Highly Dispersed Alloy Catalyst for Durability

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UTC Power
A United Technologies Company

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Project ID: fc_18_murthi

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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

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Program Objectives

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

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Current Status</th>
<th>DOE 2010 Target</th>
<th>DOE 2015 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt group metal (total content) [g/kW]</td>
<td>0.80</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Pt group metal (total loading) [mg/cm²]</td>
<td>0.64†</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Mass activity @ 900mV [A/mg_{PGM}]</td>
<td>0.28</td>
<td>0.44</td>
<td>0.44</td>
</tr>
<tr>
<td>Specific activity @ 900mV [mA/cm²]</td>
<td>0.55</td>
<td>0.72</td>
<td>0.72</td>
</tr>
<tr>
<td>Cyclic durability @ &lt;80°C / &gt;80°C [h]</td>
<td>TBD</td>
<td>5000/2000</td>
<td>5000/5000</td>
</tr>
<tr>
<td>ECA Loss* [%]</td>
<td>30</td>
<td>&lt;40</td>
<td>&lt;40</td>
</tr>
<tr>
<td>Cost [$/kW]</td>
<td>~38†</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

* 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)
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Technical Contributors

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Approach

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

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
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Overall Strategy

PtIrCo

Structural and composition optimization

Q1, ‘08

0 h

0.0 A/mgPt

Cyclic Durability

PtIrM

PtIrM scale-up and MEA optimization

Q3, ‘08

5000 h

0.44 A/mgPt

Mass activity

PtIrM

Future core shell synthesis optimization

Q3, ‘08

0.88 A/mgPt

2010 Target

PtIrM scale-up and MEA optimization

Q1, ‘08

0.88 A/mgPt

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Milestones

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone or Go/No-Go Decision</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 2008</td>
<td>Milestone: Synthesis of large scale batch (30 g) of Ir, Pd₃Co and Pd₃Fe cores</td>
</tr>
<tr>
<td>November 2008</td>
<td>Milestone: Synthesis of scaled up (5 g) batch of core/shell catalyst formulations</td>
</tr>
<tr>
<td></td>
<td>Milestone: Bench scale dispersed alloy catalyst formulation down selected</td>
</tr>
<tr>
<td></td>
<td>Go/No-Go decision: Down-selection of dispersed alloy catalyst (complete)</td>
</tr>
<tr>
<td>May 2009</td>
<td>Go/No-Go decision: Down-selection of new durable carbon</td>
</tr>
<tr>
<td></td>
<td>Milestone: Scale-up of down-selected dispersed catalyst</td>
</tr>
<tr>
<td>August 2009</td>
<td>Go/No-Go decision: Down-selection of core/shell catalyst</td>
</tr>
<tr>
<td>September 2009</td>
<td>Go/No-Go decision: UEA optimization of dispersed catalyst for single cell durability test</td>
</tr>
</tbody>
</table>
# HIGHLY DISPERSED ALLOY CATALYST

## Dispersed Catalyst Down Select Criteria

<table>
<thead>
<tr>
<th>Rank</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Weight factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Activity (A/mgPt)</td>
<td>≤ 0.2</td>
<td>0.2 – 0.3</td>
<td>0.3 – 0.4</td>
<td>0.4 – 0.45</td>
<td>≥ 0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Durability (% ECA loss after 30K cycles)</td>
<td>≥ 40 %</td>
<td>25 - 40 %</td>
<td>10 – 25 %</td>
<td>5 – 10 %</td>
<td>≤ 5%</td>
<td>0.3</td>
</tr>
<tr>
<td>Durability (% MA loss after 30K cycles)</td>
<td>≥ 40 %</td>
<td>25 - 40 %</td>
<td>10 – 25 %</td>
<td>5 – 10 %</td>
<td>≤ 5%</td>
<td>0.2</td>
</tr>
<tr>
<td>PGM Loading (wt% of Non-Pt PGM)</td>
<td>≥ 15 %</td>
<td>10 – 15 %</td>
<td>5 – 10 %</td>
<td>2.5 – 5 %</td>
<td>≤ 2.5 %</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Overall Score = Σ (Weight factor * Rank) †

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

<table>
<thead>
<tr>
<th></th>
<th>Mass Activity (RDE) (A/mgPt)</th>
<th>Durability (% ECA loss after 20 K cycles)</th>
<th>Durability (% MA loss after 20 K cycles)</th>
<th>PGM Loading (wt% of Non-Pt PGM)</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE 48 – Pt₂Ir₀.₅Co₁.₅</td>
<td>0.39</td>
<td>1 %</td>
<td>48 %</td>
<td>6 %</td>
<td>3.2</td>
</tr>
<tr>
<td>DOE 52 – Pt₂IrCr</td>
<td>0.45</td>
<td>9 %</td>
<td>49 %</td>
<td>11 %</td>
<td>3.2</td>
</tr>
</tbody>
</table>
driving forces for surface segregation:

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

- d-band center shows Pt$_2$IrCr Alloys less reactive than Pt$_3$Cr alloys
- Potential shift for Pt $\rightarrow$ Pt$^{2+}$ shows that Pt$_2$IrCr 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)
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Technical Accomplishments – Subscale MEA

