Development of Ultra-low Doped-Pt Cathode Catalysts for PEM Fuel Cells

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Columbia SC 29208.

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Project ID # FC088

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Overview

Timeline
- Start date: June 2010
- End date: May 2015
- Percent complete: 85%

Budget
- Total Funding Spent as of 3/31/2014: $2,660,608.22
- Total Project Value: $4,750,000
- Cost Share Percentage: 20.0

Barriers
A. Durability
- Retain kinetic activity and high current density performance in H₂/air after potential holding (support durability) and potential cycling (catalyst durability) experiments.

B. Cost
- Decrease in PGM content
- Cost effective synthesis procedures

C. Performance
- Obtain high current density performance in H₂/air and maintain the power density

DOE Technical Targets

<table>
<thead>
<tr>
<th>Electrocatalyst/MEA</th>
<th>2017 Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGM Loading (mg/cm²)</td>
<td>0.125</td>
</tr>
<tr>
<td>Mass Activity (A/mg_{PGM})</td>
<td>≥0.44</td>
</tr>
<tr>
<td>Mass activity and ECSA Loss after 30k Cycles (Catalyst Stability) (%)</td>
<td>≤ 40</td>
</tr>
<tr>
<td>Mass activity and ECSA Loss after 400 h (Support Stability) (%)</td>
<td>≤ 40</td>
</tr>
<tr>
<td>Potential loss after 30 k cycles (Catalyst Stability)</td>
<td>≤30 mV</td>
</tr>
<tr>
<td>Potential loss after 400 h (Support Stability)</td>
<td>≤30 mV</td>
</tr>
</tbody>
</table>

Project Lead
- University of South Carolina (USC)

Additional Interactions
- Rudiger Laufhutte (UIUC)
- Dr. Lax Saraf (Clemson University)
- Dr. Alan Nicholls (UIC)
- Electron Microscopy Center, USC
Develop cost effective high volume synthesis procedure to manufacture highly stable activated carbon composite catalyst (A-CCC) support.

- Achieve onset potential of 0.9 V vs. SHE for ORR.
- Achieve ≤30 mV loss in H₂/air after 400 h potential holding (1.2 V).

Develop low cost procedures to synthesize a catalyst with:

- Enhanced activity due to the synergistic effect of pyridinic-nitrogen catalytic sites from the support and suppressed Pt-lattice catalyst.
- Demonstrate mass activity of ≥0.44 A/mg_{PGM} in H₂/O₂ fuel cell, initial high current performance under H₂/air (<0.125 g_{PGM}/kW rated power density) and stability of mass activity (≤ 40% loss) and stability of high current density performance under H₂/air using DOE potential cycling and potential holding tests.

Develop a low cost catalyst with optimized average mass activity, stability of mass activity, initial high current performance under H₂/air (power density), catalyst and support stability able to meet 2017 DOE targets.
Approach

- Develop doped Pt/A-CCC catalyst with high activity for ORR through synergistic effect of pyridinic nitrogen containing A-CCC support and suppressed Pt-lattice catalyst.

Support Development
- Develop a corrosion resistant support with desired BET surface area to sustain potential cycling and potential holding experiments.
  - Surface modification with acid and inclusion of oxygen groups.
  - Metal-catalyzed pyrolysis with N-containing compounds to (i) dope the support, (ii) include pyridinic nitrogen active sites and (iii) increase graphitization.
  - Chemical leaching to remove excess metal used to dope the support.

