

Highly Dispersed Alloy Catalyst for Durability

2010 DOE Hydrogen Program

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Project ID: FC002

OVERVIEW

Timeline

- Start – May 1, 2007
- End – October 31, 2010
- 80% Complete

Budget

- Total project funding
 - DOE share - \$6.278 M
 - Cost share - \$2.860 M
- DOE Funding received in FY09
 - \$2.036 M
- DOE Funding for FY10
 - \$1.917 M

Barriers

Performance

- Increase catalyst activity; $\geq 0.44 \text{ A/mg}_{\text{PGM}}$

Cost

- Reduce PGM loading; $\leq 0.3 \text{ mg}_{\text{PGM}}/\text{cm}^2$

Durability

- $< 40\%$ loss in ECA and Activity under potential cycling
- $< 30 \text{ mV}$ loss in performance at 1 A/cm^2 under carbon corrosion protocol

Partners

Johnson Matthey Fuel Cells



Texas A&M University



Brookhaven National Laboratory



UTC Power

A United Technologies Company

RELEVANCE

Project Objective

Develop 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.

Task 1 – Dispersed Alloy Catalyst Development

- Modeling activity and stability of PtIrM alloys using segregation trends, d-band center, and potential shifts
- Scale-up of highly active catalysts and verification in an MEA
- MEA optimization steps to achieve high performance in H₂/air while reducing the cathode catalyst loading

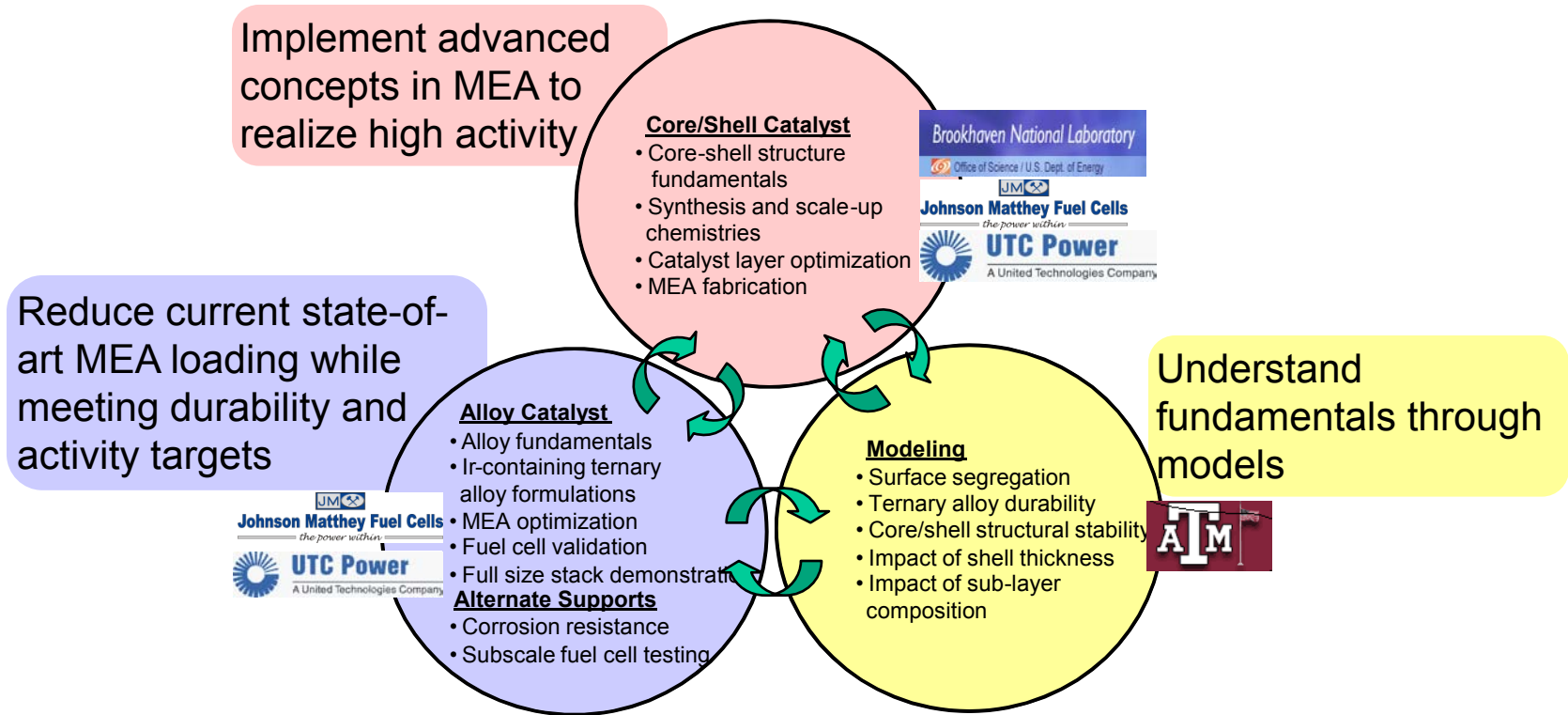
Task 2 – Core-Shell Catalyst Development

- Modeling activity and stability of Pt_{ML} on Pd_xCo and Ir cores
- Improved synthesis route for uniform Pt deposition
- Investigating the stability of scaled-up core-shell catalysts

Task 3 – Carbon Support Investigation

- Liquid Cell testing of bare carbons, Pt/C and PtM alloys/C
- Subscale MEA corrosion and durability testing of Pt/C
- MEA testing of ternary PtIrM alloys for down-selection

APPROACH



- Collaboration between UTC and JMFC to overcome activity, durability and cost barriers using new methods of formulation, fabrication and evaluation; characterization and fundamentals supported by BNL (experimental) and Texas A&M (theoretical models)
- Concurrently, the development of advanced core-shell catalysts to achieve high activity is focused at JMFC and BNL; Scale-up, incorporation in to MEA's, and verification in fuel cells is shared between JMFC and UTC
- Modeling activities at Texas A&M give valuable insight into the fundamentals for both the dispersed and core-shell catalysts to arrive at optimum systems which are verified by experimental studies

COLLABORATIONS

Partners

- 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 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 O₂ reduction reaction and stability for dissolution

