

# Highly Dispersed Alloy Catalyst for Durability

## 2010 DOE Hydrogen Program

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Project ID: FC002

# OVERVIEW

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## 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  $1 \text{ A/cm}^2$  under carbon corrosion protocol

## Partners

Johnson Matthey Fuel Cells



Texas A&M University



Brookhaven National Laboratory



# RELEVANCE

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## 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 H<sub>2</sub>/air while reducing the cathode catalyst loading

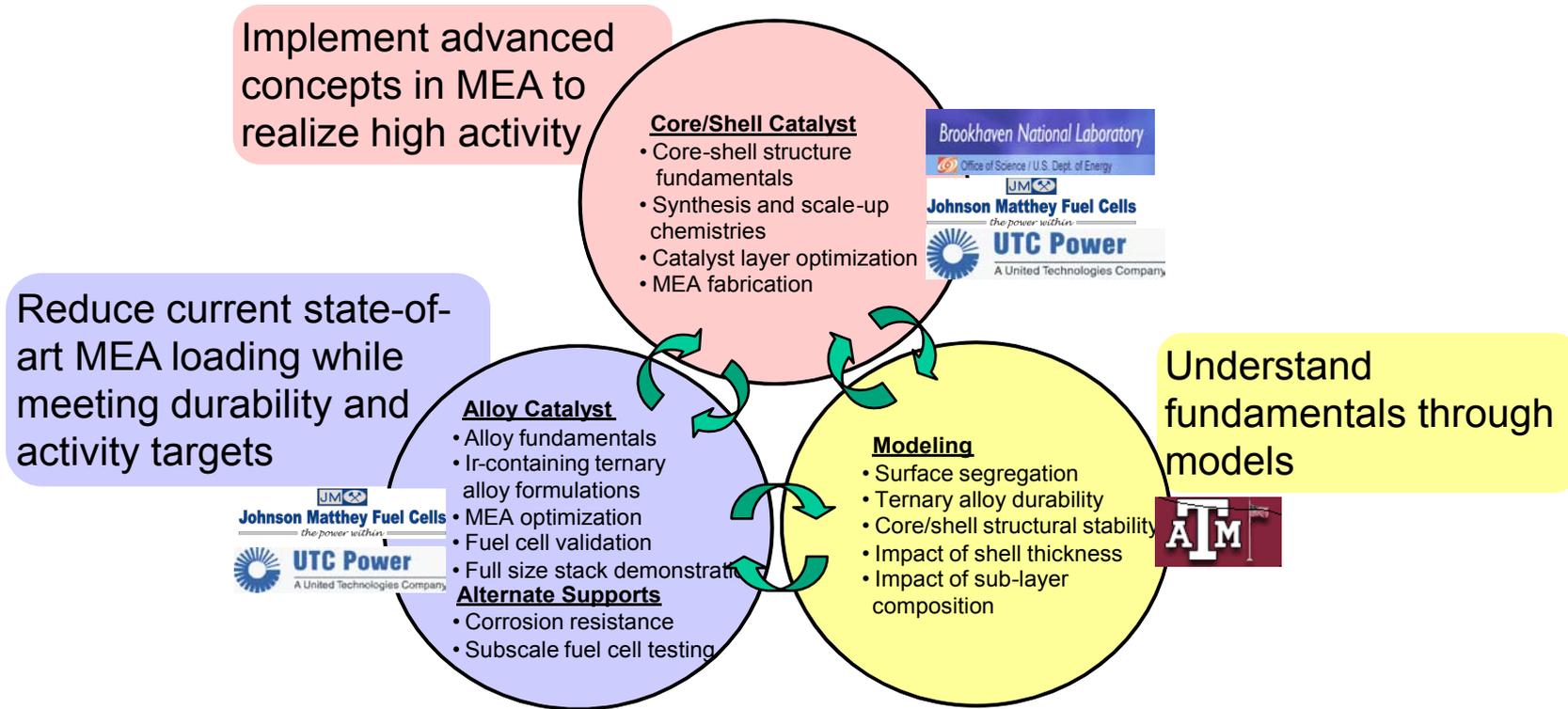
### Task 2 – Core-Shell Catalyst Development

- Modeling activity and stability of Pt<sub>ML</sub> on Pd<sub>x</sub>Co 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

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## 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 O<sub>2</sub> reduction reaction and stability for dissolution

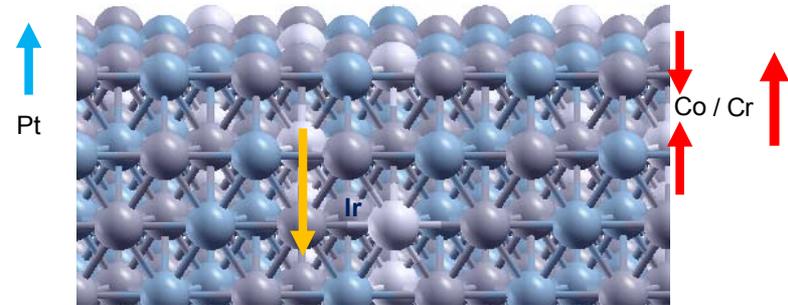
# APPROACH

## 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 <sup>2</sup> UEA of 30% Pt <sub>2</sub> 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 <sub>7</sub> IrCo <sub>7</sub> /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)