Catalyst Development
- Development of doped Pt/A-CCC catalyst.
- Two in-house developed procedures contribute to the high activity of the catalyst with the following electrocatalytic properties:
  - Enhanced activity due to synergistic effect of pyridinic nitrogen containing A-CCC support and Pt towards oxygen reduction reaction.
  - Suppressed Pt-lattice catalyst having Pt-shell/doped-metal core structure (with different doping metal content from 0 to 50%).
- In order to synthesize doped Pt/A-CCC catalyst with high activity and stability:
  - Modified polyol process was developed for uniform Pt deposition.
  - Heat treatment process was optimized to control the particle size between 3 and 5 nm.
Synthesis of Metal-doped HCC Catalyst (Doped Pt/A-CCC)

Development of Ultra-low Pt Catalysts

Development of Pt/A-CCC [Hybrid Cathode Catalyst (HCC)]

Development of metal-doped HCC (Doped Pt/A-CCC)

1. Carbon surface modification
2. Metal-catalyzed pyrolysis
3. Pt deposition
4. Controlled heating

Formation of metal-doped HCC (Pt shell doped-metal core catalyst)

Doped metal core

Metal-doped HCC
Project Timeline (According to Revised SOPO Dated 01/23/2014)

Phase II

Q1 | Q2 | Q3 | Q4 | Q5 | Q6
---|---|---|---|---|---

Task 1. Optimization studies of A-CCC support and doped Pt/A-CCC catalysts (Initial mass activity of at least 0.3 A/mg_PGM)

Task 2. Stability of mass activity of (≤40% loss of initial value) at least 0.26 A/mg_PGM after 30k cycles.

Task 3. Support stability to demonstrate 0.26 A/mg_PGM and 30-50 mV loss after 400 h.

Task 4. Initial high current density performance of at least 1.5 A/cm² at 0.6 V_{ir-free} and power density of ≤0.24 g_PGM/kW.

Task 5. Demonstration of high current density performance loss of 30-60 mV (at 0.8 A/cm²) after 30k cycles and 30-50 mV loss (at 0.8 A/cm²) after 400 h.

Task 6. Demonstration of most promising catalyst to meet initial mass activity of 0.3 A/mg_PGM, stability of mass activity of at least 0.26 A/mg_PGM and 30-60 mV loss at 0.8 A/cm² after 30k cycles.

End of task.
Development of three generations of carbon composite catalyst supports with increasing graphitization and support stability.

Two methodologies were used at USC to synthesize ultra-low Pt loading catalysts:
- Metal impregnation followed by high temperature pyrolysis and leaching (Details are given in Reviewer Only Slides 46-51).
- Metal doped Pt catalyst by diffusing the metal previously embedded in the support (USC method – This presentation)

Synthesis of catalysts with initial high kinetic activity (0.38 - 0.44 A/mg\textsubscript{PGM}) and good stability of mass activity (32 - 50% loss in mass activity) after 30k cycles.

However, high mass activity does not translate into ORR activity in high current performance under H\textsubscript{2}-air operating conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Particle size (nm)</th>
<th>Mass activity (A/mg\textsubscript{PGM})</th>
<th>Initial</th>
<th>30 k*</th>
<th>400h**</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCC</td>
<td>4.0</td>
<td>Initial 0.38</td>
<td>0.2 (47% loss)</td>
<td>0.19 (50% loss)</td>
<td></td>
</tr>
<tr>
<td>Pt-alloy/CNC</td>
<td>3.5</td>
<td>Initial 0.44</td>
<td>0.3 (32% loss)</td>
<td>0.23 (48% loss)</td>
<td></td>
</tr>
</tbody>
</table>

*30,000 cycles between 0.6 and 1.0V with rates of 50mV/s

**keep at 1.2V for 400 hours
**Technical Accomplishments**

**1. Support Development**

**Development of Activated Carbon Composite Catalyst (A-CCC) Support**

- **Surface modification** of carbon black with:
  1. O-containing group
  2. N-containing group
- **Pyrolysis**

  "Metal-catalyzed pyrolysis" 
  (Fe or Co) to increase the number of active sites by leaching

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**HIGHLIGHT:**

**BET&BJH:** The surface areas for A-CCC (fresh) and A-CCC (stabilized) are 80 and 200 m²/g. BET shows presence of mesopores after stabilization step.

