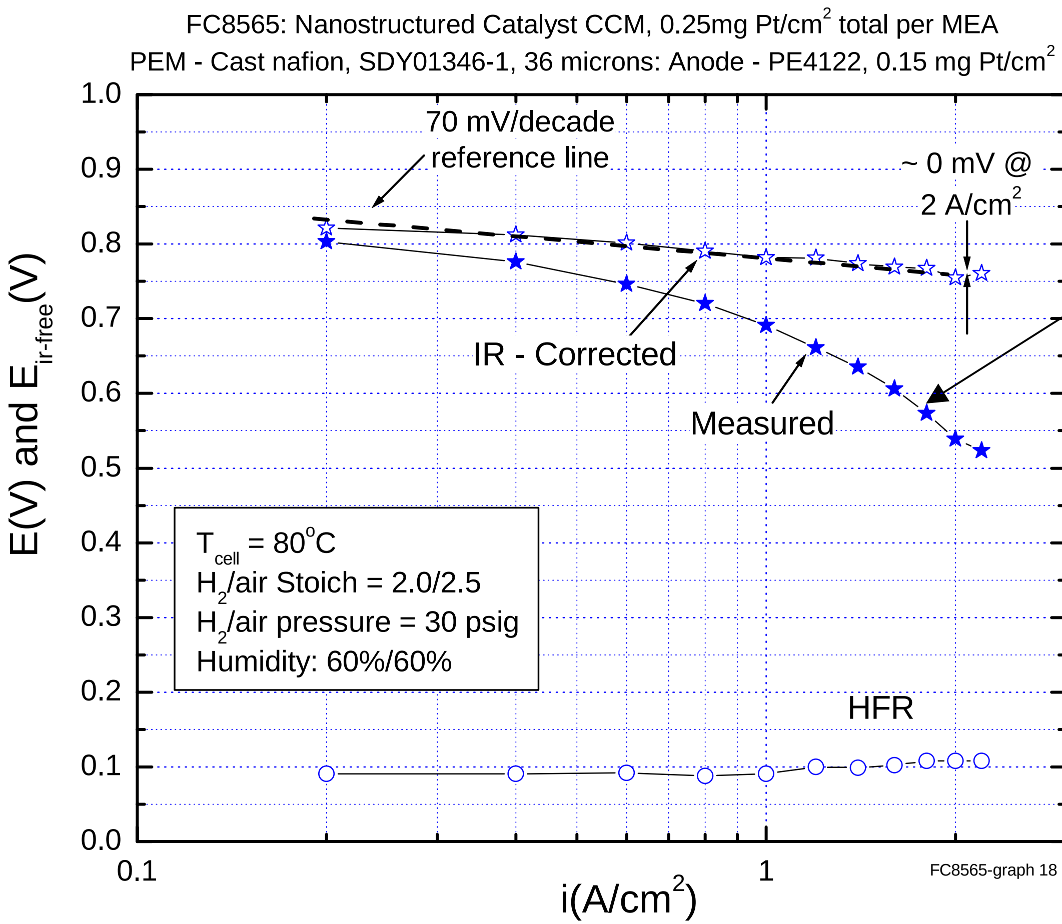
HFR = 0.10 ohm-cm² is ~ 100% higher than norm.

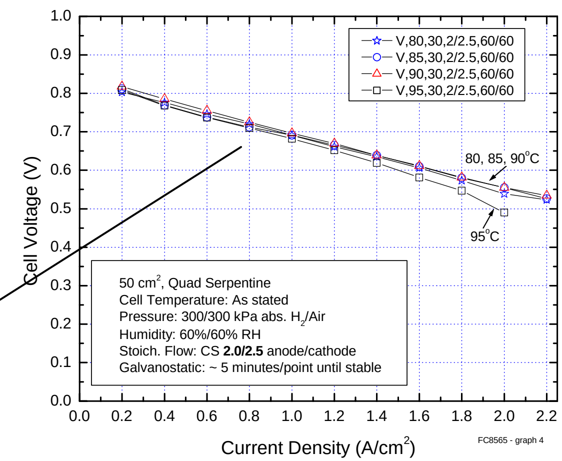


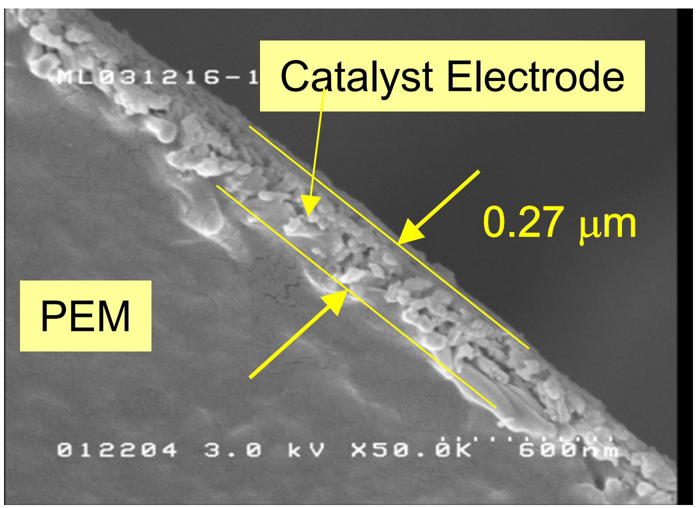
Technical Accomplishments – NSTF Catalyst – Low mass transport loss

* At the test conditions shown, there is little or no mass transport loss in the NSTF electrode layer or GDL at 2 A/cm^2, assuming a Tafel slope of ~70mV/decade .

* Mass transport losses in the NSTF catalyst coated membrane electrode layer are minimal with the catalyst composition and loading correctly matched to the whisker support particles.



