Development of Ultra-low Platinum Alloy Cathode Catalyst for PEM Fuel Cells

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Columbia SC 29208.

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Project ID # FC088
Overview

Timeline
- Start date: June 2010
- End date: Dec 2012 (Phase I)
  - May 2014 (Phase II)
- Percent complete: 50%

Barriers
- Catalyst performance
- Catalyst durability
- Scale-up synthesis procedures

Budget
- Total project funding
  - DOE share: $4,400,000
  - Contractor share: $1,100,000
- Funding received FY 11: $750,000
- Planned Funding FY 12: $1,000,000

Partners
- Yonsei University (YU), S. Korea
- Hyundai Motor Company (HMC), S. Korea (Funding ended in Dec 2011; will resume in Dec 2012)

Partners
- University of South Carolina (USC)

DOE Technical Targets

<table>
<thead>
<tr>
<th>Electro catalyst/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/mgPt)</td>
<td>0.44</td>
</tr>
<tr>
<td>ECSA Loss after 30K Cycles (Catalyst Stability) (%)</td>
<td>≤ 40</td>
</tr>
<tr>
<td>ECSA Loss after 400 h (Support Stability) (%)</td>
<td>≤ 40</td>
</tr>
</tbody>
</table>

Additional Interactions
- Rudiger Laufhutte (Univ. Illinois)
- Dr. JoAn Hudson (Clemson University)
**Objectives:** Development of high performance, low cost and durable cathode catalyst and support able to meet the 2017 DOE targets.

**Approach:**
- Optimization studies of **carbon composite catalyst (CCC)** support. (USC)
- Development of advanced hybrid catalyst based on CCC support and Pt [low Pt-alloy loading catalyst]. (USC)
- Development of **carbon nanocage (CNC)** supported Pt-alloy catalyst (Pt-alloy/CNC). (YU)
- Synthesis of corrosion resistant hybrid TiO₂–CCC support (USC)
- Development of high volume procedures for the synthesis of promising catalyst. (USC & YU)

**Primary Focus for Past Year:**
- Performance evaluation of USC Pt/C catalyst.
- Performance evaluation of CCC support. (USC)
- Evaluation of different strategies for the optimization of **hybrid cathode catalyst (HCC)** with total loadings of 0.2 mg Pt / cm² / MEA. (USC)
  - Initial and durability of kinetic mass activities.
  - Initial high current density performance in H₂-air.
- Performance evaluation of Pt-alloy/CNC catalyst activity and durability with total loadings of 0.2 mg Pt / cm² / MEA. (YU)
  - Initial and durability of kinetic mass activities.
  - Initial high current density performance in H₂-air.
<table>
<thead>
<tr>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>Q4</th>
<th>Q5</th>
<th>Q6</th>
<th>Q7</th>
<th>Q8</th>
<th>Q9</th>
<th>Q10</th>
<th>Q11</th>
<th>Q12</th>
<th>Q13</th>
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<th>Q16</th>
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<tr>
<td>9/1/10</td>
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</tr>
</tbody>
</table>

**Budget Period 1 (2.5 years)**

- Task 1: CCC support
- Task 2: Development of HCC catalysts
- Task 3: Development of Pt-alloy/CNC catalysts
- Task 4: Catalysts’ activity and durability studies
- Task 5: Development of non-carbon supported catalysts
- Task 6: High current density performance under H₂-air
- Task 7: Durability studies under H₂-air
- Task 8: Scale-up synthesis of promising catalysts

**Budget Period 2 (1.5 years)**

- Task 9: Short-stack construction and testing of 2 promising catalysts

End of task.

Go-No-Go decision for the selection of 2 promising catalysts with high mass activity, specific activity and durability.

Go-No-Go decision for the selection of 2 promising catalysts to be tested under short-stack conditions.

*Milestones are explained in slides 5 & 6*
Milestone 1: **Sep 2011**: Preparation of carbon composite catalyst (support) (Task 1)

**Status**: Achieved onset potential for oxygen reduction reaction close to 0.9 V and < 2.5% H₂O₂ production. The CCC support is stable after 10 k cycles (0.6-1.0 V) under RRDE.

Milestone 2: **Sep 2011**: Initial mass activity and specific activity (Tasks 2, 3 and 4)

**Status**: (i) Accomplished initial mass activity of 0.45 A/mgPt and specific activity of 1036 µA cm⁻² for the **USC** Pt₂Ni₁/C catalyst.

