2010 DOE Hydrogen Program Review

Advanced Cathode Catalysts and Supports for PEM Fuel Cells

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3M Company

June 8, 2010

Project ID: FC 001

Overview

Timeline

- Project start : April 1, 2007
- Project end : March 30, 2011
- 80% Complete (6/8/10)

Budget

- Total Project funding **$10.43MM**
  - $8.34 MM DOE and FFRDC
  - $2.09 MM 3M share
- Received in FY09: $2.3 MM
- Est. Funding for FY10: $1.593 MM

Partners

- Dalhousie U. (D. Stevens, J. Dahn)
- ANL (V. Stamenkovic, N. Markovic)
- JPL (C. Hays, S. R. Narayanan)
- 3M (A. Steinbach, S. Hendricks, M. Kurkowski, G. Vernstrom, A. Hester R. Atanasoski, P. Kadera, M. Debe,..)

Barriers

A. Electrode and MEA Durability

B. Stack Material & Mfg Cost

C. Electrode and MEA Performance

DOE Technical Targets

Electrocatalyst/ MEA		2010	2015
Lifetime Hrs. > 80°C		2000	5000
Mass Activity (A/mg)		0.44	0.44
PGM, (g/KW rated)		0.3	0.2
Performance (W/cm^2)	@ Rated	1	1
	@ 0.8V	0.25	0.25

Additional Current Interactions

GM Fuel Cell Activities, Nuvera Fuel Cells, other OEM's, Proton Energy Systems, Giner EC Systems LLC; LBNL, LANL; DTI

Relevance and Approach

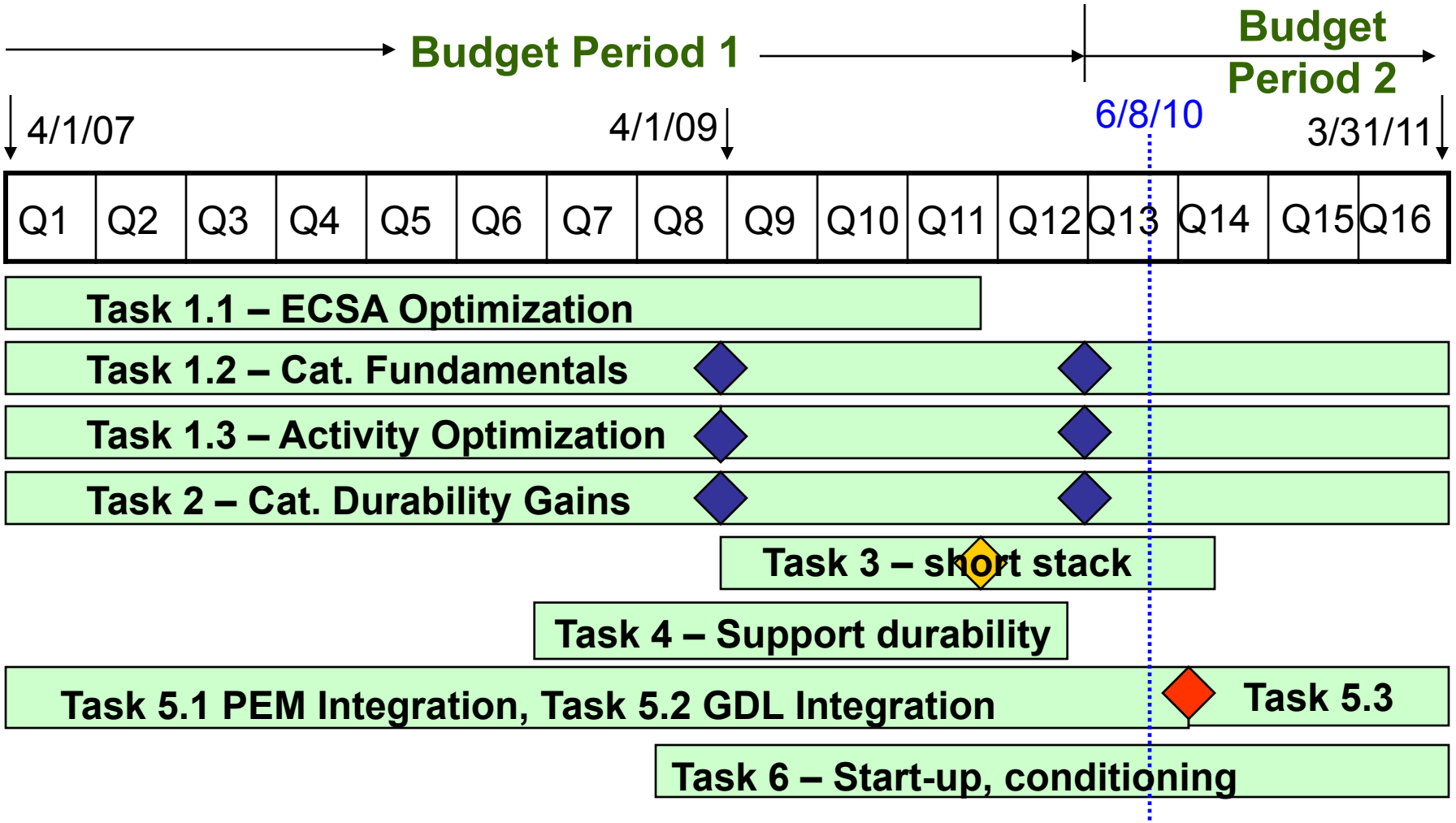
Objectives: Development of a durable, low cost, high performance cathode electrode (catalyst and support), that is fully integrated into a fuel cell membrane electrode assembly with gas diffusion media, fabricated by high volume capable processes, and is able to meet or exceed the 2015 DOE targets.

Approach: Development of advanced cathode catalysts and supports based on 3M's nanostructured thin film (NSTF) catalyst technology platform, which has already demonstrated catalyst specific activity and durability significantly higher than conventional carbon supported Pt catalysts.

Focus Topics for Past Year:

- Water management improvements for cool/wet operation through materials, electrode structure and boundary condition optimization and understanding.
- Continued multiple strategies for increasing NSTF support surface area, catalyst activity and durability, with total loadings of $\leq$ 0.25 mg-Pt/cm^2 /MEA.
- Continue fundamental studies of the NSTF catalyst activity for ORR in general and methods for achieving the entitlement activity for NSTF catalysts.
- More severe accelerated tests to benchmark the NSTF/MEA durability.
- Development of faster, easier MEA break-in conditioning protocols.
- Work with system integrators to validate NSTF functional properties/issues in short stacks.

Project Timeline and Milestones



Major Technical Accomplishments Since Last Year

- **Water management for cool/wet operation** (Task 5.2)
  - Demonstrated new paradigm for water management of thin layer electrodes based on sub-atmospheric anode pressure and high liquid water permeability anode GDL's that:
    - enables steady state current density up to 2.0 A/cm^2 at 30 to 35 ^{o}C with NSTF MEAs in 50 cm^2 single cells, and
    - 5 second 0 -1 A/cm^2 load transients at 50^{o}C and 140% RH.
  - Demonstrated gradient cathode catalyst construction that enables steady state 1 A/cm^2 at 30^{o}C, successful load transient 0 -1 A/cm^2 step at 40^{o}C, 140%RH, and which does not reduce performance at 80^{o}C over standard NSTF CCM.

- **Catalyst activity and understanding** (Task 1)
  - Increased PtCoMn mass activity 30% to 0.24 A/mg and demonstrated Pt_3Ni_7 alloy with mass activity of 0.40 A/mg and absolute activity at 900mV of 40 mA/cm^{2}w/ 0.1 mg/cm^2.
  - Developed a post fabrication treatment process that is roll-good compatible and increases ORR mass activity up to 50% for PtCoMn and the Pt_3Ni_7 alloy.
  - Made catalyst deposition process improvement that gives NSTF pure Pt performance equal to PtCoMn with much greater Pt fcc(hkl) grain sizes.
  - Identified a path forward, based on fundamental understanding of bulk crystalline Pt alloy surfaces, to potentially increase substantially the activity of nanostructured thin film catalysts to full entitlement.

Technical Accomplishments and Progress

Continued ---- Major Technical Accomplishments Since Last Year

- **Catalyst and MEA durability** (Task 2)
  - Demonstrated MEA load cycling lifetime of 5000 hours with 0.05/0.10 mg/cm^2 loaded 20 μm membrane that contained no chemical stabilizers.
  - Demonstrated that with chemical stabilizers in the membrane, the 200 hour DOE target for OCV hold under H_2/air is exceeded by a factor of ~ 3X to 4X.

- **Large area short stack test durability testing** (Task 3)
  - Initiated large area short stack testing with Nuvera to evaluate for the first time, the combination of the 3M NSTF electrode technology with the Nuvera open flow field bi-polar plate technology. Three short stacks built and BOL testing for initial understanding.

- **Membrane-electrode integration and CCM scale-up** (Task 5.1)
  - Produced 37,000 linear ft combined of NSTF substrate, coated catalyst supports, and catalyst coated membrane for process development, qualification and customer use.

- **Break-in conditioning** (Task 6)
  - Developed more user friendly MEA conditioning protocols that can provide 90% of full performance in 2 to 5 hrs. depending on the material set.

- **Demonstrated outside this contract by GM:**
  - Obtained 0.19g_{Pt}/kW in a large area stack (> 20 cells) with NSTF MEA w/0.05/0.1mg/cm^2
  - 2000 hour short stack testing, including automotive system-relevant voltage & RH cycles.
  - Demonstrated 10^{o}C cold start and -20^{o}C freeze-start capability in > 20-cell stack.

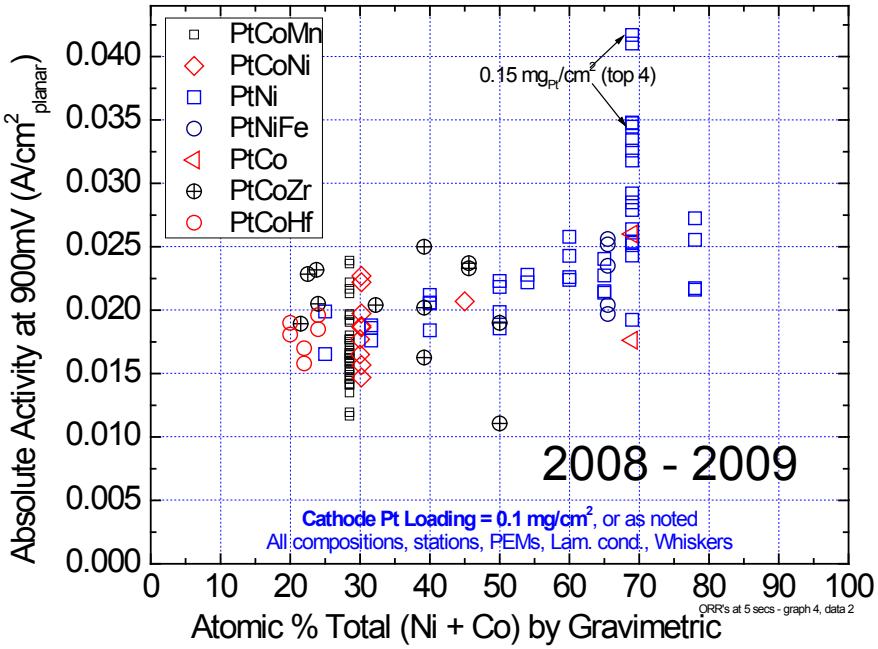
(in supplemental slides)

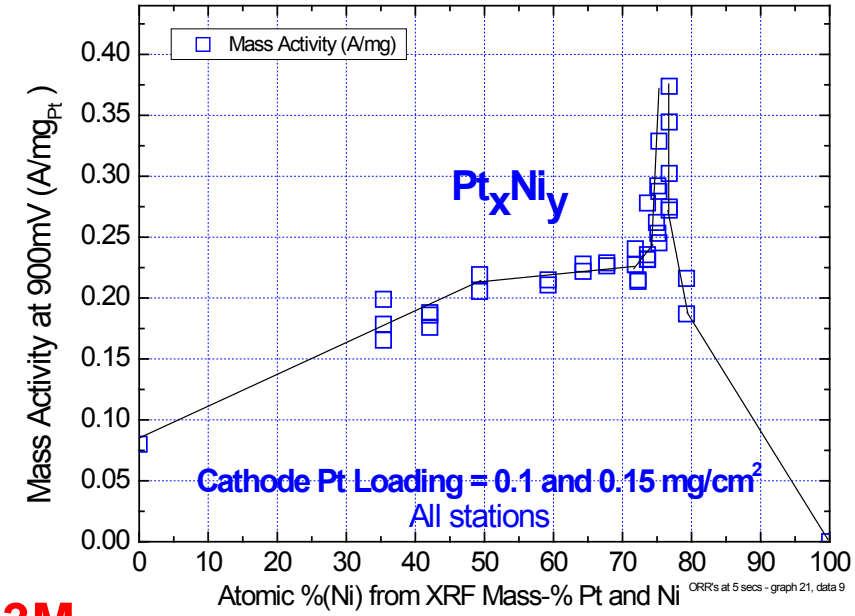
Technical Accomplishments and Progress

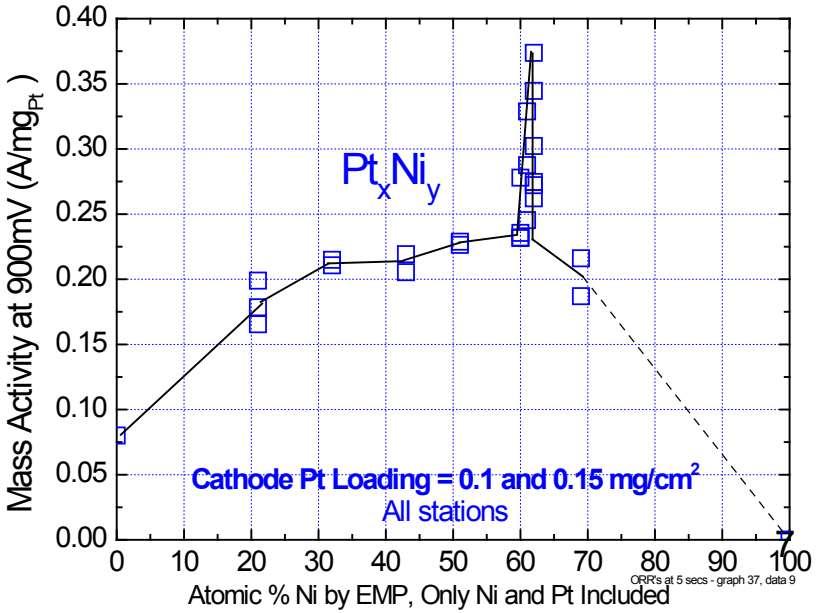
Task 1. NSTF Catalyst Activity, Surface Area, Fundamentals

First Focus Area: New Alloys

- Screening multiple new alloys revealed anomalously high ORR activity for Pt_xNi_y at high Ni content (end of 2008, early 2009, "PtM")
- We focused on studying just Pt_xNi_y to present.
- Dramatic and sharp mass activity peak at Pt_3Ni_7
- Exact position of peak depends on method used.
- Used as model system as well as potential practical catalyst.
- Definite gains in kinetic performance but not a practical catalyst yet due to performance limitations above 1 A/cm².

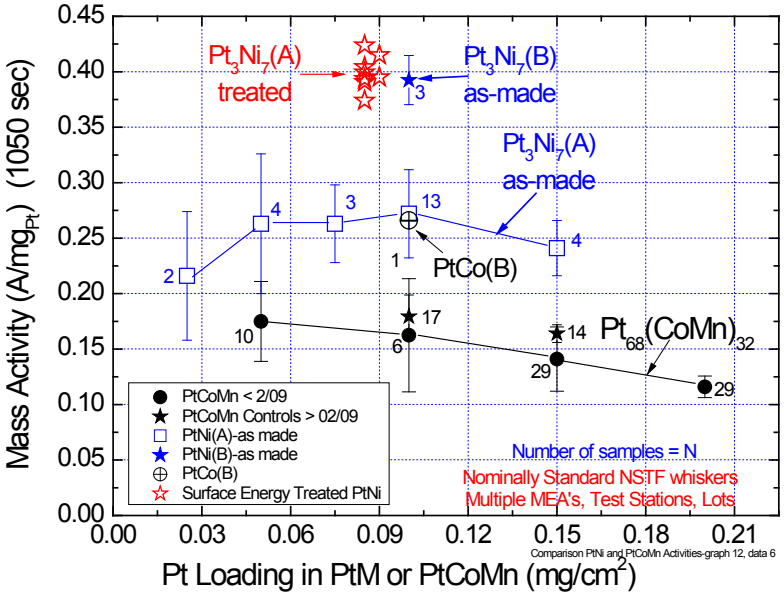






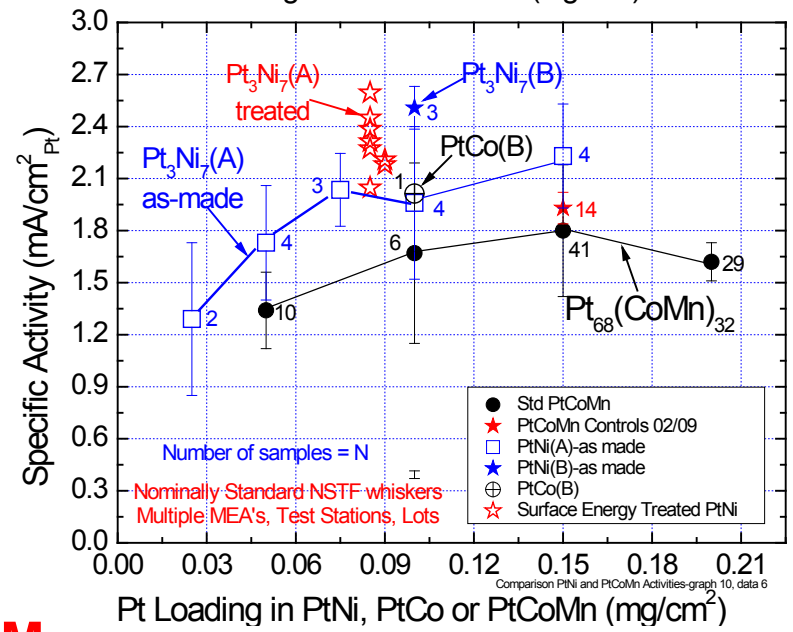
Technical Accomplishments and Progress

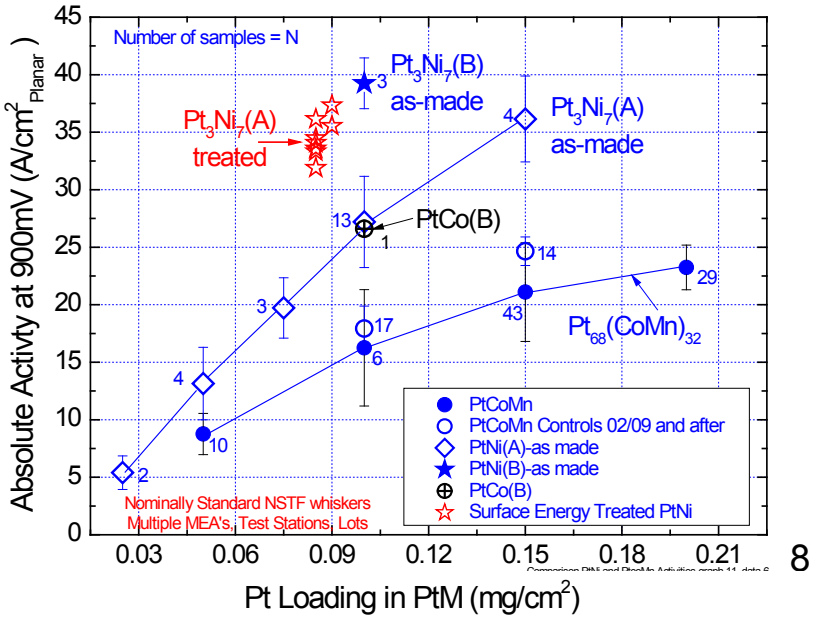
Task 1. NSTF Catalyst Activity, Surface Area, Fundamentals



Activities of PtNi vs. Std. PtCoMn

- Pt_3Ni_7 shows significant increase in activity metrics over standard $Pt_{68}(CoMn)_{32}$.
- Both specific activity and surface area are increased, roughly by the same percentage.
- The activity depends on subtleties of the process. Process B (Dalhousie batch equipment) somewhat better than process A (3M roll-good). Studying why.
- PtCo shows much weaker response vs % Co.



