Highly Dispersed Alloy Catalyst for Durability

2011 DOE Hydrogen Program

Project ID: FC002

Vivek S. Murthi

UTC Power

A United Technologies Company

May 10, 2011

OVERVIEW

Timeline

- Start – May 1, 2007
- End – October 31, 2011
- 90% 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 A/cm^2 under carbon corrosion protocol

Budget

- Total project funding
  - DOE share - $5.878 M
  - Cost share - $2.086 M
- DOE Funding received in FY10
  - $1.278 M
  - No cost extension in place

Partners

Johnson Matthey Fuel Cells

Texas A&M University

Brookhaven National Laboratory

UTC Power
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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

- ❑ Effect of transition metals
  - Membrane doping studies with Co and Cr ions
- ❑ MEA optimization of 30%Pt_2IrCr/C_{KB}
  - Effect of ink formulations (I/C ratio, EW), GDL comparison
- ❑ Load cycling in full size MEA
  - UTC vs. DOE protocol comparisons with Pt baselines
  - 30%Pt_2IrCr/C_{KB} load cycling of JM scaled-up MEA

Task 2 – Core-Shell Catalyst Development

- ❑ Pt Electroless deposition (ELD) methods
- ❑ Methods to improve core stability
- ❑ Durability testing on various core-shell materials.

Task 3 – Alternative Carbon Support

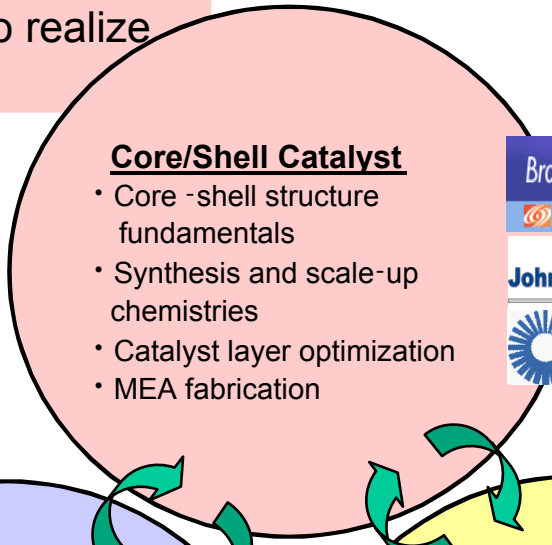
- ❑ Transfer of best alloy onto best carbon support
- ❑ Subscale MEA Corrosion Testing

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

Brookhaven National Laboratory
Office of Science / U.S. Dept. of Energy
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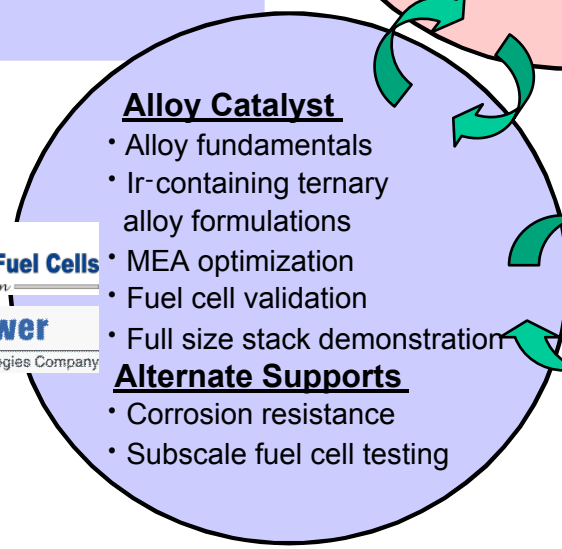

Alloy Catalyst
- Alloy fundamentals
- Ir-containing ternary alloy formulations
- MEA optimization
- Fuel cell validation
- Full size stack demonstration

Alternate Supports
- Corrosion resistance
- Subscale fuel cell testing

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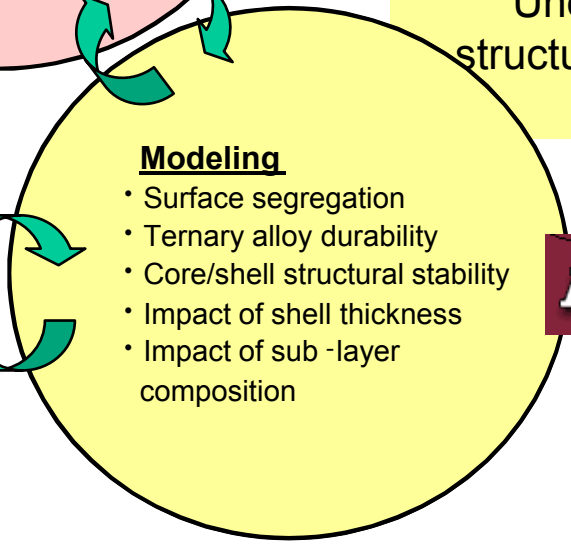


Modeling
- Surface segregation
- Ternary alloy durability
- Core/shell structural stability
- Impact of shell thickness
- Impact of sub -layer composition

