2012 Annual Merit Review
DOE Hydrogen and Fuel Cells and Vehicle Technologies Programs

Advanced Cathode Catalysts and Supports for PEM Fuel Cells

Mark K. Debe
3M Company
May 15, 2012

Project ID: FC 001

Overview

Timeline

- Project start : April 1, 2007
- Project end : (98% complete)
  - Original - March 31, 2011
  - w/No Cost Ext. – June 30, 2012

Budget

- Total Project funding **$10.742 MM**
  - $8.593 MM DOE and FFRDC
  - $2.148 MM 3M share
- Allocated in FY11: $ 450,000
- Invoiced in FY11: $ 852,888
- Remaining for FY12: $ 244,704

Partners

- Dalhousie U. (J. Dahn, D. Stevens)
- JPL (C. Hays)
- ANL (N. Markovic, V. Stamenkovic)
- GM (E. Thompson, stack testing)

Barriers

A. Electrode and MEA Durability

B. Stack Material & Mfg Cost

C. Electrode and MEA Performance

DOE Technical Targets

Electrocatalyst / MEA	2017	2020
Lifetime w/cycling (Hrs)	5000	5000
% Loss in mass activity	< 40	< 40
Mass Activity @ 0.9V (A/mg)	0.44	0.44
Total PGM (g/KW rated)	0.125	0.125
Performance (W/cm^2) @ Rated Power / @ 0.8V	1 / 0.24	1 / 0.24

Additional Interactions

Nuvera Fuel Cells, Other OEM's, Proton Onsite, Giner Inc., ANL (Ahluwalia modeling group)

- Project Management - 3M (A. Steinbach, M. Kurkowski, S. Hendricks, A. Hester, P. Kadera, G. Vernstrom, M. Debe)

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.

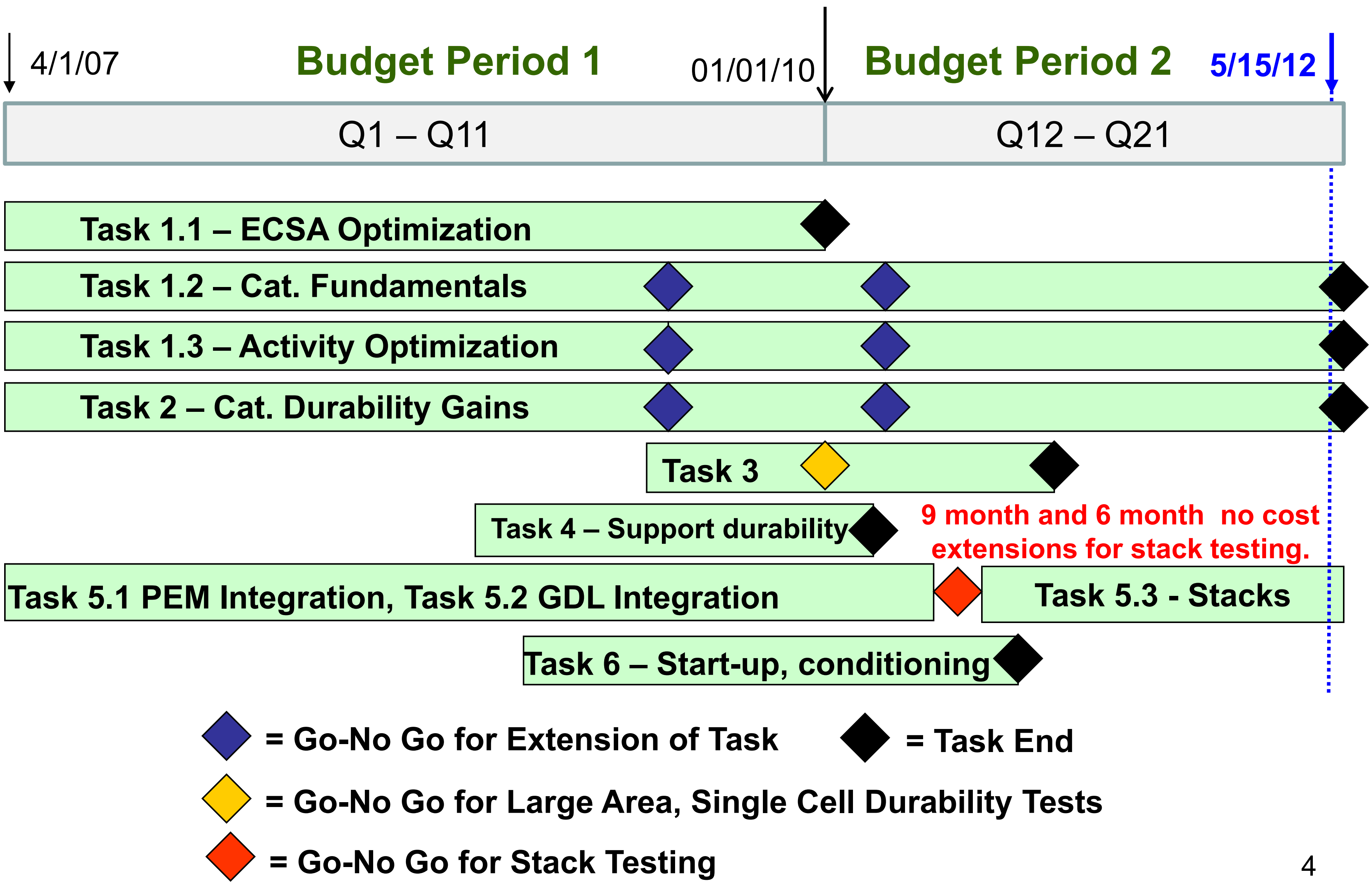
Approach:

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:

- Short stack testing with PtCoMn based NSTF electrodes
  - Completion of 1st short stack testing for performance
  - Down-selection and fabrication of final MEA components for 2nd durability stack
  - Initiation of 2nd stack durability cycling protocol
- Development work on Pt_3Ni_7 NSTF catalysts
  - Work towards optimization of deposition and annealing processes
  - Work towards optimization of *ex-situ* de-alloying and roll-to-roll pilot level scale-up
  - Addressing membrane integration issues

Relevance and Approach: Project Timeline and Milestones



Technical Accomplishments and Progress

Major Technical Accomplishments Since Last Review (5/10/11)

- ❑ **Short stack testing with PtCoMn based NSTF electrodes** (Task 5.3)
  - Completed 1st 29 cell rainbow short stack performance testing at GM to down-select the MEA configuration. Down-selection from 6 to 1 configurations successfully made.
  - Initiated durability cycling tests with 2nd short stack (20 cells with one type of 3M MEA).
- ❑ **Met 2017 CV cycling and OCV targets with MEA type used in 2nd short stack testing**
  - 30,000 CV cycle test: Demonstrated 10 $\pm$ 7 mV loss at 0.8 A/cm^2, 16 $\pm$ 2% loss of EC surface area, and 37 $\pm$ 2 % loss of mass activity (Task 2).
  - Met 3M OCV hold test: 570 hours with OCV loss = 13 % under 50 kPa H_2 overpressure
- ❑ **Development work on Pt_3Ni_7 NSTF catalysts** (Task 1)
  - Extended enhanced catalyst deposition process improvement (P1) from pure Pt and PtCoMn to Pt_3Ni_7 , obtaining same dramatic gains in Pt(hkl) grain size with simpler, more cost effective coating process.
  - Screened over 100 different de-alloying conditions for impact on fuel cell performance.
  - Developed 240x faster *ex-situ* de-alloying process than initial nitric acid bath conditions.
  - Developed roll-to-roll pilot level scale-up with 240x faster dealloying process conditions.
  - Achieved 0.4 – 0.45 A/mg-Pt mass activity with 100% roll-to-roll fabricated, dealloyed and SET- "annealed" catalyst at 0.121 mg/cm^2 loading of Pt_3Ni_7 for cathode use.
  - Achieved 0.16 g_{Pt}/kW at 0.65 V,80 ^oC and 200kPaa using 0.15 mg/cm^2 total Pt in MEA.
- ❑ **Developed model to explain a fundamental NSTF extended surface catalyst property**
  - Higher current density at low loadings due to ensemble packing of NSTF ext. surface cat.

Technical Accomplishments and Progress

Short stack 1 testing (2 week plan, 4.5 months actual)

Objective: Test 6 MEA configurations and down-select to 1 based on beginning of life performance, for final Stack 2 testing.

CCM ID	PEM	Anode	Cathode	S1622 Cells
Config. 1	3M-24um (w/add. 2)	0.05 P1 PtCoMn	0.15 P4 PtCoMn + SET	9-12
	3M-24um (w/add. 1)	0.05 P1 PtCoMn		
Config. 2	3M-24um (w/add. 2)	0.05 P1 PtCoMn	0.10 P1 PtCoMn	5-8, 22-25
Config. 3	3M-S	0.05 P1 PtCoMn	0.15 P1 PtCoMn	13-16
		0.05 P1 PtCoMn		
Config. 6	3M-X	0.05 P1 PtCoMn	0.15 P1 PtCoMn	17,18
Config. 7		0.05 P1 PtCoMn	0.10 P1 PtCoMn	19-21
Config. 8	3M-24um (w/add. 1)	0.05 P1 PtCoMn	0.15 P1 PtCoMn	1-4, 26-29

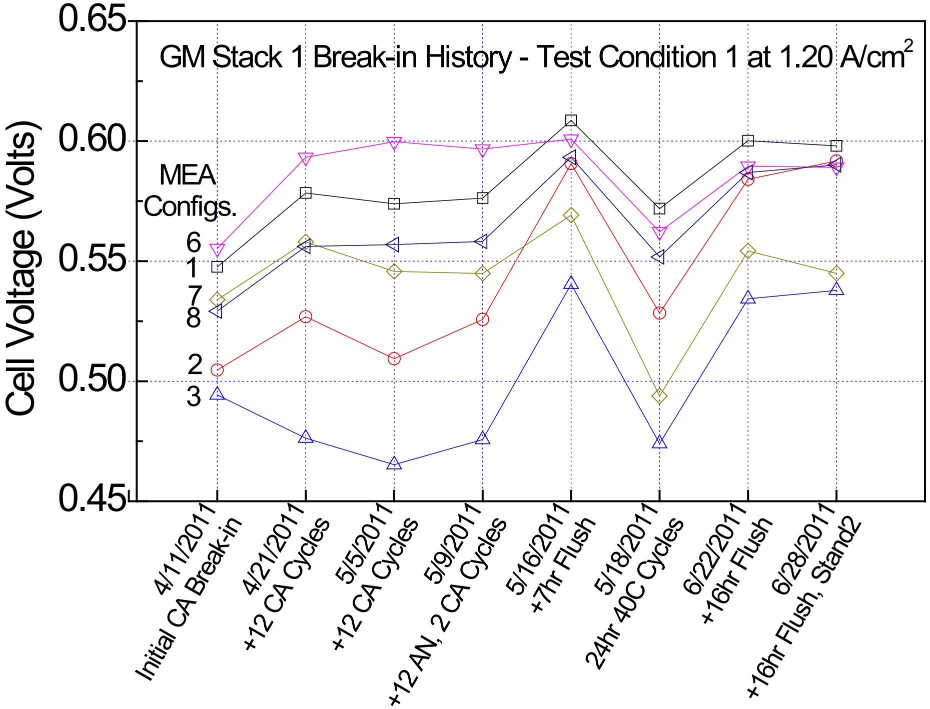
- Stack 1 : 29 cells
- Break-in conditioning
- Extensive “debugging” of low performance at GM, 3M.
- Beginning Of Life testing from 4/10/11 to 6/28/11.
- Reversible decay tests from ~ 7/21/11 to 8/3/11.
- Durability test protocol development completed 8/29/11.

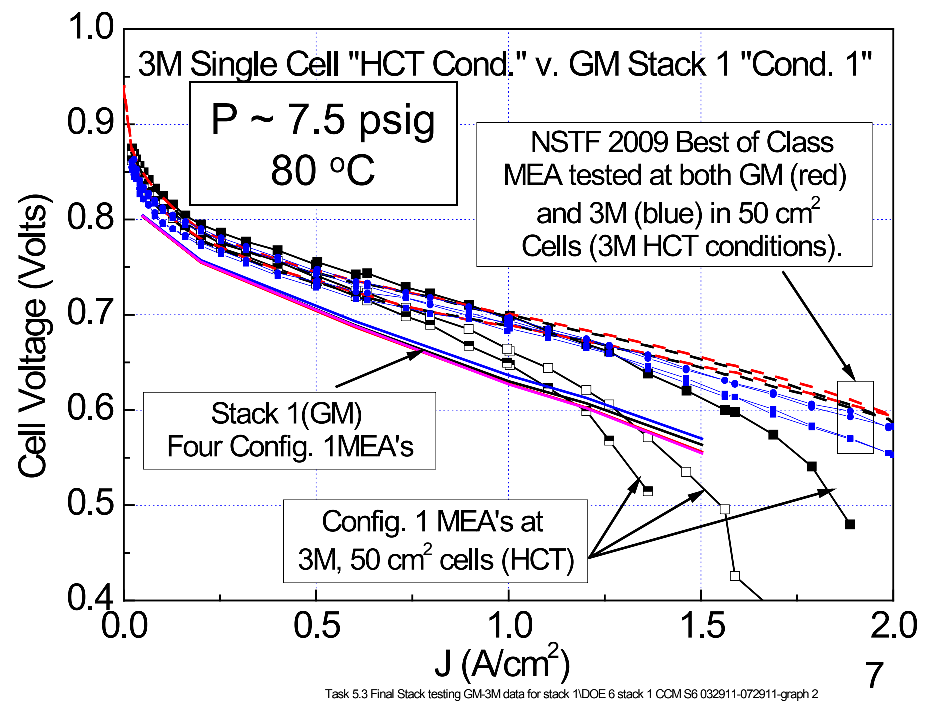
- The various configurations showed a wide range of performances which facilitated the MEA configuration down-selection for Stack 2 durability testing.
- MEA Configuration 1 performed best, had best stability under all GM tests conditions.(MEA Config. 1 was down-selected, but not ultimately used in Stack 2).
- For all GM test conditions, the stack performance of each MEA configuration was significantly lower than the same MEA’s in 50 cm^2 cells tested at 3M.

Technical Accomplishments and Progress

Short stack 1 testing: issues

- Break-in conditioning was problematic - test station water identified as an issue.
- Best MEA performances (MEA Config. 1) were much worse than past history with 50 cm^2 single cells at both GM and 3M at low pressures (bottom right figure).
- Config. 1 MEA's (same lot as in stacks) also underperformed 3M expected results
- Catalyst ORR metrics and surface area's, and CCM's SEM characterization were normal.
- Possible reasons for under-performance: (3M high current test (HCT) ≈ GM conditions)
  - More complete conditioning possible with single cells; water purity
  - Differences due to stack vs. single cell flow field effects (see Stack 2 discussion).
  - Membrane ionomer properties or contamination.

