

Highly Dispersed Alloy Catalyst for Durability

Vivek S. Murthi



May 20, 2009

Project ID: fc_18_murthi

Overview

Timeline

- Start – May 1, 2007
- End – April 30, 2010
- 66% Complete

Budget

- Total project funding
 - DOE share - \$6.278M
 - Cost share - \$2.860M
- DOE Funding for FY08
 - \$1,163 K
- DOE Funding received in FY09
 - \$2,140 K

Barriers

- A. Performance
 - Increase catalyst activity
- B. Cost
 - Reduce PGM loading
- C. Durability
 - Increase cyclic durability

Partners

- Johnson Matthey Fuel Cells



- Texas A&M University



- Brookhaven National Laboratory



Program Objectives

Develop structurally and compositionally advanced cathode catalyst that will meet DOE 2010 targets for performance and durability

Characteristics	Current Status	DOE 2010 Target	DOE 2015 Target
Pt group metal (total content) [g/kW]	0.80	0.3	0.2
Pt group metal (total loading) [mg/cm ²]	0.64 [‡]	0.3	0.2
Mass activity @ 900mV [A/mg _{PGM}]	0.28	0.44	0.44
Specific activity @ 900mV [mA/cm ²]	0.55	0.72	0.72
Cyclic durability @ <80°C / ≥80°C [h]	TBD	5000/2000	5000/5000
ECA Loss* [%]	30	<40	<40
Cost [\$/kW]	~38 [†]	5	3

* 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 \$ 47.67/g (Pt = \$1166.22/Troy Oz; Ir = \$ 316.58/troy oz)

Technical Contributors

UTC Power Corporation:

Vivek S. Murthi, Elise Izzo, Carmen Perez-Acosta, Wu Bi, Sathya Motupally, Tom Jarvi

Johnson Matthey Fuel Cells:

Sarah Ball, Rachel O'Malley, Sarah Hudson, Brian Theobald, Dave Thompsett, Graham Hards

Brookhaven National Lab:

Wei-Ping Zhou, Miomir Vukmirovic, Jia Wang, Dong Su, Yimei Zhu, Radoslav Adzic

Texas A&M University:

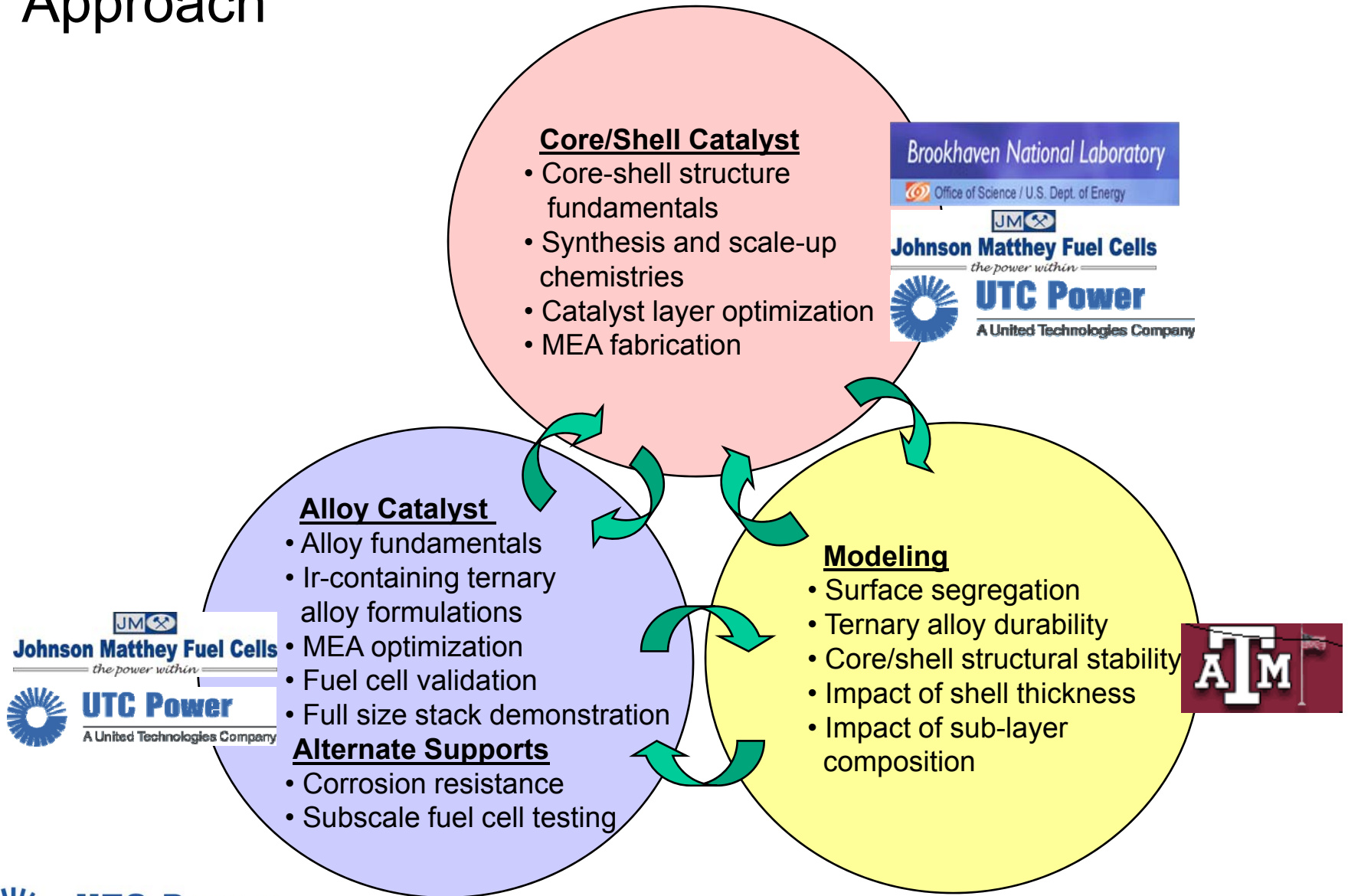
Perla B. Balbuena, Gustavo Ramirez-Caballero, Yuguang Ma, Rafael Callejas-Tovar, Julibeth Martinez de la Hoz