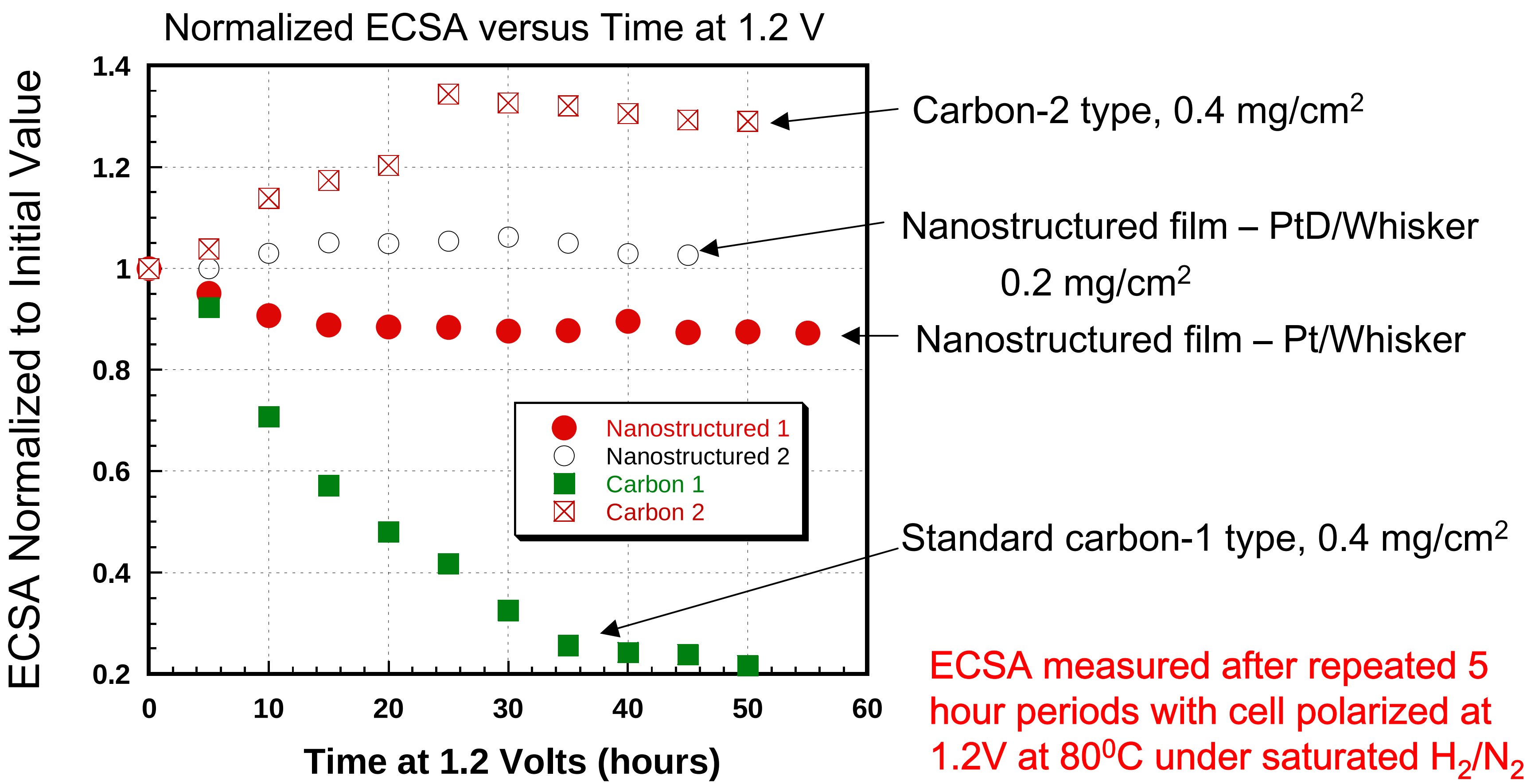




Technical Accomplishments – NSTF Catalyst – Surface area (ECSA) stability

1.2 volts electrochemical stress test has been applied to carbon supports and the nanostructured thin film catalysts.

Nanostructured films are more electrochemically stable against loss of surface area than a standard carbon supported Pt catalyst and similar to carbon-2 type.

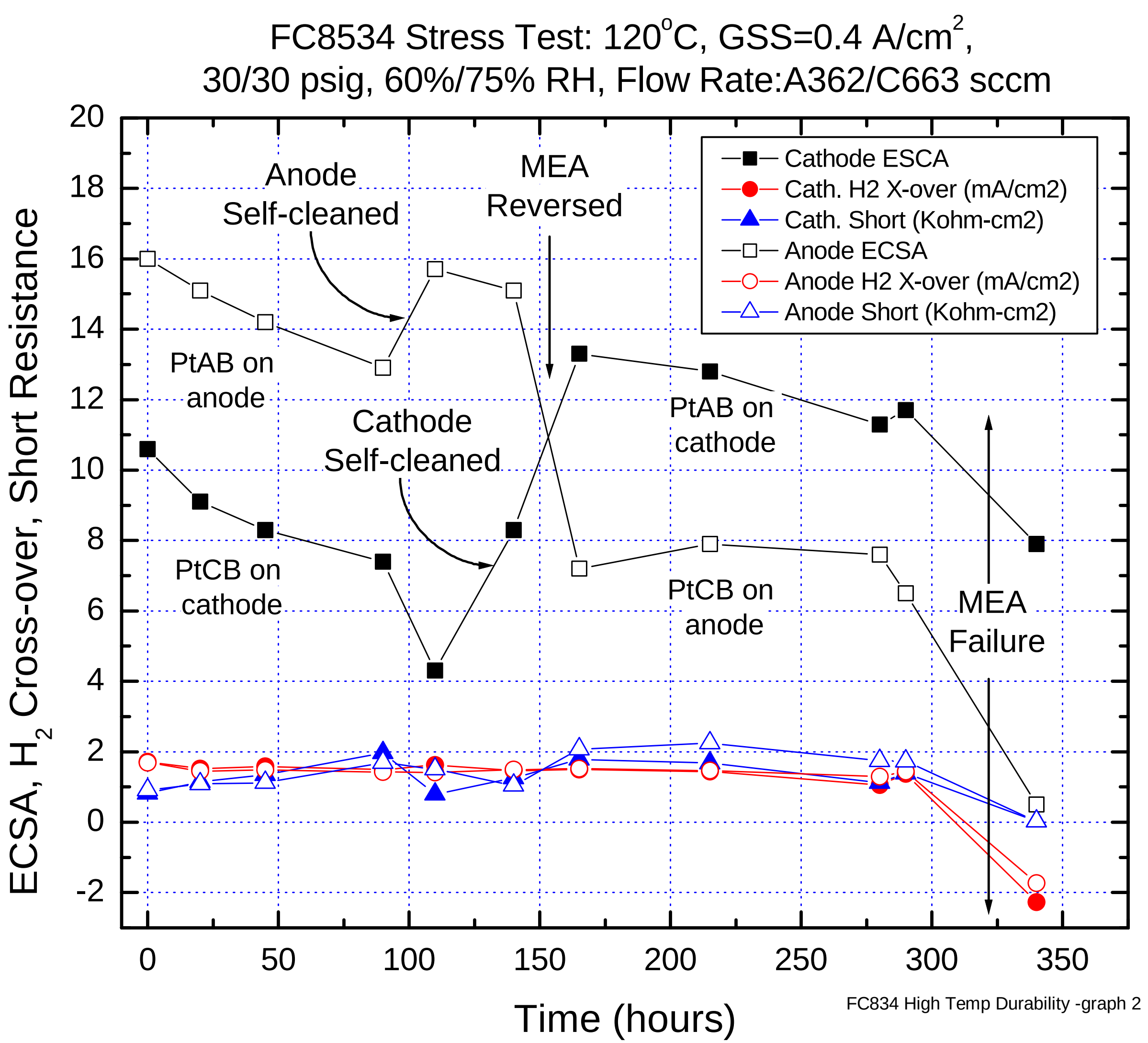


ECSA measured after repeated 5 hour periods with cell polarized at 1.2V at 80^0C under saturated H_2/N_2.

Technical Accomplishments – NSTF Catalyst – Surface area (ECSA) stability

Surface area stability at 120°C and water balance conditions:

- Multiple MEA's tested
- The H_2 cross-over and short resistances extracted with the ECSA were very stable until the MEA failed completely.
- Both anode and cathode show some decay in surface area initially, then "self-cleaned" and ECSA recovered.
- PtCB ECSA ~ 80% of initial value after > 100 hours at 120°C. Dropped another 6% over next 125 hours.