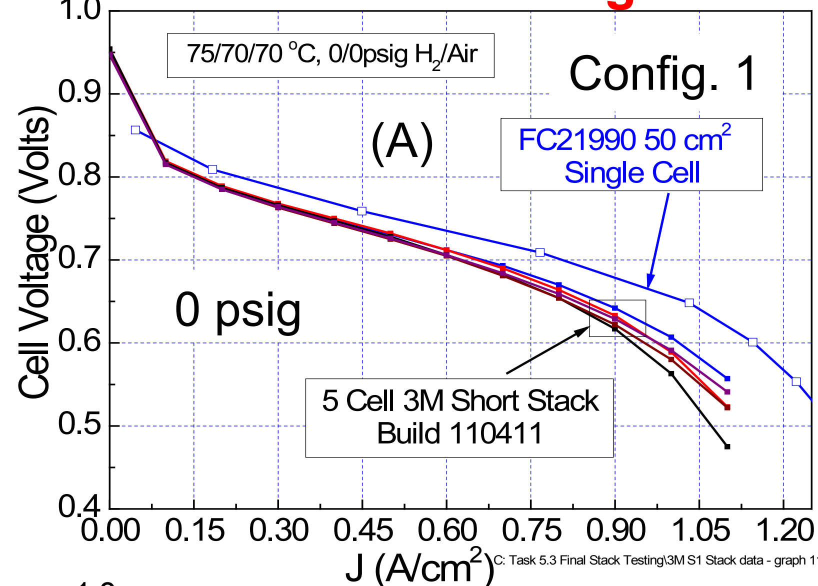


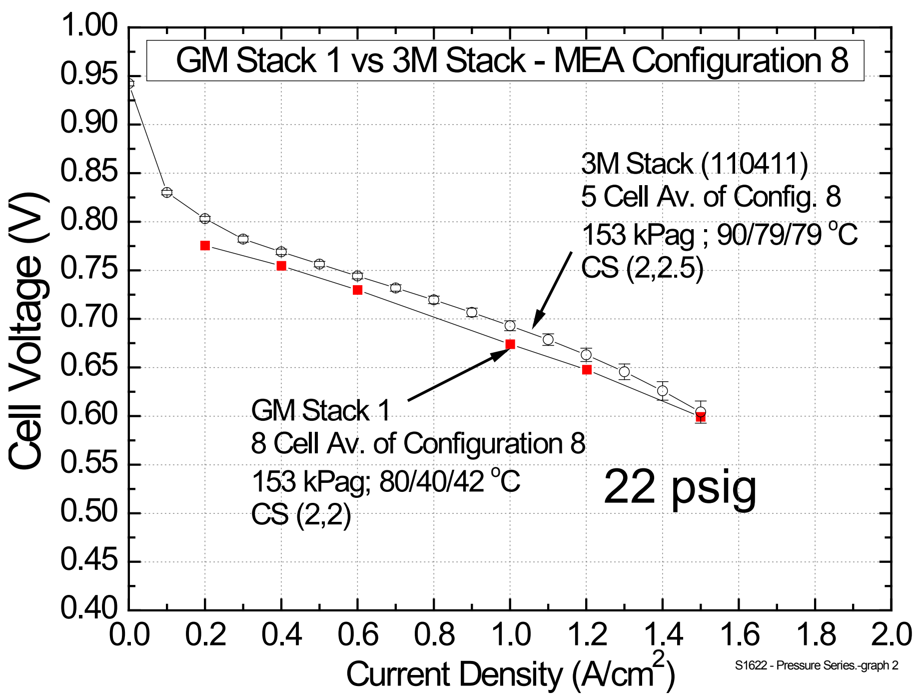


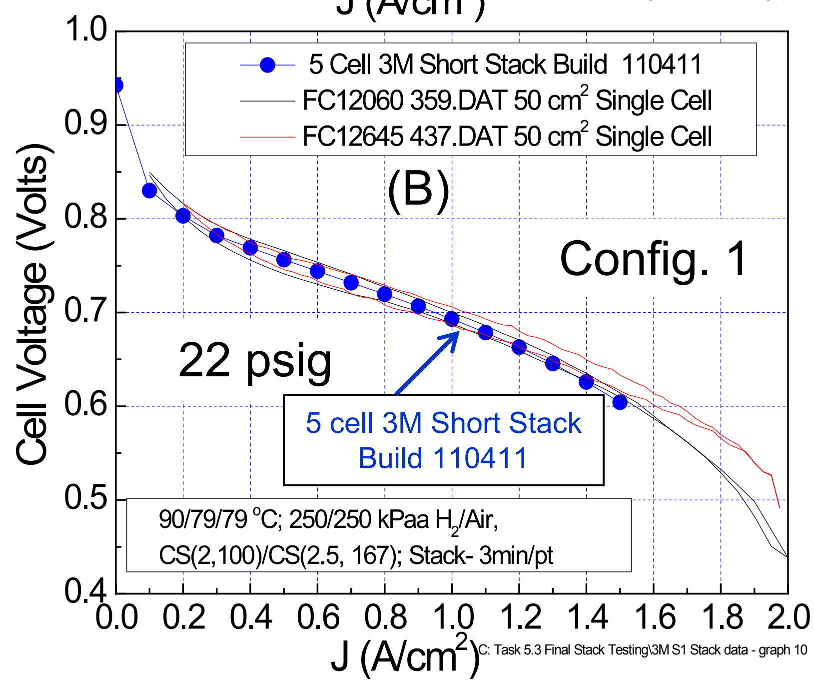
Technical Accomplishments and Progress

Short stack 1 testing: comparison with 3M short stack testing

- With configuration 1 MEA, 3M's 312 cm^2 short stack gives similar performance to 50 cm^2 single cells at high pressure but not at low pressure (3M Stack flow fields very similar to single 50 cm^2 cell) (A,B).
- 3M short stack gives higher performance than GM short stack (C).
- These results suggest possible flow field effect contribution to under-performance.





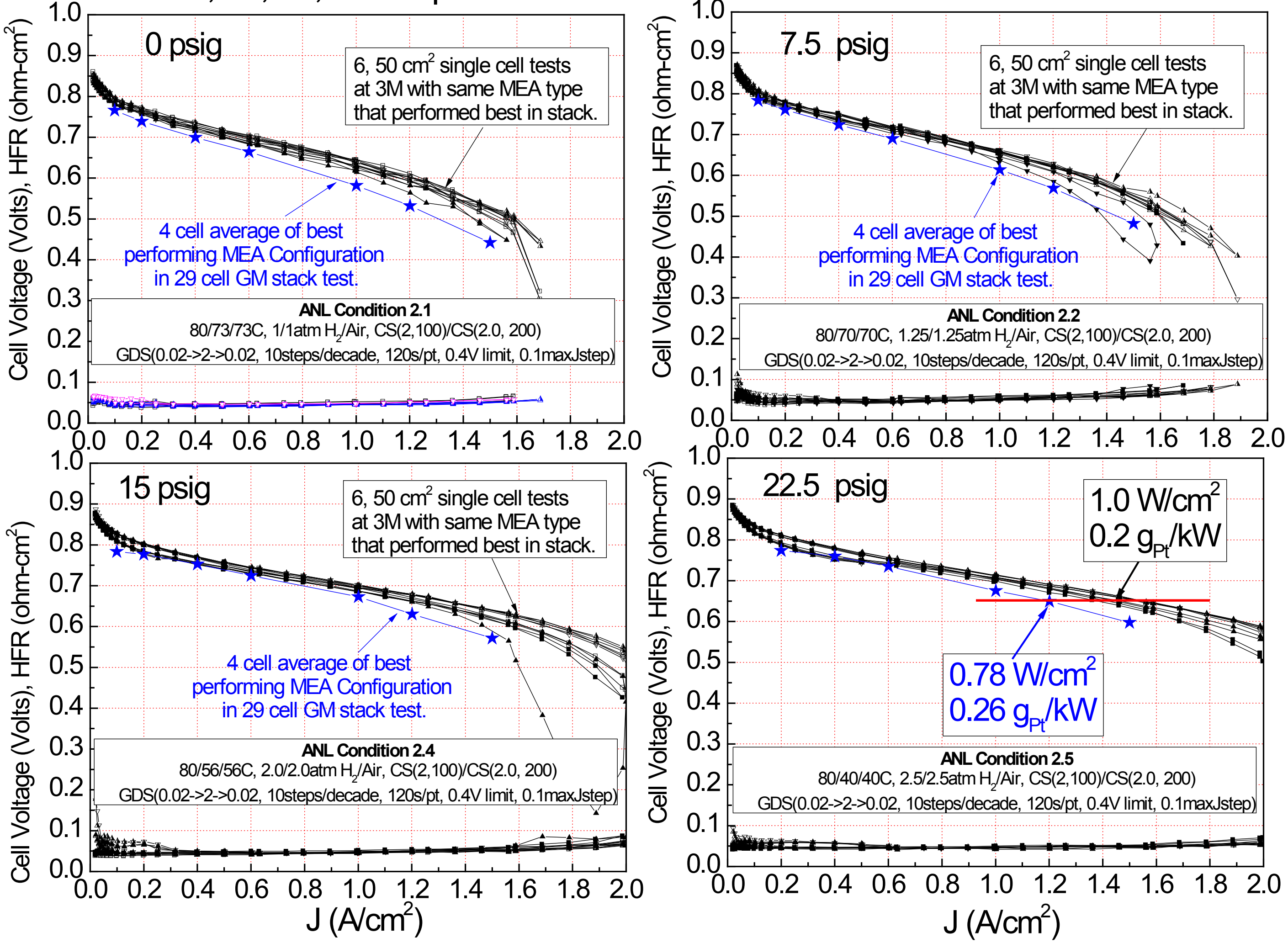


Technical Accomplishments and Progress

Short stack 1 testing: GM stack vs 3M 50 cm² cells - ANL pressure series.

- ❑ MEA configuration 1 average performance improves with pressure similarly in GM stack as in 3M single cell, using ANL test conditions, but stack still lags single cells.

Case 2.1,2.2,2.4,2.5 - Impact of Pressure



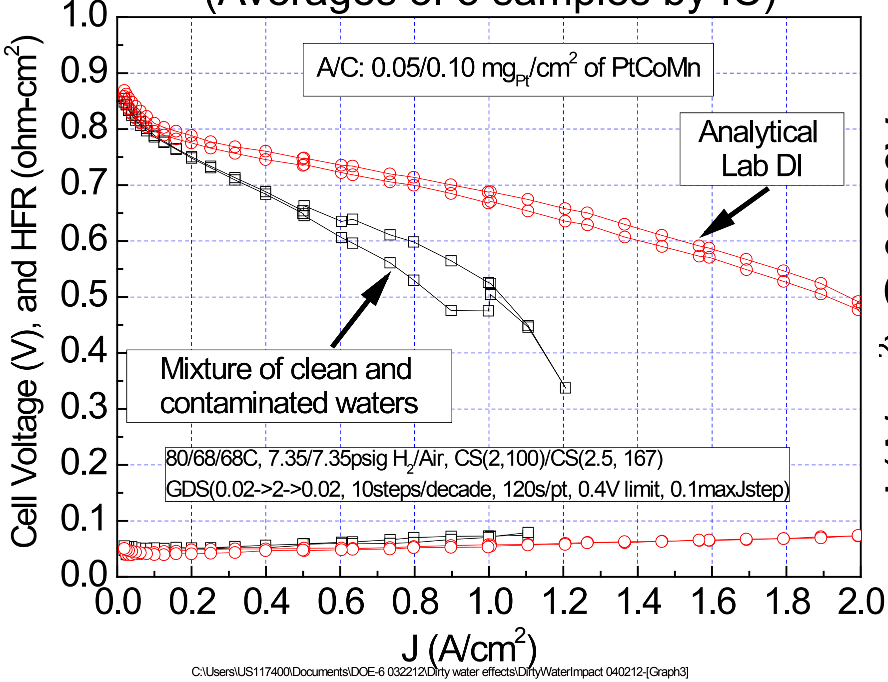
- GM stack data is 4 cell average of the best performing MEA configuration type 1.
- Test conditions are those from A NL (Ahluwalia) systems modeling group.
- Strong effect of pressure consistent with mass transport issues.
- Cell compression in GM stack evaluated and believed not to be an issue.

Task 5.3 Final Stack Testing\GM-3M data for Stack 1\ANL Systems Model - graph 13

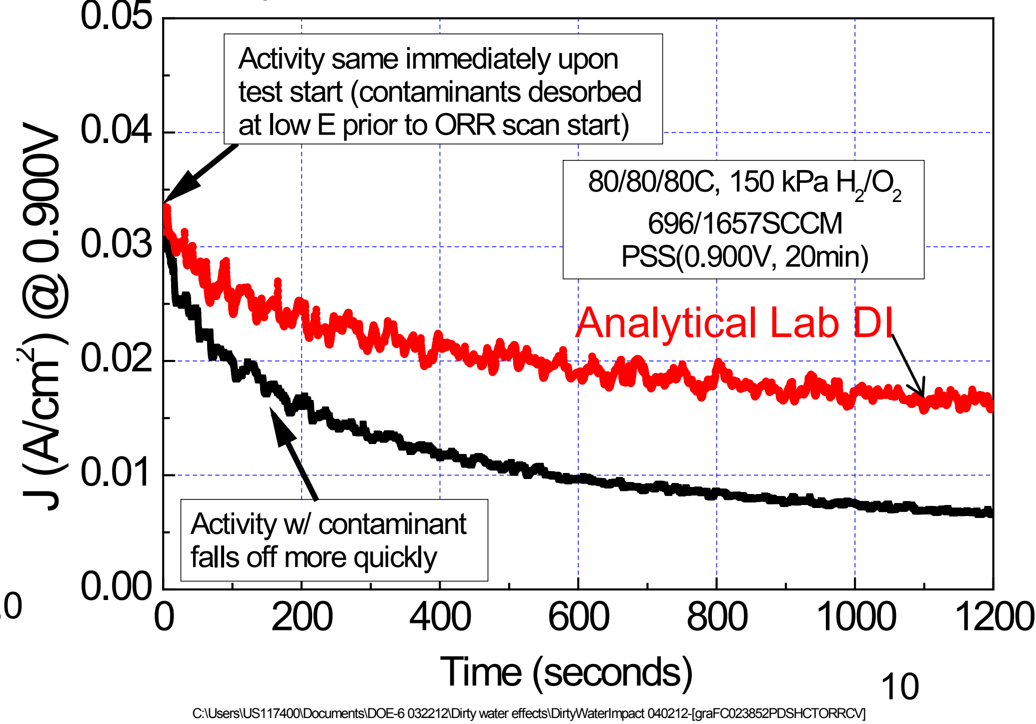
Short stack 1 testing: Illustration of water contamination effect

- Effect of contamination at 3M Laboratory water (18 Mohm-cm, but new unit):
  - High current density performance in galvanodynamic scans dramatically affected.
  - Activity measurements at 900mV show co-adsorption of OH^- and probably Cl^-.

Analytical Lab DI (red curve): 1.2 ± 0.5 μM Cl^-
Contaminated waters : 16.9 ± 0.3 μM Cl^-
(Averages of 5 samples by IC)



ORR Absolute Activity @ 1050s:
Contaminated DI: 7.5mA/cm²-planar
Analytical Lab DI: 17.6mA/cm²-planar



Technical Accomplishments and Progress

Short stack 2 testing: Objectives, status and issues

Objective: Demonstrate 3000 hours of durability load cycling using 29 cell short stack with 20 cells devoted to the down-selected 3M MEA.

