2006 DOE Hydrogen Program Review

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

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3M Company

May 17, 2006

Project ID # FC19

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start 1/1/02
- Project end 6/30/06
- 97.5% complete

Barriers

A. Durability
B. Stack Material & Mfg Cost
C. Electrode Performance

Budget

- Total Project funding
  - $6.99 million DOE
  - $2.03 million Contractor share
- Received in FY05: $1.86 million
- Funding for FY06: $ 0.33 million

MEA Technical Targets *(2010)*

- Durability w/cycling: > 5000 hrs,
- Cost: $15/kW,
- PGM Total: 0.5 g/ kW rated

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 < ~ 120ºC under sub-saturated inlet conditions with start-stop cycling, and pilot-scale production levels.

b) **Task 2:** Finish characterization of new proton conducting electrolytes and incorporation into membranes for operation at T > 120ºC, based on non-aqueous proton conduction mechanisms.

Plan and Approach

Tasks 1 and 3: 80 < T < 120ºC MEA by roll-good processes

a) Develop advanced 3M - NanoStructured Thin Film Catalysts (NSTFC) 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.

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

c) Match the 3M PEM and 3M NSTF catalyst for optimum performance, durability, and start-up.

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

e) Stack testing advanced MEAs from d).

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

Complete characterization of membranes comprising polymers blended with stable non-volatile 3M superacids, and new heteropolyacid additives for proton transport under hotter, drier conditions.

Current Year Technical Accomplishments - Summary

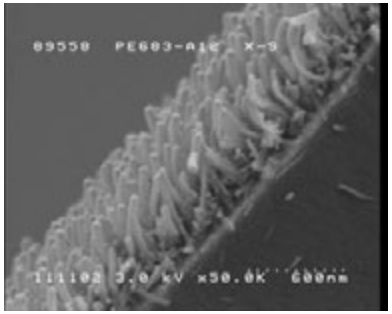
- Down-selected NSTF ternary PtC_xD_y catalyst for best performance and durability and demonstrated mass activity of 0.25 A/mg-Pt (at 900mV) when loading and NSTF whisker-support particle surface areas were better matched.
- NSTF catalysts shown to have significantly enhanced stability against surface area loss from Pt dissolution when compared to conventional Pt/C dispersed catalysts under both accelerated CV cycling from 0.6 to 1.2 volts, and real time, air/air start-stop durability cycles.
- NSTF catalyst support-whiskers shown to have total resistance to corrosion when held at potentials up to 1.5 volts for 3 hours.
- 3M PEM demonstrated over 5,000 hour lifetime under automotive operating conditions with load cycling at 80 ^oC, and 64 ^oC dew points.
- 3M PEM (730EW) demonstrated > 100 mS/cm conductivity at 120 ^oC, 80 ^oC DP, 250kPa.
- 3M PEM(840EW) and NSTF catalyst have been integrated for best performance, durability and fastest start-up, using all roll-good fabricated pilot scale processing.
- MEA having NSTF catalyst and 3M PEM operated for > 800 hours with cycling from 0.1 to 2 A/cm^2, and mean current density of $1A/cm^2$, under totally dry H_2/O_2, at 15 psig and 65-70^oC, with minimal permanent loss of performance. Still going.

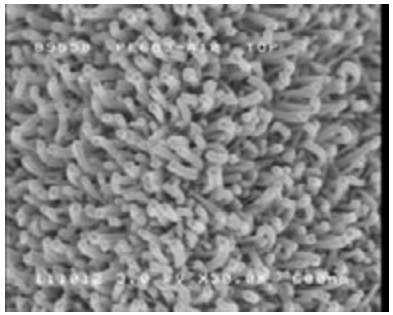
Technical Accomplishments - NSTF Mass Activities

Mass and specific activities of NSTF catalysts depend on the surface area of the supporting whisker. Whisker lengths and areal number density were controlled in first study of effect on activities.

