Highly Dispersed Alloy Catalyst for Durability

2012 DOE Hydrogen Program

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UTC Power
A United Technologies Company

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Project ID # FC002

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OVERVIEW

Timeline

- Start – May 1, 2007
- End – April 30, 2012
- 94% Complete

Barriers

Performance

- Increase catalyst activity; ≥ 0.44 A/mg_{PGM}

Cost

- Reduce PGM loading; ≤ 0.3 mg_{PGM}/cm^2

Durability

- < 40% loss in ECA and Activity under potential cycling
- < 30 mV loss in performance at 1.5 A/cm^2 under carbon corrosion AST protocol

Budget

- Total project funding
  - DOE share - $5.878 M
  - Cost share - $2.086 M
- Funding received in FY11: $0
- Planned Funding in FY12: $0
  - No cost extension in place

Partners

Johnson Matthey Fuel Cells

Texas A&M University

Brookhaven National Laboratory

COLLABORATIONS

- UTC Power (Industry):
  - Dispersed alloy and core-shell catalyst synthesis, RDE activity/durability measurements and characterization
  - Carbon support screening and corrosion testing
  - MEA optimization to improve electrode structure for cell performance
  - Sub-scale, single cell and stack testing
- Johnson – Matthey Fuel Cells (Industry):
  - Catalyst scale-up synthesis (dispersed and core-shell systems)
  - MEA optimization to improve electrode structure
- Brookhaven National Lab (Federal):
  - Investigate the activity and stability of novel core-shell catalyst systems
  - Synchrotron in-situ EXAFS and TEM-EELS to understand the surface characteristics of dispersed alloy and core-shell systems validating the modeling results
- Texas A&M University (Academia):
  - Computational calculations to understand activity and stability benefits of dispersed alloy and core-shell catalysts in terms of their activity for O_2 reduction reaction and stability against dissolution

HIGHLY DISPERSED ALLOY CATHODE CATALYST

Outline

Project Objective

Develop a compositionally advanced cathode catalyst on a support that will meet DOE activity, durability and PGM loading targets in a structurally optimized MEA capable of performing at high current density.

- ❑ Approach
- ❑ 2011 & 2012 Milestones and Current Status
- ❑ Task 1: Dispersed Alloy Catalyst Development
- ❑ Summary

APPROACH

Implement advanced concepts in MEA to realize high activity

Reduce current MEA loading while meeting durability and activity targets

Understand catalyst structure fundamentals through models

Core/Shell Catalyst
- Core -shell structure fundamentals
- Synthesis and scale-up chemistries
- Catalyst layer optimization
- MEA fabrication

Alloy Catalyst
- Alloy fundamentals
- Ir-containing ternary alloy formulations
- MEA optimization
- Fuel cell validation
- Full size stack demonstration

Alternate Supports
- Corrosion resistance
- Subscale fuel cell testing

Modeling
- Surface segregation
- Ternary alloy durability
- Core/shell structural stability
- Impact of shell thickness
- Impact of sub -layer composition

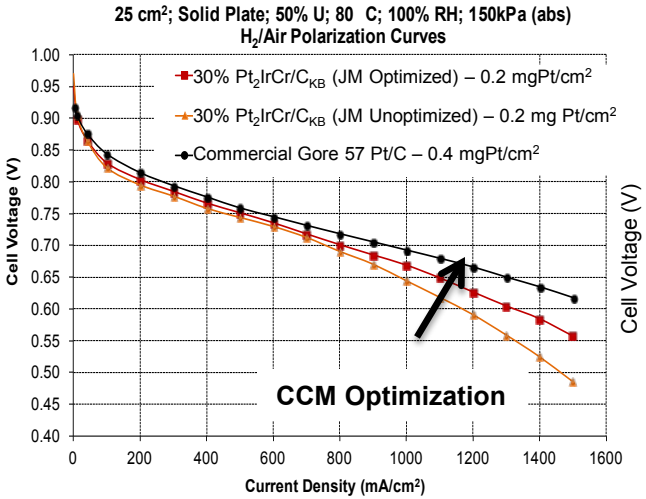
APPROACH

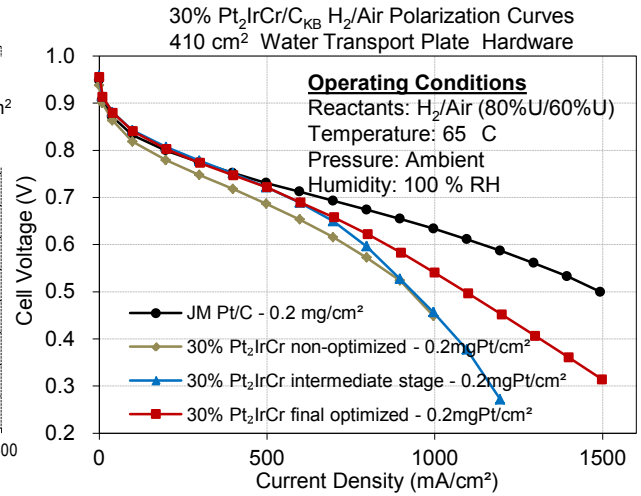
Milestones and Accomplishments

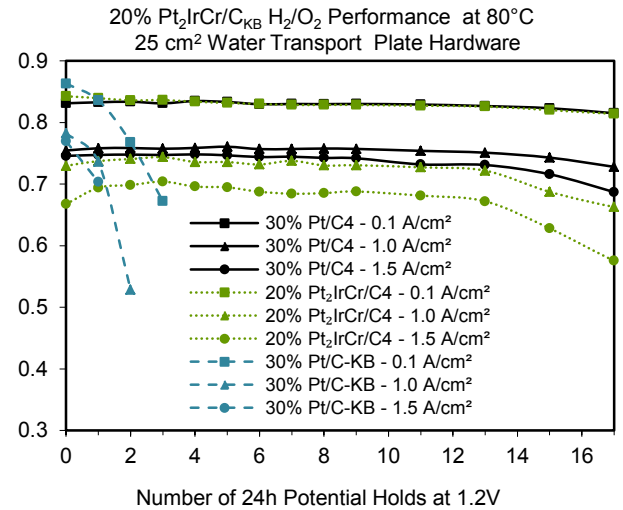
Month/Year	Milestone or Go/No-Go Decision	Status/Comments
April 2010	Milestone: Completion of all modeling work (alloy and core-shell) and publication of results	Task Complete
June 2010	Milestone: Scale-up of alloy catalyst on durable carbon support and sub-scale MEA testing	Scale-up complete; Sub-scale corrosion completed January 2011;
June 2010	Milestone: Scale-up of 30% Pt_2IrCr on KB alloy catalyst	Complete
November 2010	Go/No-Go decision: Down-selection and MEA optimization of core-shell catalysts for single cell durability test	**No-Go Decision;** Very low durability under MEA conditions
December 2010	Milestone: Single cell validation of dispersed alloy catalysts	Complete
April 2011	Stack Demonstration of alloy catalyst	**Accumulated 2000 hours of load cycling for the Pt_2IrCr alloy catalyst; Tear-down complete**
July 2011	MEA optimization of 20% $Pt_2IrCr/C4$ alloy catalyst and single cell durability test	**No-Go**; Estimated performance after optimization is still lower than commercial Pt/C.
October 2011	MEA optimization of 30% Pt_2IrCr/C_{KB}	**Completed Dec 2011; Performance with improved MPL concept GDL – in progress**
April 2012	Performance data of optimized MEA in a multi-cell stack with the alloy catalyst	**On-track; April 2012**