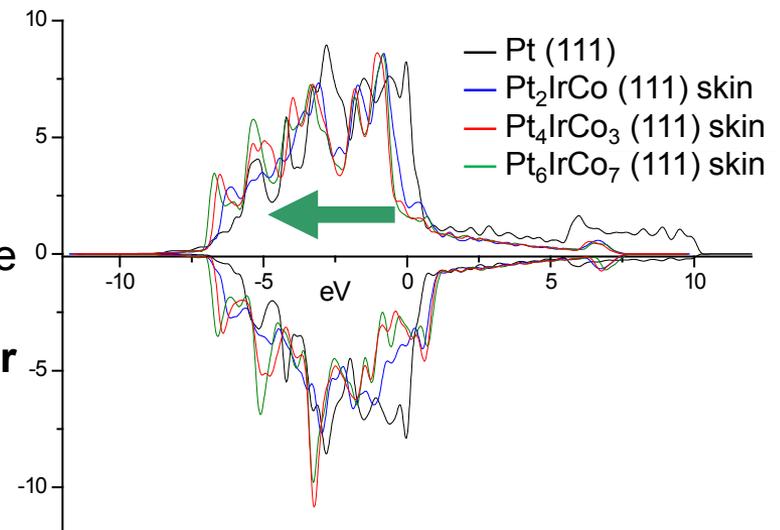
- i. Favors Pt-skin
- ii. Pt segregation significantly reduced at low Ir content
- iii. **Compared to PtIrCo alloys, the trend to form Pt-skin is reduced**

O<sub>2</sub> and O adsorption trends in PtIrM (M = Co/Cr)

Pt(111) > Pt<sub>3</sub>M skin > Pt<sub>2</sub>IrM skin > Pt<sub>4</sub>IrM<sub>3</sub> skin > Pt<sub>6</sub>IrM skin > PtM skin

- Excess of e<sup>-</sup> on surface Pt atoms; deficit of e<sup>-</sup> in Co/Cr subsurface atoms
- Ir induces a larger negative d-band center shift → weaker O, OH, and H<sub>2</sub>O 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
- **Pt<sub>6</sub>IrCo<sub>7</sub> and Pt<sub>6</sub>IrCr<sub>7</sub> 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

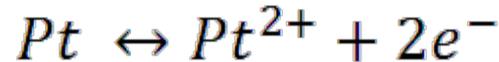
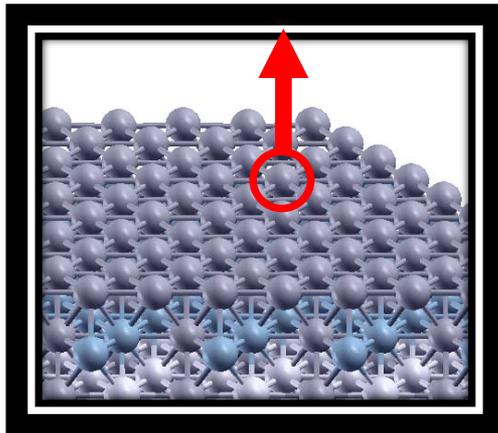


# TECHNICAL ACCOMPLISHMENTS

## Task 1: Electrochemical Stability – PtIrM Alloys

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

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



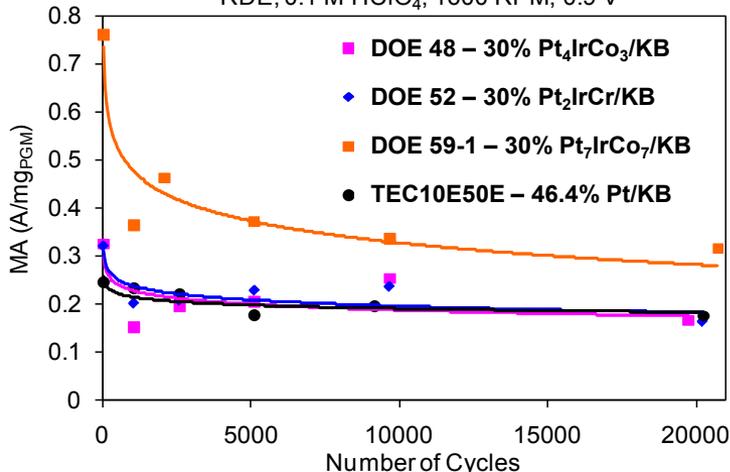
$$\Delta U = - \frac{\mu_{Pt, alloy} - \mu_{Pt, pure}}{2e}$$