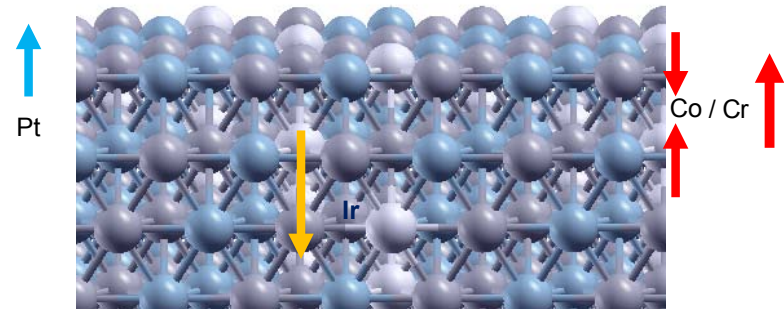
APPROACH

Milestones and Accomplishments

Month/Year	Milestone or Go/No-Go Decision	Status/Comments
May 2009	<u>Go/No-Go decision</u> : Down-selection of new durable carbon	Completed May 2009. Down-selected a carbon (C4) that Meets DOE's corrosion targets and verified a 30% Pt/C4. Currently working to scale-up alloy on C4
May 2009	<u>Milestone</u> : Scale-up of down-selected dispersed catalyst	Completed May 2009, for both catalysts. Currently testing performance and durability of first trial 410 cm ² UEA of 30% Pt ₂ IrCr/KB
August 2009	<u>Go/No-Go decision</u> : Down-selection of core/shell catalyst	New Go/No-Go: April 2010;
September 2009	<u>Go/No-Go decision</u> : UEA optimization of dispersed catalyst for single cell durability test	New Go/No Go: April 2010. Task extended for new alloy formulation: 30% Pt ₇ IrCo ₇ /KB
April 2010	<u>Milestone</u> : Completion of all modeling work and publication of results	On-track
April 2010	<u>Go/No-Go decision</u> : Down-selection of core/shell catalyst	Pushed back for further development ; project extension till Oct. 2010.
May 2010	<u>Milestone</u> : Scale-up of alloy catalyst on durable carbon support and sub-scale MEA testing	On-track
October 2010	<u>Milestone</u> : Single cell validation of dispersed alloy catalysts and Stack Demonstration	On track; catalyst system in stack TBD

TECHNICAL ACCOMPLISHMENTS

Task 1: Segregation Trends and Electronic Effect



Ir in PtIrCo (Vacuum)

- i. Favors Pt-skin
- ii. Reduces lattice mismatch
- iii. **Significant Pt segregation at low Ir content**

Ir in PtIrCr (Vacuum)

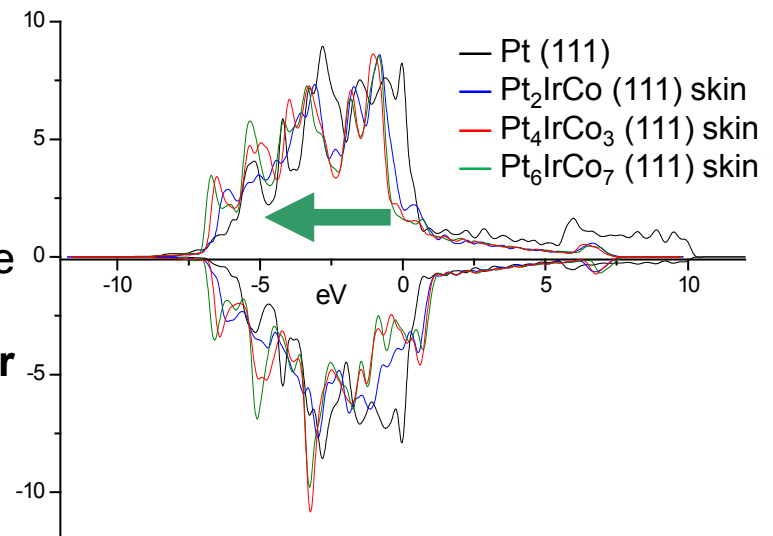
- i. Favors Pt-skin
- ii. Pt segregation significantly reduced at low Ir content
- iii. **Compared to PtIrCo alloys, the trend to form Pt-skin is reduced**

O₂ and O adsorption trends in PtIrM (M = Co/Cr)

Pt(111) > Pt₃M skin > Pt₂IrM skin > Pt₄IrM₃ skin > Pt₆IrM skin > PtM skin

- Excess of e⁻ on surface Pt atoms; deficit of e⁻ in Co/Cr subsurface atoms
- Ir induces a larger negative d-band center shift → weaker O, OH, and H₂O adsorption thus enhancing ORR activity
- When Cr is on the surface, the d-band center shift of the Pt atoms is smaller than those on the Pt-skin surfaces
- **Pt₆IrCo₇ and Pt₆IrCr₇ shows very large d-band center shift and excess of charge on Pt surface atoms predicting a very high activity**

DOS of Pt-skin Surfaces

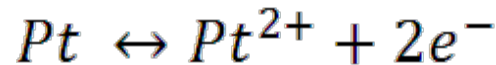
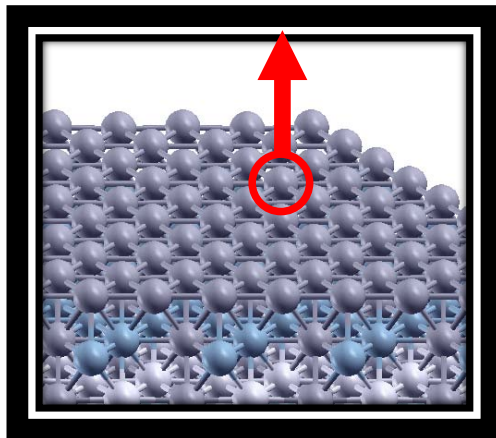


TECHNICAL ACCOMPLISHMENTS

Task 1: Electrochemical Stability – PtIrM Alloys

System	μ_{Pt} (eV)	$\Delta\mu$ (eV)	ΔU (V) (under O)
Pt(111)	-6.64	0	0
Pt/Pt ₂ IrCo(111)	-7.00	-0.36	0.18
Pt/Pt ₄ IrCo ₃ (111)	-7.04	-0.40	0.20
Pt/Pt ₆ IrCo ₇ (111)	-6.91	-0.27	0.14