TECHNICAL ACCOMPLISHMENTS

2008 - 2011: Alloy Catalyst Development





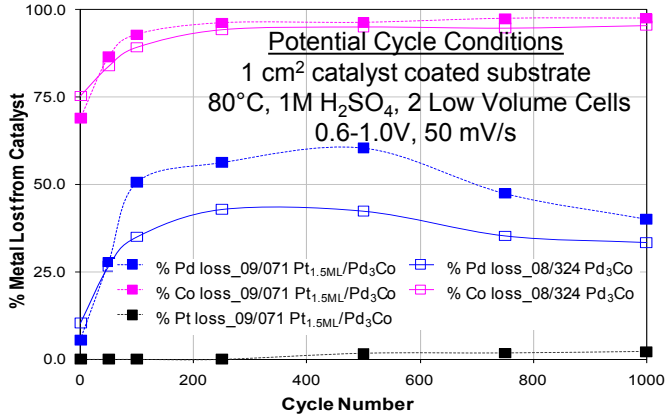


- 30% Pt_2IrCr /C_{KB} has best durability among studied alloys in both RDE and MEA cycling
- Clear evidence of improvement for high current density performance in H_2/Air from sub-scale catalyst layer optimization steps
- A performance gap of 94 mV vs. baseline Pt/C (0.2 mg/cm^2) @ 1 A/cm^2 in full-scale single cells
- Down-selected stable carbon C4: Carbon that meets DOE carbon corrosion target (< 30 mV loss in performance at 1.5 A/cm^2 under carbon corrosion AST protocol)
  - C4 showed significant corrosion stability
  - No performance loss until 300 hours of 1.2 V holds (13 cycles)
  - Large gap in air performance curves observed for Pt/C4 compared to Pt/CKB.
  - Lower ECA and MA than same catalyst on KB due to poor dispersion and large particles.

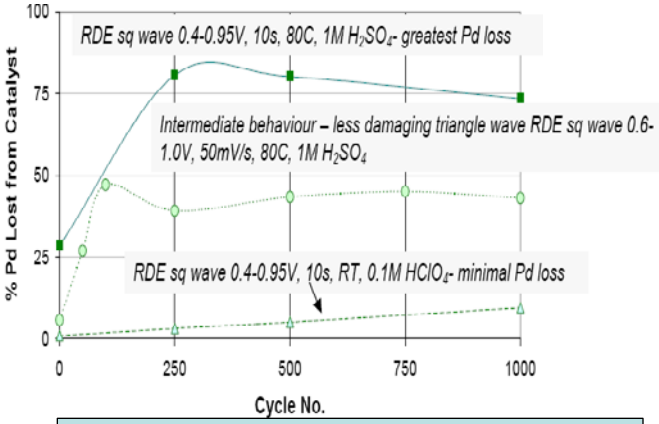
TECHNICAL ACCOMPLISHMENTS

2008 - 2011: Core-Shell Catalyst Development

Activities Leading to No-Go Decision



JM 09/71 $Pt_{1.5ML}/Pd_3Co$



Pd_3Co and Pd_3Fe cores identified from modeling to have ~5xPt MA

Multiple Core preparation methods, Pt coating & Characterization

- Activity in MEA<<RDE
- LEIS and voltammetry identified Co on surface
- Stability and activity of Pd_3Co = Pd_3Fe
- Significant Pd dissolution in liquid cell @ 80°C, 1M H_2SO_4, 0.6-1.0V cycles

No-Go Pd_3Cr shows Pd dissolution

No-Go on Pt_{ML}/Pd_3Fe due to concern for Fe leaching in MEA

Pd plates onto Pt surface during cycling if above a certain Pd^{2+} concentration

Pt_{ML}/Ir core has small MA benefit

No-Go Pd dissolution observed under multiple test protocols for UPD lab scale and scale-up catalysts

No benefit from acid leaching Pd_3Co cores before Pt deposition results

Pt_{ML}/Ir has good stability and no MEA to RDE gap

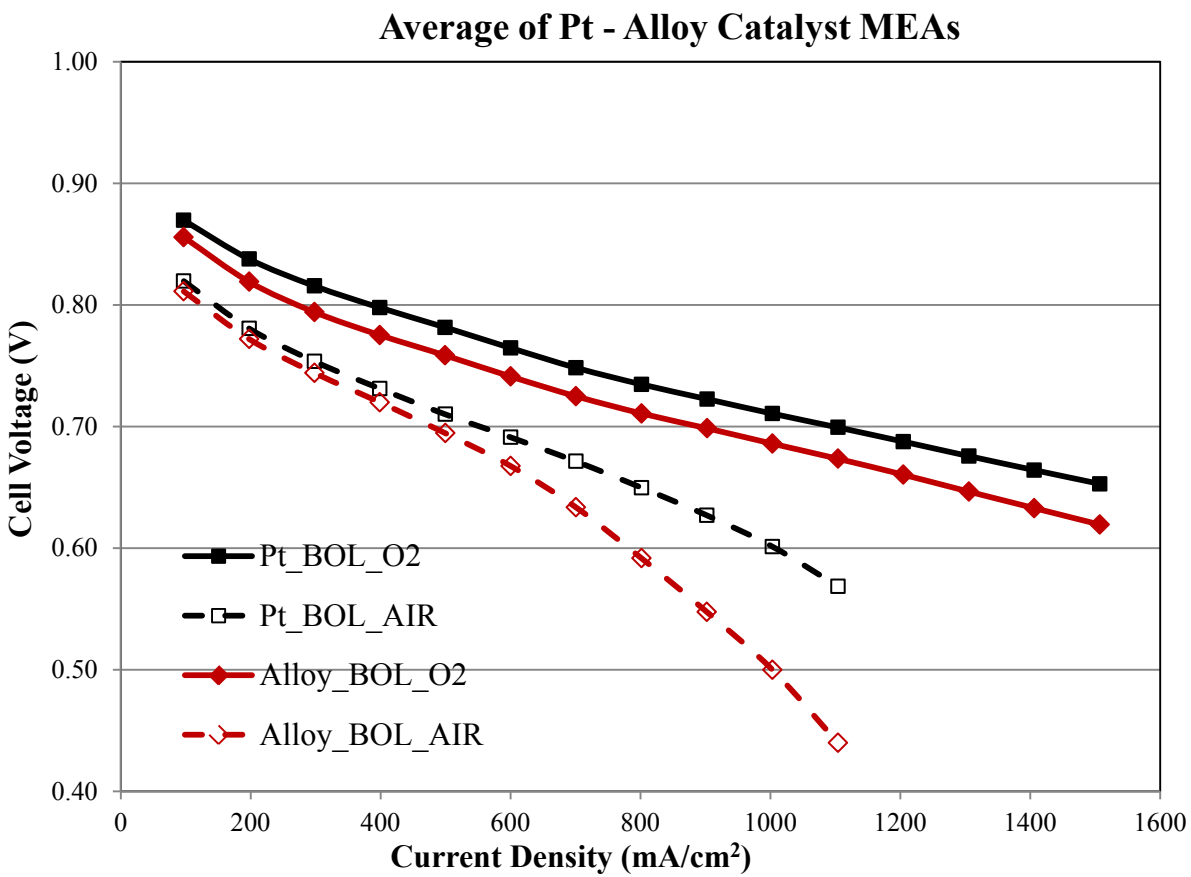
Non-uniform shell thickness for scale-up catalysts; varies between 0 – 2 ML