HIGHLY DISPERSED ALLOY CATALYST



DOE Hydrogen Program

Approach

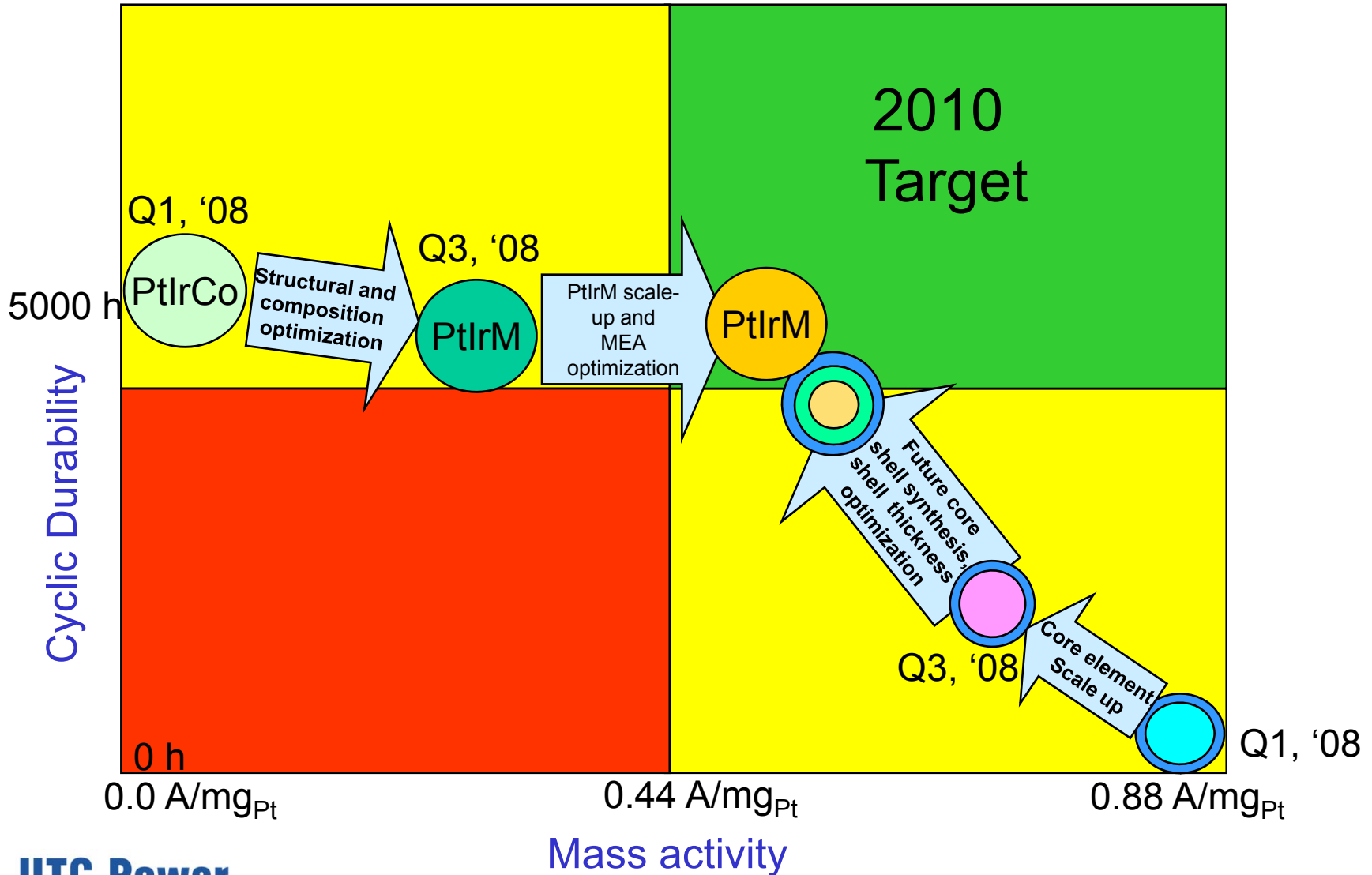


HIGHLY DISPERSED ALLOY CATALYST



DOE Hydrogen Program

Overall Strategy

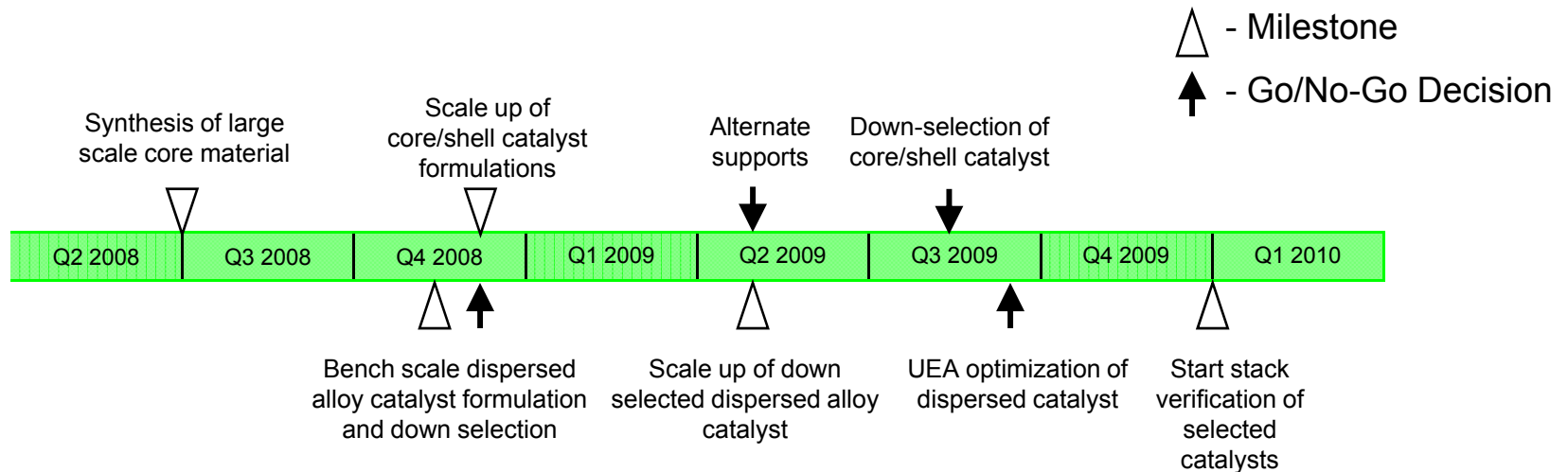


HIGHLY DISPERSED ALLOY CATALYST



DOE Hydrogen Program

Milestones



Month/Year	Milestone or Go/No-Go Decision
July 2008	Milestone: Synthesis of large scale batch (30 g) of Ir, Pd ₃ Co and Pd ₃ Fe cores
November 2008	Milestone: Synthesis of scaled up (5 g) batch of core/shell catalyst formulations Milestone: Bench scale dispersed alloy catalyst formulation down selected Go/No-Go decision: Down-selection of dispersed alloy catalyst (complete)
May 2009	Go/No-Go decision: Down-selection of new durable carbon Milestone: Scale-up of down-selected dispersed catalyst
August 2009	Go/No-Go decision: Down-selection of core/shell catalyst
September 2009	Go/No-Go decision: UEA optimization of dispersed catalyst for single cell durability test