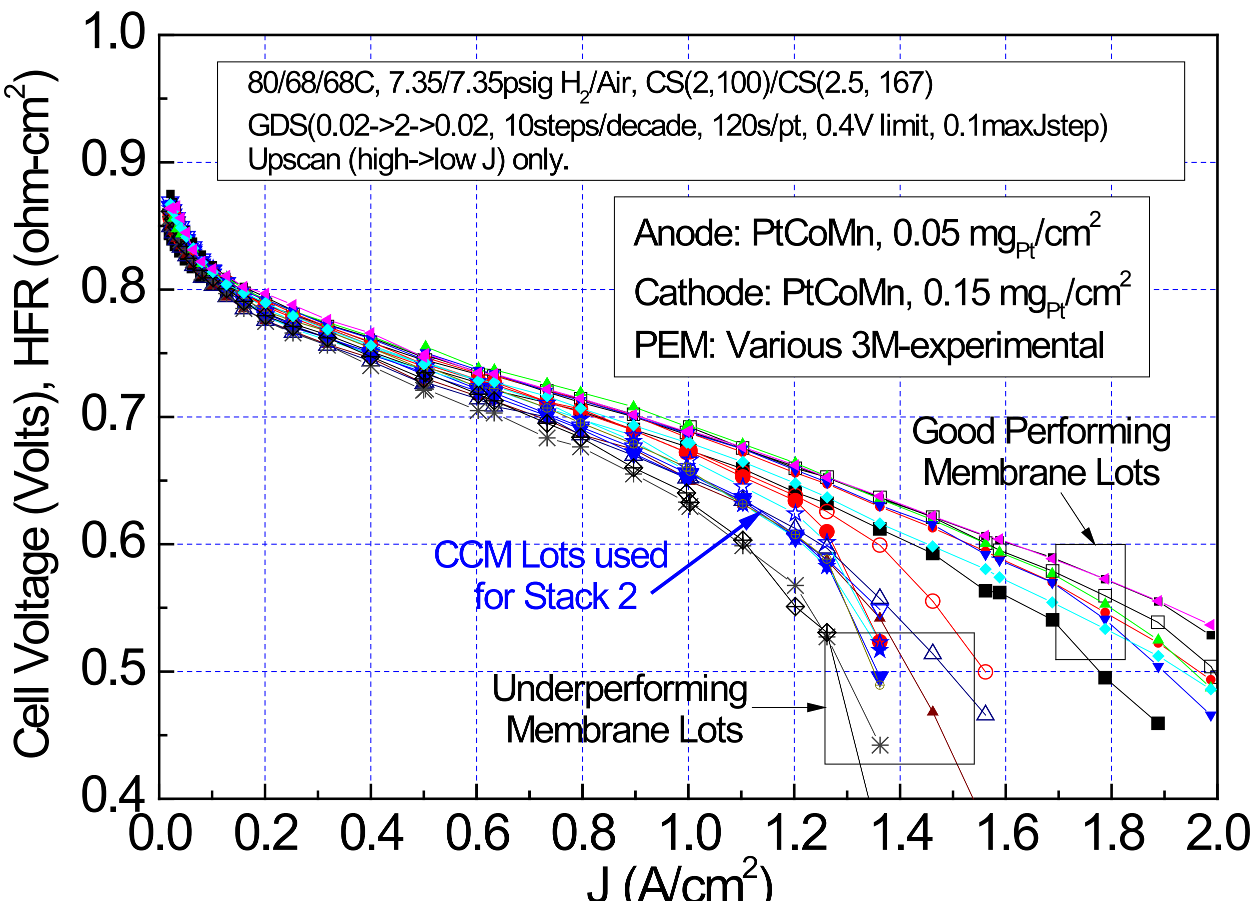
Status and Issues:

- CCM production issues and membrane availability forced a change in final MEA configuration from the original down-selected configuration (1) to a combination of configurations of 1 and 3, using new, 3M experimental membrane.
- CCM's and GDL's delivered to GM on 1/15/12, ~ 6 months after plan.
  - New GM stack plates fabricated
  - Stack 2 build completed on 2/1/12
  - Break-in conditioning completed ~ 3/1/12. Durability testing started 3/16/12.
  - 3M discovered after shipment, that CCM's sent used an underperforming membrane lot
    - Impact is significant loss of high current density performance in 50 cm^2 cells.
    - Likely possibility that stack 2 durability testing will be negatively impacted.
    - However single cell MEA accelerated stress tests still meet 2017 targets.
- Stack 2 Performance to date
  - Stack 2 performance fell below that of stack 1 under most conditions tested.
  - First four sets of stack 2 durability cycling completed, 350 hours, by 3/29/12.
  - Significant decay rates observed during first four sets of 1500 durability cycles/set.
  - GM replaced 3 weak cells at 350 hours. Stack restarted 4/11/12.
  - Some improvement under some conditions after re-start.

Technical Accomplishments and Progress

Short stack 2 testing: Issues – Background for Underperforming MEA's

- Gradual performance decay over much of 2011 realized in this project's single cell testing
- Myriad other CCM component changes masked what was occurring
- Also question about possible DI water quality in this time period, but not confirmed.
- Discovery of membrane performance issue after shipment of MEA's for Stack 2
- Problem traced to inadvertent release of experimental PEM lot that had been put on-hold.

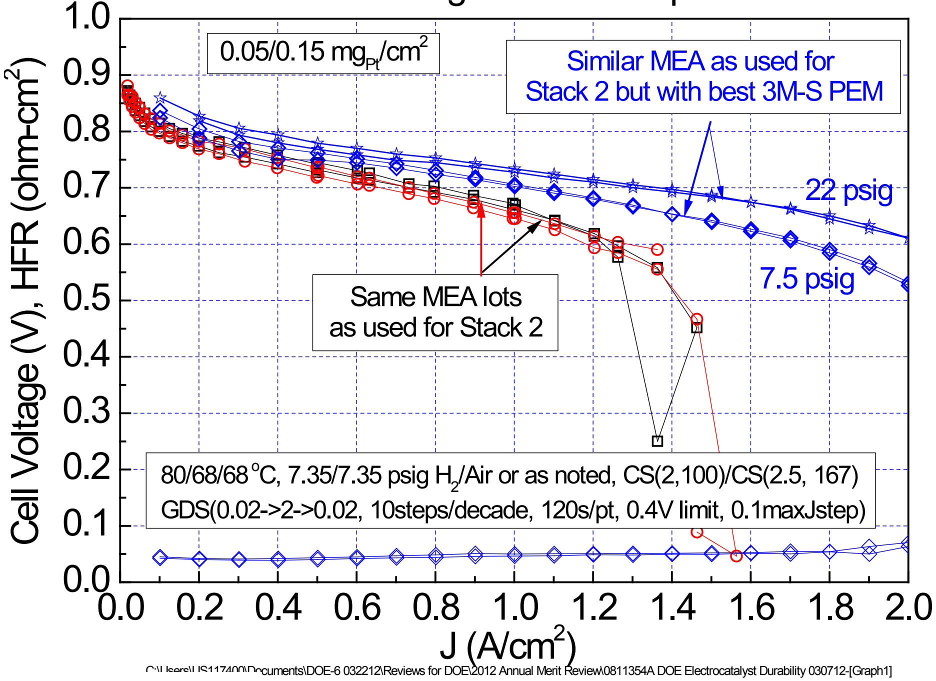


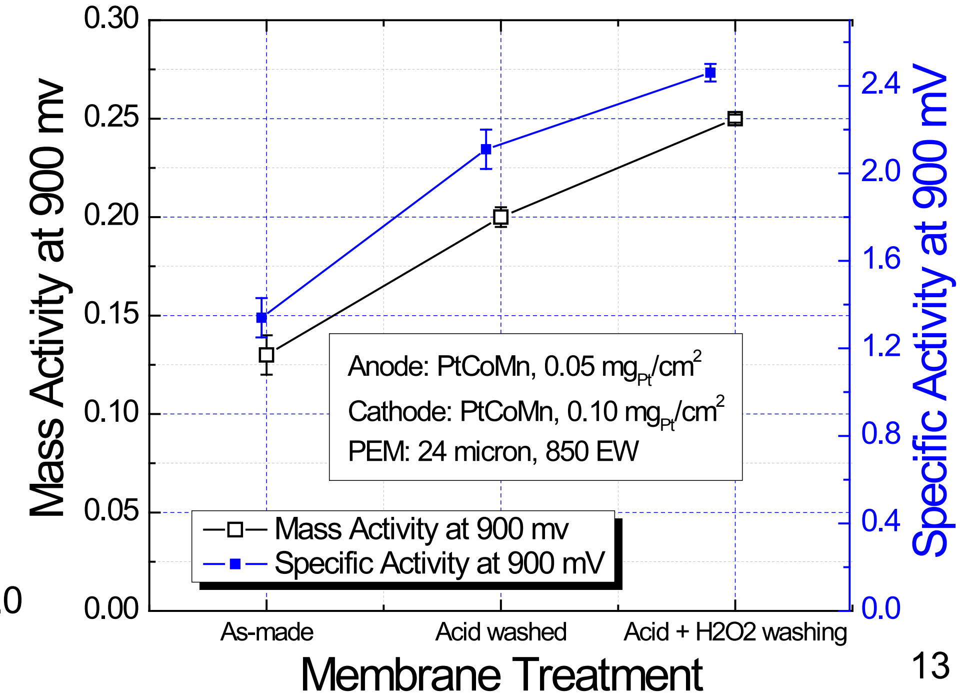
- Most obvious effect of membrane lot issue is loss of high current density performance.
- 50 cm^2 cell tests of CCM's from same lot as used for Stack 2 (blue stars) show:
  - Catalyst specific and mass activities were a little low in as-made membranes.
  - ECSA's and HFR are both normal.

Technical Accomplishments and Progress

Short stack 2 testing: Issues - Membrane performance issue

- 50 cm^2 single cell tests with best 3M-S experimental PEM (high performing) and similar catalysts show significantly better performance over that of MEA's used in stack 2 (left figure).
- Limiting current density and ORR activities are strongly affected.
- Membrane cleaning (regular 3M PEM w/ same ionomer lot as stack 2 PEM) has large effect on PtCoMn ORR specific and mass activity:
  - Activities in as-made PEM are below historical averages (2011 AMR, slide 17) of 1.75 mA/cm^2_{Pt} and 0.16 A/mg_{Pt} by -24% and -16% respectively.
  - Acid washing increases the mass and specific activities above the historical values.
  - Acid + peroxide cleaning increases the specific and mass activities to +40% and +60% above the historical values respectively.
- Membrane cleaning does not improve the reduced limiting current density issue!

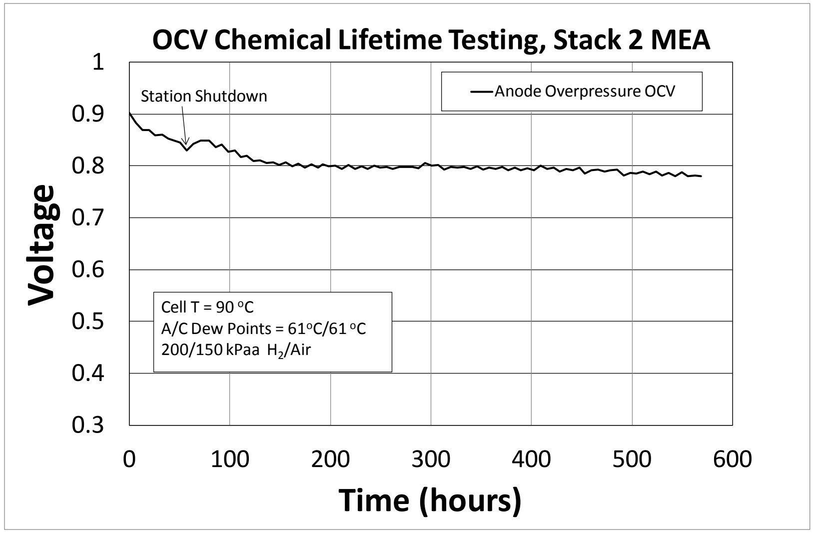


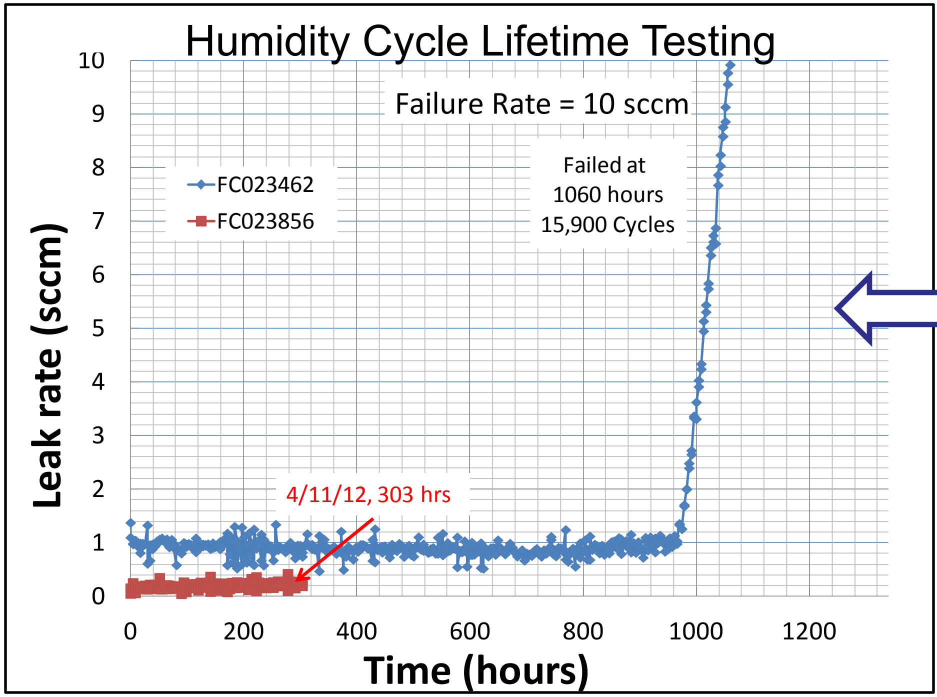


Technical Accomplishments and Progress

Short stack 2 testing: RH Cycling and OCV Hold lifetime tests with Stack 2 MEA

- ❑ RH cycle tests of MEAs from same lot of CCM as used for Stack 2 are still being completed:
  - The first CCM failed (developed hole) after 1060 hours or 15,900 cycles, short of 20,000 cycle target (see bottom left and right).
  - Second CCM just starting and has lower leak rate to start (see bottom left, red curve.)
- ❑ OCV Hold test of MEA from same lot of CCM as used for Stack 2 has passed 500 hr target (see top right).





**RH Cycle Running Conditions:

- Wet Stream: 1000 sccm, 150%RH
- Dry Stream: 2000sccm, 0%RH
- 80°C Cell Temperature, 0/0psi
- 2 min wet, 2 min dry cycle
- Leak check every 5 hours (physical sccm leak measurement instead of crossover current measurement across MEA)

** Based on: Table D-4 Membrane Mechanical Cycle and Metrics, (Test using a MEA)Table revised December 10, 2009, Target Tables from U. S. Drive Fuel Cell Technical Team Technology Roadmap.