No-Go Pd loss observed for Pd and Ir ion washed Pd_3X cores

No-Go on Pt_{ML}/Ir core due to low cost benefit and limited Ir resources

TECHNICAL ACCOMPLISHMENTS

Task 1: Pt_2IrCr/C_{KB} 20-Cell Stack Performance



Stack Operating Conditions	
No. of Pt_2IrCr alloy cells	16
No. of Pt baseline cells	4
Pt_2IrCr alloy cells Loading	0.3 mg_{PGM}/cm^2
Pt baseline cells Loading	0.2 mg_{PGM}/cm^2
Hardware	WTP
Reactants	H_2/Air
Avg. Temperature	70°C
Pressure	Ambient
Humidity	100% RH

Pt_2IrCr/C_{KB} vs. Pure Pt Activity

- BOL Performance of the alloy catalyst is lower than the Pt catalyst (100 mV performance gap at 1 A/cm^2)
- Oxygen permeability and proton concentration losses in the cathode due to Cr ion contamination in the 30%Pt_2IrCr/C_{KB}

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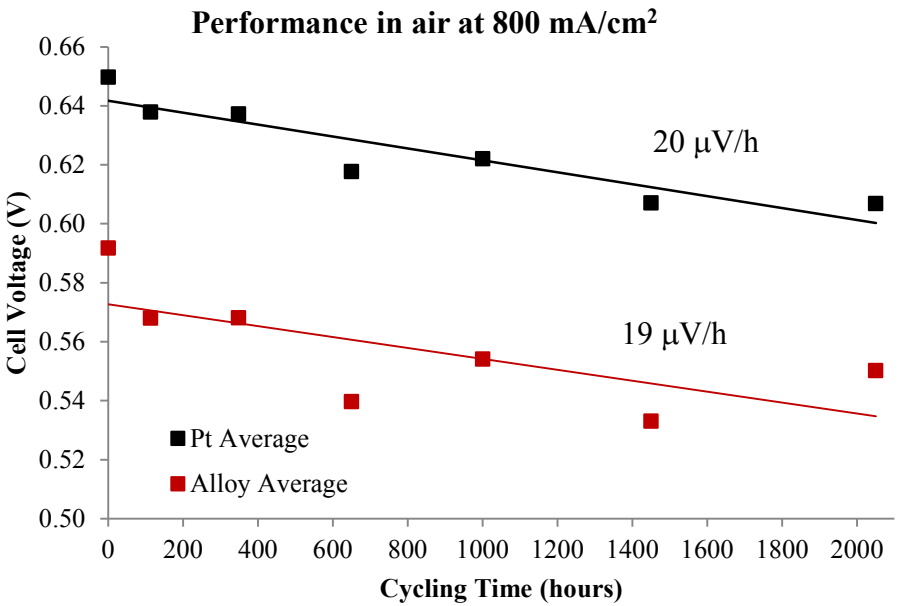
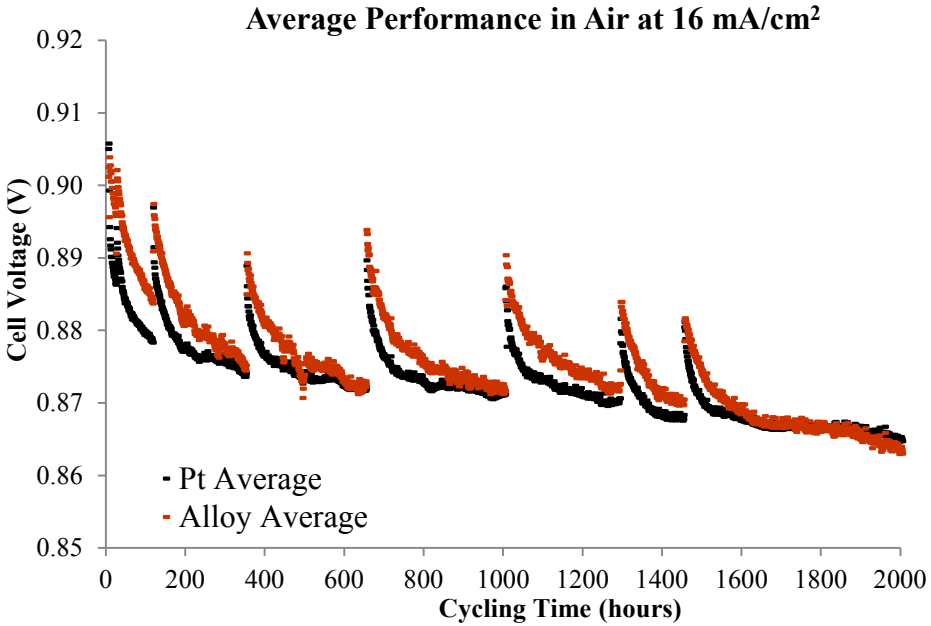
TECHNICAL ACCOMPLISHMENTS