System	μ_{Pt} (eV)	$\Delta\mu$ (eV)	ΔU (V) (under O)
Pt(111)	-6.64	0	0
Pt/Pt ₂ IrCr(111)	-7.63	-0.99	0.5
Pt/Pt ₄ IrCr ₃ (111)	-7.21	-0.57	0.29
Pt/Pt ₆ IrCr ₇ (111)	-7.67	-1.03	0.52



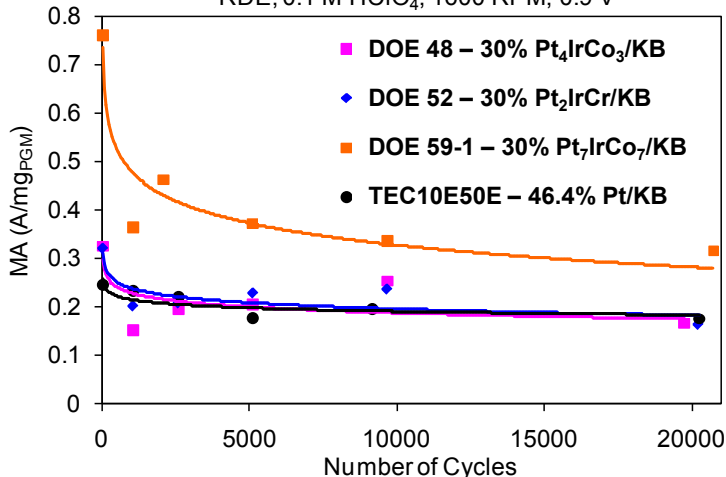
$$\Delta U = - \frac{\mu_{Pt, alloy} - \mu_{Pt, pure}}{2e}$$

- Potential shift (in vacuum and under O) indicates that Ir stabilizes Pt atoms, with a maximum as Ir content varies
- Pt atoms more stable on PtIrCr skin surfaces than PtIrCo**

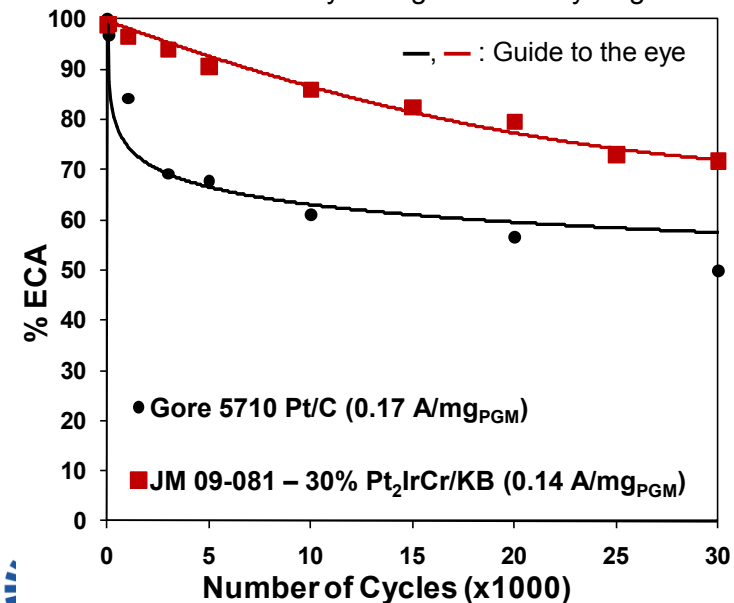
2008 and 2009 ACCOMPLISHMENTS

Task 1: PtIrM Alloys

Mass Activity Decay during Potential Cycling
RDE, 0.1 M HClO₄, 1600 RPM, 0.9 V



ECA Decay during Potential Cycling



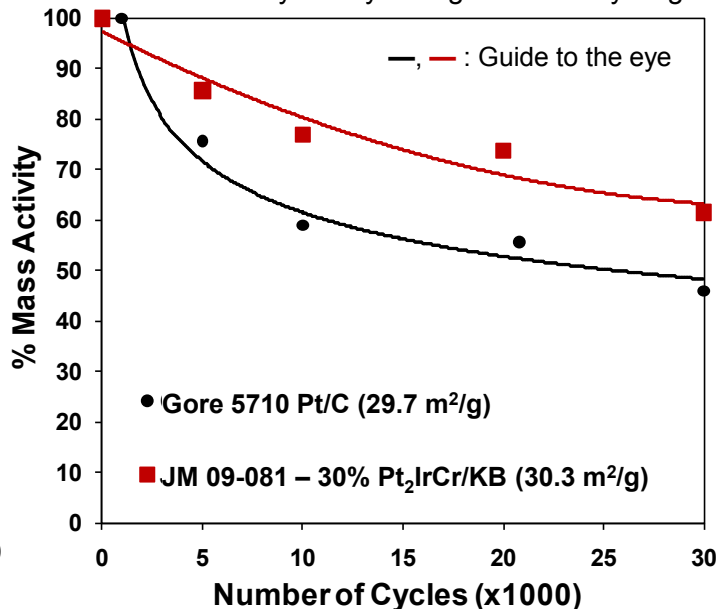
Previous Accomplishments

- ❑ First batch of 30% Pt₇IrCo₇/KB showed high mass activity (0.7 A/mg_{PGM}) and ECA in RDE

Current Scale-up of Dispersed Catalyst

- ❑ 30% Pt₂IrCr /KB has best durability in both RDE and MEA cycling
- ❑ Mass activity and ECA are lower than RDE values
 - Possible causes include
 1. Instability of alloy during MEA fabrication process
 2. Low utilization of catalyst, as seen by the low ECA
 - MEA – RDE gap under investigation

