

Highly Dispersed Alloy Catalyst for Durability

2011 DOE Hydrogen Program
Project ID: FC002

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UTC Power

A United Technologies Company

May 10, 2011

OVERVIEW

Timeline

- Start – May 1, 2007
- End – October 31, 2011
- 90% Complete

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

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



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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%Pt₂IrCr/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%Pt₂IrCr/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



Core/Shell Catalyst

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



Understand catalyst structure fundamentals through models

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



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 O₂ reduction reaction and stability against dissolution

APPROACH

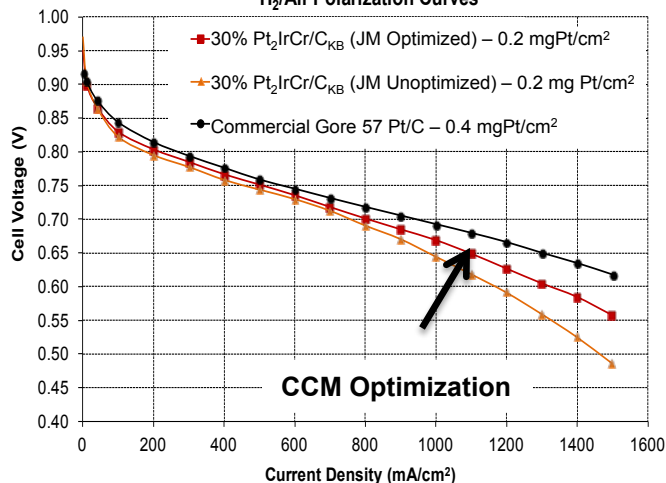
Milestones and Accomplishments

| Month/Year | Milestone or Go/No-Go Decision | Status/Comments |
|---------------|--|---|
| April 2010 | <u>Milestone</u> : Completion of all modeling work and publication of results | Task Complete |
| June 2010 | <u>Milestone</u> : 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 | <u>Milestone</u> : Scale-up of 30% Pt ₂ IrCr on KB | Complete |
| November 2010 | <u>Go/No-Go decision</u> : 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 | <u>Milestone</u> : 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 ₂ IrCr/C4 and single cell durability test | On Track |

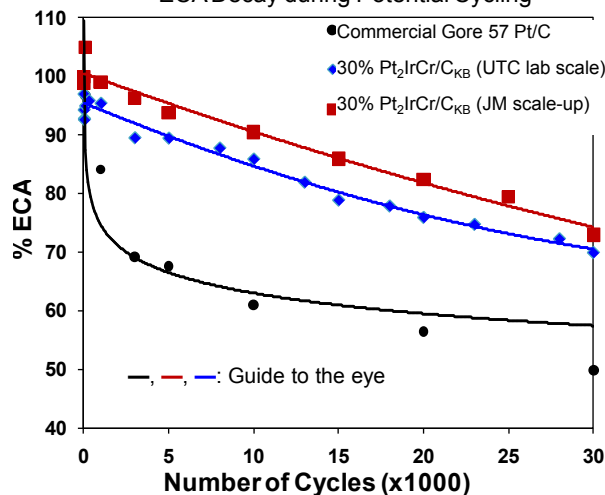
TECHNICAL ACCOMPLISHMENTS

2008 - 2010: Formulation, Scale-up and Optimization

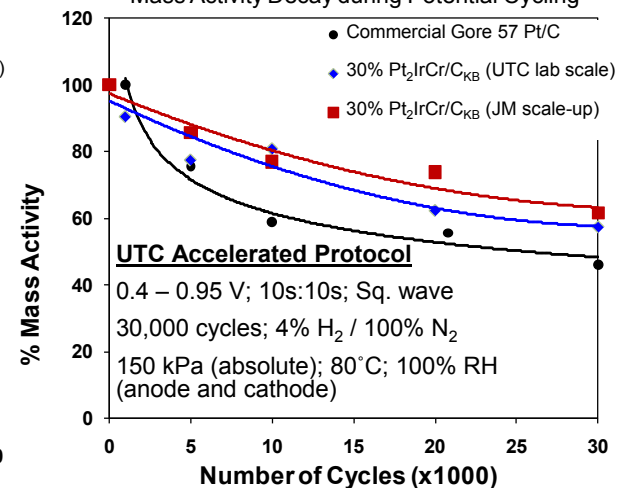
25 cm²; Solid Plate; 50% U; 80 \bar{S} ; 100% RH; 150kPa (abs)
H₂/Air Polarization Curves