Technical Accomplishments and Progress

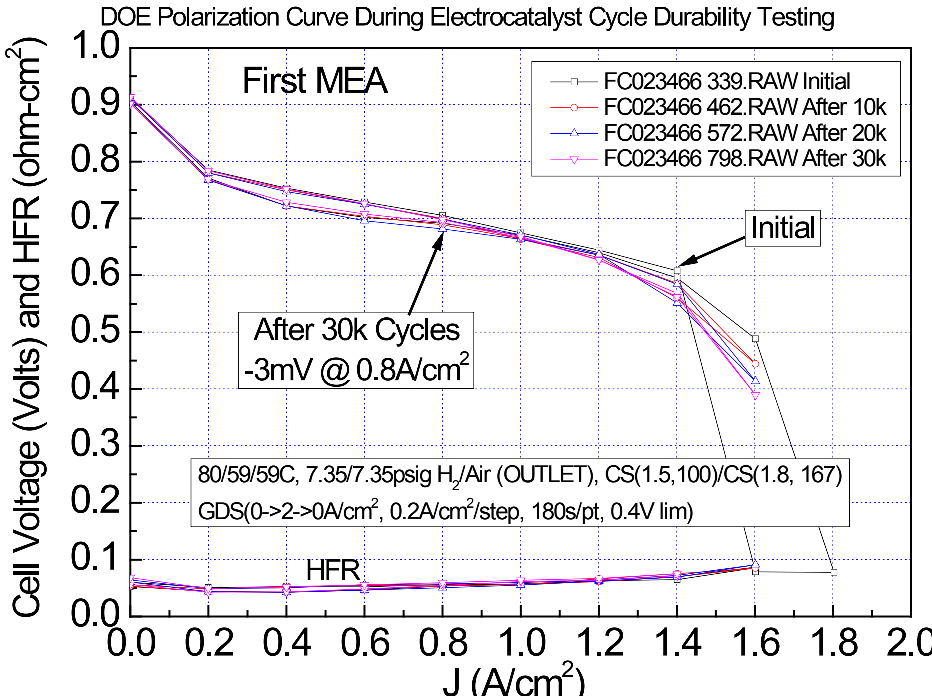
Stack 2: Objectives, status and issues: Cathode CV cycling stress test

Test Protocol (US Drive FC Tech. Team)

30,000 saw-tooth cycles at 50 mV/sec;
0.6 - 1.0 - 0.6 V; 80/80/80 °C, 50 cm^2
100/100 kPa H_2/N_2; 200/200SCCM.

2 MEA's : definition (same as used in Stack 2)

Cathode Catalyst: 0.15 mg/cm^2 PtCoMn (P4+SET)
Anode catalyst: 0.05 mg/cm^2 PtCoMn (P4)
GDL's: 3M standard 2979 on A/C
PEM: 3M-Supported with additive, 18 micron thick



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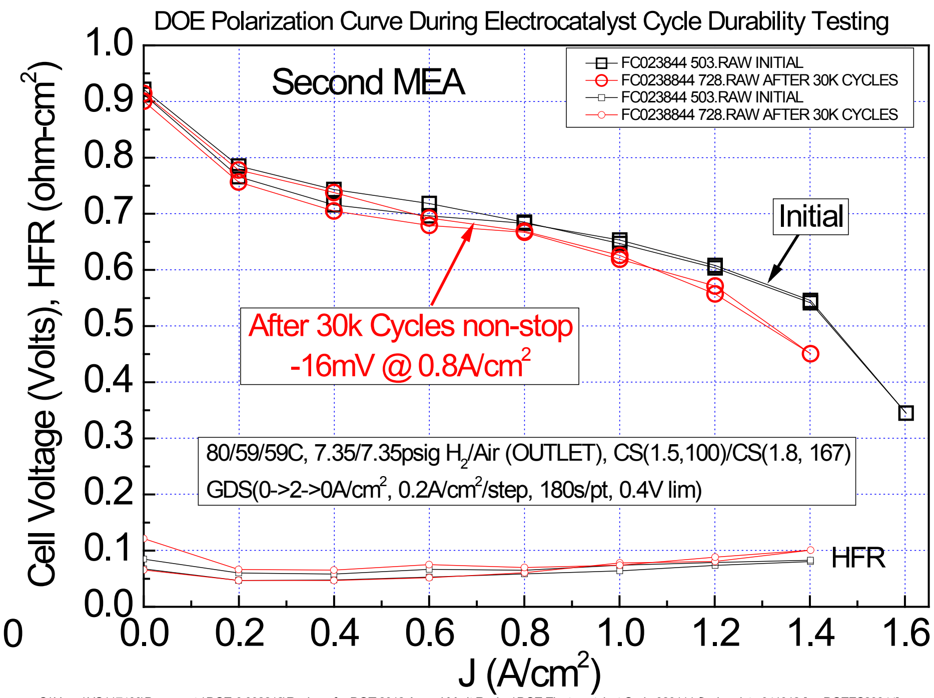

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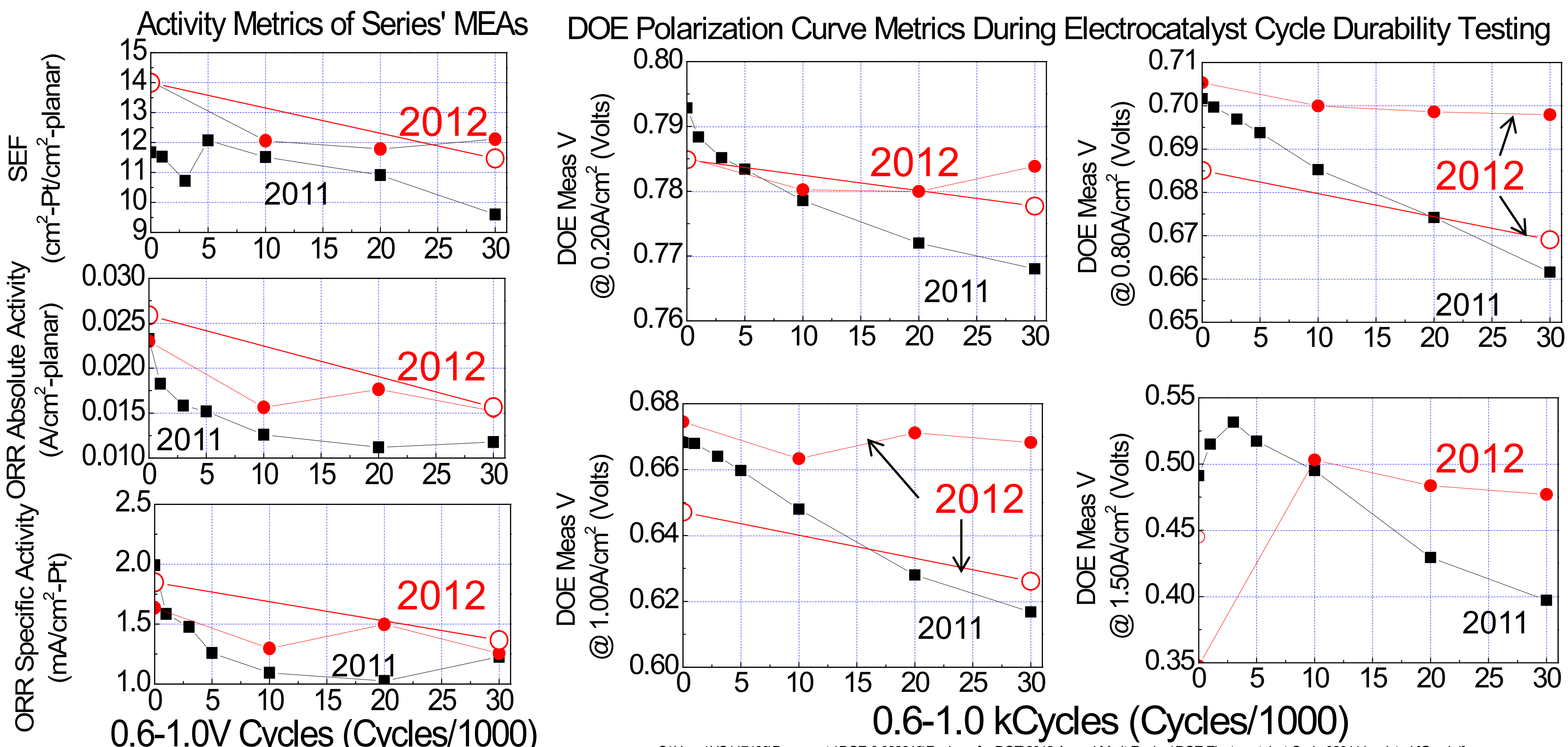
- First MEA polarization curves taken periodically using both DOE and 3M (HCT) protocols.
- Second MEA ran 30,000 cycles without stopping to save time. Both exceed 2017 targets.

Technical Accomplishments and Progress

Stack 2: Objectives, status and issues: Cathode CV cycling stress test

- **Stack 2 type MEA's meet all 2017 targets for this test, even with contaminated PEM.**
  - Surface area losses of (-14, -18)% meet 2017 target (≤ 40% loss of initial area).
  - DOE Polarization curve voltage losses at 0.8 A/cm^2 of (-3, -16)mV meet target (≤ 30 mV).
  - Mass activity loss of (-34, -39)% meet 2017 target (≤ 40% loss of initial mass activity).

ORR and Polarization Curve Metrics vs Number of Cycles (2012 vs 2011)



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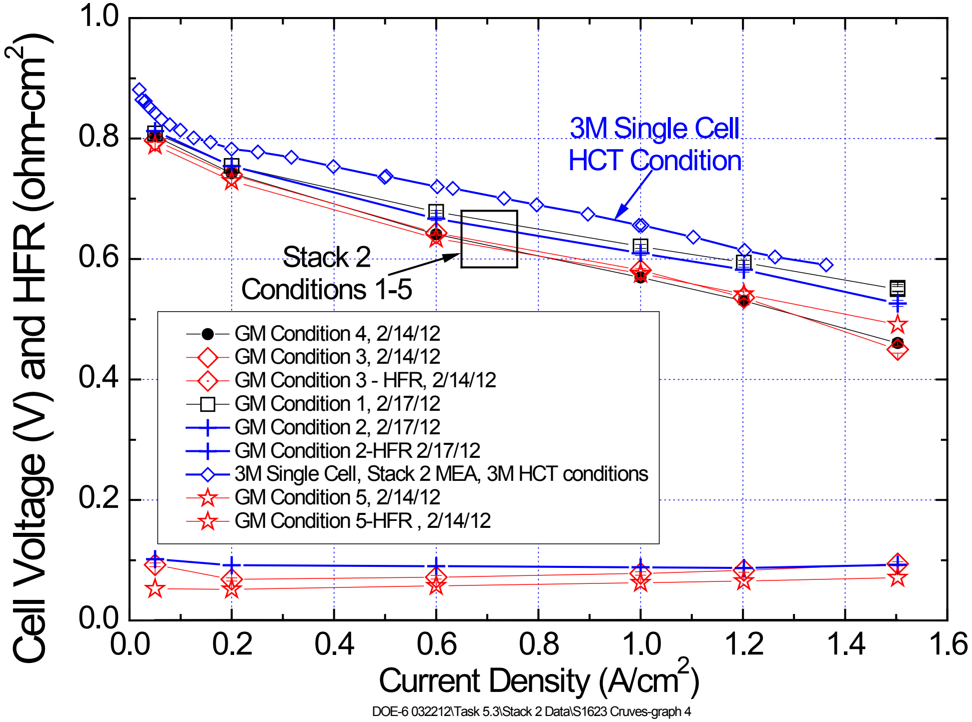
Technical Accomplishments and Progress

Short stack 2 testing: Beginning of Life Performance

❑ Stack 2 testing beginning of life performance and testing conditions

- Stack 2 performance was evaluated under five different sets of operating conditions (table).
- Stack 2 performance was much lower than expected under all conditions.
- Stack 2 performances did not vary significantly from driest to wettest conditions.
- Stack 2 performances under-performed 3M 50 cm^2 single cell with same MEA lot as in stack.
- Stack 2 performances were generally below stack 1 performances at start of durability cycling.
- Average H_{upd} cathode surface areas were ~ normal at 8.2 m^2/g.
- Shorting resistances were lower than standard MEA's. Compression paper results normal.



Stack Cond.	T (°C)	An/Ca St.	An RH in (%)	Can RH out (%)	Pressure
1	~ 82	~1.5/1.8	25	82	Variable
2	~ 75	~1.5/1.8	30	85	Variable
3	~ 65	~2 /1.8	30	≥100	Variable
4	~ 78	~1.5/1.8	20	65	Variable
5	~ 78	~2.0/1.8	≥100	≥100	Variable

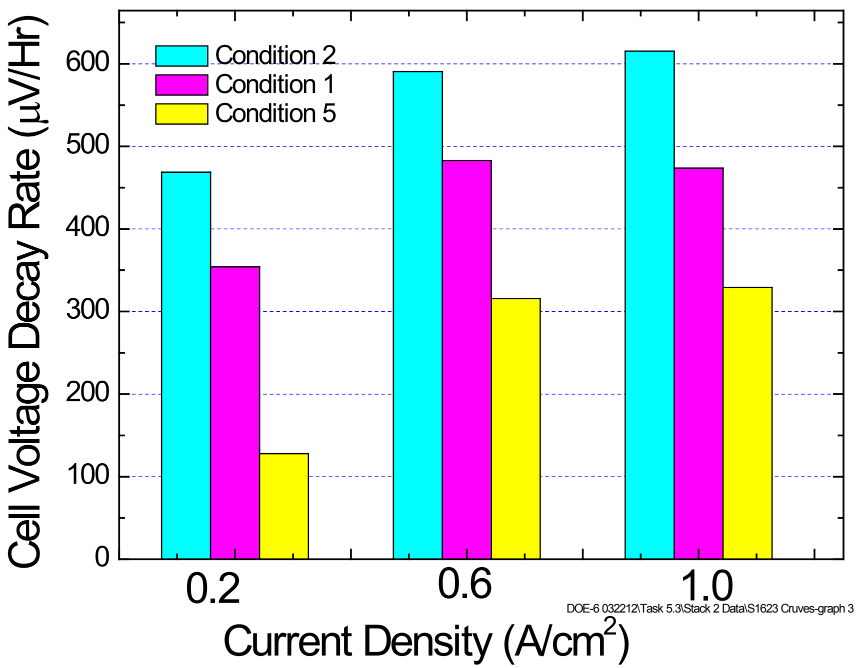
3M Single Cell HCT Cond.:
T (°C) Cell/An/Ca DP's = 80/68/68 °C,
H_2/air pressure = 150/150 kPaa
An/Ca Stoichs. = 2/2.5