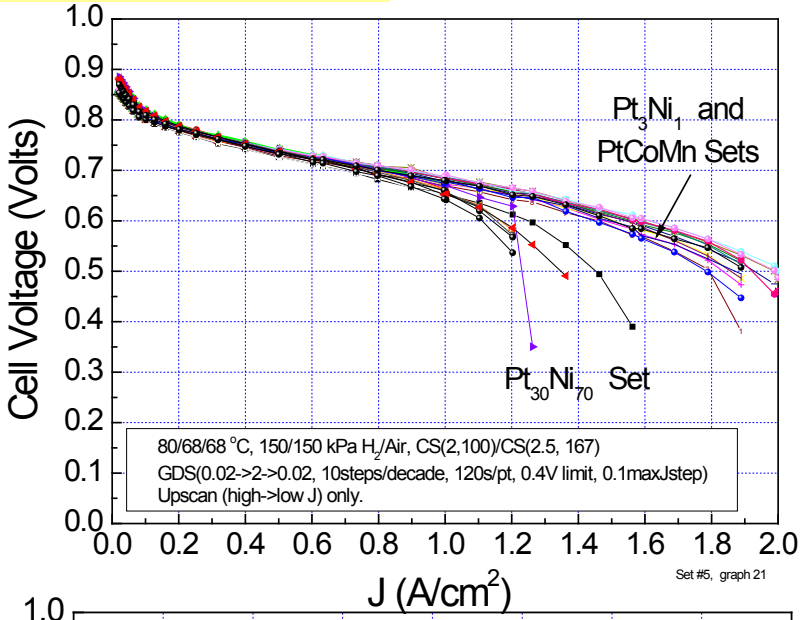


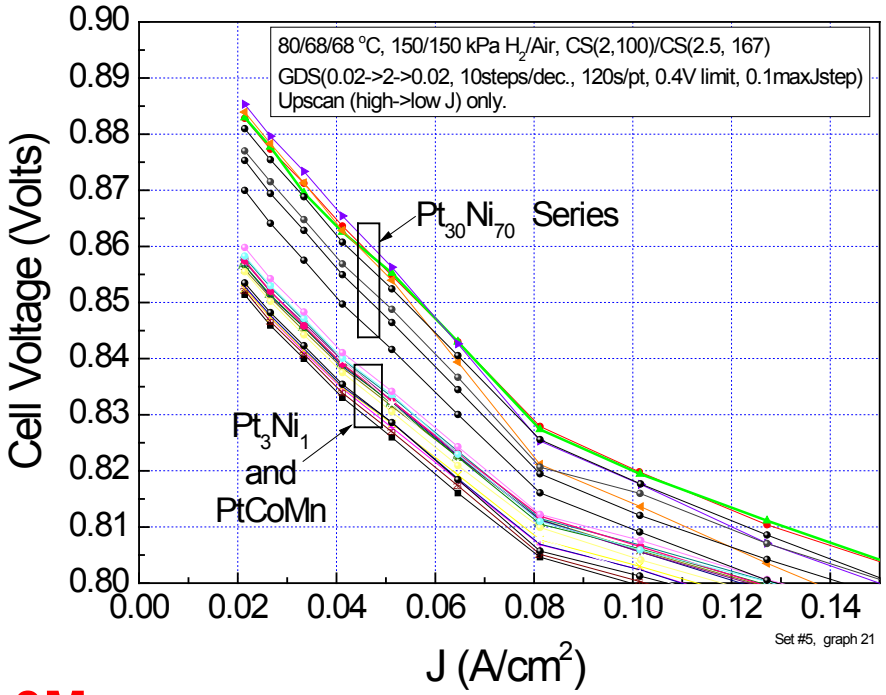
Technical Accomplishments and Progress

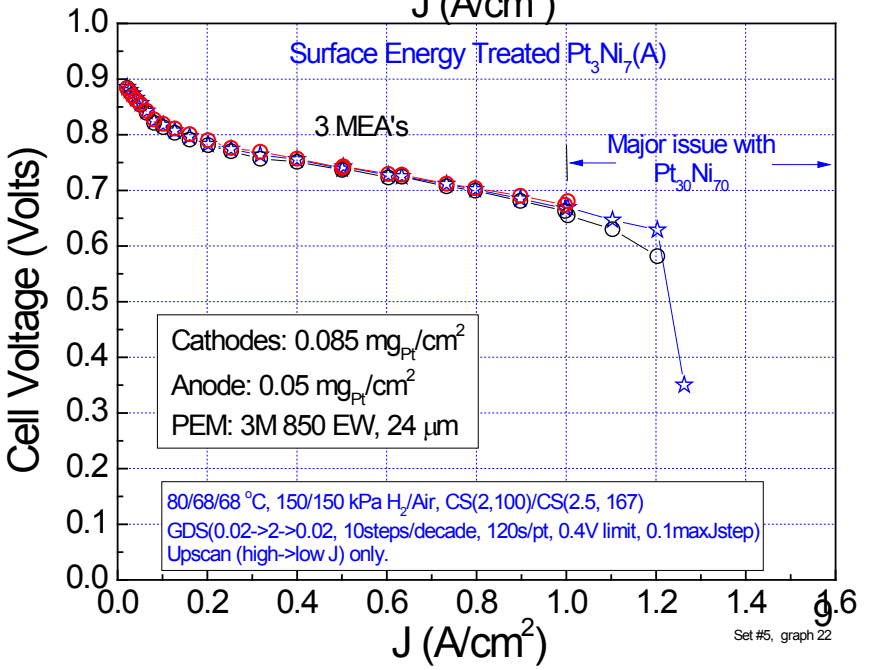
Task 1. NSTF Catalyst Activity, Surface Area, Fundamentals

Limitations of Pt_3Ni_7

- Higher mass activity of Pt_3Ni_7 translates to higher H_2/air polarization curve kinetics.
- However, the main issue is loss of high current density performance due to excess Ni dissolving into the membrane.
- Acid washing pre-treatment helps but not completely and is not a desirable process.
- It may not be possible to stabilize the excess Ni. It is a very novel system.





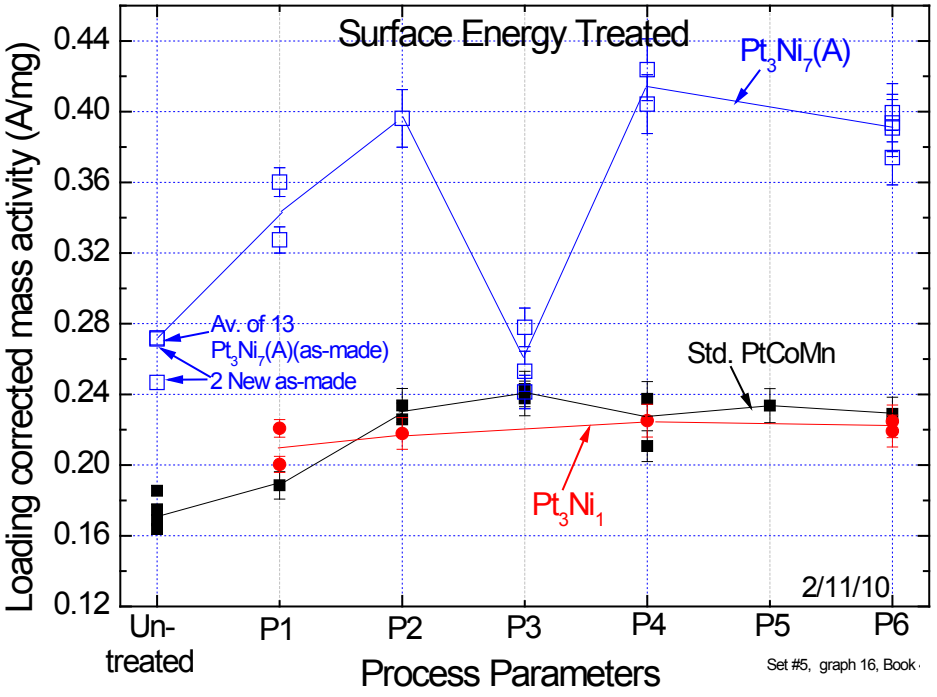


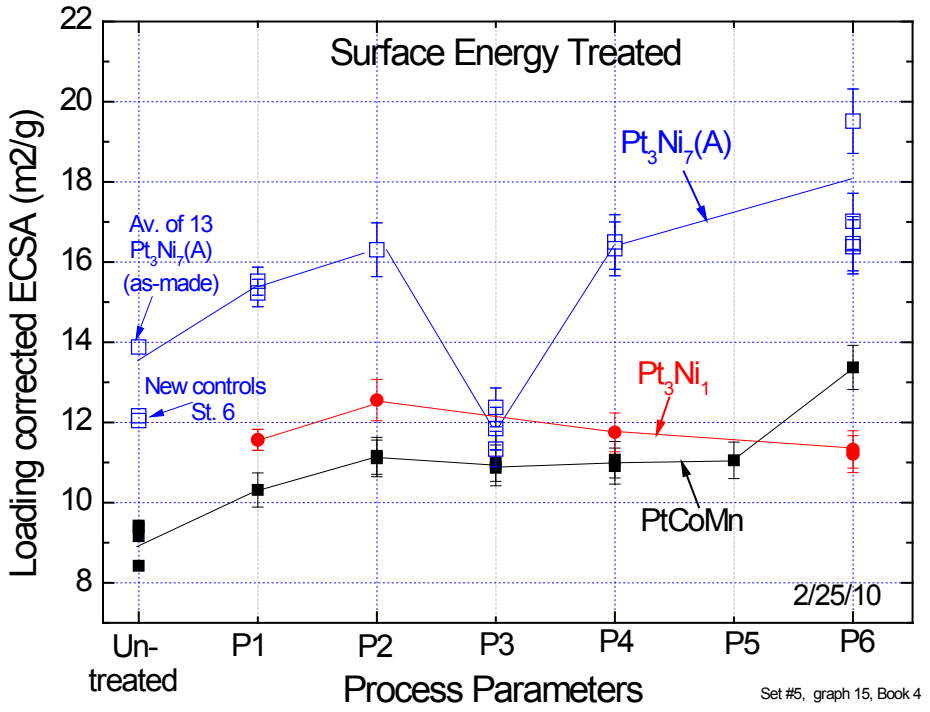
Technical Accomplishments and Progress

Task 1. NSTF Catalyst Activity, Surface Area, Fundamentals

Second Area of Focus: Catalyst post processing for simulated annealing

- Fundamental studies of bulk crystalline alloys show benefit of annealing (ANL).
- We focused on development of a roll-good compatible surface energetic treatment to simulate catalyst annealing. It has been successful in showing similar gains in activity:
  - Increases Pt_3Ni_7 (A) activity to equal that of Pt_3Ni_7 (B) (see previous slide, red stars.)
- Mass activity increases are due to both increases in ECSA and specific activity.
- $Pt_{30}Ni_{70}$ benefits the most, and is sensitive to the parameter conditions used.
- The process is still being optimized in a batch mode.



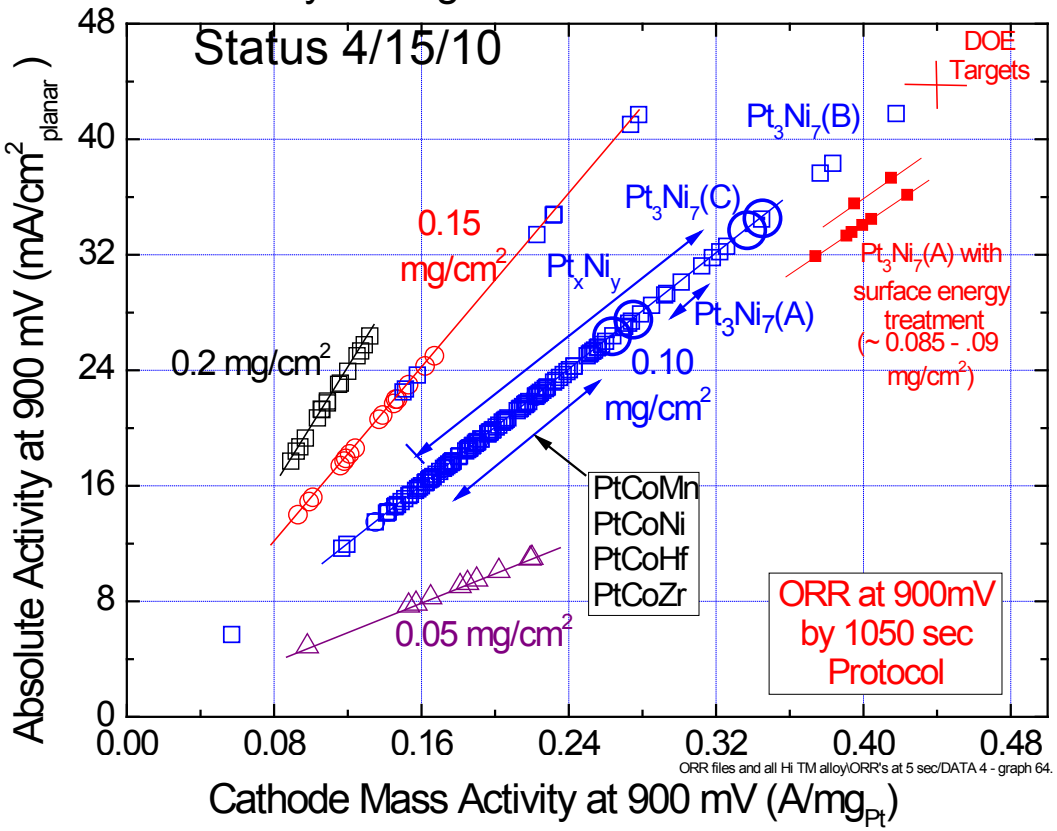


Technical Accomplishments and Progress

Task 1. NSTF Catalyst Activity, Surface Area, Fundamentals

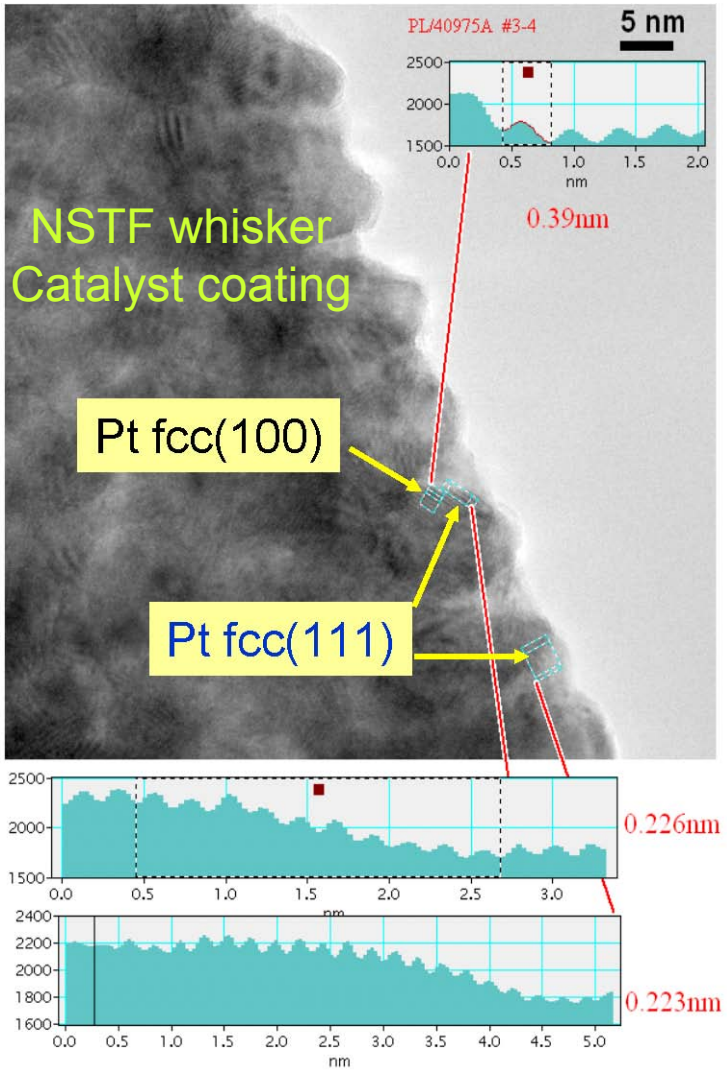
Status of Activities vs. Targets

- The PtNi alloys' absolute activity and mass activity are approaching more closely the DOE targets.
- Post treatment process improvements still anticipated.
- New look at fundamentals of NSTF activity pointing to new focus direction to reach entitlement potential of NSTF catalysts in general.



Towards Future Gains

Increasing the fractional surface area that has the preferred fcc(111) facets.