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

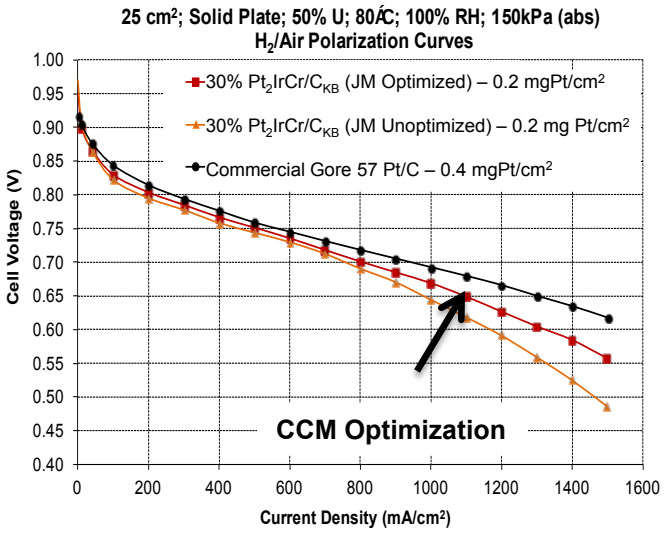
APPROACH

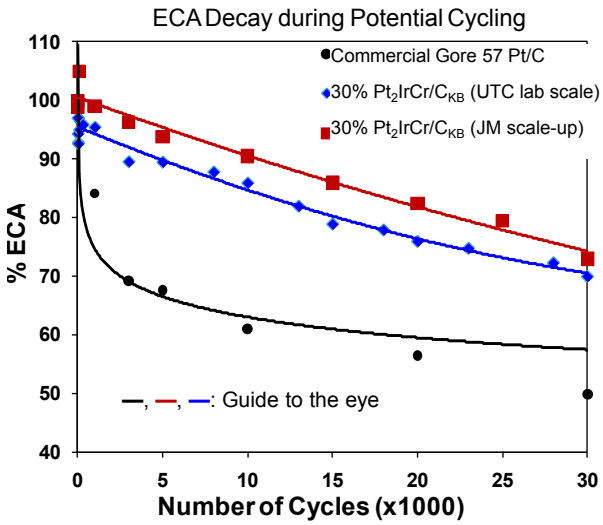
Milestones and Accomplishments

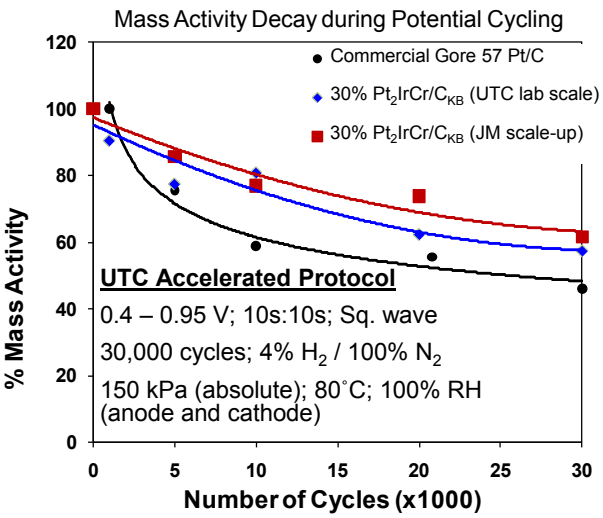
Month/Year	Milestone or Go/No-Go Decision	Status/Comments
April 2010	Milestone: Completion of all modeling work and publication of results	Task Complete
June 2010	Milestone: Scale-up of alloy catalyst on durable carbon support and sub-scale MEA testing	Scale-up complete; Sub-scale corrosion test by January 2011; MEA optimization in-progress
June 2010	Milestone: Scale-up of 30% Pt_2IrCr on KB	Complete
November 2010	Go/No-Go decision: Down-selection and MEA optimization of core-shell catalysts for single cell durability test	**No-Go Decision;** Investigating alternate core-shell synthesis methods
December 2010	Milestone: Single cell validation of dispersed alloy catalysts	Complete
April 2011	Stack Demonstration	BOL complete; Durability testing currently underway
October 2011	MEA optimization of 20% Pt_2IrCr/C4 and single cell durability test	On Track