Task 1: Pt_2IrCr/C_{KB} Durability in 20-Cell Stack

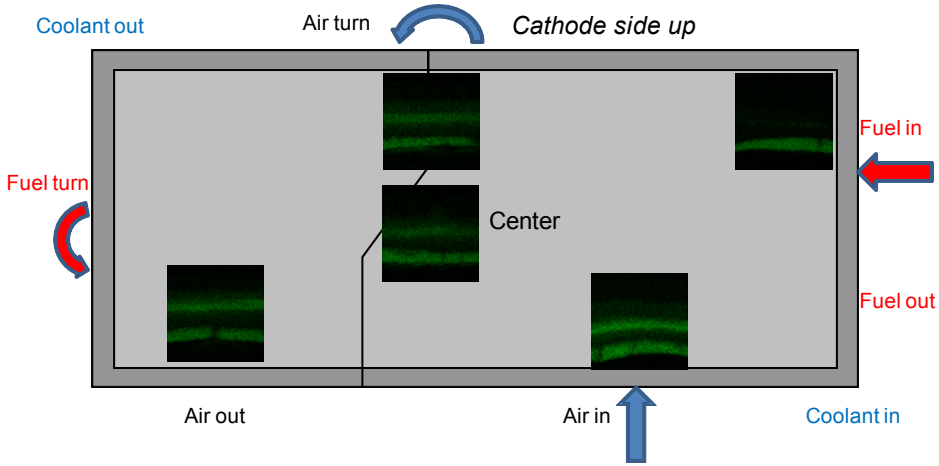


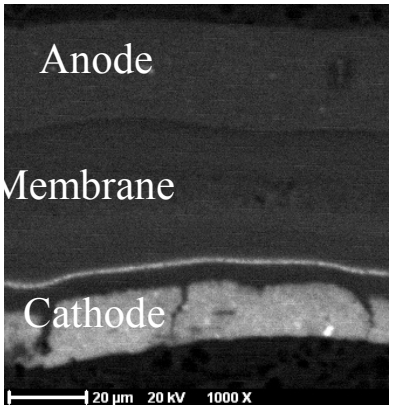


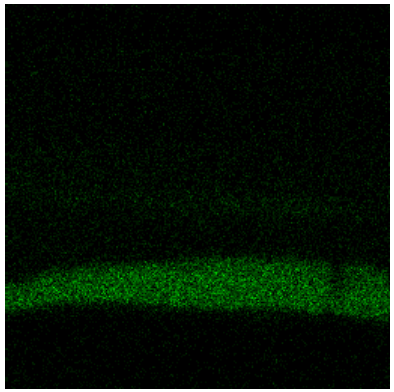
- Pt_2IrCr Durability in short stack
  - 2000 hrs of durability test completed under UTC DOE-AST drive cycle protocol
  - Both Pt and Pt alloy show performance recovery after periodic diagnostic tests with removal of catalyst surface oxides
  - During load cycling, Pt alloy shows slow voltage decay at low current density
    - — Surface oxides buildup on the alloy catalyst surface was slower than Pt. However, with the extended period of load cycling, both ORR activities approached the same level
  - Pure Pt shows better performance at high current density compared to Pt alloy
  - Overall rate of degradation is similar for Pt_2IrCr and Pt

TECHNICAL ACCOMPLISHMENTS

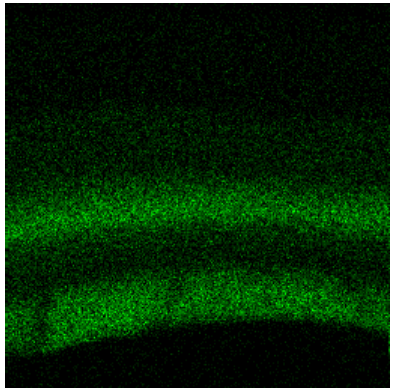
Task 1: Pt_2IrCr/C_{KB} 20-Cell Stack Teardown Analysis



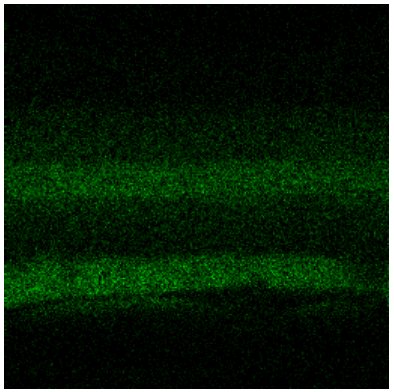




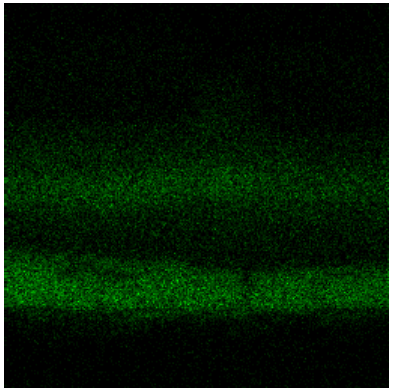
Fuel In



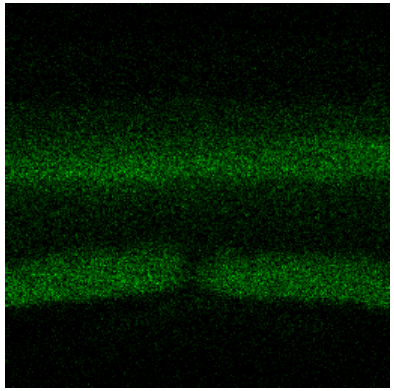
Air In



Air Turn



Center



Air Out

EMPA Cr map in the MEA relative to fuel/air flow

- Majority of the Cr leaching was observed at the air inlet

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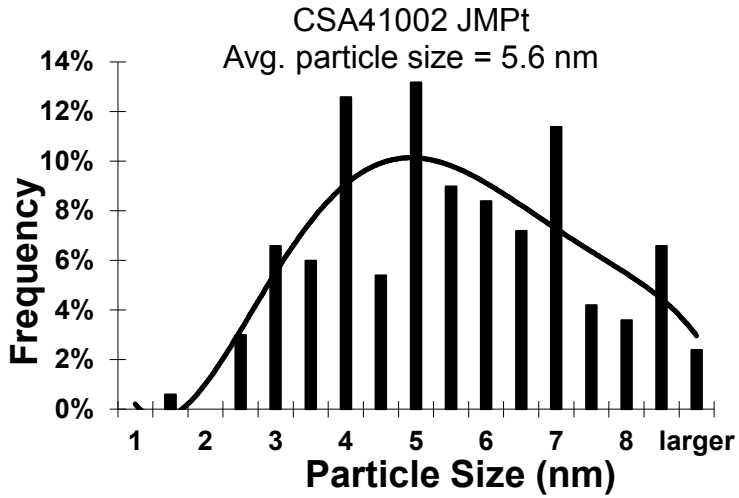
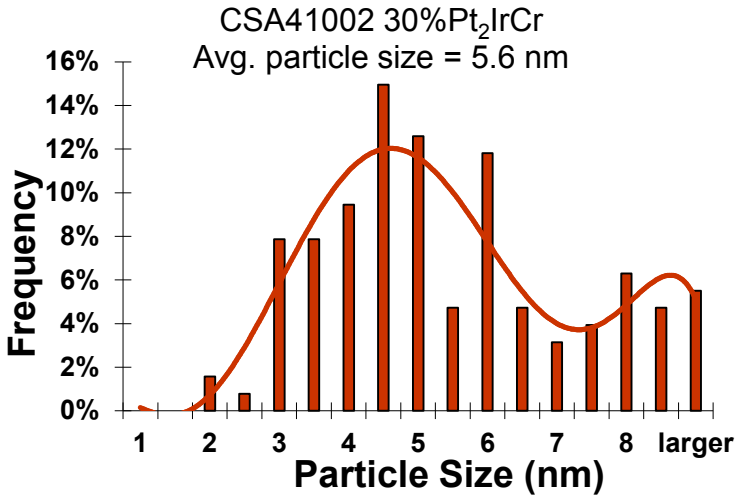
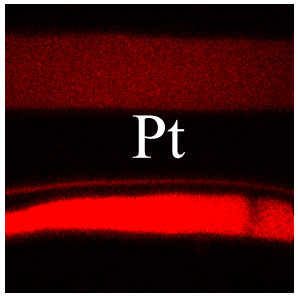
TECHNICAL ACCOMPLISHMENTS