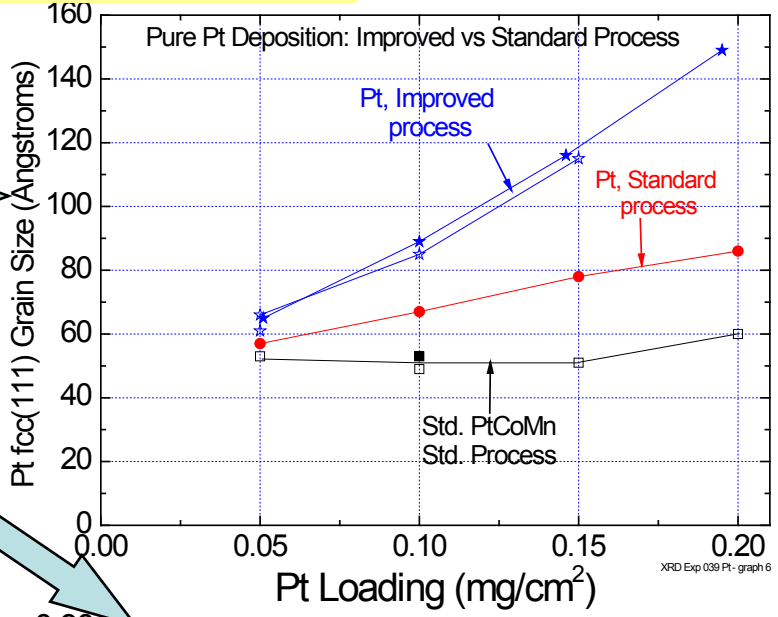


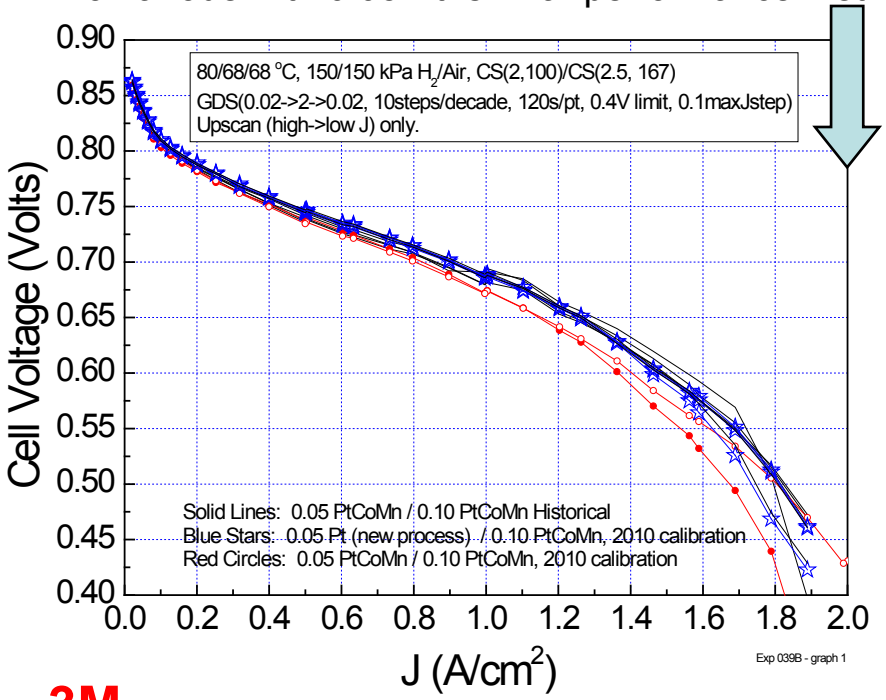
Technical Accomplishments and Progress

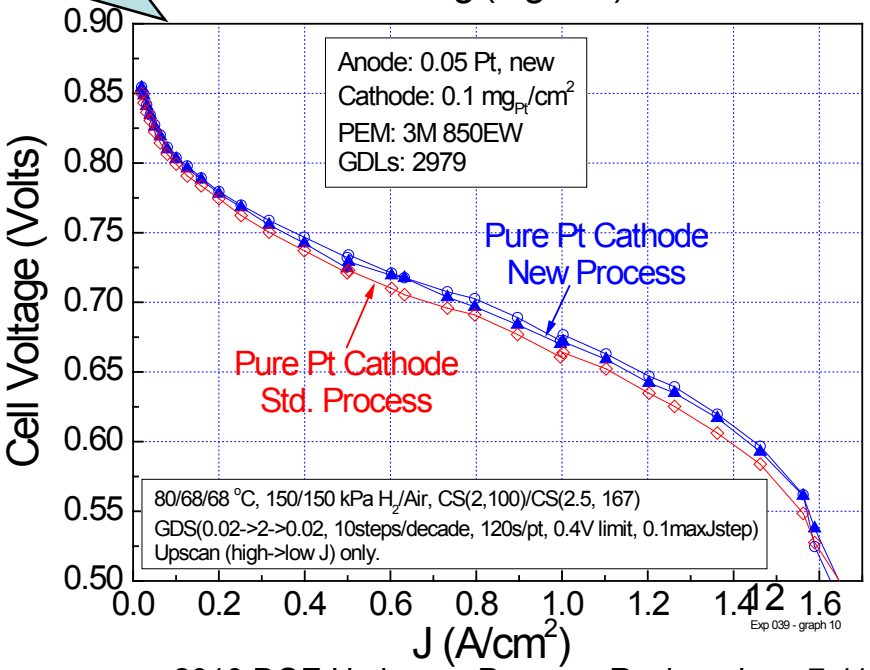
Task 1. NSTF Catalyst Activity, Surface Area, Fundamentals

Pure Pt and Process Improvements

- NSTF-Pure Pt revisited with improved, simpler process.
- Improved process significantly increases Pt grain sizes over standard deposition process.
- Pure Pt at loadings of 0.1 and 0.15 mg/cm^2 yield very similar polarization curves to standard PtCoMn at 0.10 mg/cm^2 of Pt to up to ~1.4 A/cm^2.
- Impact of new process on Pt alloys to be determined.
- Pure Pt cathodes by the new process are slightly improved over pure Pt by the standard process.
- No negative impact replacing 0.05 mg/cm^2 PtCoMn on anode with 0.05 Pt: similar performance metrics.







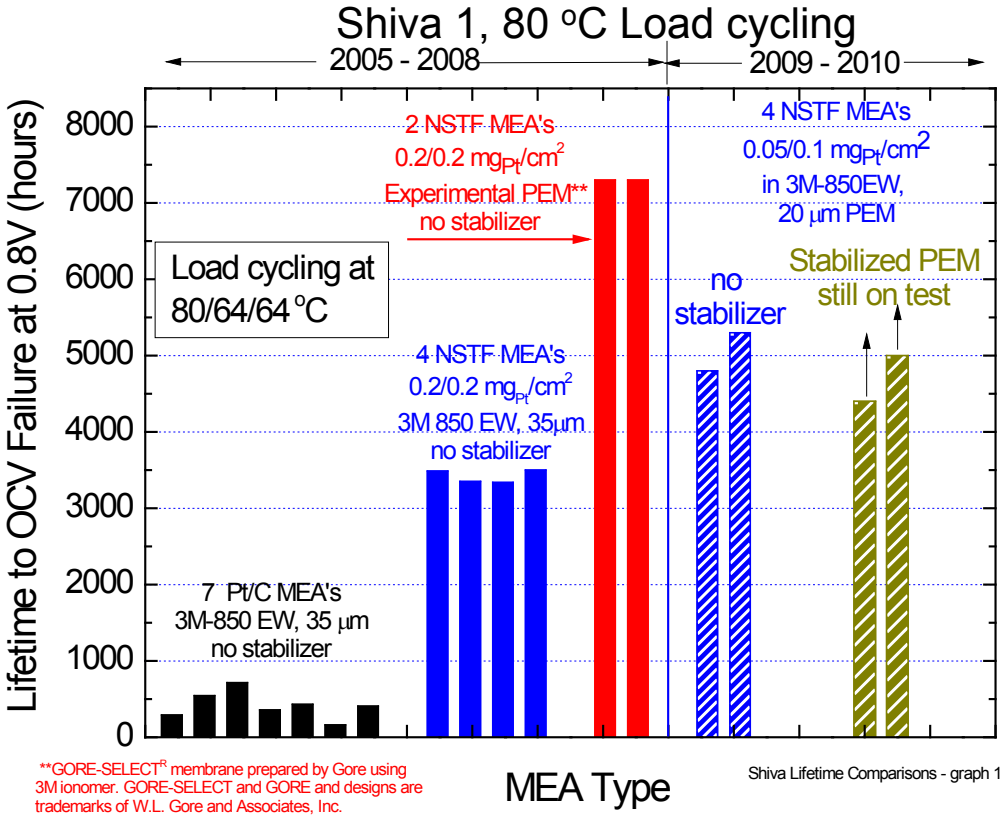
Technical Accomplishments and Progress

Task 2 – Accelerated Durability Testing

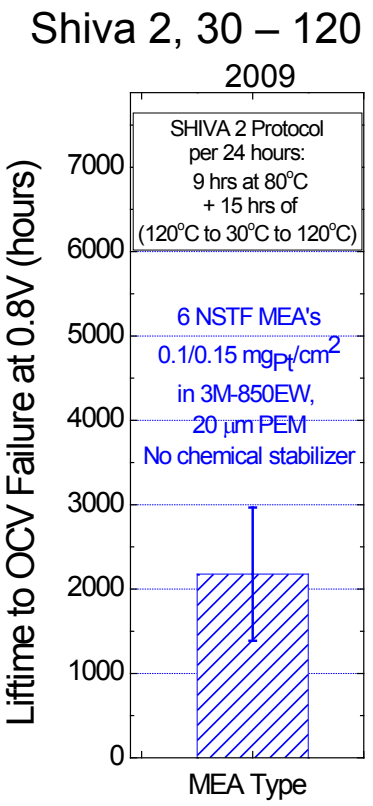
Three Tests Continued Since Last AMR:

1) Load cycling on SHIVA 1 & 2: 80 °C, and 30 to 120 °C protocols
2) CV Cycling: Catalyst alloys types, deposition process differences, cell effects
3) OCV hold at 90 °C under H_2/Air: Catalyst alloys, PEM additives, catalyst loadings

1. Accelerated Load Cycling Lifetime Testing



**GORE-SELECT® membrane prepared by Gore using 3M ionomer. GORE-SELECT and GORE and designs are trademarks of W.L. Gore and Associates, Inc.

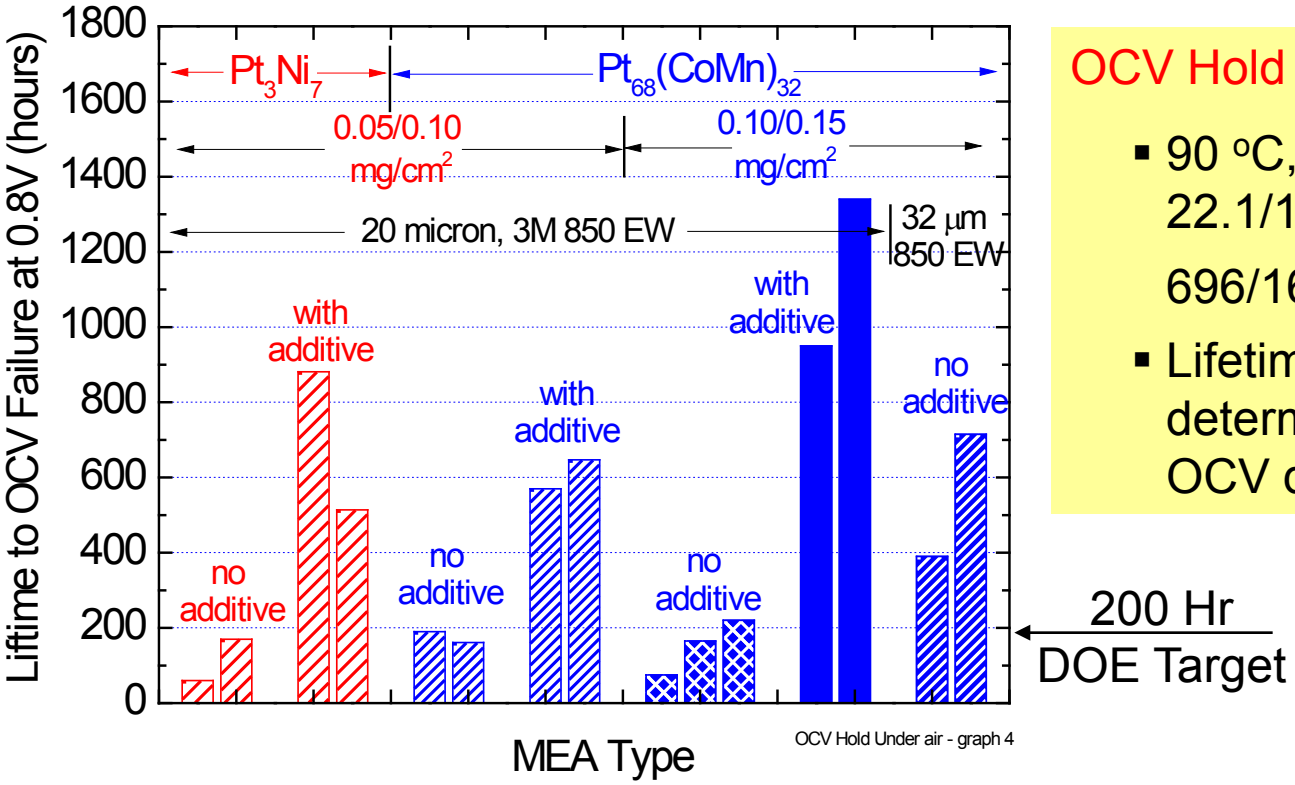


(Protocols in additional slides section)

Task 2 – Accelerated Durability Testing

2. OCV Hold Test Update

- PEM chemical additive required to consistently exceed 200 hour target by 3 to 4 x with 20μm, 850EW PEM and NSTF PtNi or PtCoMn at any loading.
  - With additive, PtNi life is slightly better than PtCoMn (698±184 vs 610±40 hrs. at 0.1mg/cm^2).
  - With additive and 20 μm PEM, 0.10/0.15 PtCoMn has longer lifetime (1,145±195 hrs) than 0.05/0.10PtCoMn (Av = 610±40 hrs)
- Thicker membrane and higher loading can meet the target with no additive.



OCV Hold Lifetime Under H_2/Air

- 90 °C, 30/30% RH, 22.1/14.7psig H_2/Air, 696/1657 SCCM,
- Lifetime estimated by visually determined onset of rapid OCV decay to 800 mV.

Technical Accomplishments and Progress

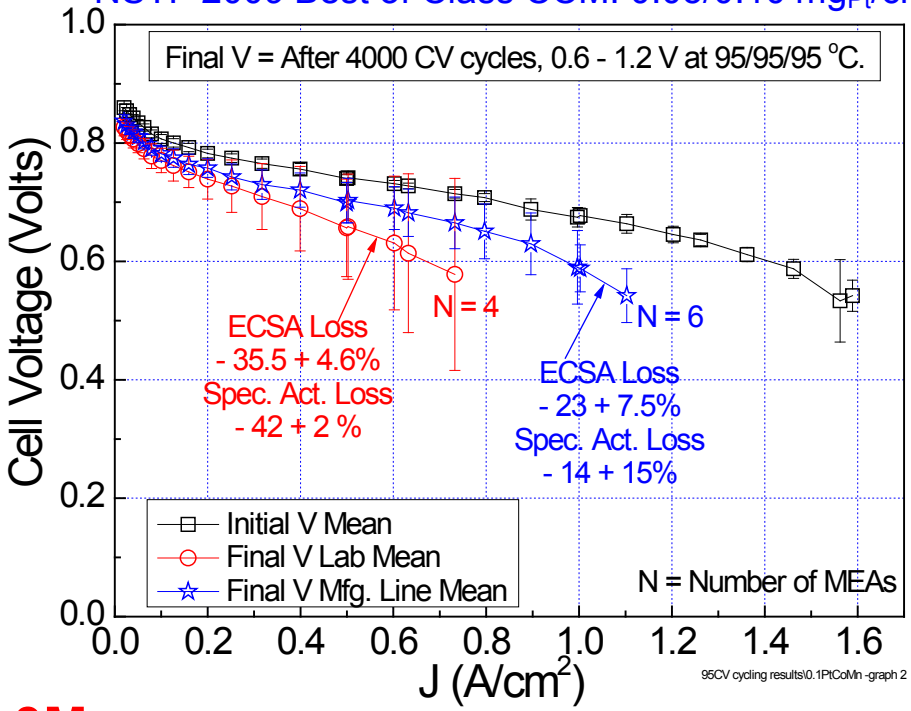
Task 2 – Accelerated Durability Testing

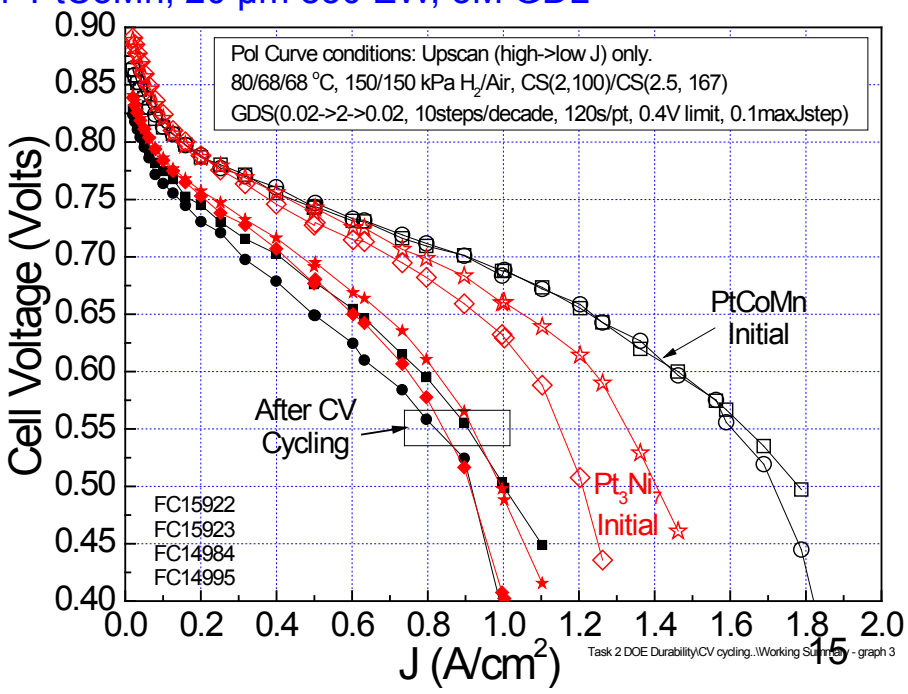
3. CV High Voltage Cycling Test Update – more severe 95 °C conditions

- Nine more PtCoMn samples tested at more severe conditions since last year
  - Multiple materials differences in membrane and catalyst lots, test cells, …
  - Results show stability of mfg. line produced catalysts is statistically better than lab made: -23% to -36% loss of ECSA depending on mfg line vs. lab made catalysts and CCM.
  - Small effects due to membrane lot, test cell, catalyst process differences
- Pt_3Ni_7 performance metrics no worse under high voltage cycling test than PtCoMn

Voltage Cycling Protocol:

- 95/95/95 °C, 200/200 kPa H_2/N_2 , 800/1800SCCM, 4000 CV Cycles: (1.2->0.6->1.2V, 20mV/s).
- NSTF 2009 Best of Class CCM: 0.05/0.10 mg_{Pt}/cm^2 PtCoMn, 20 µm 850 EW, 3M GDL





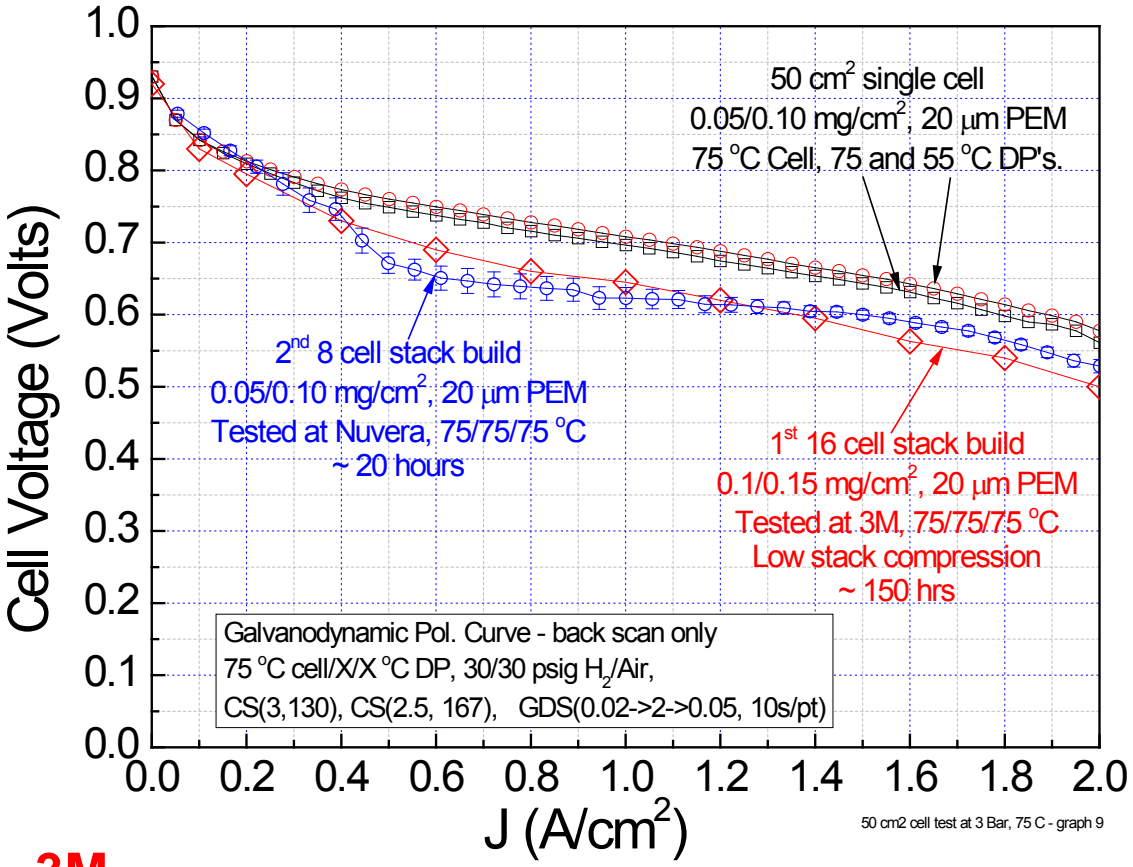
Technical Accomplishments and Progress

Task 3 Full Size (> 250 cm²) Single or Multi-Cell Tests

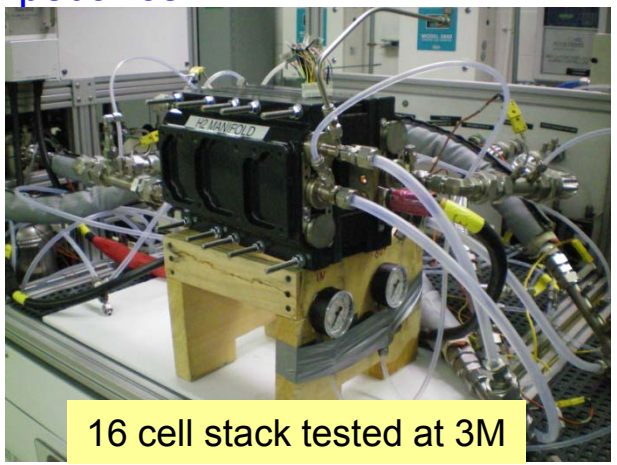
3M NUVERA FUEL CELLS

Subtask 3.2 Large area short stack durability tests

- Initiates subtask 3.2 for preliminary large area electrode testing prior to final Task 5.3.
- Key opportunity to evaluate for the first time, the combination of the 3M NSTF electrode technology with the Nuvera open flow field bi-polar plate technology.
- Project began ~ Sept. 2009. Short stack testing at both 3M and Nuvera now underway.
- Evaluating the NSTF 2008/9 Best of Class MEA's with Andromeda Stack technology.



