Power for the Real World

2011 Annual Merit Review
DOE Hydrogen and Fuel Cells and
Vehicle Technologies Programs

Advanced Cathode Catalysts and Supports for PEM Fuel Cells

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3M Company
May 10, 2011

Powered by 3M

Project ID: FC 001

DOE Hydrogen Program

Overview

Timeline

- ❑ Project start : April 1, 2007
- ❑ Project end : (86% complete)
  - Original - March 31, 2011
  - w/No Cost Ext. – Dec. 31, 2011

Budget

- ❑ Total Project funding **$10.742 MM**
  - $8.593 MM DOE and FFRDC
  - $2.148 MM 3M share
- ❑ Allocated in FY10: $ 1,205,281
- ❑ Invoiced in FY10: $ 1,303,430
- ❑ Remaining for FY11: $1,439,013

Partners

- ❑ Dalhousie University (J. Dahn, D. Stevens)
- ❑ JPL (C. Hays)
- ❑ ANL (N. Markovic, V. Stamenkovic)
- ❑ Project Management – 3M

Barriers

A. Electrode and MEA Durability

B. Stack Material & Mfg Cost

C. Electrode and MEA Performance

DOE Technical Targets

Electrocatalyst/ MEA		2015 old	2015 new
Lifetime Hrs, > 80°C		5000	5000
Mass Activity(A/mg)		0.44	0.44
PGM, (g/KW rated)		0.2	0.125
Performance (W/cm^2)	@ Rated	1	1
	@ 0.8V	0.25	0.25

Additional Interactions

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

Relevance and Approach

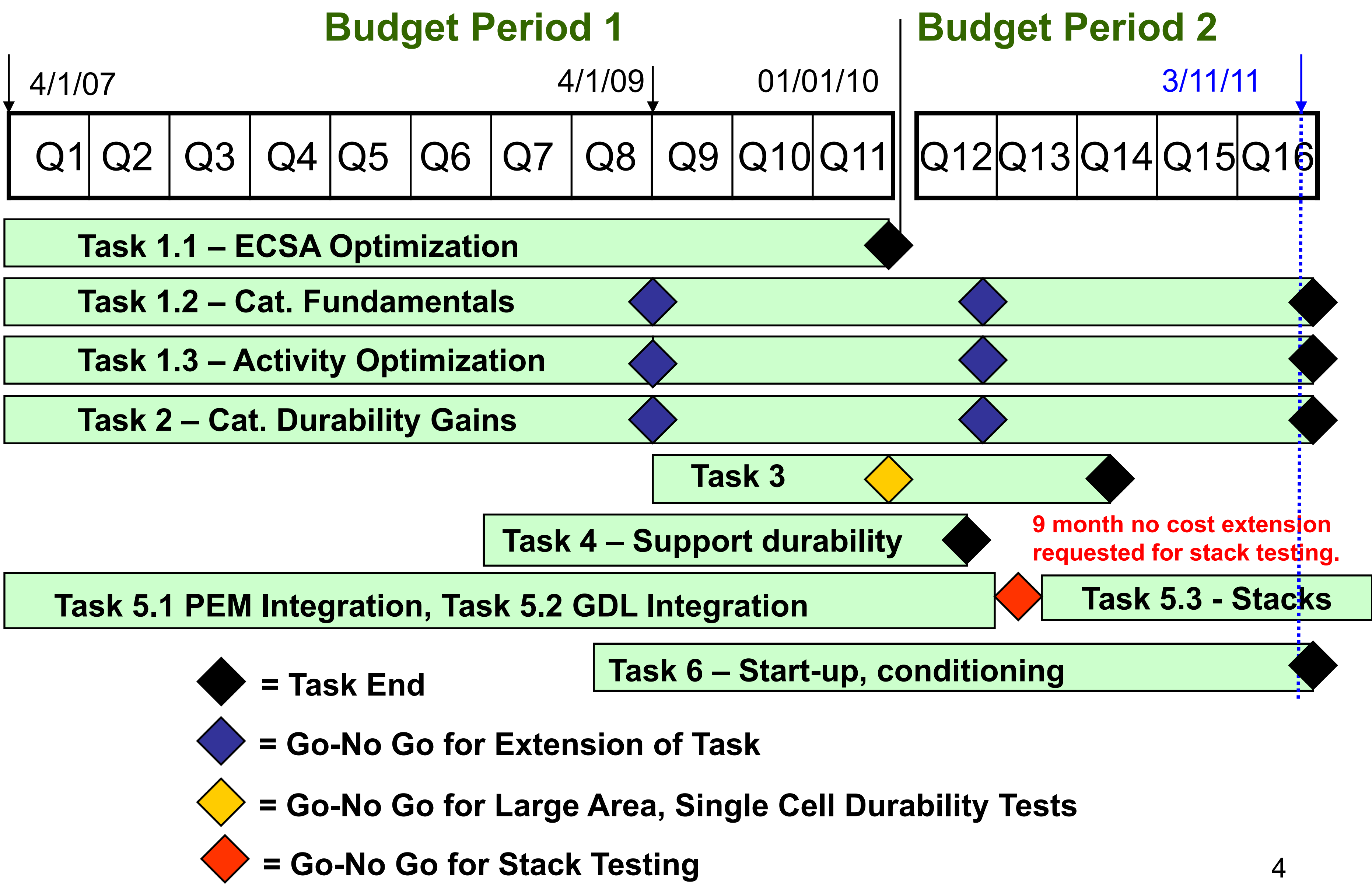
Objectives: Development of a durable, low cost, high performance cathode electrode (catalyst and support), that is fully integrated into a fuel cell membrane electrode assembly with gas diffusion media, fabricated by high volume capable processes, and is able to meet or exceed the 2015 DOE targets.

Approach: Development of advanced cathode catalysts and supports based on 3M's nanostructured thin film (NSTF) catalyst technology platform. Optimize integration with membrane and gas diffusion media for best overall MEA performance, durability and cost.

Primary Focus Topics for Past Year:

- Water management improvements for cool/wet transient operation through materials, electrode structure and boundary condition optimization and understanding.
- Continued multiple strategies for increasing NSTF catalyst activity, surface area and durability, with total loadings of $\leq$ 0.25 mg-Pt/cm^2 /MEA.
  - Focus on key NSTF alloy catalyst compositions and process improvements discovered and developed in 2009/2010.
- Continued AST's to benchmark durability of new NSTF MEA configurations
- Down-select components for new 2010 "best of class" MEA for final stack testing in 2011.
- Continue fundamental studies of the NSTF catalyst activity for ORR in general, and methods for achieving the entitlement activity for NSTF catalysts.

Relevance and Approach: Project Timeline and Milestones



Major Technical Accomplishments Since Last Review (6/8/10)

- **Water management for cool/wet transient operation** (Task 5.2)
  - Developed key strategy for reducing cathode flooding at cool temperatures by taking product water out the anode, the **"water-out-anode" mode**.
    - Demonstrated that anode GDL was most critical component for water-out-anode strategy. Significantly improved cool/wet performance at ambient pressure.
    - Developed cathode gradient catalyst hybrid construction that also dramatically helps water management at low temperature as well as high temperature.

- **New catalyst activity and understanding; annealing and process scale-up** (Task 1.3)
  - Extended enhanced catalyst deposition process improvement (P1) from pure Pt to PtCoMn and obtained same dramatic gains in Pt(hkl) grain size and surface smoothing with simpler, more cost effective coating process.
  - Surface Energy Treatment (SET) process scaled up for roll-to-roll catalyst annealing. Significantly improves ORR activity of some alloys, more than others.
  - Demonstrated Pt_3Ni_7 alloy catalyst mass activities in 50cm^2 cells ranging from 0.35 $\pm$ 0.06 A/mg to 0.59 $\pm$ 0.08 A/mg at 3M and GM depending on lab, protocol and loading measurement. Gain in ORR activity derived from SET catalyst annealing process.
  - Validated Pt_3Ni_7 alloy peak composition in compositional spread RDE measurements on NSTF whiskers (Dalhousie).
  - Obtained first confirmation of Pt_3Ni_7 composition at nm scale of whiskerettes and Pt enrichment of whiskerette tips (JPL/Cal Tech).

Technical Accomplishments and Progress

Continued ---- Major Technical Accomplishments Since Last Year

- **Catalyst and MEA durability with preliminary 2010 "best of class MEAs" (**Task 2)
  - OCV Hold: Demonstrated 12 ± 5 % OCV voltage loss after 500 hours at 250/200 kPa H_2/air, 90°C, 30%RH.
  - 1.2 V hold: Demonstrated 10 mV loss at 1.5 A/cm^2, 10% loss of ECSA and 10 % loss of mass activity after 400 hr at 1.2 V at 80C, 150kPa, 100% RH.
  - 30,000 CV cycles: Demonstrated 40 mV loss at 1.5 A/cm^2, 18% loss of EC surface area, and 48 % loss of mass activity under 30,000, 0.6-1.0-0.6 V cycles at 50mV/sec, 80/80/80°C.
  - Demonstrated load cycling lifetimes of 9000 hours with 2009 "Best of Class" catalyst loadings (0.05 / 0.10 mg/cm^2) in non-supported 3M PEM with chemical stabilizers.
- **Membrane-electrode integration and CCM scale-up** (Task 5.1)
  - Produced 49,000 linear ft combined of NSTF substrate, coated catalyst supports, and catalyst coated membrane for process development, qualification and customer use.
- **2010 "Best of class" MEA Down-selection for Final Stack Testing (**Task 5.3)
  - Defined and implemented major screening programs for integration of all MEA components for 2010 best of class MEA for final stack testing.
  - Final short stack testing activities initiated at GM.

Technical Accomplishments and Progress

Topics Discussed in This Update

Task 1.3 - Catalysts for increased ORR activity and stability

- As-deposited Pt_3Ni_7 (2 slides)
- Catalyst deposition process advances: New P1 process vs. standard P4 (4 slides)
- Surface energy treatment (SET) process for catalyst annealing (4 slides)

Task 2 – Durability testing

- Membrane durability : OCV hold - 90°C, 30% RH, 22.1/14.7 psig H_2/air (2 slides)
- Support stability : 1.2 V hold (new DOE test protocol) (2 slides)
- Catalyst stability against dissolution: CV cycling (2 slides)
  - 0.6 – 1 V, 30,000 cycles at 80°C
- Load cycling : MEA lifetime (1 slide)

Task 5.1/5.2/5.3 – All Aspects of MEA integration and Preparation for Final Stack Testing

- 2010 "Best of Class" Down-select for final stack testing (5 slides)
  - Objective, Process and Schedule
  - MEA component factors and testing criteria
  - Example of component screening results

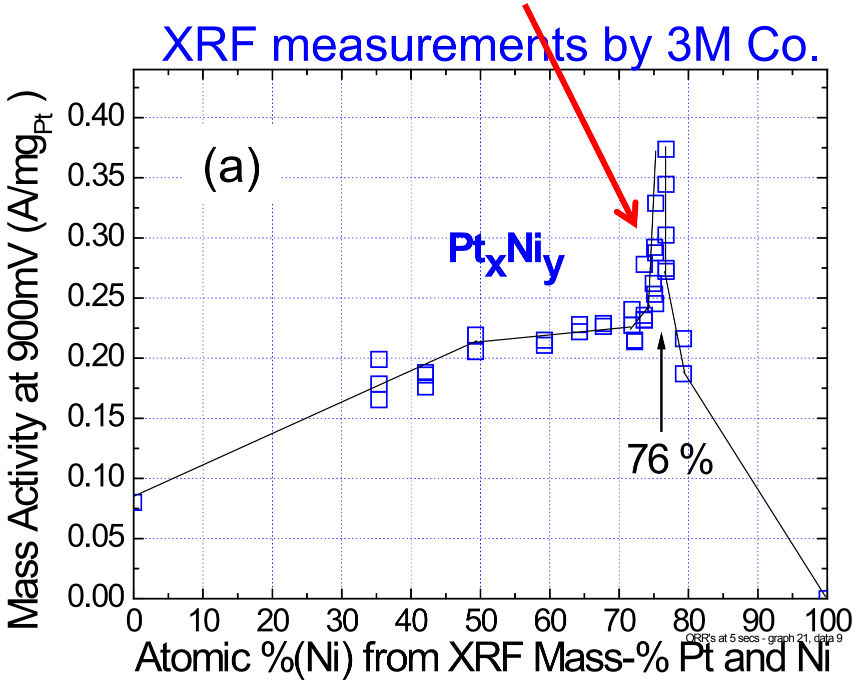
Too much material, only high level summary of the down-select process.

Task 1.3 – New catalysts for increased ORR activity and stability

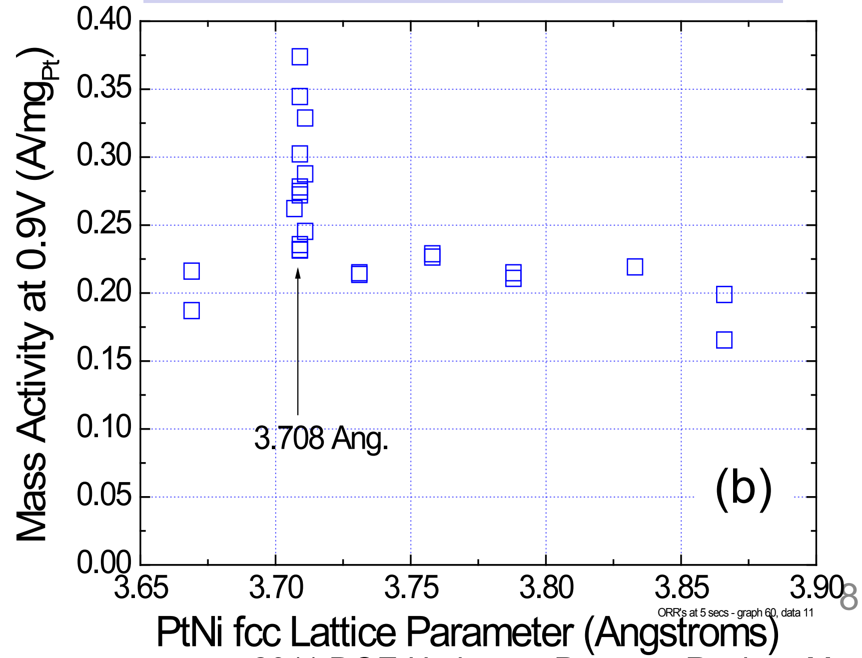
❑ Uniqueness of as-deposited Pt_xNi_{1-x} : x = 0.30

- Utilized XRF and EMP to measure compositions more precisely.
- Finite peak width can now be resolved with higher resolution (gravimetric only ± 5%)
- Found that exact position of peak depends on method used.
  - By XRF, peak appears to be at 76 at.% Ni in as-made catalyst.
  - By EMP, peak appears to be at 62 at.% Ni in as-made catalyst.
  - Gravimetric most accurate and in-between, so chose to call this Pt_3Ni_7.