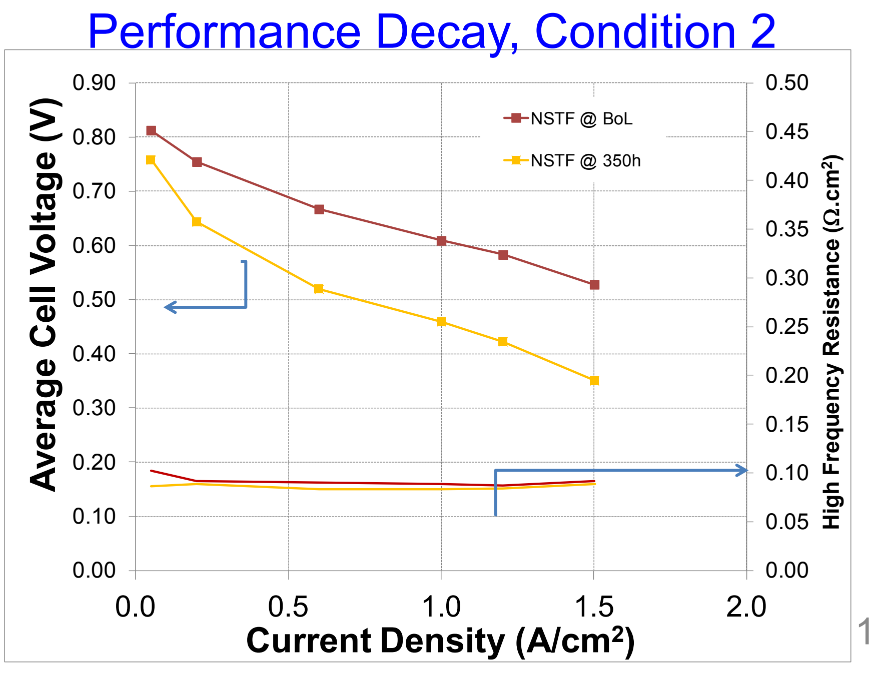
Technical Accomplishments and Progress

Short stack 2 testing: Durability cycling status

❑ **Stack 2 showed significant degradation after each of four, 1500 cycle sets:**

- Durability cycling modified US Drive Fuel Cell Tech Team recommended protocol:
  - Higher pressure, controlled current ramp rate, voltage control, fine tuning…
- Results after 4 sets of 1500 cycles:
  - Crossover leak rate of stack and hydrogen take-over in cells were high
  - HFR increased with time but cannot account for lost performance
  - 2 point (beginning and end) decay rates for 4 Cycle sets over 250 hours are much higher (3x-8x) than expected (bar-graph).
  - There are significant fluctuations in performances between each of the 4 Cycle sets.
  - After replacing weak cells 4/12/12, 100mV increase at 1.5 Acm^2 under Cond. 2.

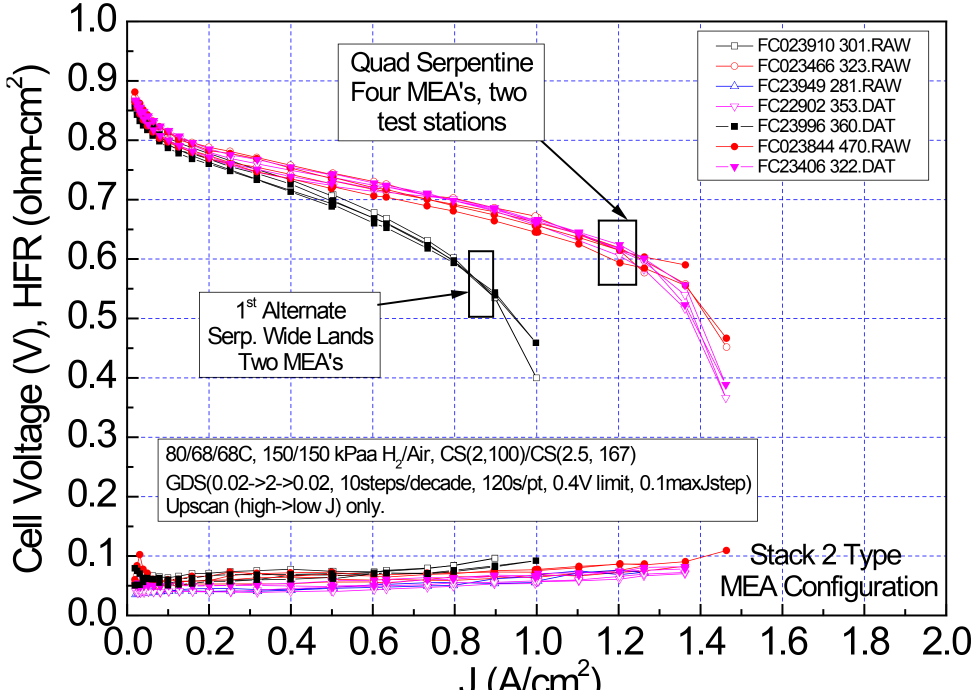




Technical Accomplishments and Progress

Short stack 2 testing: Issues – Investigating possible flow field effects

- Impact of flow field: Study started 3/25/12 comparing 1st of 9 different types of flow field
- Tests are using the same MEA lot as used for Stack 2. Testing on multiple stations.
- First alternate FF completed and compared to 3M standard 50 cm^2 quad-serpentine:
  - Main difference is width of lands and channel dimensions:
    - **Quad-Serpentine:** 4 parallel channels, 10 loops; Channel W, D; Land = 0.8 mm,1 mm; 0.8 mm
    - **First Alternate Serpentine:** 6 parallel channels, 2 loops; Channel W,D; L = 2 mm, 0.25 mm; 2 mm
  - Both types have similar pressure drops (see figure on right).
  - Much poorer performance at 150kPaa pressure with wide lands of first alternate serpentine.
  - Performance with alternate FF improves only slightly with pressure increases (not shown).



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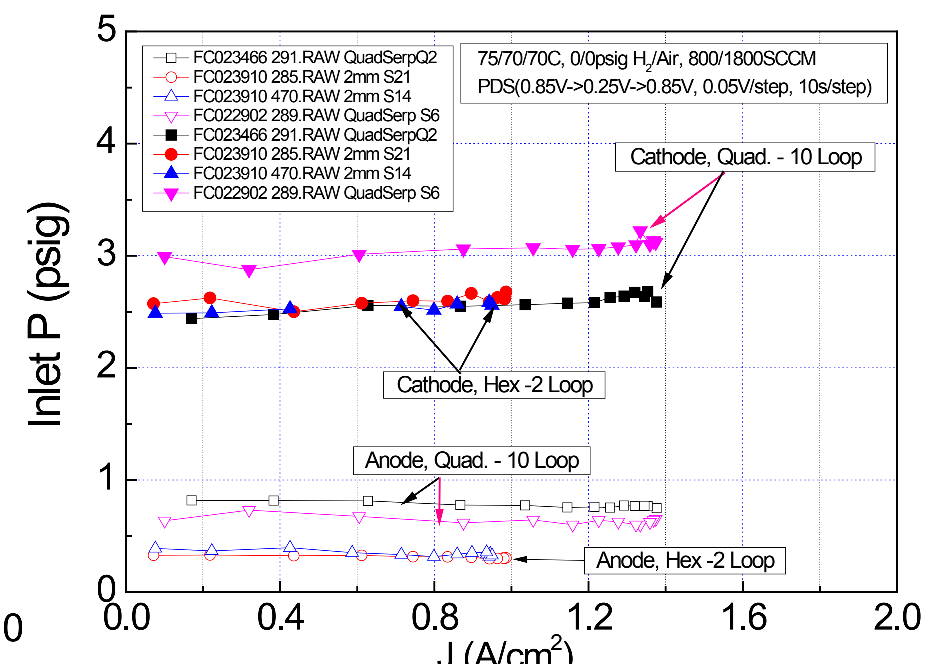

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Technical Accomplishments and Progress

Pt_3Ni_7 Development: Dealloying experiments and process scale-up

Objective: Study NSTF Pt-Ni alloy system to understand how to achieve stable nanoporosity that will increase surface area, specific activity and maintain stable high current density performance while being practicably scalable.

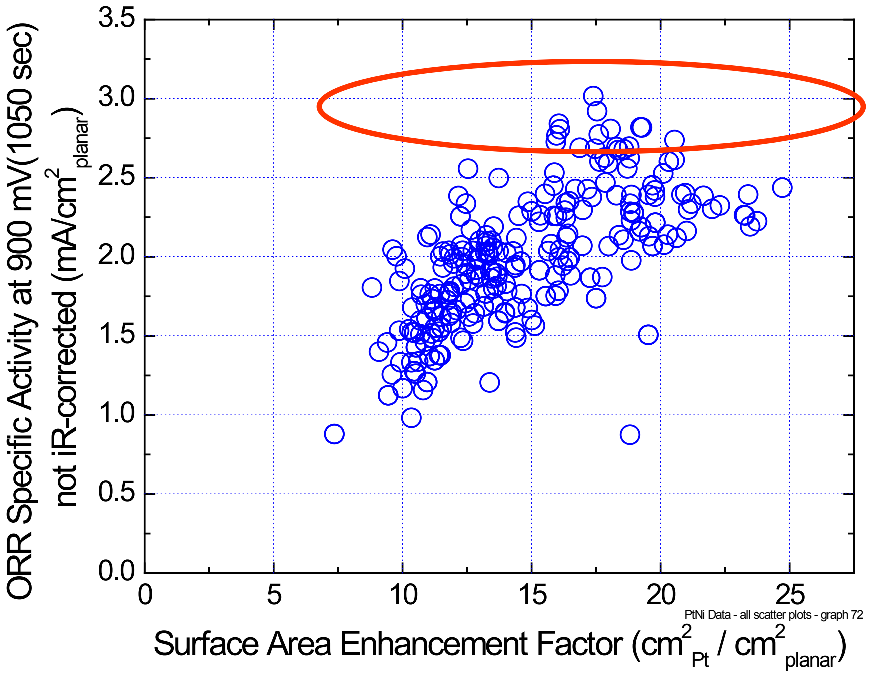
Approach: Use *ex-situ* methods to remove excess Ni from as-made Pt_3Ni_7 catalysts:

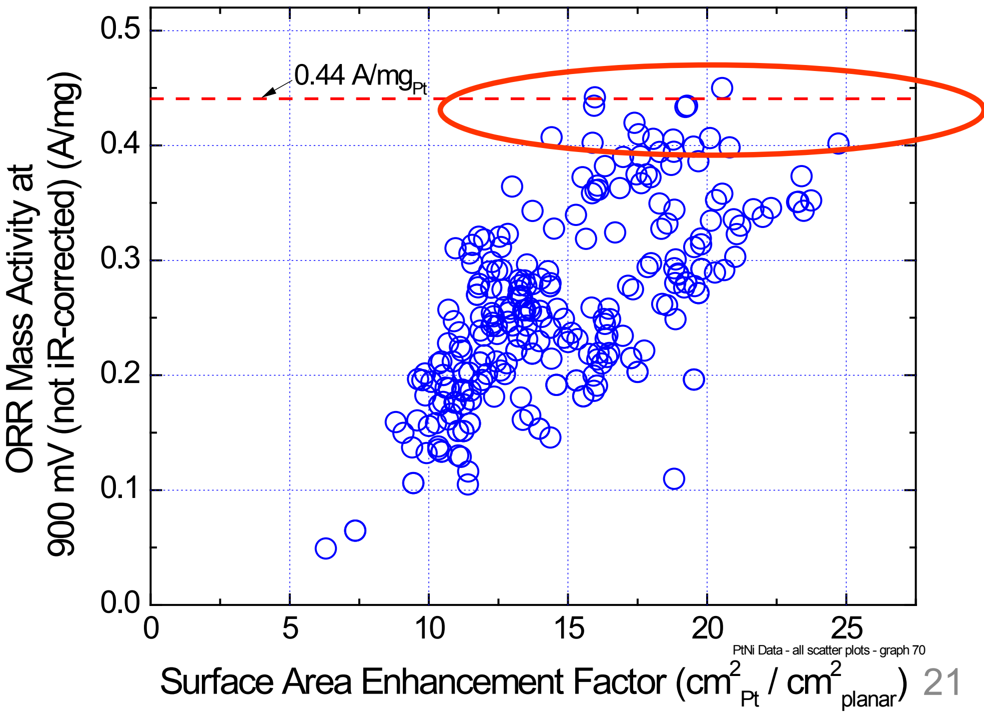
- ❑ Catalyst material factors
  - Loading (0.075, 0.10, 0.125, and 0.15 mg/cm^2)
  - Alloy homogeneity - Catalyst deposition process (P1 vs. P4 process)
  - Post-fabrication annealing – SET process
- ❑ Dealloying processes and conditions investigated
  - Electrochemical (ex-situ CV Cycling)
  - **Acid Washing (composition, concentrations, time, temperature)**
    - Batch treatment (Pt/Ni loadings vs time, acid composition and concentrations)
    - Requirements for roll-to-roll processing at reasonable web speeds
- ❑ Roll-to-roll scale-up capability (pilot level)
  - Facilities identification within 3M, equipment modifications, pretrial web-runs
  - Multiple trial runs, correlation of Pt/Ni dissolution rates with batch experiments
- ❑ Fuel cell testing and property characterization (XRD, XRF, TEM)
  - Correlation of ORR metrics and limiting currents with dealloying/SET processing
  - H_2/O_2 testing diagnostics of limiting currents
  - Correlation of Pt_3Ni_7 fcc(hkl) grain sizes, lattice parameters and compositions

Technical Accomplishments and Progress

Pt_3Ni_7 Development: Dealloying experiments and process scale-up

- **Results:** Fuel cell metrics correlated as "global" summaries
  - Over 100 different combinations of bath compositions, concentrations, times, roll-to-roll dealloy web speeds, and SET treatment process parameters for four loadings of Pt_3Ni_7 were tested in duplicate in 50 cm^2 fuel cells.
  - 16 ORR relevant kinetic and performance metrics were extracted from the PDS and GDS polarization curves and correlated with materials and process parameters (all proprietary).
  - Critical metrics may be plotted w/o identifying material/process factors=> 38 scatter-plots.
  - Example scatter plots follow. Show that roll-to-roll dealloying and SET processes were found which generate Pt_3Ni_7 ORR specific activities up to 3 mA/cm^2_{Pt} (left), and mass activities between 0.4 and 0.45 A/mg_{Pt} (right).