Technical Accomplishments – NSTF Catalyst – Composition stability

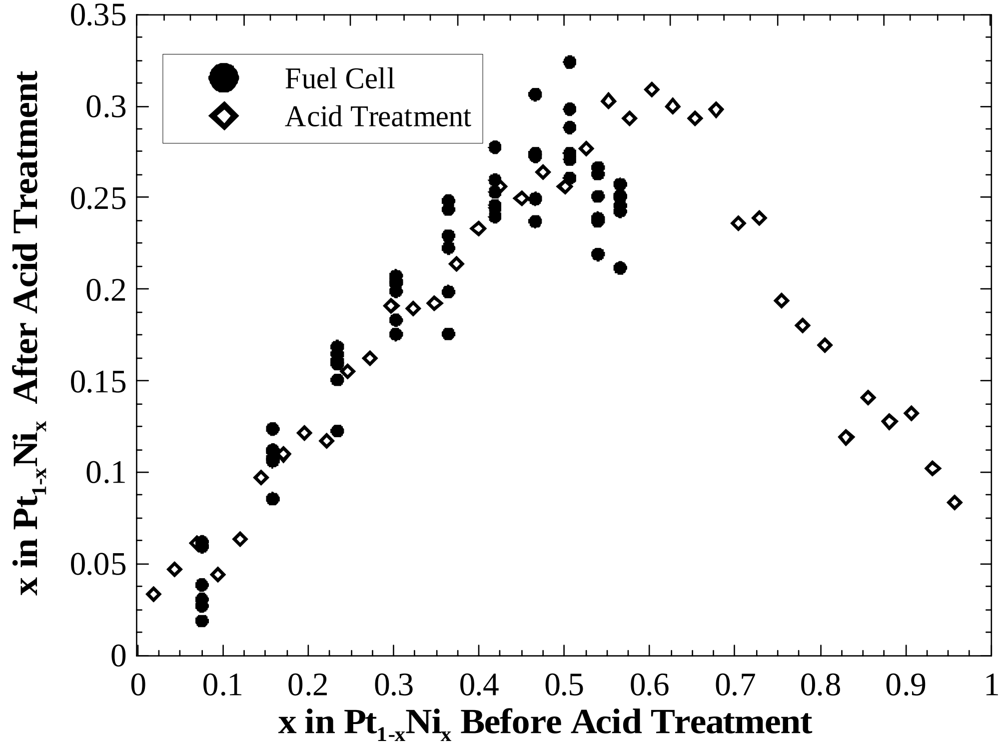
Dalhousie has done extensive characterization of combinatorial libraries of various binary and ternary NSTF catalysts for:

- Surface and bulk compositions and structure – comparing as-made with acid soaked and fuel cell tested catalysts,
- Lattice constants vary with Pt and TM atomic fractions, before and after acid exposure,
- PtXY form random, solid solutions,
- Extent of bulk or surface depletion of TM depends on initial amount,
- Same stable PtTM phases obtained after acid washing as after fuel cell operation.

- x_{after} in $Pt_{1-x}A_x$ of the $Pt_{1-x}A_x$ library plotted versus x_{before} in $Pt_{1-x}A_x$ for a library used in a fuel cell, and an identical library treated with 1M H_2SO_4 at 80°C for 10 days. (A = Ni or Fe)

- The data points after acid treatment show no evidence for the presence of surface A atoms at any point in the library.