Pt_3Ni_7 at peak by gravimetric at.%



ECS Trans., **33** 143 (2010), and J. Electrochem. Soc. (Accepted)

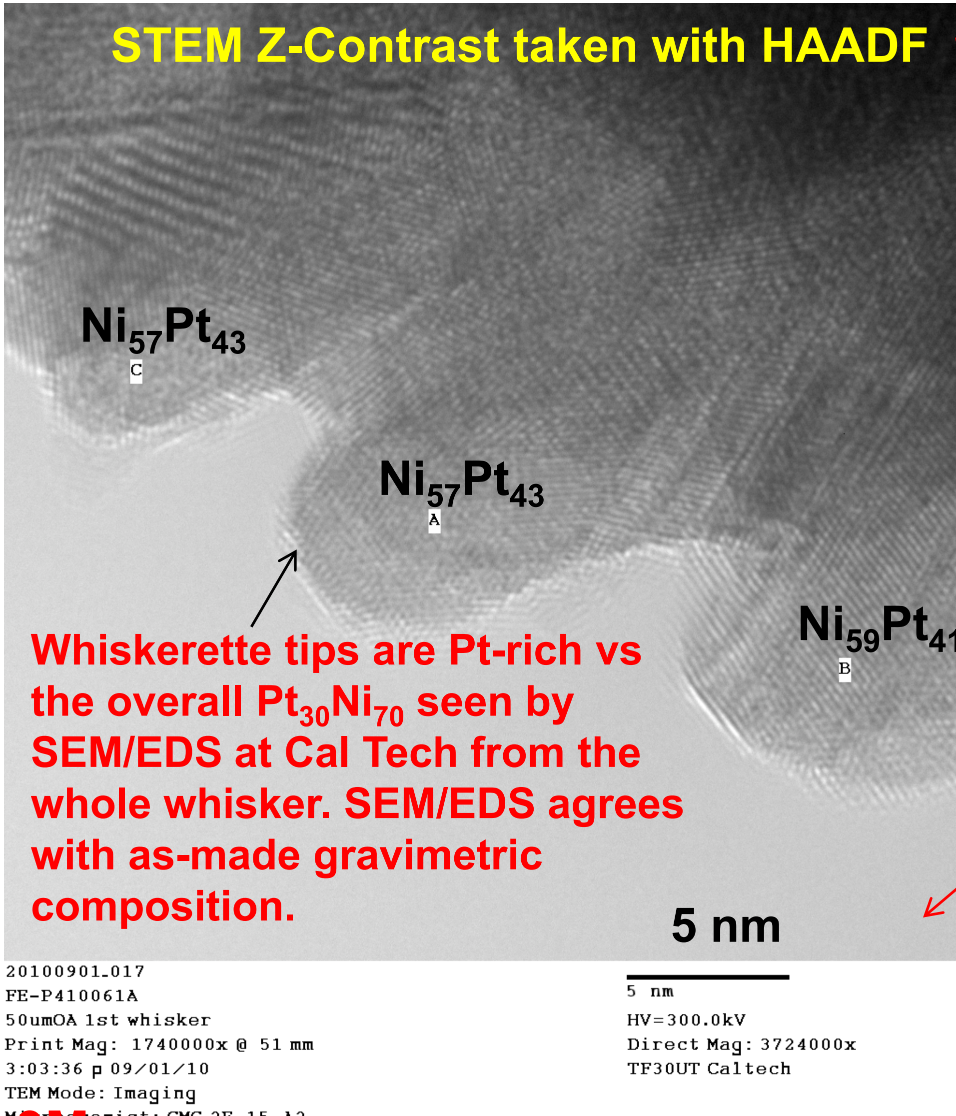


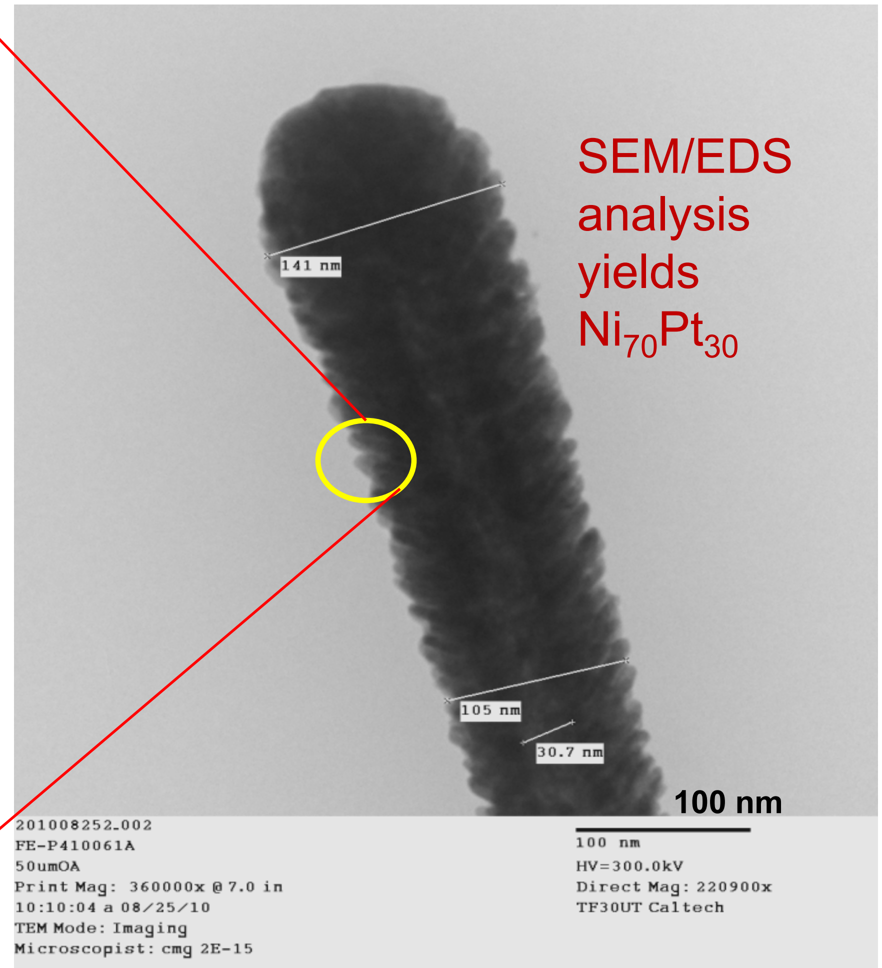
Technical Accomplishments and Progress

Task 1.3 – New catalysts for increased ORR activity and stability

- TEM by Carol Garland (Cal Tech), Charles Hays (JPL)

$Pt_{30}Ni_{70}$ coated NSTF whiskers from 3M production line process P4.





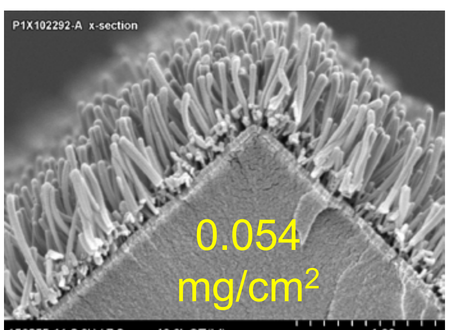
Improved catalysts for increased ORR activity and stability – P1 vs P4

Catalyst deposition process advances: New P1 vs Std. P4

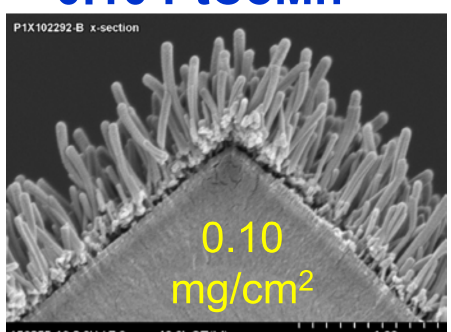
- P4 = Standard alloy roll-to-roll sputter deposition process
- P1= Simpler, more cost effective process than P4
  Impact: faster; larger grain sizes; smoother surface morphology
- Now applied to $Pt_{68}Co_{29}Mn_3$ as well as pure Pt.
- SEM shows no difference in P1 vs P4 NSTF catalyst microstructure:

PtCoMn by P1 Deposition Process

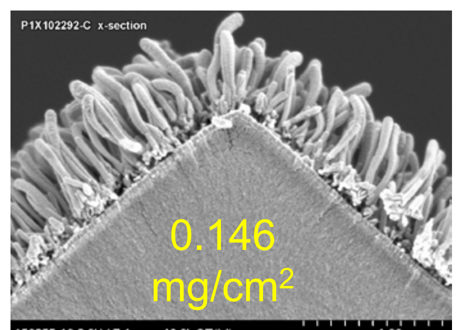
0.05 PtCoMn



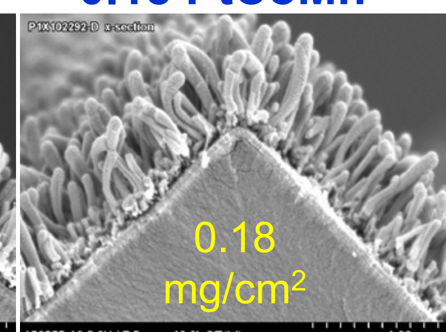
0.10 PtCoMn



0.15 PtCoMn



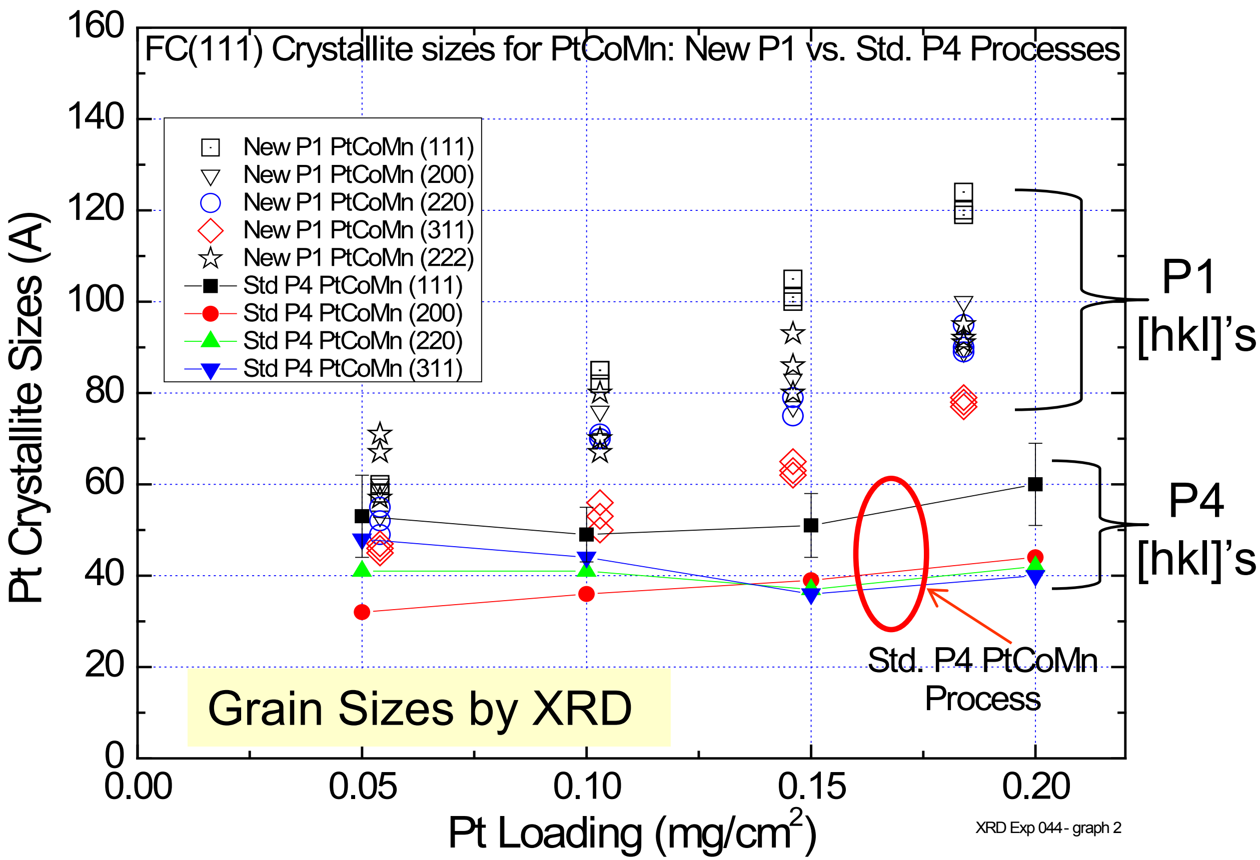
0.18 PtCoMn

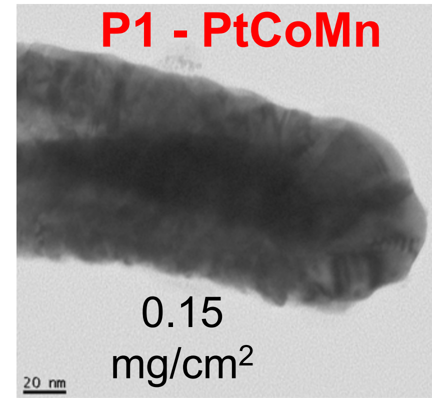


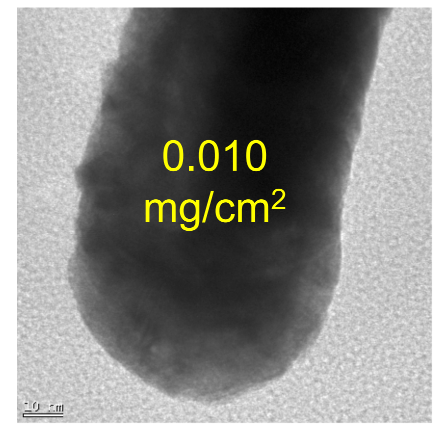
Technical Accomplishments and Progress

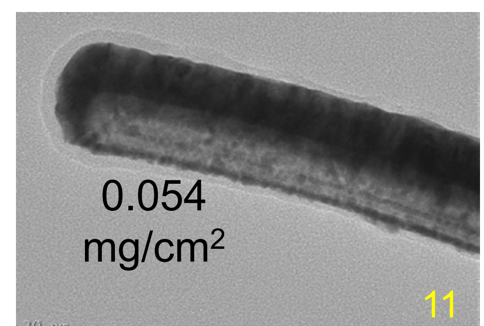
Improved catalysts for increased ORR activity and stability – P1 vs P4

- P1 process develops much larger fcc(hkl) grain sizes in NSTF-PtCoMn
- All [hkl] grain sizes increase with loading, not so with P4 process.
- TEM shows absence of NSTF "whiskerettes" on sides of whiskers and larger grains in catalyst coating, consistent with XRD.
- Aspects of P1 process also providing "annealing –like" conditions.