**HRTEM:** Graphitic carbon containing carbon nano fibers/tubes are formed during metal catalyzed pyrolysis.

**ADVANTAGE:** The BET surface area and the pore-size of the A-CCC support can be tailored to achieve uniform Pt deposition (3-5 nm).
Technical Accomplishments

1. Support Development
Metal inclusion and Estimation of Metal Content in A-CCC Support

**ICP analysis**

<table>
<thead>
<tr>
<th>Support</th>
<th>Co amount (wt%)</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-CCC H800</td>
<td>4.76%</td>
<td>137</td>
</tr>
<tr>
<td>A-CCC H900</td>
<td>6.84%</td>
<td>131</td>
</tr>
<tr>
<td>A-CCC H1000</td>
<td>8.13%</td>
<td>125</td>
</tr>
<tr>
<td>A-CCC H1100</td>
<td>10.69%</td>
<td>85</td>
</tr>
</tbody>
</table>

**HIGHLIGHT**

- Cobalt amount in the support increased with the increase in heat treatment temperature.
- BET surface area decreased at temperatures >900 °C.
Graphitic carbon formation through metal-catalyzed pyrolysis.

Co particles are embedded in the bulk of the carbon during pyrolysis in the presence of Co-N chelate compound.

Carbon nano fiber can be formed in the presence of Co at relatively low temperature (~800°C) which is more stable than amorphous carbon.

The A-CCC catalyst showed an onset potential of \textbf{0.9 V vs. RHE} and well-defined kinetic and mass transfer regions.
Technical Accomplishments

1. Support Development

Support Stability—1.2 V Potential Holding

**Mass Activity Loss of 40% doped Pt/A-CCC**

<table>
<thead>
<tr>
<th>Mass Activity (A/mg_{PGM})</th>
<th>Pt/A-CCC</th>
<th>Pt/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.25</td>
<td>Loss</td>
</tr>
<tr>
<td>400h</td>
<td>0.17</td>
<td>72%</td>
</tr>
</tbody>
</table>

**HIGHLIGHT:** (Status against 2017 DOE targets)

- The mass activity decreases from 0.25 to 0.17 A/mg_{PGM} (32% mass activity loss) after 400 h.
- The potential loss is 27 mV after 400 h potential holding against the 2017 DOE target of 30 mV loss after 400 h, respectively.
- The rated power density is 0.18 g_{PGM}/kW.
- Commercial Pt showed 72% mass activity loss, 71% ECSA loss and no activity after 400 h.

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**DOE Test Protocol**

Hold at 1.2 V for 400 h, H_{2}/N_{2}, 80°C, 150 kPa, 100% RH, single cell 25 cm²

**Polarization:**

- H_{2}/O_{2} (2/9.5 stoic.), 80°C, 100% RH, 150 kPa
- H_{2}/air (2/2 stoic.) 40% RH, 80°C, 170 kPa

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**Power Density: 0.18 g_{PGM}/kW**

**ViR-free loss**

\[ V_{iR-free} = 0.8A/cm^{2} (mV) \]

(2.0/2.0 stoic.)

<table>
<thead>
<tr>
<th>Initial</th>
<th>689</th>
</tr>
</thead>
<tbody>
<tr>
<td>400h</td>
<td>662</td>
</tr>
</tbody>
</table>

**Visible**

689 (27 mV loss) No Activity
HIGHLIGHT:
- Surface modification increases the hydrophilicity of graphitic carbon.
- Uniform particle distribution with an average particle size of 2-3 nm is achieved with the USC developed modified polyol process.
- No loss in H$_2$/O$_2$ fuel cell performance after 30k cycles using DOE potential cycling test.
Technical Accomplishments

2. Catalyst Development

**Doped Pt Catalyst Development**

Development of a Process to Control the Particle Size During High Temperature Pyrolysis

- **Conventional Pyrolysis**
  - Fresh catalyst
  - 800°C for 0.5 h

- **Modified Pyrolysis**
  - 800°C for 1.0 h

**HIGHLIGHT:**
- Normal heat-treatment results in 10 to 20 nm particles.
- The new process yields uniform particle size distribution with ~3.4 nm doped-Pt catalyst particles.