Four Types of NSTF Whisker Supports Were Studied

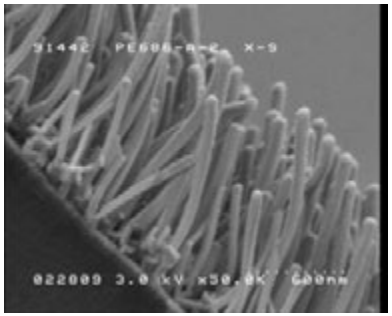
PE683A NSTF whisker supports

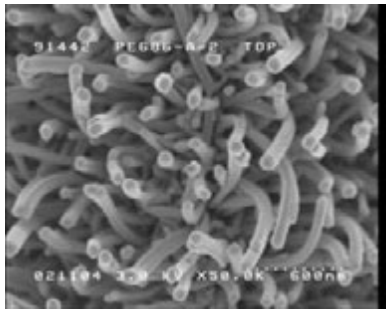


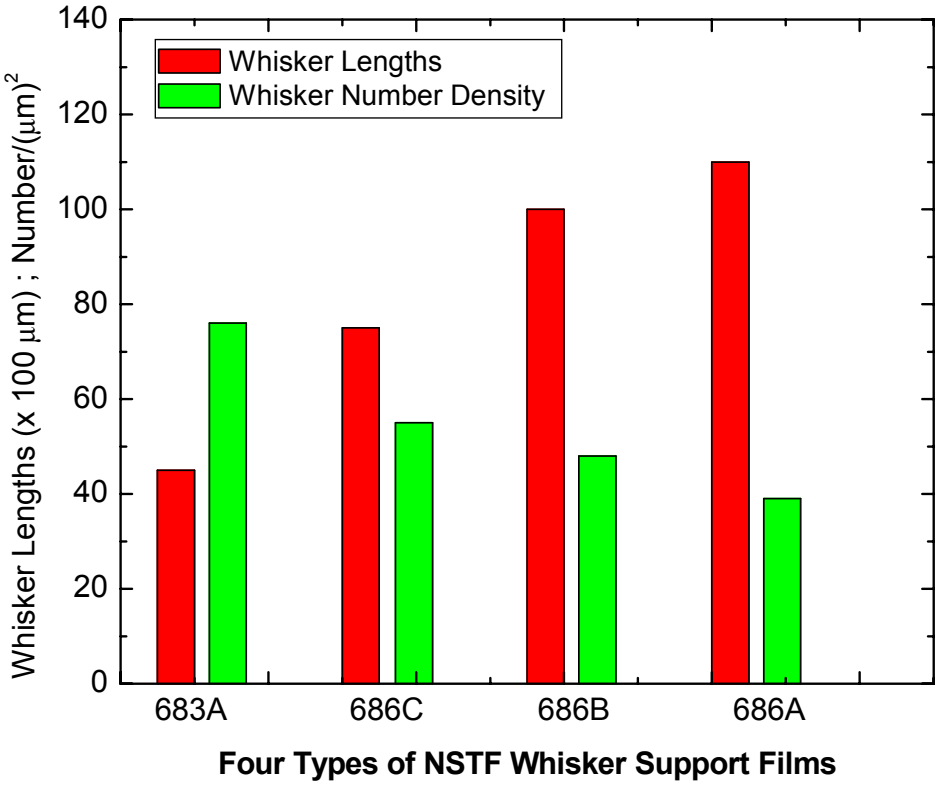


Examples of Two Types

PE686A NSTF whisker supports







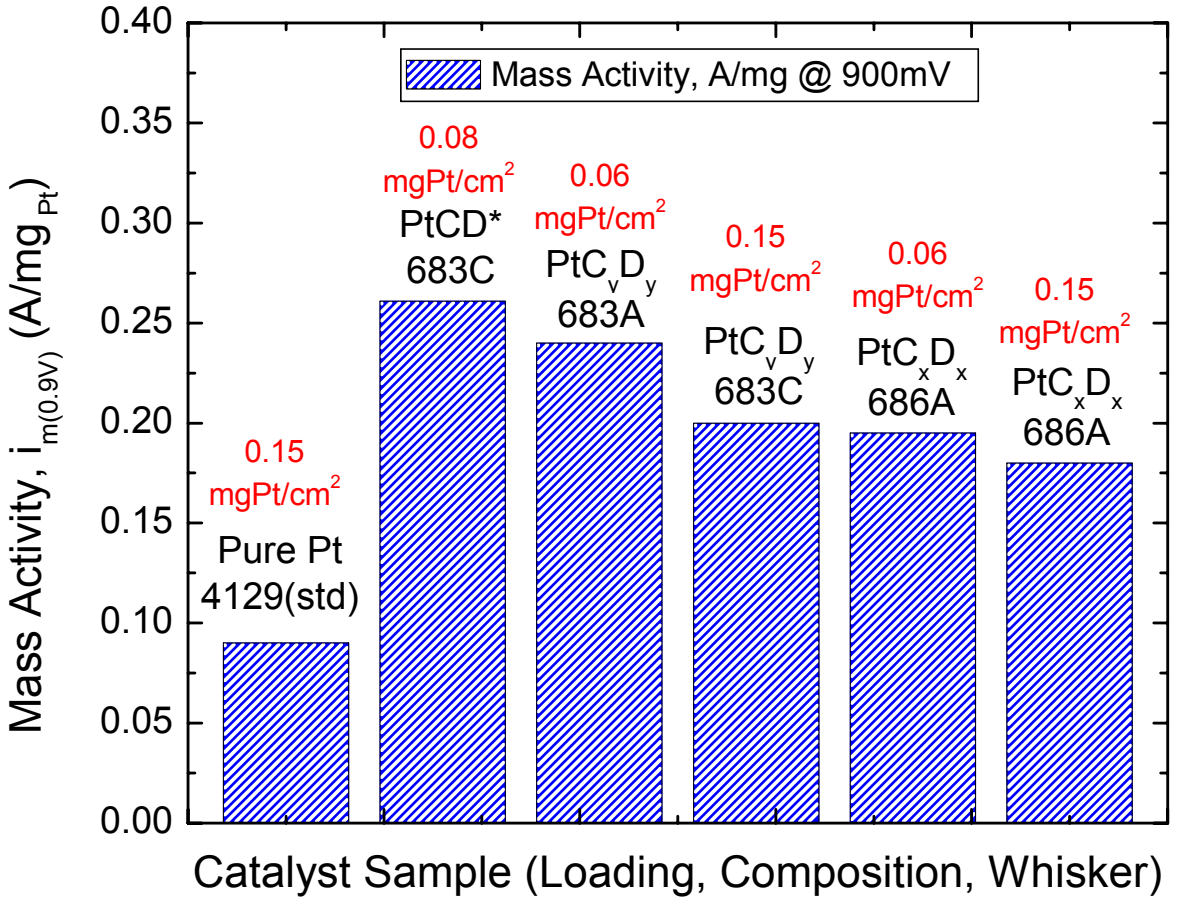
Four Types of NSTF Whisker Support Films

Technical Accomplishments - NSTF Mass Activities

NSTF mass activities at 900mV, 150kPa H_2/O_2, are ~ 2.5 x standard Pt/C.

Better matching catalyst loading to the surface area of the NSTF whisker support film increases mass activity:

- Mass activities of NSTF ternaries are ~ 2.5 x plain NSTF Pt.
- Mass activities > 0.25 A/mg-Pt obtained with 0.08mg/cm² PtC_xD_y ternary.
- Mass activities ~ same obtained with state-of-art Pt_xCo_{1-x} /C (TKK)
- Whisker support structure, and ternary composition also are factors



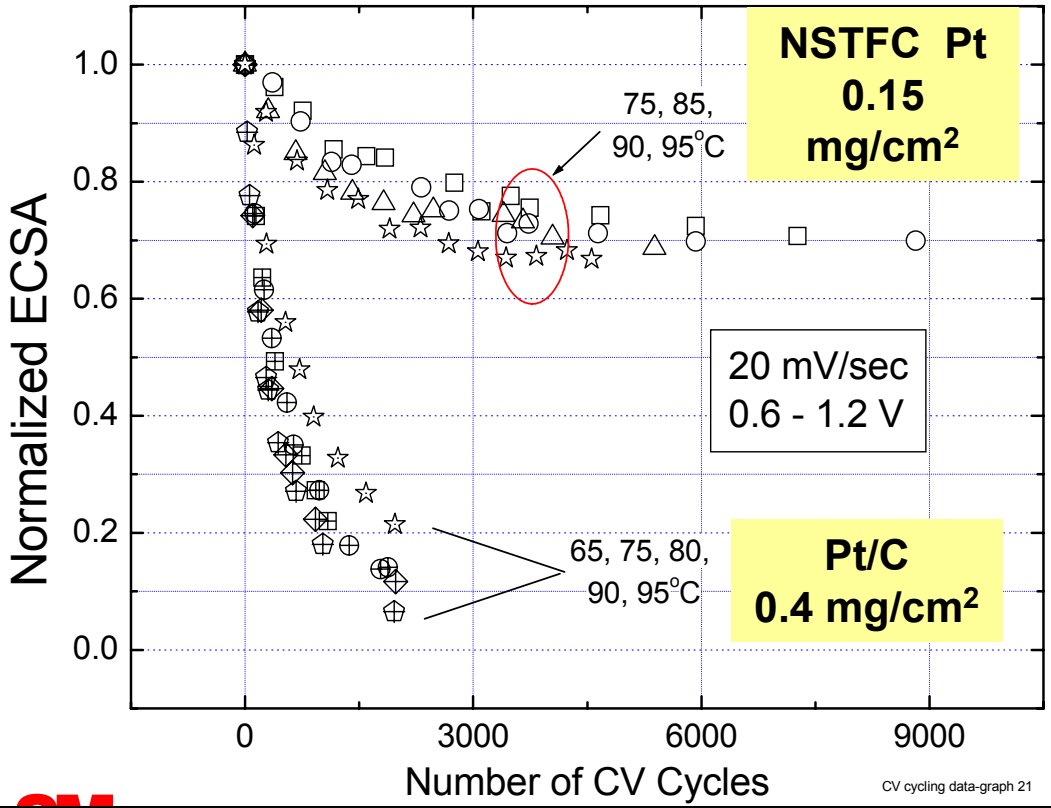
Whisker lengths, densities, mass activities-graph 2

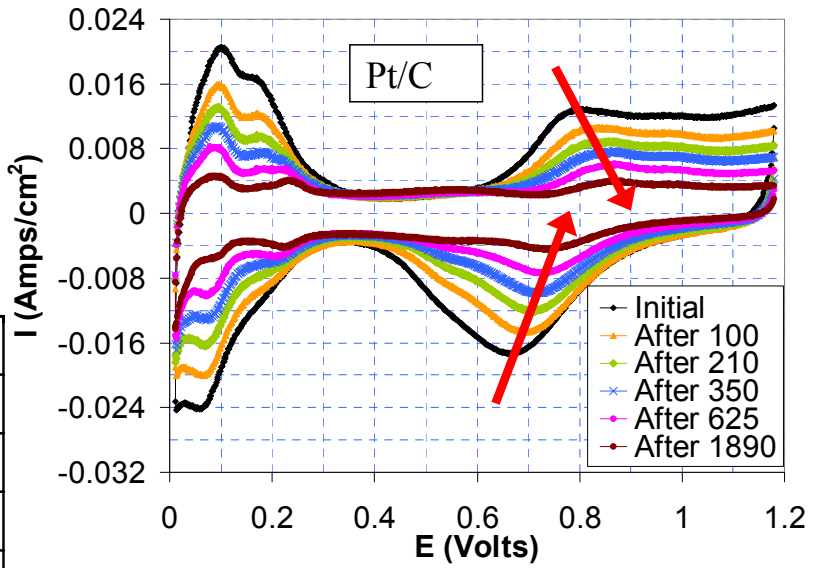
Technical Accomplishments - NSTFC Durability – CV cycling