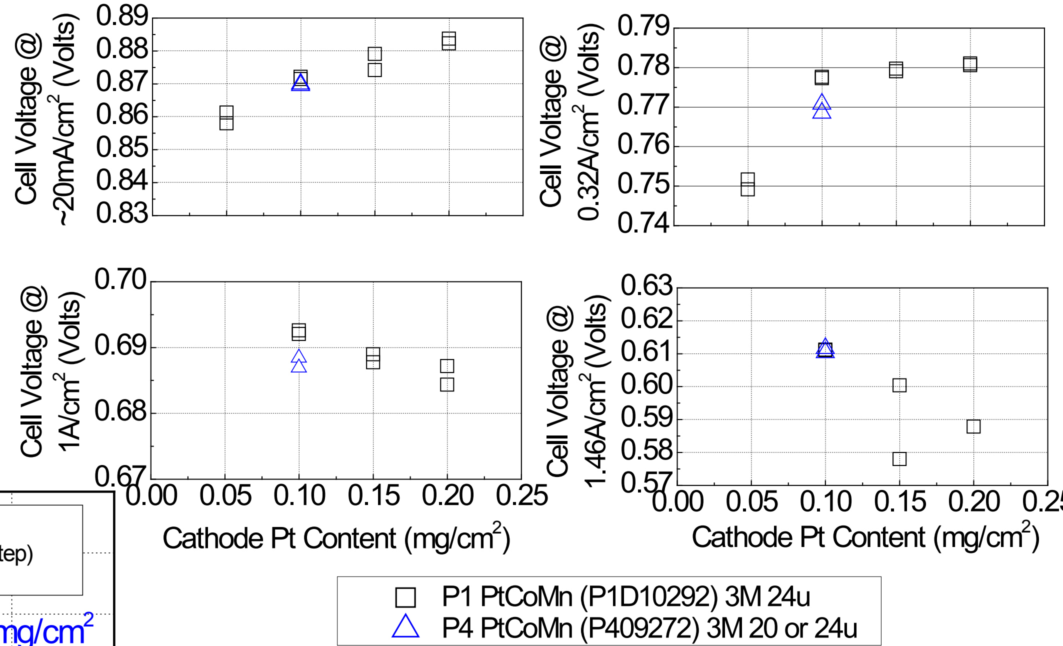
Technical Accomplishments and Progress

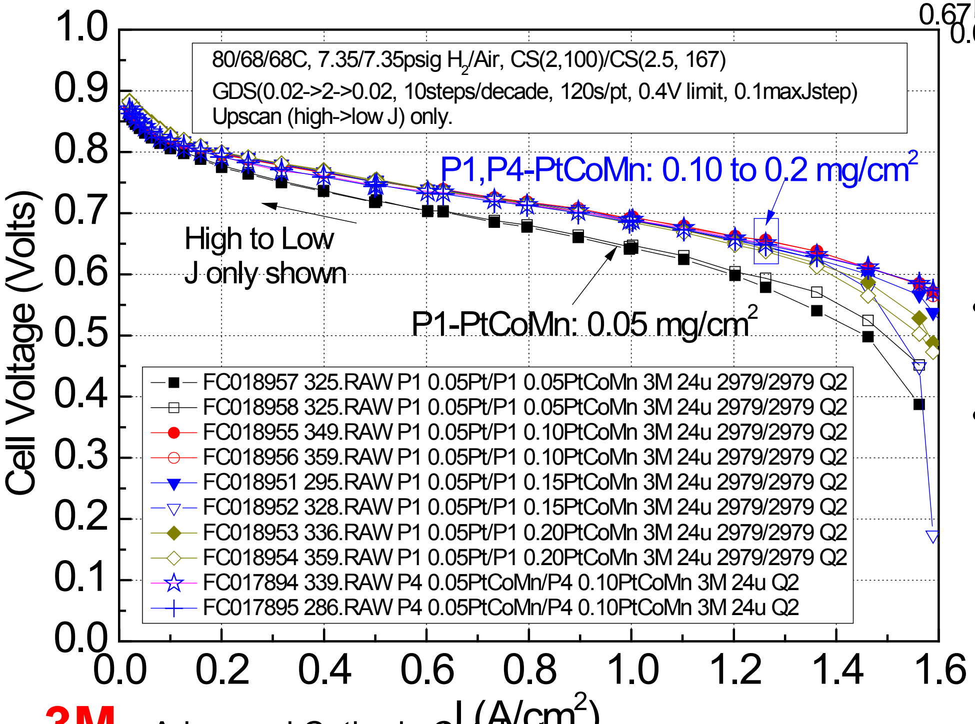
Improved catalysts for increased ORR activity and stability – P1 vs P4

Performance Metrics Comparisons, P1 vs P4 Processes for NSTF Cathodes

GDS polarization curves.

- Generally similar high current density performance between P1 loading series (0.1, 0.15 and 0.2 mg/cm^2) and P4 standard PtCoMn at 0.10 mg/cm^2
- P1- PtCoMn cathode performance with 0.05 mg/cm^2 is significantly lower than P1-PtCoMn at three higher loadings.





GDS polarization curves metrics.

- P1 – process yields ~10 mV improvement at 0.32 A/cm^2 and 5 mV at 1A/cm^2 v. P4 process.
- P1 and P4 processed catalysts have very similar performance at very low (0.02) and very high (1.5 A/cm^2) J.

MEA's: 3M-24 micron PEM, 3M Std. GDL's

Improved catalysts for increased ORR activity and stability – P1 vs P4

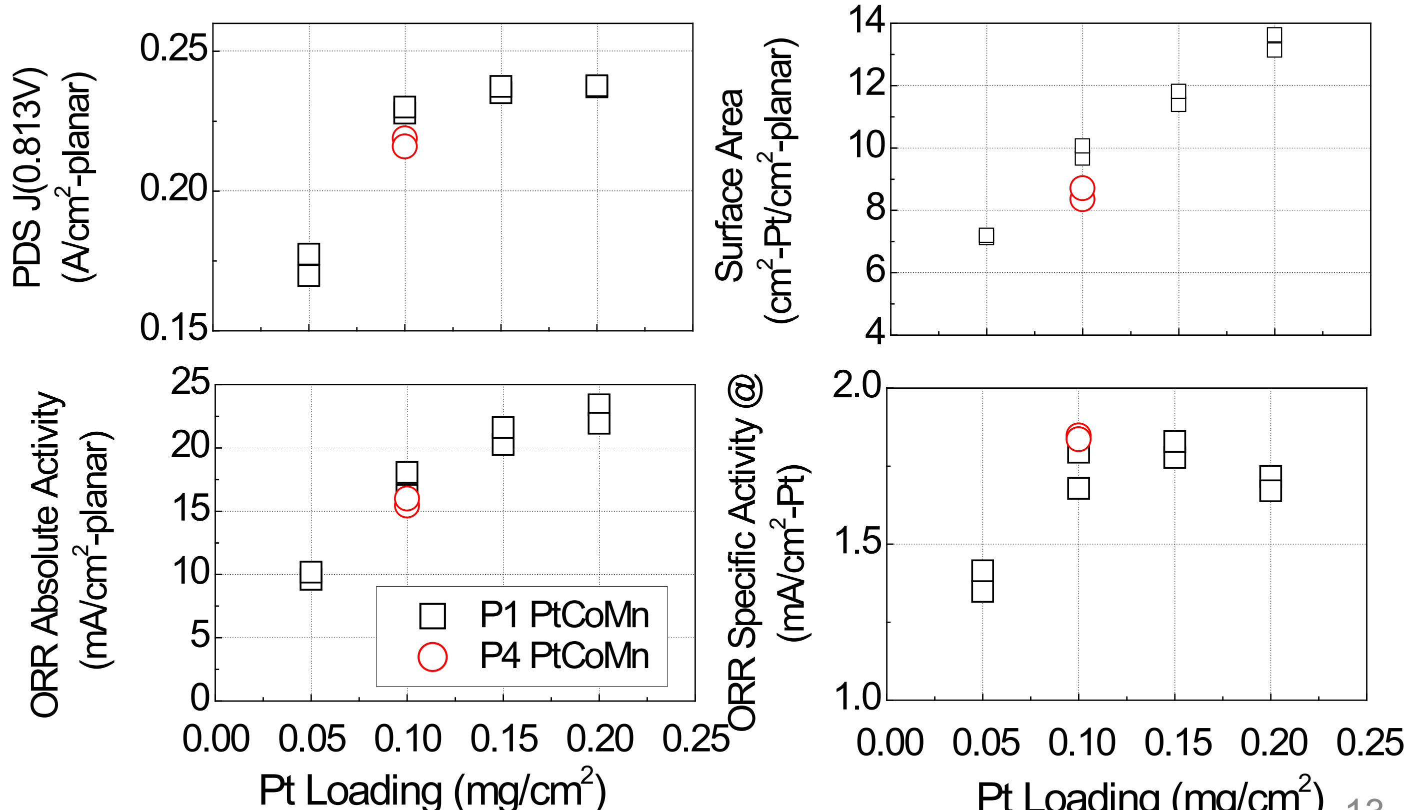
PtCoMn : Comparison of P1 (0.05 to 0.20 mg/cm^2_{Pt}) to P4 (0.10 mg/cm^2_{Pt})

- Steady increase in P1 PtCoMn ORR kinetics as loading increases.
- At 0.1 mg/cm^2, P1-PtCoMn (squares) has slightly higher SEF and PDS polarization curve response than P4 PtCoMn (circles),
- Absolute and specific activities are very similar.

Conclusion:

- Slight benefits and no penalties for simpler, faster P1 process for depositing alloys.

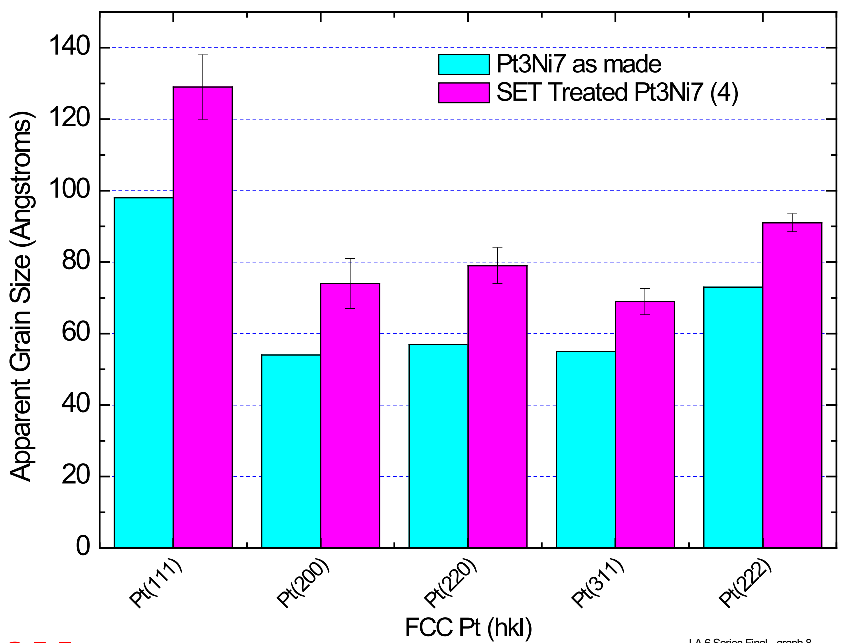
ORR Metrics



Improved catalysts for increased ORR activity and stability – SET

❑ Surface Energy Treatment (SET) Post processing

- SET process effectively anneals the as-made NSTF catalyst layer
- Applied to P4 and P1 made catalysts before making CCM's
- Applied so far to as-deposited $Pt_{68}Co_{29}Mn_3$ and Pt_3Ni_7
- Roll-to-roll capable process–scaled up on pilot scale coating line March, 2011.

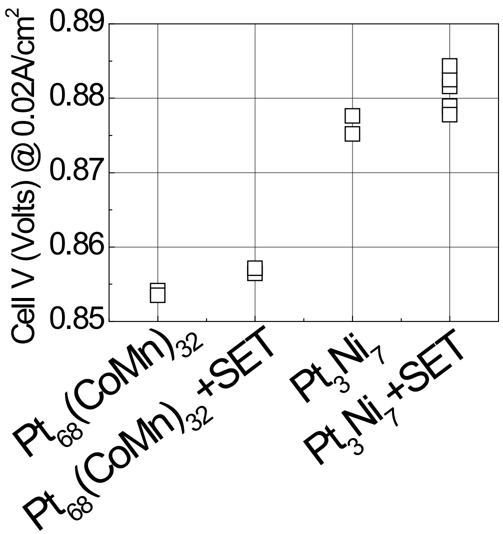


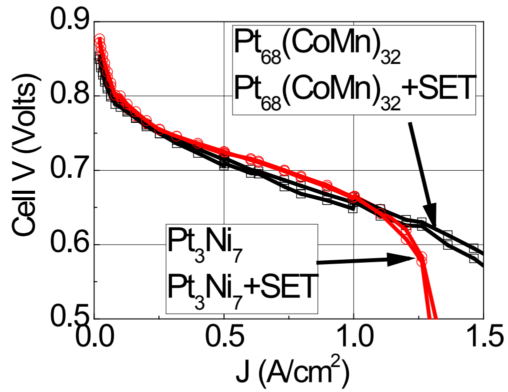
- SET process slightly increases Pt(hkl) grain sizes over as-made P1- PtCoMn and P4 - Pt_3Ni_7

Technical Accomplishments and Progress

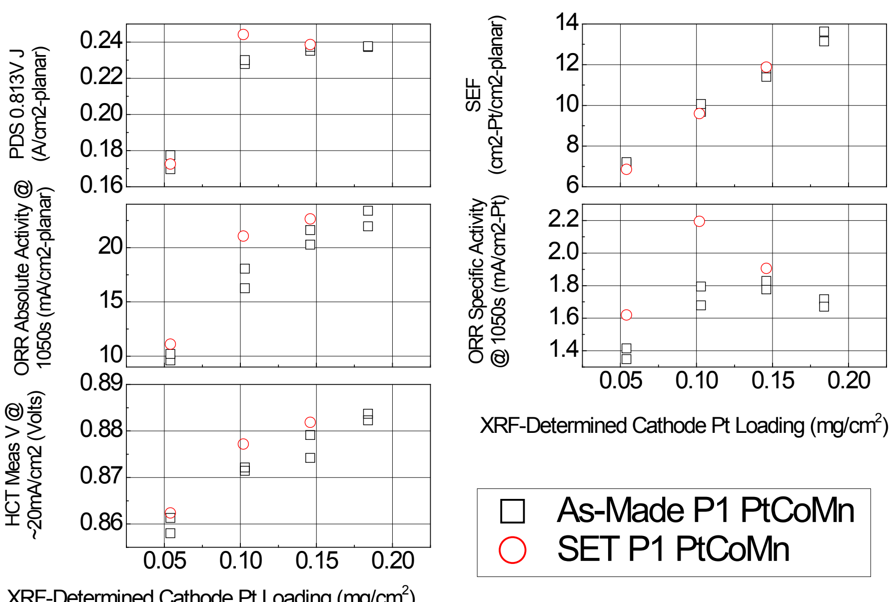
Improved catalysts for increased ORR activity and stability – SET