- Similar effects for PtXY ternaries

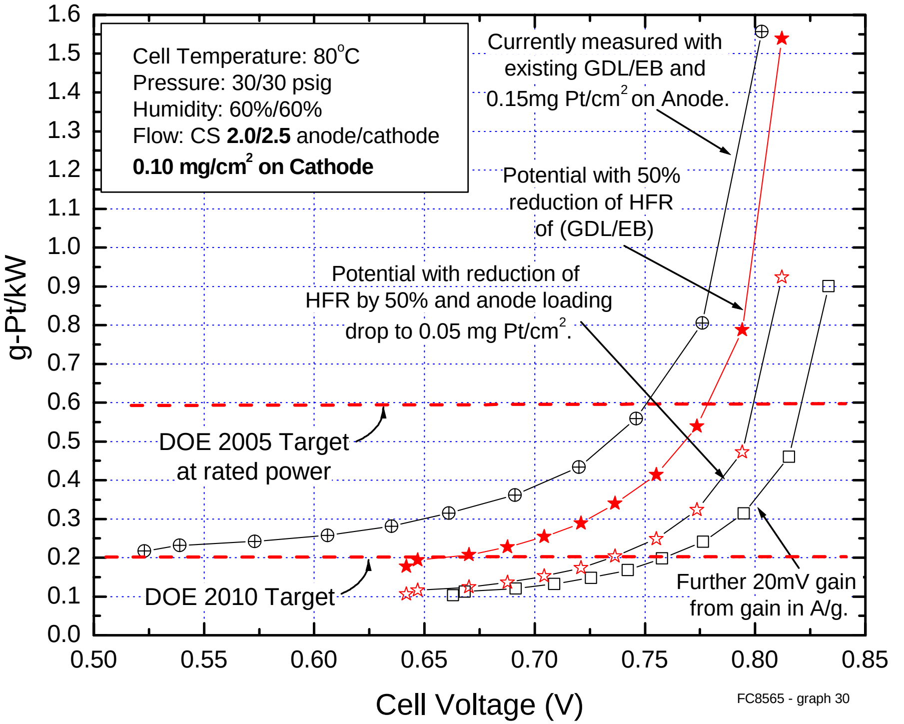


Technical Accomplishments – Definition of Potential Pathway to DOE Targets

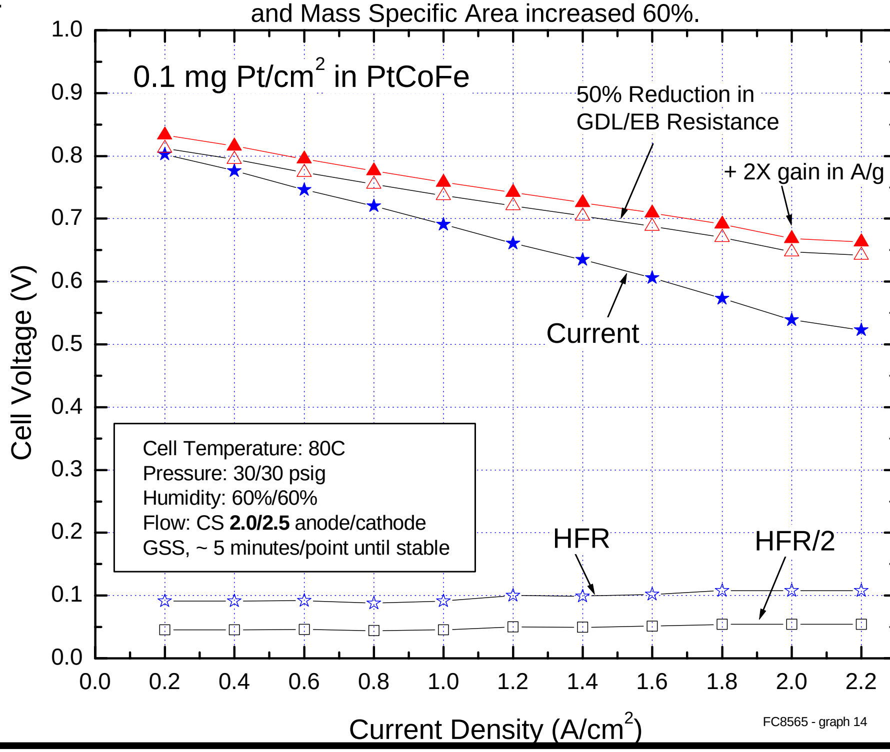
1) Reduce EB/GDL impedances by 50% while maintaining the high permeability.
2) Reduce anode loading to 0.05 mg/cm² with same performance currently achieved with 0.15 mg/cm².
3) Double mass activity (A/g) by increasing mass specific area (m²/g) 60% and specific activity 35% while maintaining 5x gain in specific activity (A/cm²-Pt).
4) Integrated MEA with NSTF/3M-PEM optimized for higher T, lower RH operation and minimal F^- release.

NSTF Pt specific power density entitlement is < 0.2 gPt/kW for cell voltages < 0.75 V for conditions shown with current development status.

FC8565: Pt-Specific Power Densities (g_{Pt}/kW) achievable with HFR reduced 50% with improved GDL/EB, reduced anode loading, and 2x Gain in Mass Activity.



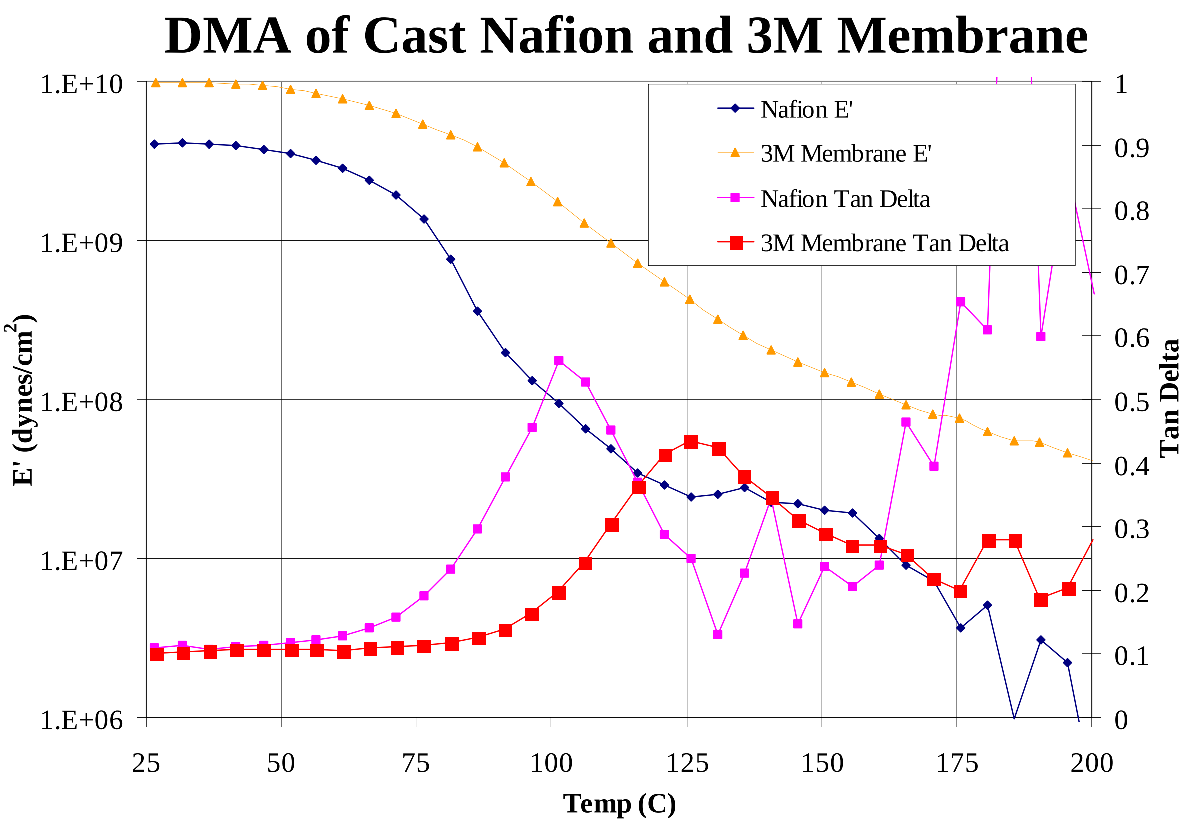
FC8565: Projected performance improvements assuming HFR is Reduced by 50%, Specific Activity increased 33% and Mass Specific Area increased 60%.



Selected Technical Accomplishments – Membranes - PEM for 85<T<120°C

- Demonstrated new PEM with higher Tg,Modulus and equivalent conductivity/permeability to cast Nafion at same EW. New PEM shows lower F^- release rates in fuel cell testing.
- Additives to 3M PEM substantially increase oxidative stability and further reduce F^- release.
- Lower EW PEM's fabricated with lower resistance under hotter, drier conditions.
- Optimum PEM processing methods identified with NSTF catalysts for rapid start-up.
- Optimum PEM processing methods identified for further reduction of F^- release rates.

- Tg of 3M membrane is 25 ^{0}C higher than same equivalent weight Nafion.
- Modulus of 3M membrane > 10X higher than Nafion at 120 °C, dry.