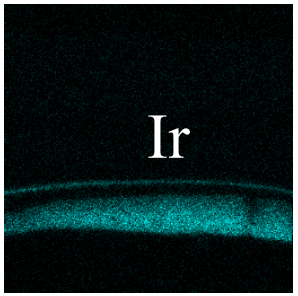
Task 1: Pt_2IrCr/C_{KB} 20-Cell Stack Teardown Analysis





Pt_2IrCr - 29.9% Pt,14.8% Ir, 4.0% Cr;	Pt	Ir*	Cr
Initial wt.%	61.4	30.4	8.2
Initial atomic ratio	1	0.50	0.50
Final wt.%	71.0 (±0.6)	24.2 (±1.8)	4.8 (±1.3)
Final atomic ratio	1	0.35	0.25





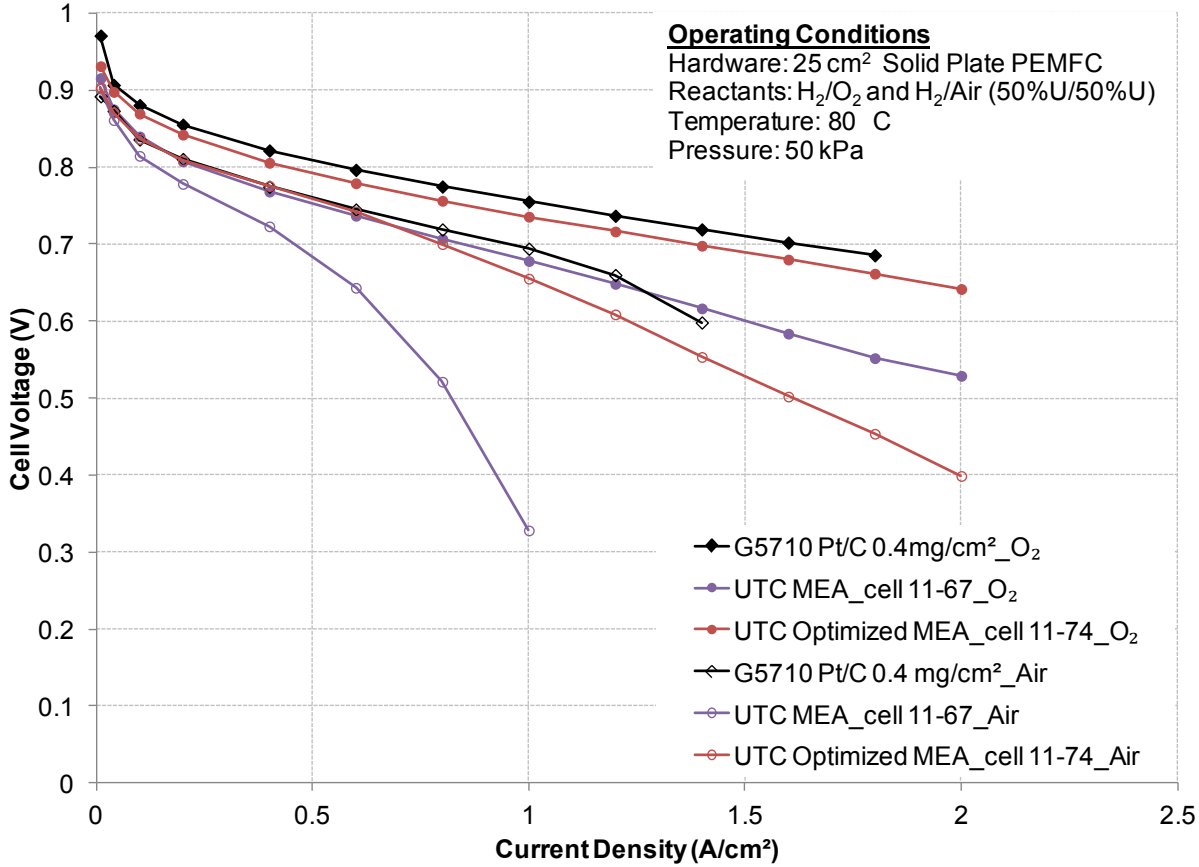
EMPA map Pt and Ir

- ❑ No significant particle size increase observed for the alloy catalyst (~5 to 5.6 nm)
- ❑ Pt/C particle size increased from ~2 nm to 5.6 nm
- ❑ Primary durability loss in the alloy catalyst due to transition metal alloy dissolution (~50% loss)

* Some overlap in Pt and Ir emission lines expected

TECHNICAL ACCOMPLISHMENTS

Task 1: Pt_2IrCr/C_{KB} Sub-Scale MEA Optimization



- Nafion® 1100 EW in cathode electrode (Cell 11-67) shows lower activity and performance compared to cell 11-74 (1000 EW).
- Performance at 100 mA/cm^2 is 0.87V for cell 11-74 compared to 0.84V for cell 11-67 for a loading of 0.3mg$_{PGM}$/cm^2