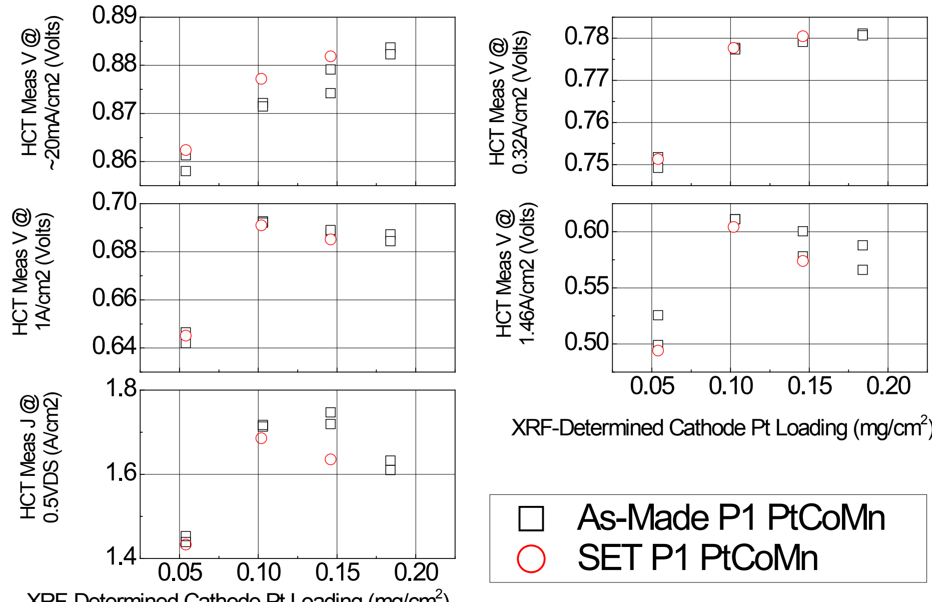
SET post process applied to P1-PtCoMn, Pt_3Ni_7





- SET process slightly increases fuel cell H_2/air kinetic region of as-made P1- PtCoMn and Pt_3Ni_7 .
- SET - Pt_3Ni_7 improves fuel cell H_2/air kinetics by 25 mV over as-made PtCoMn.
- SET of Pt_3Ni_7 improves 0.9 V O_2 ORR activity by up to 3x (next slide)



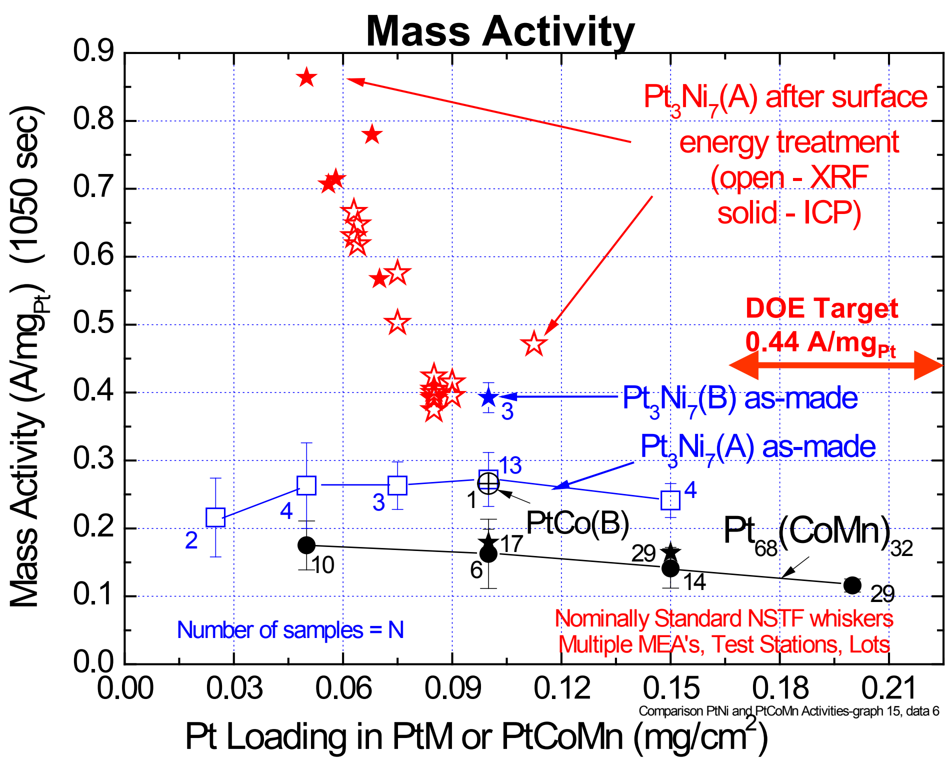


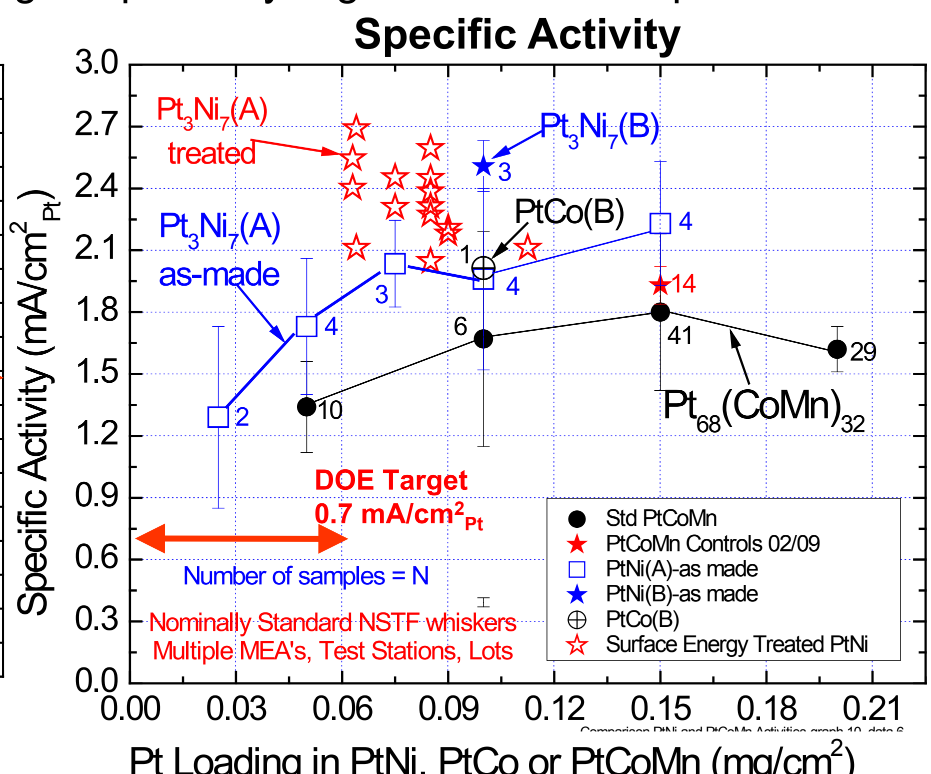
Technical Accomplishments and Progress

Improved catalysts for increased ORR activity and stability – SET Pt_3Ni_7

- ORR activity gains of SET-Pt_3Ni_7 vs as-made $Pt_{68}(CoMn)_{32}$ and Pt_3Ni_7

- Pt_3Ni_7(A) and PtCoMn all made on production equipment as roll-goods.
- Pt_3Ni_7 shows significant increase in activity metrics over standard $Pt_{68}(CoMn)_{32}$.
- SET treatment of roll-good process A catalyst dramatically improves activity
- XRF and ICP loading values in good agreement for SET post processed Pt_3Ni_7
- Note: SET “annealing” parameters varying for new samples shown: strong gain in A/mg vs decreasing loading not just a function of loading but probably slight differences in process.





Technical Accomplishments and Progress

Improved catalysts for increased ORR activity and stability – SET Pt_3Ni_7

❑ ORR Mass Activity at Comparison of Pt_3Ni_7 at 3M and GM

- 4-sample subset of SET Pt_3Ni_7 series was measured at both 3M and GM in 50 cm^2 cells.
- 3M and GM XRF/ICP mass loadings used to determine mass activities.
- Mass-corrected values depend on measurement protocol, but range from 0.35 to 0.59 A/mg.

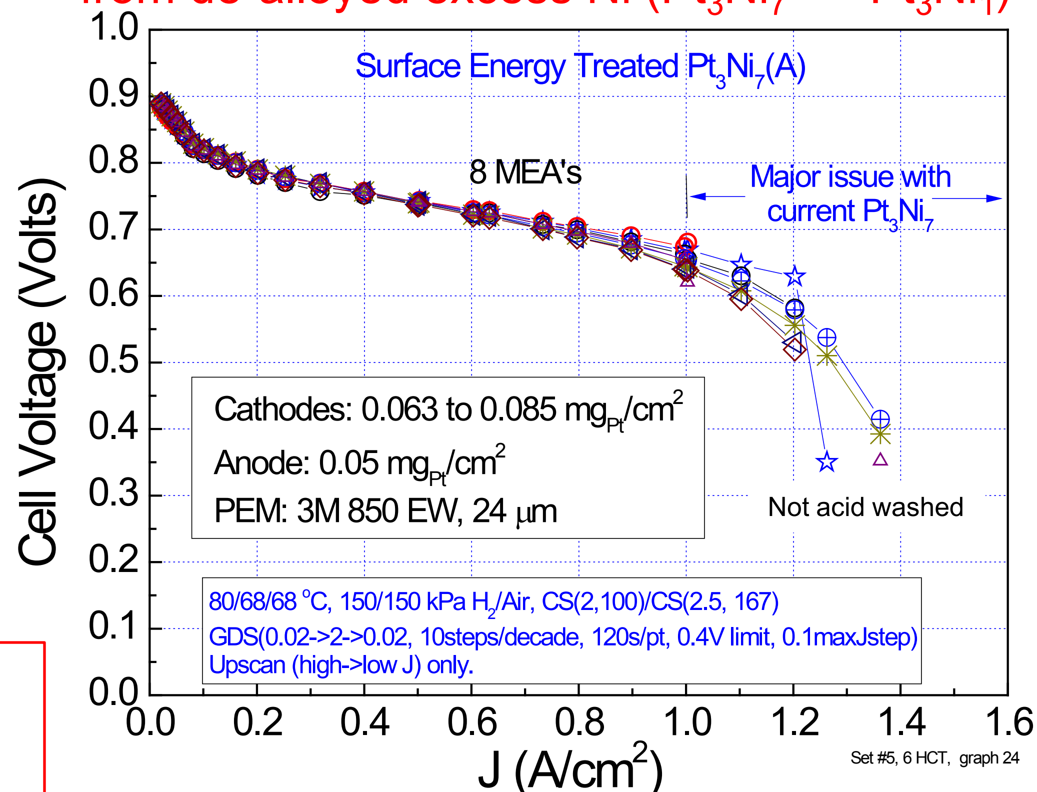
3M XRF/ICP Loading-Normalized Mass Activity Values:

- 3M w/3M protocol = 0.59 ± 0.08 A/mg.
- GM w/3M protocol = 0.51 ± 0.06 A/mg
- GM w/GM protocol = 0.43 ± 0.06 A/mg

GM ICP Loading-Normalized Mass Activity Values:

- GM w/3M protocol, = 0.42 ± 0.08 A/mg
- GM w/ GM protocol = 0.35 ± 0.06 A/mg

❑ Major Issue - Reduced limiting current from de-alloyed excess Ni (Pt_3Ni_7 => Pt_3Ni_1)



- Current as-made Pt_3Ni_7 alloys suffer from much reduced limiting current density, J_{Lim}
- J_{Lim} decreases as the amount of transition metal increases. Acid washing can help.
- Needs optimized *ex-situ* de-alloying process.

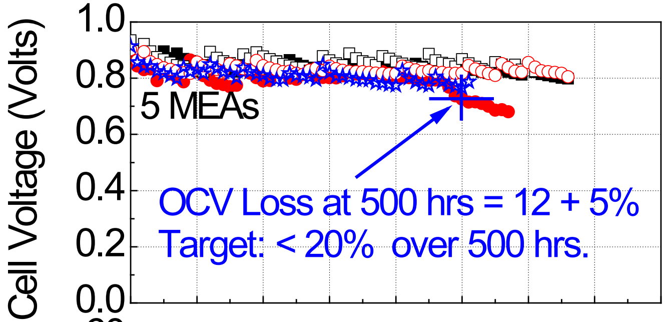
Improved catalysts for increased ORR activity and stability

- Accelerated Durability Tests with "Preliminary 2010 Best of Class" Down-Selected MEA Components:

  1. MEA /Membrane durability : OCV hold, 500 hours
     - 90^{o}C, 30% RH, 22.1/14.7 psig H_2/air
     - Targets: $\leq$ 20% loss of OCV after 500 hours
  2. Catalyst support stability: 1.2 V hold, 400 hours
     - 1.2 V for 400 hours; 80/80/80 ^{o}C; 7.35/7.35 psig H_2/N_2, 696/1657 SCCM.
     - Targets: $\leq$ 40% activity; $\leq$ 30mV loss at 1.5 A/cm^2; $\leq$ 40% loss ECSA
  3. Catalyst stability against dissolution: CV cycling, 30,000 cycles
     - 0.6 - 1.0 - 0.6 V; 30,000 cycles at 50 mV/sec; 80/80/80 ^{o}C ; 100/100 kPa, H_2/N_2; 200/200SCCM.
     - Targets: $\leq$ 40% activity; $\leq$ 30mV loss at 0.8 A/cm^2; $\leq$ 40% loss ECSA
  4. MEA Load cycling: 3M Protocol, Updated Historical MEA lifetimes
     - 80/64/64^{o}C, Constant Flows (Stoichs: 1.7 to 15); OCV, 0.2 < J < 1 A/cm^2

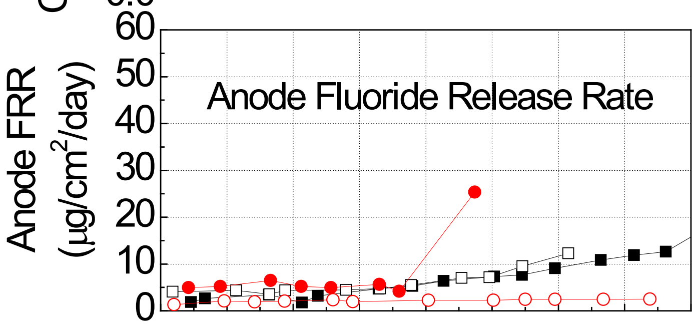
Improved catalysts for increased ORR activity and stability – OCV Hold

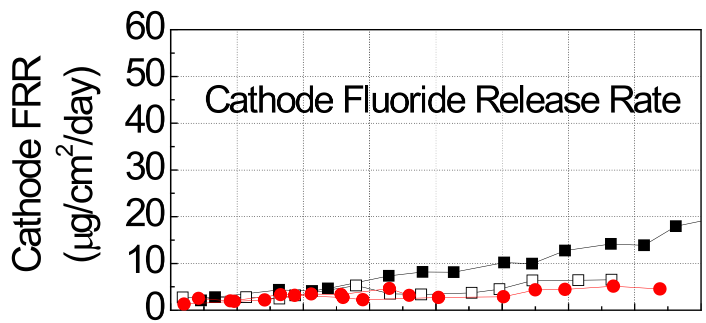
- OCV Hold with "Preliminary 2010 Best of Class" : First five MEA's exceed x-over 500 hour target. Sixth one allowed to run until x-over = 20 mA/cm² – reached 1300 hrs on 3/30/11.