ECA Decay during Potential Cycling



Mass Activity Decay during Potential Cycling



- ❑ 30% Pt₂IrCr /C_{KB} has best durability among studied alloys in both RDE and MEA cycling
- ❑ Clear evidence of improvement for high current density performance in H₂/Air from preliminary catalyst layer optimization steps
- ❑ Half-loading (0.2mg_{Pt}/cm²) alloy catalyst MEA's can achieve comparable initial performances to a standard Gore 57 (0.4mg_{Pt}/cm²)
- ❑ 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) Pt₈IrCo₂/C4 shows only 12 mV loss at 1.5 A/cm² in O₂



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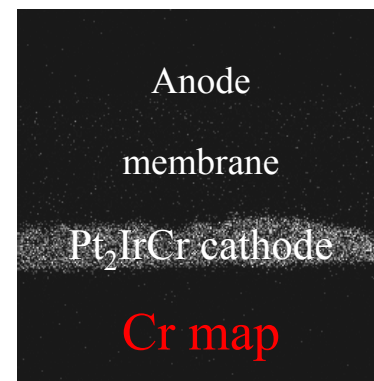
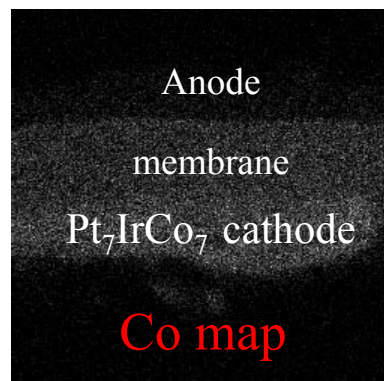
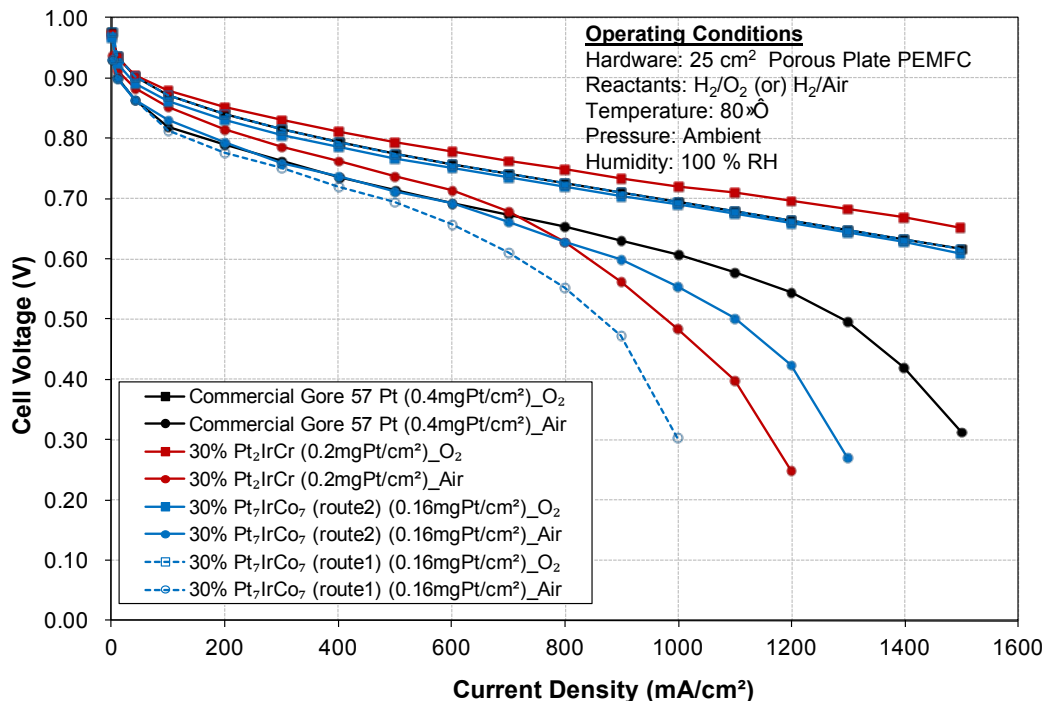
TECHNICAL ACCOMPLISHMENTS