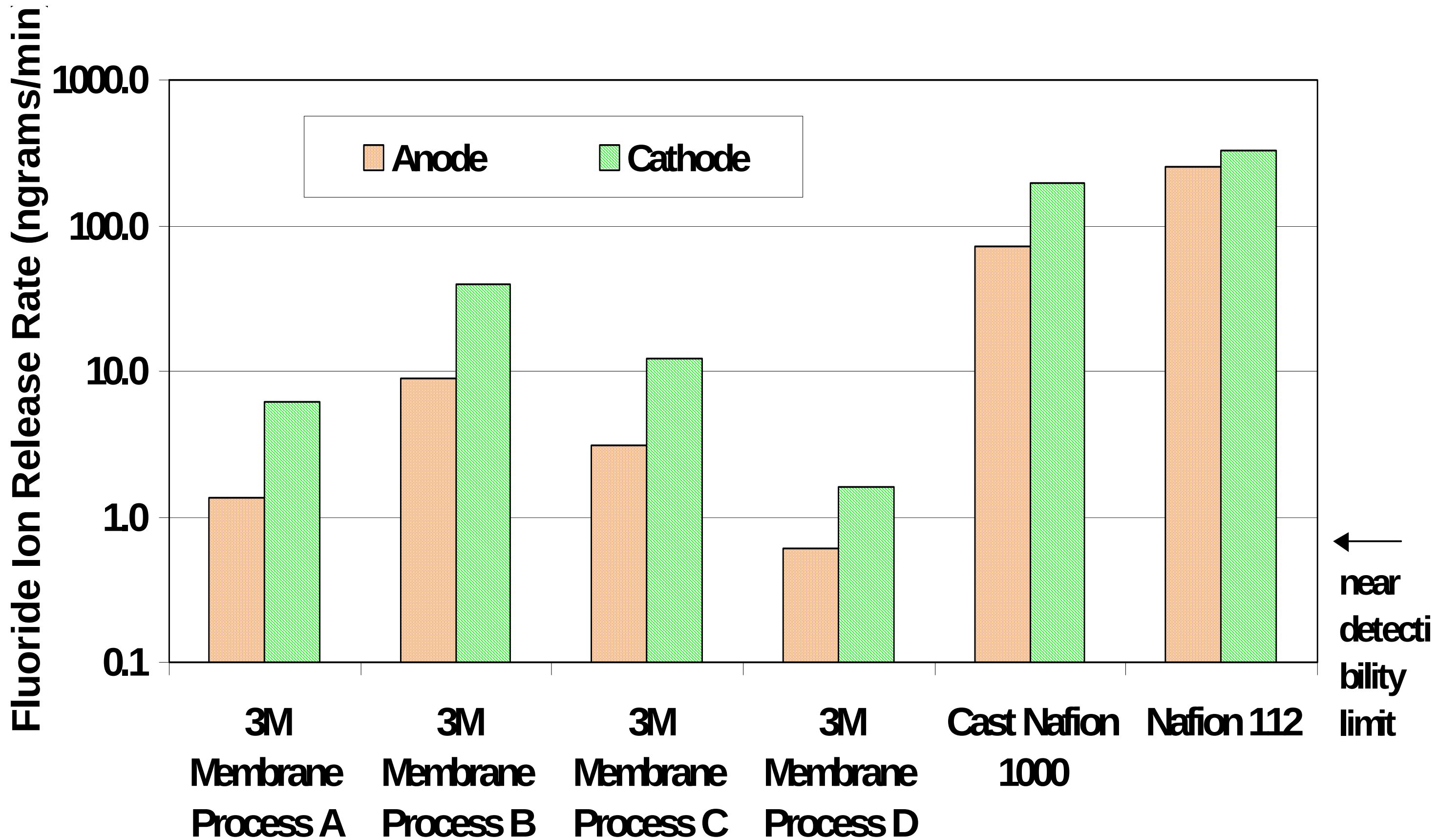


Technical Accomplishments - PEM for 85<T<120°C – F^- Release Rates

Fluoride release of various membranes.

Rates reflect F^- ion concentration in water collected in accelerated fuel cell testing at **80°C**, with 60°C dewpoint on anode and cathode.

- **Fluoride concentration in effluent water is up to >100 x lower for 3M membrane than Nafion.**
- **These 3M membranes are neat, no additives for oxidative stability.**

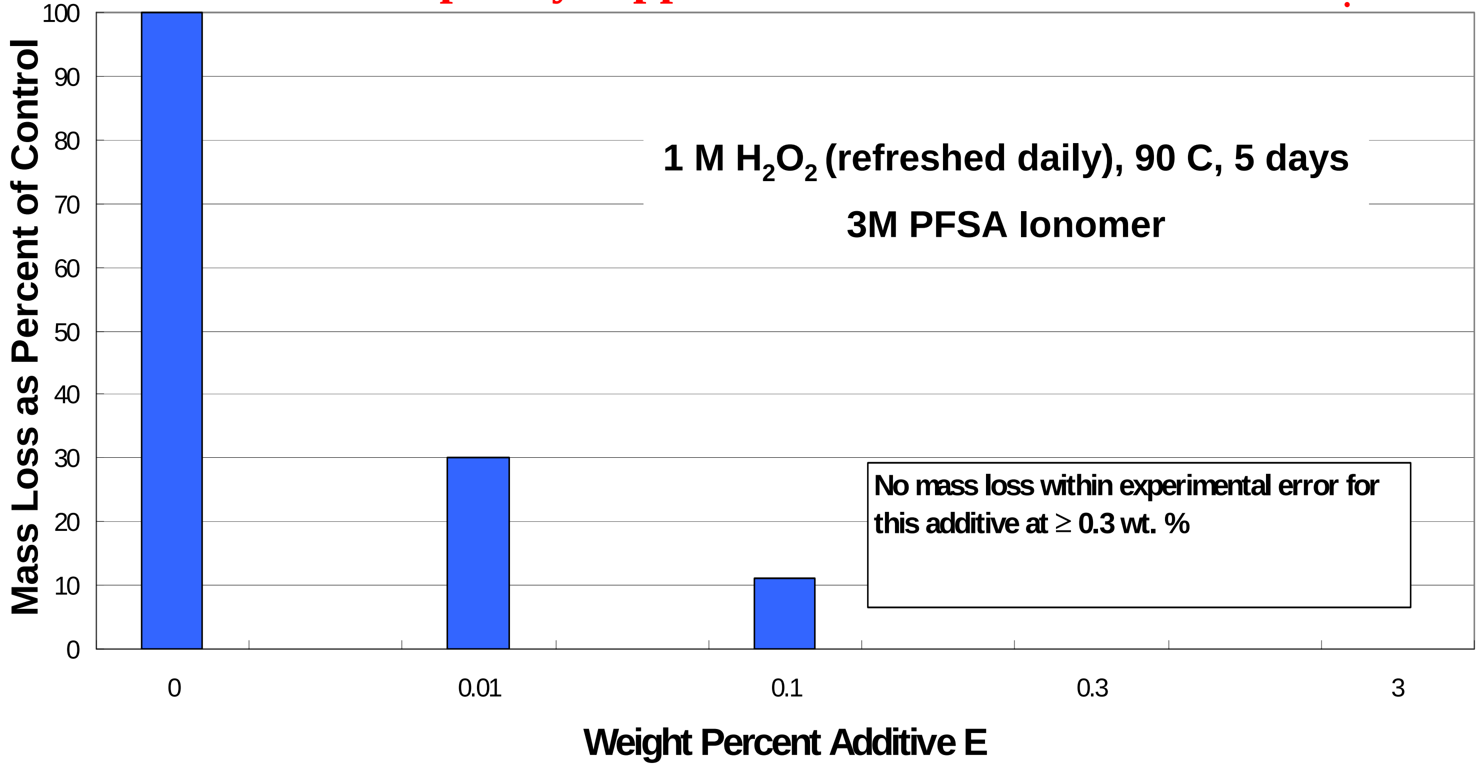


Technical Accomplishments - PEM for 85<T<120ºC – Oxidative stability

Adding Additives to the 3M membrane can give further oxidative stability:

- **~ 2 dozen additives screened by mass-loss in H_2O_2 soak**
- **5 primary candidates down-selected for MEA fuel cell F^- release tests**