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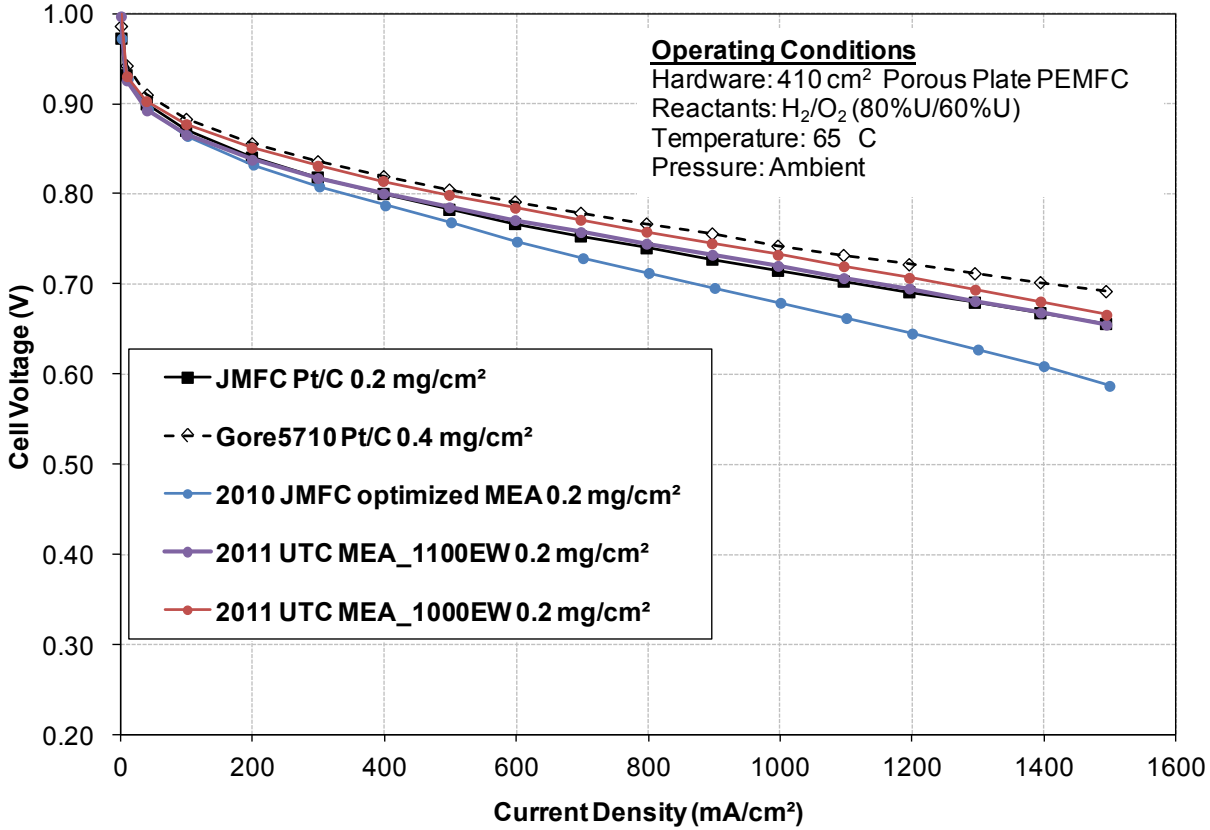
TECHNICAL ACCOMPLISHMENTS

Task 1: Pt_2IrCr/C_{KB} Single Cell MEA Performance



- Mass activity of 2011 UTC MEA (1000EW) is 0.24 A/mg_{Pt} (0.17 A/mg_{PGM}) with loading of 0.2 mg_{Pt}/cm^2 (0.3 mg_{PGM}/cm^2); ~ 35% improvement in mass activity compared to 2010 JMFC optimized MEA
- Mass activity of JM Pt 0.2 mg_{Pt}/cm^2 is 0.19 A/mg_{Pt}

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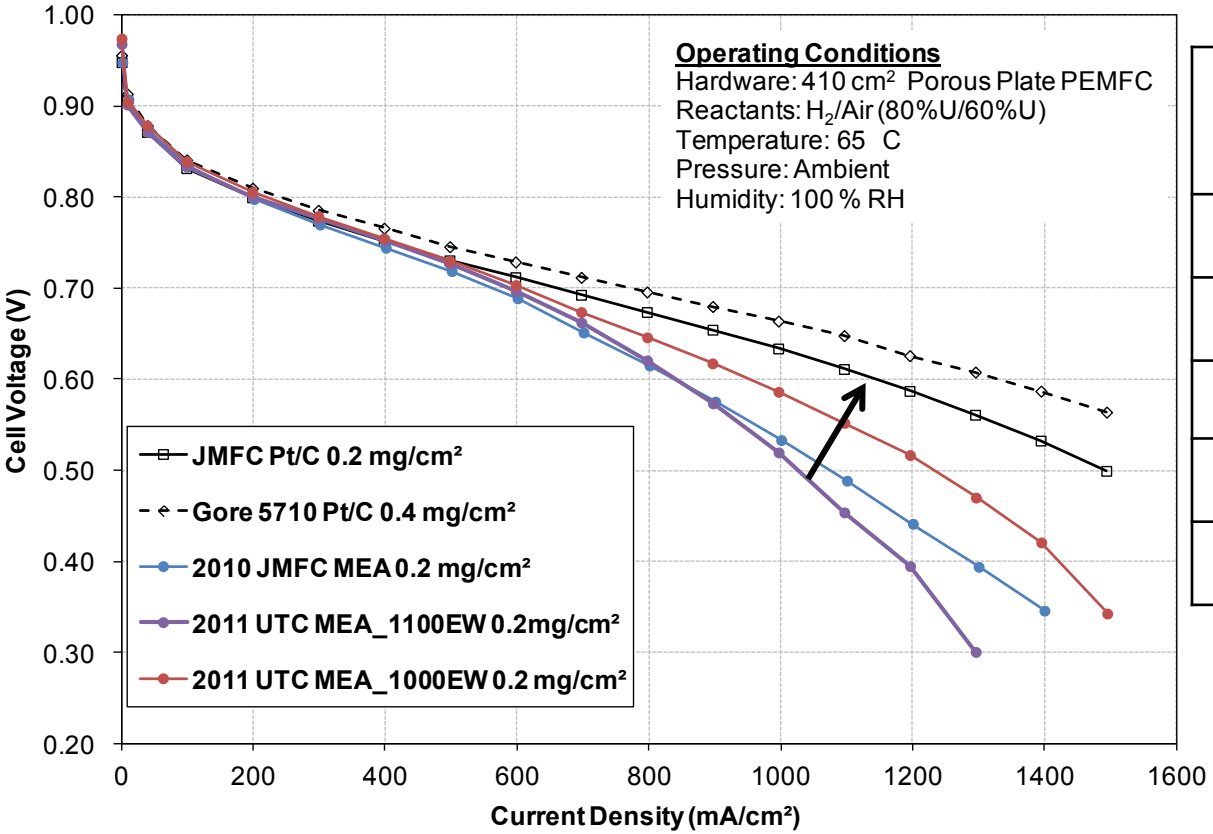
TECHNICAL ACCOMPLISHMENTS

Task 1: Pt_2IrCr/C_{KB} Single Cell MEA Performance



Cell	Voltage at 0.1A/cm² In H_2/O_2 (V)	Voltage at 1A/cm² In H_2/Air (V)	iR at 1A/cm² In H_2/Air (V)
JM Pt/C (0.2)	0.871	0.634	0.079
Gore5710 Pt /C(0.4)	0.883	0.664	0.062
JMFC MEA	0.864	0.533	0.093
UTC MEA 1100EW	0.866	0.520	0.076
UTC MEA 1000EW	0.886	0.586	0.084

- 2011 UTC optimized MEA (1000EW) is the highest performance for Pt_2IrCr/C alloy catalyst in H_2/air in a WTP cell
- 53 mV increase in performance at 1A/cm² in H_2/air compared to 2010 JMFC optimized MEA