HIGHLY DISPERSED ALLOY CATALYST



Dispersed Catalyst Down Select Criteria

Rank	1	2	3	4	5	Weight factor
Mass Activity (A/mg_{Pt})	≤ 0.2	0.2 – 0.3	0.3 – 0.4	0.4 – 0.45	≥ 0.5	0.4
Durability (% ECA loss after 30K cycles)	≥ 40 %	25 - 40 %	10 – 25 %	5 – 10 %	≤ 5%	0.3
Durability (% MA loss after 30K cycles)	≥ 40 %	25 - 40 %	10 – 25 %	5 – 10 %	≤ 5%	0.2
PGM Loading (wt% of Non-Pt PGM)	≥ 15 %	10 – 15 %	5 – 10 %	2.5 – 5 %	≤ 2.5 %	0.1

Overall Score = Σ (Weight factor * Rank) †

† Go-No Go decision made after considering the individual ratings

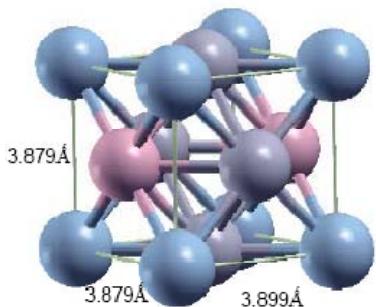
	Mass Activity (RDE) (A/mgPt)	Durability (% ECA loss after 20 K cycles)	Durability (% MA loss after 20 K cycles)	PGM Loading (wt% of Non-Pt PGM)	Score
DOE 48 – Pt ₂ Ir _{0.5} Co _{1.5}	0.39	1 %	48 %	6 %	3.2
DOE 52 – Pt ₂ IrCr	0.45	9 %	49 %	11 %	3.2

HIGHLY DISPERSED ALLOY CATALYST



DOE Hydrogen Program

Modeling Pt₂IrCr Activity and Stability



$\Delta U(V)$ for the reaction $Pt \rightarrow Pt^{+2} + 2e^-$ on the alloy surface compared to that on pure Pt (111)

System	$\Delta U(V)$
Pt	0
Pt ₂ IrCr-Pt ₂ IrCr-Pt ₂ IrCr	0.45
Pt ₄ -PtIrCr ₂ -PtIr ₂ Cr	0.02
Pt ₃ Cr-Pt ₃ Cr-Ir ₃ Cr	0.40

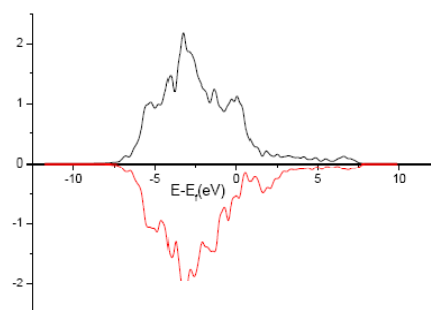
Thermodynamic stability of these surfaces (segregation trend under adsorbed oxygen) follows the order:
Pt₃Cr > Pt₂IrCr > Pt-skin

driving forces for surface segregation:

- large atomic size
- low surface energy
- small heat of alloy formation

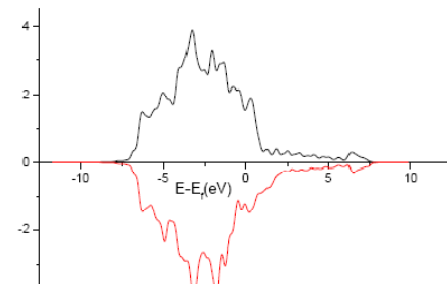
- d-band center shows Pt₂IrCr Alloys less reactive than Pt₃Cr alloys
- Potential shift for Pt → Pt²⁺ shows that Pt₂IrCr more stable

For the non-segregated surface, the potential shift is positive, indicating that the Pt atoms on that surface have less tendency to dissolve than on pure Pt(111)



Non-segregated Surface
Pt₂IrCr-Pt₂IrCr-Pt₂IrCr

d-band center for surface Pt atoms: **-2.30eV**



Segregated Surface
Pt₄-PtIrCr₂-PtIr₂Cr

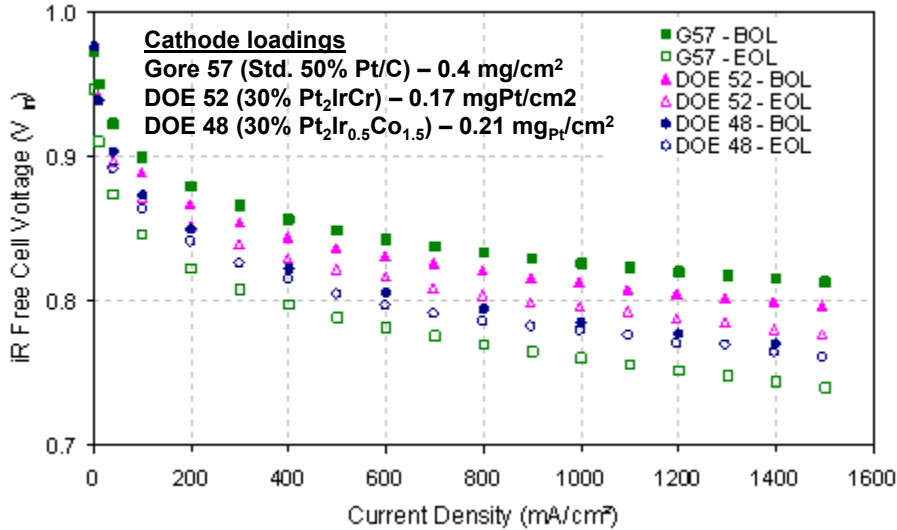
d-band center for Surface Pt atoms: **-2.31eV**