MEA definitions

Anode catalyst: P1 – Pt or PtCoMn, 0.05 mg/cm²
PEM: 3M-S with additive
Cathode Catalyst: P1 - PtCoMn , 0.15 mg/cm²
Cathode GDL's: 3M standard
Anode GDL's: 3M standard and Type B





OCV Hold at : **

Cell T = 90 °C,

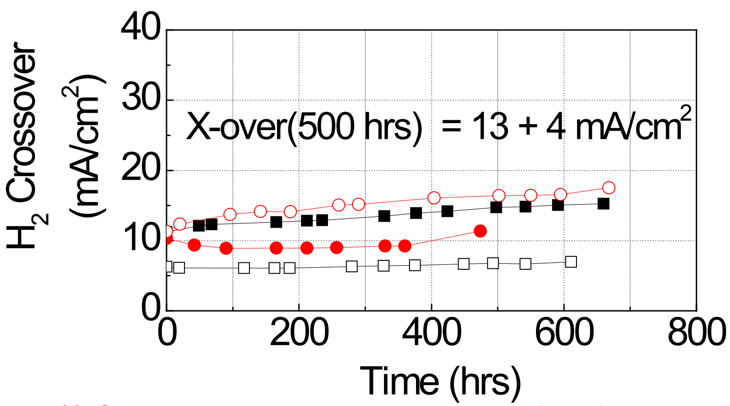
%RH = 30/30%

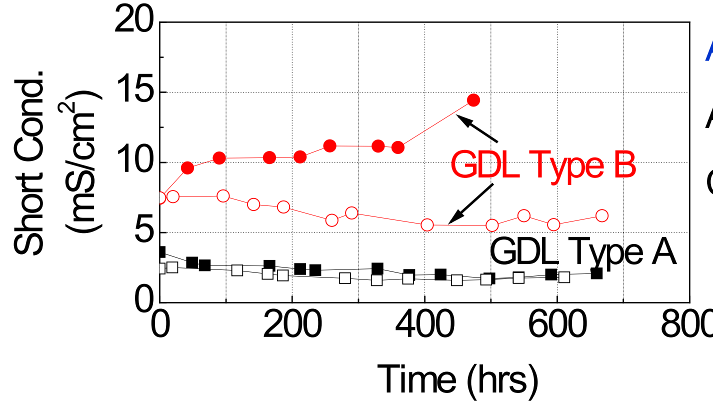
H_2 inlet = 250 kPa

Air Inlet = 200 kPa

Anode Flow = 696 sccm

Cath. Flow = 1657SCCM





** Crossover values are measured at the same operating conditions as used for the OCV hold test (but with N_2 on cathode). So crossover and shorting values appear much worse than if we used the prescribed USFCC method (ambient pressure, room T).

Technical Accomplishments and Progress

Improved catalysts for increased ORR activity and stability – 1.2 V Hold 400 hrs

- Polarization curves taken periodically using both DOE and 3M protocols.
- Pol. Curves show little effect of 1.2 V hold for 435 hrs.
- Metrics exceed Targets.

MEA definitions

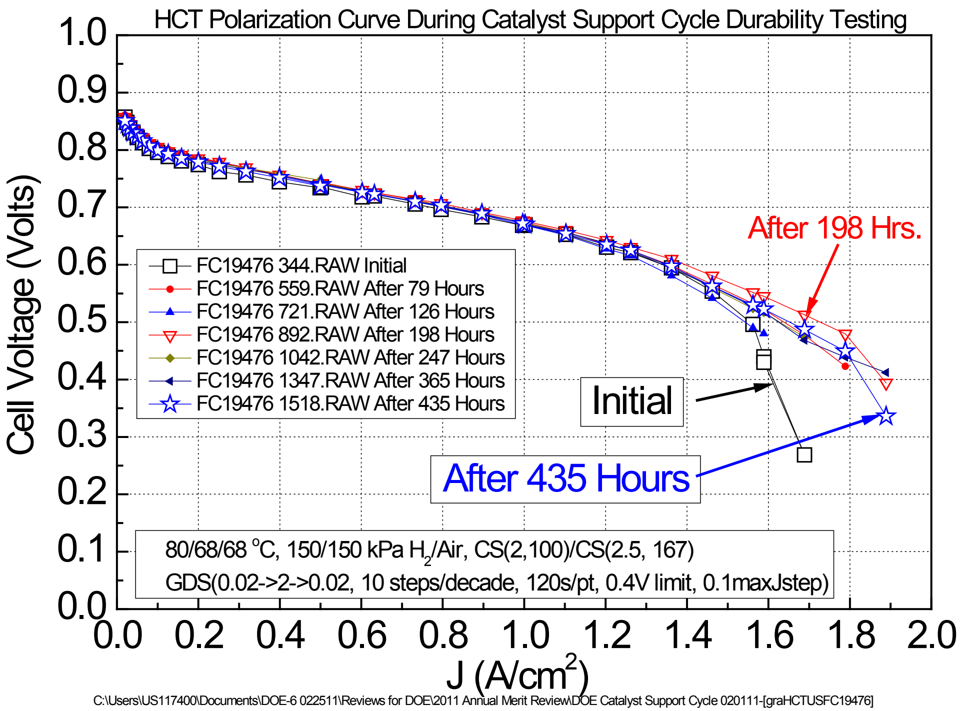
Anode catalyst: P1 – PtCoMn, 0.05 mg/cm^2

PEM: 3M-Supported with additive

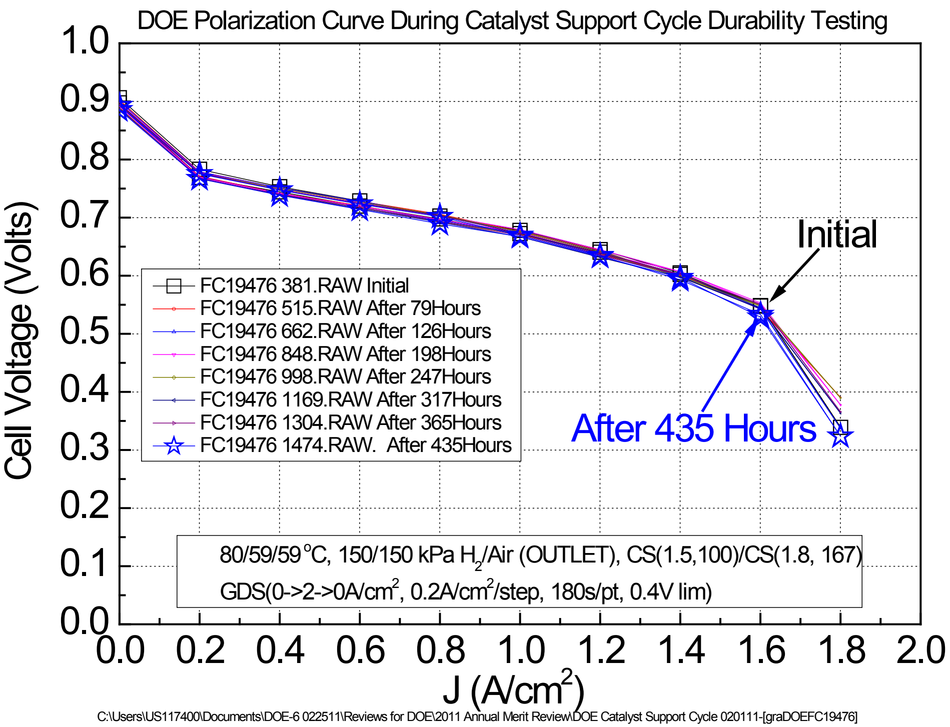
Cathode Catalyst: P1 - PtCoMn , 0.15 mg/cm^2

Anode/Cathode GDL's: 3M standard

3M Std. Pol. Curve Protocol



DOE Pol. Curve Protocol

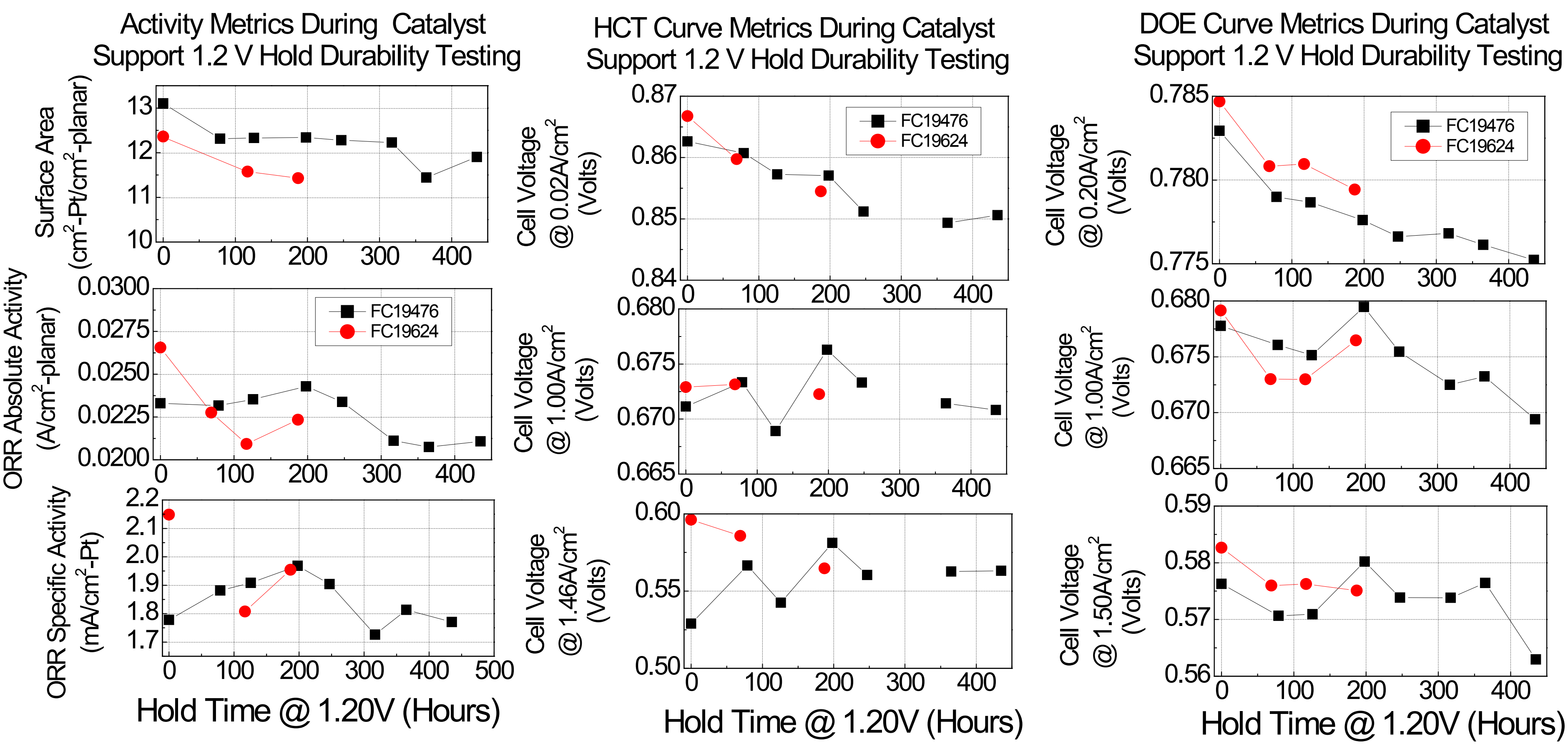


Technical Accomplishments and Progress

Improved catalysts for increased ORR activity and stability – 1.2 V Hold 400 hrs

- Surface Area loss of 10% exceeds target (< 40% loss)
- DOE Pol. curve loss of ~10mV at 1.5 A/cm^2 exceeds target (< 30 mV loss)
- Specific activity loss of 0% exceeds target (< 40% loss)
- Second sample test underway.

ORR and Polarization Curve Metrics vs Number of Hours at 1.2 V



Technical Accomplishments and Progress

Improved catalysts for increased ORR activity and stability – CV Cycle

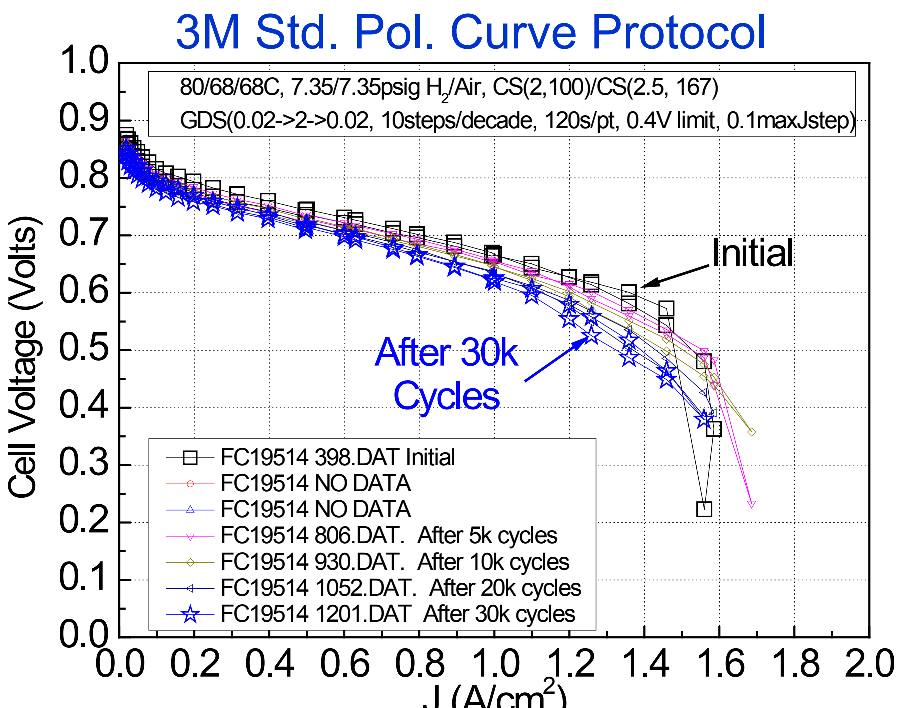
Test Protocol

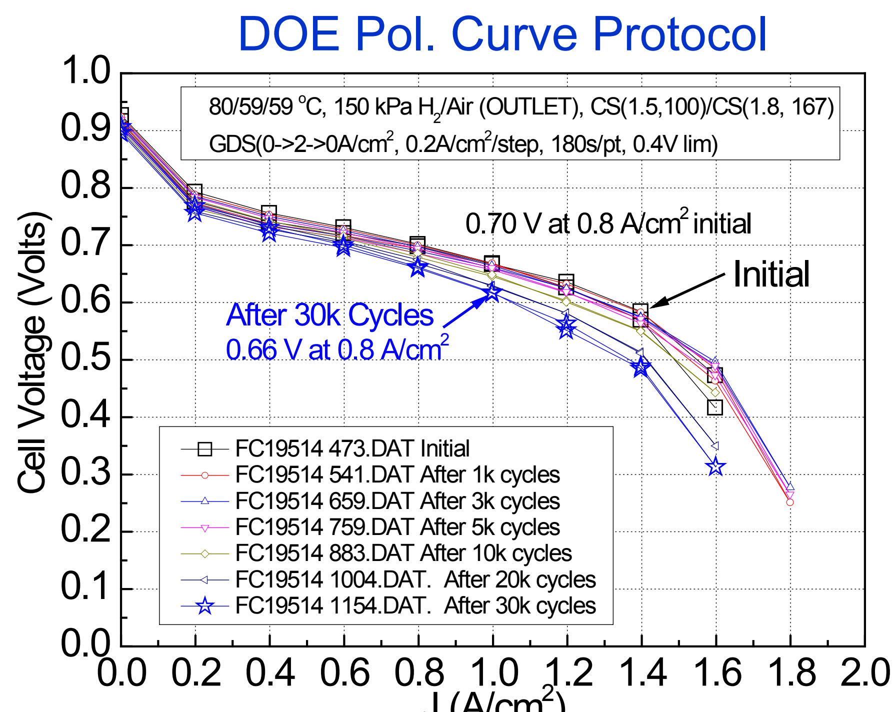
30,000 cycles at 50 mV/sec;
0.6 - 1.0 - 0.6 V; 80/80/80 °C
100/100 kPa H_2/N_2,
200/200SCCM.