- Two16 cell and one 8 cell stacks built
- No "fit-n-function" issues
- No contamination issues in 3000 hrs. of assembled shelf time -1st 16 cell.
- Test condition tuning needed to remove flooding at mid-currents.
- Large opportunity to reduce Impedance.

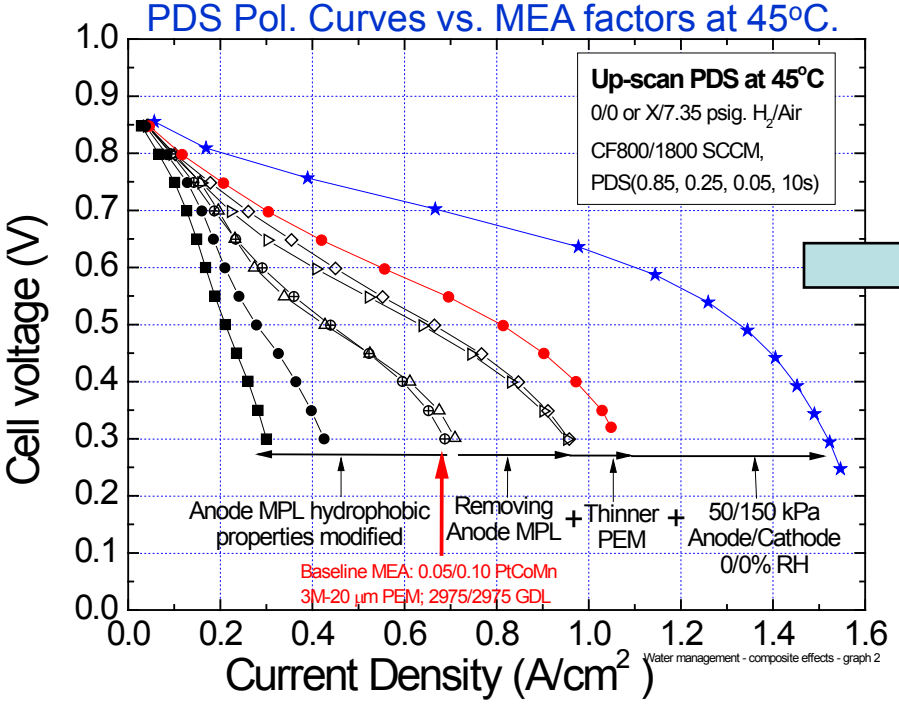

16 cell stack tested at 3M

Technical Accomplishments and Progress

Task 5.2. NSTF MEA Water Management for Cool / Wet Operation

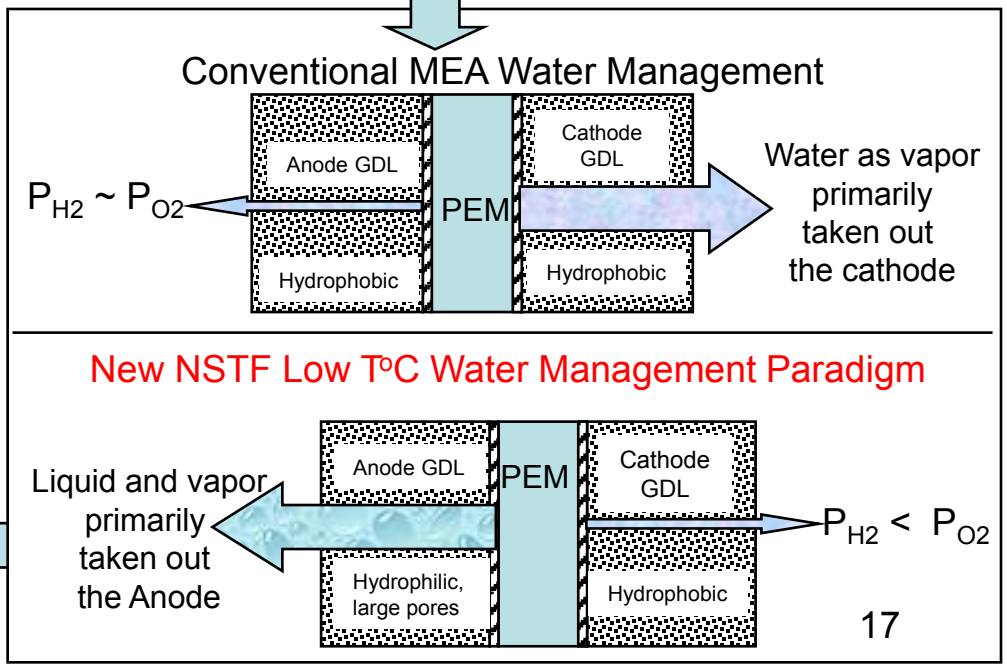
Change Material Factors and Operating Conditions to Move Water Out the Anode

PDS Pol. Curves vs. MEA factors at 45°C.



Important Factors to Reduce Cathode Flooding Under Cool, Wet Conditions.

- Eliminate anode MPL and PTFE
- Use thinner membrane
- Utilize natural hydrophilicity of NSTF catalyst
- Use cathode-to-anode overpressure
- Use sub-atmospheric anode pressure
- Use anode GDL paper with high K_{H2O}



Reducing impedance for water migration from the cathode through the PEM and anode GDL:

Three most critical parameters

- $P_{cathode} > P_{anode}$
- $P_{anode} \leq 1$ atm
- Anode GDL with high permeability for liquid water

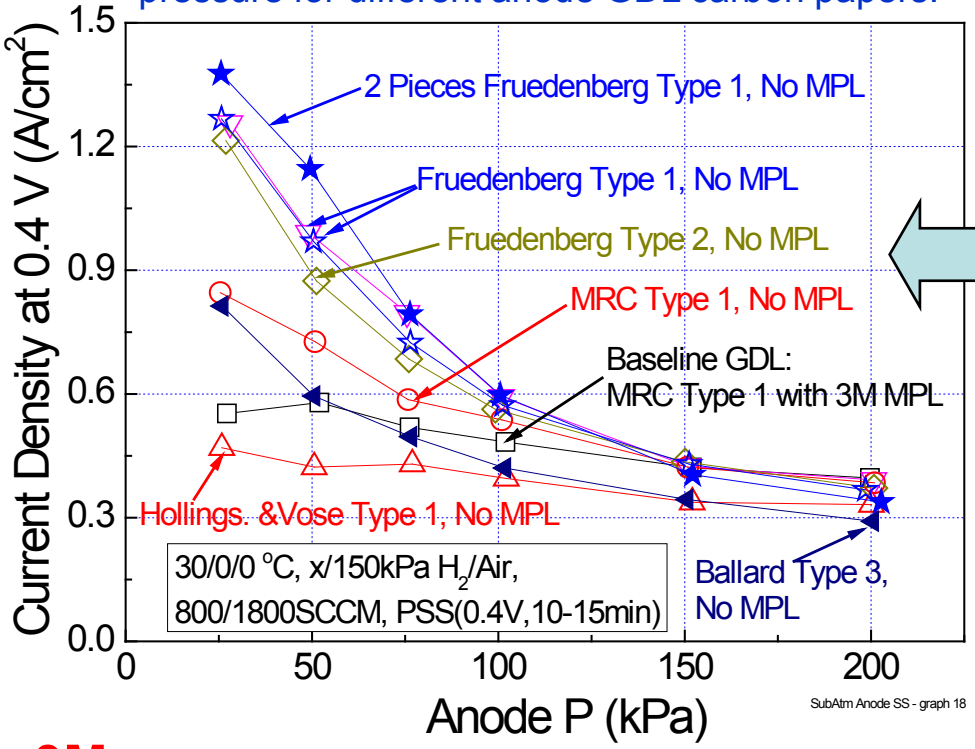
Technical Accomplishments and Progress

Task 5.2. NSTF MEA Water Management for Cool / Wet Operation

Steady state current density: Impact of anode pressure and GDL type

- Low temperature operation critical for rapid stack start-up at T < 60 °C.
- Cathode flooding is significantly reduced by moving water out the anode at low temperatures.
- Sub-atmospheric H_2 pressure can dramatically improve liquid water movement out the anode.
- Low anode GDL impedance for liquid water flow is critical for this benefit of low P_{anode}.
- Removing the MPL, no PTFE and choosing liquid permeability, K_{H20} are critical.

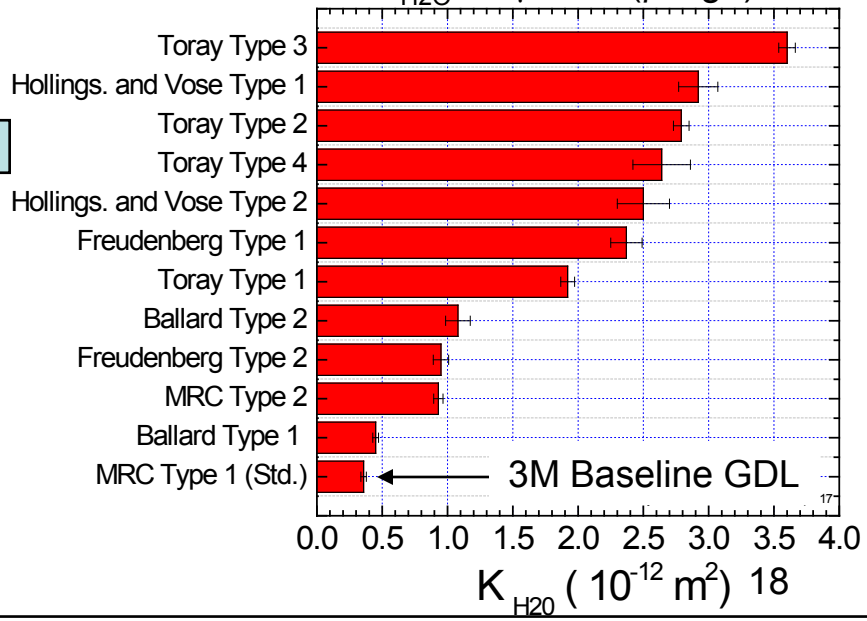
Steady state current density at 0.4 V vs. anode pressure for different anode GDL carbon papers.



Water permeability for series of different GDL carbon papers, used as-received, no PTFE or MPL.

Darcy's Equation: $v(m/sec) = -(K/\mu)dP/dx$

$K_{H2O} = - \mu\, mx / (\rho^2 Agh)$



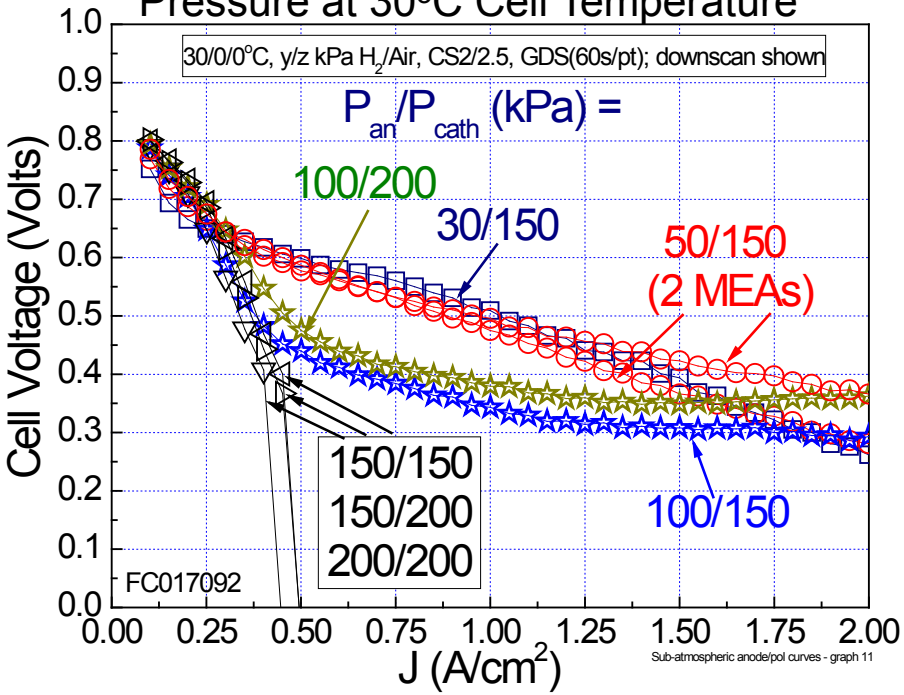
Technical Accomplishments and Progress

Task 5.2. NSTF MEA Water Management for Cool / Wet Operation

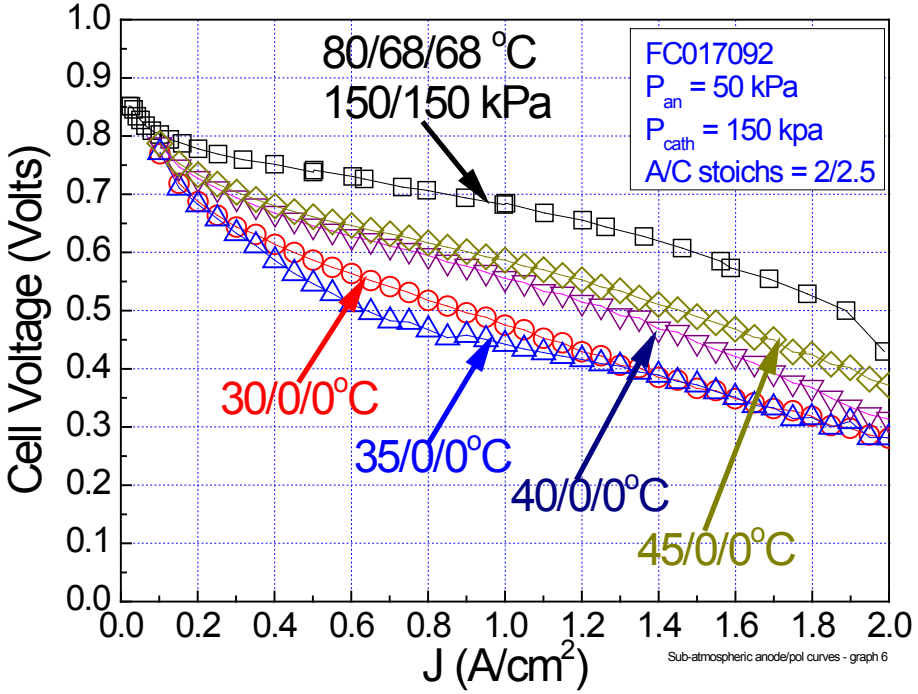
30 °C to 45 °C Pol. Curves: Impact of anode/cathode pressure

- NSTF 2009 "best of class" CCM with Freudenberg Type 1 GDL on the anode is stable at 30 °C to 2 A/cm^2, even with ambient pressure anode (100 kPa) if $P_{cath} \geq 150$ kPa.
- Operating with 50 kPa absolute H_2 improves performance in the mid-range.
- No loss of performance at high temperatures with new anode GDL

GDS Pol. Curves vs. Anode/Cathode Pressure at 30°C Cell Temperature



GDS Pol. Curves vs. Cell Temperature with 50 kPa Anode Pressure



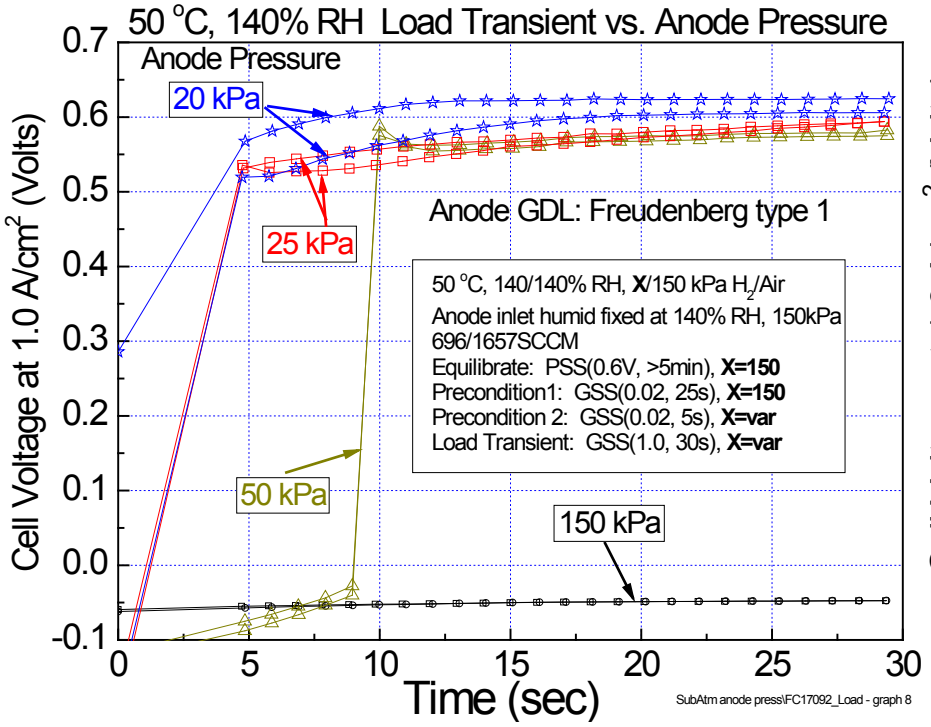
NSTF MEA: 2009 "Best of Class" CCM with 0.05/0.10 mg_{Pt}/cm^2 of PtCoMn on 3M 850EW, 20 µm PEM; Cathode GDL = Baseline 2979; Anode GDL = Freudenberg Type 1

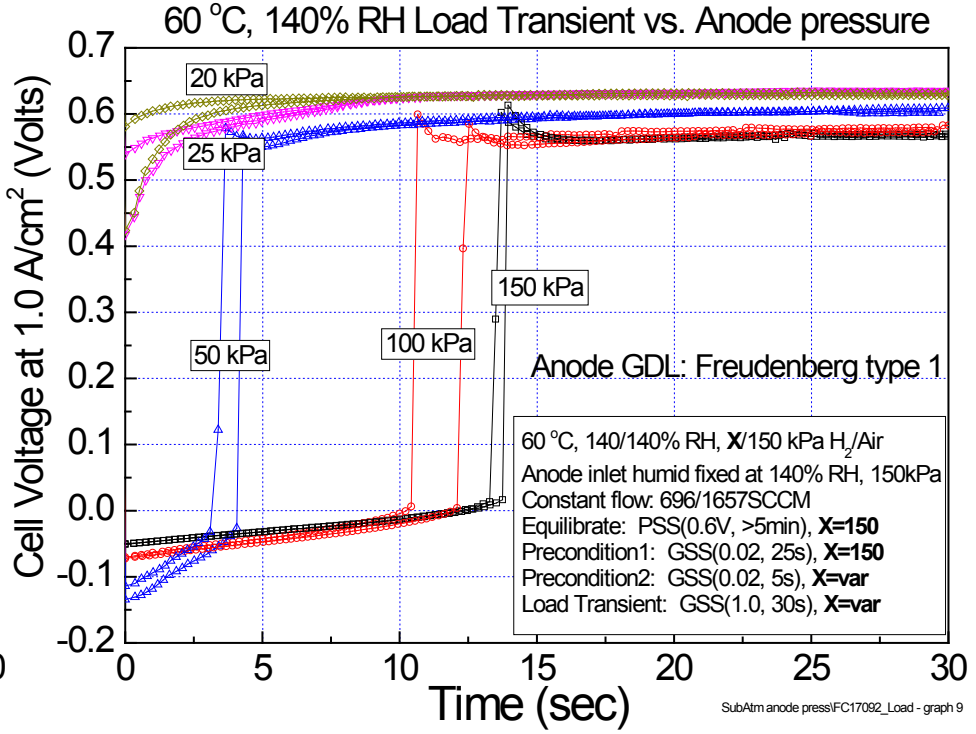
Technical Accomplishments and Progress

Task 5.2. NSTF MEA Water Management for Cool / Wet Operation

50 °C and 60 °C Wet Load Transient Responses: 0.02 → 1 A/cm² step

- Reduced anode pressure greatly improves load transient performance at 140% RH.
- "Steady state" performance is also improved w/ reduced anode pressure (+60 mV as anode pressure decreases from 100 kPa to 25 kPa.)
- Reduced anode pressure also assists load transients at 50 °C, 140% RH.