HIGHLY DISPERSED ALLOY CATALYST



DOE Hydrogen Program

Technical Accomplishments – Subscale MEA



UTC Accelerated Protocol

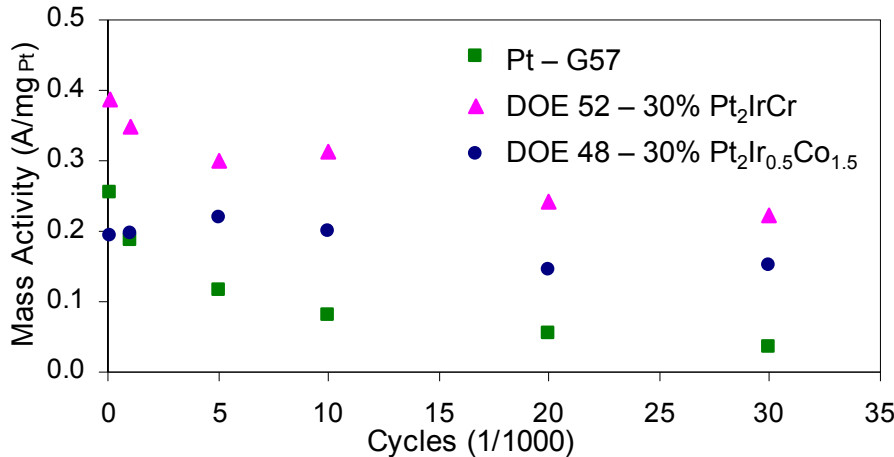
0.4 – 0.95 V; 10s:10s; Sq. wave

30,000 cycles; 4% H₂ / 100% N₂

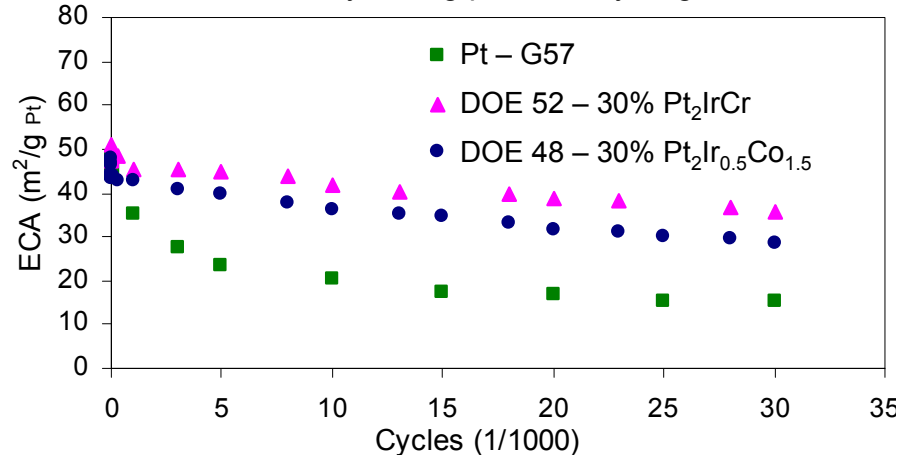
150 kPa (absolute); 80°C; 100% RH (anode and cathode)

- Ir prevents transition metal leaching and Pt dissolution
- Cr has added benefits in MEA
 - low Fluoride Emission Rates
 - higher oxide stability
- **Pt₂IrCr gave best durability in both RDE and MEA cycling**