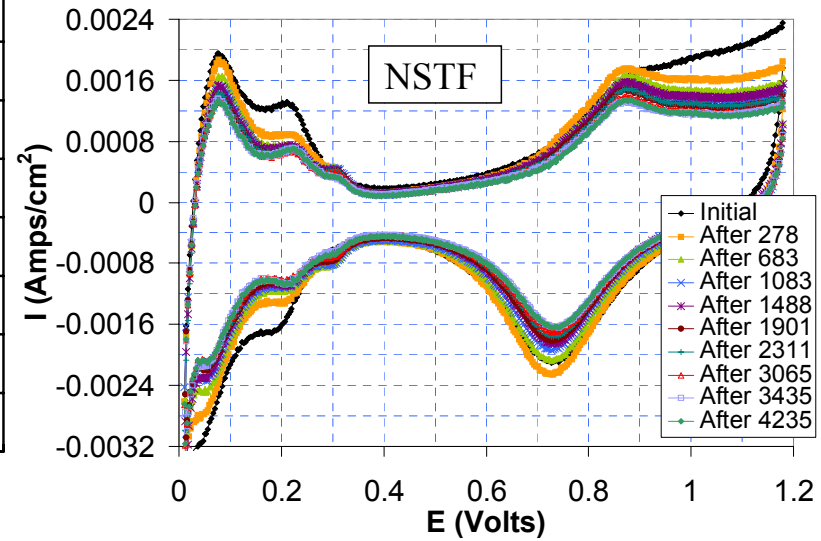
CV's Conditions:
20 mv/sec, T = 80°C ,
Anode/Cathode: H_2/N_2 ,
RH:100/100%

CV changes from Pt/C during 1890 cycles, and (bottom) NSTF MEA through 4235 cycles.

Normalized Surface Area versus Number of Cycles at Various Temperatures under Voltage Cycling.

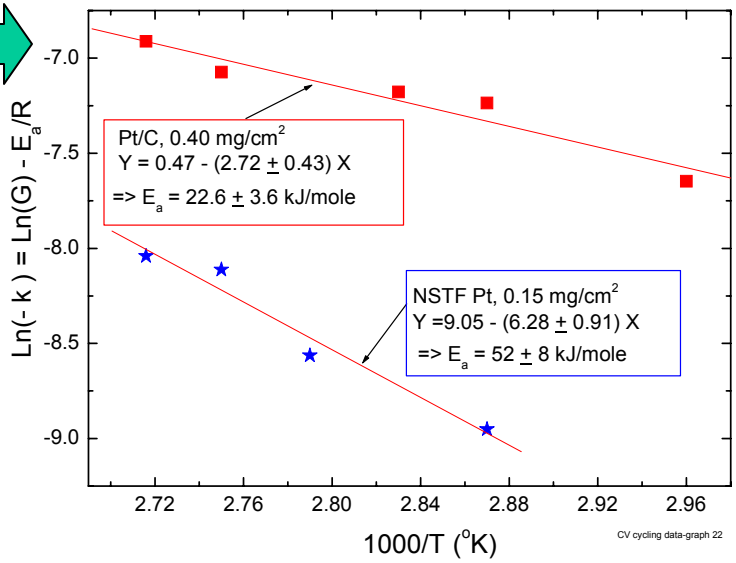




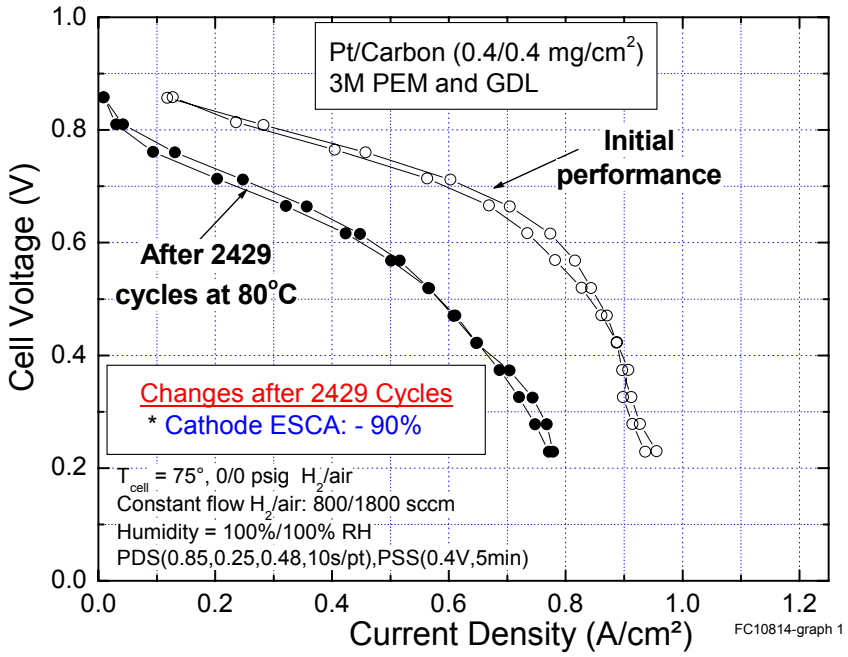


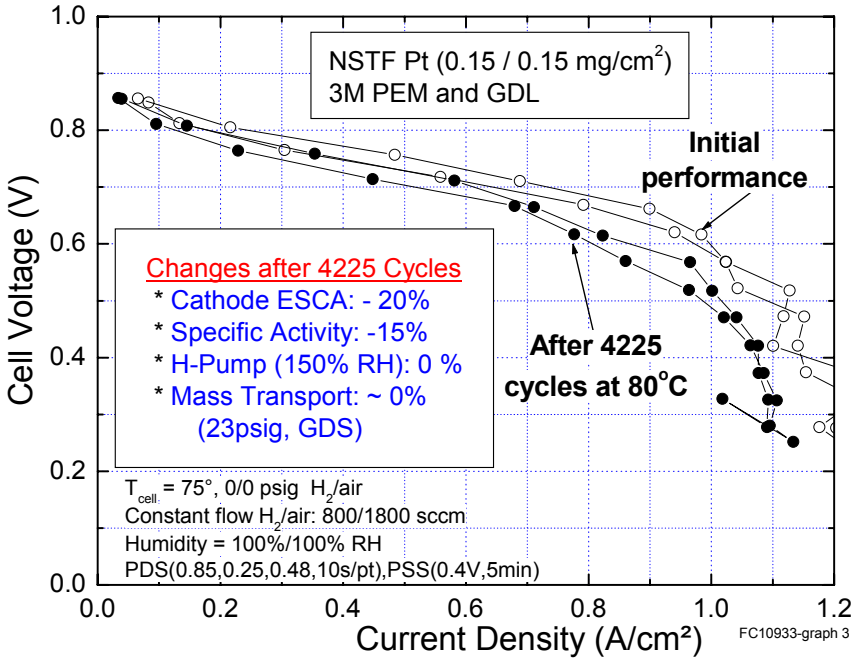
Technical Accomplishments - NSTF Durability – CV cycling

First Order Kinetic Rate Model of Surface Area Loss:
NSTF = 52 kJ/mole vs. Pt/C = 23 kJ/mole



- Pt/C polarization curves show significant performance degradation after 2429 cycles at 80°C. ECSA drops 90% from 297 to 33 cm²/cm².
- NSTF polarization curves show much less performance loss after 4225 cycles at 80°C. ECSA drops 20% from 13.2 to 10.4 cm²/cm².





Summary of CV Cycling Comparisons

- NSTF-Pt catalysts (0.15 mgPt/cm^2) are much more resistant to loss of surface area from high voltage cycling than are Pt/Carbon (Ketjen Black) with 0.4 mg Pt/cm^2 loading.
- The NSTF-Pt asymptotically approaches a maximum of ~ 33% surface area loss in 9000 cycles, while the Pt/C loses ~ 90% of the initial surface area in 2000 cycles
- The activation energy for surface area loss is twice as high for NSTF (52 vs 23kJ/mole) reflecting a slower rate of surface area loss for NSTF.
- The surface area loss appears to be primarily by agglomeration. Surface Area loss of Pt/C = 90%/2500 cycles, versus NSTF = 20%/4225 cycles
- Both anode and cathode Pt/C crystallite sizes increase 380% and 300%, but the NSTF crystallite sizes increase only ~ 10% and 68% respectively.
- The increased Pt/C particle size does not increase catalyst specific activity or catalyst utilization to equal that of the NSTF.