MEA definition

Anode catalyst: P1 - 0.05 mg/cm^2 PtCoMn
GDL's: 3M standard
PEM: 3M-Supported with additive
Cathode Catalyst: P1 - 0.15 mg/cm^2 PtCoMn

- Polarization curves taken periodically using both DOE and 3M (HCT) protocols.
- Pol. Curves show clear effect of CV cycling through 30,000 cycles.



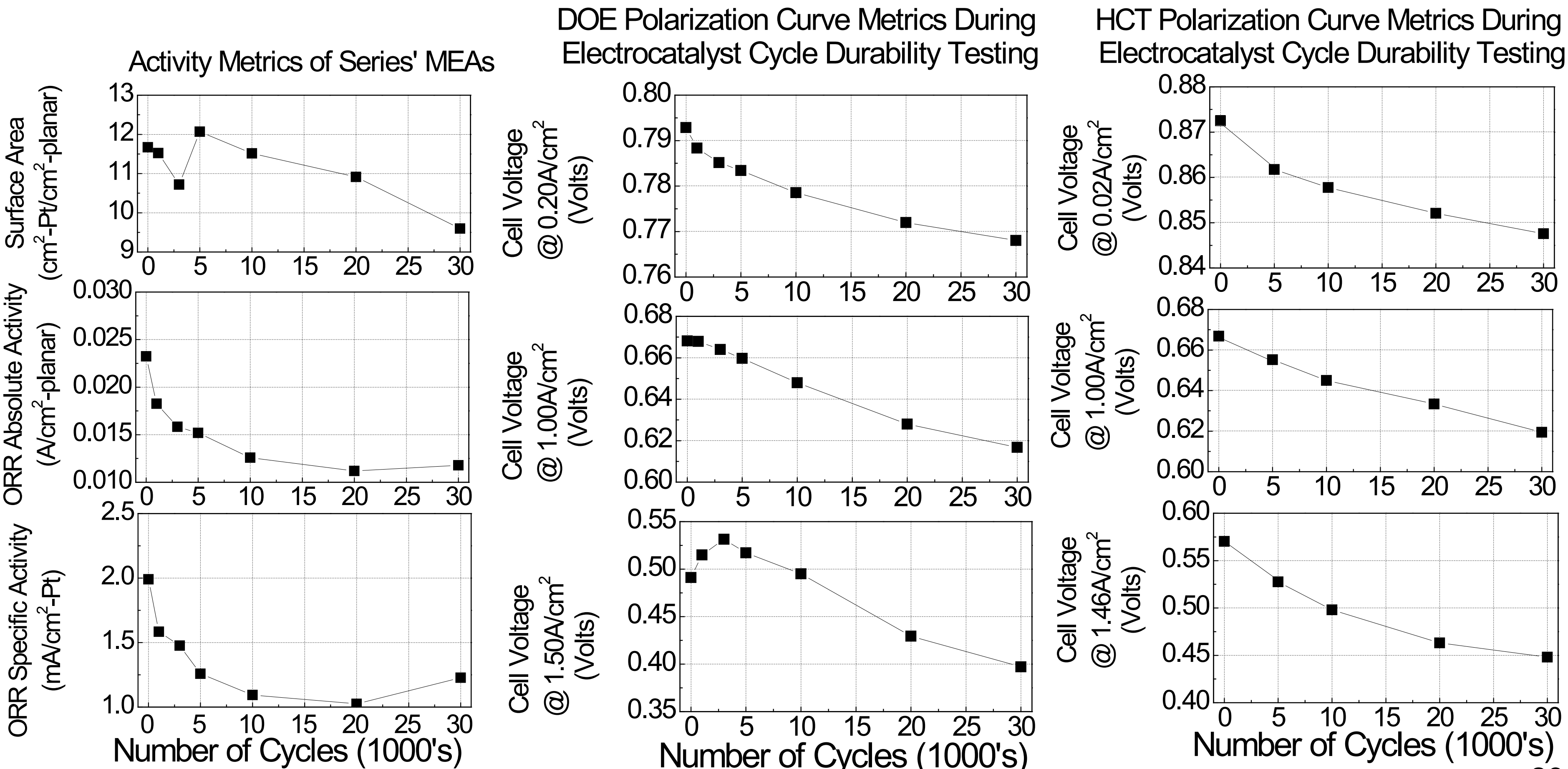


Technical Accomplishments and Progress

Improved catalysts for increased ORR activity and stability – CV Cycle

- Surface area loss of 18% exceeds target (≤ 40% loss of initial area).
- DOE Pol. curve loss of 40 mV at 0.8 A/cm^2 does not meet target (≤ 30 mV loss).
- Mass activity loss of 48% does not meet target (≤ 40% loss of initial catalytic activity).

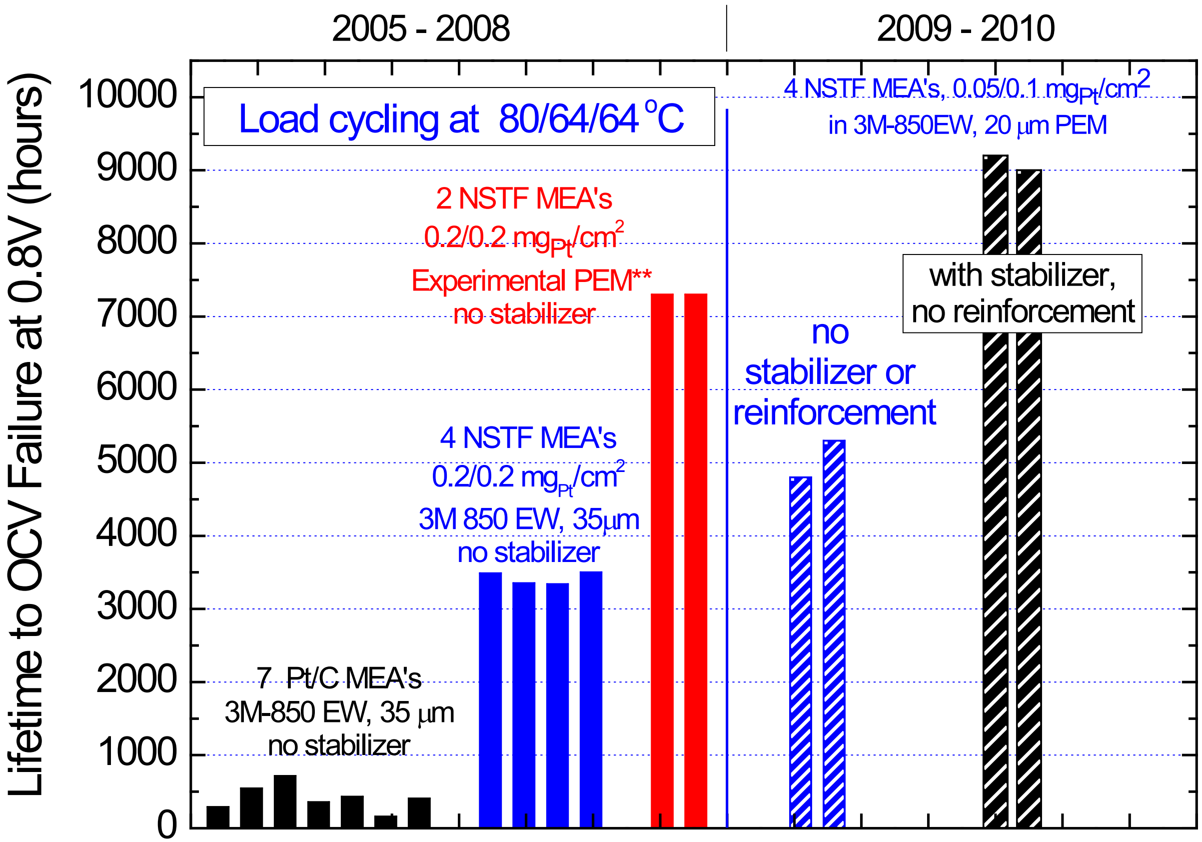
ORR and Polarization Curve Metrics vs Number of Cycles



Technical Accomplishments and Progress

3M Accelerated Load Cycling Lifetime Testing – Historical Update

- NSTF MEA's lifetimes without chemical stabilizers exceeded 5000 hours under load cycling accelerated testing, 7000 hours with reinforcement and no stabilizers.
- Now completed: 2009 Best of Class MEA (0.05/0.10 mg/cm^2 PtCoMn) with chemical stabilizers in 24 µm 3M PEM, but no reinforcement, reached 9000 hours before cross-over failure.



SHIVA 1 Load Cycle Protocol 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

Technical Accomplishments and Progress

Task 5.1/5.2/5.3 – MEA Integration and Final Stack Testing

❑ 2010 "Best of Class" MEA component down-selection process

- **Objective:** Down-select all final MEA component sets for NSTF 2010 best of class MEA for final stack testing at GM.
- **MEA component sets in down-selection process:** (primary focus ~ 9 months)
  - Cathode catalyst: composition, loading, deposition process, post process
  - Anode catalyst: composition and deposition process (finalized)
  - PEM: thickness, supported vs un-supported, chemical additive levels, etc.
  - Anode GDL: Backing layer type, MPL properties
  - Cathode GDL: Backing layer type and MPL properties, Interfacial coatings
- **Target date** for final component sets roll-good manufactured: March 18, 2011.

❑ Final Stack Testing

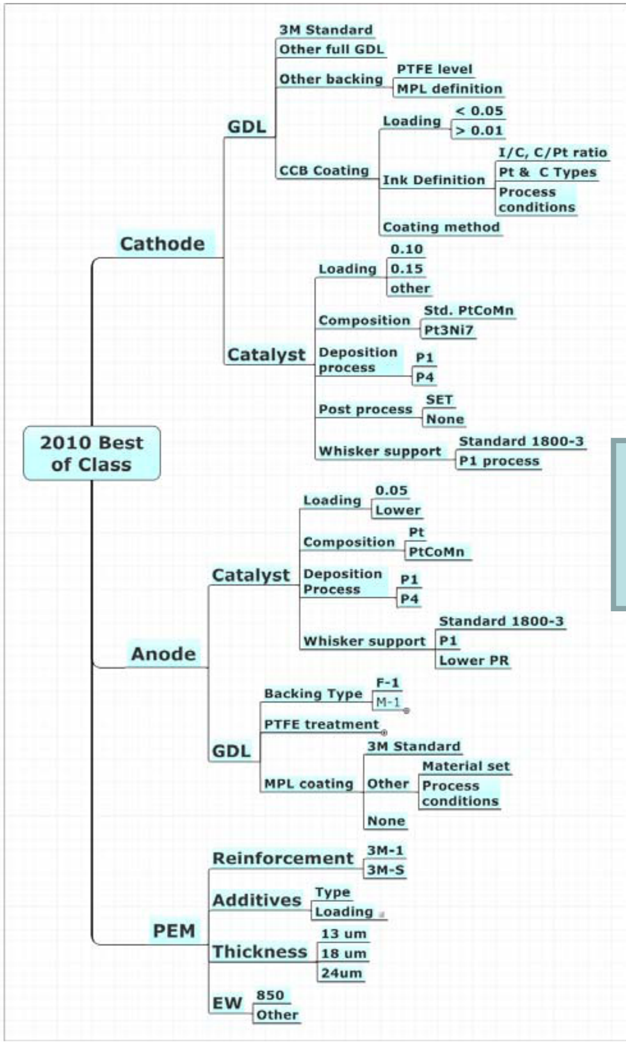
- **Planned schedule** for stack testing: April 1 to Dec. 31, 2011.
- **Testing Objectives:**
  - Stack #1: 29 cell Rainbow, 6 MEA component sets, ~ 200 hrs, BOL
  - Stack #2: 29 cell, 1 to 2 MEA component sets, ~ 3300 hrs durability

Technical Accomplishments and Progress

Task 5.1/5.2/5.3 – MEA Integration for Final Stack Testing

❑ 2010 Best of Class" MEA component down-selection process

Material set studies completed in last half-year as part of MEA down-select process:



100's of MEA's

- Anode GDL backing types from vendors – multiple series
- PTFE treatment of anode GDL backing layers
- MPL basis weights and roll-to-roll coating parameter series
- Anode GDL shorting mitigation strategies
- PEM equivalent weights, supported vs non-supported series
- PEM thickness series
- 3M standard PEM + additive series
- 3M-S + additive series
- Cathode P1-PtCoMn loading series
- Cathode P1 vs P4 processing conditions
- SET processing parameters for P1-PtCoMn
- SET processing parameters for Pt_3Ni_7
- Cathode Hybrid CCB loading series
- Cathode Hybrid CCB Pt/C type series
- Cathode Hybrid CCB ink composition series
- Cathode Hybrid CCB coating process series
- 3M-S CCM production series
- Hybrid + Anode GDL combined series
- SET + P1 combined series
- Anode catalyst PtCoMn vs Pt series
- Pt_3Ni_7 -PEM thickness interaction series
- CCM lamination material set series
- many others

Technical Accomplishments and Progress

Task 5.1/5.2/5.3 – MEA Integration for Final Stack Testing

❑ Component Down-Select - General Test Protocols and Criteria Summary

- **Conditioning:** Thermal Cycles
- **Potentiodynamic Scans:** 75/70/70C, 0/0psig H_2/Air, 800/1800SCCM, PDS(10s/pt)
- **ORR Activity:** 80/80/80C, 150/150kPa H_2/O_2, 696/1657SCCM, PSS(0.900V_{MEAS}, 20min). Estimate of shorting and crossover at same conditions by CV (0.65-0.085V, 2mV/s)
- **ECSA:** 70/70/70C, 100/100kPa H_2/N_2, 800/1800SCCM, CV (0.65-0.085V, 100mV/s). Average of up-scan and down-scan H_{UPD} charge of short, crossover corrected CVs, 210μC/cm^2_{Pt}.
- **HCT (GDS polarization curves):** 80/68/68C, 7.5/7.5psig H_2/Air, CS2/2.5, GDS(120s/pt)
- **Startup Transient + Cool Poteniostatic Scans (PSS):**
  - Precondition: 80C, 30/30% RH, 696/1657SCCM H_2/Air, 100/100kPa, GSS(0.05, 10min)
  - Startup Transient: 30C, 100/100% RH, 100/150kPa,696/1657SCCM H_2/Air, PSS(0.4V, 10min)
  - CoolPSS: xC (x=30->50), 100/100 or 0/0% RH, 100/150kPa, 696/1657SCCM H_2/Air, PSS(0.4V, 10min)
- **T Sens:** xC (x=80->30->80) 100/100% RH, 100/100kPa, 800/1800SCCM H_2/Air, PSS(0.6V, 15min)
- **Reversible Stability:**
  - Degradation: 90/90/90C, 1044/2485SCCM H_2/Air, 200/200kPa, GDS(0->1.5, 120s/pt), 10 hours
  - Performance Check: HCT
- **Load Transient:** xC, y/y% RH (y=140, 100, or 0), 150/150kPa, 696/1657SCCM H_2/Air, PSS(0.6V,5min),GSS(0.02,30s), GSS(1.0,30s)
- **Humidification Sensitivity:** 90C, x/xC dewpoint (x=90,77,65,59,49C), 200/200kPa, CS2/2 H_2/Air, GSS(1.2,30min/pt)