TECHNICAL ACCOMPLISHMENTS

2008 - 2010: Formulation, Scale-up and Optimization





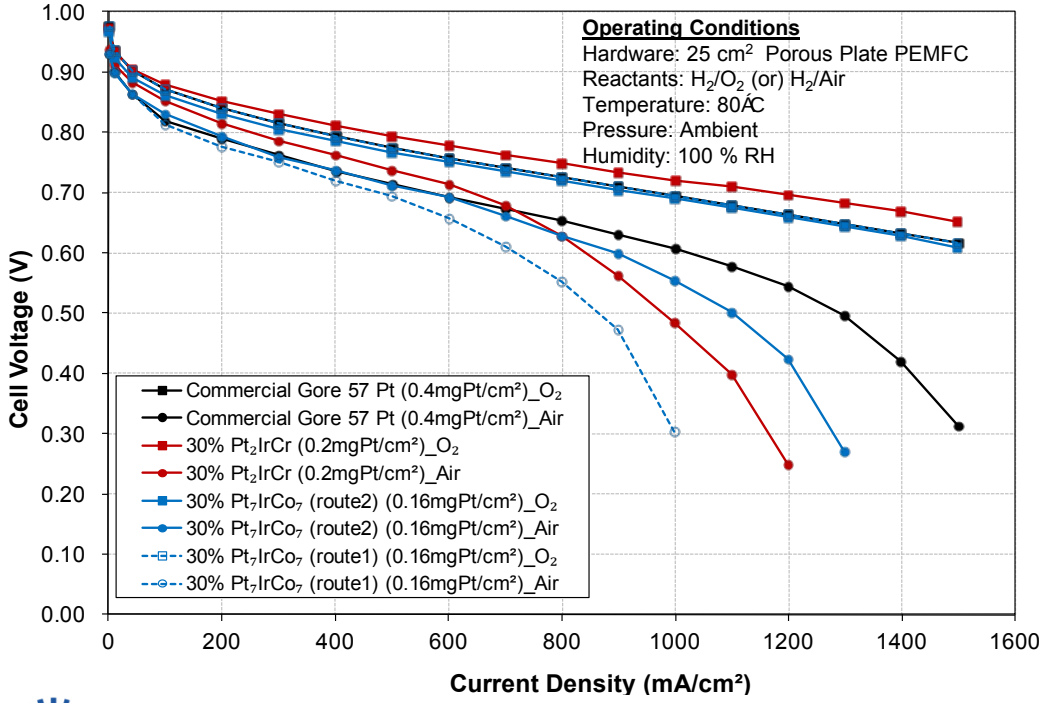


- 30% Pt_2IrCr /C_{KB} has best durability among studied alloys in both RDE and MEA cycling
- Clear evidence of improvement for high current density performance in H_2/Air from preliminary catalyst layer optimization steps
- Half-loading ($0.2mg_{Pt}/cm^2$) alloy catalyst MEA's can achieve comparable initial performances to a standard Gore 57 ($0.4mg_{Pt}/cm^2$)
- Down-selected stable carbon C4: Carbon that meets DOE Target
  - C4 showed significant corrosion stability
  - No performance loss until 300 hours of 1.2 V holds (13 cycles)
  - After 17 cycles (408 hours) Pt_8IrCo_2/C4 shows only 12 mV loss at 1.5 A/cm² in O_2

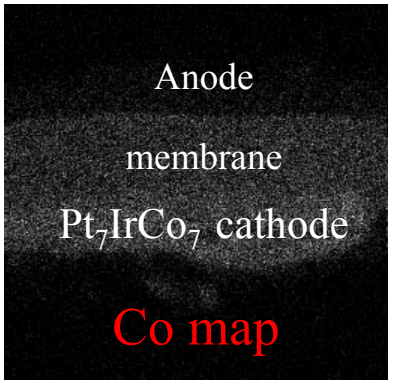
TECHNICAL ACCOMPLISHMENTS

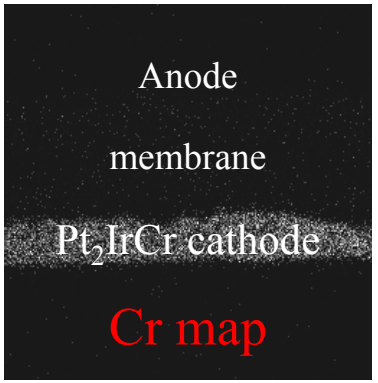
Task 1: Pt_2IrCr/C_{KB} vs. Pt_7IrCo_7/C_{KB}

- ❑ 30% Pt_2IrCr/C_{KB} shows higher kinetic performance than other developed alloys
- ❑ Mass transport can be improved with MEA optimization
- ❑ 30% Pt_2IrCr/C_{KB} was down-selected for further MEA optimization



- ❑ Lower Stability of Co than Cr in acidic environments
  - 45-75% Co and 25% Cr loss from catalysts in 1M H_2SO_4
  - 48% Co and 15% Cr loss from catalysts into ink solvent/Nafion
  - Cr or Co ions in MEAs have detrimental impact on cell performance
  - Lower stability of Co than Cr in fresh MEAs (stored more than 90 days)