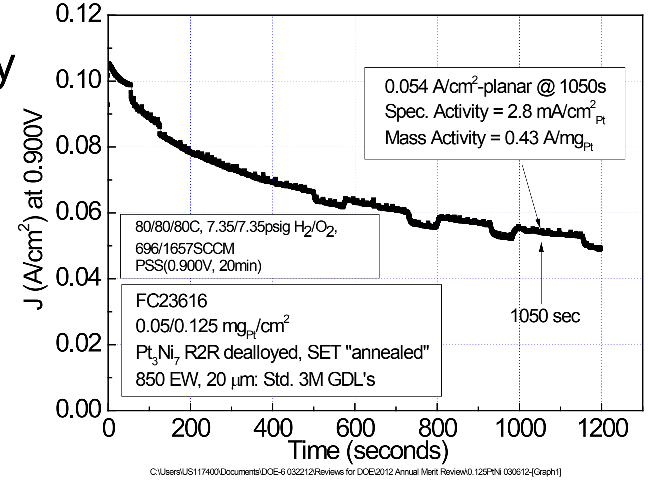




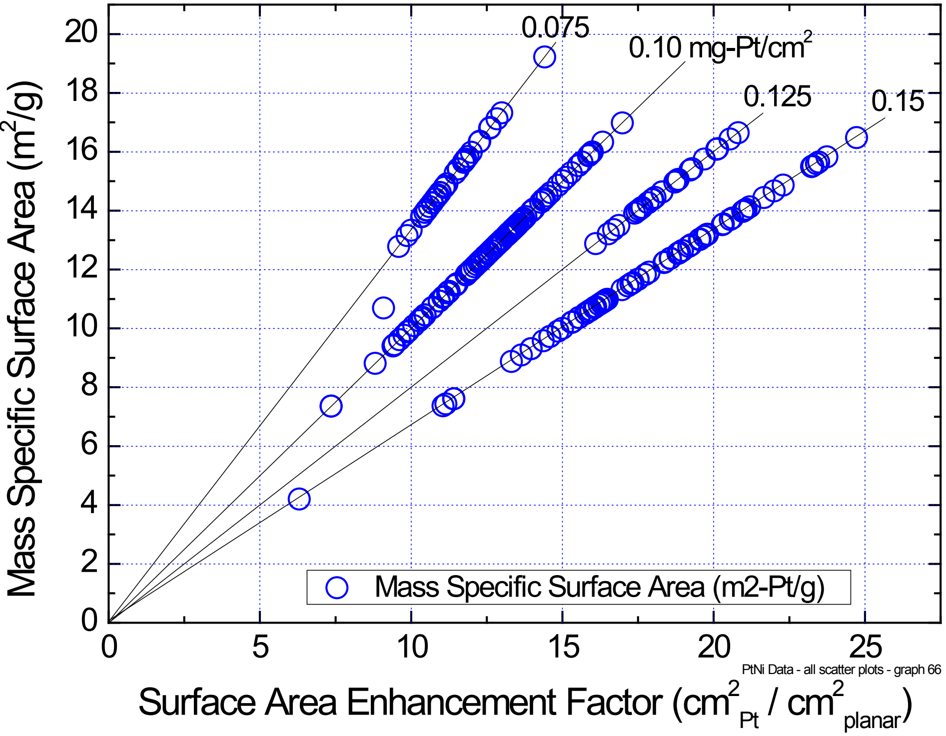
Technical Accomplishments and Progress

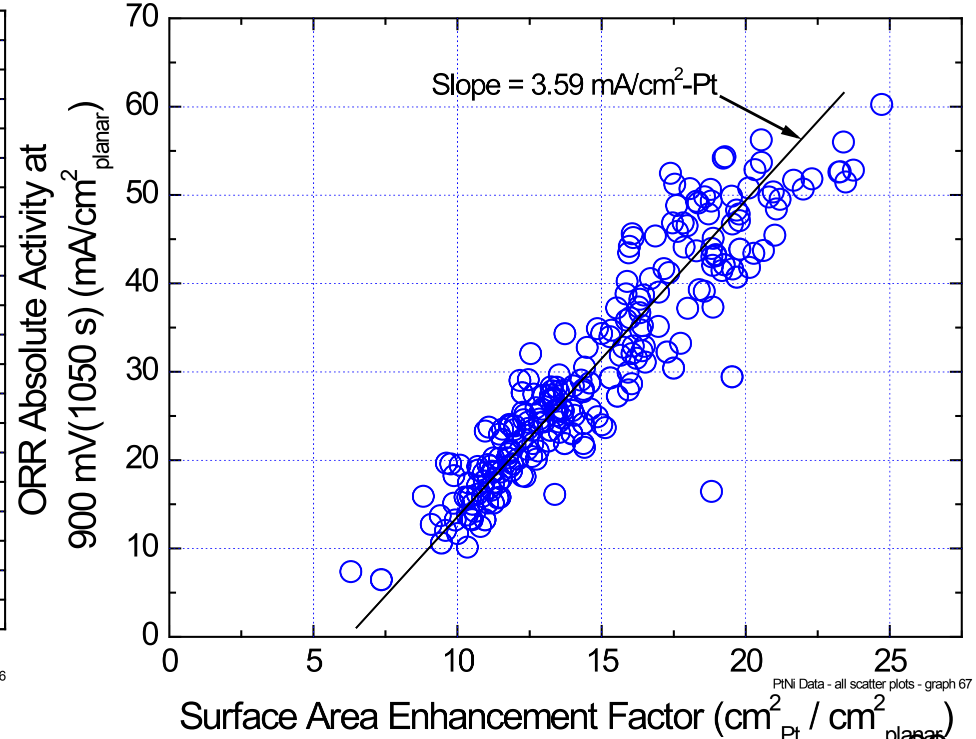
Pt_3Ni_7 Development: Dealloying experiments and process scale-up

- **Results:** Fuel Cell testing global summary
  - Surface area enhancement (SEF) factors up to 25 cm^2_{Pt}/cm^2_{planar} were generated, with mass specific surface areas of 15-20 m^2/g_{Pt} common for the highest mass activities (bottom left.)
  - The absolute activity at 900 mV is highly linear with SEF with a slope of a pseudo-specific activity of 3.6 mA/cm^2_{Pt} (bottom right).



ORR activity measure-ment protocol



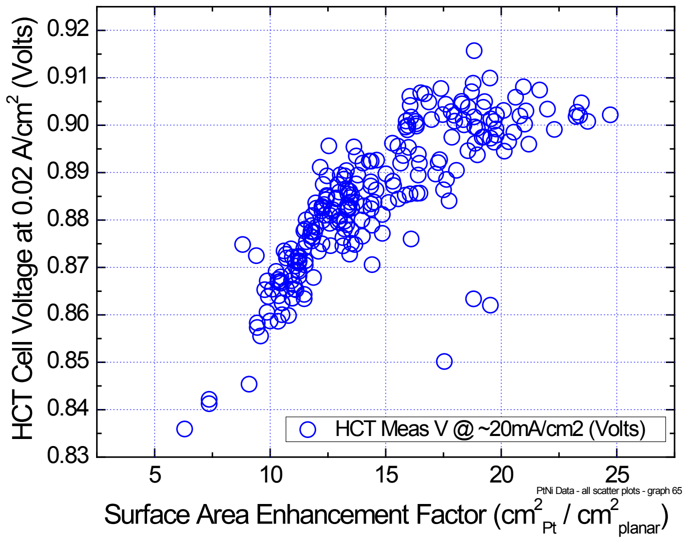


Technical Accomplishments and Progress

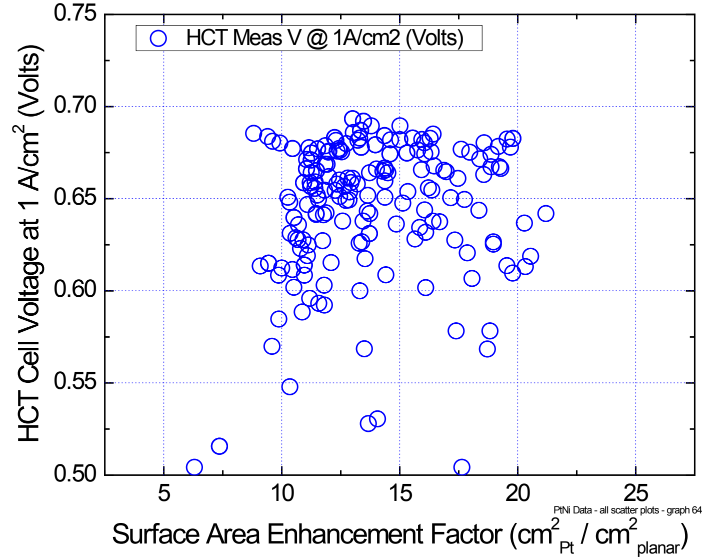
Pt_3Ni_7 Development: Dealloying experiments and process scale-up

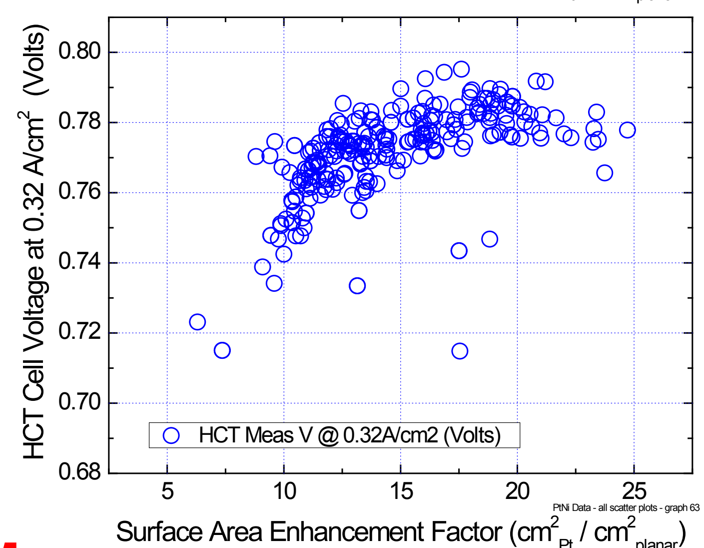
- **Results:** Fuel Cell global summary

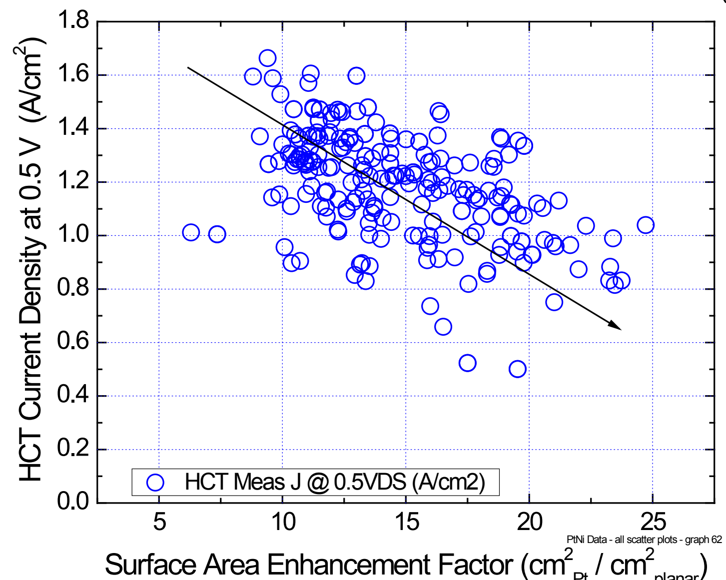
- Low current voltages correlate with SEF, but progressively less and less up to 1 A/cm².



- Above 1 A/cm² the cell voltages depict an inverse dependence on surface area.





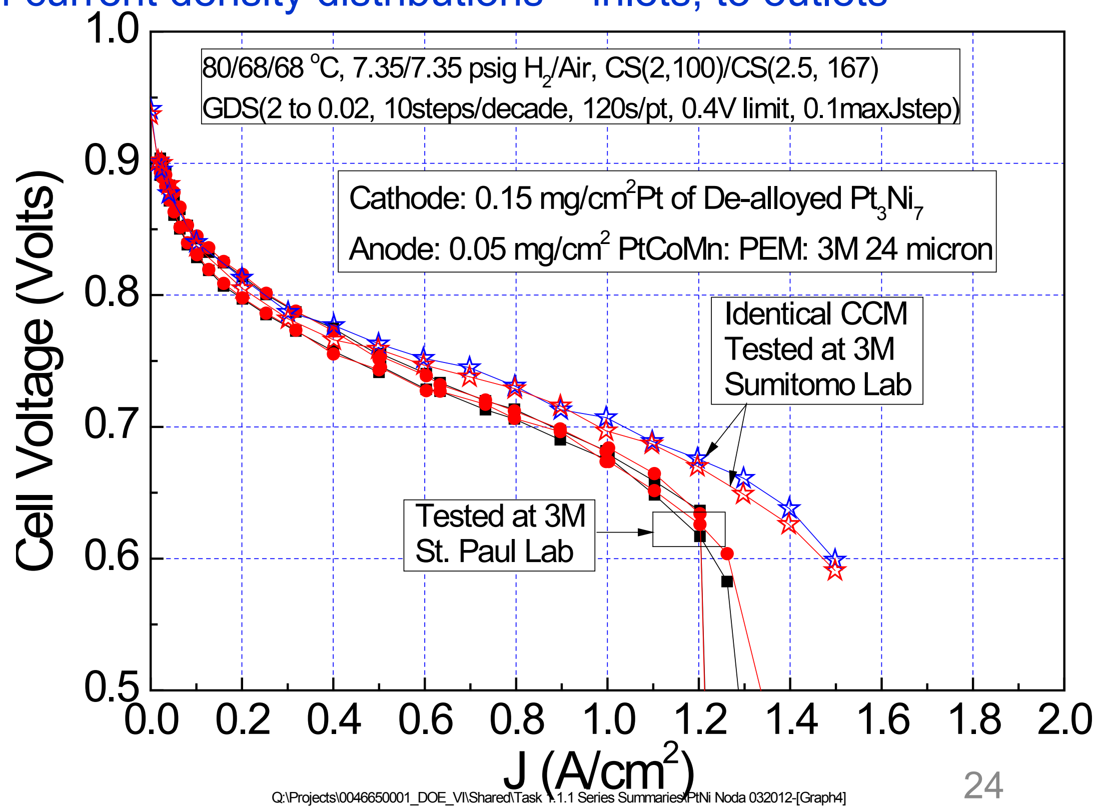


- Excess Ni at higher loadings further reduces limiting currents.