- 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**

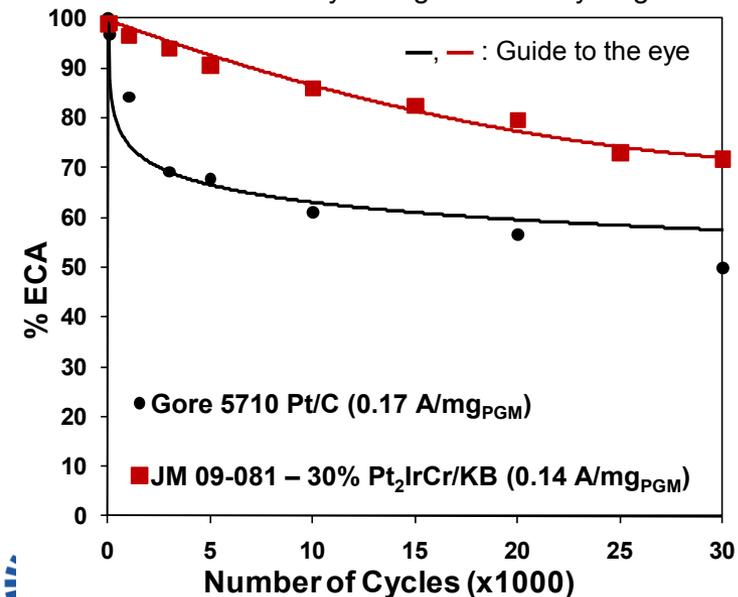
# 2008 and 2009 ACCOMPLISHMENTS

## Task 1: PtIrM Alloys

Mass Activity Decay during Potential Cycling  
RDE, 0.1 M HClO<sub>4</sub>, 1600 RPM, 0.9 V



ECA Decay during Potential Cycling



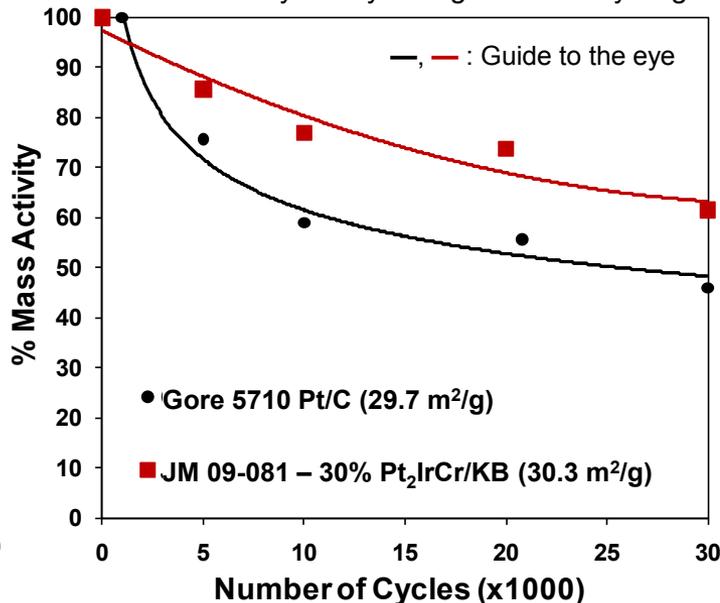
### Previous Accomplishments

- ❑ First batch of 30% Pt<sub>7</sub>IrCo<sub>7</sub>/KB showed high mass activity (0.7 A/mg<sub>PGM</sub>) and ECA in RDE

### Current Scale-up of Dispersed Catalyst

- ❑ 30% Pt<sub>2</sub>IrCr /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

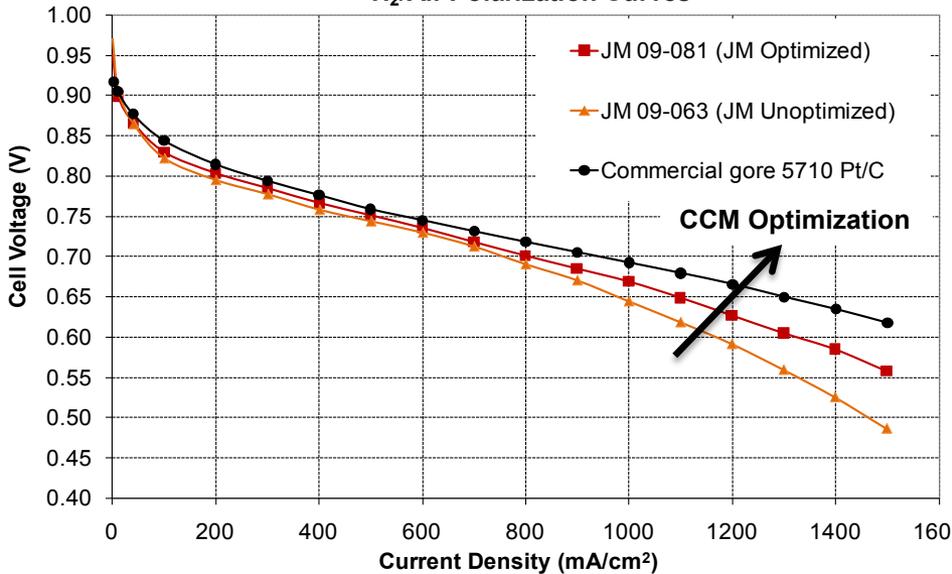
0.4 – 0.95 V; 10s:10s; Sq. wave  
30,000 cycles; 4% H<sub>2</sub> / 100% N<sub>2</sub>  
150 kPa (absolute); 80°C; 100% RH  
(anode and cathode)