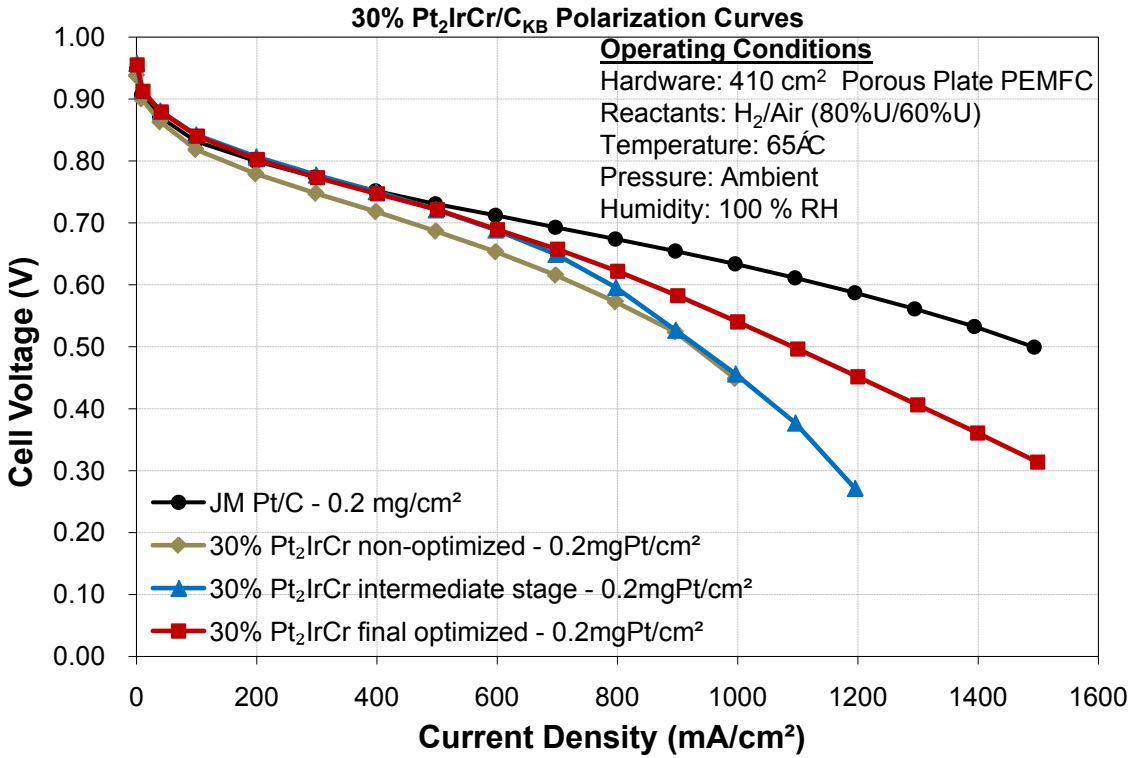




EMPA elemental map
of fresh MEAs after ~90 days

TECHNICAL ACCOMPLISHMENTS

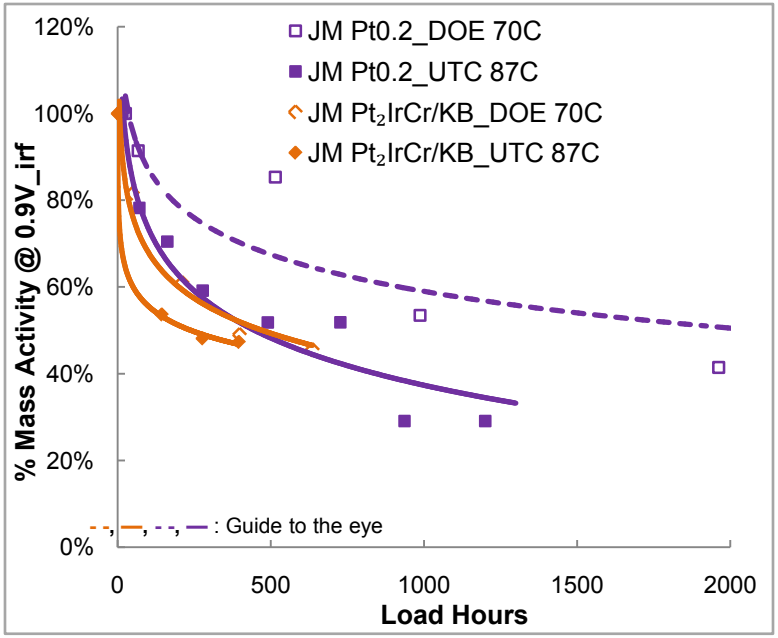
Task 1: Pt_2IrCr/C_{KB} Single-Cell MEA Optimization