UTC Accelerated Protocol

- Ir prevents transition metal leaching and Pt dissolution
- Cr has added benefits in MEA
  - low Fluoride Emission Rates
  - higher oxide stability
- Pt$_2$IrCr gave best durability in both RDE and MEA cycling
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Down-selected PtIrM/C Alloys

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

Stable ECA after particle reaches 4-5 nm

30% Pt₆IrCo₇ (DOE 59-1)
- Higher initial Mass Activity
- Stable ECA ~70 m²/gₚt
- Currently optimizing heat treatment impact for trade-off of performance and durability

Final MA = 0.4 A/mgₚt

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JM Scale-up: 30% Pt$_2$Ir$_{0.5}$Co$_{1.5}$ and 30% Pt$_2$IrCr

Pt$_2$Ir$_{0.5}$Co$_{1.5}$ (DOE 48)
Mass activity of scale up batch in RDE similar to lab scale synthesis

Pt$_2$IrCr (DOE 52)
Initial preparation attempt (batch 1) showed multi phased particles; second attempt successful; optimization of synthesis procedure in progress
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Pd₃Co/Ptₘₐₙₐₜ - JM Scale-up

0.25 monolayer of oxygen

<table>
<thead>
<tr>
<th>System</th>
<th>μₚₜ (eV)</th>
<th>Δμ (eV)</th>
<th>ΔU (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt (0 ML)</td>
<td>-6.98</td>
<td>-0.72</td>
<td>0.36</td>
</tr>
<tr>
<td>Pt (0.25ML)*</td>
<td>-6.26</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pt(shell)-Pd(core)</td>
<td>-6.42</td>
<td>-0.16</td>
<td>0.08</td>
</tr>
<tr>
<td>Pt(shell)-Pt₃Co</td>
<td>CVT1</td>
<td>-6.46</td>
<td>-0.20</td>
</tr>
<tr>
<td>(core)</td>
<td>CVT2</td>
<td>-6.46</td>
<td>-0.20</td>
</tr>
<tr>
<td>Pt(shell)-Pt₃Fe</td>
<td>CVT1</td>
<td>-4.88</td>
<td>1.38</td>
</tr>
<tr>
<td>(core)</td>
<td>CVT2</td>
<td>-6.49</td>
<td>-0.23</td>
</tr>
</tbody>
</table>

Pt becomes less stable compared with in vacuum; Pd and Pd₃Co cores can increase Pt stability

Durability to potential cycling

After 6500 cycles

- ΔE₁/₂ ≈ -13 mV
- 30 % loss in mass activity (at 0.9 V)
- 53 % loss in ECSA
- 25 % increase in specific activity

Durability

At 0.9 V vs. RHE after 6500 cycles, initial activity is 0.11 mA cm⁻², while after 6500 cycles, it is 0.09 mA cm⁻².
After potential cycling

1. Decrease in particle size of Pd<sub>3</sub>Co core
2. Particle density (TEM) decreases significantly
3. Pt layer seems to grow preferentially on one side of the particles
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Pd₃Co/Pt₂ML Core/Shell Stability

**Voltammetry curves for Pt₂ML/Pd₃Co/C in 0.1 M HClO₄ after potential cycles (0.6 – 0.95 V square wave with 30 sec pulse); RT**

**ORR curves for Pt₂ML/Pd₃Co/C in 0.1 M HClO₄ at 1600rpm after potential cycling. Scan rate: 10 mV/s; RT**

**Potential shift with different Pt shell thickness – in vacuum**

<table>
<thead>
<tr>
<th>ΔU (V)</th>
<th>1 layer</th>
<th>2 layers</th>
<th>3 layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(shell)-Co(core)</td>
<td>-0.54</td>
<td>-0.56</td>
<td>-1.95</td>
</tr>
<tr>
<td>Pt(shell)-Fe(core)</td>
<td>-1.10</td>
<td>-1.05</td>
<td>-2.79</td>
</tr>
<tr>
<td>Pt(shell)-Pd(core)</td>
<td>0.20</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Pt(shell)-Pd₃Co(core)</td>
<td>0.21</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Pt(shell)-Pd₂Fe(core)</td>
<td>-0.51</td>
<td>0.08</td>
<td>0.07</td>
</tr>
</tbody>
</table>

**In vacuum**
Monolayer Pt leads to highest stability for Pd and Pd₃Co core

- Pt₂ML/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%
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Pd$_3$Co/Pt$_{\text{ML}}$ - Activity in MEA’s

All core shell catalysts show enhancement over Pt only
Best mass activity Pt$_{\text{ML}}$/Ir core shell
Pt$_{\text{ML}}$/Pd$_3$Co and Pt$_{\text{ML}}$/Pd$_3$Fe show equivalent performance

49 cm$^2$ active area MEAs, $\text{H}_2/\text{O}_2$ stoich 2/10, 80°$\text{C}$, 150 kPa$_{\text{abs}}$, 100% RH
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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
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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
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