Mass Activity Decay during potential cycling



ECA Decay during potential cycling



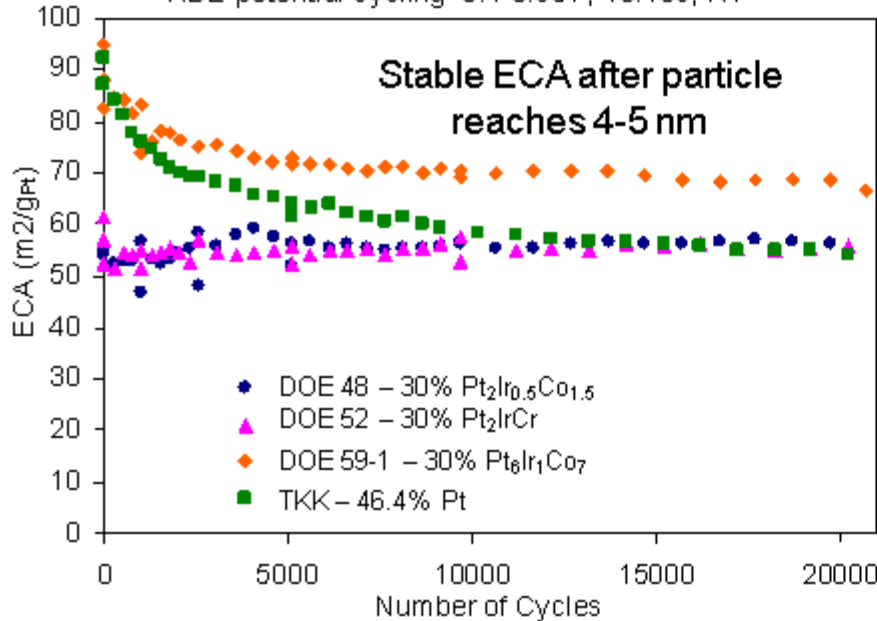
HIGHLY DISPERSED ALLOY CATALYST



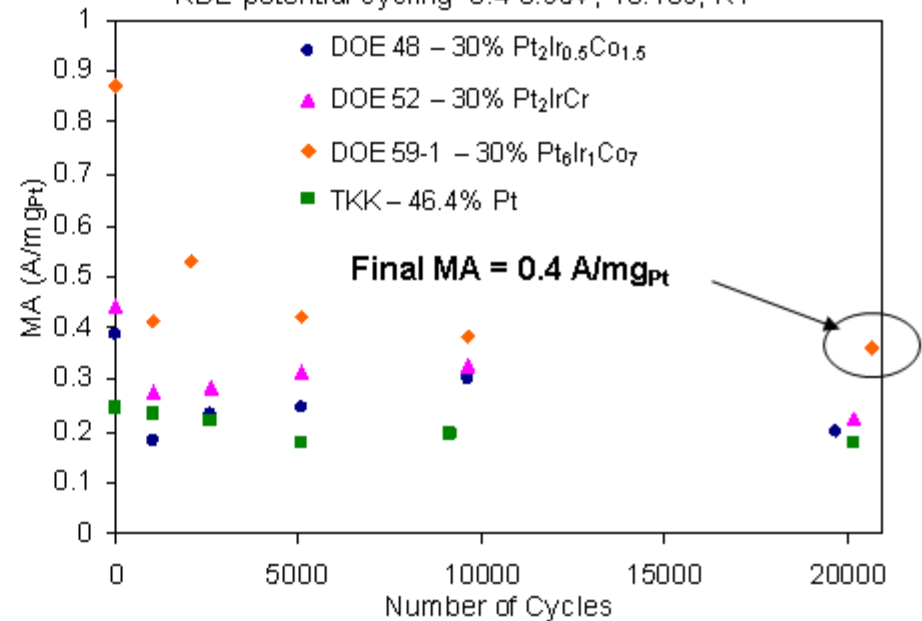
DOE Hydrogen Program

Down-selected PtIrM/C Alloys

RDE potential cycling 0.4-0.95V, 10:10s, RT



RDE potential cycling 0.4-0.95V, 10:10s, RT



30% Pt₆IrCo₇ (DOE 59-1)

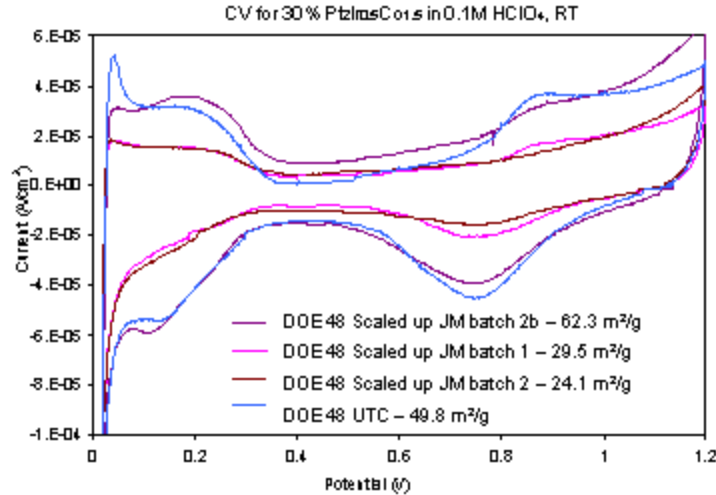
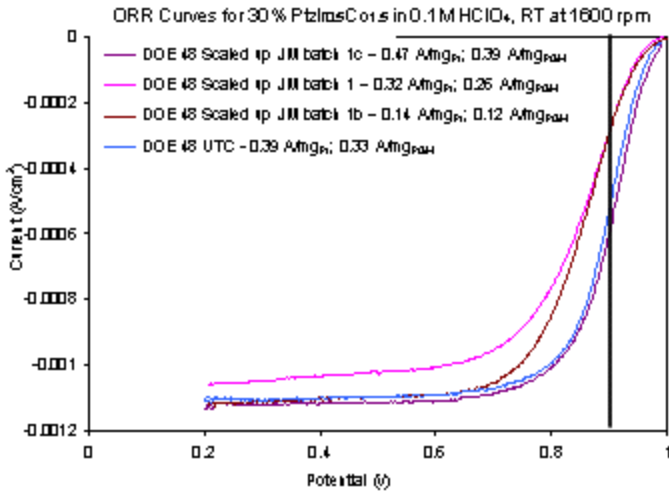
- Higher initial Mass Activity
- Stable ECA ~70 m²/g_{Pt}
- Currently optimizing heat treatment impact for trade-off of performance and durability

HIGHLY DISPERSED ALLOY CATALYST



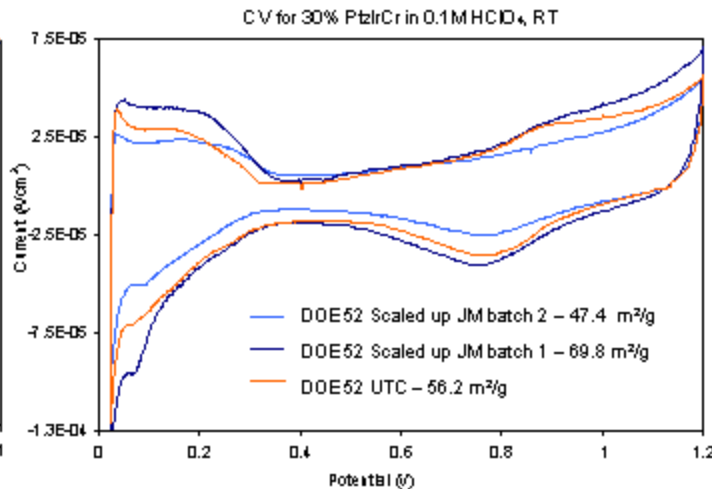
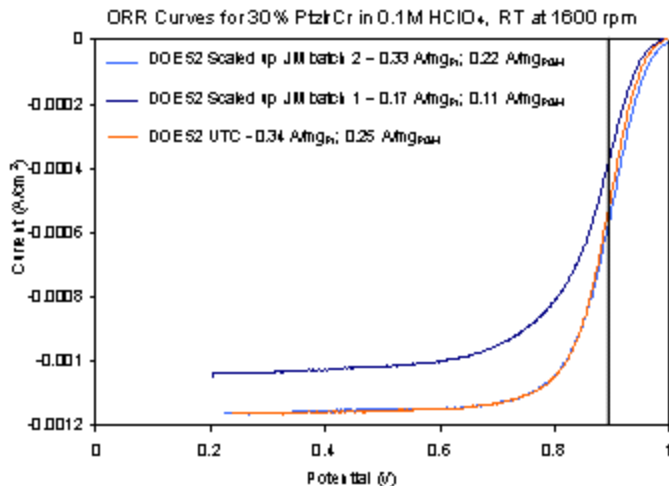
DOE Hydrogen Program

JM Scale-up: 30% Pt₂Ir_{0.5}Co_{1.5} and 30% Pt₂IrCr



Pt₂Ir_{0.5}Co_{1.5} (DOE 48)

Mass activity of scale up batch in RDE similar to lab scale synthesis



Pt₂IrCr (DOE 52)

Initial preparation attempt (batch 1) showed multi phased particles; second attempt successful; optimization of synthesis procedure in progress



UTC Power

A United Technologies Company

This presentation does not contain any proprietary, confidential, or otherwise restricted information