Mass Activity Decay during Potential Cycling



UTC Accelerated Protocol

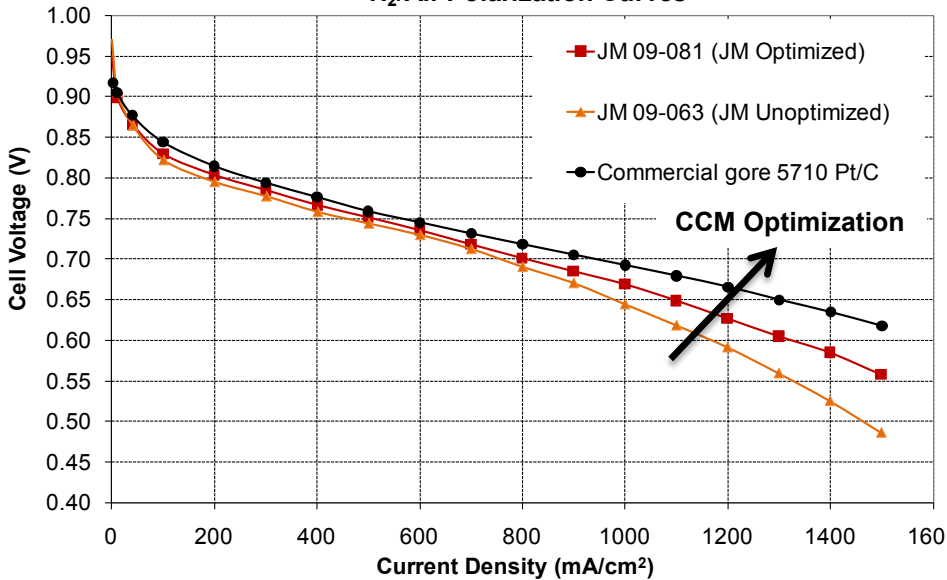
0.4 – 0.95 V; 10s:10s; Sq. wave
30,000 cycles; 4% H₂ / 100% N₂
150 kPa (absolute); 80°C; 100% RH
(anode and cathode)



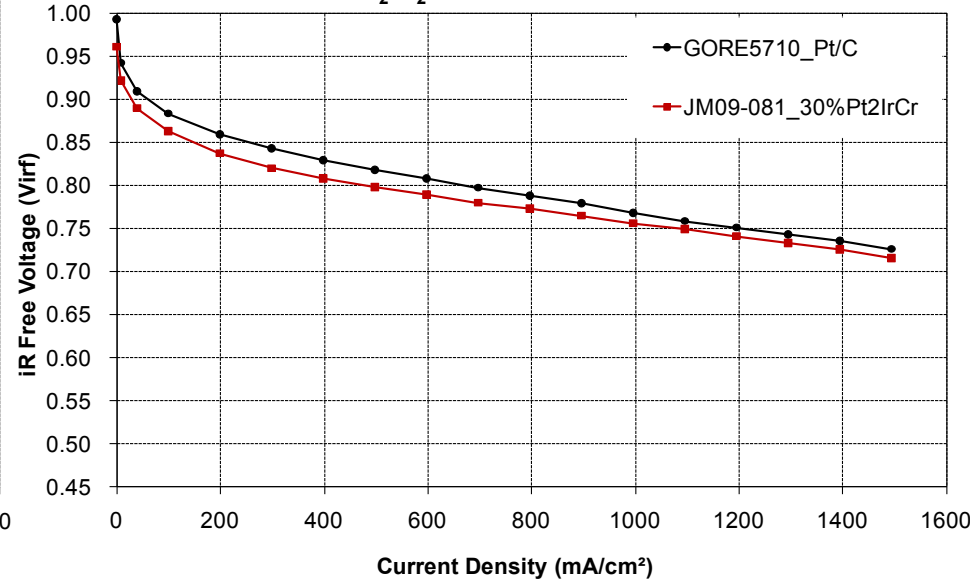
TECHNICAL ACCOMPLISHMENTS

Task 1: Scale-up and Optimization of 30% Pt₂IrCr

25 cm²; Solid Plate; 50% U; 80 °C; 100% RH; 150kPa (abs)
H₂/Air Polarization Curves



410 cm²; Water Transport Plate, 65 °C, 100kPa(abs.)
H₂/O₂ Polarization Curves

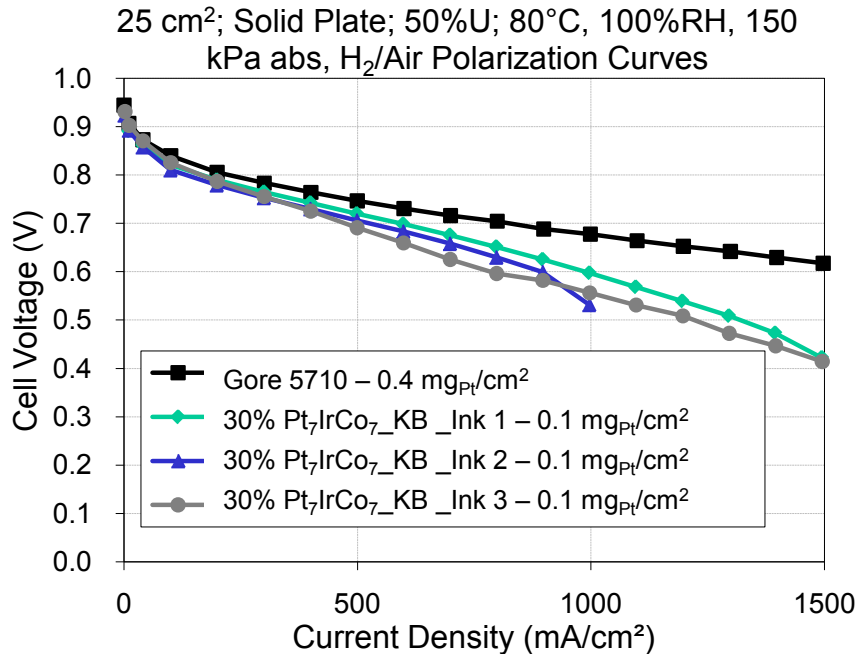


Catalyst	CCM Details	ECA	MA	MA
		m ² /g _{Pt}	A/mg _{Pt}	A/mg _{PGM}
30% Pt ₂ IrCr/KB	JM 09-063_unoptimized MEA 0.20mg/cm ²	35.0	0.234	0.156
30% Pt ₂ IrCr/KB	JM 09-081_optimized MEA 0.21mg/cm ²	28.4	0.210	0.140
Gore 5710 Pt/C	Commercial MEA in SP 0.4 mg/cm ²	29.7	0.172	0.172
30% Pt ₂ IrCr/KB	JM 09-081_unoptimized MEA in WTP 0.2 mg/cm ²	26.6	0.144	0.095
GORE 5710 Pt/C	Commercial MEA in WTP 0.4mg/cm ²	51.3	0.132	0.132