Technical Accomplishments and Progress

Task 5.1/5.2/5.3 – MEA Integration for Final Stack Testing

- 2010 Best of Class" MEA component down-selection process

Example 1: Outcome of Down-Select Process for Type A PEM additive

Results : PEM additive type A at optimum wt%, vs no-additive

HCT-GDS 0.32 A/cm^2	HCT-GDS 1.0 A/cm^2	HCT-GDS 1.46 A/cm^2	HCT-GDS 2.0 A/cm^2
Hot/Dry Steady State	Hot/Wet Steady State	Cool/Dry Steady State	Cool/Wet Steady State
Hot/Dry Transient	Hot/Wet Transient	Cool/Dry Transient	Cool/Wet Transient
Shorting	Reversible Stability	CV cycling	OCV Hold

Better than control
Worse than control
Same as control

MEA Tested = 0.05 Pt/0.15 PtCoMn, 3M 24 µm, H2315/2979

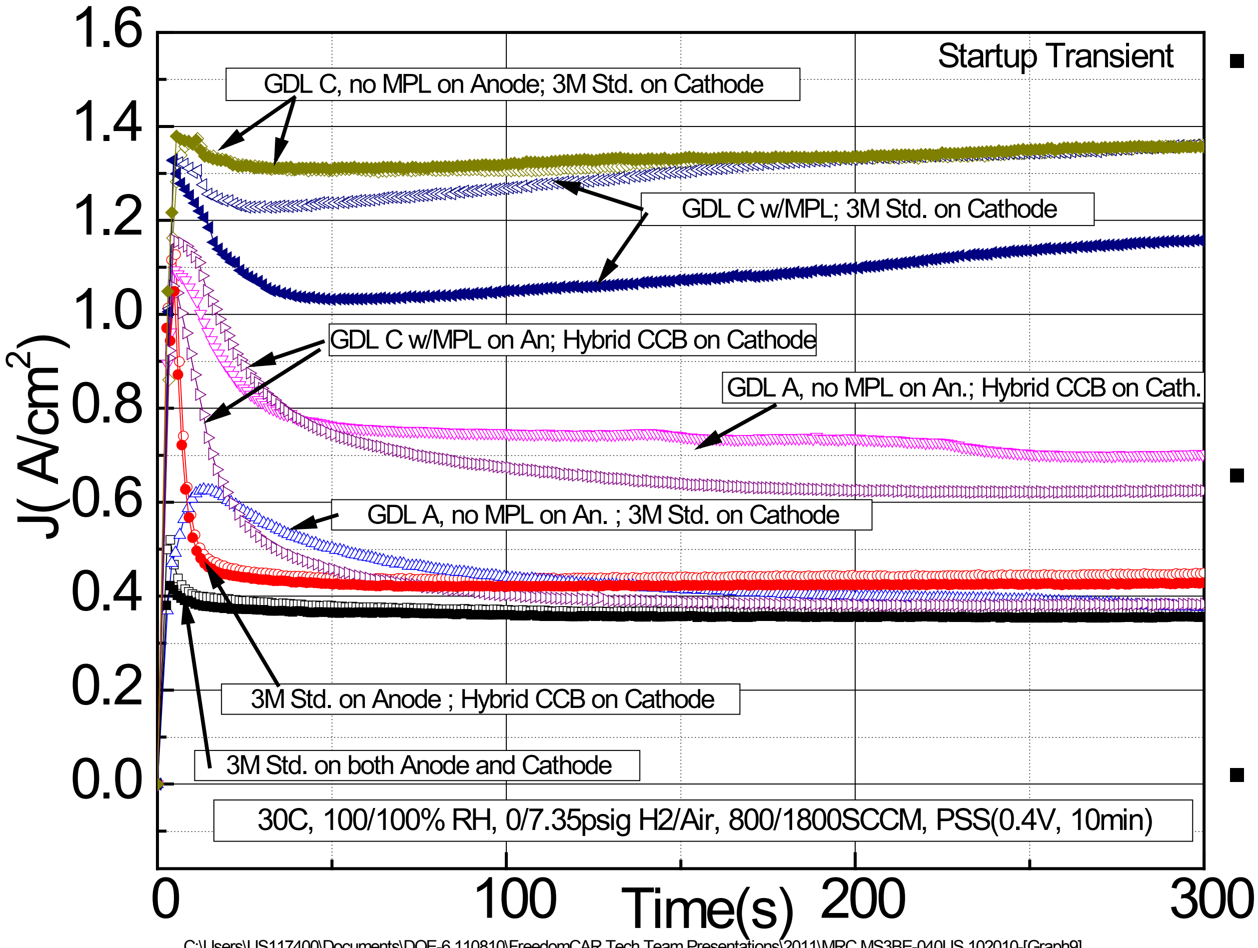
Conclusion: Very promising, no negative issues identified.

Task 5.1/5.2/5.3 – MEA Integration for Final Stack Testing

❑ 2010 Best of Class" MEA component down-selection process

Example 2: Anode GDL Options for improved water management

Impact of anode GDL on start-up transient and steady state current density at 30 °C, 100% RH and ambient anode pressure:



- Anode GDL backing layer is the most significant component affecting control of water flow from cathode to anode and thereby water management with ultra-thin electrodes.
- Startup transient current of experimental GDL C is more than 2x better than any other, including those with the Hybrid B on the cathode.
- GDL type C resistance still a little too high, so not down-selected for final stacks.

Collaborations

Subcontractors

- Dalhousie University : Subcontractor. Focused on Pt_3Ni_7 studies. Funding ended Dec., 2010.
- ANL (Markovic/Stamenkovic group): Subcontractor, periodic measurements in 2010.
- NASA-JPL: Subcontractor, periodic interactions in 2010. TEM, co-deposition of Pt_3Ni_7 in 2010.

System Integrators and stack manufacturers (partial list)

- GM Fuel Cell Activities-Honeoye Falls: 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 – collaborative work under Task 3 concluded by mid-2010.
- Proton Energy Systems – Collaboration outside of DOE H_2 program. Performance testing of NSTF MEAs in electrolyzers. Continuous testing and periodic interaction past year.
- Giner EC Systems, LLC – Collaboration outside of DOE H_2 program. Performance testing of NSTF MEAs in electrolyzers. Periodic testing and interaction past year.

National Laboratories

- ANL(Ahluwalia) – Supplied extensive NSTF fuel cell performance data for ANL systems modeling.
- LBNL, LANL, UTC– Collaborative interactions outside this contract under LBNL project "FC fundamentals at Low and Subzero temperatures."
- NIST – Samples and data supplied to NIST for optical method development for CCM Pt loading measurement done under FC Manufacturing

Future Work (3/11/11 to 12/31/11)

- **2010 Best of Class MEA Down-Selection**
  - ✓ Conclude current activities to down-select the remaining MEA components for final stack testing at GM:
  - ✓ Define 6 MEA configurations for rainbow short stack BOL testing.
  - ✓ Select final MEA configuration for long term testing,
  - ✓ Fabricate final MEAs sufficient for both stacks.

- **Final Stack Testing**
  - ✓ Secure 9 month no cost extension with Golden, CO office.
  - ✓ Deliver MEA media to stack integrator by 3/25/2011 for BOL stack and final MEA configuration for long term durability stack testing, targeting 3300 hrs by 12/31/11.
  - ✓ Execute testing plan.

- **Continue limited effort on one or two key issues related to anode GDL for water management and long term irreversible voltage decay.**

- **Prepare and Submit Final Report**

Project Summary : Status Against DOE Targets – March, 2011 (blue = new)

Characteristic	Units	Targets 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	0.125	< 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 GM short stack
PGM Total Loading	mg PGM / cm^2 total	0.125	0.15 – 0.20, A+C with current PtCoMn alloy
Mass Activity (150kPa H_2/O_2 80°C. 100% RH, 1050 sec)	A/mg-Pt @ 900 mV, 150kPa O_2	0.44	0.24 A/mg in 50 cm^2 w/ PtCoMn > 0.43 A/mg in 50 cm^2 with SET Pt_3Ni_7
Specific Activity (150 kPa H_2/O_2 at 80°C, 100% RH)	μ A/cm^2-Pt @ 900 mV	720	2,100 for PtCoMn, 0.1mg_{Pt}/cm^2 2,500 for new Pt_3Ni_7, 0.1mg_{Pt}/cm^2
Durability: 30,000 cycles 0.6 -1.0V, 50mV/sec,80/80/80°C, 100kPa,H_2/N_2	- mV at 0.8 A/cm^2 - % ECSA loss - % Mass activity	< 30mV < 40% < 40 %	- 40 mV loss at 1.5 A/cm^2 - 18% loss ECSA - 48 % loss mass activity
Durability: 1.2 V for 400 hrs. at 80°C, H_2/N_2, 150kPa, 100% RH	- mV at 1.5 A/cm^2 % ECSA loss % Mass activity	< 30mV < 40% < 40%	- 10 mV loss at 1.5 A/cm^2 -10% loss ECSA -10 % loss mass activity
Durability: OCV hold for 500 hrs. 250/200 kPa H_2/air, 90°C, 30%RH	H_2 X-over mA/cm^2 % OCV loss	< 20 < 20 %	13 $\pm$ 4 mA/cm^2 at 500 hrs (5 MEAs) -12 $\pm$ 5 % OCV loss in 500 hrs
Durability under Load Cycling (membrane lifetime test)	Hours, T $\leq$ 80°C Hours, T > 80°C	5000 5000	9000 hrs, 3M PEM (20μm, 850 EW w/ stabilizers), 50cm^2, 80/64/64 °C 2000 hrs (OEM short stack,0.1/0.15)

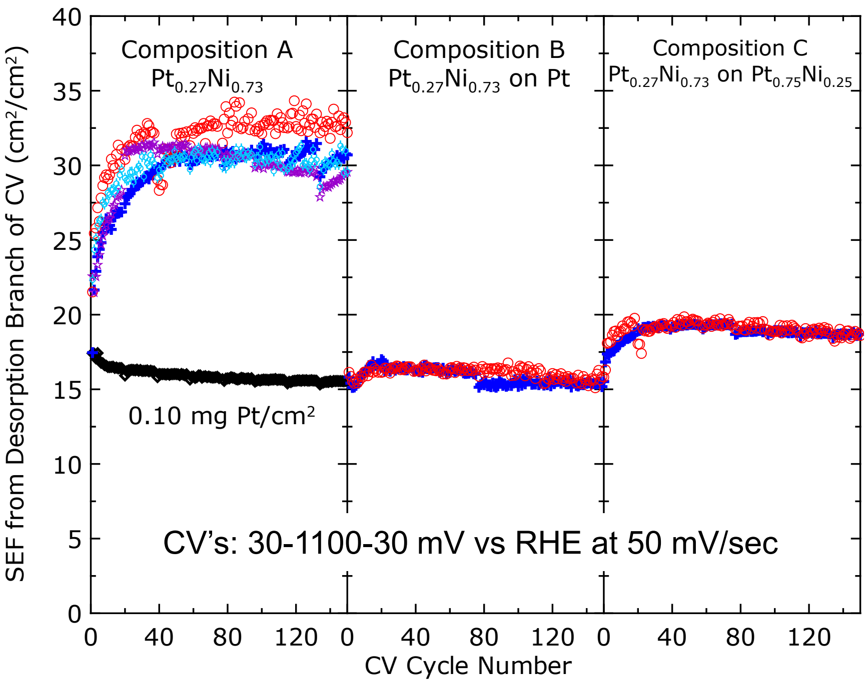
Technical Back-Up Slides

Task 1.3 – New catalysts for increased ORR activity and stability – Pt_3Ni_7 work at Dalhousie University

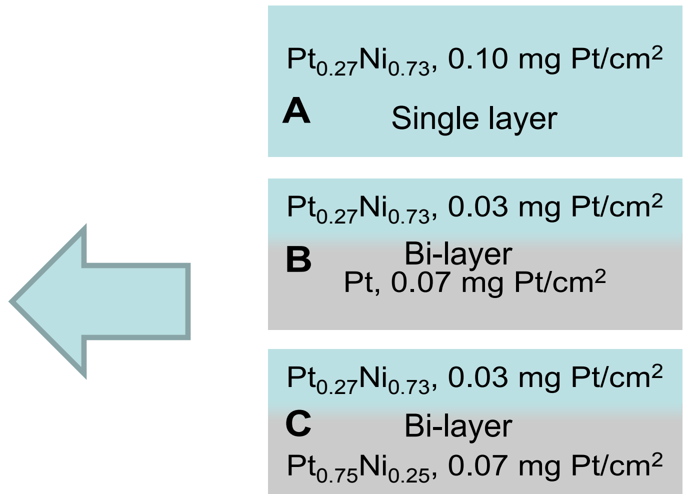
❑ Uniqueness of as-deposited Pt_xNi_{1-x} : x = 0.30

- ECSA of Composition A is much larger than bi-layer constructions B or C.
- Results imply a highly porous Pt-skin type model in which Ni dissolution occurs throughout the deposited film creating a high catalytic surface area. Suggests all the area is H_{upd} active.
- Ni dissolution from the entire Pt_3Ni_7 layer is required to generate the high surface area and activity.
- Not all of the Ni is however lost. The results suggest that the remaining Ni modifies the electronic properties of the Pt surface to increase the activity of the catalytic sites relative to Pt.