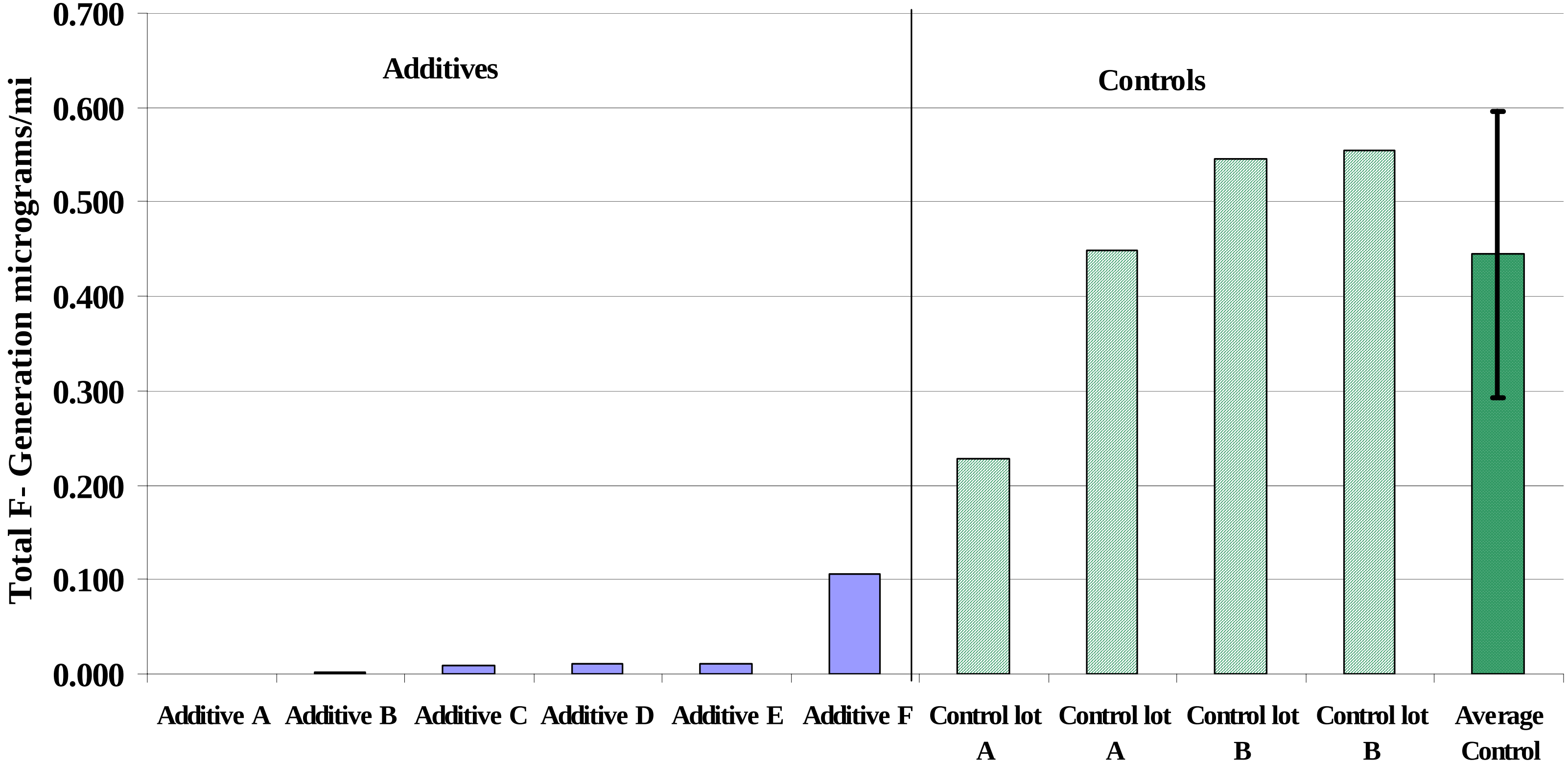
- **Additive A was effective even at 0.01 wt. %.**
- **Mass loss completely suppressed at ≥ 0.3 wt. % Additive E.**



Technical Accomplishments - PEM for 85<T<120^{o}C – Oxidative stability

Fluoride Release 90/60/60^o C, Load cycled from 0 to 0.5 A/cm^2
50 cm^2 cell, Dispersed catalyst, 0.4/0.4 Pt/Pt, 800/1800 SCCM H_2/air

- All five additives were effective in reducing F^- release rates below controls
- F^- release rates in operating fuel cell reduced by 1-2 orders of magnitude.