- ❑ Clear evidence of improvement for high current density performance in H₂/air from catalyst layer optimization steps
- ❑ Half-loading (0.2mg_{Pt}/cm²) alloy catalyst MEA's can achieve comparable initial performances to a standard Gore 5710 (0.4mg_{Pt}/cm²) in 25cm² solid plate (SP) and first attempt 410cm² WTP cell

TECHNICAL ACCOMPLISHMENTS

Task 1: RDE to MEA Gap – PtIrM Alloys



Catalyst	RDE		MEA*	
	ECA	MA	ECA	MA
	m ² /g _{Pt}	A/mg _{PGM}	m ² /g _{Pt}	A/mg _{PGM}
Gore 5710 Pt/C	89	0.20	42	0.19
30% Pt ₂ IrCr/KB	49	0.31	29	0.13
30% Pt ₇ IrCo ₇ /KB [‡]	75	0.48	44	0.21

* Average ECA and MA based on three or more MEAs

[‡] Most recent batch

- ❑ Mass activity and ECA are lower than RDE values for alloy catalysts
 - Possible causes include
 1. Instability of alloy during MEA fabrication process
 2. Low utilization of catalyst, as seen by the low ECA
- ❑ Initial investigation into MEA fabrication suggests different ink formulations can significantly increase both mass transport properties and kinetic performance of alloy catalysts
- ❑ A gap may still exist between RDE and MEA for alloy catalysts
- ❑ Extensive investigation currently underway

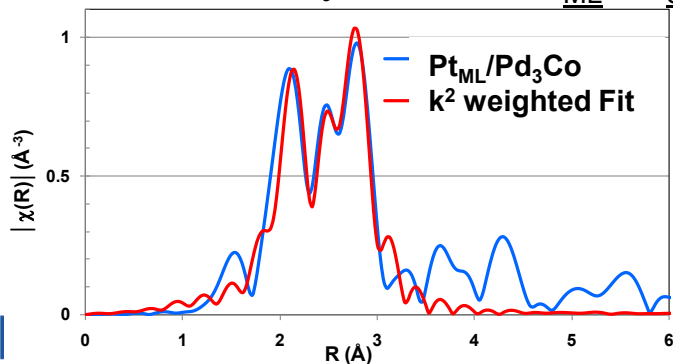
TECHNICAL ACCOMPLISHMENTS

Task 2: Pt_{ML}/Pd₃X Core-Shell – Fundamentals

Stability of Pd/Co in Pd ₃ Co relative to pure Pd/Co	ΔU (V) (under Vacuum)	Stability of Pd/Cr in Pd ₃ Cr relative to pure Pd/Cr	ΔU (V) (under Vacuum)
Pd	0.08	Pd	0.07
Co	0.32	Co	-0.04
$(\Delta U_{Pd} - \Delta U_{Co})_{alloy}$	1.00	$(\Delta U_{Pd} - \Delta U_{Cr})_{alloy}$	1.81

- ❑ Leaching trend: Cr > Co > Pd; predicted trend in agreement with recent JM experiments showing dissolution of Cr >> dissolution of Co
- ❑ Adsorption energies suggest both core-shell Pt/Pd₃Co and Pt/Pd₃Cr more active than pure Pt
- ❑ OH, O, and water adsorption in Pt/Pd₃Co weaker than in Pt/Pd₃Cr
- ❑ **Overall activity/stability favors Pt/Pd₃Co**

In-Situ XAS Analysis of JM Pt_{ML}/Pd₃Co



Fit Pt L3 and Pd K data concurrently with constraints

$$N_{Pt-Pt} = 6.5 (\pm 1.3)$$

$$N_{Pt-Pd} = 2.0 (\pm 1.0)$$

$$R_{Pt-Pt} = 2.736 \text{ \AA} (\pm 0.006) (< \text{Pt } 2.76 \text{ \AA})$$

$$R_{Pt-Pd} = R_{Pd-Pt} = 2.727 \text{ \AA} (\pm 0.007)$$

**Coordination number of Pt (6.5)
suggests 1 ML of Pt**



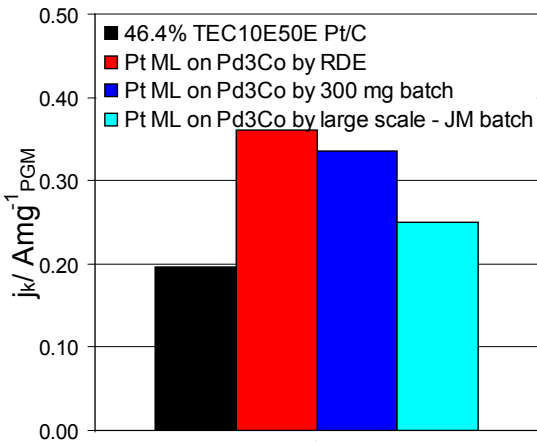
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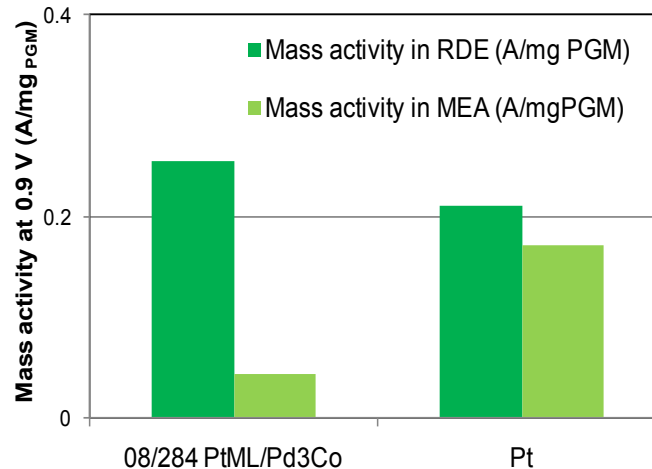
TECHNICAL ACCOMPLISHMENTS