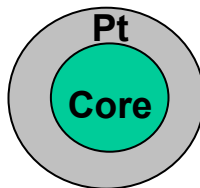
HIGHLY DISPERSED ALLOY CATALYST



DOE Hydrogen Program

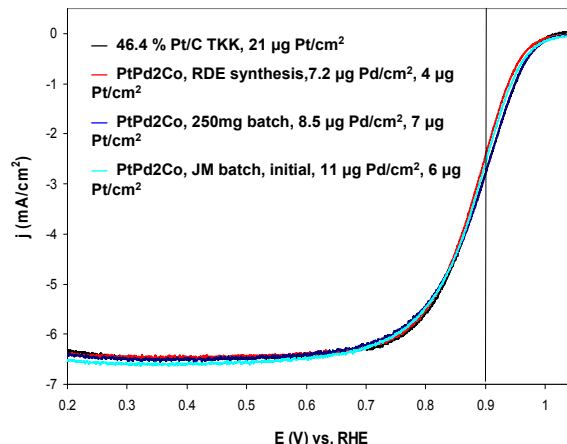
Pd₃Co/Pt_{ML} - JM Scale-up

0.25 monolayer of oxygen

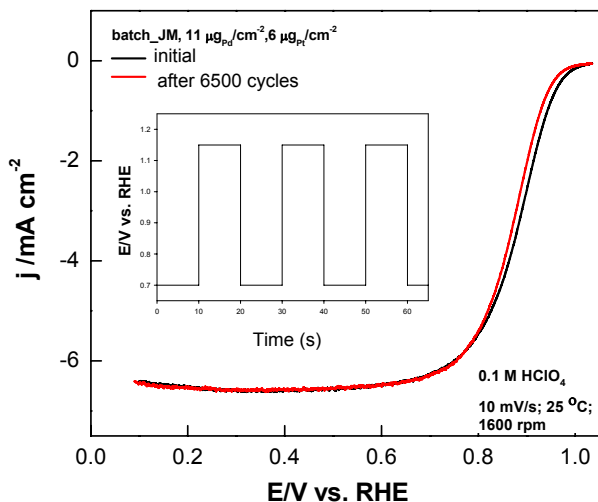


System	μ_{Pt} (eV)	$\Delta\mu$ (eV)	ΔU (V)	
Pt (0 ML)	-6.98	-0.72	0.36	
Pt (0.25ML)*	-6.26	0	0	
Pt(shell)-Pd(core)	-6.42	-0.16	0.08	
Pt(shell)- Pd ₃ Co (core)	CVT1 CVT2	-6.46 -6.46	-0.20 -0.20	0.10 0.10
Pt(shell)- Pd ₃ Fe (core)	CVT1 CVT2	-4.88 -6.49	1.38 -0.23	-0.69 0.12

In the presence of oxygen Pt becomes less stable compared with in vacuum; Pd and Pd₃Co cores can increase Pt stability



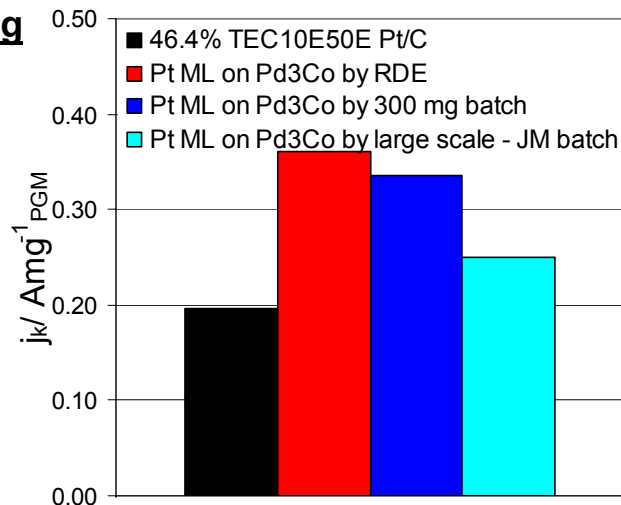
Durability



Durability to potential cycling

After 6500 cycles

- $\Delta E_{1/2} \approx -13$ mV
- 30 % loss in mass activity (at 0.9 V)
- 53 % loss in ECSA
- 25 % increase in specific activity



UTC POWER

A United Technologies Company

This presentation does not contain any proprietary, confidential, or otherwise restricted information

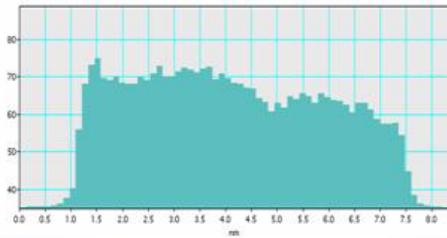
HIGHLY DISPERSED ALLOY CATALYST



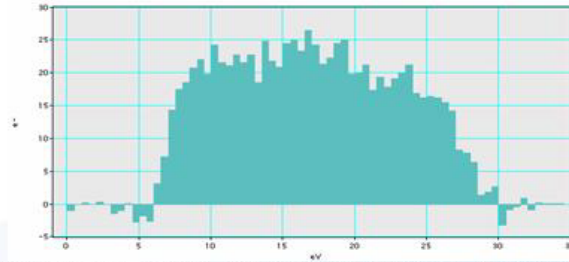
DOE Hydrogen Program

Pd₃Co/Pt_{ML} - Fundamentals

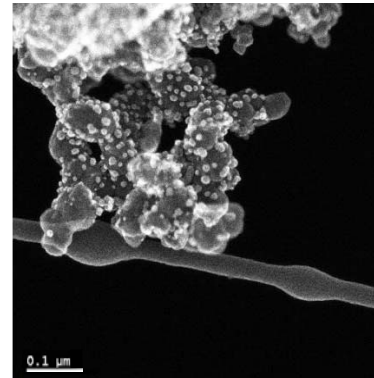
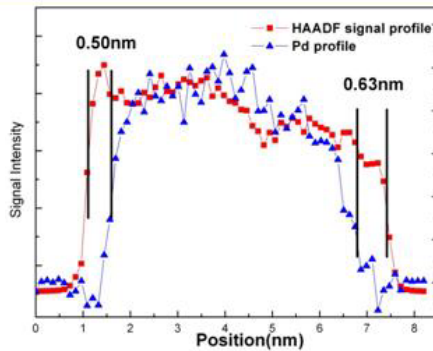
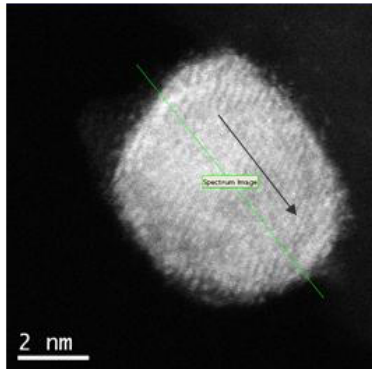
HAADF-STEM Signal