(ii) Accomplished initial 0.44 A/mgPt and specific activity of 1023 µA cm⁻² for **YU** Pt₂Ni₁/CNC catalyst.

(iii) The initial mass activity values for **USC** Pt₂Ni₁/C catalyst and **YU** Pt₂Ni₁/CNC satisfy the 2017 DOE mass activity target of 0.44 A/mgPt.

Milestone 3: **Jun 2012**: Durability of kinetic mass activity at least 0.24 A mg⁻¹Pt after 30 k cycles tested according to DOE protocol (0.6-1.0 V). (Task 4)

**Status**: Achieved 0.3 A mg⁻¹Pt after 30 k cycles for Pt₂Ni₁/CNC (**YU**) catalyst in 25 cm² cell. Need similar or higher performance for USC HCC catalysts and to be confirmed in a 50 cm² cell in at least two laboratories.

The durability of mass activity and support stability for USC catalysts are planned to be accomplished in June 2012 and will be reported in July 2012 quarterly report.

**Jun 2012**: GO/NO-GO decision for Milestones 2 and 3

Selection of HCC and Pt-M/CNC catalysts. The goal is to maintain high activity and achieve ≤40% loss of initial catalytic activity after 30 k cycles.

**Possible solution**: Development of corrosion resistant supports such as TiO₂-CCC and activated graphitic carbon (AGC). (Task 5)
Technical Accomplishments and Progress

Milestones

- **Milestone 4: Dec 2012:** Initial high current density performance in H₂-air (80 °C, 100% / 40% RH, 150 kPaₐₚₑₛ. outlet pressure, 1.5/1.8 stoic.). *(Task 6 and 7)*  
  **Status:** (i) Achieved 1.25 A cm⁻² @ 0.58 Vᵦᵣ-free in 25 cm² cell at PGM loading of 0.125 mgPt cm⁻² for **USC** Pt₂Ni₁/C catalyst.  
  (ii) Achieved 1.03 A/cm² @ 0.7 Vᵦᵣ-free in 25 cm² cell at PGM loading of 0.1 mgPt cm⁻² for **Yonsei University** Pt₂Ni₁/CNC catalyst. (Need improvements and to be performed in 50 cm² cell in at least two laboratories.)

- **Milestone 5: Dec 2012:** Scale-up synthesis and durability of promising catalysts with optimum high current density performance in H₂/air. *(Task 8)*  
  **Status:** Scale-up synthesis of HCC and Pt₂Ni/CNC: On going catalyst durability under high current region in H₂-air for USC Pt₂Ni/C and Pt₂Ni/CNC catalysts: Started in March 2012.

**Dec 2012: GO/NO-GO decision for Milestones 4 and 5**  
**Criteria:** Selection of two most promising catalysts with (i) high kinetic mass activity, (ii) ≤40% loss of initial catalytic activity after 30 k cycles, (iii) initial high current density performance of at least 1.5 A cm² at 0.58 Vᵦᵣ-free under H₂/air (1.5/1.8 stoic.), 80 °C, 40% RH, 150 kPaₐₚₑₛ. outlet pressure.
Highlight

OCV decreases from 1.009 V to 0.943 V as the initial Pt loading increases from 30 wt% to 60 wt%.

Effect of initial Pt loading on polarization performance and OCP in H₂-O₂
The catalyst mass activity increases as the Pt loading decreases.

Pt utilization increases as the Pt loading decreases.

<table>
<thead>
<tr>
<th>Pt loading (mg/cm²)</th>
<th>Current Density @0.9V (A/cm²)</th>
<th>Mass Activity (A/mg)</th>
<th>ECSA Fuel Cell/RDE (m²/g)</th>
<th>Utilization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.012</td>
<td>0.24</td>
<td>70.18/85.00</td>
<td>82.56</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0185</td>
<td>0.185</td>
<td>67.86/85.00</td>
<td>79.83</td>
</tr>
<tr>
<td>0.2</td>
<td>0.03</td>
<td>0.15</td>
<td>49.45/85.00</td>
<td>58.18</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0321</td>
<td>0.107</td>
<td>47.63/85.00</td>
<td>56.04</td>
</tr>
<tr>
<td>0.4</td>
<td>0.035</td>
<td>0.0875</td>
<td>41.08/85.00</td>
<td>48.33</td>
</tr>
</tbody>
</table>

- At 0.6V iR-free, the current density increases from 700mA/cm² to 1300mA/cm² as the Pt loading increases from 0.05mgPt/cm² to 0.4mgPt/cm².
Technical Accomplishments and Progress
MEA Optimization Studies (Effect of Membrane)

Membrane optimization studies to increase the OCP and MEA performance at high current density was studied using NRE212 membrane and proprietary membrane (PM).