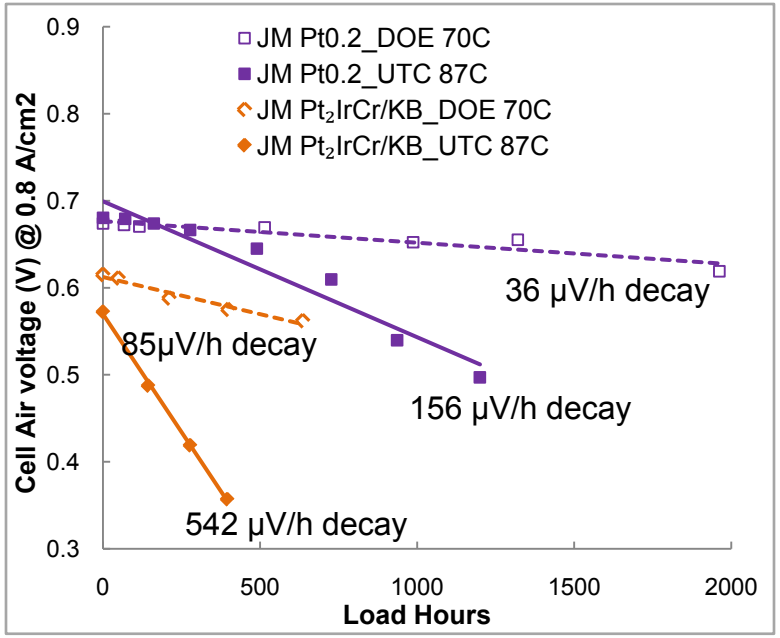


- Performance optimizations in full-scale single cells
  - Improved electrode structure (ink formulation, I/C ratio, Nafion® EW) and GDL (hydrophobicity)
  - Increased catalyst utilization from 26 to 42 m^2/g_{Pt}
  - Higher mass activity from 0.11 to 0.2 A/mg_{Pt}
  - Reduced mass transport resistance by 91 mV @ 1 A/cm^2
  - A performance gap of 94 mV vs. baseline Pt/C (0.2 mg/cm^2) @ 1 A/cm^2

TECHNICAL ACCOMPLISHMENTS

Task 1: Pt_2IrCr/C_{KB} Durability in Full-Size MEA





Durability protocol

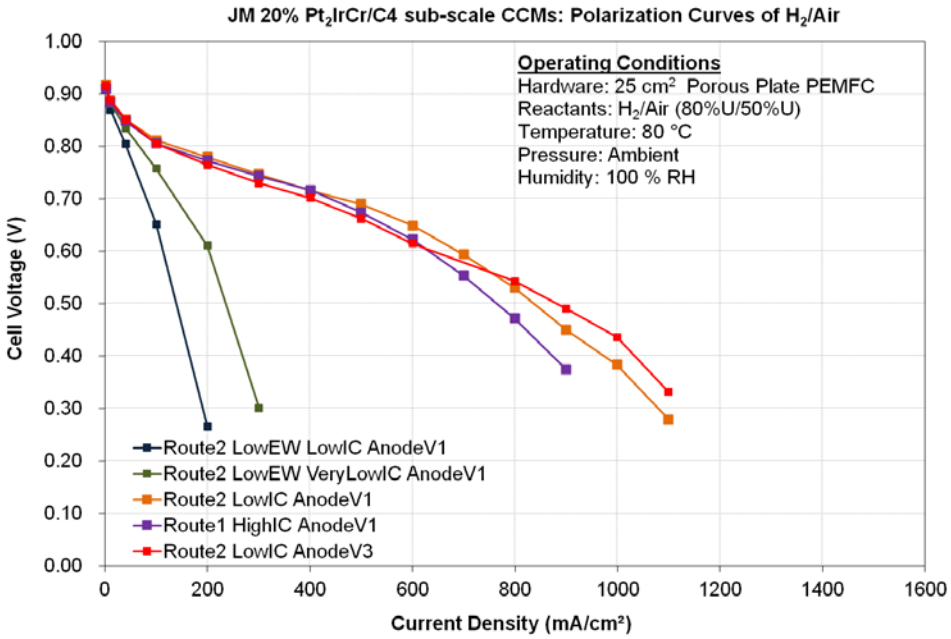
- Modified DOE protocol: ~33-100 %RH cycle, 20-100 mA/cm^2 (dry) & 20-1000 mA/cm^2 (wet) load cycle, average 70 ºC, ambient pressure
- UTC protocol: current cycles up to 800 mA/cm^2, average 87 ºC, ambient pressure

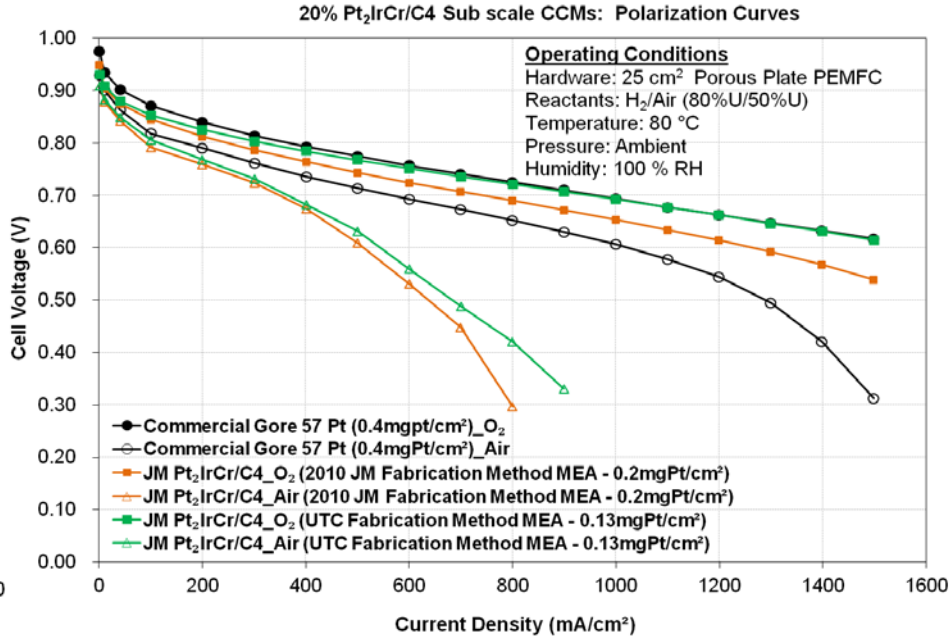
❑ Pt_2IrCr/C_{KB} vs. Pure Pt durability