**Particle Size / nm**

- $d_{avg} = 2.5-3.4$ nm

**Frequency / %**

10-20 nm Particles

~3.5 nm Particles
Technical Accomplishments

2. Catalyst Development
Doped Pt Catalyst Development

Formation of doped Pt/A-CCC catalyst-Effect of Heat-treatment

Heat treatment time (h) | Pt peak (deg) | PtCo peak (deg) | Particle size (nm) |
--- | --- | --- | --- |
0 | 67.3 | -- | 2.5 |
0.5 | 67.9 | 69.4 | 2.8 |
1 | 67.8 | 69.5 | 3.9 |
2 | -- | 69.4 | 3.9 |
4 | -- | 69.5 | 4.5 |

Co doped Pt Composition | Pt$_{1.3}$Co$_{1}$/C
--- | ---
Co amount in the CCC (wt%) | 10.32%
Pt amount (wt%) | 30
Support(C+Co) amount (%) | 70
Carbon amount (wt%) | 62.776
Cobalt amount (wt%) | 7.224
Pt amount (mol ratio) | 0.154
Co amount (mol ratio) | 0.123
Pt/Co mol ratio | 1.3

HIGHLIGHT
- XRD shows the presence of Pt and PtCo phases after 0.5 h heat treatment.
- Single-phase Co-doped Pt is formed after 2 h.
- The shift in 2θ can be varied by adjusting the heat treatment time.
Co is present within the A-CCC support and diffuses during controlled annealing in the presence of a protective coating to form Co-doped Pt catalyst.

Line scan confirms the existence of Co in the core and a Pt-shell thickness of 0.5-0.8nm (Core-shell structure).
Technical Accomplishments

3. Catalyst Durability

Catalyst Durability Studies of Doped Pt/A-CCC (0.6-1.0 V Cycling)

H₂-O₂ Performance of Doped Pt/A-CCC

![Graph showing H₂-O₂ performance of doped Pt/A-CCC catalysts.]

Mass Activity Loss of Doped Pt/A-CCC

![Graph showing mass activity loss of doped Pt/A-CCC catalysts.]

HIGHLIGHT: (Status against 2017 DOE targets)

- **H₂-O₂**: The initial cell potential at 2 A/cm² current density is 0.701 V$_{\text{ir-corr}}$ initially and 0.669 V$_{\text{ir-corr}}$ after 30k potential cycling corresponding to a loss of 32 mV.

- **Mass Activity**: The initial mass activity of the Co-doped Pt/A-CCC catalyst is 0.408 A/mg$_{\text{PGM}}$. After 30k cycles, the mass activity decreased to 0.23 A/mg$_{\text{PGM}}$, which corresponds to 43.6% decay from the initial value.

**DOE Accelerated Stress Test Protocol**

- 0.6 ~ 1.0 V, 50mV/s, 30,000 cycle,
- H₂/N₂, 80°C, 100% RH, single cell 25cm²
- Polarization : H₂/O₂, 750/750 sccm, 100% RH, 80°C
- Pt mass activity : H₂/O₂, 2/9.5 stoic, 100% RH, 80°C, 150kPa backpressure
HIGHLIGHT:

- The doped Pt/A-CCC catalyst exhibits potential loss of 79 mV (from 0.700 V_{iR-free} to 0.621 V_{iR-free}) after 30k cycles at 0.8 A/cm².
- Pt/C showed no activity after 30k cycles.