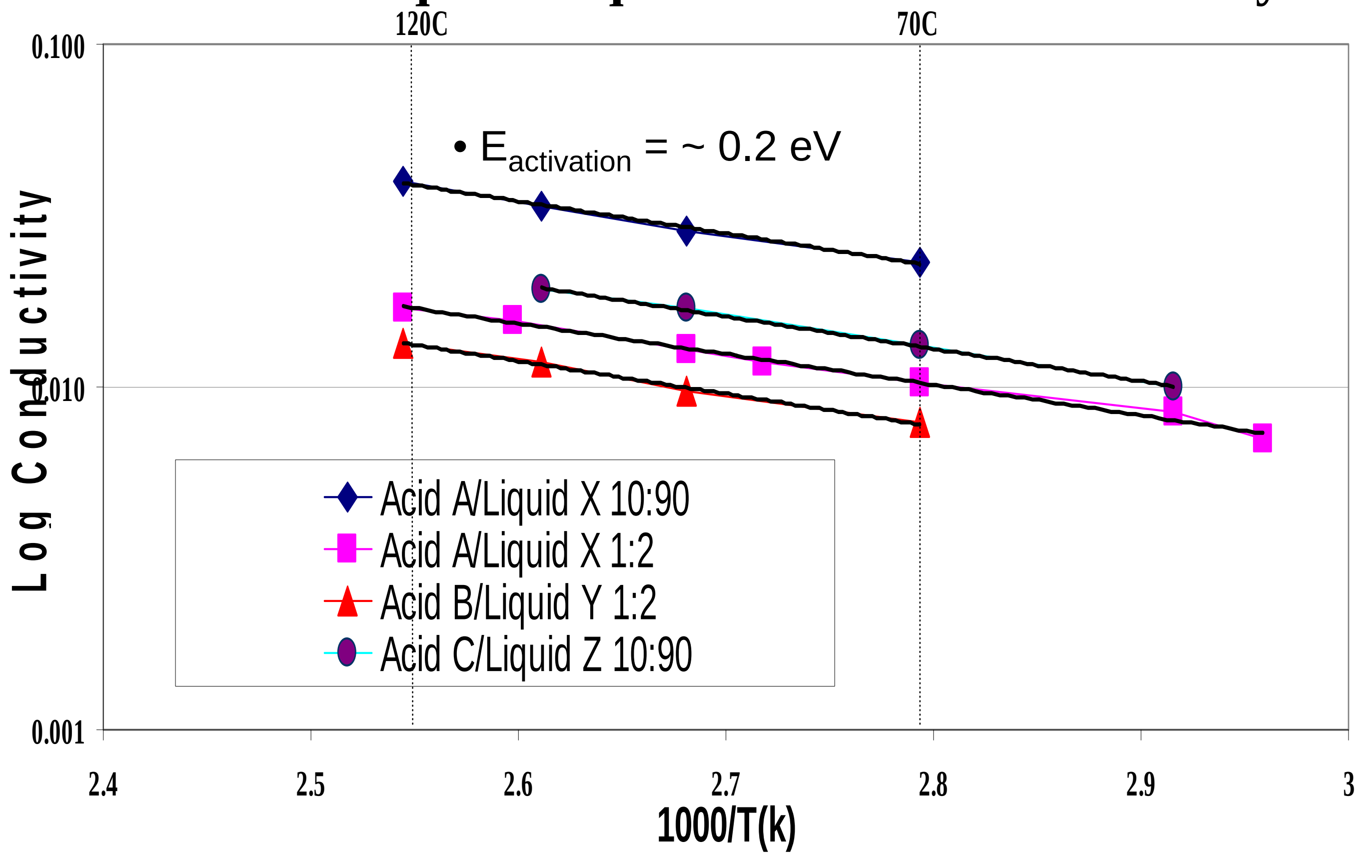


Selected Technical Accomplishments – Non-aqueous Membranes for T > 120ºC

- Three basic approaches: Conductivity enhancing additives in -
  a) polymers and b,c) two types of inorganic composites
- Fundamental characterization of proton conduction in liquid cells and MD modeling
- Basic membrane conductivity characterization as a function of temperature
- Membrane formation and electrolyte incorporation process development

- **Ab initio calculations by J. W. Halley (U. of MN) give close correspondence, about 0.3 eV for the Acid A/ Liquid X system.**
- **Concentration effects and Monte Carlo simulations also being studied.**

Acid/Liquid –Liquid Cell Proton Conductivity

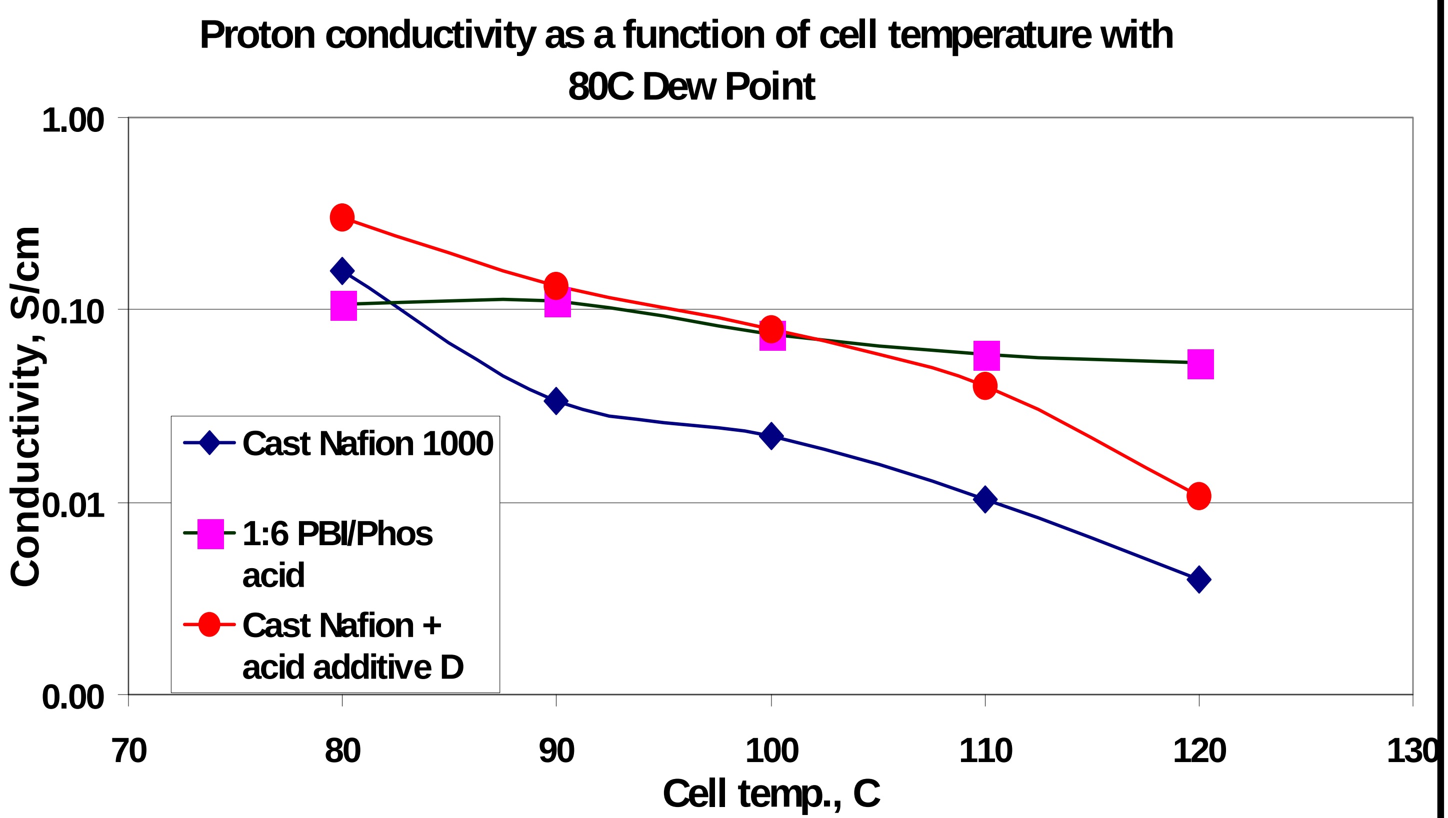


Selected Technical Accomplishments – Non-aqueous Membranes for T > 120°C

Task 2 – Liquid additive in polymer approach
Basic Membrane Conductivity Testing

- T < 100°C : Conductivity of Acid D/Nafion membrane is higher than Nafion 1000 or PBI-6PA membrane.
- T > 100°C : Conductivity is higher than Nafion but below PBI-6PA.