Technical Accomplishments – NSTFC Stop/Start Durability

Real-time Cycling Test to Simulate Automotive Stop-Start

- **NSTF significantly more stable than Pt/C – consistent with Accelerated CV cycling**
- **NSTF Performance loss after 300 cycles is reversible, not permanent like for Pt/C**
- **XRD and CV ECSA imply NSTF catalyst crystallite sizes are increased by SS-cycling.**

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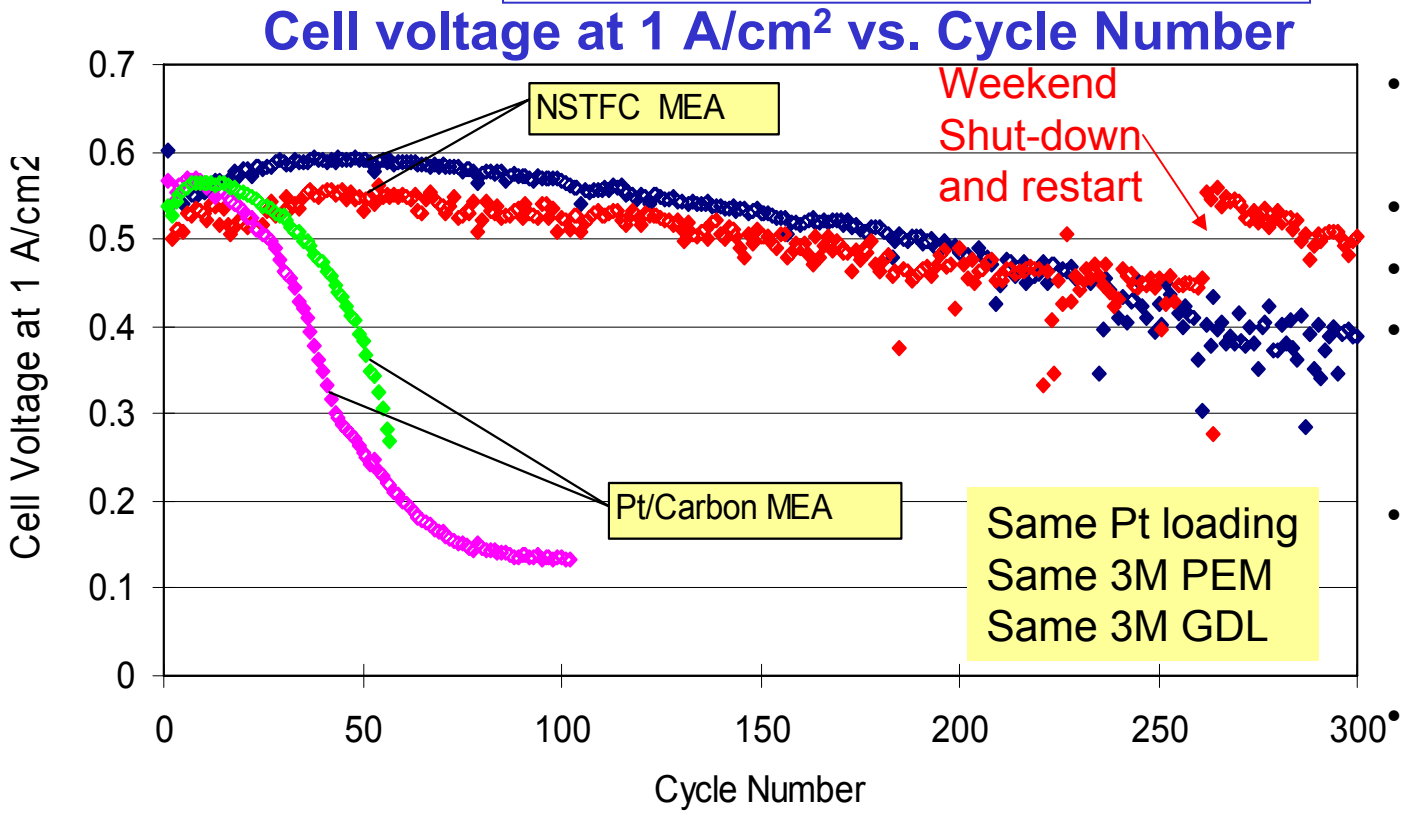
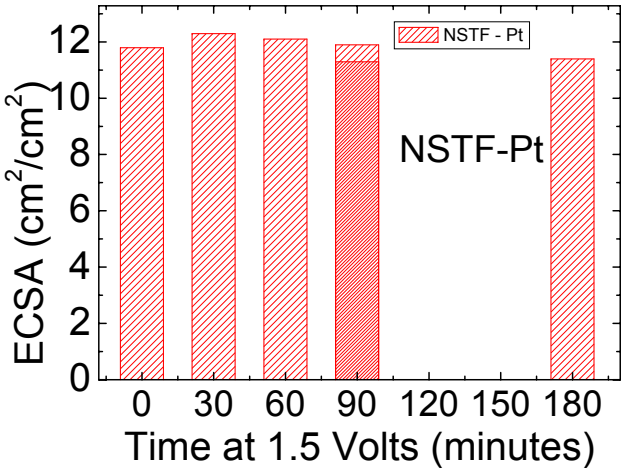


- Proprietary protocol – H_2/air cycled to anode
- ~ 20 min./ cycle
- T = 80 °C
- Stopping and cooling cell recovers all NSTFC 1 A/cm² performance.
- ~ -20% loss of ECSA correlates with change seen with CV cycling
- Pt/Carbon performance not recoverable.

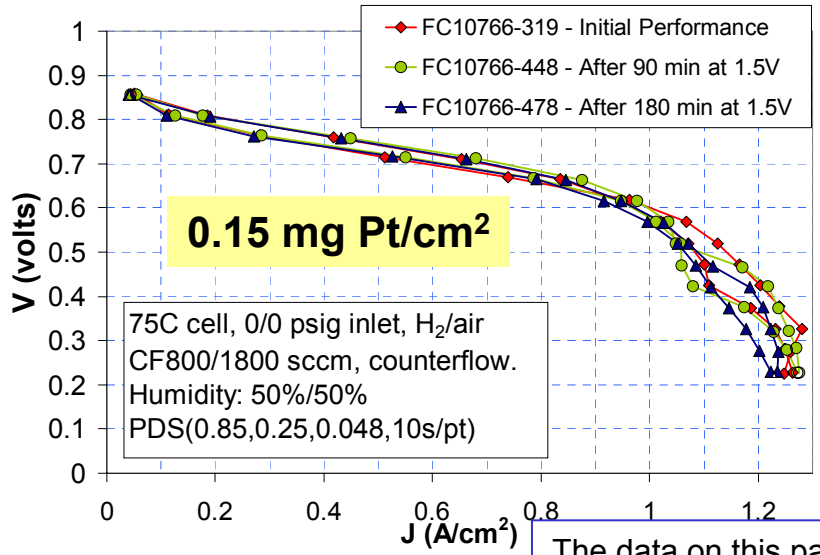
Technical Accomplishments – NSTF Support Durability

Applied Voltage = 1.5 V; 500 sccm H_2 / N_2 on An/Cat; Cell T = 80°C ; %RH: 100%

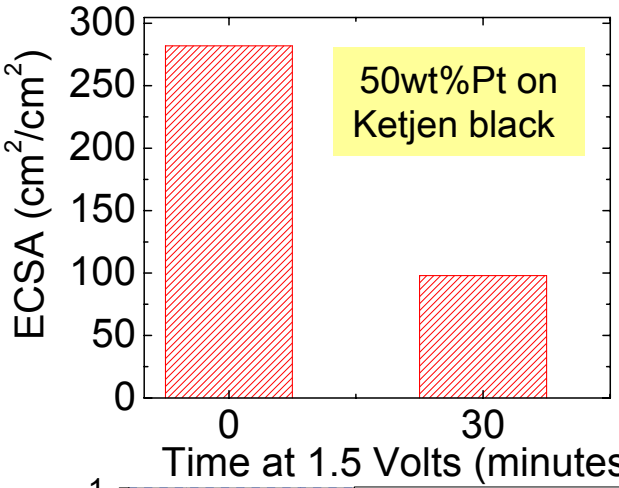
NSTF ECSA and Performance Show No Decay After 3 Hours at 1.5 V.