Task 1: $\text{Pt}_2\text{IrCr}/\text{C}_{\text{KB}}$ vs. $\text{Pt}_7\text{IrCo}_7/\text{C}_{\text{KB}}$

- ❑ 30% $\text{Pt}_2\text{IrCr}/\text{C}_{\text{KB}}$ shows higher kinetic performance than other developed alloys
- ❑ Mass transport can be improved with MEA optimization
- ❑ 30% $\text{Pt}_2\text{IrCr}/\text{C}_{\text{KB}}$ was down-selected for further MEA optimization

- ❑ Lower Stability of Co than Cr in acidic environments

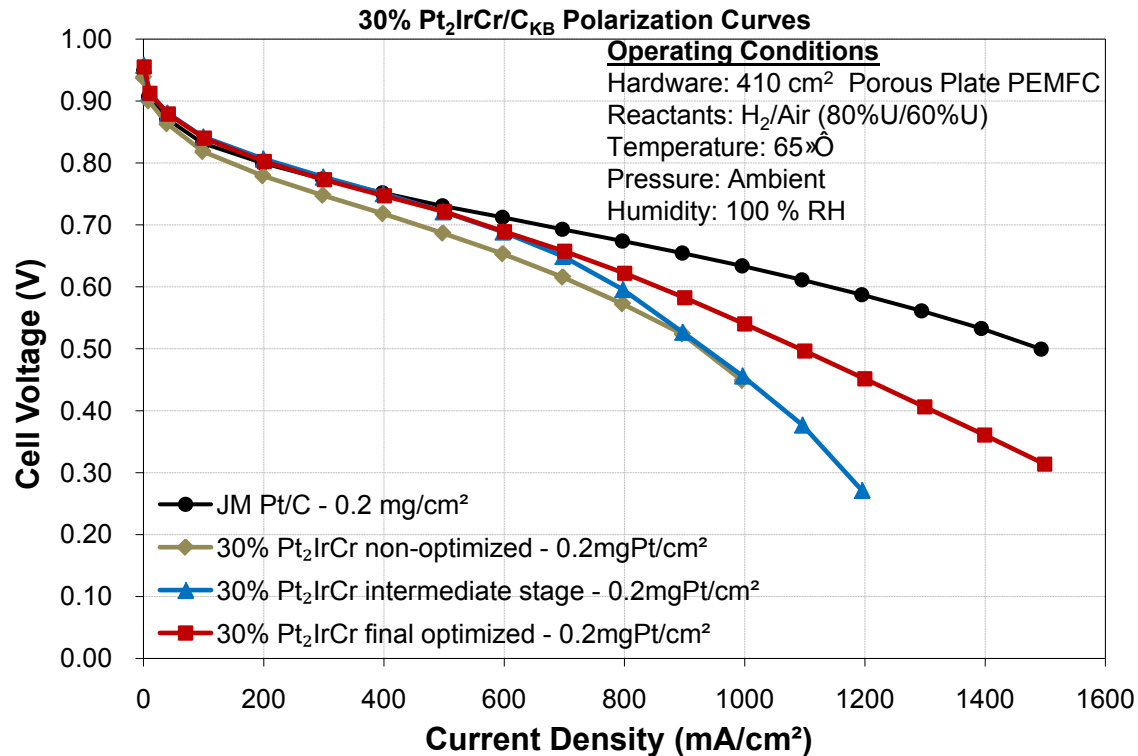
- 45-75% Co and 25% Cr loss from catalysts in 1M H_2SO_4
- 48% Co and 15% Cr loss from catalysts into ink solvent/Nafion
- Cr or Co ions in MEAs have detrimental impact on cell performance
- Lower stability of Co than Cr in fresh MEAs (stored more than 90 days)