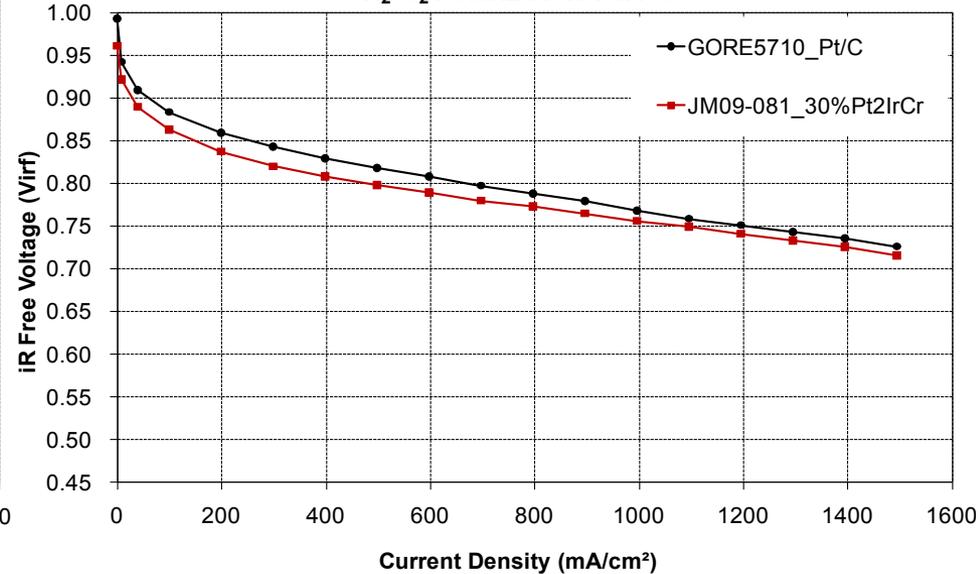
# TECHNICAL ACCOMPLISHMENTS

## Task 1: Scale-up and Optimization of 30% Pt<sub>2</sub>IrCr

25 cm<sup>2</sup>; Solid Plate; 50% U; 80 °C; 100% RH; 150kPa (abs)  
H<sub>2</sub>/Air Polarization Curves



410 cm<sup>2</sup>; Water Transport Plate, 65 °C, 100kPa(abs.)  
H<sub>2</sub>/O<sub>2</sub> Polarization Curves

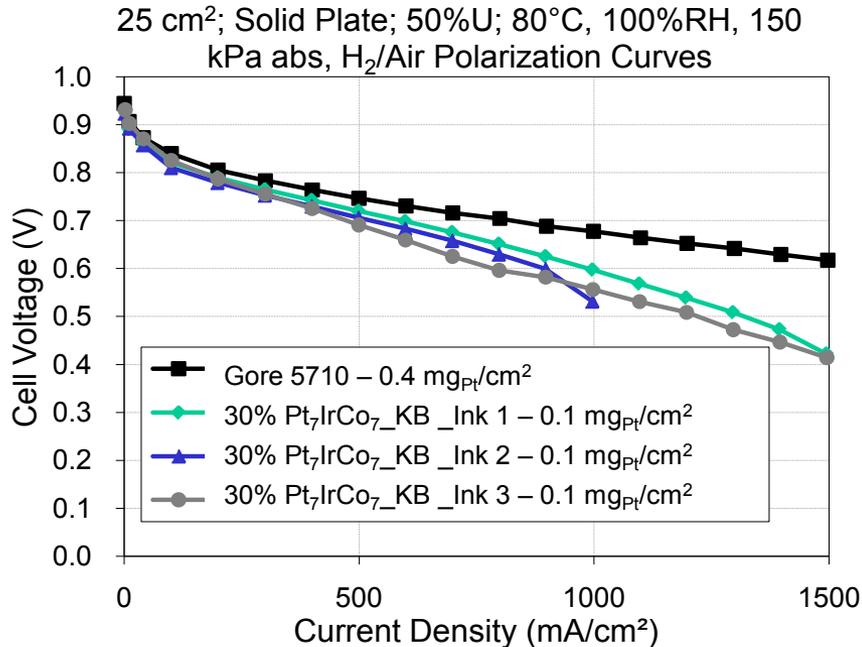


Catalyst	CCM Details	ECA	MA	MA
		m <sup>2</sup> /g <sub>Pt</sub>	A/mg <sub>Pt</sub>	A/mg <sub>PGM</sub>
30% Pt <sub>2</sub> IrCr/KB	JM 09-063_unoptimized MEA 0.20mg/cm <sup>2</sup>	35.0	0.234	0.156
30% Pt <sub>2</sub> IrCr/KB	JM 09-081_optimized MEA 0.21mg/cm <sup>2</sup>	28.4	0.210	0.140
Gore 5710 Pt/C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

- ❑ Clear evidence of improvement for high current density performance in H<sub>2</sub>/air from catalyst layer optimization steps
- ❑ Half-loading (0.2mg<sub>Pt</sub>/cm<sup>2</sup>) alloy catalyst MEA's can achieve comparable initial performances to a standard Gore 5710 (0.4mg<sub>Pt</sub>/cm<sup>2</sup>) in 25cm<sup>2</sup> solid plate (SP) and first attempt 410cm<sup>2</sup> WTP cell