Task 2: Activity of Pt_{ML}/Pd₃Co Core – Shell

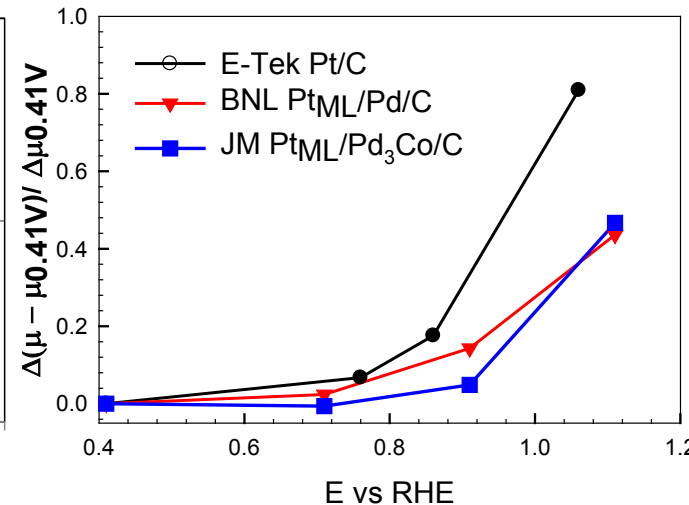
Previous RDE Results



Mass Activity Comparison - RDE vs MEA



In-situ XANES $\Delta\mu$ Analysis

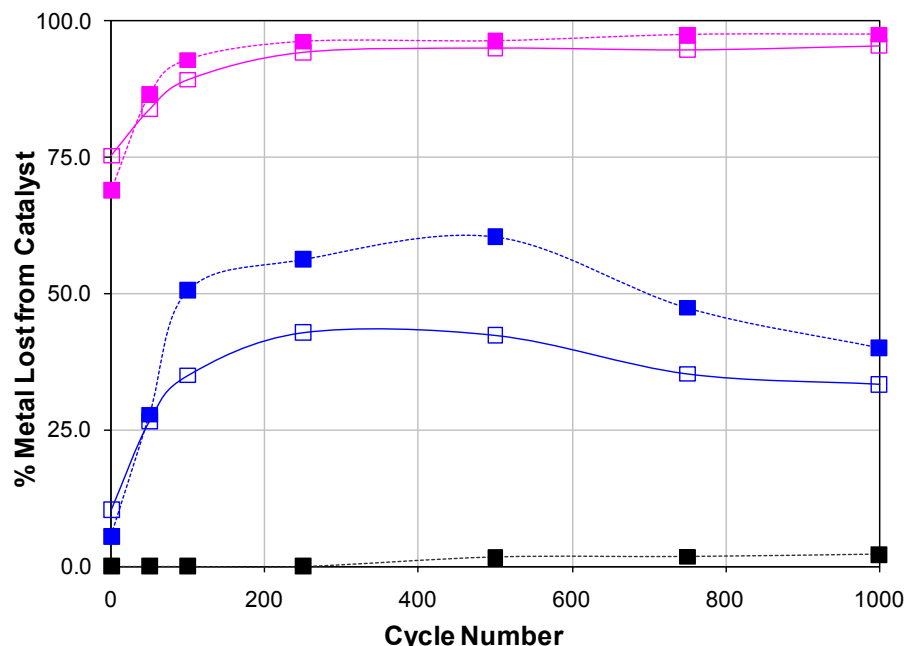


- ❑ RDE and microscopy characterization (2008 report) imply similar properties for Pt coating via BNL and JM routes for Pt_{ML}/Pd₃Co
- ❑ **Substantially lower activity of Pt_{ML}/Pd₃Co in MEAs (0.044 A/mg_{PGM}) vs RDE (0.254 A/mg_{PGM})** due to
 - Instability/restructuring of Pt_{ML}/Pd₃Co at 80°C under MEA test conditions
 - Incomplete Pt shell
- ❑ XANES ($\Delta\mu$) Analysis of JM Pt/Pd₃Co shows higher stability towards oxidation of Pt/Pd₃Co compared with pure Pt (in agreement with modeling results)

TECHNICAL ACCOMPLISHMENTS

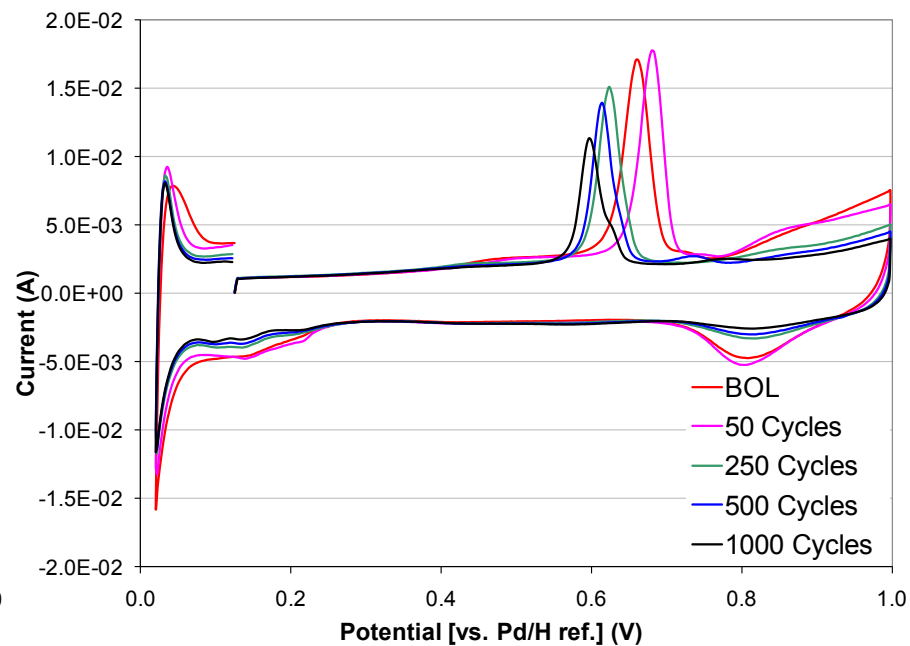
Task 2: Stability of Pt_{ML}/Pd₃Co Core – Shell

Stability of Pt, Pd and Co during Potential Cycling
0.6 – 1.0V, 50mV/s, 1M H₂SO₄, 80°C



■ % Pd loss_09/071 Pt_{1.5ML}/Pd₃Co □ % Pd loss_08/324 Pd₃Co
■ % Co loss_09/071 Pt_{1.5ML}/Pd₃Co □ % Co loss_08/324 Pd₃Co
■ % Pt loss_09/071 Pt_{1.5ML}/Pd₃Co