EMPA elemental map
of fresh MEAs after ~90 days

TECHNICAL ACCOMPLISHMENTS

Task 1: Pt₂IrCr/C_{KB} Single-Cell MEA Optimization

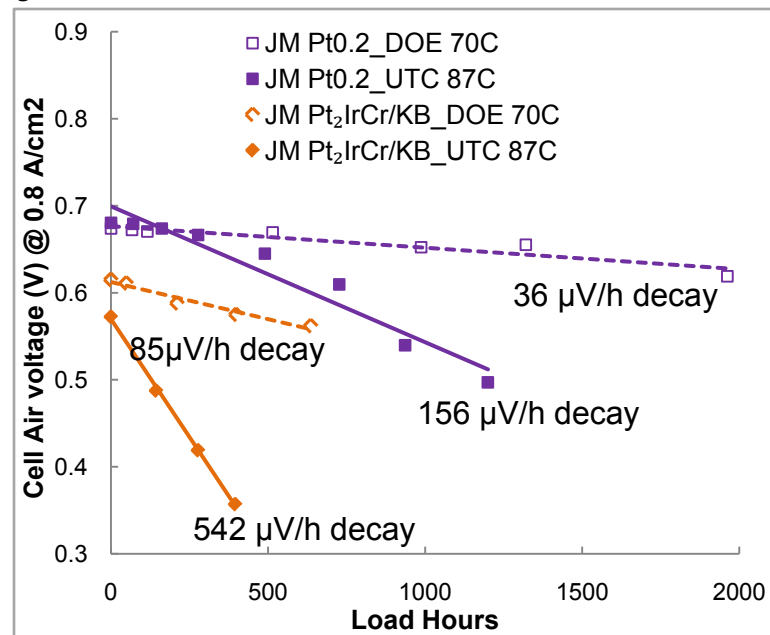
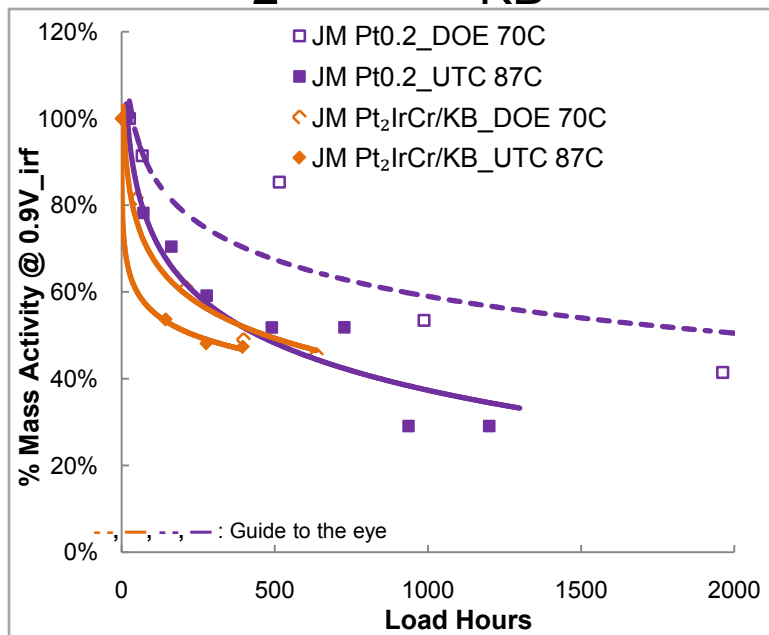


□ Performance optimizations in full-scale single cells

- Improved electrode structure (ink formulation, I/C ratio, Nafion® EW) and GDL (hydrophobicity)
- Increased catalyst utilization from 26 to 42 m²/g_{Pt}
- Higher mass activity from 0.11 to 0.2 A/mg_{Pt}
- Reduced mass transport resistance by 91 mV @ 1 A/cm²
- A performance gap of 94 mV vs. baseline Pt/C (0.2 mg/cm²) @ 1 A/cm²