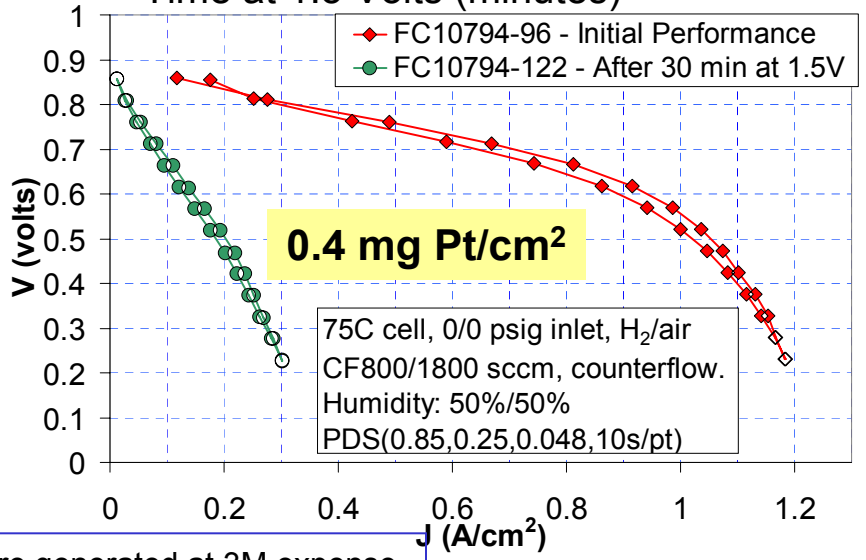
No Carbon to Corrode



Pt/C ECSA and Performance Decay Significantly after just 30 minutes at 1.5 V.



Carbon Corrosion



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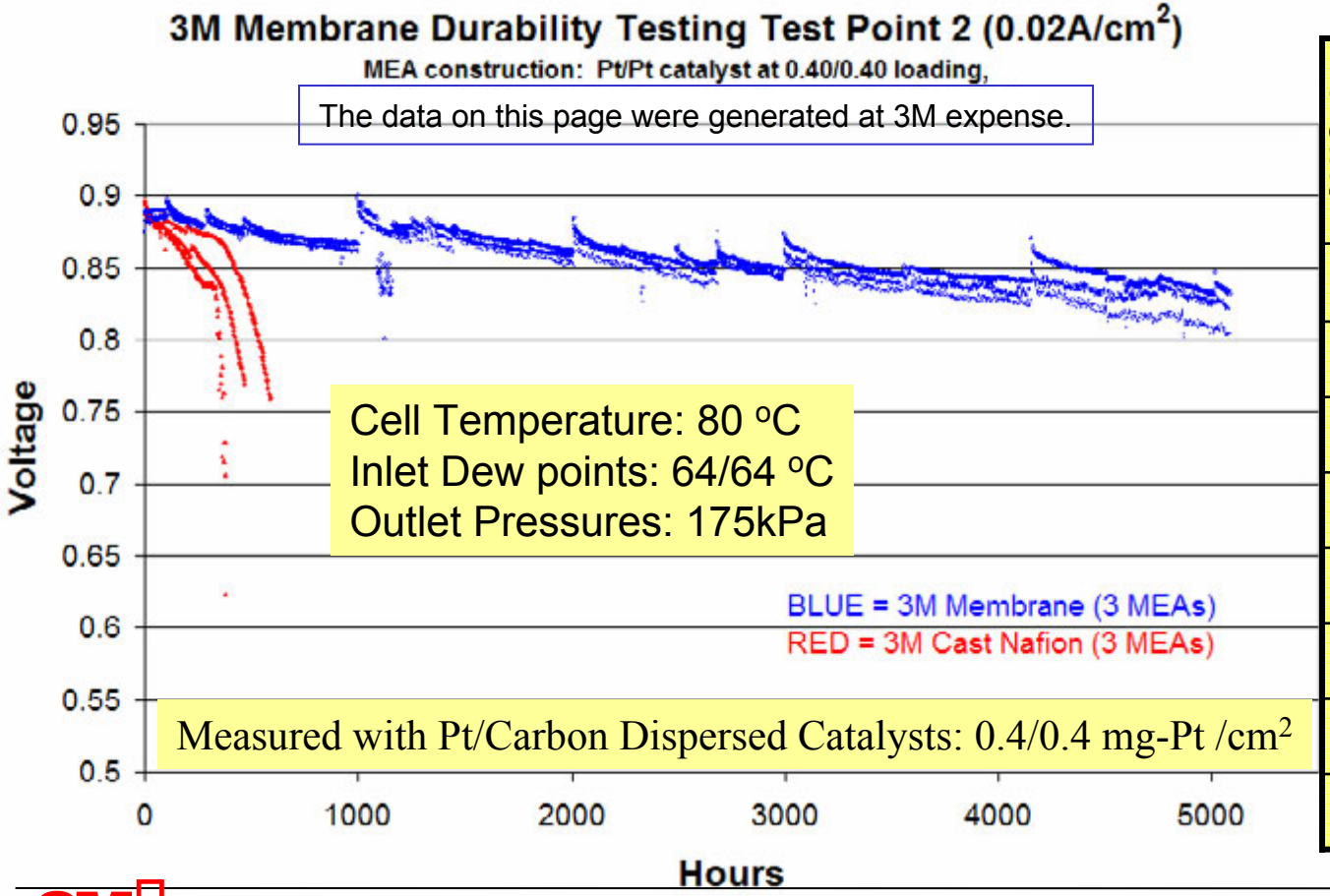
Technical Accomplishments – PEM Durability

Under load-cycling tests, the 3M PEM has demonstrated > 5000 hours lifetime, where failure is defined when V(0.02 A/cm^2) becomes < 800 mV.

Utilizing a multi-cell test station, several MEAs are run in separate cells in continuous fashion under the following conditions:

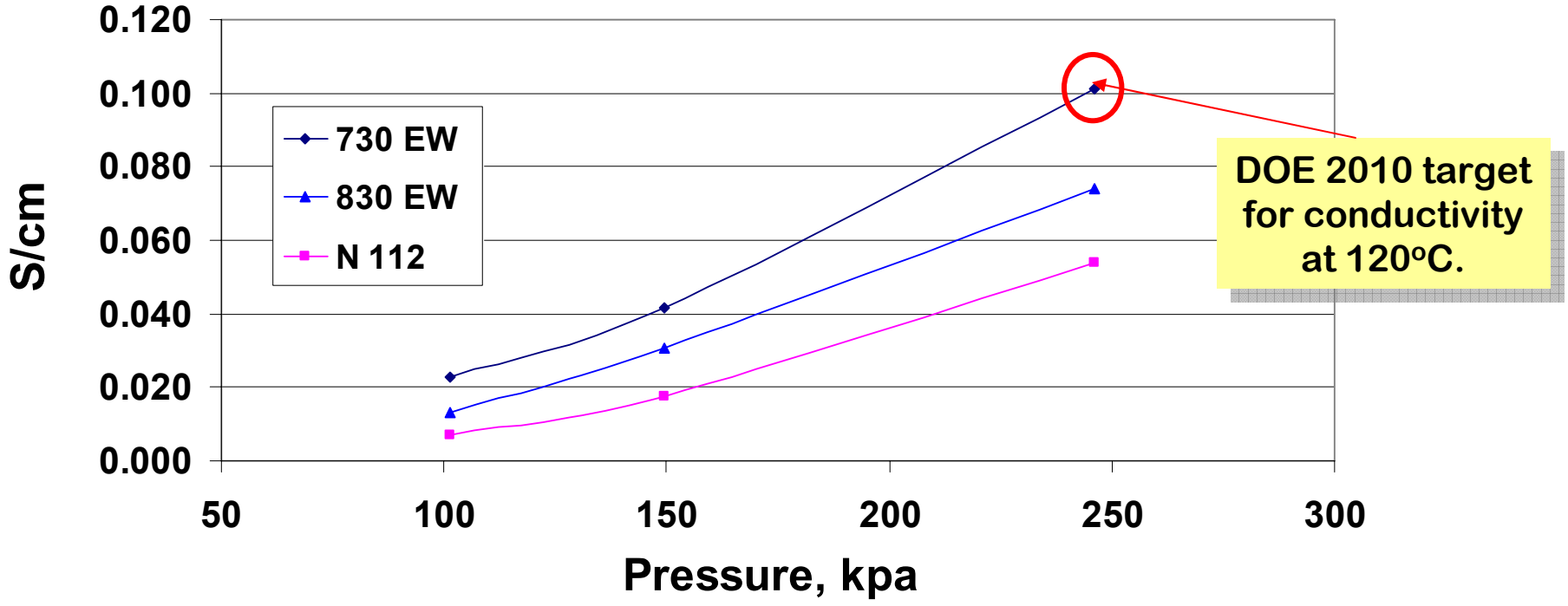


Test Point	J (A/cm^2)	Duration (min)	Stoich.
1	0.20	5	5
2	**0.02**	**20**	**15**
3	0.80	15	1.7
4	0.80	10	3
5	0.02	20	15
6	0.80	15	1.7
7	0.20	20	5
8	1.00	20	1.7

Technical Accomplishments – PEM Conductivity

3M PEM with 730 EW meets the DOE 2010 target for membrane conductivity at 120°C.

Proton Conductivity as a function of pressure at 120°C, (water content = 80˚C DP at 250 kPa)



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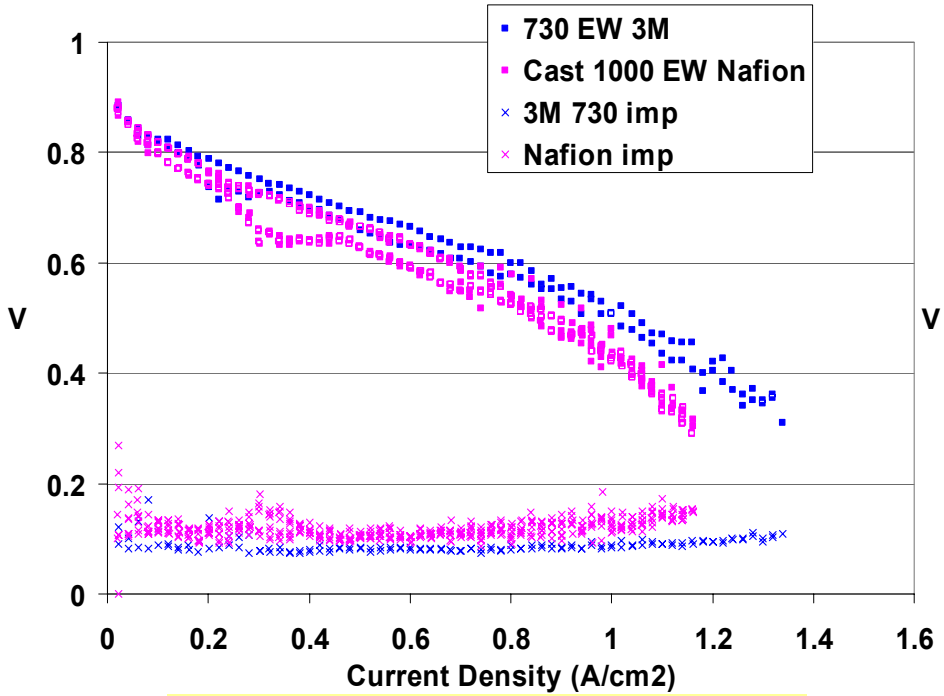
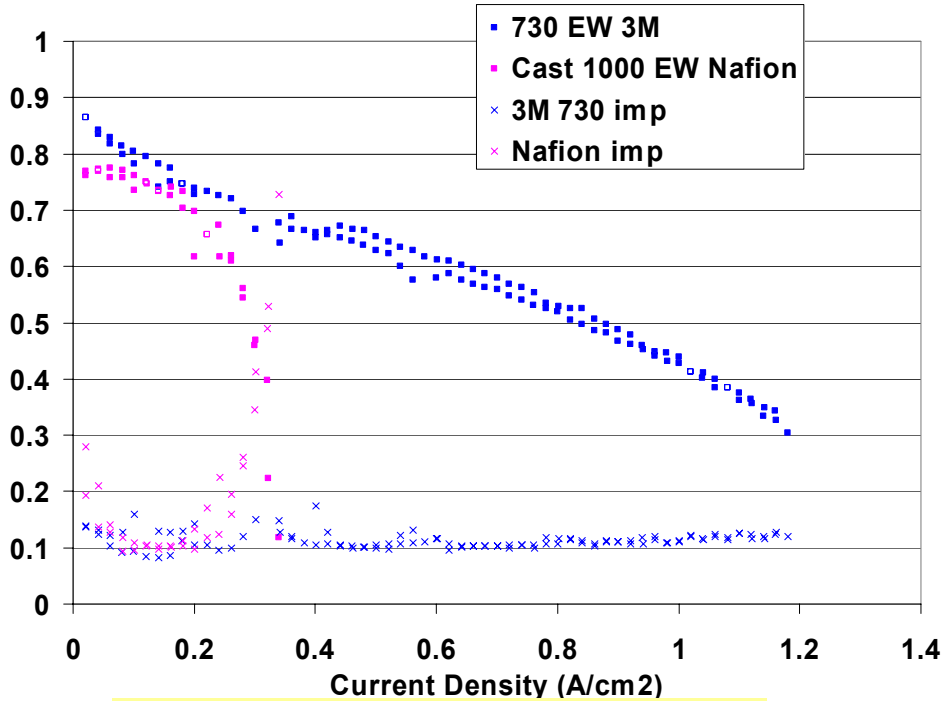
Technical Accomplishments – Membrane Performance - Hot and Drier

Fuel cell performance is much higher for lower EW membranes under hot, dry conditions.



730 EW ionomer, 120˚ C, 250 kPa, **20 % RH**



730 EW ionomer, 120˚ C, 250 kPa, **10 % RH**

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Technical Accomplishments – Real Time Durability Test

NSTF/3M PEM MEA durability test under dry H_2/O_2 with periodic cycling: Loss of –11μV/hr at 1 A/cm² over 815 hours through 4/20/06 (still running).

- NSTF PtCxDy ternary and 3M PEM based MEA.
- Totally dry H_2/O_2, 200 kPa, 65-70 °C.
- 1 hour repetitive GSS (0.7 or 0.9 A/cm²) and GDS scans (0.1-2 A/cm²): Mean J =0.99 A/cm²
- Stop, cool for 1.5 hours, and restart every 100 - 125 hours fully recovers performance
- Over 1400 cycles between ~ 0.87V and ~ 0.5 V in 820 hours.