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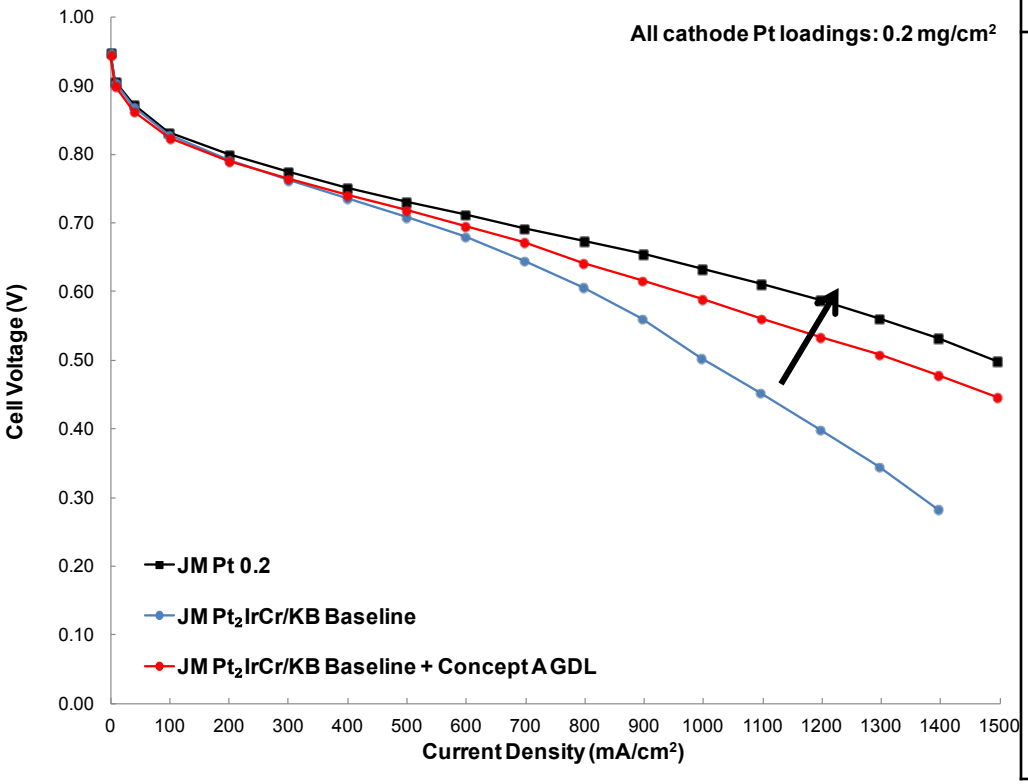
TECHNICAL ACCOMPLISHMENTS

Task 1: Pt_2IrCr/C_{KB} MEA Performance Improvement



Task	Sub-task Current Status
MEA optimization for Pt_2IrCr/C_{KB}	❖ Down-selection of Decal materials and fabrication
	❖ Catalyst/electrode decal acid treatment
	❖ MEA Ink properties: 1. Ink mixing time 2. Solvents
	❖ Pt Loading in MEA
	❖ Modified thin UTC MPL
	❖ Thinner durable membrane
	❖ Cathode layer additives
	❖ Ionomer optimization
	❖ Optimized MEA and UTC MPL technology for GDL

❑ Improved performance by **85 mV** at 1A/cm^2 using a modified GDL with a thinner MPL

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HIGHLY DISPERSED ALLOY CATALYST

2012 Summary

Catalyst	Concept	Tasks	Reasons
Pt-alloy catalyst on high surface area carbon (KB)	MEA optimization via combination of CL and MPL modifications	1. Membrane (<30 um) 2. Cathode catalyst layer additives 3. Ionomer optimization 4. UTC MPL technology for GDL improvements	1. Thinner durable membrane to improve performance 2. Control hydrophobicity of CL 3. For higher catalyst utilization and conductivity in CL 4. Multi-cell stack with alloy catalysts combining new electrode structure and improved GDL to resolve flooding issues; On-track to be completed by April 2012

- ❑ Demonstrate improved performance in a full size WTP cell for 30% Pt_2IrCr/C_{KB}
  - MEA optimization → improved performance at 1A/cm^2 is **53 mV**
  - Modified GDL with a thinner MPL → improved performance by **85 mV** at 1A/cm^2
  - Full size MEA performance of the optimized MEA and UTC MPL technology for GDL (in-progress)
  - Multi-cell stack performance of optimized MEA (to be completed by April 2012)
- ❑ Completed stack testing and teardown to understand degradation mechanisms
  - Primary durability loss in the alloy catalyst due to transition metal alloy dissolution
  - No significant change in average alloy particle size

PROJECT SUMMARY

Relevance:

Develop structurally and compositionally advanced cathode catalyst layers that will meet DOE targets for performance and durability in real-life conditions in an MEA and 20-cell stack tests.

Approach:

Complete fundamental modeling, experimental studies that elucidate the structure of a catalyst after synthesis, their stability during processing and fuel cell operation.

Technical Accomplishments and Progress:

(1) Completed stack testing and teardown to understand degradation mechanism for Pt_2IrCr alloy under an AST protocol: Primary durability loss in the alloy catalyst due to transition metal alloy dissolution

(2) Completed demonstration of improved MEA performance at high current density in a full size WTP cell for the 30% Pt_2IrCr/C_{KB}

(3) Current core-shell method was a No-Go after extensive physical characterization and stability testing of various core-shell materials

(3) Successfully identified a stable carbon support (C4) that meets DOE Target. However, No-Go decision made due to large gap in air performance, lower ECA and MA compared to the same catalyst on KB.

Technology Transfer/Collaborations:

Active partnerships with JMFC, BNL and Texas A&M to develop a more active and durable cathode catalyst layer. Technology transfer through team meetings, presentations and publications.

Suggested Future Research for Alloy Catalysts:

A focus on MEA optimization during the early stages of catalyst development is essential to identify and understand the limits of alloy catalysts and their impact on the high current density performance.

HIGHLY DISPERSED ALLOY CATALYST

Activities and Learnings: Dispersed Alloy Catalysts

- Ir induces a larger negative d-band center shift → weaker O, OH, and H_2O adsorption energies thus enhancing ORR activity. d-band center shows Pt_2IrCr alloys less reactive than Pt_3Cr alloys. Potential shift for Pt → Pt^{2+} shows that Pt_2IrCr more stable
- Pt_6IrCo_7 shows very large d-band center shift and excess of charge on Pt surface atoms predicting a very high activity.
- Bimodal distribution shows higher initial mass activity than monomodal – primarily due to small particle size Pt

- Significant impact of Co/Cr on catalyst activity when in catalyst layer compared to membrane. Cell resistance and gas permeability affected when in membrane.
- Higher mass activity loss rates during load cycling at higher operation temperature

- Catalyst utilization and electrode structure in the MEA by optimizing ink formulations and processing methods significantly impact the selection of new catalyst systems and their performance under high current density operations of a fuel cell stack