- 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)

TECHNICAL ACCOMPLISHMENTS

Task 3: 20% Pt_2IrCr/C4 Sub-Scale MEA Optimization



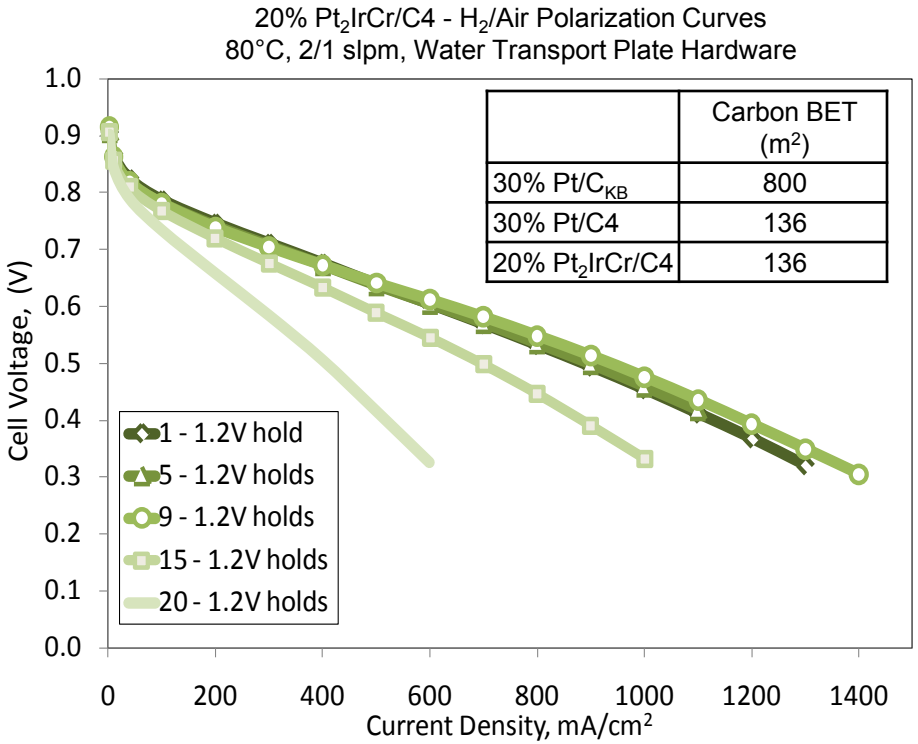


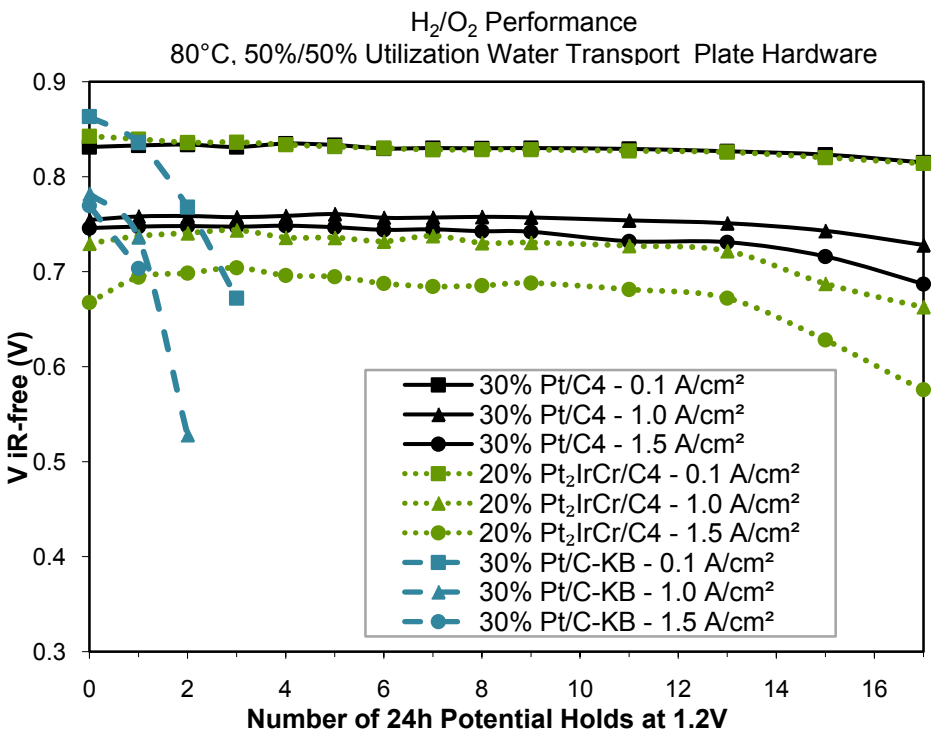
- Performance optimizations in sub-scale WTP cells
  - Improve electrode structure of cathode based on ink formulation, I/C, Nafion® EW, cathode GDL (hydrophobicity) and anode versions
  - Improved mass activity compared to the Pt/C4 catalyst
  - A large air performance gap observed compared to Pt/C_{KB} and Pt/C4 systems (0.2 mg/cm^2) at high current densities
  - Preliminary MEA fabrication at UTC shows that opportunities exist for further performance improvement at UTC – main focus in 2011