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Current density at 0.7V (mA/cm²)</th>
<th>OCV (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion® NRE 212</td>
<td>2050</td>
<td>1.038</td>
</tr>
<tr>
<td>Proprietary membrane</td>
<td>2500</td>
<td>0.965</td>
</tr>
</tbody>
</table>

**Highlight**
- PM increases the current density by 450mA/cm² at 0.7V while OCV decreases.

**Technical Accomplishments and Progress**

**MEA Optimization Studies (Effect of Membrane)**

**MEA specifications & Test conditions**
- Cathode: 0.15mgPt/cm² / Anode: 0.1mgPt/cm² / 46wt% Pt/C
- NRE 212 vs. Proprietary membrane/10BC/CCM/25cm²
- Flow rate: Anode: H₂ 750sccm / Cathode: O₂ 750sccm
- Back pressure: None / RH: 100% / Cell temp.: 80°C

**Highlight**
- At 0.6Vᵋᵣ-free, 0.15mgPt/cm² on PM shows 500mA/cm² higher current density when compared with 0.4mgPt/cm² on NRE212 membrane.
Technical Accomplishments and Progress

MEA Optimization Studies (Effect of non-carbon Support)

**Highlights**
- Pt/TiO₂ shows low mass transport loss.
- Pt/TiO₂ shows OCV close to 1.0V.
- Pt/TiO₂ shows power density 1.15W/cm².

**MEA specifications & Test conditions**
- Anode: 0.5mgPt/cm², Pt/C/Nafion 112/5cm²
- Anode: H₂ 150sccm / Cathode: O₂ 150sccm
- Back pressure: None / RH: 100% / Cell temp.: 75°C

**Comparison of Accelerated Corrosion Test Results of Pt/C and Pt/TiO₂ Catalysts (Potential Holding at 1.2 V)**

- Pt/C shows 93% loss in ECSA at Tc = 80h.
- Pt/TiO₂ shows ~20% loss in ECSA at Tc = 80h.
- Potential loss of 100mV was observed for Pt/C after 40hrs.
- No Potential loss is observed for Pt/TiO₂.

**Technical Accomplishments and Progress**

**MEA Optimization Studies (Effect of non-carbon Support)**

- Initial state 7000 cycle 10mTiO₂
- After test 7000 cycles

- Pt/TiO₂ electrode retained a similar morphology and catalyst layer thickness (1µm) before and after accelerated durability test.
Objective: Combine the catalytic activity of Pt/Pt-alloy with that of carbon composite catalyst (CCC) thus forming a hybrid cathode catalyst (HCC) having ultra-low Pt loading.

**Technical Accomplishments and Progress**

**Synthesis of HCC**

**Carbon modification** (Step 1)

- **Surface modification** of carbon black with:
  (i) **O**-containing group
  (ii) **N**-containing group
- **Pyrolysis**

**Carbon composite Catalyst** (Step 2)

- **“Metal-catalyzed pyrolysis”** (Fe or Co) to increase the number of active sites by leaching
- **Pt deposition**
- **Pyrolysis**

**Hybrid cathode catalysts (HCC)** (Step 3)

- **Pt deposition**

The advantages of this approach are:

(i) no leaching step is necessary in order to remove the un-reacted transition metal.

(ii) no increase of Pt particle size in step 3.

(iii) avoids destruction of Pt-alloy catalyst/carbon support interaction.

(iv) easy to scale-up.

Technical Accomplishments and Progress
Performance Evaluation of Carbon Composite Support

TEM

**HIGHLIGHT:**
- Metal atoms are covered with several graphitic layers.
- Nanostructured fibers of graphitic carbon was formed as a result of metal-catalyzed pyrolysis.
- XPS indicated that the high-temperature pyrolysis increased the Lewis basicity due to the increased concentration of pyridinic-type nitrogen.