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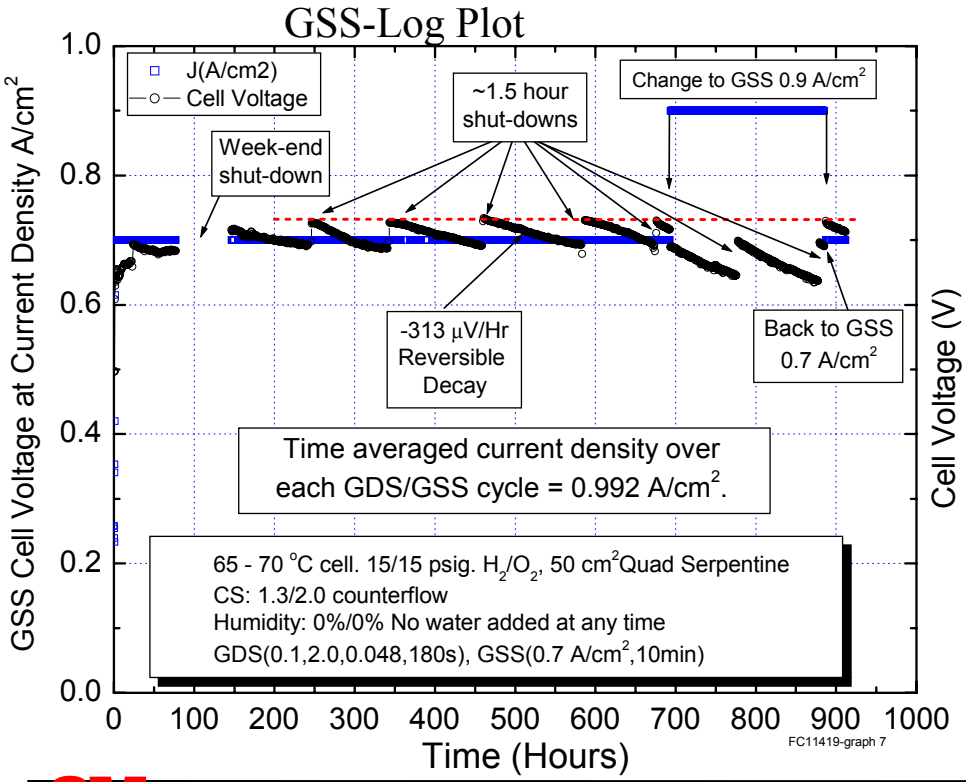
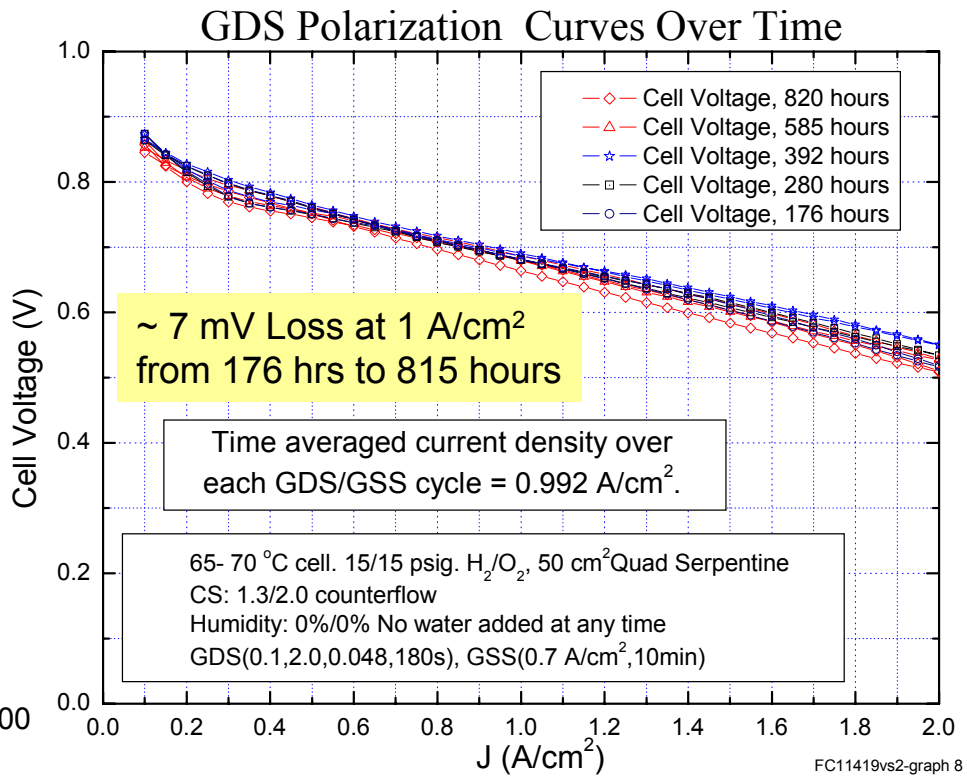


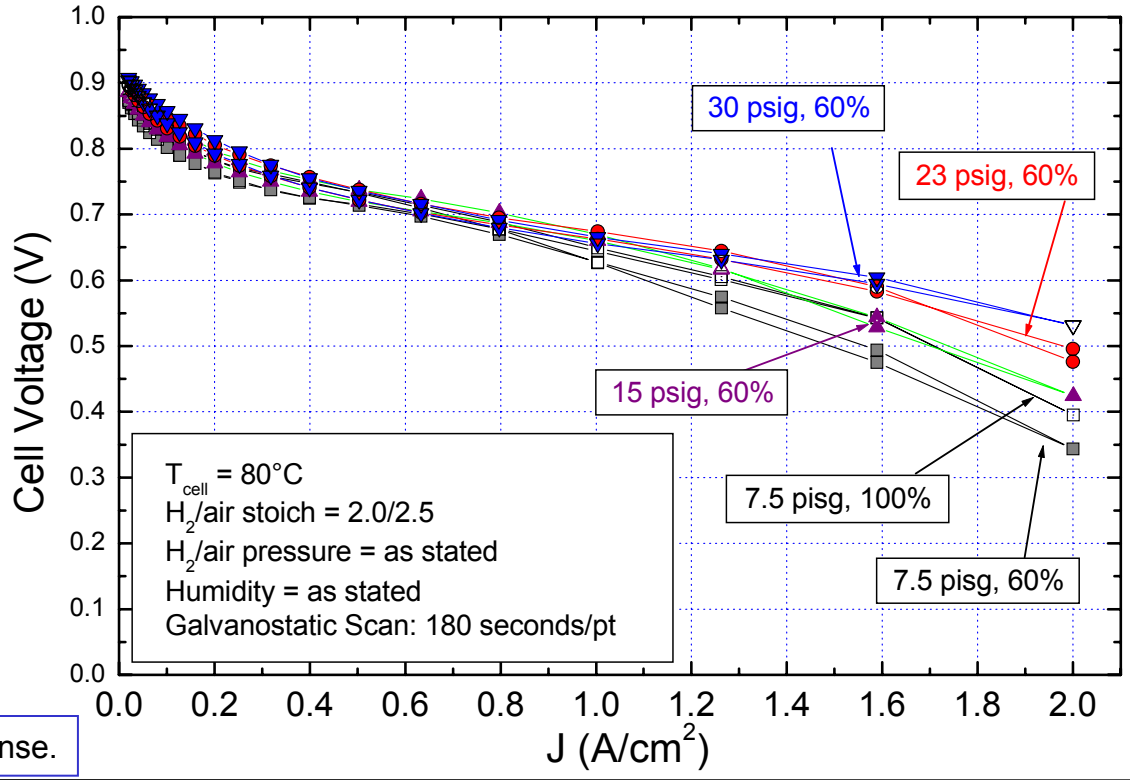


Technical Accomplishments - NSTF CCM Scale-up

Conclusions:

- All process steps in NSTF CCM roll-good fabrication have broad parameter windows
- Pilot line fabricated roll-good CCM performance matches hand-formed MEA's.
- MEA components are all manufacturable by high volume methods.

- Roll-good MEA, tested as fabricated, made with NSTF PtCD catalyst at 0.2mg/cm^2 on cathode and 3M 980EW PEM, can hit 1.5 A/cm^2 at 600mV under 250kPa H_2/air.



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Project Summary and Future Work

Relevance: Has demonstrated the feasibility for achieving the 2010 durability, performance and cost targets specified by DOE with MEA's designed for high volume manufacturability.

Technical Accomplishments and Progress: Project has met its objectives by demonstrating that a) non-carbon supported, thin film catalysts can simultaneously achieve high mass activities and high durability under stop-start and high potential conditions, b) PEM lifetimes under load-cycling can exceed 5000 hrs, and PEM conductivities can remain high under hot, dry operating conditions.

Technology Transfer/Collaborations: Active interactions with automotive fuel cell system integrators have specified performance and durability tests for membrane, catalyst and catalyst supports that were used to demonstrate significant enhancements of the approach in these areas.