DOE Accelerated Stress Test Protocol

0.6 ~ 1.0 V, 50mV/s, 30,000 cycle, H₂/N₂, 80°C, 100 % RH, single cell 25cm²

H₂/air: 2.0/2.0 stoic, 40% RH, 80°C, 170 kPa

- The particle size increased from ~3.4 nm to 5-7 nm after 30k cycles
Technical Accomplishments
Catalyst Development
Doped Pt Catalyst Development
Formation of doped Pt/A-CCC₁ catalyst—Effect of leaching

<table>
<thead>
<tr>
<th></th>
<th>Pt (wt%)</th>
<th>Co (wt%)</th>
<th>Molar ratio (XRF)</th>
<th>Molar ratio (ICP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>78.4</td>
<td>21.6</td>
<td>Pt : Co = 1:0.93</td>
<td>Pt : Co = 1:1</td>
</tr>
<tr>
<td>HT800°C</td>
<td>78.4</td>
<td>21.6</td>
<td>Pt : Co = 1:0.93</td>
<td>Pt : Co = 1:0.85</td>
</tr>
<tr>
<td>Leach 0.5h</td>
<td>85.1</td>
<td>14.9</td>
<td>Pt : Co = 1:0.59</td>
<td>Pt : Co = 1:0.59</td>
</tr>
<tr>
<td>Leach 12h</td>
<td>88.8</td>
<td>11.2</td>
<td>Pt : Co = 1:0.42</td>
<td>Pt : Co = 1:0.43</td>
</tr>
</tbody>
</table>

HIGHLIGHT:

- **XRD** shows after high temperature pyrolysis, Co present within the A-CCC₁ support diffused to the surface and doped into Pt lattice which is confirmed by the Pt peak shift in the XRD from 39.7° for pure Pt to 41.2° for the Co-doped Pt.

- **XRF & ICP** analysis show that 37% Co was removed from the catalyst after 0.5 h. Further leaching for 12h did not leach out all the transition metal (only 18% more Co is leached out). 45% Co remains in the catalyst corresponding to a **Pt to Co ratio of 1 to 0.43**. The Co dissolution rate in the first half an hour is 49 times higher than the remaining 11.5 hours.

- **HRTEM** shows 3 to 6 nm doped Pt catalyst particles after controlled heat treatment process.
HIGHLIGHT:

- **Mass activity** increased from 0.22 to 0.35 A/mg$_{\text{PGM}}$ after Co-doping. Leaching leads to better catalytic activity at 0.9 V (0.47 A/mg$_{\text{PGM}}$).

- **H$_2$/air performance**: At 0.6 V$_{\text{ir-free}}$, the current densities are 0.68, 1.00, 1.45 and 1.70 A/cm$^2$ for fresh, heat-treated, leached for 0.5h and leached for 12h catalysts, respectively. The 12 h leached catalyst showed initial power density of **0.196 g$_{\text{PGM}}$/kW** (rated power).

- **Catalyst stability**: Doped Pt/A-CCC$_1$ (12 h leached) catalyst showed 7 mV potential loss after 10k cycles.
Collaborations

Characterization and Interactions

- **Rudiger Laufhutte** (University of Illinois, Urbana-Champaign): ICP analysis of doped Pt catalysts.

- **Alan Nicholls** (University of Illinois, Chicago): HRTEM & XEDS mapping.

- **Lax Saraf & Haijun Qian** (Clemson University): Transmission Electron Microscopy analysis.

- **EM Center** (University of South Carolina): HR-TEM analysis

- **Scribner Associates**: Design and construction of fuel cell test stations according to USC requirements.