TECHNICAL ACCOMPLISHMENTS

Task 1: Pt₂IrCr/C_{KB} Durability in Full-Size MEA



Durability protocol

- Modified DOE protocol: ~33-100 %RH cycle, 20-100 mA/cm² (dry) & 20-1000 mA/cm² (wet) load cycle, average 70 °C, ambient pressure
- UTC protocol: current cycles up to 800 mA/cm², average 87 °C, ambient pressure

□ Pt₂IrCr/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)



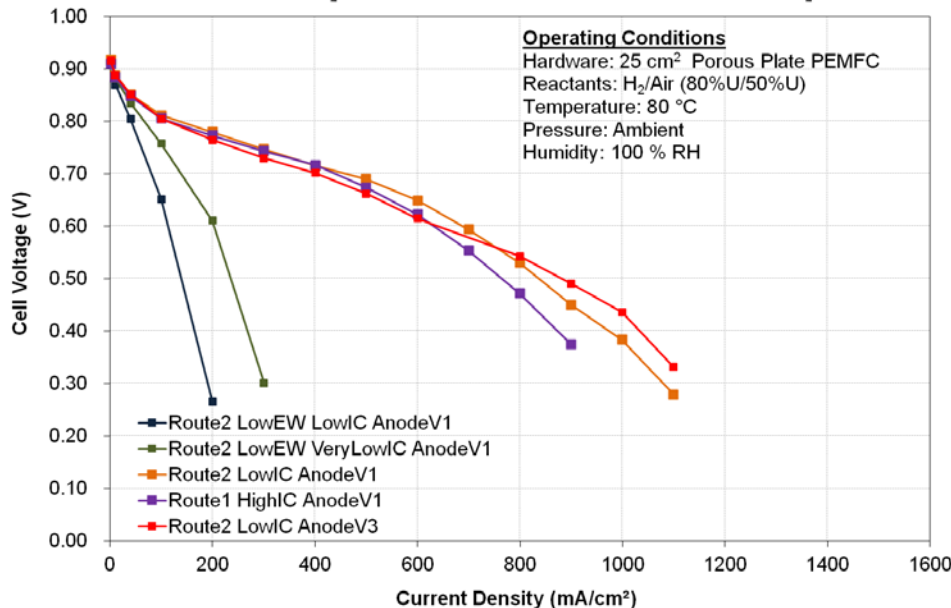
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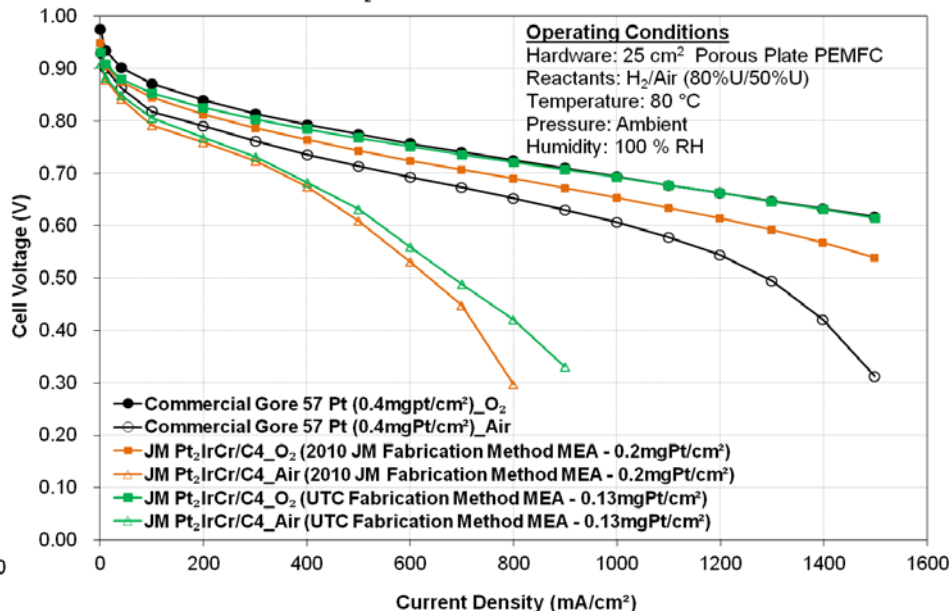
TECHNICAL ACCOMPLISHMENTS