TECHNICAL ACCOMPLISHMENTS

Task 3: $Pt_2IrCr/C4$ Corrosion Testing in WTP

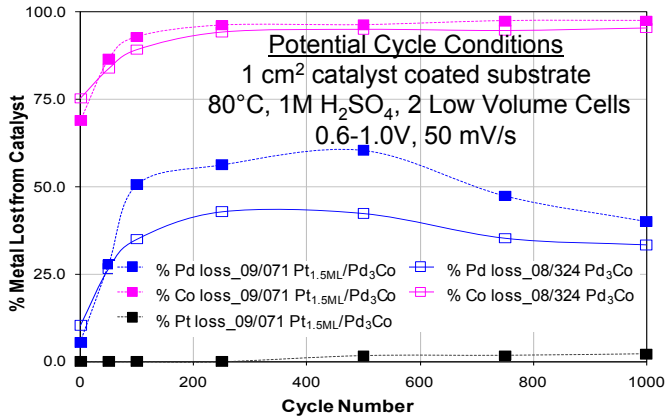
- Scaled-up 20% $Pt_2IrCr/C4$ has lower performance due to low loading and non-optimized MEA
- Performance for C4 begins to decay only after 300h
- There is no thinning of catalyst layers for C4 after 408h
- Limited activity decay during testing
  - This catalyst and carbon combination is kinetically stable
  - MEA optimization to improve high current density performance (Main focus in 2011)

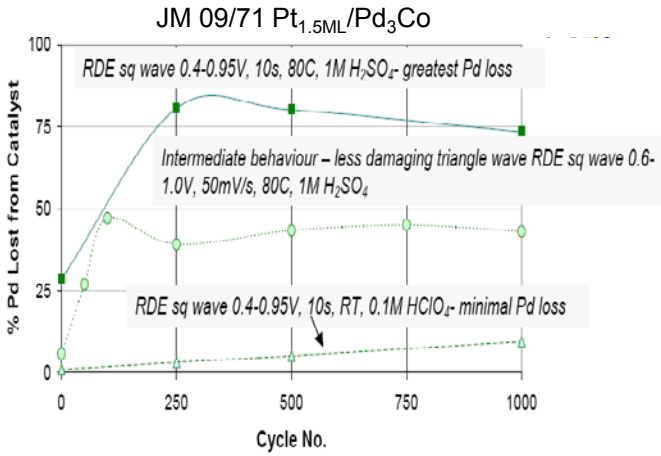




CORE-SHELL ELD METHOD

Activities Leading to No-Go Decision





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

CURRENT TECHNICAL STATUS

Electrocatalyst Targets	Previous Status	Current Status	DOE 2010 Target	DOE 2015 Target
Pt group metal (total content) [g/kW]	0.50	0.50	0.3	0.2
Pt group metal (total loading) [mg/cm^2]	0.40Ä	0.40§	0.3	0.2
Mass activity @ 900mV [A/mg$_{PGM}$]	0.14	0.20	0.44	0.44
Specific activity @ 900mV [mA/cm^2]	0.50	0.94	0.72	0.72
Cyclic durability @ <80°C / ≥80°C [h]	N/A	400	5000/2000	5000
ECA Loss* [%]	30	30	<40	<40
Cost [$/kW]	~26†	~26†	5	3
Carbon Support Durability iR free O_2 performance loss at 1.5 A/cm^2 after 400h at 1.2 V [mV]	59	92‡	<30	<30

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

† 5 year average PGM price $ 51.55/g (Pt = $1234.33/Troy Oz; Ir = $ 369.06/troy oz); costs not projected to high volume

§ Based on current scaled-up 30% Pt_2IrCr MEA ; Anode/Cathode loading – 0.1/0.3 mg/cm^2 (PGM)

‡ 40 mV iR free O_2 performance loss at 1.5 A/cm^2 after 360 hours at 1.2 V

- **30% Pt_2IrCr/C_{KB} – Stack durability demonstration in progress**
- **Scaled-up a 200g batch of 20%Pt_2IrCr/C4; MEA optimization activities in progress**
- **No-Go decision for core-shell catalysts (JM fabrication method)**

FUTURE WORK

Task 1: Dispersed Catalyst Work

- Short stack durability testing of 30% Pt_2IrCr/C_{KB}

Task 2: Core-Shell Catalyst Development

- Investigate alternate core-shell synthesis methods
- Subscale performance of core-shell catalyst

Task 3: Stable Carbon Support

- MEA optimization for 20% $Pt_2IrCr/C4$ “best catalyst on best carbon support”
  - Ink formulation and processing methods
  - Thin and durable membrane down-selection
  - Cathode Ionomer selection, EW and I/C ratio
  - Cathode and Anode GDL development for high performance
- Durability testing of optimized MEA

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 full-size MEA optimization of 30% Pt_2IrCr/C_{KB} along with full size durability testing and a 20-cell stack performance demonstration.