Surface area enhancement factor (SEF) from H_{upd} RDE measurements of the three NSTF alloy and pure Pt coated whisker compositions A, B, C on GC disks



Schematic illustration of three NSTF compositions prepared and tested on RDE's



Gary Chih-Kang Liu, D.A. Stevens, J. C. Burns, R.J. Sanderson, George Vernstrom, R.T. Atanasoski, M.K. Debe and J. R. Dahn, "Oxygen reduction activity of dealloyed $Pt_{1-x}Ni_x$ catalysts," J. Electrochem. Soc., accepted for publication

Technical Back-Up Slide

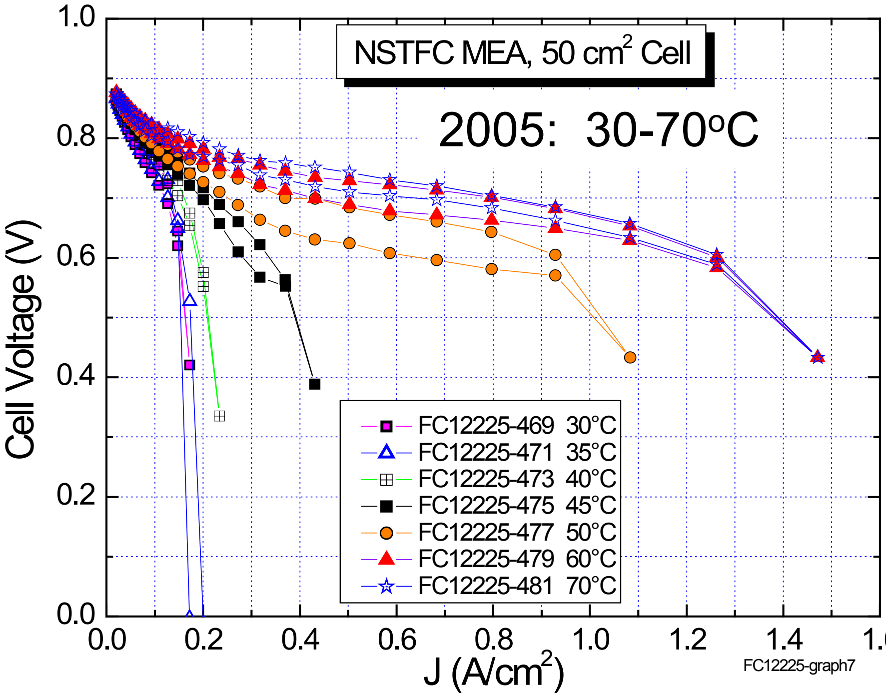
Task 5.1/5.2/5.3 – MEA Integration for Final Stack Testing

❑ 2010 Best of Class" MEA component down-selection process

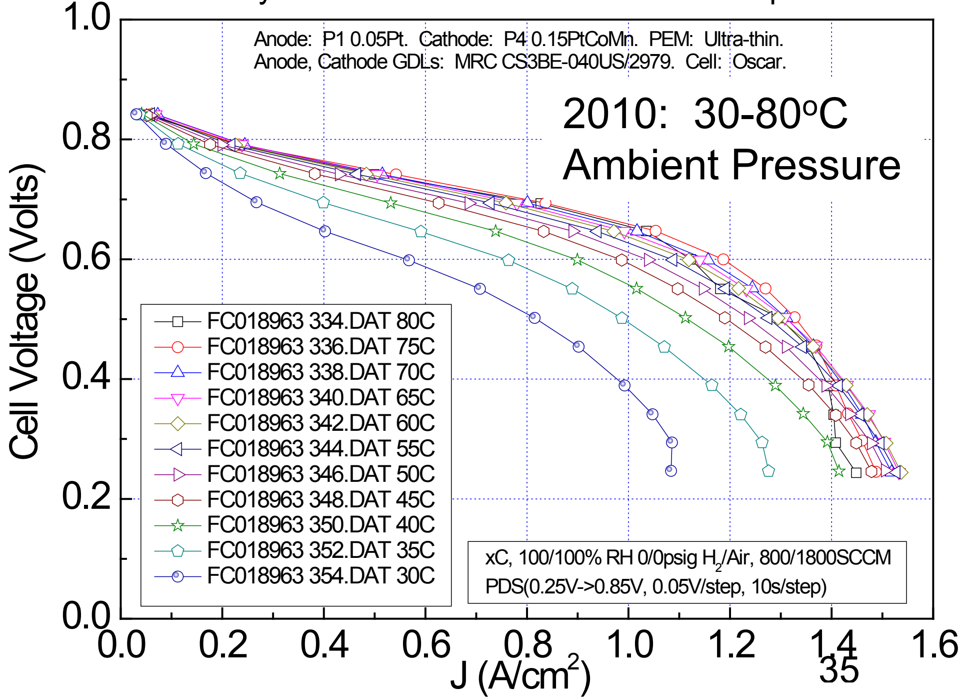
Example 3: PEM Factors for CCM parameter screening in 50 cm^2 fuel cell tests

- Improved Anode GDL + Thinner Membrane significantly improves performance at on Low Temperature and Ambient Pressure.
- Performance in bottom right slide similar to that of MEA with dispersed electrodes.

35 µm PEM, 0.2 mg/cm^2 PtCoMn
3M Std. GDLs on anode/cathode



13 µm PEM, 0.15 mg/cm^2 PtCoMn
GDL C on anode, 3M Std. GDL on cathode



Task 5.1/5.2/5.3 – MEA Integration for Final Stack Testing

2010 Best of Class" MEA component down-selection process

Example 4: Cathode GDL Options

Cathode GDL Options:

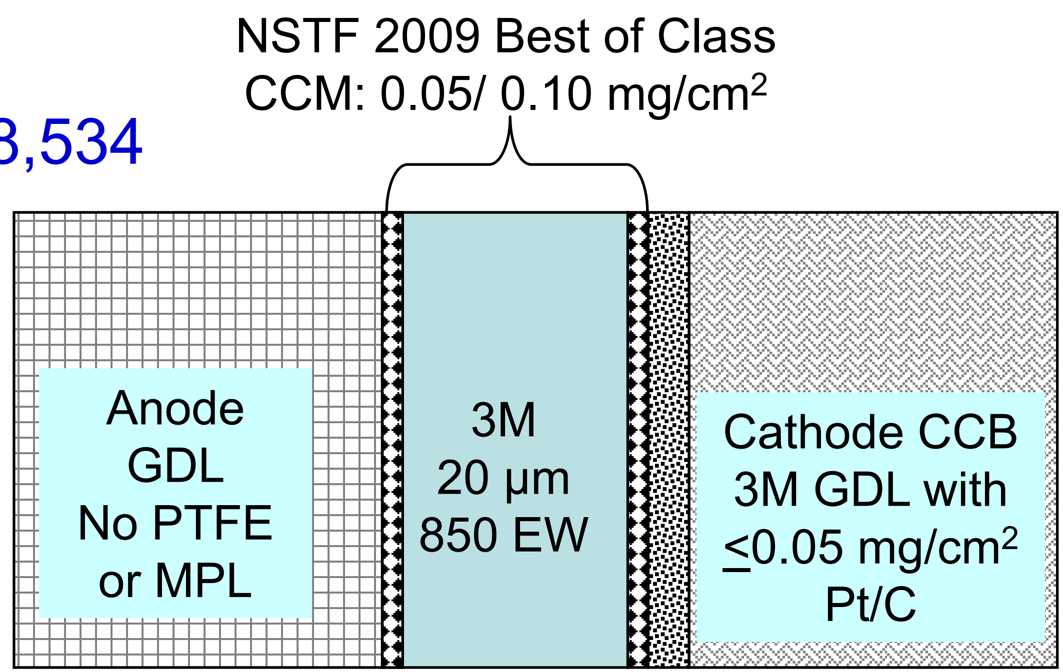
- Backing type: Fixed, 3M Standard
- Hydrophobic treatment - % PTFE
- MPL type – probably fixed
- Hybrid vs non-hybrid (Hybrid CCB)
  - Pt/C type and loading, I/C ratio,
  - C diluent fraction
  - Coating chemistry and method

Deciding Factors:

- Water management metrics (enhanced water out the cathode)
- ORR metrics
- HCT metrics (Mass transfer overpotential) at high temperature
- Pt loading cost/benefit ratio
- Accelerated stress tests

Hybrid Type B: US 6,238,534

- Anode = NSTF Pt, 0.05 mg/cm^2
- **Cathode = 3M Gradient** = NSTF + Pt/C (CCB on 3M GDL)
- PEM = 3M 20 μm,
- Anode GDL = MPL-free type A used as-received

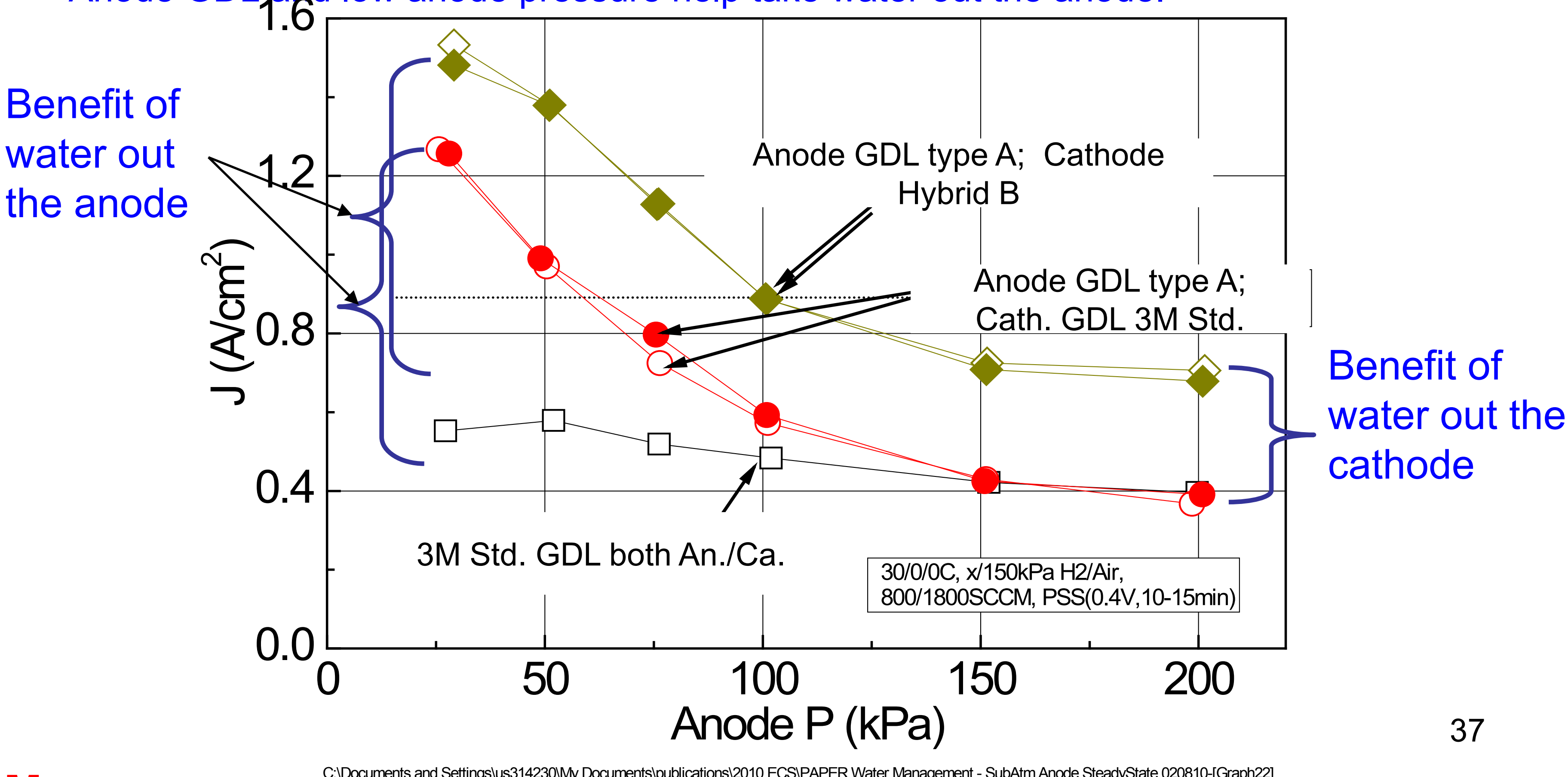


Task 5.1/5.2/5.3 – MEA Integration for Final Stack Testing

❑ 2010 Best of Class” MEA component down-selection process

Example 4: Cathode GDL Options: Hybrid B: 30°C Steady State vs. P_{Anode}

- Hybrid B MEA’s show significant low Temperature benefit relative to NSTF CCM-only.
- Water management effects of cathode CCB and Anode GDL, P_A appear primarily additive:
  - CCB helps take water out cathode
  - Anode GDL and low anode pressure help take water out the anode.



Task 5.1/5.2/5.3 – MEA Integration for Final Stack Testing

❑ 2010 Best of Class" MEA component down-selection process

Low Temperature Water Management Summary

- Strategies to increase the fraction of water moving out the anode and decrease the liquid water moving out the cathode are most effective for increasing cool, wet limiting currents.
  - Natural NSTF hydrophilic property enables this approach
  - Best strategy in principle for any MEA if it can be done – harvests product water to humidify PEM, decreases O_2 mass transport impedance on the cathode.
- Novel effect of sub-atmospheric anode pressure (P_A) operation demonstrated:
  - Several-fold increase in room temperature limiting current
  - P_A effect sensitive to temperature, anode GDL properties. **Useful for screening GDL's.**
  - Conventional "thick" dispersed electrode MEAs do not show same benefit.
  - Water balance mechanistic study
    - Reduced anode pressure decreases total water flux out cathode.
    - Simple model suggests performance improvement due to decreased *liquid* product water flux through cathode GDL.
- Material Factors
  - **Anode GDL backing layer appears to be most significant component affecting control of water flow from cathode to anode at ambient pressure.**
  - Continuing to screen new vendor supplied GDL backing layers and 3M MPL's for best performance and minimal negative factors such as shorting.

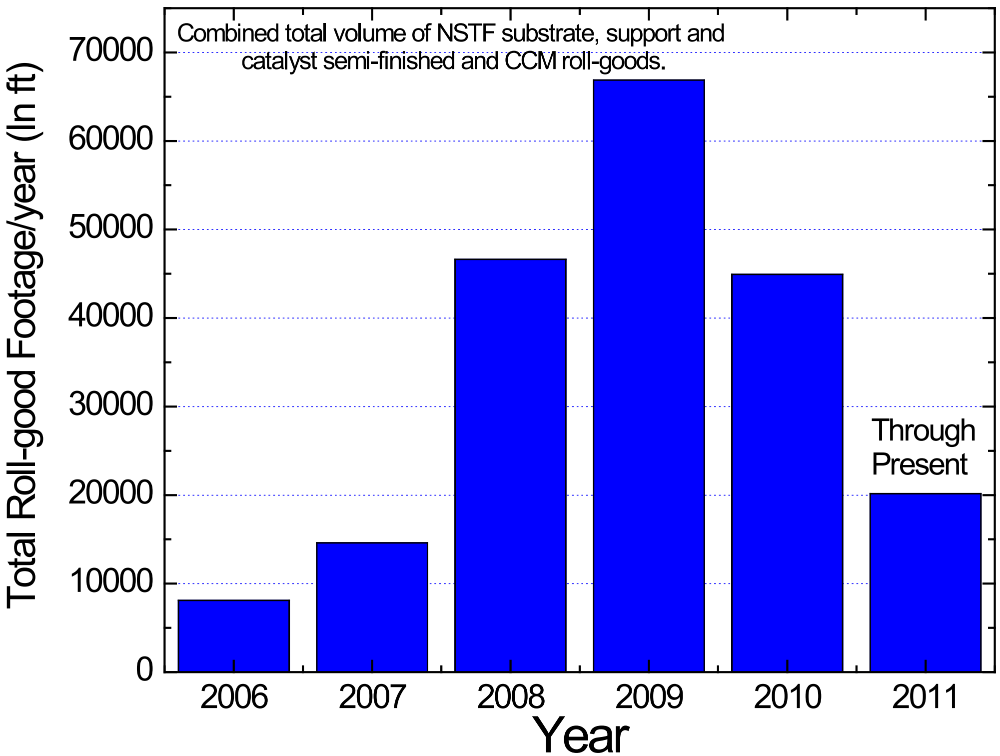
Technical Back-Up Slide

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

NSTF CCM Scale-up Status:

- Process improvements continuously being implemented for roll-good CCM component fabrication, quality and cost improvements.

- Produced 202,000 linear ft combined of NSTF substrate, coated catalyst supports, and catalyst coated membrane for process development, qualification and customer use since tracking started in 2006.



Thru Feb. 10 2011

MCTS
Catalyst Coated MCTS
\+ CCM
202,000 lin ft