- Conductivity of Membrane with Acid D is highly stable at all conditions.
- Acid additive D is stable by TGA to > 250 °C

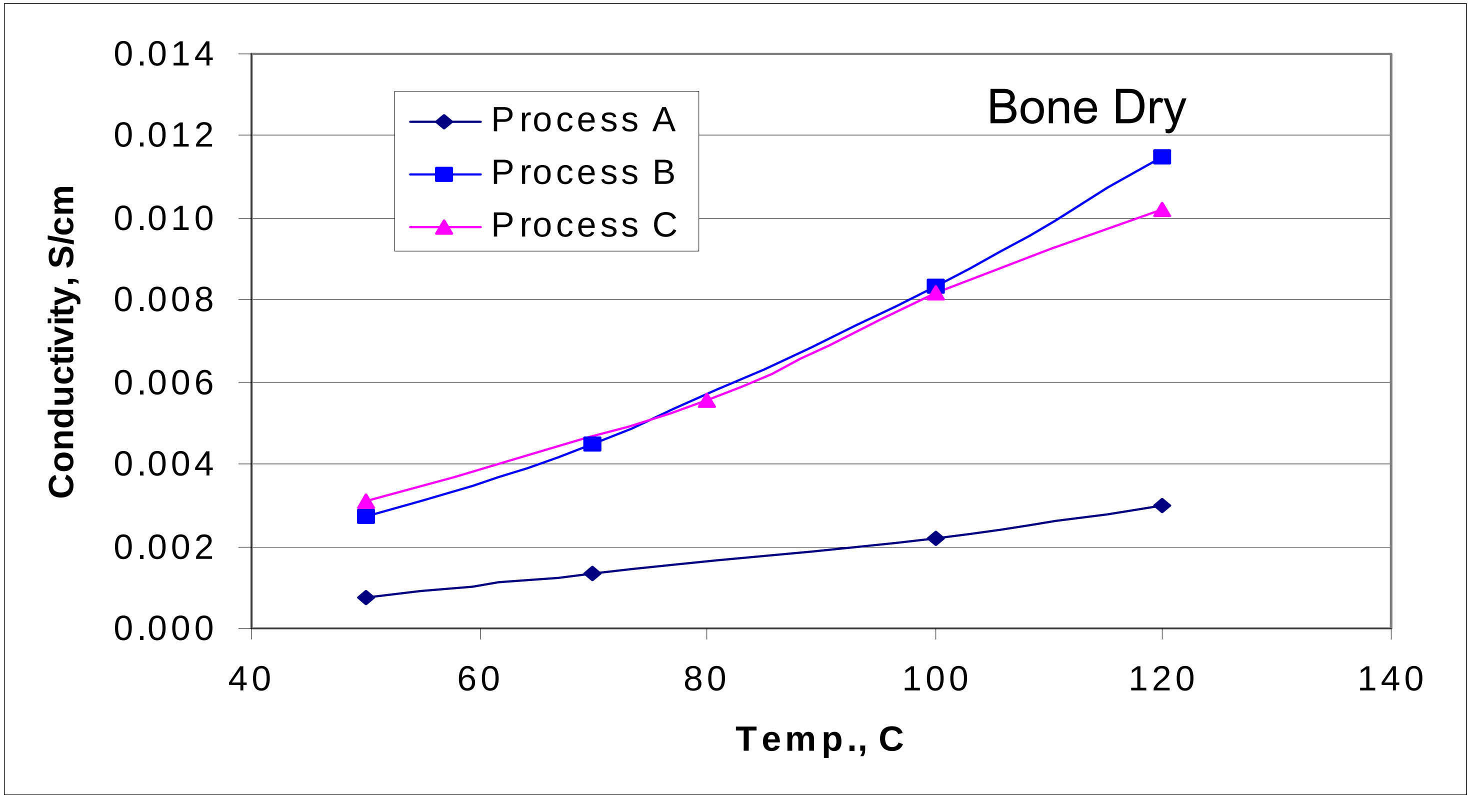


Selected Technical Accomplishments – Non-aqueous Membranes for T > 120^{o}C

Task 2 – Electrolytes in type 1 inorganic oxide composite approach
Basic Membrane Conductivity Testing – Bone Dry.

Processing conditions affect stability of composite, conductivity, and imbibing of electrolyte.

Electrolyte: Acid A/Liquid X, 90:10



Interactions and Collaborations

Advanced Catalysts: Fabrication, Fundamental Characterization, Understanding

Dalhousie University: Prof. Jeff Dahn - Combinatorial materials fabrication and characterization of Pt ternary catalysts applied to 3M NSTF support films.

Lawrence Berkeley National Lab: P. Ross, N. Markovic, et al. - RRDE measurements of specific activities and other fundamental properties of 3M NSTF catalysts.

U. of Illinois, Urbana : Prof. A. Wieckowski - High resolution STEM and RAIR characterization of 3M NSTF catalysts.

Brookhaven National Laboratory: J. McBreen - EXAFS, XANES of 3M NSTF catalysts.

Advanced Membranes: Fundamentals

U. of Minnesota: Prof. Woods Halley - Theory and simulation studies for non-aqueous membrane based proton conduction.

CWRU: Prof. T. Zawodzinski - Fundamental experimental studies of proton transport in liquid and solid proton conductors, and fundamental studies of catalyst/electrolyte ORR.

MEA Modeling: 3D Mixed Phase Modeling of Operating MEA

U. of Miami: Prof. H. Liu - Extend existing 3M/U. of Miami developed MEA model to determine optimum component properties for dry operation, adapt to treat ultra-thin electrode layers.

Air Management: Modeling and Hardware Development

***Vairex* Corp.:** Understanding and development of an air management system designed for optimized performance of 3M MEA's operating under hot, dry conditions

Response to Previous Year Reviewers' Comments

Q1, Q2, & Q5: Positive comments. No questions or criticisms offered.

Q3: Question about the reality of the lower F^- generation rate for 3M's PFSA membrane.

Response: We have generated and shown subsets of extensive data bases documenting the reduced F^- generation rate of the 3M PFSA membrane.

Q4: "3M appears to be very possessive relative to industrial collaboratives. 3M needs to open up its innovations (re:polymers and catalysts) to neutral 3rd parties."

Specific recommendations…: "3M's innovations should be independently verified because, if proven out, their developments could have major impact."

Weaknesses: "Needs to open up on the technical innovation to third party industrial firms."

Response: We have benefited this year significantly from the independent validation by LBNL of our NSTF catalysts' enhanced specific activity. We are working with selected customers outside the contract to incorporate NSTF catalyst based MEA's into their future products.

Future Work

- Remainder of FY 2004

  85 ^oC < T<120 ^oC MEA :

  - Advanced NSTF catalysts:

    Complete PtAB down-selection process for highest specific activity and high temperature stability, optimize NSTF whisker support for increased m^2/g, optimize EB/GDL for reduced resistance, high permeability, low RH operation.
  - PEM's: Down-selection process completed for membrane EW and additives.
  - MEA integration: Optimize NSTF/PEM/GDL interface
  - Pilot level scale-up: Fabricate pilot-scale quantities of roll-good fabricated MEA.

  T>120 ^oC MEA :

  - Proton conduction: Continued fundamental studies of mechanisms in additives.
  - Membrane matrix formation: Focus on identified critical issues for existing approaches.
  - Membrane electrolyte: Synthesis and membrane matrix imbibing or filling.
  - MEA evaluation: Accelerate fuel cell testing and in-situ characterization.
  - PEM/Catalyst: Initiate studies of electrolyte/catalyst interface effects on ORR.

- FY 2005
  - Complete short stack testing of T <120 ^oC MEA, using large area MEA's.
  - Scale-up and optimization of component processes for T <120 ^oC roll-good MEA.
  - Down-select MEA components for T > 120 ^oC MEA's.
  - Complete full high temperature characterization of down-selected, T > 120 ^oC MEA in medium sized area MEA's.