HIGHLY DISPERSED ALLOY CATALYST

Activities and Learnings: Core-Shell Catalysts

- Pd and Pd_3Co cores increase Pt stability whereas Co, and Pd_3Fe cores decrease stability. Adsorption energies suggest both Pt/Pd_3Co and Pt/Pd_3Cr more active than pure Pt
- A clear correlation between the segregation energies of the core elements under oxygen and the dissolution trends observed experimentally

- RDE and microscopy characterization imply similar properties for Pt coating via UPD and JM routes for Pt_{ML}/Pd_3Co
- HAADF and EELS line scan results show that the shell thickness is not uniform; vary between 0.4 – 1.0 nm. Particle size and density decreases significantly after cycling. Pt shell with 1 layer shows highest activity compared to 2 and 3 layers

- Substantially lower activity of scaled Pt_{ML}/Pd_3Co in MEAs vs 0.7A/mg_{Pt} (0.254 A/mg_{PGM}) in RDE
- Substantial Co and Pd loss on exposure to acid. Higher temperature and more concentrated electrolyte contribute to Pd dissolution – more damaging than room temperature RDE testing

HIGHLY DISPERSED ALLOY CATALYST

Activities and Learnings: Durable Carbon Supports

- Pt on C4 showed significant corrosion stability. Lower ECA and MA than same catalysts on KB due to poor dispersion and large particles.

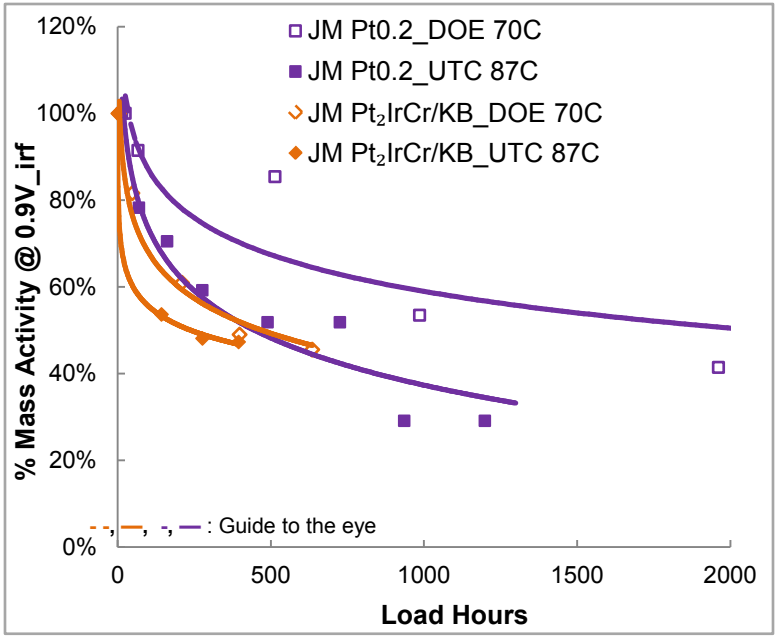
- No trend observed for weight loss and CO_2 loss vs. BET surface area of Carbon.
- Large particle observed from TEM, 7-8 nm. Scaled up 30% Pt/C4 has a particle size of ~3.6 nm.

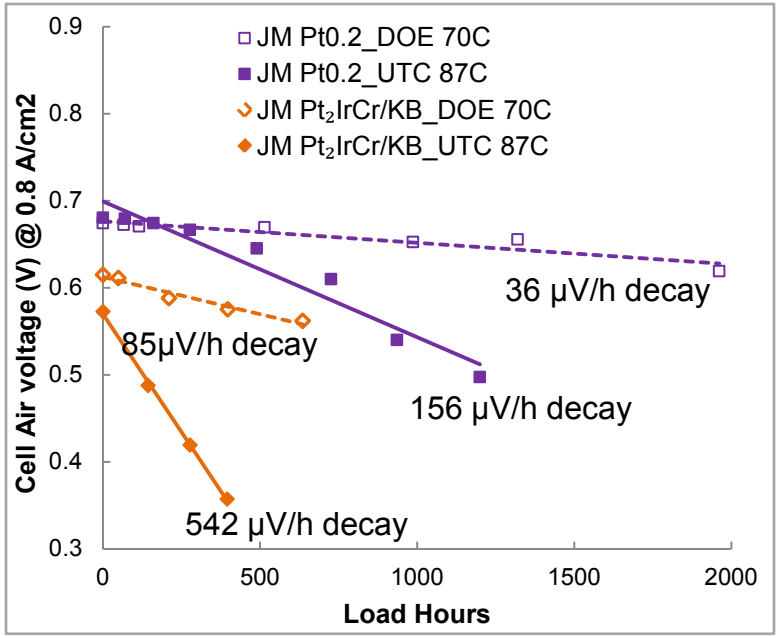
- There is no thinning of catalyst layers. Performance for C4 begins to decay only after 300h. However, large air performance gap observed for Pt/C4 compared to $Pt/C_{KB.}$

Technical Back-up Slides

Durability in Full-Size MEA

JM 30% Pt_2IrCr/C_{KB}





<u>Durability protocol</u>

- Modified DOE protocol: ~33-100 %RH cycle, 20-100 mA/cm^2 (dry) & 20-1000 mA/cm^2 (wet) load cycle, average 70 ºC, ambient pressure
- UTC protocol: current cycles up to 800 mA/cm^2, average 87 ºC, ambient pressure

❑ Pt_2IrCr/C_{KB} vs. Pure Pt durability

- Higher rate of mass activity and high-current density performance loss for Pt-alloy than pure Pt
- Mass activity of Pt and Pt-alloy reaches the same value after decay
- Degradation rates increased with temperature in both Pt and Pt-alloys
- Cr loss into MEA (leads to increase in cell resistance and oxygen gain)

HIGHLY DISPERSED ALLOY CATALYST

Response to 2011 DOE Merit Review Feedback

- Data regarding iridium or chromium dissolution has been obtained based on EMPA elemental mapping after full-size and stack durability testing.
- Scale-up of a Pt_2IrCr alloy on the down-selected Carbon (C4) is complete. Subscale corrosion test completed in Jan 2011; MEA optimization of 20% Pt_2IrCr/C4 is still below DOE target due to large gap in air performance, lower ECA and MA compared to the same catalyst on KB.
- Fundamental study to understand the durability of transition metals in PtIrM alloys (M=Cr, Co) show lower Stability of Co than Cr in acidic environments.
- ***Completed 2000 hr of durability testing in a short stack under the AST drive cycle protocol and identified transition metal alloy dissolution as the primary degradation mechanism in the alloy catalyst***

- **The core-shell approach**
  - Current core-shell method was a No-Go after extensive physical characterization and stability testing of various core-shell materials

- **Improve high current density performance via MEA optimization**
  - Demonstrated 53 mV improvement in high current density performance for a full size optimized MEA .
  - A further ~85mV improvement in high current density performance achieved using a modified thin microporous layer containing GDL