- **Fuel Cell Technologies**: Design and construction of 25 and 50 cm² single cells according to USC specifications.
### Technical Accomplishments

#### Summary of Accomplishment of Doped Pt/A-CCC Cathode Catalyst

<table>
<thead>
<tr>
<th>Metric</th>
<th>Units</th>
<th>Status (FY2014)</th>
<th>Commercial Pt/C</th>
<th>2017 DOE target</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial Mass Activity</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Mass activity</td>
<td>A/mg$<em>{PGM}$ @ 900 mV$</em>{ir}$</td>
<td>0.25~0.47</td>
<td>0.18</td>
<td>≥0.44</td>
</tr>
<tr>
<td><strong>Catalyst Stability (0.6-1.0 V cycling)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Loss in catalyst activity</td>
<td>% loss after 30k cycles</td>
<td>43%</td>
<td>68%</td>
<td>≤40%</td>
</tr>
<tr>
<td>Loss in ECSA</td>
<td>% loss after 30k cycles</td>
<td>15%</td>
<td>80%</td>
<td>≤40%</td>
</tr>
<tr>
<td>Potential loss @ 800 mA/cm$^2$</td>
<td>mV loss after 30k cycles</td>
<td>79 mV</td>
<td>No Activity</td>
<td>≤30 mV</td>
</tr>
<tr>
<td><strong>Support Stability (1.2 V holding)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Loss in catalyst activity</td>
<td>% loss after 400 h</td>
<td>32%</td>
<td>72%</td>
<td>≤40%</td>
</tr>
<tr>
<td>Loss in ECSA</td>
<td>% loss after 400 h</td>
<td>6%</td>
<td>71%</td>
<td>≤40%</td>
</tr>
<tr>
<td>Potential loss @ 800 mA/cm$^2$</td>
<td>mV loss after 400 h</td>
<td>27 mV</td>
<td>No Activity</td>
<td>≤30 mV</td>
</tr>
<tr>
<td><strong>PGM Content and PGM Loading</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PGM total content (Power Density)</td>
<td>g$_{PGM}$/kW (rated)</td>
<td>0.18~0.24</td>
<td>0.3</td>
<td>≤0.125</td>
</tr>
<tr>
<td>PGM total loading</td>
<td>mg$<em>{PGM}$/cm$^2</em>{geo}$</td>
<td>0.2</td>
<td>0.2</td>
<td>≤0.125</td>
</tr>
</tbody>
</table>
Task 1: Synthesis of metal doped Pt/A-CCC (HCC) catalysts

Task 2. Optimization studies of selected catalysts

- Initial and durability of mass activity and high current performance under H₂-air under potential cycling condition (0.6-1.0 V, 30k cycles).
- Increase the performance of Pt-M/A-CCC catalysts as a function of concentration of doped metal in the A-CCC support and pyrolysis temperature.

Task 3. Optimization of high volume production procedures for the A-CCC support and doped Pt/A-CCC catalysts.

Task 4. Performance evaluation of two selected catalysts

   a) Durability of high current performance under H₂-air
   b) Catalyst down selection

The goal is to select a best performing catalyst to demonstrate the following characteristics in single cells:

(According to Revised SOPO Dated 01/23/2014)

(i) initial mass activity of 0.3 A/mg$_{\text{PGM}}$ and stability of mass activity of at least 0.26 A/mg$_{\text{PGM}}$ after 30k cycles

(ii) initial high current density performance of at least 1.5 A/cm$^2$ at 0.6 V$_{\text{ir-free}}$

(iii) stability of high current density of only 30-60 mV loss at 0.8 A/cm$^2$ following accelerated stress testing.

(iv) Evaluation of reproducibility of support and catalyst performance.

Deliverables:

- Supply of a most promising catalyst for independent evaluation. The amount to be determined by the DOE.
Publications Resulted from the Current Project


7. Development of Hybrid Cathode Catalyst for PEM Fuel Cells, Taekeun Kim, Won Suk Jung, Tianyuan Xie, Akos Kriston, Prabhu Ganesan, David Gamliel, Brian Murphy and Branko N. Popov, *222nd ECS Meeting*, Honolulu, HI, October 7-12, 2012.


Team Members who contributed to this presentation

University of South Carolina
Branko N. Popov, Tae-keun Kim, Won-suk Jung, Xie Tianyuan, Joseph Rotchford, Akos Kriston and Prabhu Ganesan

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