# TECHNICAL ACCOMPLISHMENTS

## Task 1: RDE to MEA Gap – PtIrM Alloys



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

\* Average ECA and MA based on three or more MEAs

<sup>‡</sup> 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

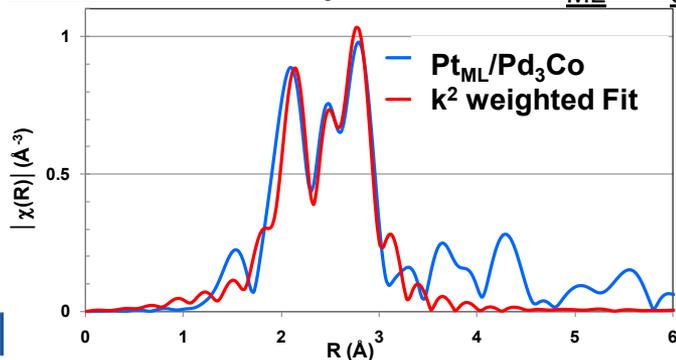
# TECHNICAL ACCOMPLISHMENTS

## Task 2: Pt<sub>ML</sub>/Pd<sub>3</sub>X Core-Shell – Fundamentals

Stability of Pd/Co in Pd <sub>3</sub> Co relative to pure Pd/Co	$\Delta U$ (V) (under Vacuum)	Stability of Pd/Cr in Pd <sub>3</sub> Cr relative to pure Pd/Cr	$\Delta U$ (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/Pd<sub>3</sub>Co and Pt/Pd<sub>3</sub>Cr more active than pure Pt
- ❑ OH, O, and water adsorption in Pt/Pd<sub>3</sub>Co weaker than in Pt/Pd<sub>3</sub>Cr
- ❑ **Overall activity/stability favors Pt/Pd<sub>3</sub>Co**