NSTF MEA: 2009 "Best of Class" CCM with 0.05/0.10 mg_{Pt}/cm^2 of PtCoMn on 3M 850EW, 20 µm PEM; Cathode GDL = 3M Baseline; Anode GDL = Freudenberg Type 1

Technical Accomplishments and Progress

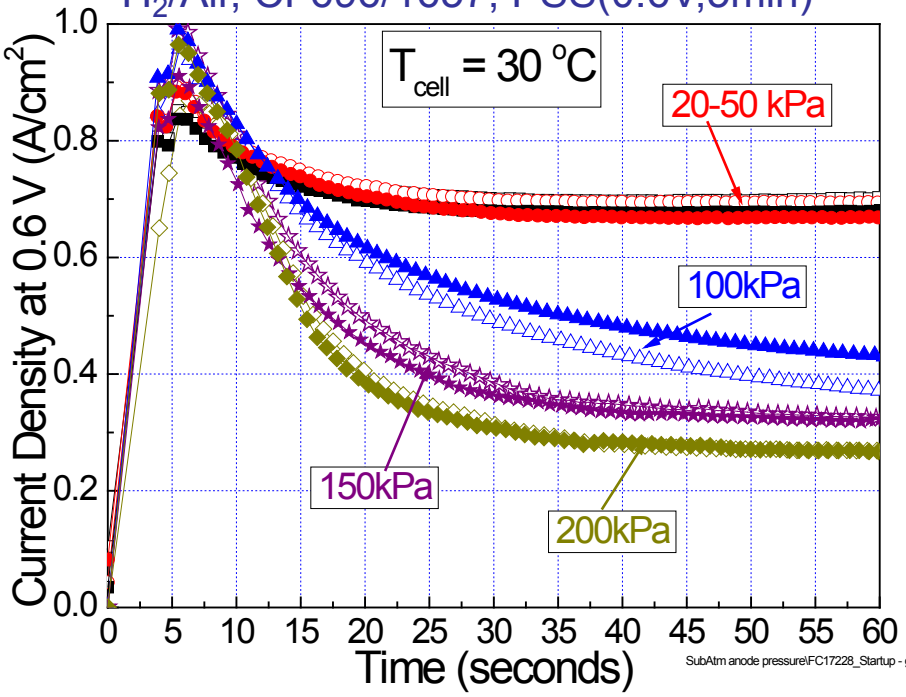
Task 5.2. NSTF MEA Water Management for Cool / Wet Operation

10 °C to 30 °C Dry Start-up Transient Responses: ~ 0.85 V → 0.6 V step

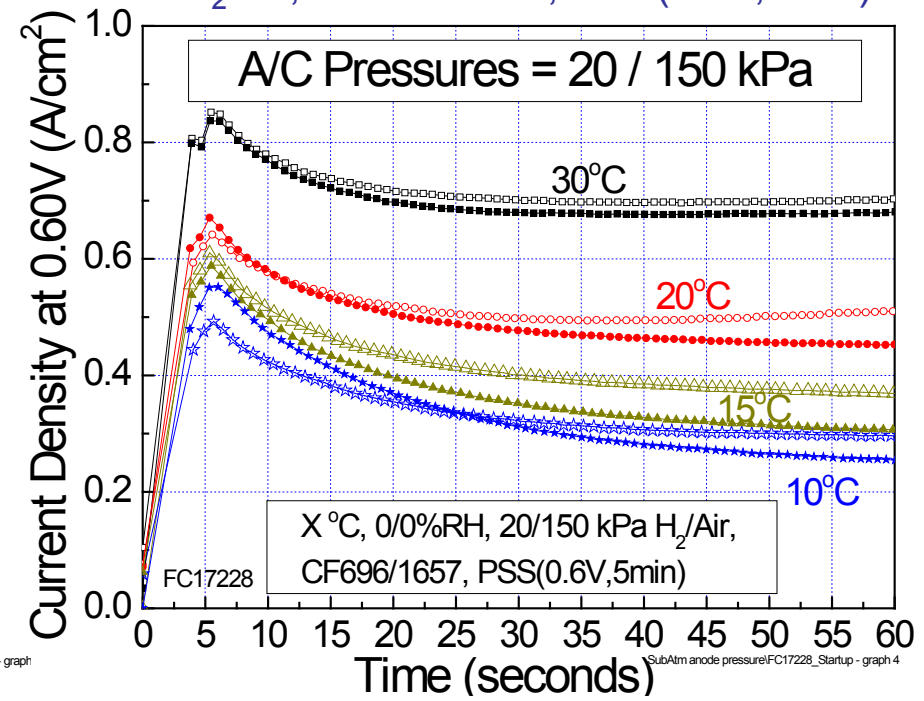
- Test used to mimic system start-up from ambient temperatures.
- MEAs were first preconditioned, cooled to 30 °C, then immediately "started" w/ dry gas.
- Anode pressure has little impact on the "peak" J, but has a strong influence for longer times.

Precondition: 80 °C, 30/30% RH, 696/1657SCCM, GSS(0.05, 5min)

Startup Trans: 30 °C, 0/0%RH, x/150 kPa H_2/Air, CF696/1657, PSS(0.6V,5min)



Startup Trans: X °C, 0/0%RH, 20/150 kPa H_2/Air, CF696/1657, PSS(0.6V,5min)



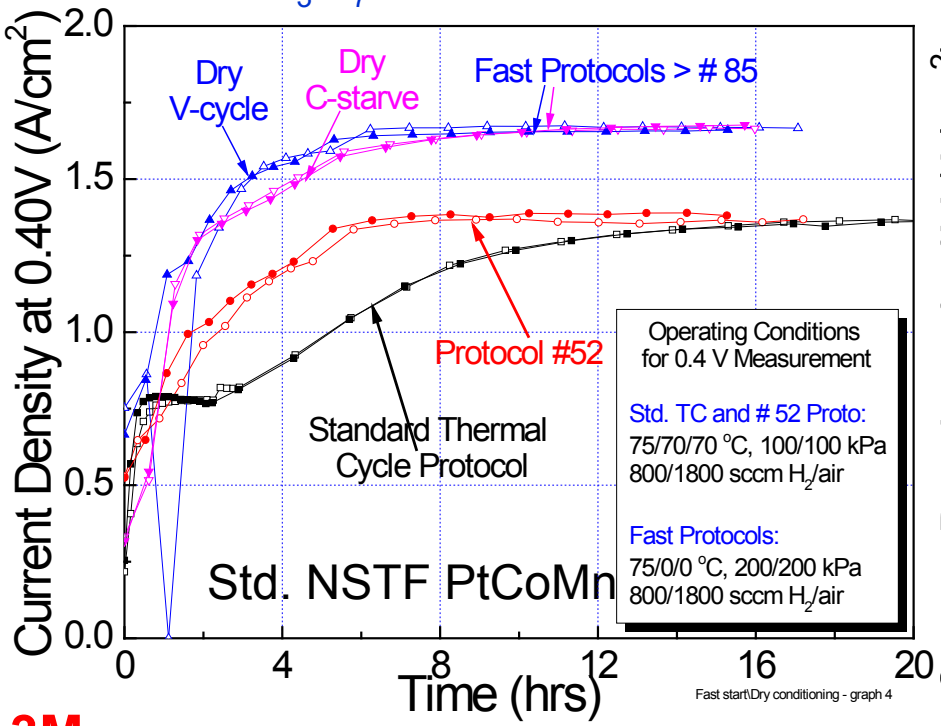
NSTF MEA: 2009 "Best of Class" CCM with 0.05/0.10 mg_{Pt}/cm^2 of PtCoMn on 3M 850EW, 20 µm PEM; Cathode GDL = Baseline 2979; Anode GDL = Freudenberg Type 1

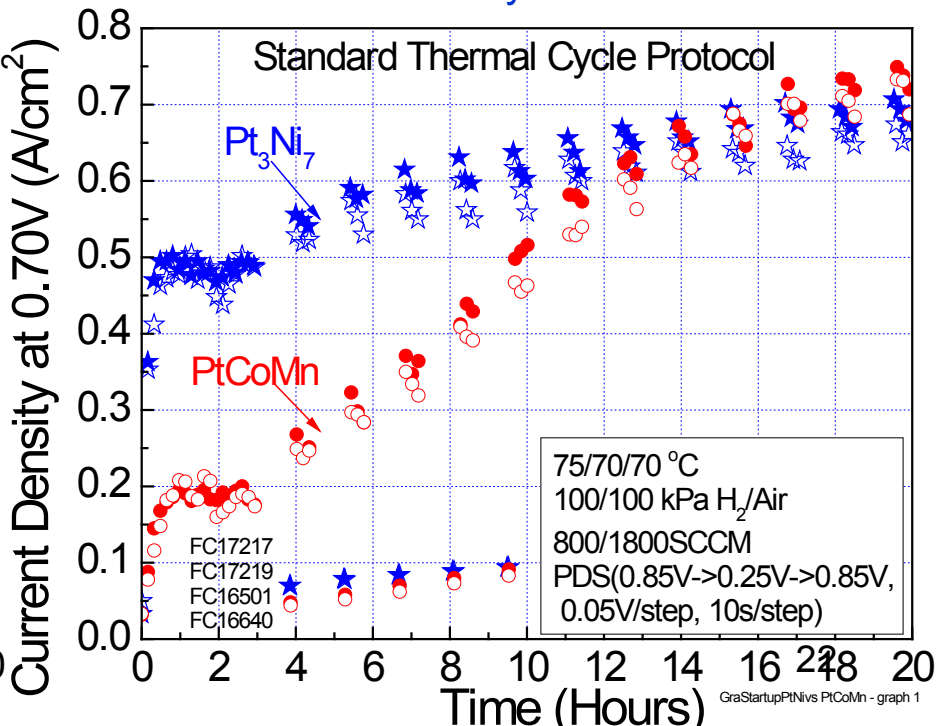
Technical Accomplishments and Progress

Task 6 MEA break-in conditioning

Objective: Dramatically reduce the time and simplify the process for initial break-in conditioning of NSTF catalyst based MEA's.

- Task formally started 3/1/2009 but significant pre-history at 3M
- Standard Protocol from 2000 → Used "Thermal Cycling" protocol w/ water flushing (~ 40 hrs)
- Materials, process factors and test station operational protocols are all important
- Over 80 new protocols evaluated, ~ half since start of task.
- Status: - Conditioning time for PtCoMn reduced by ~ 5x, water flushing eliminated.
  - Multiple performance metrics evaluated and parity nearly met on multiple stations
  - Communicating latest dry, current cycling protocol to customers
  - Pt_3Ni_7 conditions faster than PtCoMn under standard thermal cycles





Collaborations

Subcontractors

- Dalhousie University : Subcontractor, extensive year-round continuous collaboration
- ANL (Markovic/Stamenkovic group): Subcontractor, full year collaboration but periodic
- NASA-JPL: Subcontractor, partial year collaboration due to funding break

System Integrators and stack manufacturers (partial list)

- GM Fuel Cell Activities -Honeoye Falls: Extensive collaboration outside of DOE H_2 program with materials generated at 3M under this contract. Multi-year single cell performance and activity validations, stack testing, cold/freeze start and water management evaluations, PEM and GDL integration, durability testing, fundamental modeling studies.
- Nuvera Fuel Cells – Large area short stack testing-combining open flow field with NSTF MEAs for first time, continuous collaboration past half year.
- Proton Energy Systems – Performance testing of NSTF MEAs in electrolyzers. Continuous testing and periodic interaction past year.
- Giner EC Systems, LLC – Performance testing of NSTF MEAs in electrolyzers. Periodic testing and interaction past year.

National Laboratories

- LBNL, LANL, UTC– Collaborative interactions under LBNL project “FC fundamentals at Low and Subzero temperatures.”
- NIST – Sample supplied for optical method development for CCM Pt loading detection

Future Work

Water Management Improvement

- Continue to combine the improvement factors now identified that significantly enhance cool operation and load transient start-up; determine best synergistic combinations towards the 2010 best of class MEA for final stack testing.

Cathode Catalyst Mass Activity Gain

- Continue to fabricate and optimize catalyst compositions, structures and fabrication processes to exceed target mass activity of 0.44 A/mg_{Pt} and which meet all other performance requirements.
- Down-select the final catalyst and configuration to be scaled-up for the final stack testing.

MEA Integration

- Down-select the final 2010 Best of Class MEA (catalysts for each electrode, membrane, GDLs for each electrode, processes, …) under Task 5, for final stack testing.

Stack testing

- Continue Task 3 short stack evaluations with 2009 Best of Class MEA, upgrading to 2010 best of class MEA.
- Identify OEM stack for final stack testing under Subtask 5.3.

Start-up conditioning and reversible stability

- Continue to develop simplified break-in conditioning protocols and catalyst/membrane components to reduce MEA break-in conditioning time to < 3 hours for full performance.

Project Summary : Status Against DOE Targets – April, 2010 (red = new)

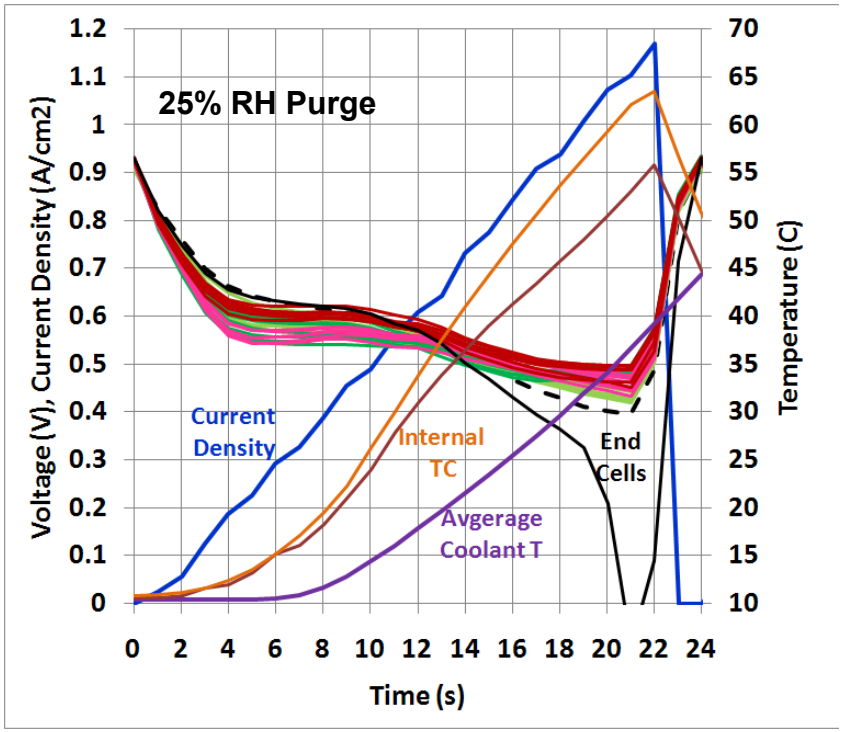
Characteristic	Units	Targets 2010 / 2015	Status: Values for roll-good CCM w/ 0.15mg_{Pt}/cm^2 per MEA or as stated
PGM Total Content	g_{Pt}/kW_e rated in stack	0.3 / 0.2	< 0.18g_{Pt}/kW for cell V < 0.67 V in 50 cm^2 cell at 150kPa inlet. 0.19g_{Pt}/kW, 400 cm^2 OEM short stack
PGM Total Loading	mg PGM / cm^2 total	0.3 / 0.2	0.15, A+C with current PtCoMn alloy
Durability under Load Cycling (membrane lifetime test)	Hours, T ≤ 80°C Hours, T > 80°C	5000 / 5000 2000 / 5000	5000 hrs, 3M PEM (20µm, 850 EW no stabilizers), 50cm^2 , 80/64/64 °C 2000 hrs (OEM short stack,0.1/0.15)
Mass Activity (150kPa H_2/O_2 80°C. 100% RH, 1050 sec)	A/mg-Pt @ 900 mV, 150kPa O_2	0.44 / 0.44	0.24 A/mg in 50 cm^2 w/ PtCoMn 0.40 A/mg in 50 cm^2 with new Pt_3Ni_7
Specific Activity (150 kPa H_2/O_2 at 80°C, 100% RH)	µ A/cm^2-Pt @ 900 mV	720 / 720	2,100 for PtCoMn, 0.1mg_{Pt}/cm^2 2,500 for new Pt_3Ni_7, 0.1mg_{Pt}/cm^2
Accel. Loss: 30,000 cycles, 0.7 – 0.9V step, 30 s hold at 80/80/80°C	- mV at 0.8 A/cm^2 % ECSA loss	< 30mV < 40% / 40 %	~ 0 mV / -10mV, Cat=0.15/0.1 mg/cm^2 ~ 0% / -22%, Cat=0.15/0.1 mg_{Pt}/cm^2
Accel. Loss: 200 hr hold @ 1.2 V at 95°C, H_2/N_2, 150kPa, 80% RH	- mV at 1.5 A/cm^2 % ECSA loss	< 30mV < 40% / 40%	+ 25mV gain at 1.5 A/cm^2 ~ - 17% loss (Cath. = 0.15 mg/cm^2)
OCV hold without PEM failure under 250/200 kPa H_2/air, 90°C, 30%RH	Hours mA/cm^2	200 < 20	610/1200 for Cath. = 0.1/0.15mg_{Pt}/cm^2 H_2 Crossover < 20 mA/cm^2, F^- ion release rate < 0.5 µg/cm^2-day
Accel. Loss: 4,000 cycles 0.6 -1.2V, 20mV/sec, 95/95/95°C, 200kPa,H_2/N_2	Specific Activity % ECSA loss	?? ??	-14 ± 15% loss in mA/cm^2 $_{Pt}$ - 23 ± 8 % loss of $cm^2{}_{Pt}$ / $cm^2{}_{planar}$

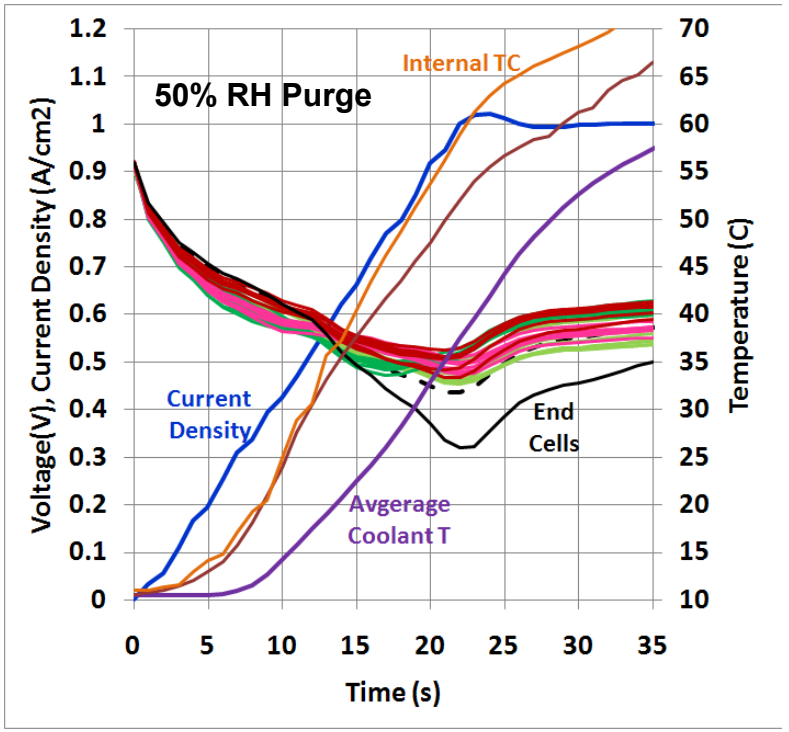
Supplemental Slides

GM Automotive Short Stack Test - Work done outside the 3M/DOE contract.