CO stripping voltammetry at 10 mV/s



- Significant surface area loss over 1000 cycles – 60% CO peak area loss
- **Clear evidence of substantial Co and Pd loss on exposure to acid**
- Presence of Pt does not reduce Pd dissolution – but minimal Pt dissolution



UTC Power

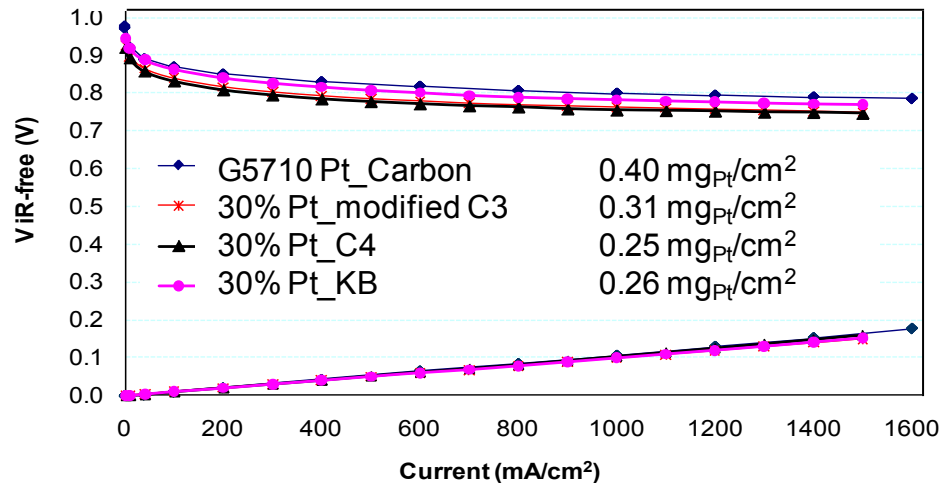
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*Decrease in solution Pd content at > 500 cycles- under investigation

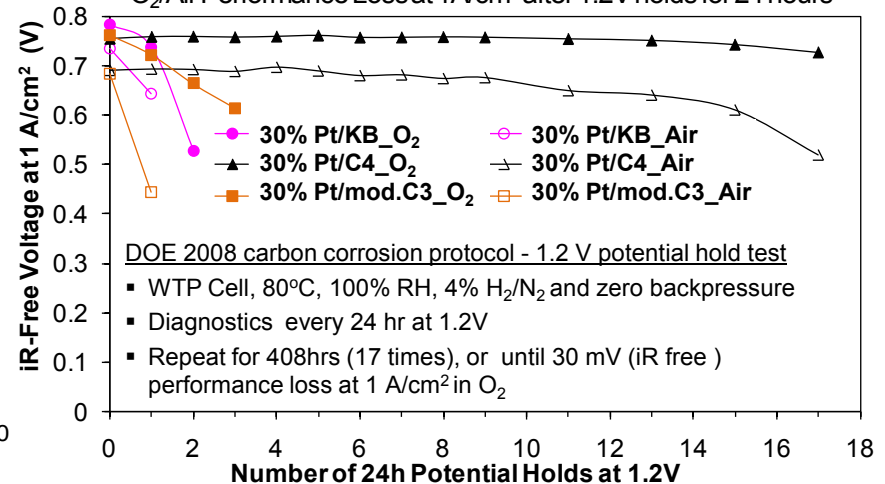
TECHNICAL ACCOMPLISHMENTS

Task 3: Down-selecting Alternate Carbon Support

BOL Performance in H₂/O₂, 50%U, 80°C, WTP



O₂/Air Performance Loss at 1A/cm² after 1.2V holds for 24 hours

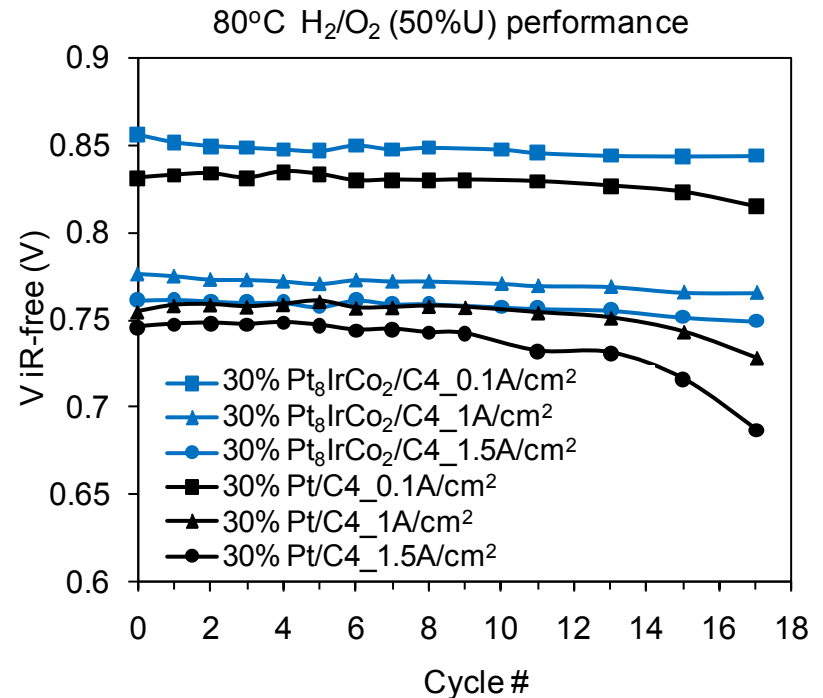
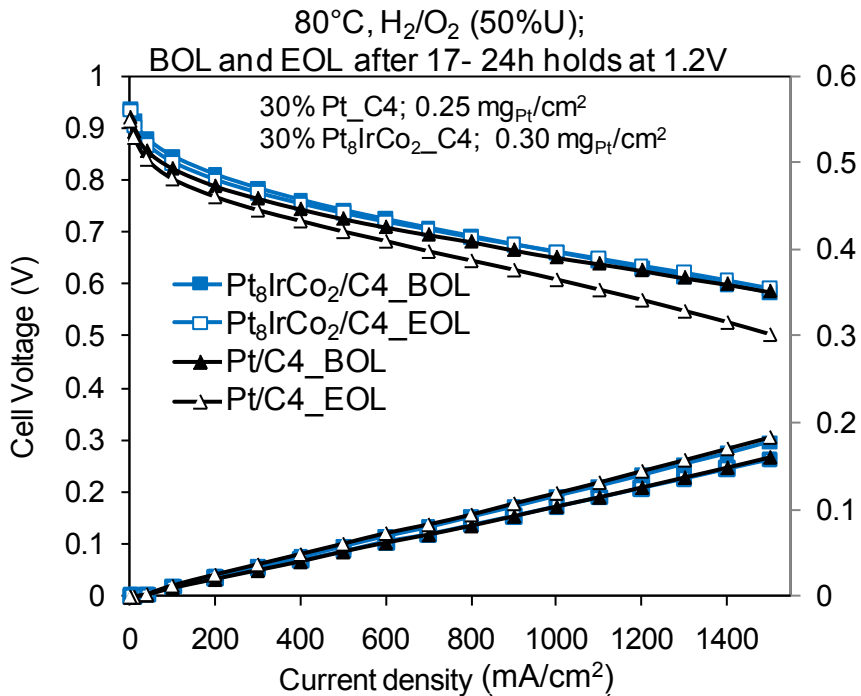