Pt_3Ni_7 Development: Dealloying experiments and process scale-up

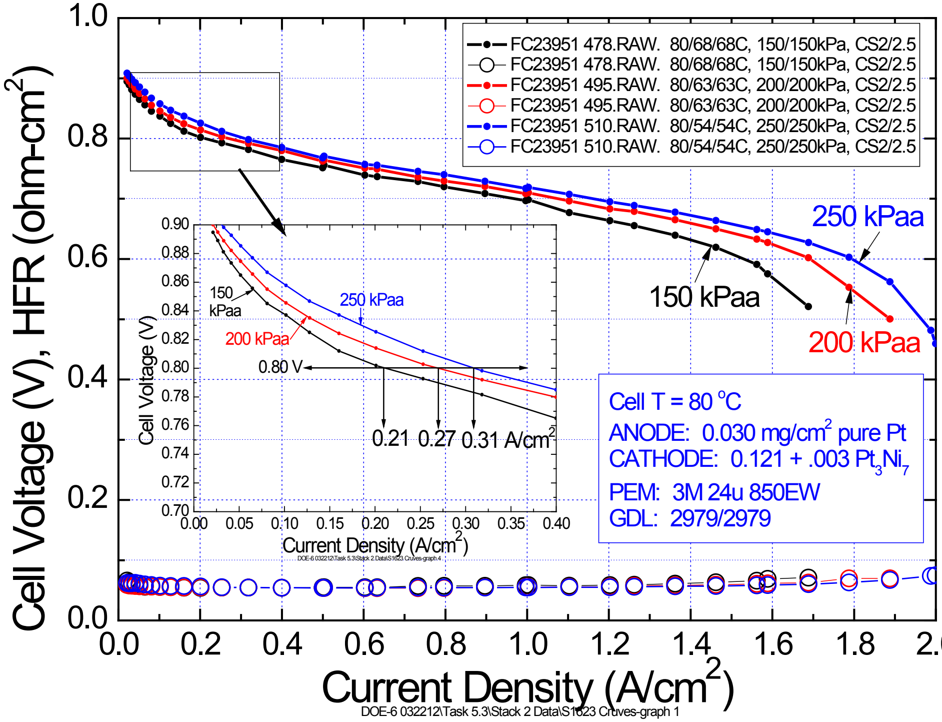
- **Results:** Fuel Cell results for best configuration
  - The limiting current is still much lower than it should be. Some mechanism other than mass transport is operative, e.g. :
    - Concentration polarization due to excess Ni in the vicinity of the catalyst surface
    - Test station effects and conditioning protocols, as demonstrated in the figure below.
    - Water cleanliness, particularly Cl- that affect GDS maximum curves in 3M labs.
    - Flow fields and non-uniformity of current density distributions – inlets, to outlets
    - Membrane properties

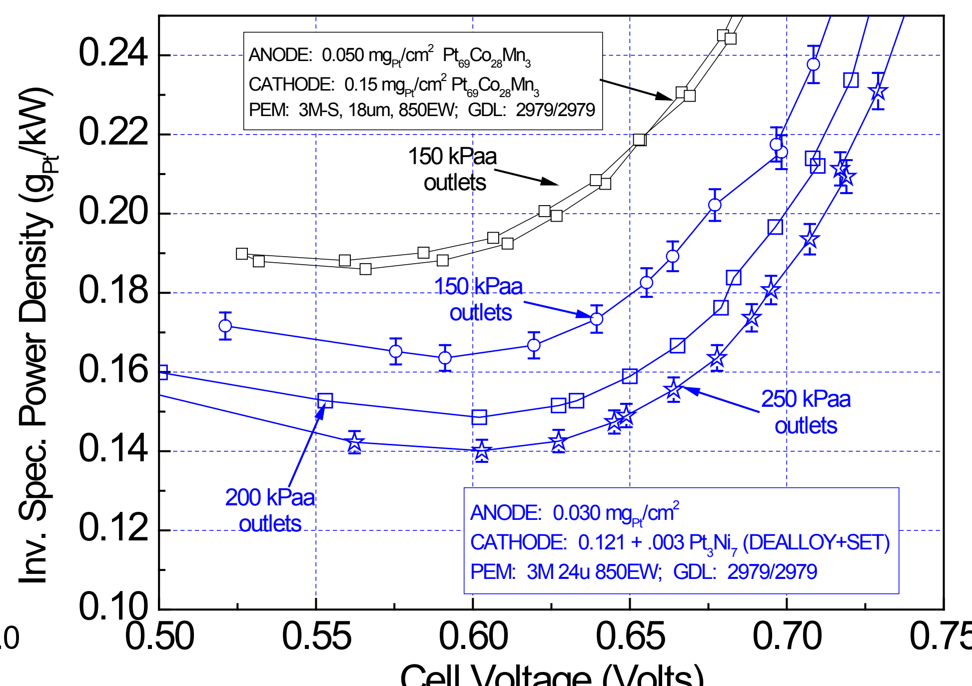
- **Results:** Different limiting currents observed at 3M St. Paul and 3M Sumitomo:
  - Identical MEA's
  - Same 50 cm^2 FCT cells
  - Same GDS protocol
  - Different conditioning
  - Different humidification approach



Pt_3Ni_7 Development: Toward 2012 Best of Class Pt/Pt_3Ni_7 CCM configuration.

- The best overall performance to date is obtained with Pt_3Ni_7 on the cathode that has been roll-to- roll dealloyed and SET treated with best conditions explored thus far. MEA below used:
  - Anode = 0.03 mg/cm² NSTF-Pt ; Cathode = 0.121 ± 0.003 mg/cm² of NSTF Pt_3Ni_7 (by ICP)
  - PEM = Standard 3M-24 μm, 850 EW ; GDL's = 3M standard 2979 ; FF = 3M standard Quad-serpentine.
  - Inverse Specific Power density = **0.14 – 0.18 g_{pt}/kW** over 0.6 – 0.65 V and 150 to 250 kPaa operating ranges at 80°C , with **0.151 ± 0.003 mg_{Pt}/cm^2** total loading per MEA (right graph).
  - Pt_3Ni_7 gives **0.21 to 0.31 mA/cm² at 0.8 V** ("1/4 power") over 150 to 250 kPaa pressure (outlet control).
  - These Pt_3Ni_7 cathodes show limiting current improvements over last year, but there is still opportunity for further gains. (Temperature sensitivity over 80 – 95°C at 150 kPaa shown in Back-up Slides, # 34)





Collaborations Over Life of Project

Subcontractors

- Dalhousie University : Subcontractor. Focused on Pt_3Ni_7 studies. Funding ended Dec., 2010.
- ANL (Markovic/Stamenkovic group): Subcontractor, periodic measurements in 2010, 2011.
- 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. Final short stack testing: Done under this project, Task 5.3.
- 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 OnSite – Collaboration outside of DOE H_2 program. Performance testing of NSTF MEAs in electrolyzers. Continuous testing and periodic interaction past year.
- Giner Inc., 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 (4/11/12 to 6/30/12)

- ❑ **Final Stack Testing**
  - **Complete stack testing at GM – decision of when to stop**
  - **Understand issues with performance and decay**
    - **Complete flow field study**
    - **Apply load cycling protocol to 50 cm^2 cells w/ MEA's having high-performing PEM's.**

- ❑ **Characterize Pt_3Ni_7 dealloyed (R2R) materials under DOE durability accelerated stress tests.**

- ❑ **Prepare Final Report**

Project Summary : Status Against DOE Targets – March, 2012 (blue = new)

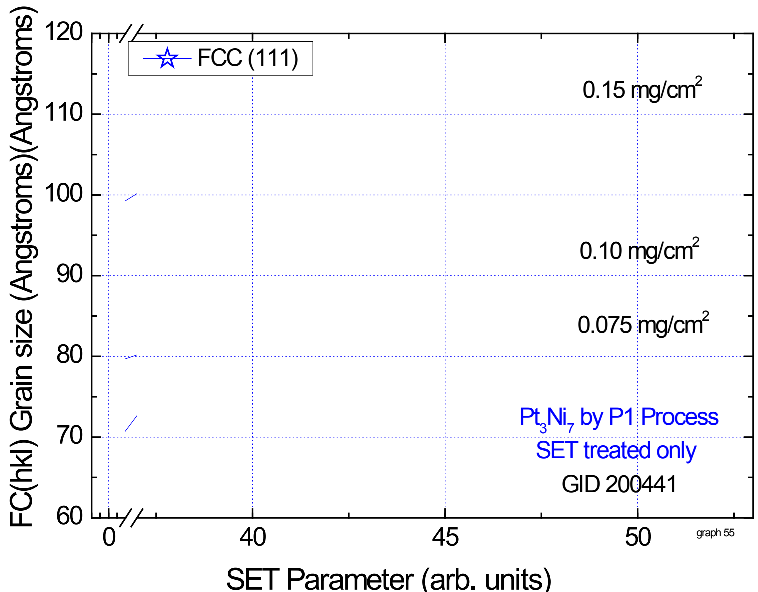
Characteristic	Units	Targets 2017	Status: Values for roll-good CCM w/ $0.15 mg_{Pt}/cm^2$ per MEA or as stated
PGM Total Content	g_{Pt}/kW_e rated in stack	0.125	0.14 - 0.18 g_{Pt}/kW for cell 0.6 < V < 0.65 at 80 °C and 150kPaa to 250 kPaa outlet. Pt_3Ni_7, 50 cm^2 cell w/ 0.15 mg/cm^2 total Pt.
PGM Total Loading	mg PGM / cm^2 total	0.125	0.15 to 0.20, A+C with PtCoMn alloy 0.15 A+C with Pt/Pt_3Ni_7
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 R2R Pt_3Ni_7
Specific Activity (150 kPa H_2/O_2 at 80°C, 100% RH)	mA/cm^2-Pt @ 900 mV	0.720	2.1 for PtCoMn, $0.1 mg_{Pt}/cm^2$ 2.7-3.0 for R2R Pt_3Ni_7, $0.125 mg_{Pt}/cm^2$
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 %	10 ± 7mV loss at 0.8 A/cm^2 16 ± 2% loss ECSA, PtCoMn 37 ± 2% 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 ± 4 mA/cm^2 at 500 hrs (5 MEAs) 12 ± 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)

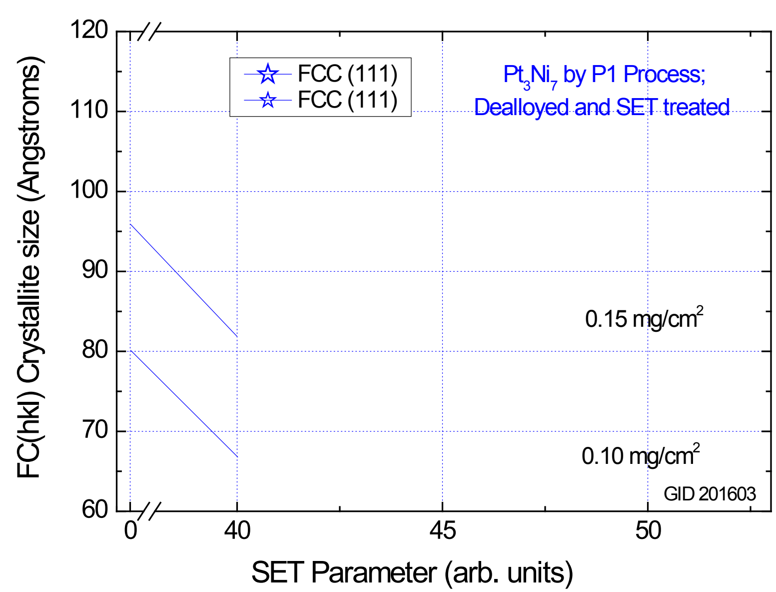
Technical Back-Up Slides

Technical Accomplishments and Progress – Back up Slide

Pt_3Ni_7 Development: Dealloying experiments and process scale-up

- **Results:**
  - Hundreds of lab batch dealloying, with XRF Pt/Ni atomic fraction measurements completed.
  - Process chemistry identified to reduce dealloy time by factor of 1/240, feasible for roll-to-roll.
  - Roll-to-roll (R2R) equipment identified and modifications made for down-selected chemistry.
  - Four R2R dealloying experiments completed and optimum conditions determined.
  - Combination of R2R dealloying and SET processing completed multiple times using full width roll-goods.
- **XRD results for SET treated and dealloyed Pt_3Ni_7**
  - FCC(111) crystallite sizes increase with loading and SET treatment of as-made catalysts as historically seen for PtCoMn and Pt_3Ni_7 (left figure).
  - SET and dealloying treatment produces smaller crystallites, independent of SET parameters.

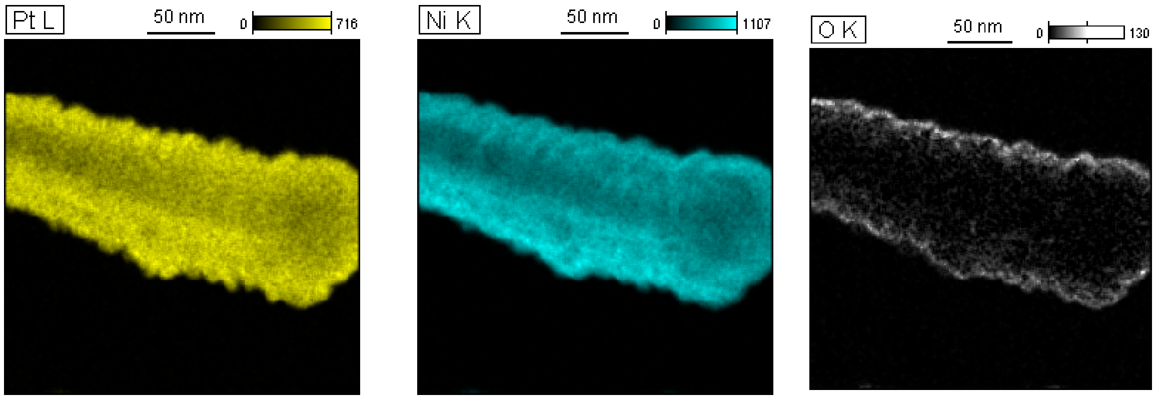




Technical Accomplishments and Progress

Pt_3Ni_7 Development: Dealloying experiments and process scale-up

- **Results:** TEM Images Characterization
  - HAADF images may suggest less density of the PtNi in the R2R dealloyed whiskers
  - Whiskerettes appear more “feathery” after SET treatment (see bottom three images).



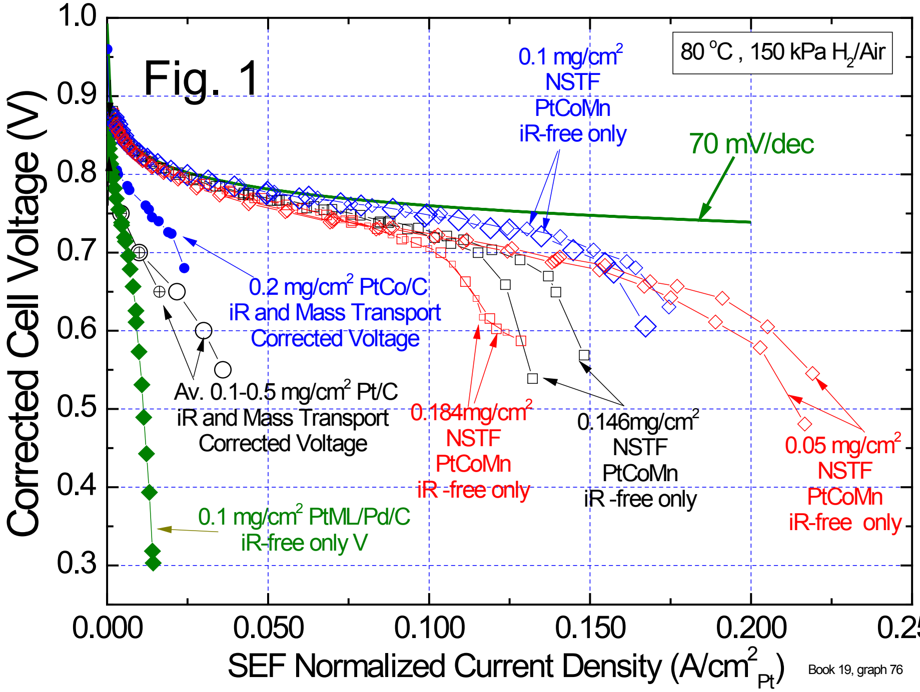
- Pt and Ni distribution appears uniform (first two images left).
- Oxygen is restricted to surface of whisker coatings (last image left).