Remaining Work on This Project:

- Complete short stack testing (3-5 kW) in automotive quality stack, and deliver to Argonne National Laboratory for evaluation: (by June 30, 2006)
- Complete and submit final report: (by Sept. 30, 2006)

Proposed Future Research: Further optimize NSTF multi-element catalysts and supports for mass activities approaching entitlement values and further enhanced corrosion resistance. Integrate the NSTF catalysts with tailored membranes designed for hotter, drier conditions and optimized GDL's.

Project Summary- NSTF Cat. Characteristics vs DOE Targets

Table 3.4.13. [1] Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Units	2010/2015 Stack Targets	3M 2006 Status (50 cm^2 cell)
PGM Total Content	g/kW rated in stack	0.5 / 0.4	**0.33** for V < 0.72 volts
PGM Total Loading	mg PGM/cm^2 electrode area	0.3 / 0.2	**0.21**
PGM Cost	$/kW @ $15/g	8 / 6	**6**
Durability with cycling At operating T ≤ 80°C At operating T > 80°C	Hours	 5000 2000	**TBD** under specified conditions
Mass Activity (150kPa H_2/O_2 80°C. 100% RH)	A/mg-Pt @ 900 mV	0.44 / 0.44	**0.25**
Specific Activity (150kPa H_2/O_2 80°C. 100% RH)	µA/cm^2-Pt @ 900 mV,	720 / 720	**2,470** (0.08 mg-Pt/cm^2)
ECSA loss by Stop/Start	% ECSA loss	< 40	30 (Per protocol of slides 8 or 11)
Electrochemical support loss at high potentials	mV after 100 hrs @ 1.2 V	< 40	< 10 projected (Per protocol of slide 12)

Project Summary- 3M PEM Characteristics vs DOE Targets

Table 3.4.12. [1] Technical Targets: Membranes for Transportation Applications

Characteristic	Units	2010/2015 Target	3M 2006 Status (50 cm^2 cell)
Membrane Conductivity at:	S/cm	0.10 / 0.10	**> 0. 10** @ 120°C w/ 80°C DP, 250kPa,
Operating Temperature			
Room Temperature	S/cm	0.07 / 0.07	0.12 saturated
-20 °C	S/cm	0.01/ 0.01	TBD
Operating Temperature	°C	≤ 120	≤ **120**
Inlet water vapor partial pressure	kPa (absolute)	1.5 / 1.5	TBD
Oxygen cross-over	mA/cm^2	2 / 2	Expected to be similar for PFSA
Hydrogen cross-over	mA/cm^2	2 / 2	**< 2** @ 70 °C, saturated
Durability with load cycling	Hours, T ≤ 80 °C Hours, T > 80 °C	5000 2000 / 5000	> 5000 > 4,000

[1] DOE HFCIT Multi-Year Research, Development and Demonstration Plan

Publications & Presentations

1. M. K. Debe, A. K. Schmoeckel, G. D. Vernstrom and R. Atanasoski, "High Voltage Stability of NanoStructured Thin Film Catalysts for PEM Fuel Cells," submitted J. Power Sources, March, 2006, and presented 2005 Fuel Cell Seminar, Palm Springs, California, Nov. 14 - 18, 2005.
2. M. K. Debe, A. K. Schmoeckel, S. M. Hendricks, G. D. Vernstrom, G. M. Haugen and R. T. Atanasoski, "Durability Aspects of Nanostructured Thin Film Catalysts for PEM Fuel Cells," presented at Symposium on Durability and Reliability of Low-Temperature Fuel Cell Systems, 208th ECS meeting, Oct. 16 - 21, 2005, Los Angeles, CA.
3. J. McBreen, M. Balasubramanian, W.-S. Yoon, K. Y. Chung, H. S. Lee, and X. Q. Yang, R.T.Atanasoski, A.K. Schmoeckel, G.D. Vernstrom, and M.K. Debe, "PEM Fuel Cells: Materials Issues," Fifth International Symposium on Proton Exchange Membrane Fuel Cells, In Honor of Dr. Subramanian Srinivasan, 208th ECS Meeting, Los Angeles, CA, Oct. 16 - 21, 2005.
4. J.R. Dahn, D.A. Stevens, A. Bonakdarpour, E.B. Easton, M.T. Hicks, G.M. Haugen, R.T. Atanasoski and M.K. Debe, "Development of Durable and High-Performance Electrocatalysts and Electrocatalyst Support Materials," Symposium on Durability and Reliability of Low-Temperature Fuel Cell Systems, 208th ECS meeting, Oct. 16 - 21, 2005, Los Angeles, CA.
5. F. Meng, S. Dec, M. Frey, S. Hamrock, J. Turner, and A. Herring, "Spectroscopic Studies of Heteropoly Acid doped 3M Perfluorinated Sulfonic Acid Polymer Membranes," 208th Meeting of the Electrochemical Society, Los Angeles, CA, Oct. 18, 2005. A paper of the same title was also submitted to *Proceeding of the Electrochemical Soc.*
6. S. Hamrock, "The Development of New PEM Fuel Cell Membranes at 3M," Golden Gate Polymer Forum, 25th Anniversary Symposium, Oct. 23, 2005, San Francisco, CA.
7. A. M. Herring, J. A. Turner, S. F. Dec, F. Meng, J. Horan, N. Aieta, R. J. Stanis, "The Use of Heteropoly Acids in the Production of High Performance PEM Fuel Cell Components," 2005 Fuel Cell Seminar, Nov. 15, Palm Springs, CA.
8. S. Hamrock, "New PFSA membranes with Improved Durability," Pacific Polymer Conference IX, Maui, Hawaii, Dec. 12, 2005.
9. M. K. Debe, "Advanced Catalyst and Membrane Technology with Enhanced Performance and Durability for Automotive Requirements," at 4th Internationa. Fuel Cell Workshop 2005, Kofu, Japan, Sept. 23-24, 2005.
10. A. Herring, J. Turner, S. Dec, J. Malers, F. Meng, J. Horan and N. Aieta,"The Use of Heteropoly Acids in Composite Membranes for Elevated Temperature or Low Humidity PEM Fuel Cell Operation," 2nd International Conference on Polymer Batteries and Fuel Cells, Las Vegas, NV, June 13, 2005.
11. M. A. Yandrasits,"Mechanical Property Measurements of PFSA Membranes at Elevated Temperatures and Humidities," 2nd International Conference on Polymer Batteries and Fuel Cells, Las Vegas, NV, June 14th 2005.
12. M. K. Debe,"Prospects and Challenges for PEM Fuel Cells with a Focus on MEA Development for Automotive Applications," Invited Plenary Lecture, 2005 Annual Meeting of the North American Membrane Society, Providence, RI, June 15, 2005.

Critical Assumptions and Issues

1) Stack testing of the NSTF MEAs currently underway will be using a 3.5 to 5kW short-stack version of a new design that has not previously been tested with this or any type of MEA. It is a short stack version of full 70kW automotive prototype, meeting stringent power density (volumetric and gravimetric) targets. It requires full 7-layer MEA's with integrated gaskets for proper operation. Development of the methodologies to make 7-layer NSTF MEA's is being done for the first time, and outside the contract, to enable the stack testing. There is very little time left in the contract to work out issues that might arise by the combination of these new 7-layer MEAs and new stack design.

2) Work on stack testing has been delayed for two reasons. First we waited until the new automotive stack hardware was finally available, which did not occur until early April, 2006. Second, we have delayed in order to incorporate the best and latest version of an integrated MEA containing the 3M NSTF catalyst and 3M PEM combination. These MEA's will be roll-good fabricated on a very tight schedule on pilot production equipment to just match the readiness of the new stack. This timing will only allow 2 to 3 stack builds and evaluations before the end of the contract June 30, 2006, by which time it must be delivered to Argonne National Lab. There is little if any time for solving any problems.

3) The latest and best MEA roll-good components to be used in the stack testing will be fabricated on actual production equipment. If there are delays due to scheduling conflicts or equipment failures, then again we may not make the desired time-line.