### In-Situ XAS Analysis of JM Pt<sub>ML</sub>/Pd<sub>3</sub>Co



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**



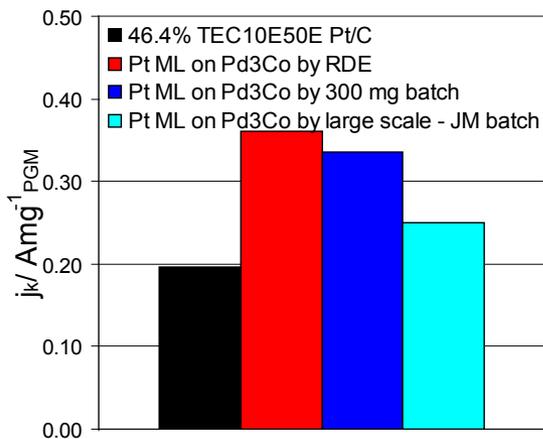
UTC

A United Technologies Company

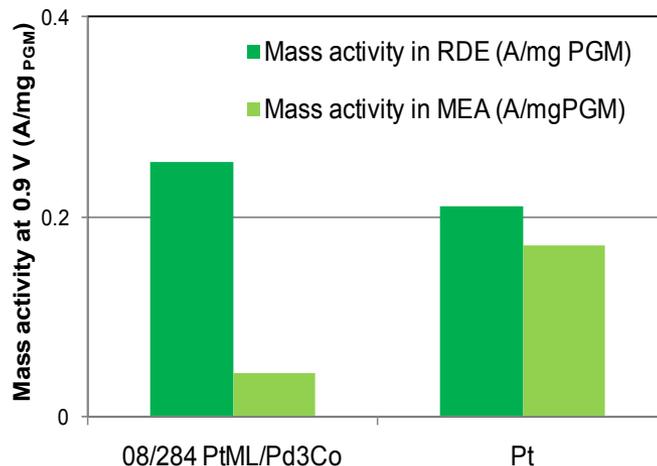
# TECHNICAL ACCOMPLISHMENTS

## Task 2: Activity of Pt<sub>ML</sub>/Pd<sub>3</sub>Co Core – Shell

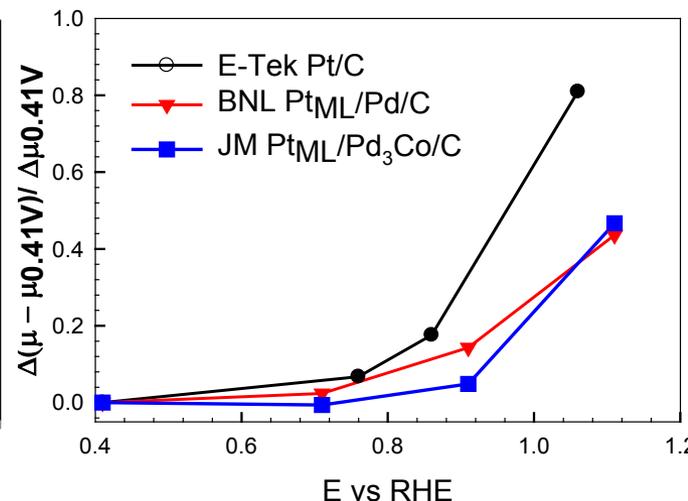
### Previous RDE Results



### Mass Activity Comparison - RDE vs MEA



### In-situ XANES $\Delta\mu$ Analysis

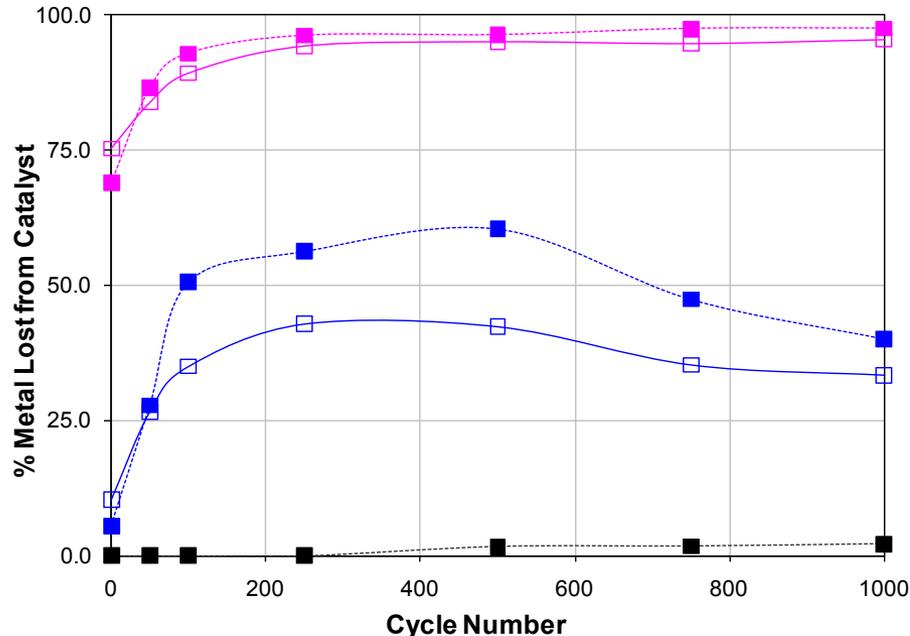


- ❑ RDE and microscopy characterization (2008 report) imply similar properties for Pt coating via BNL and JM routes for Pt<sub>ML</sub>/Pd<sub>3</sub>Co
- ❑ **Substantially lower activity of Pt<sub>ML</sub>/Pd<sub>3</sub>Co in MEAs (0.044 A/mg<sub>PGM</sub>) vs RDE (0.254 A/mg<sub>PGM</sub>)** due to
  - Instability/restructuring of Pt<sub>ML</sub>/Pd<sub>3</sub>Co at 80°C under MEA test conditions
  - Incomplete Pt shell
- ❑ XANES ( $\Delta\mu$ ) Analysis of JM Pt/Pd<sub>3</sub>Co shows higher stability towards oxidation of Pt/Pd<sub>3</sub>Co compared with pure Pt (in agreement with modeling results)

# TECHNICAL ACCOMPLISHMENTS

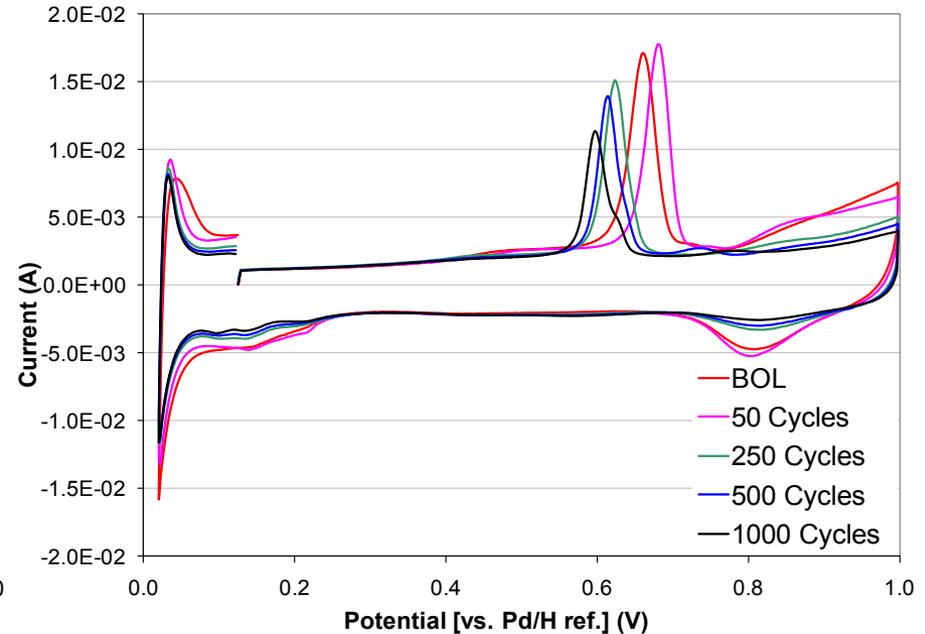
## Task 2: Stability of Pt<sub>ML</sub>/Pd<sub>3</sub>Co Core – Shell

Stability of Pt, Pd and Co during Potential Cycling  
0.6 – 1.0V, 50mV/s, 1M H<sub>2</sub>SO<sub>4</sub>, 80°C