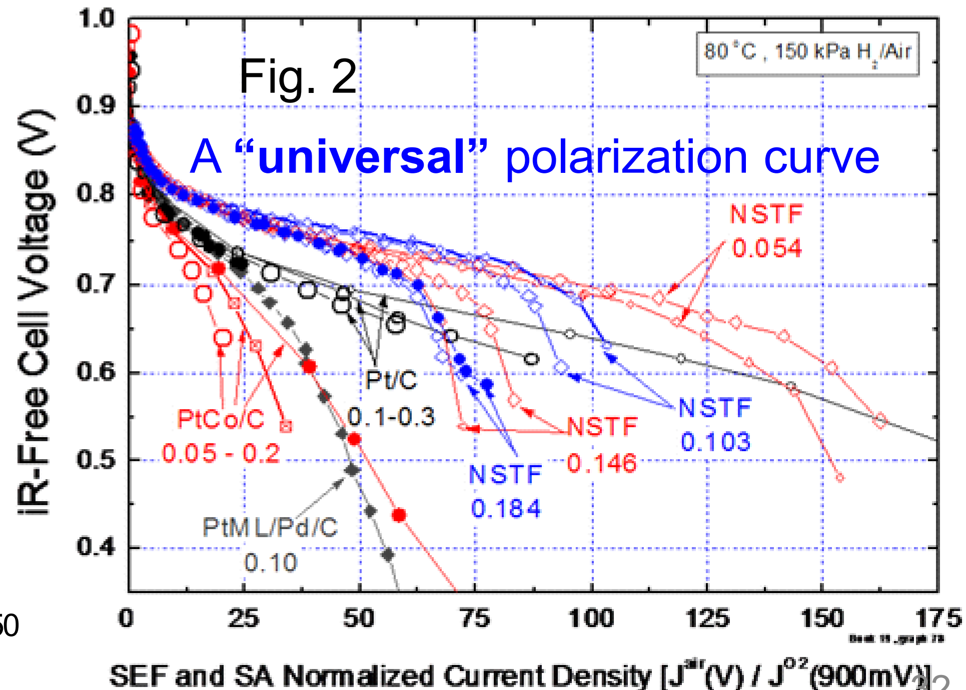
Technical Accomplishments and Progress

NSTF Fundamentals: Extended Surface Catalyst fundamental properties

Ref: Mark K. Debe, "Effect of Electrode Structure Surface Area Distribution on High Current Density Performance of PEM Fuel Cells," *J. Electrochemical Society* **159**(1) B54-B67 (2011).

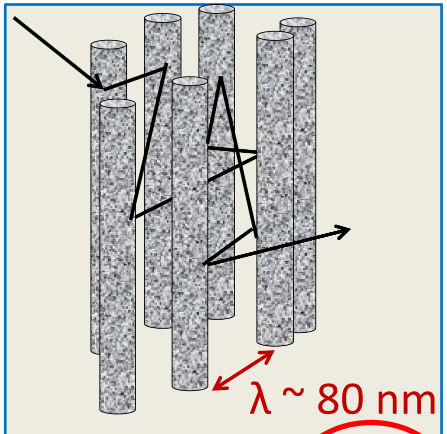
- Loss of high current density with cathode loadings below 0.2 mg_{Pt}/cm^2 in Pt/C electrodes is an issue.
- We show this effect is much less at a given loading with the NSTF catalyst type electrodes (Figs. 1 and 2 below)
- We develop a model based on elementary kinetic gas theory and known molecule/surface interaction mechanisms that take place in the Knudsen regime to explain these differences.
- The close packed nature of the extended NSTF catalysts and their spacing on the order of the Knudsen length enables O_2 molecules to make many more surface collisions per unit time (see cartoons on next slide).
- When modeled the result is an additional pre-exponential scaling factor in the Butler-Volmer equation related to a distance metric, ρ_s describing the catalyst surface area distribution, (see bottom graphs on next slide.)
- The model is able to predict the correct heat of enthalpy for O_2 physisorption and the observed ratio of current densities at V(iR-free) = 0.7 V for NSTF compared to Pt/C dispersed electrodes in the 0.05 to 0.15 mg_{Pt}/cm^2 range from published data for eleven different catalyst types and cathode loadings below 0.2 mg/cm^2, (shown in graph immediately below).

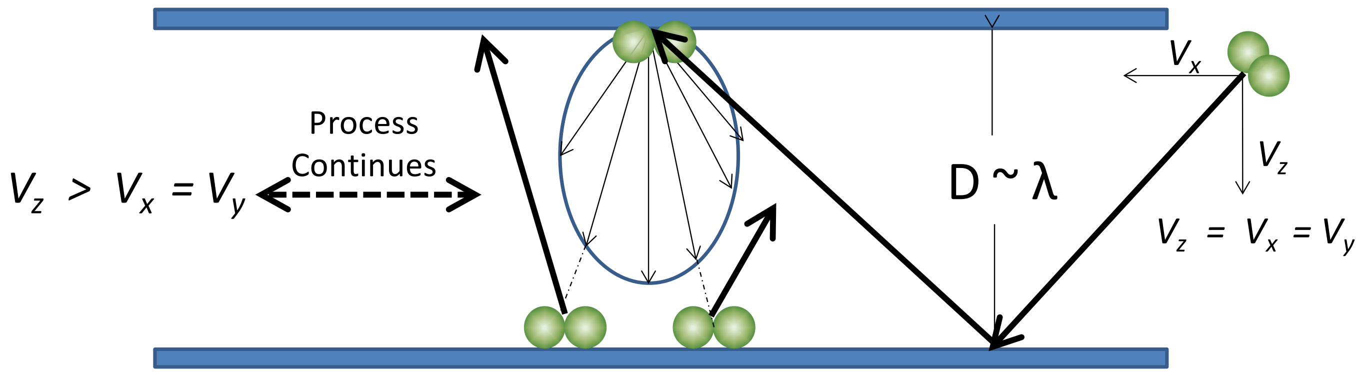




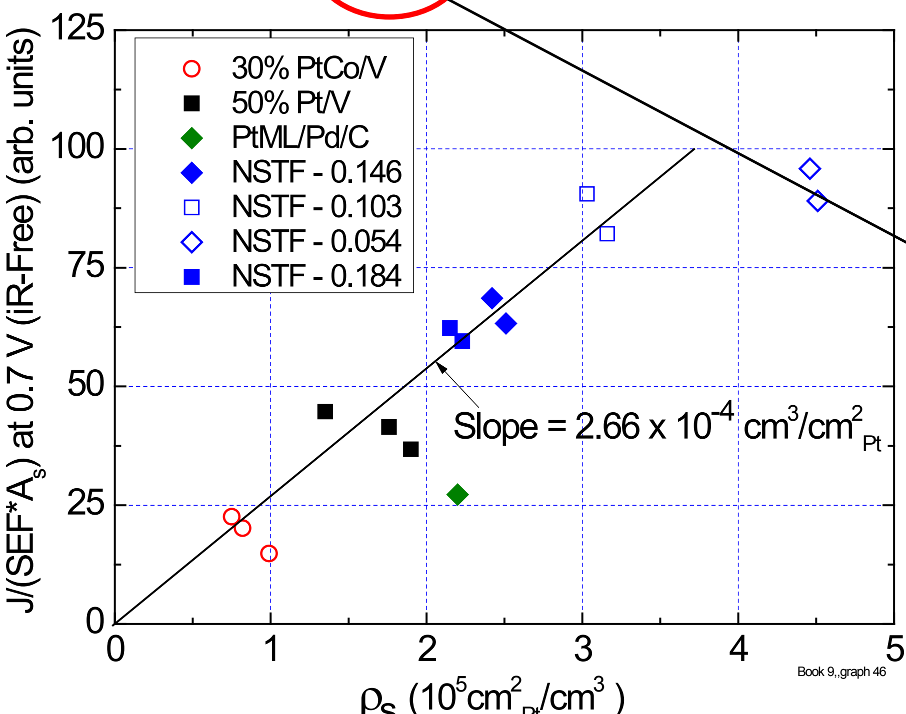
Technical Accomplishments and Progress

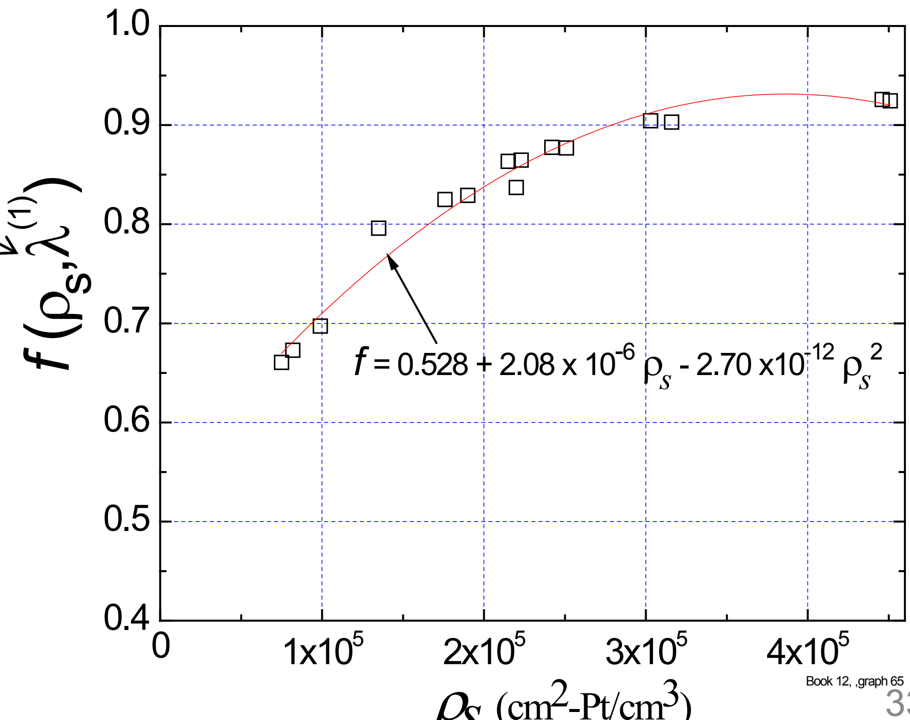
Model Development: Extended Surface Catalyst Fundamental Properties





$$J(A/cm^2_{planar}) = f(d_s)S(cm^2_{Pt}/cm^2_{planar})[i_o(A/cm^2_{Pt})\ p^{\gamma}_{O_2}\ (1-\Theta_{ad})^x \exp\left(-\frac{\beta F\eta}{RT}\right)\exp\left(-\frac{\gamma\Delta G_{ad}}{RT}\right)]$$

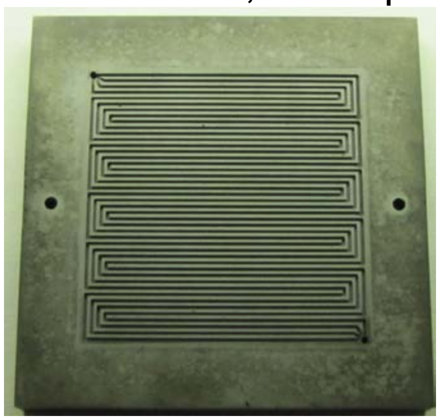




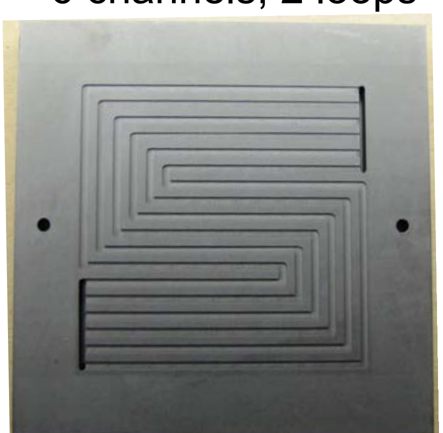
Technical Accomplishments and Progress

Short stack 2 testing: Issues – Investigating possible flow field effects

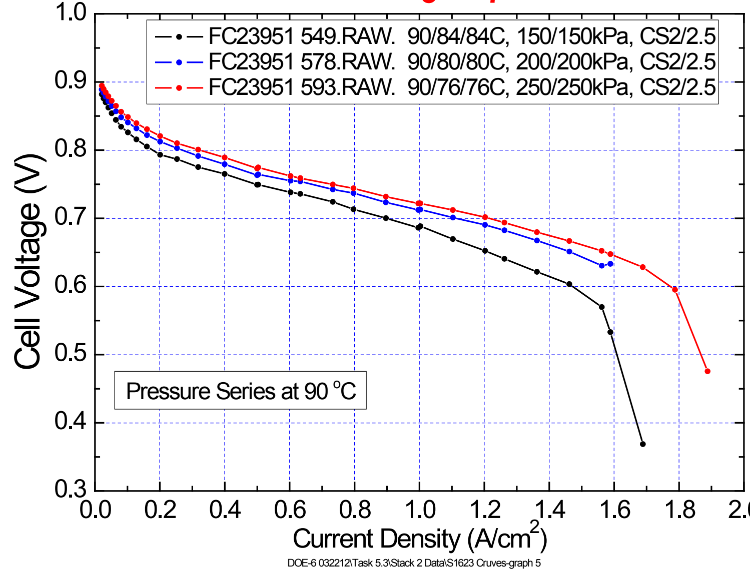
3M Std. Quad-Serpentine
4 channels, 10 loops

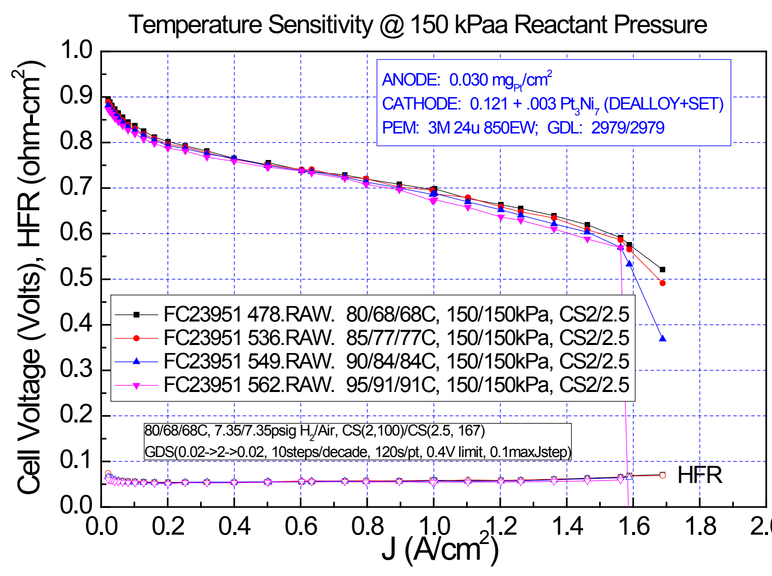


1st Alternative FF
6 channels, 2 loops



Pt_3Ni_7 Development: Toward 2012 Best of Class Pt/Pt_3Ni_7 CCM Configuration.





- Top: Pressure series at 90 °C for 0.03/0.121 Pt/Pt_3Ni_7 based MEA.
- Bottom: 0.03/0.121 Pt/Pt_3Ni_7 based MEA shows very little sensitivity over temperature range of 80 to 95 °C (inlet RH controlled to give ~ 100% outlet RH at each temperature.)