Cold Start (10 °C) Performance

Purge: High flow rates, 0.05 A/cm², 76C, Cathode Inlet P = 215kPa, 1800s
Cold Start: Wide Open Throttle at 10C



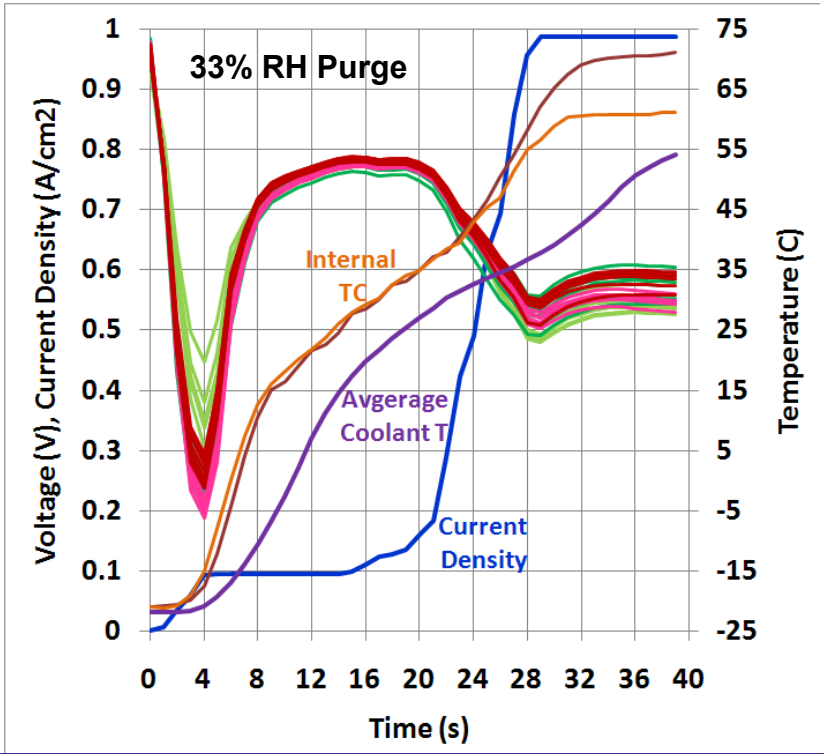


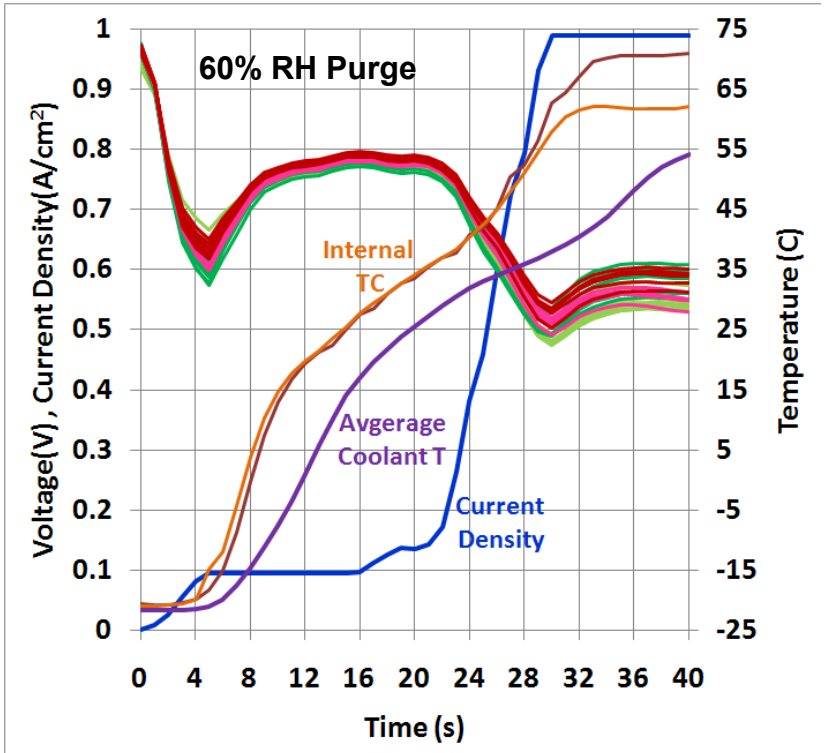
❑ NSTF-specific enabling technology was developed and implemented to demonstrate cold-start of NSTF (under ideal purge conditions) from 10C.

GM Automotive Short Stack Test – Work done outside the 3M/DOE contract.

Freeze-Start (-20C) Performance

Purge: High flow rates, 0.05 A/cm², 76C, Cathode Inlet P = 215kPa, 1800s
Freeze Start: -20C, idle at 0.1 A/cm², Wide Open Throttle at 20C





- NSTF-specific enabling technology was developed and implemented to demonstrate freeze start of NSTF from -20C.
  - Given the transient nature of cold/freeze start, system-level demonstration is desired (testing is planned for 2010 pending success of 80C performance optimization of enabling technology with NSTF)

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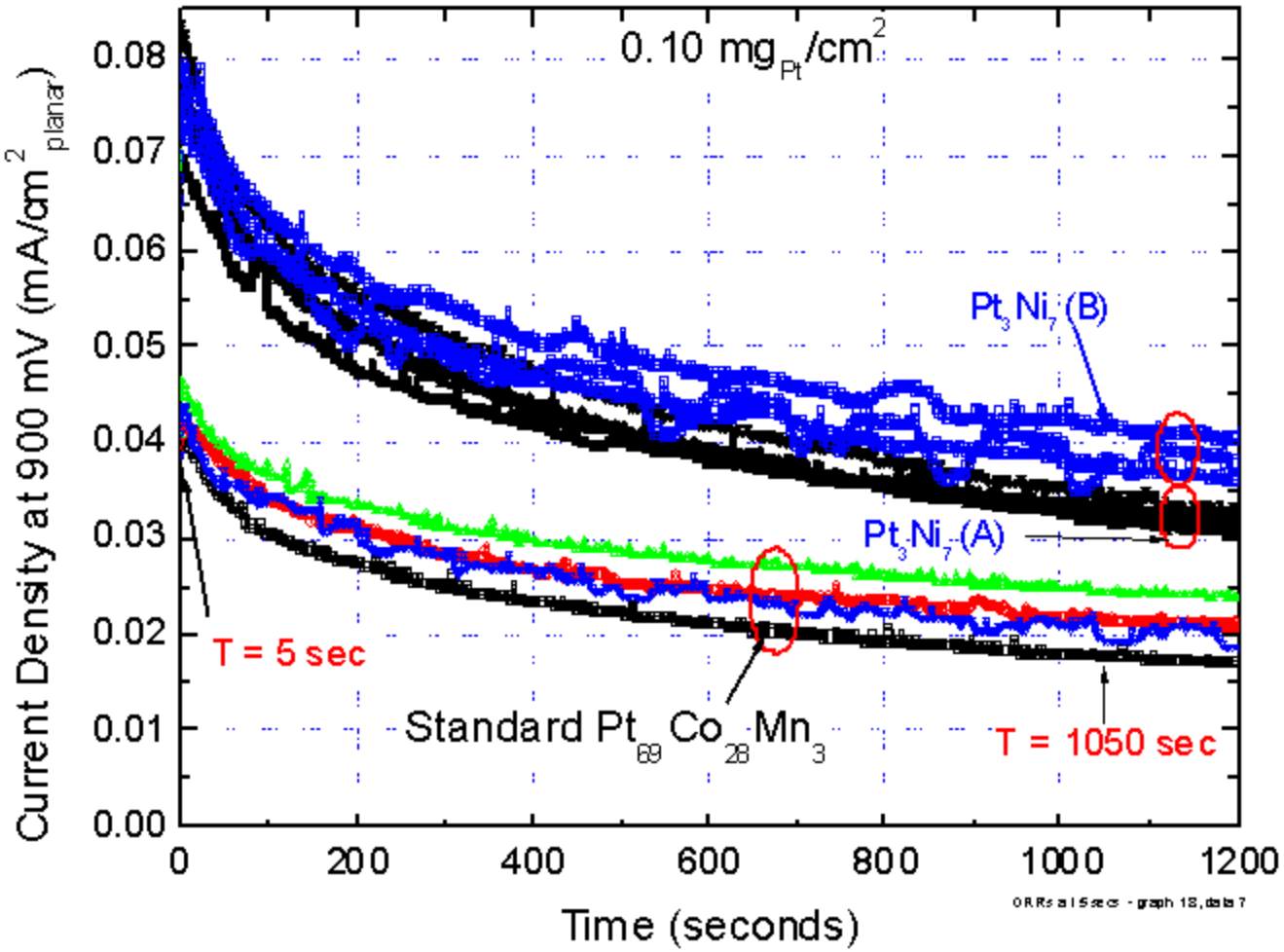
Technical Accomplishments and Progress

Task 1. NSTF Catalyst Activity, Surface Area, Fundamentals

Absolute 900 mV activity current densities for the PtNi and PtCoMn Catalysts

Cell potential set to 0.9 V at t ~ 0 sec.

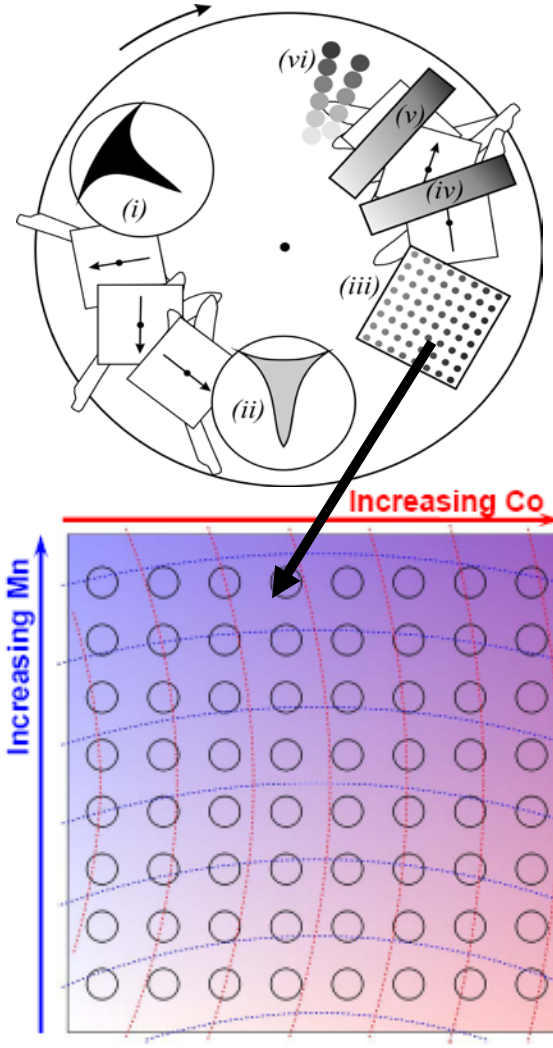


150 kPa H_2/O_2
100% RH

Technical Accomplishments and Progress

Task 1. NSTF Catalyst Activity, Surface Area, Fundamentals

Advanced catalysts by compositional spread screening at Dalhousie University



Background

- 64-electrode arrays of thin film catalysts deposited onto NSTF whiskers, made into MEAs at 3M, tested at Dal. U.
- 158 libraries fabricated and made into CCM through 2/28/10.

Since last AMR:

- Effect of sputtering gas on different alloys
- Generating constant Pt composition binary alloys spreads large enough to make 50 cm^2 electrodes. These are coated onto NSTF sheets for testing at 3M.
- Also coated catalyst compositional spreads onto NSTF whisker coated glassy carbon disks.

DALHOUSIE UNIVERSITY *Inspiring Minds*

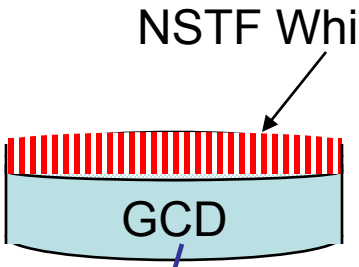
- David Stevens
- Robbie Sanderson
- Gary Liu
- Stephen Wang
- Nils van der Bosch
- Jeff Dahn

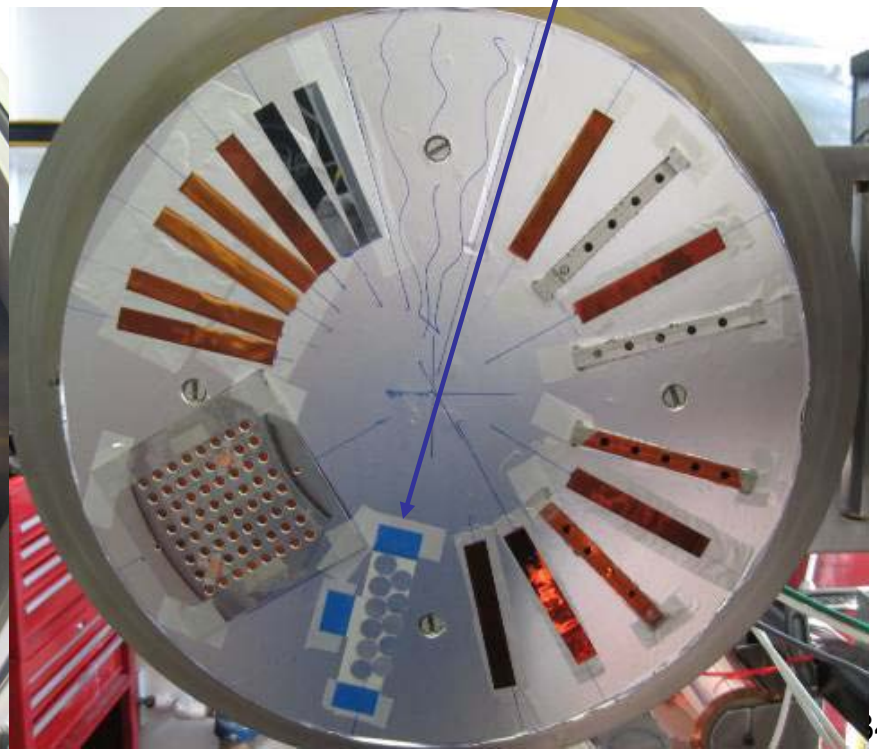
Technical Accomplishments and Progress

Task 1. NSTF Catalyst Activity, Surface Area, Fundamentals

DALHOUSIE UNIVERSITY *Inspiring Minds*

- Dalhousie is also capable of excellent RRDE characterization. Now applied to NSTF routinely.
- New aspect is that 3M grows the whiskers directly on the glassy carbon disk.
- Dalhousie applies the catalyst to be studied to the whiskers by sputtering. Then characterizes in multi-RRDE facilities.





Technical Accomplishments and Progress

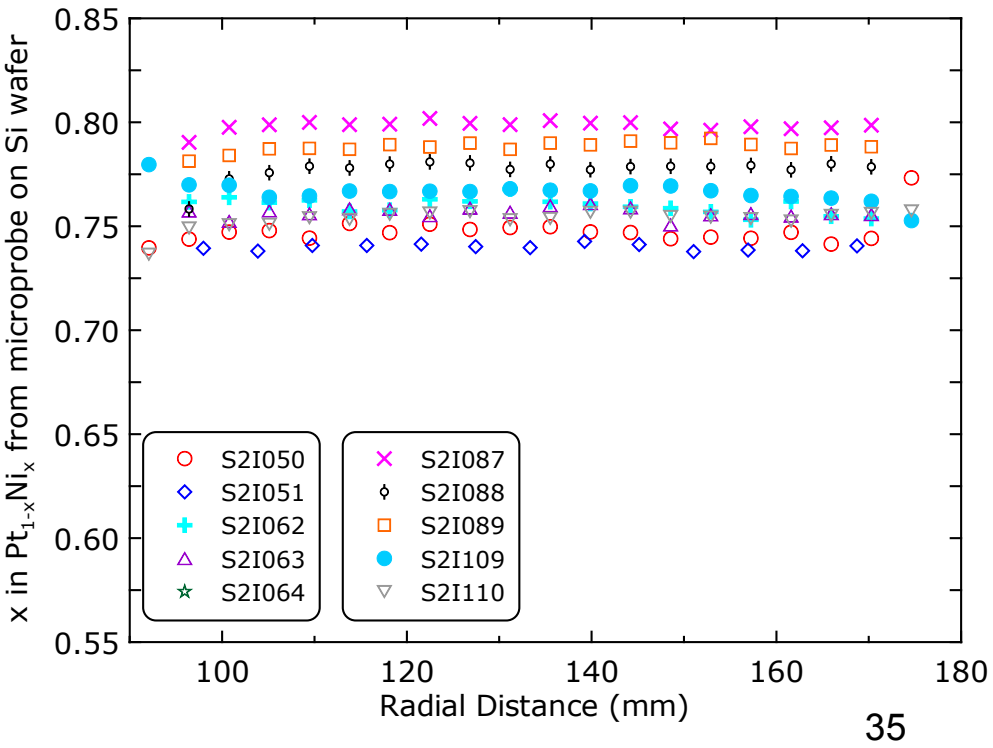
Task 1. NSTF Catalyst Activity, Surface Area, Fundamentals

DALHOUSIE UNIVERSITY *Inspiring Minds*

Key Dalhousie Effort in 2009/10:

- Focus on PtNi system to assist 3M to determine source of unique activity of Pt_3Ni_7.
- Extend study to PtCo to see if it performs similarly.

- Dalhousie fabricated PtNi coated GC disk samples around critical Pt_3Ni_7 composition. Use different deposition constructions.
- Determined exact compositions per disk location by electron microprobe analyses.
- Characterize alloy lattice parameters and grain sizes per disk location and thus composition.
- Measure RDE activity and ECSA versus disk location.
- Perform CV high voltage cycling on RDE disks and monitor changes in activity and ECSA with composition.