(2) Decided the current core-shell method was a No-Go after extensive physical characterization and stability testing of various core-shell materials

(3) Successfully deposited our best catalyst onto our most durable carbon support.

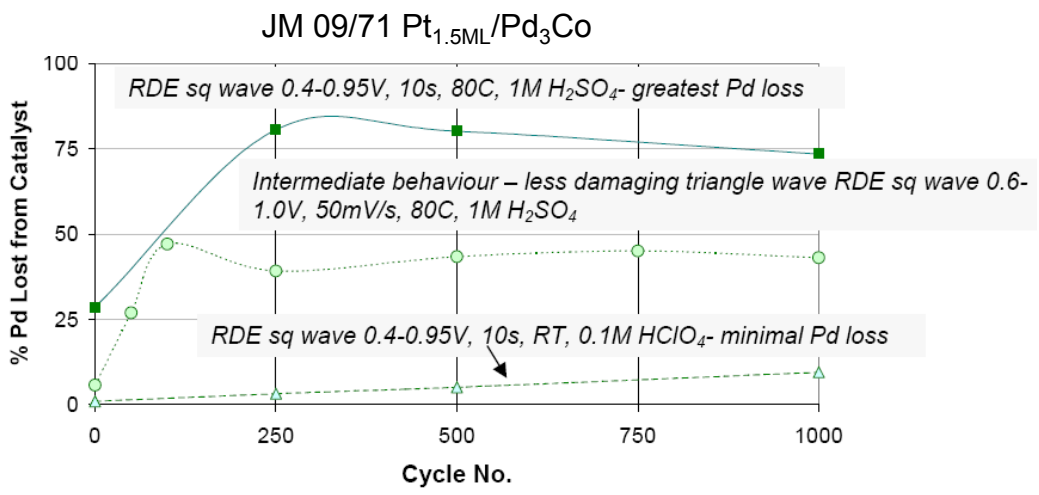
Technology Transfer/Collaborations: Active partnerships with JMFC, BNL and Texas A&M to develop a more active and durable cathode catalyst layer. Technology transfer through team meetings, presentations and publications.

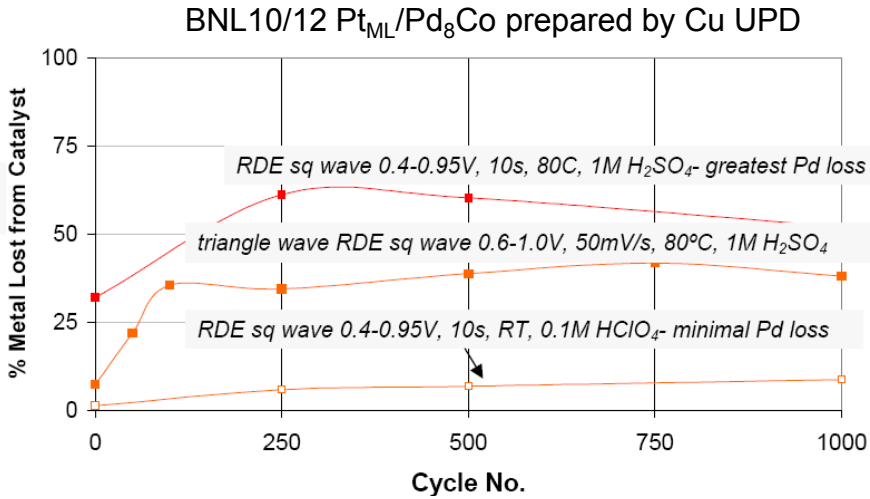
Proposed Future Research: Focus will be on further improving MEA performance for the best alloy on our most durable support while wrapping up the program with durability testing in both a short full-size MEA stack and the fully optimized single cell MEA.

Technical Back-up Slides

CORE-SHELL ELD METHOD

Pd loss due to temperature, electrolyte or cycle regime





- Stability of JM 09/71 $Pt_{1.5ML}/Pd_3Co$ and BNL 10/12 Pt_{ML}/Pd_8Co tested under 3 different cycling regimes show similar behavior
- Higher temperature and more concentrated electrolyte contribute to Pd dissolution – substantially more damaging than room temperature RDE testing
- Explains low performance in MEAs vs RDE
- "Cation-wash" procedure for improving the stability of core-shell nanoparticle catalysts - unsuccessful

- Task 3: Core/shell catalyst – **No-Go Decision for Single-cell/Stack testing**