Task 3: 20% Pt₂IrCr/C4 Sub-Scale MEA Optimization

JM 20% Pt₂IrCr/C4 sub-scale CCMs: Polarization Curves of H₂/Air



20% Pt₂IrCr/C4 Sub scale CCMs: Polarization Curves



□ 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/cm²) at high current densities
- Preliminary MEA fabrication at UTC shows that opportunities exist for further performance improvement at UTC – main focus in 2011



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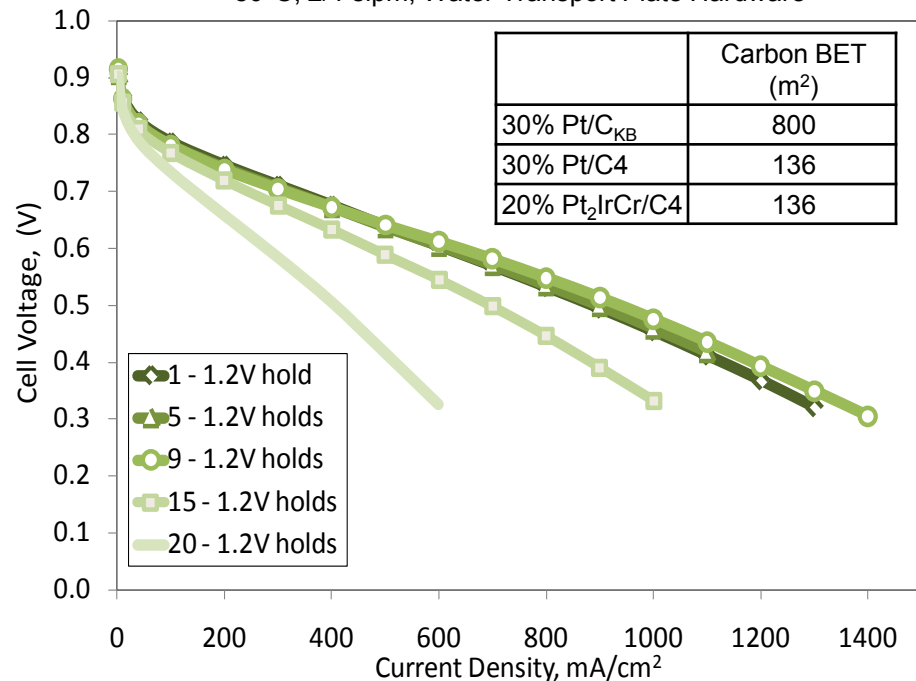
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TECHNICAL ACCOMPLISHMENTS