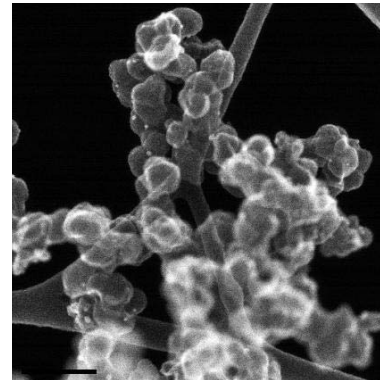
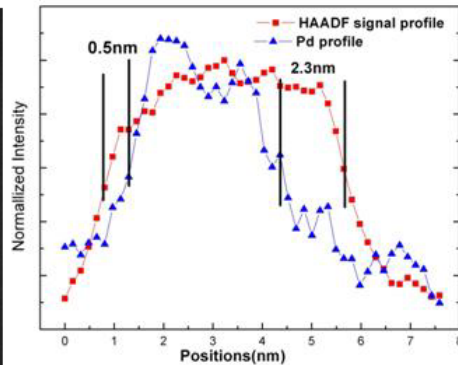
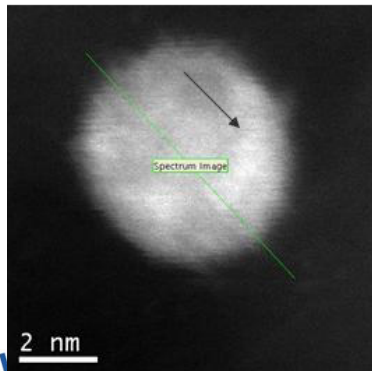
Pd EELS Profile



1. HAADF signal indicates the size of nanoparticles; Pd EELS signal shows the composition of Pd
2. Core – Shell structure resolved and thickness of shell measured



1. HAADF and EELS line scan results prove the core-shell structure of Pt on Pd
2. Shell thickness is not uniform; may vary between 0.5 – 0.8 nm

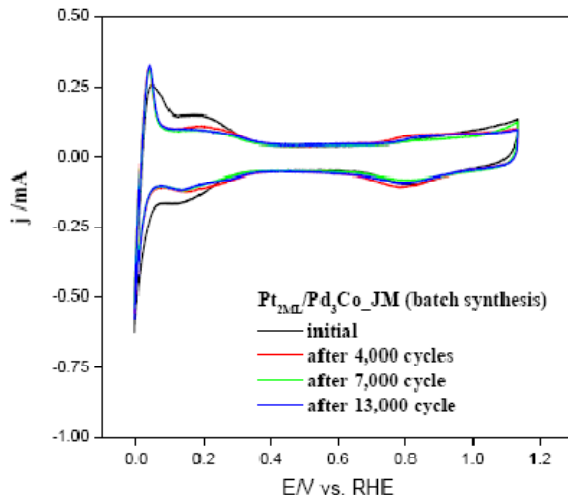


After potential cycling

1. Decrease in particle size of Pd₃Co core
2. Particle density (TEM) decreases significantly
3. Pt layer seems to grow preferentially on one side of the particles

Pd₃Co/Pt_{2ML} Core/Shell Stability

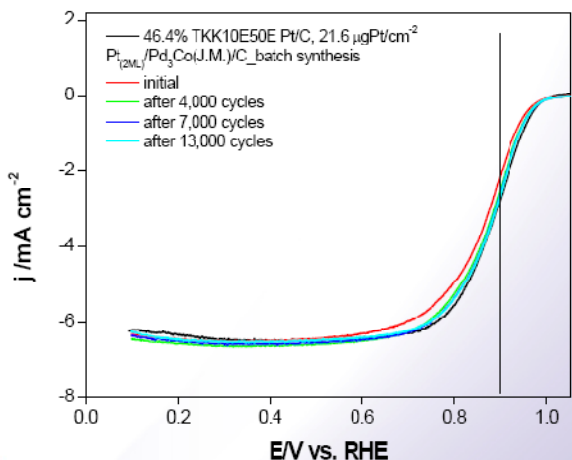
Voltammetry curves for Pt_{2ML}/Pd₃Co/C in 0.1 M HClO₄ after potential cycles (0.6 – 0.95 V square wave with 30 sec pulse); RT



Potential shift with different Pt shell thickness – in vacuum

	ΔU (V)		
	1 layer	2 layers	3 layers
Pt(shell)-Co(core)	-0.54	-0.56	-1.95
Pt(shell)-Fe(core)	-1.10	-1.05	-2.79
Pt(shell)-Pd(core)	0.20	0.02	0.02
Pt(shell)-Pd ₃ Co(core)	0.21	0.06	0.06
Pt(shell)-Pd ₃ Fe(core)	-0.51	0.08	0.07

ORR curves for Pt_{2ML}/Pd₃Co/C in 0.1 M HClO₄ at 1600rpm after potential cycling. Scan rate: 10 mV/s; RT



In vacuum

Monolayer Pt leads to highest stability for Pd and Pd₃Co core

- Pt_{2ML}/Pd₃Co synthesized with mediated growth method (100 mg JM batch) shows improved stability
- The total surface area loss was ~ 40% after 13,000 cycles while the ORR specific activity at 0.9 V was increased by ~ 80%