Carbon	BET surface area m ² /g _{carbon}
Ketjen Black	800
Aerogel	600
Nanoblack	250
C4	136
C5	195
Modified C1	55
Modified C2	97
Modified C3	122

- ❑ Ex-situ testing of eight carbons completed
 - Down-selected two carbons for subscale MEA corrosion testing, Modified C3 and C4
- ❑ BOL performance of Pt on Ketjen Black higher than modified C3 and C4
 - Due to smaller Pt particles and ultimately higher mass activity
- ❑ Large O₂ performance loss after only one potential hold for both KB and modified C3
- ❑ Pt on C4 showed significant corrosion stability
 - No performance loss until 300 hours of 1.2 V holds (13 cycles)
 - After 17 cycles (408 hours) only 27 mV loss at 1.0A/cm² in O₂
 - Down-selected C4 as final carbon that meets DOE Target

TECHNICAL ACCOMPLISHMENTS

Task 3: Improving Activity of Catalyst on New Support



	Catalyst Formulation	Particle size (TEM)	ECA m ² /g _{Pt}	MA A/mg _{Pt}	MA A/mg _{PGM}
DOE 67-1	30% Pt/C ₄	4.85	45.7	0.09	0.09
DOE 68-1	30% Pt ₃ Co/C ₄	5.96	33.1	0.23	0.23
DOE 99B	30% Pt ₈ IrCo ₂ /C ₄	7.35	29.7	0.18	0.16

- Alloy on C₄, 30% Pt₈IrCo₂
 - Better initial performance, 2x Pt based MA of Pt/C₄
 - More stable during potential holds
 - No mass transport loss for alloy at high C.D
- Current focus is on understanding the stability of the alloy vs large particle size Pt/C₄ and mechanism for high current density performance loss

CURRENT TECHNICAL STATUS

Electrocatalyst Targets	Previous Status	Current Status	DOE 2010 Target	DOE 2015 Target
Pt group metal (total content) [g/kW]	0.80	0.50	0.3	0.2
Pt group metal (total loading) [mg/cm ²]	0.64 [‡]	0.40	0.3	0.2
Mass activity @ 900mV [A/mg _{PGM}]	0.28	0.14	0.44	0.44
Specific activity @ 900mV [mA/cm ²]	0.55	0.50	0.72	0.72
Cyclic durability @ <80°C / ≥80°C [h]	TBD	TBD	5000/2000	5000/5000
ECA Loss* [%]	30	30	<40	<40
Cost [\$/kW]	~41 [†]	~26 [†]	5	3

Carbon Targets	Current Status	DOE 2010 Target
Durability – iR free O ₂ performance loss at 1 A/cm ² after 400h at 1.2V	27 mV	<30 mV

* Durability data measured after 30K cycles on UTC defined accelerated test protocol

[‡]Anode/Cathode loading – 0.4/0.24 mg/cm² (PGM)

[†] 5 year average PGM price \$ 51.55/g (Pt = \$1234.33/Troy Oz; Ir = \$ 369.06/troy oz)

Based on current scaled-up 30% Pt₂IrCr MEA ; Anode/Cathode loading – 0.1/0.3 mg/cm² (PGM).

- 30% Pt₂IrCr /KB – best durability in both RDE and MEA cycling**
- Scale-up of highly active (0.7 A/mg_{PGM}) Pt₇IrCo₇, in progress**
- Down-selected a carbon, C4, that meets DOE 2010 Targets**

Task 1: Dispersed Catalyst Work

- Further RDE and MEA testing of scaled up batch of 30% Pt₇IrCo₇
- Stability of Ir and Co/Cr in alloys
- Completion of all modeling work and publication of results (April 2010)
 - Composition of various PtIrM alloy catalysts during potential cycling to be fed into the models developed at TAMU
- Dispersed Catalyst CCM optimization
 - Investigating MEA fabrication process to understand gap between MEA and RDE data
 - Electrode structure optimization for water-transport-plate cells
 - Performance modeling
 - GDL selection and final UEA optimization
- Single cell validation of dispersed alloy catalysts and Stack Demonstration (October 2010)

Task 2: Core-Shell Catalyst Development

- Performance testing of Pt_{ML}/Ir core-shell CCM's
- Establish performance and stability comparison between Pd₃Co coated via JM and BNL routes
- Go/No-Go: If DOE mass activity target met in subscale MEA, final scale-up and MEA optimization will proceed (April 2010)

Task 3: Carbon corrosion

- Completion of scale-up alloy catalyst on durable carbon support, MEA optimization and subscale durability testing (October 2010)

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 MEA and 20-cell stack test.

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 scale-up of a 30% Pt₂IrCr/C ternary alloy catalysts and preliminary optimization of cathode catalyst layers in a subscale MEA for performance in H₂/air. Began work on optimizing a full-size UEA.
- (2) Scaled-up a Pt_{ML}/Pd₃Co/C core-shell catalyst to a 5g batch.
- (3) Down-selected a durable carbon support capable of meeting DOE durability targets.

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.

Proposed Future Research: Continue to experimentally verify the modeling data for core-shell stability and understand alloy durability and impact on MEA performance. Incorporate alternate durable support, optimize electrode structure and performance modeling to improve overall catalyst performance in an MEA