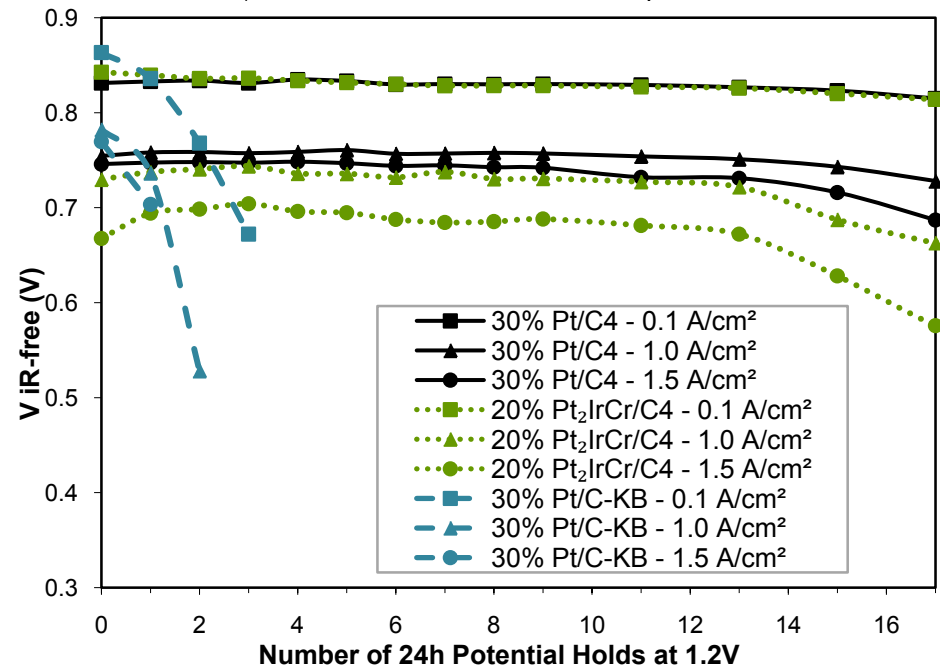
Task 3: Pt₂IrCr/C4 Corrosion Testing in WTP

- Scaled-up 20% Pt₂IrCr/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)

20% Pt₂IrCr/C4 - H₂/Air Polarization Curves
80°C, 2/1 slpm, Water Transport Plate Hardware

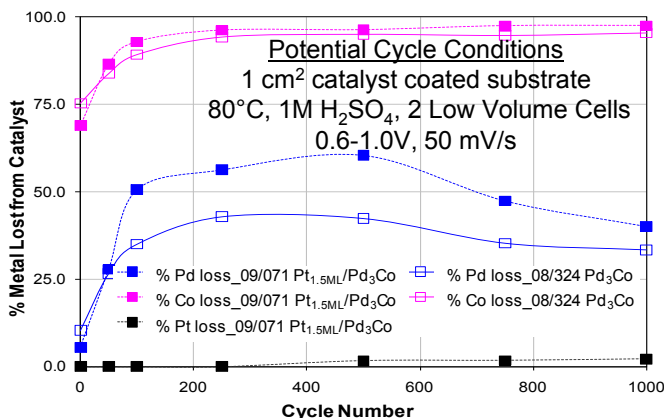


H₂/O₂ Performance
80°C, 50%/50% Utilization Water Transport Plate Hardware



CORE-SHELL ELD METHOD

Activities Leading to No-Go Decision



Pd₃Co and Pd₃Fe cores identified from modeling to have ~5xPt MA

Multiple Core preparation methods, Pt coating & Characterization

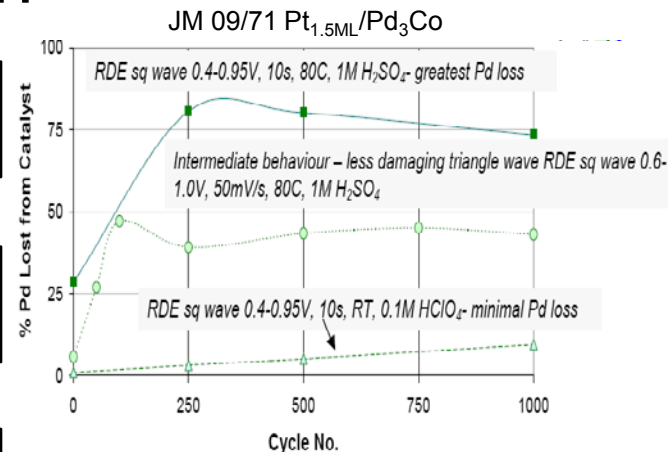
- Activity in MEA << RDE
- LEIS and voltammetry identified Co on surface
- Stability and activity of Pd₃Co = Pd₃Fe
- Significant Pd dissolution in liquid cell @ 80°C, 1M H₂SO₄, 0.6-1.0V cycles