■ % Pd loss\_09/071 Pt<sub>1.5ML</sub>/Pd<sub>3</sub>Co    □ % Pd loss\_08/324 Pd<sub>3</sub>Co  
■ % Co loss\_09/071 Pt<sub>1.5ML</sub>/Pd<sub>3</sub>Co    □ % Co loss\_08/324 Pd<sub>3</sub>Co  
■ % Pt loss\_09/071 Pt<sub>1.5ML</sub>/Pd<sub>3</sub>Co

CO stripping voltammetry at 10 mV/s

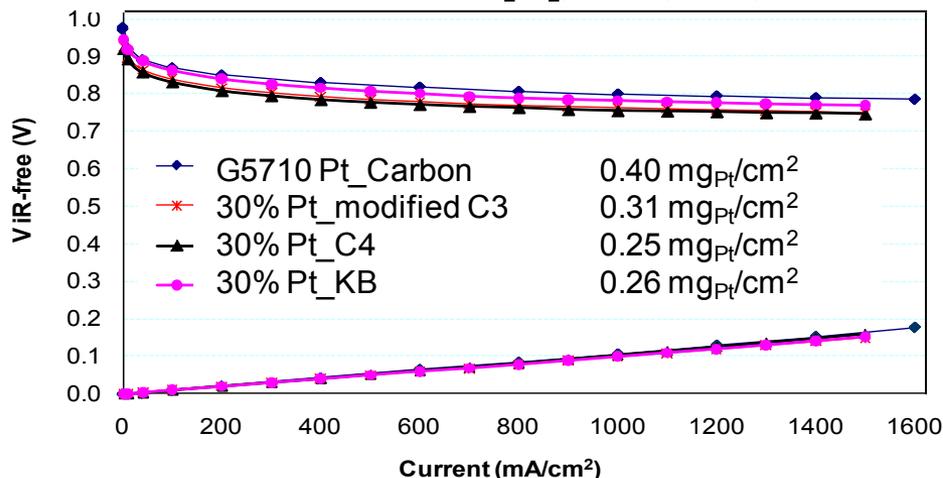


- ❑ Significant surface area loss over 1000 cycles – 60% CO peak area loss
- ❑ **Clear evidence of substantial Co and Pd loss on exposure to acid**
- ❑ Presence of Pt does not reduce Pd dissolution – but minimal Pt dissolution

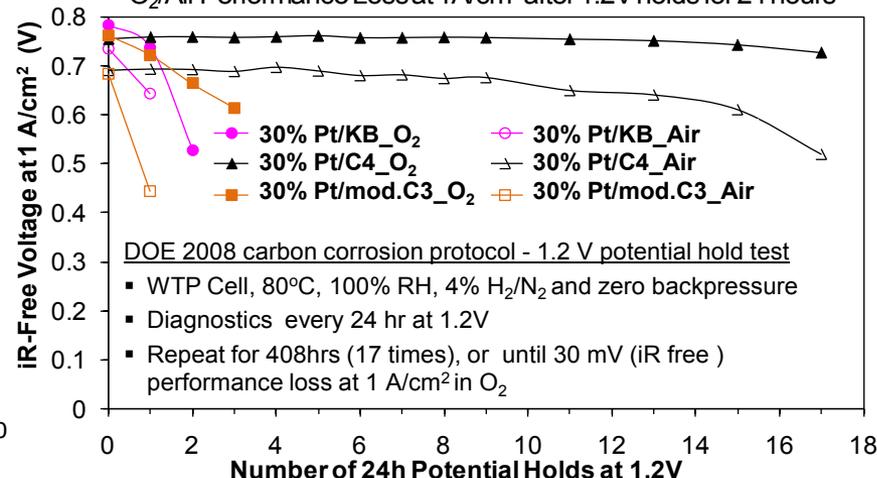
# TECHNICAL ACCOMPLISHMENTS

## Task 3: Down-selecting Alternate Carbon Support

BOL Performance in H<sub>2</sub>/O<sub>2</sub>, 50%U, 80°C, WTP



O<sub>2</sub>/Air Performance Loss at 1A/cm<sup>2</sup> after 1.2V holds for 24 hours