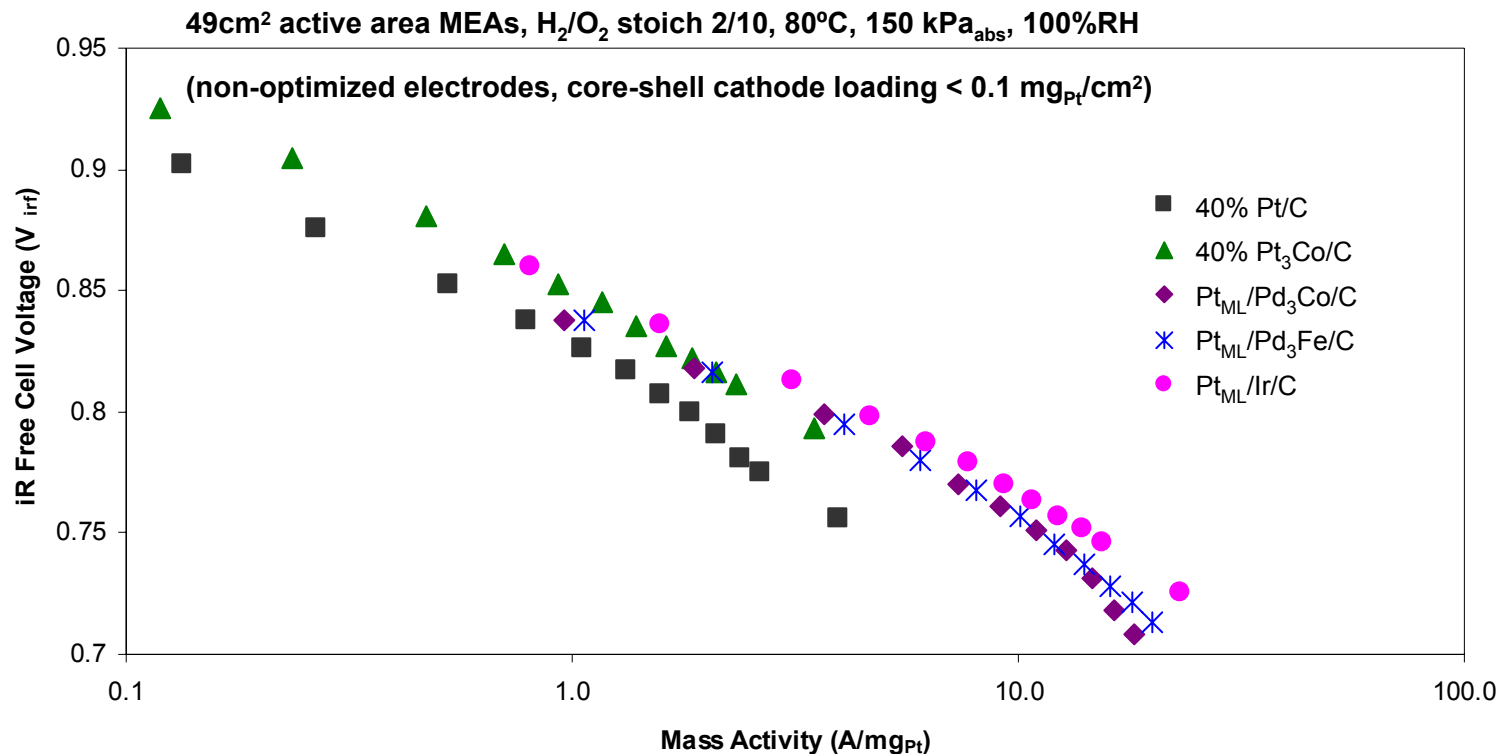


HIGHLY DISPERSED ALLOY CATALYST



DOE Hydrogen Program

Pd₃Co/Pt_{ML} - Activity in MEA's



- All core shell catalysts show enhancement over Pt only
- Best mass activity Pt_{ML}/Ir core shell
- Pt_{ML}/Pd₃Co and Pt_{ML}/Pd₃Fe show equivalent performance



UTC Power

A United Technologies Company

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Future Work

□ FY 2009

– Dispersed Alloy Catalyst

- Fundamental study on heat treatment process to improve activity and durability
- Fundamental effect of Ir-containing alloys on durability benefit

– Core/Shell Catalyst

- Explore new core materials based on modeling results
- New chemistries to obtain uniform Pt coating with improved mass activity

– Carbon support

- Liquid cell corrosion testing to down-select more durable carbon support
- Optimize synthesis to maximize activity

□ FY 2010

– Dispersed Alloy Catalyst

- Validate selected catalysts in a single-cell fuel cell under new DOE protocol
- Stack verification of selected catalysts

– Core/Shell Catalyst

- Down-select, scale-up and optimize MEA layer
- Full size (400cm²) single cell verification

– Carbon support

- Verification of down-selected carbon in sub-scale MEA

Project Summary

- **Relevance:** Work to develop a more active and durable catalyst that meets and surpasses the DOE 2010 targets for performance and durability in real-life conditions in a 20-cell stack test.
- **Approach:** Complete fundamental modeling and experimental studies that elucidate how the structure of a catalyst and its support behave during synthesis, processing and operation.
- **Technical Accomplishments and Progress:** Demonstrated catalyst mass activities that surpass the DOE 2010 target for dispersed catalysts ($\geq 0.7 \text{ A/mg}_{\text{PGM}}$) in RDE testing. Reproduced mass activities of almost $0.3 \text{ A/mg}_{\text{PGM}}$ for our down-selected catalyst in both RDE and subscale MEA testing (3X a standard Pt only catalyst). Scaled-up a core-shell catalyst to a 5g batch. Began work on optimizing the catalyst layer for full-scale MEA testing.
- **Technology Transfer/Collaborations:** Active partnerships with Johnson Matthey Fuel Cells, Brookhaven National Laboratory, and Texas A&M University with the ultimate goal to develop a more active and durable catalyst through team meetings, presentations and publications.
- **Proposed Future Research:** Continue to experimentally verify the modeling data for core-shell stability and activity benefits of dispersed alloys. Use modeling to investigate stable non-PGM cores for core-shell catalyst systems.

Supplemental Slides

HIGHLY DISPERSED ALLOY CATALYST



DOE Hydrogen Program

Cycling Protocol and Durability Modeling

	2007 DOE Protocol	UTC Accelerated Protocol †	2008 Modified Protocol #
Cycle	30 s at 0.7 V; 30 s at 0.9 V (60 s/cycle)	10 s at 0.4; 10 s at 0.95 V (20 s /cycle)	0.6 – 1.0 V at 50 mV/s (16 s /cycle)
Wave Shape	Square	Square	Triangle
Number	30,000	30,000	30,000
Fuel/Oxidant	100% H ₂ / 100% N ₂	4% H ₂ in N ₂ / 100% N ₂	100% H ₂ / 100% N ₂
Pressure Temperature and % RH	150 kPa (absolute) 80°C 100% (anode and cathode)	150 kPa (absolute) 80°C 100% (anode and cathode)	100 kPa (absolute) 80°C 100% (anode and cathode)

† Cycling below 0.9V leads to reduced Pt dissolution

2008 DOE Accelerated Testing Protocol – more aggressive

Pt dissolution rate depends on the initial particle size and the potential window of cycling