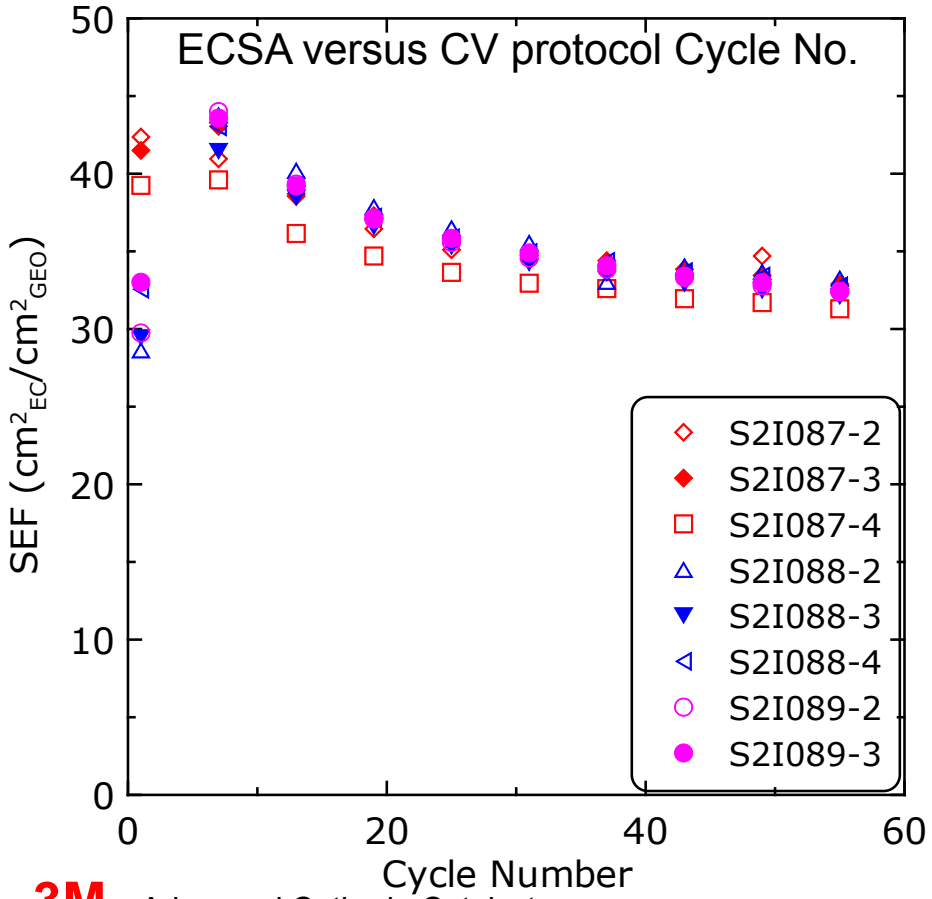


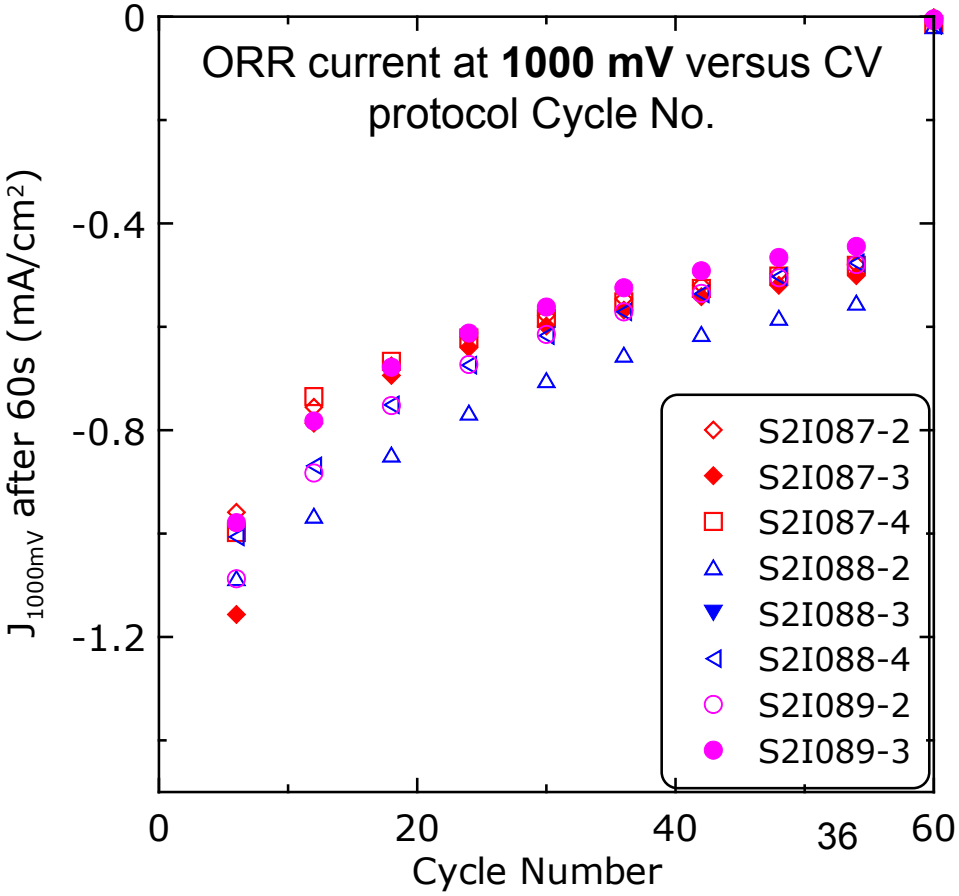
Technical Accomplishments and Progress

Task 1. NSTF Catalyst Activity, Surface Area, Fundamentals

PtNi Gradient Composition Sputtering Runs on GC disks:
ECSA and ORR activity stability with accelerated high voltage cyclic voltammetry (CV) cycling

- RDE surface areas are much higher than 3M measures in fuel cells, 250% larger.
- Very high kinetic currents – measured at 1000 mV !
- Stability of alloy/intermixed compositions due to high voltage CV cycling extracted.





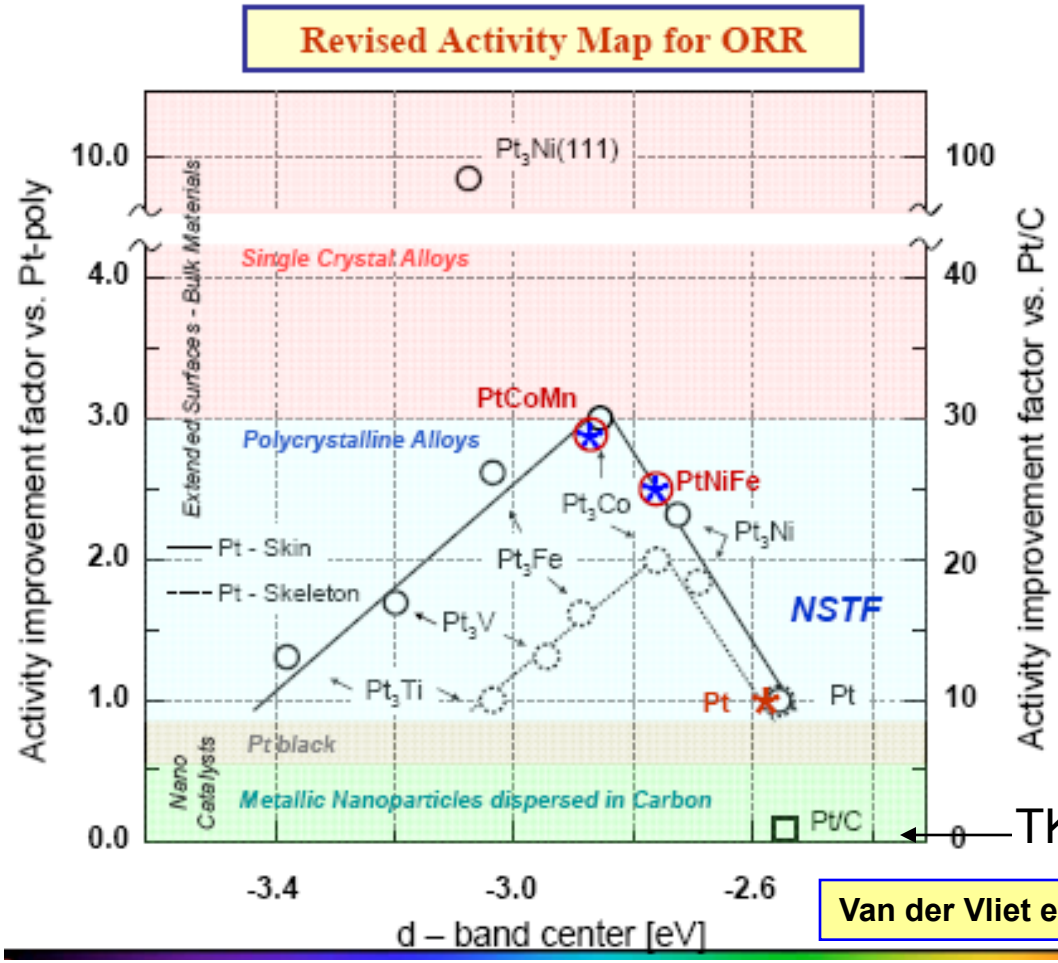
Technical Accomplishments and Progress

Supplemental Slide

Argonne NATIONAL LABORATORY

Task 1. NSTF Catalyst Activity, Surface Area, Fundamentals

- ANL/3M paper at Fall 2009 ECS meeting showed this "Volcano Plot"
- Compares ANL measured NSTF alloy activities and ANL extended surface (bulk) catalyst activities to TKK 5nm Pt/C dispersed catalyst, all measured at ANL.



- $Pt_3Ni_1(111)$ single crystal surface activity is ~100 x more active for ORR than the Pt/C by ANL.
- 3M NSTF PtCoMn and PtNiFe appeared to fit their model for polycrystalline alloys
- Still potential for > 3X more to make NSTF equal to single crystal. Work in progress.

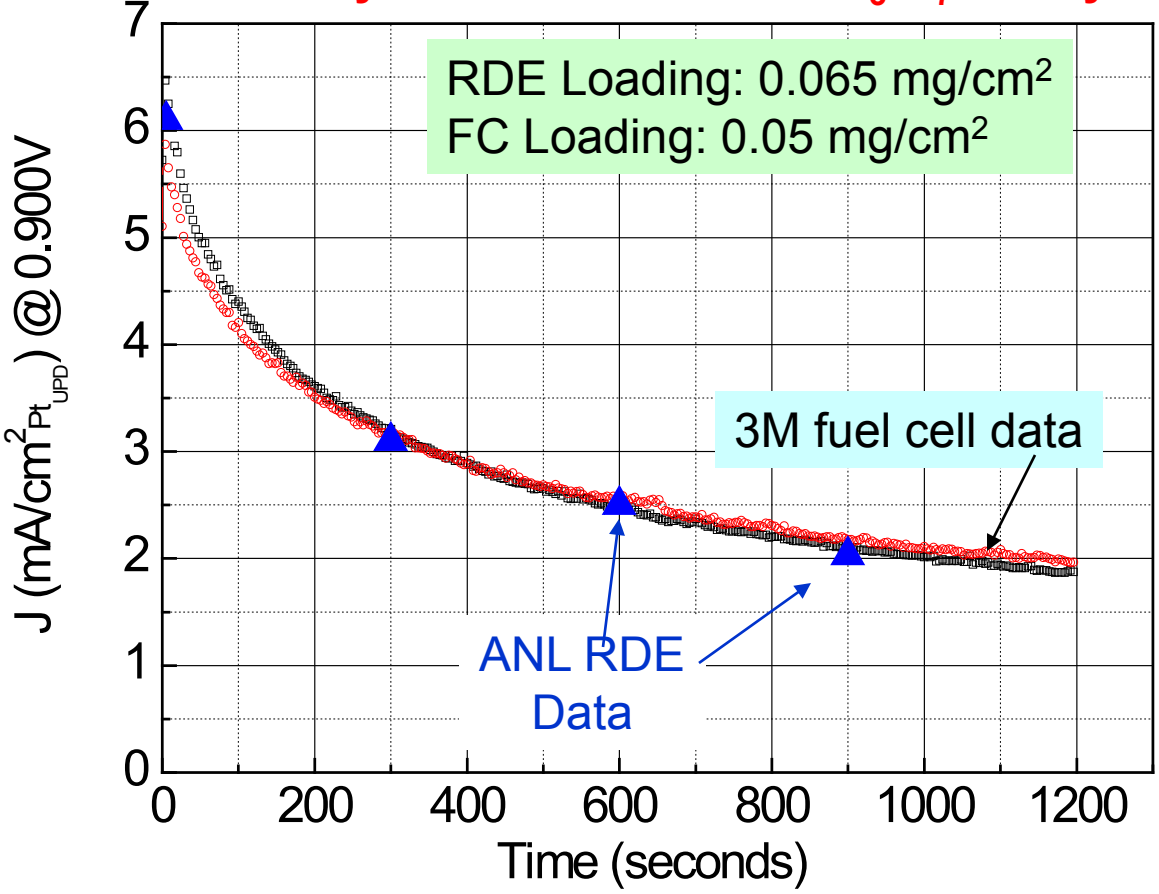
TKK 5nm Pt/C = 1

Van der Vliet et al., 216th ECS Meeting, Vienna, Oct. 2009

Technical Accomplishments and Progress

Task 1. NSTF Catalyst Activity, Surface Area, Fundamentals

ORR Activity Protocol- Comparison of RDE and Fuel Cell Activity Measurements for Pt_3Ni_7 Catalyst.

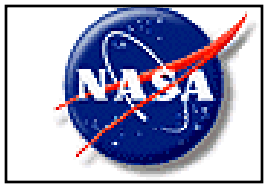


15 min Potential HOLD at 900mV in ANL RDE #90512-1; NSTF PtNi

Excellent quantitative agreement of RDE and Fuel Cell current density decay rate as a function of time at 900mV under the ORR protocol.

Technical Accomplishments and Progress

Task 1. NSTF Catalyst Activity, Surface Area, Fundamentals



JPL

JPL: Charles C. Hays, S. R. Narayanan

- JPL did not receive funding from April 2 to mid-October 2009
- Fractional FTE working on project.
- Therefore limited ability to work on tasks detailed in June 30, 2009 review:

1) Preparation of Pt_3Co and Pt_3Ni samples on NSTF coated glass carbon disks for testing at Dalhousie (see Task 1.2) with their multi-gun deposition capability by:
   a) co-deposition (simulating single target deposition)
   b) and multi-layering deposition
2) Arc-melting precise alloy disks for both fundamental RDE characterization and multi-element sputtering targets they can use to apply to 50 cm^2 samples for 3M to evaluate directly.

- Item 1) completed by JPL, sent to Dalhousie for RDE testing as part of round robin study.
  - Sample was ion-gun sputtered from a single Pt_3Co target
  - Higher Pt loading than typically used (~ 0.34 vs 0.1 mg/cm^2)
  - RDE measurements at Dalhousie of JPL sample show very high ECSA and activity due to high loading.
- Item 2) and other tasks to be completed pending additional funding,

Technical Accomplishments and Progress

Task 2 – Accelerated Durability Testing

Shiva 1: 80 °C Load cycling protocol at 80/64/64 °C

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

Shiva 2: 30 – 120 °C load cycling protocol

Cycles/Day	Cell Temp	Conditions Description	Time
1	80	Long scan @ 0.6A/cm2 to used collect fluoride data	4.5 hrs
1	80	Short anode overpressure OCV to monitor lifetime	5 min
4	120	Hot Temperature Low RH to degrade MEA (up to 80°C dewpoint)	15 hrs
	30	Low Temperature to Thermal and Humidity Cycle MEA	
2	80	Load Cycle at Various RH to monitor performance	4.5 hrs

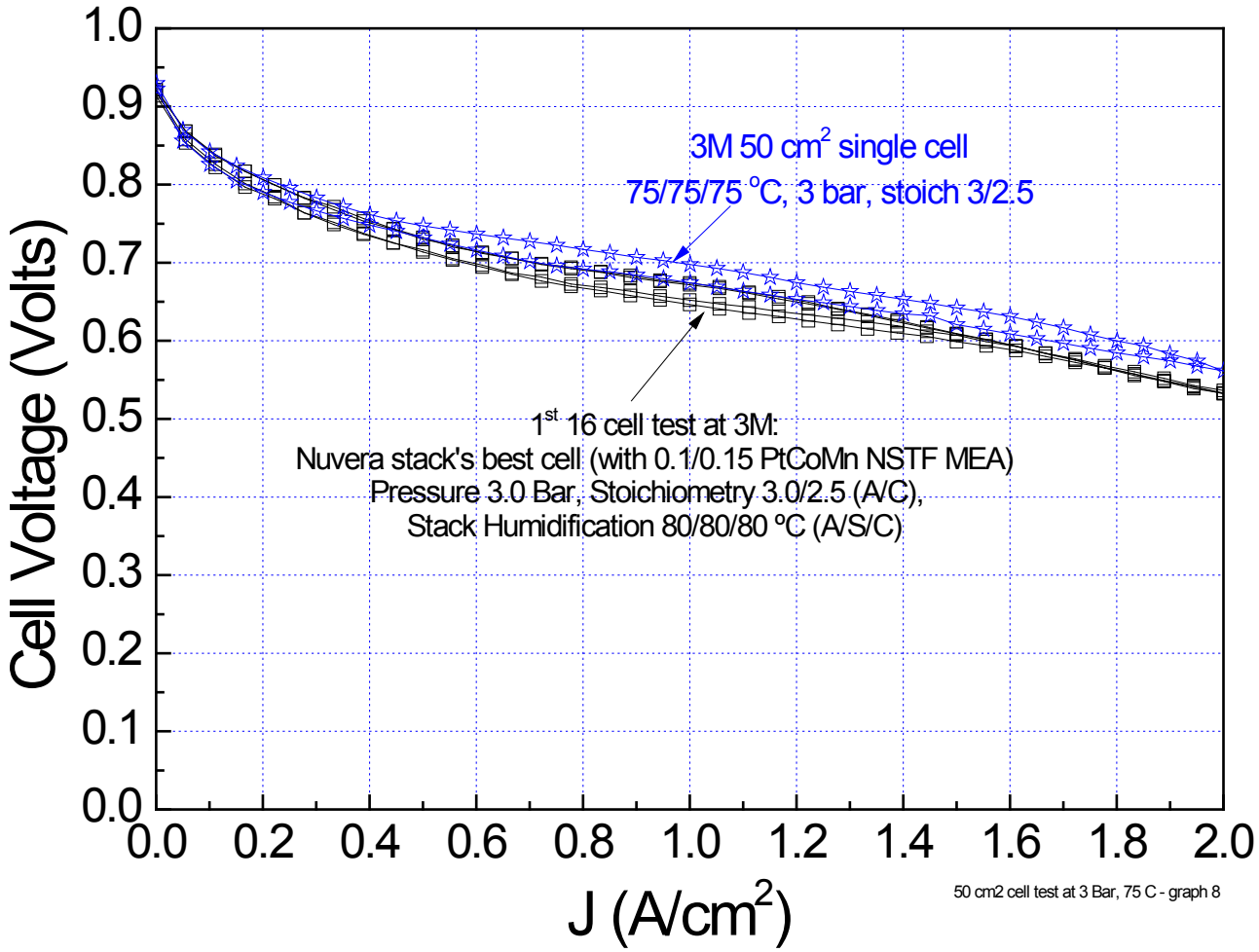
Task 3 Full Size (> 250 cm^2) Single or Multi-Cell Tests

3

NUVERA FUEL CELLS

Subtask 3.2 Large area short stack durability tests

- Under improved operating conditions with the 1st stack, the best cell performance approaches the single cell results more closely.