No-Go Pd₃Cr shows Pd dissolution

Pd plates onto Pt surface during cycling if above a certain Pd²⁺ concentration

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

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



No-Go on Pt_{ML}/Pd₃Fe due to concern for Fe leaching in MEA

Pt_{ML}/Ir core has small MA benefit

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

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

No benefit from acid leaching Pd₃Co cores before Pt deposition results

No-Go Pd loss observed for Pd and Ir ion washed Pd₃X cores



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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] | 0.40 ^h | 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 |
| <u>Carbon Support Durability</u> 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% Pt₂IrCr MEA ; Anode/Cathode loading – 0.1/0.3 mg/cm² (PGM)

‡ 40 mV iR free O₂ performance loss at 1.5 A/cm² after 360 hours at 1.2 V

- ☐ **30% Pt₂IrCr/C_{KB} – Stack durability demonstration in progress**
- ☐ **Scaled-up a 200g batch of 20%Pt₂IrCr/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% Pt₂IrCr/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% Pt₂IrCr/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% Pt₂IrCr/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.

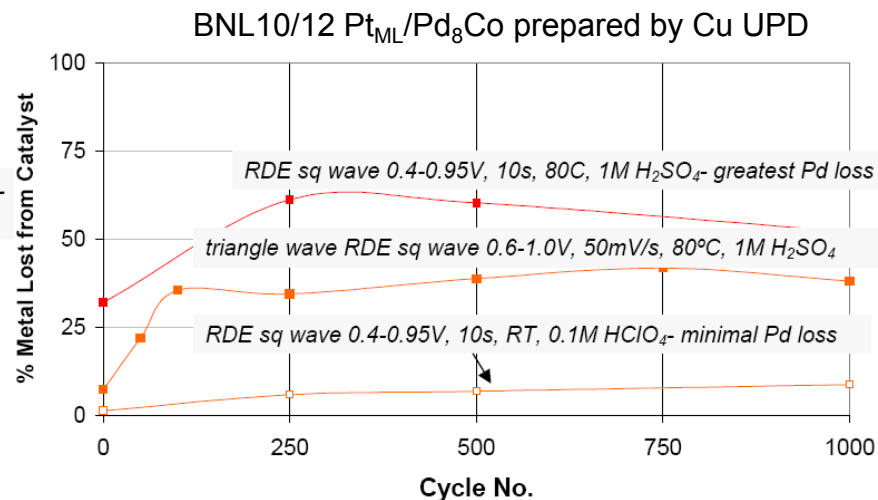
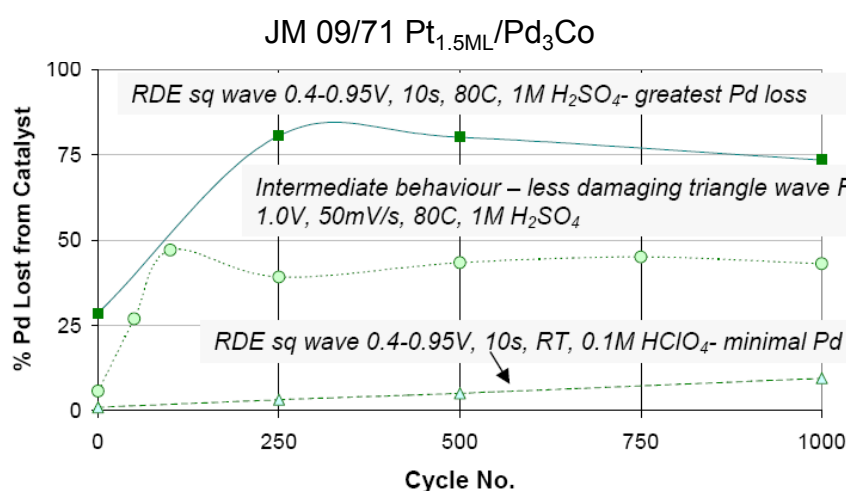
Technology Transfer/Collaborations: Active partnerships with JMFC, BNL and Texas A&M to develop a more active and durable cathode catalyst layer. Technology transfer through team meetings, presentations and publications.

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}/Pd₃Co and BNL 10/12 Pt_{ML}/Pd₈Co 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**