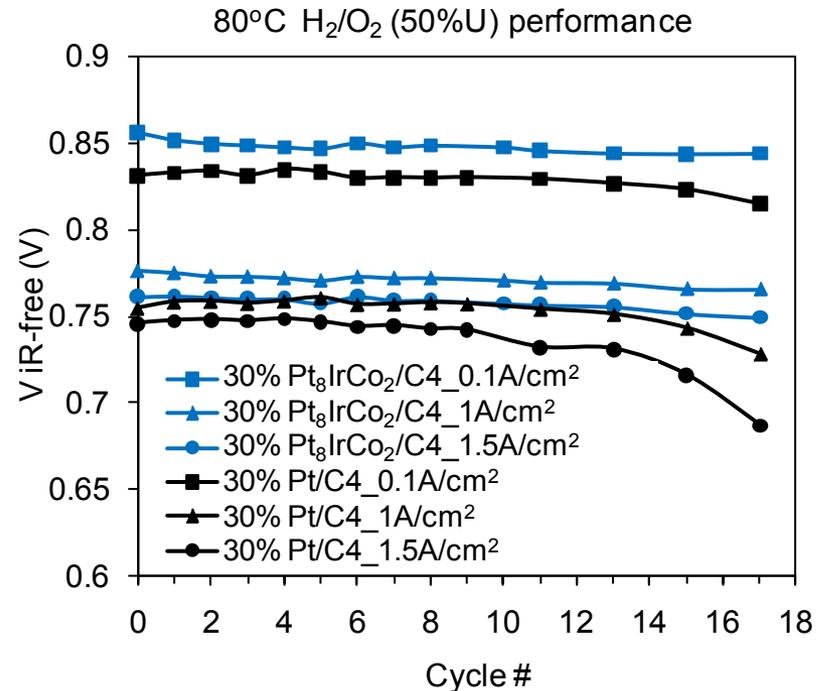
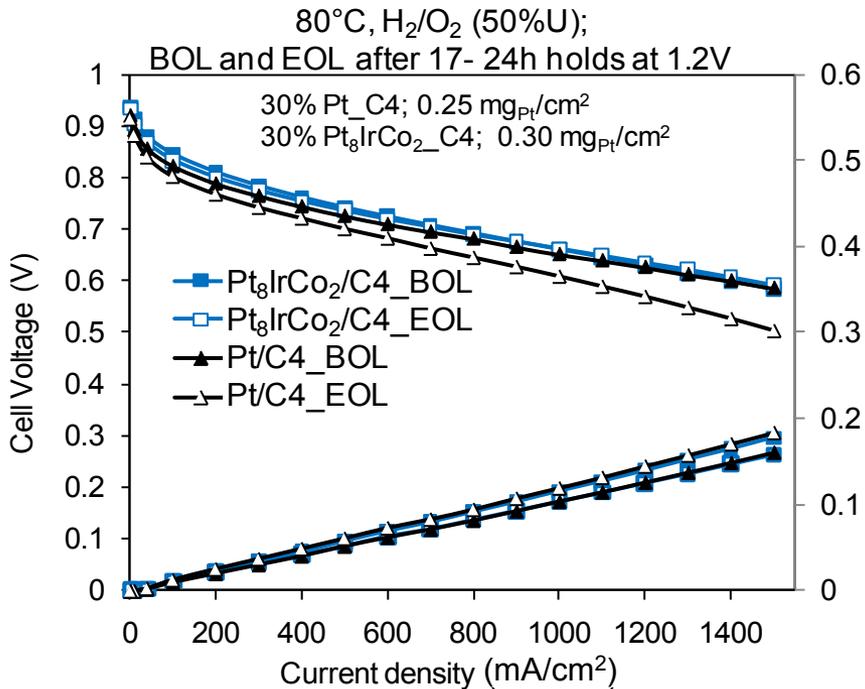


Carbon	BET surface area m <sup>2</sup> /g <sub>carbon</sub>
Ketjen Black	800
Aerogel	600
Nanoblack	250
C4	136
C5	195
Modified C1	55
Modified C2	97
Modified C3	122

- ❑ 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 O<sub>2</sub> 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/cm<sup>2</sup> in O<sub>2</sub>**
  - **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 <sup>2</sup> /g <sub>Pt</sub>	MA A/mg <sub>Pt</sub>	MA A/mg <sub>PGM</sub>
DOE 67-1	30% Pt/C4	4.85	45.7	0.09	0.09
DOE 68-1	30% Pt <sub>3</sub> Co/C4	5.96	33.1	0.23	0.23
DOE 99B	30% Pt <sub>8</sub> IrCo <sub>2</sub> /C4	7.35	29.7	0.18	0.16

- Alloy on C4, 30% Pt<sub>8</sub>IrCo<sub>2</sub>
  - 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 <sup>2</sup> ]	0.64 <sup>‡</sup>	0.40	0.3	0.2
Mass activity @ 900mV [A/mg <sub>PGM</sub> ]	0.28	0.14	0.44	0.44
Specific activity @ 900mV [mA/cm <sup>2</sup> ]	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 <sup>†</sup>	~26 <sup>†</sup>	5	3

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

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

<sup>‡</sup> Anode/Cathode loading – 0.4/0.24 mg/cm<sup>2</sup> (PGM)

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

Based on current scaled-up 30% Pt<sub>2</sub>IrCr MEA ; Anode/Cathode loading – 0.1/0.3 mg/cm<sup>2</sup> (PGM).

- 30% Pt<sub>2</sub>IrCr /KB – best durability in both RDE and MEA cycling**
- Scale-up of highly active (0.7 A/mg<sub>PGM</sub>) Pt<sub>7</sub>IrCo<sub>7</sub>, 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% Pt<sub>7</sub>IrCo<sub>7</sub>
- 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<sub>ML</sub>/Ir core-shell CCM's
- Establish performance and stability comparison between Pd<sub>3</sub>Co 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

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**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% Pt<sub>2</sub>IrCr/C ternary alloy catalysts and preliminary optimization of cathode catalyst layers in a subscale MEA for performance in H<sub>2</sub>/air. Began work on optimizing a full-size UEA.
- (2) Scaled-up a Pt<sub>ML</sub>/Pd<sub>3</sub>Co/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