Technical Accomplishments and Progress

Task 5.1 NSTF/PEM Integration and Process Scale-up Related Activities

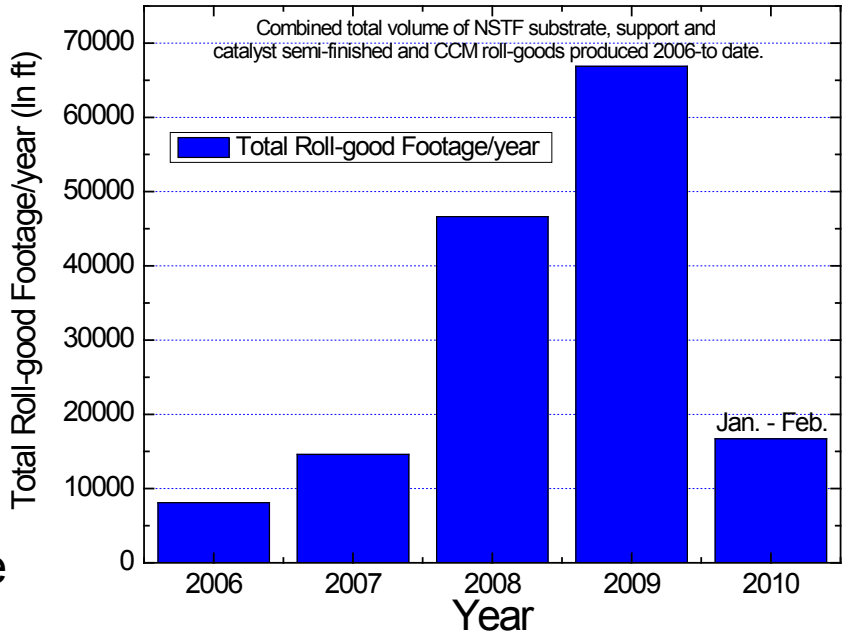
Focus Areas Since Last Annual Review:

PEM integration:

- Evaluations of NSTF with other low EW 3M PEM's
- Evaluations with experimental PEM's.
- Catalyst coated membrane formation

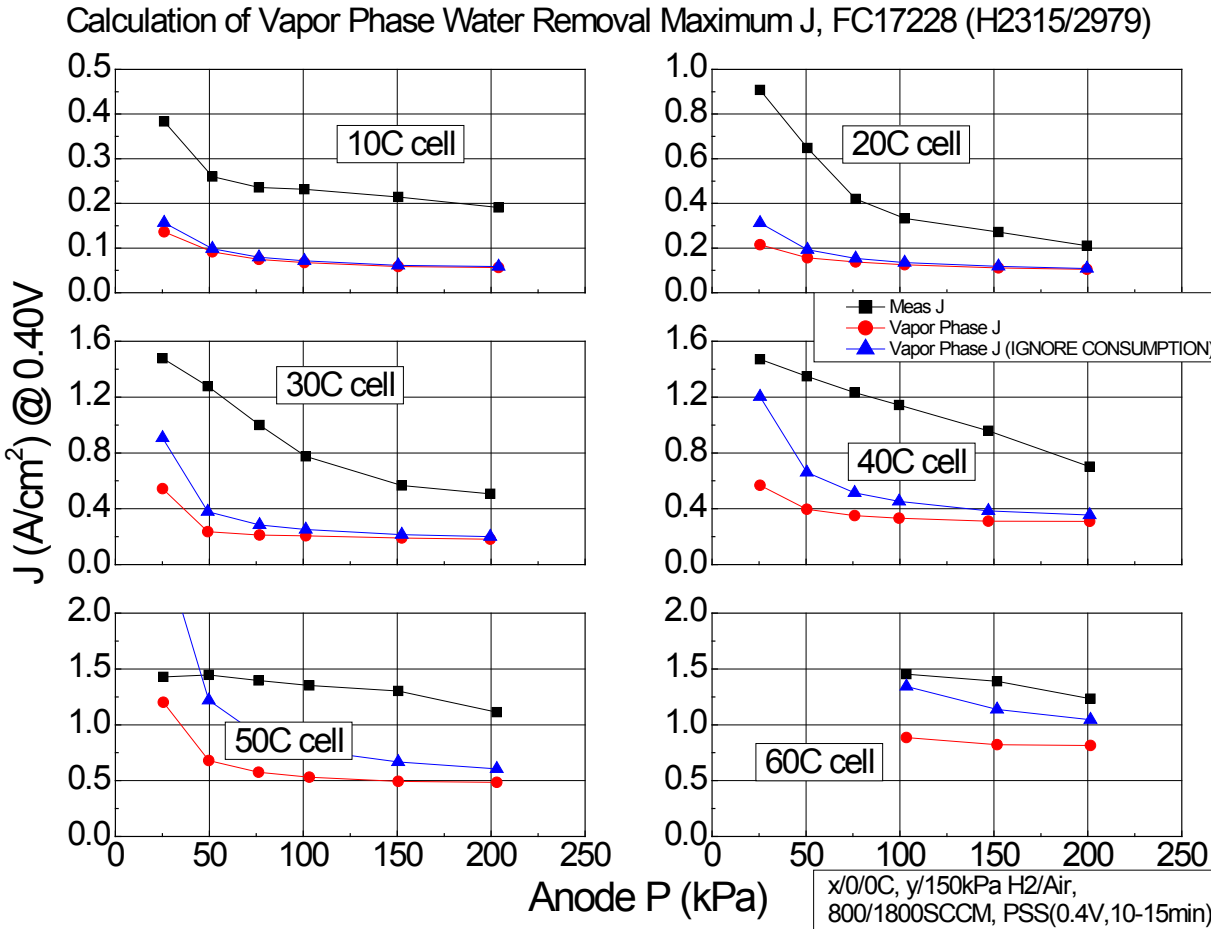
Membrane-electrode integration and CCM scale-up:

- Process improvements implemented for roll-good CCM component fabrication and CCM fabrication.
- Produced 37,000 linear ft combined of NSTF substrate, coated catalyst supports, and catalyst coated membrane for process development, qualification and customer use since last FCTT review (partially produced for the current contract).



Technical Accomplishments and Progress

Task 5.2. NSTF MEA Water Management for Cool / Wet Operation



Steady State vs. Anode Pressure and Cell Temperature:

Compares Vapor Phase –Only Supported Current Density to Measured Current Density.

- As the anode pressure is decreased, it's capability to remove water via vapor phase increases. To evaluate the magnitude of the vapor phase removal, the above charts compare the measured J (black) to the calculated maximum J which could be supported by vapor phase alone, calculated either on the cell outlet boundary conditions (red), or to the cell inlet conditions (ignore gas consumption, blue).
- These calculations indicate that vapor phase removal is a minority fraction until 50-60 °C. Additionally, the increase in measured J with decreasing Pa is generally faster and of a different shape than the vapor phase removal J profiles.
- While vapor phase removal likely is beneficial, it does not appear to be the most important mode to enable the improved performance, which reinforces the concept of liquid water removal via the anode.

Technical Accomplishments and Progress

Task 5.2. NSTF MEA Water Management for Cool / Wet Operation

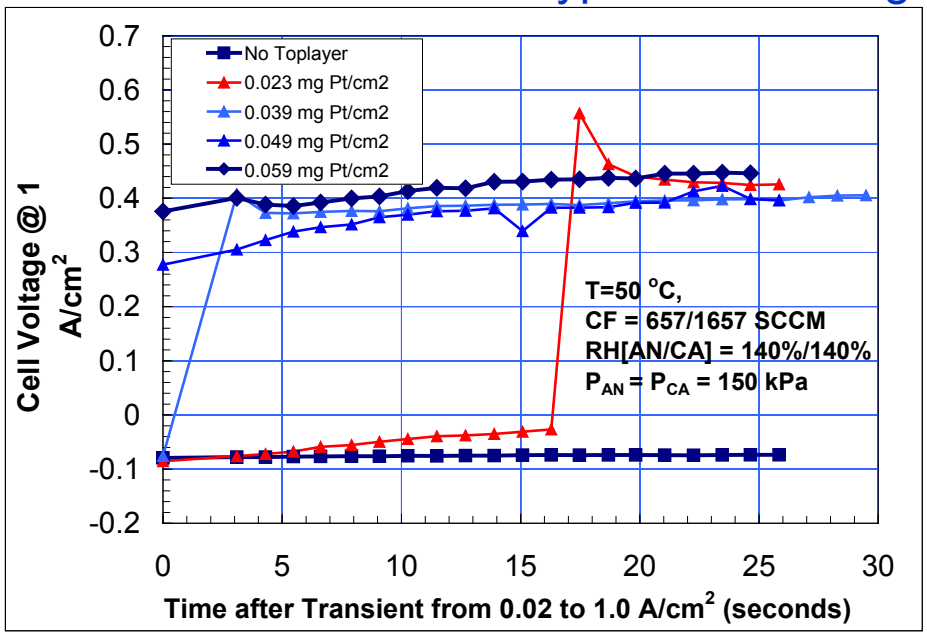
Alternative approach for improved NSTF water management investigated:

- Cathode Modification Instead of Anode GDL/Pressure-

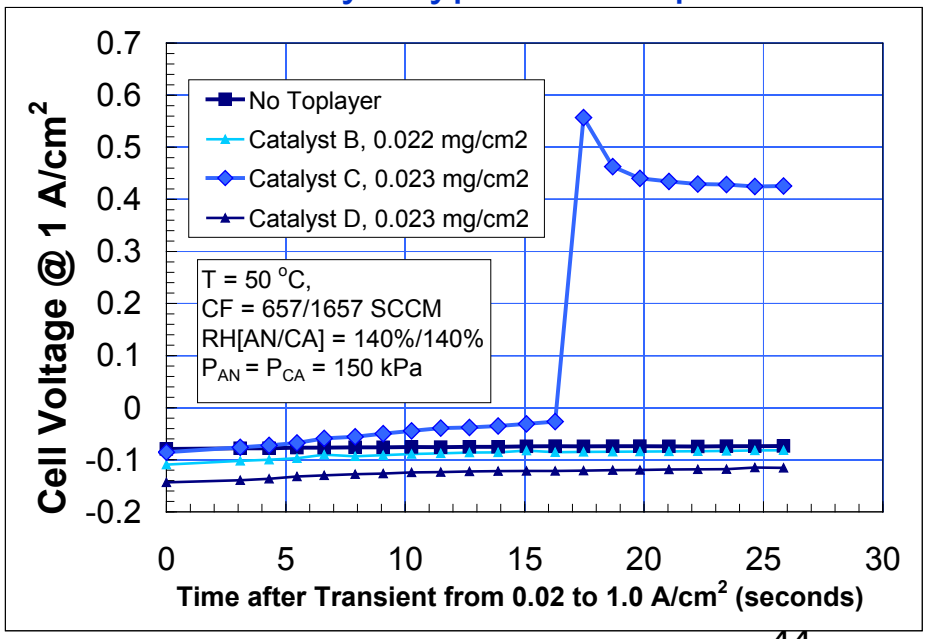
- A hybrid or gradient cathode catalyst: NSTF + top layer Pt/C catalyst (re: US 6,238,534)
- Best gradient construction found also passes 50 °C Wet Load Transient with one specific type of Pt/C catalyst (type C in bottom right graph).

50 °C Wet Load Transient
NSTF CCM: 0.05/0.10 PtCoMn in 20 µm 3M 850 EW PEM

Transient behavior with type C vs loading



Pt/C catalyst type C is Superior



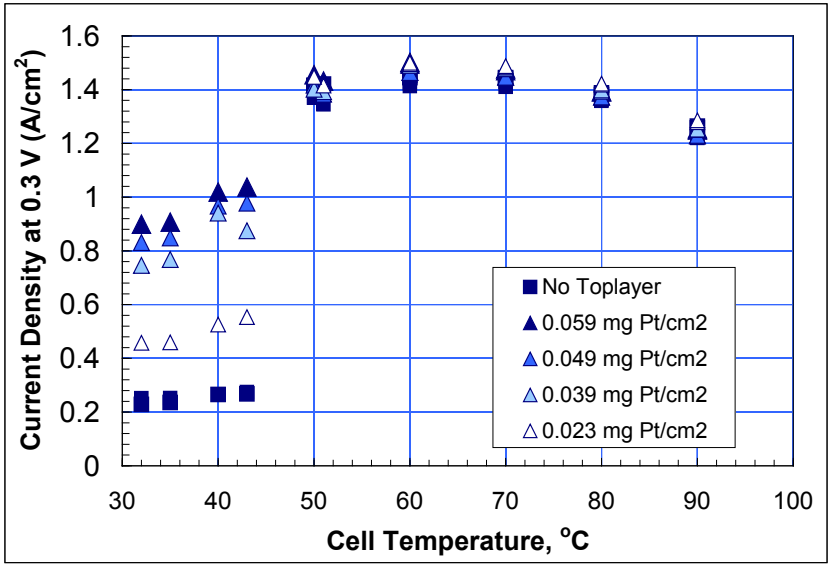
Technical Accomplishments and Progress

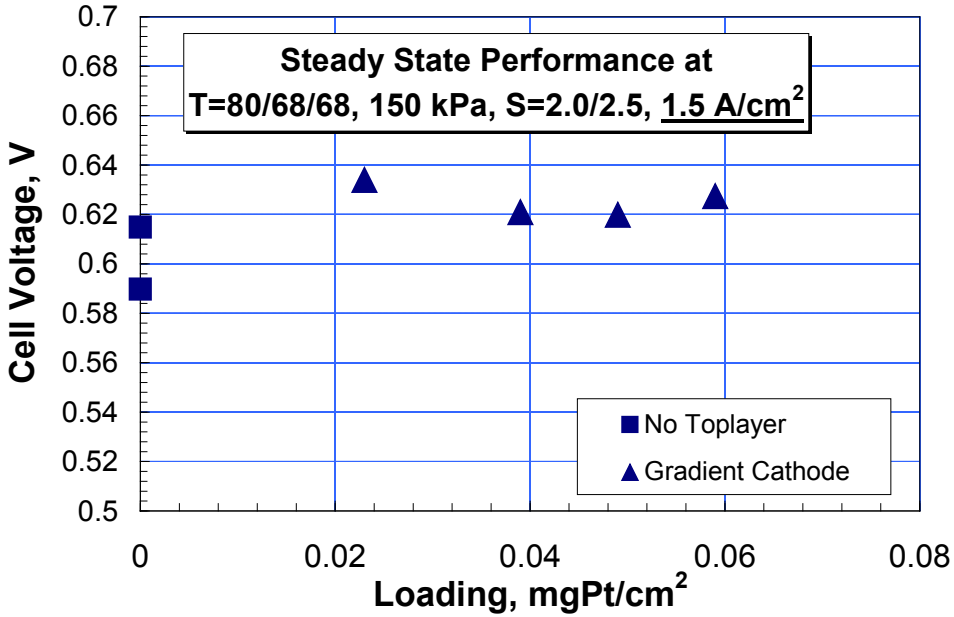
Task 5.2. NSTF MEA Water Management for Cool / Wet Operation

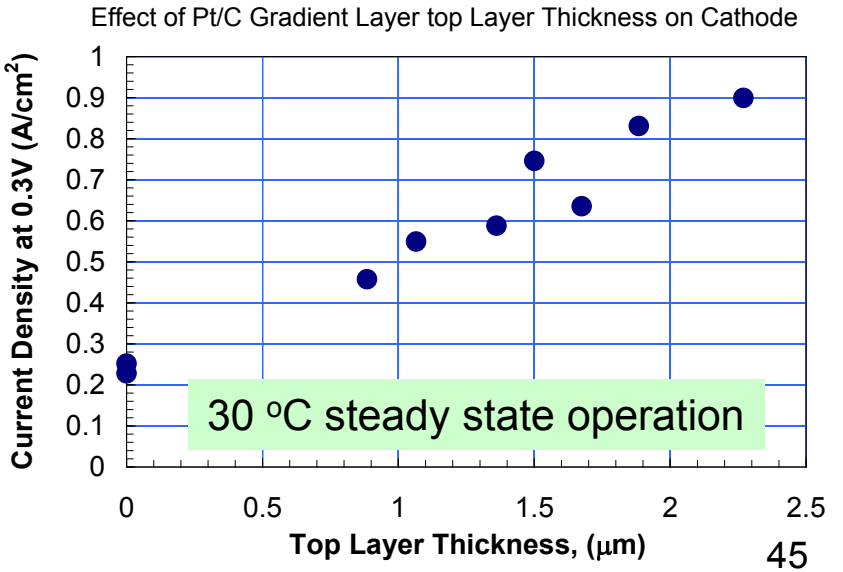
Alternative approach for improved NSTF MEA water management investigated: (continued)

- Cathode Modification Instead of Anode -

- A hybrid or gradient cathode catalyst: NSTF + top layer Pt/C catalyst (re: US 6,238,534)
- Best gradient construction (on 2009 best of class CCM) can give 1 A/cm^2 at 30 °C with no loss of performance at 80 °C compared to just baseline NSTF (2009 best of class CCM).
- Type of Pt/C catalyst is critical for best effect, and higher loading helps proportionately.







Technical Accomplishments and Progress

Task 6. MEA break-in conditioning

Protocols

- Protocols' primary repeat sections are shown.
- Protocols are repeated until stable performance is achieved.
- Reactant flows shown for 50cm^2 cell.

Standard Thermal Cycle

```
//WARMUP WITH  POL. CURVES AND V HOLDS//
SET_CELL_TEMPERATURE (75C)
SET_ANODE_FLOW (800SCCM)
SET_CATHODE_FLOW (1800SCCM)
SET_ANODE_HUMIDIFICATION (70C)
SET_CATHODE_HUMIDIFICATION (70C)
SET_ANODE_PRESSURE (0 psig)
SET_CATHODE_PRESSURE (0 psig)
COUNT= (0); WHILE_COUNT_< (4)
    COUNT+1 ()
    POL. CURVE (0.85V->0.25V->0.85V, 0.05V/STEP, 10S/STEP)
    V=0.4V,5min
END_WHILE_COUNT ()
//COOL TO ROOM T, GASES OFF, LIQ WATER INJECT//
SET_CELL_TEMPERATURE (25C)
SET_ANODE_FLOW (0SCCM)
SET_CATHODE_FLOW (0SCCM)
SET_ANODE_HUMIDIFICATION (0.26CC/MIN)
SET_CATHODE_HUMIDIFICATION (0.40CC/MIN)
J=0A/cm2, 45min
```

Fast Condition (Dry, Starve)

```
//WARMUP WITH J (CURRENT DENSITY) CYCLE//
SET_CELL_TEMPERATURE (75C)
SET_ANODE_FLOW (140SCCM)
SET_CATHODE_FLOW (124SCCM)
SET_ANODE_HUMIDIFICATION (DRY)
SET_CATHODE_HUMIDIFICATION (DRY)
SET_ANODE_PRESSURE (14.7 psig)
SET_CATHODE_PRESSURE (14.7 psig)
COUNT= (0); WHILE_COUNT_< (22)
    COUNT+1 ()
    J=0A/cm2, 2s
    J=0.1A/cm2, 10s
    J=0.2A/cm2, 3s
END_WHILE_COUNT ()
//PERFORMANCE CHECK//
SET_ANODE_FLOW ( 800SCCM)
SET_CATHODE_FLOW (1800SCCM)
V=0.4V, 5min
//MORE J CYCLE AT 75C//
SET_ANODE_FLOW (140SCCM)
SET_CATHODE_FLOW (124SCCM)
COUNT= (0); WHILE_COUNT_< (22)
    COUNT+1 ()
    J=0A/cm2, 2s
    J=0.1A/cm2, 10s
    J=0.2A/cm2, 3s
END_WHILE_COUNT ()
//COOL CELL TO 55C WITH J CYCLE//
SET_CELL_TEMPERATURE (55C)
COUNT= (0); WHILE_COUNT_< (44)
    COUNT+1 ()
    J=0A/cm2, 2s
    J=0.1A/cm2, 10s
    J=0.2A/cm2, 3s
END_WHILE_COUNT ()
```