**RRDE Stability Test for CCC**
- 0.1 M HClO$_4$, 5 mV/s
- RPM: 1600
- Loading: 120 µg/cm$^2$
- Cycling: 0.6 to 1 V vs. RHE

**HIGHLIGHT:**
- CCC support showed onset potential of 0.9 V vs. RHE for ORR.
- The support is stable after 10K potential cycles between 0.6 and 1.0 V vs. RHE.
Technical Accomplishments and Progress
RRDE Comparison Studies of CCC, 5% Pt/C and 5% Pt/CCC Catalysts

RRDE Comparison

RRDE Stability Test for 5% Pt/CCC

HIGHLIGHT:
• CCC, 5% Pt/C and 5% Pt/CCC show onset potential of 0.9, 0.985 and 1.0 V vs. RHE, respectively, for ORR.
• The potential at 2 mA/cm² is 0.707, 0.793 and 0.873 V for CCC, 5% Pt/C and 5% Pt/CCC, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>10 Cycles</th>
<th>100 Cycles</th>
<th>100000 Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECSA [m²/g]</td>
<td>67.2 (100 %)</td>
<td>67.2 (100%)</td>
<td>61.8 (92 %)</td>
<td>55.1 (82 %)</td>
</tr>
</tbody>
</table>
**Technical Accomplishments and Progress**

**Comparison of 30% Pt/C and 30% Pt/CCC Catalysts (Effect of Catalytically Active CCC Support)**

**Highlight:**
The 30% Pt$_{1.3}$Co$_1$/CCC (HCC) catalyst shows 30% current density increase at 0.7 V and 40% current density increase at 0.7 $V_{\text{Ir-free}}$ when compared to the 30% Pt/C catalyst.
Technical Accomplishments and Progress
Comparison of Electrochemical Properties of Different HCC Catalysts

HIGHLIGHT:
USC catalysts show ECSA in the range from 34.6 – 72.9 m²/g.

HIGHLIGHT:
USC catalysts show mass activities in the range from 0.35 to 0.45 A mg⁻¹ Pt⁻¹.

Technical Accomplishments and Progress
Comparison of Electrochemical Properties of Different HCC Catalysts

HIGHLIGHT:
USC catalysts show ECSA in the range from 34.6 – 72.9 m²/g.

HIGHLIGHT:
USC catalysts show mass activities in the range from 0.35 to 0.45 A mg⁻¹ Pt⁻¹.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>OCV (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30% Pt₃Co₁/CCC</td>
<td>1.010</td>
</tr>
<tr>
<td>30% Pt₃Ni₁/CCC</td>
<td>0.995</td>
</tr>
<tr>
<td>46% Pt₃Cu₁/CCC</td>
<td>0.976</td>
</tr>
<tr>
<td>46% Pt₂Ni₁/C</td>
<td>0.971</td>
</tr>
<tr>
<td>46% Pt/C</td>
<td>0.975</td>
</tr>
</tbody>
</table>

H₂ - O₂ fuel cell
H₂/O₂ (750/750 sccm)
80 °C, 100% RH, no back press.
Anode: 46% Pt/C (0.1 mg/cm²)
Cathode: HCC catalysts (0.125 mg/cm²)
Membrane: Nafion NRE 212

Current density/mA cm⁻²
Potential/V vs. RHE
0.1 M HClO₄ ECSA-RRDE
50 mV/s, 20 µg/cm²

Mass activity
H₂/O₂ (2/9.5 stoic.)
80 °C, 100% RH
150 kPa abs.

Technical Accomplishments and Progress
Comparison of Electrochemical Properties of Different HCC Catalysts
Technical Accomplishments and Progress

Comparison of Electrochemical Properties of HCC Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Particle size (nm)</th>
<th>Mass activity (A/mgPt)</th>
<th>Specific Activity (µA/cm²)</th>
<th>ECSA in RDE (m²/g)</th>
<th>ECSA in MEA (m²/g)</th>
<th>Utilization (%)</th>
<th>Current density @ 0.7 V (A/cm²) H₂/O₂ (750/750 sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30% Pt₁₃Co₁/CCC</td>
<td>3.6</td>
<td>0.41</td>
<td>1198</td>
<td>34.55</td>
<td>33.14</td>
<td>95.90</td>
<td>2.15</td>
</tr>
<tr>
<td>30% Pt₃Ni₁/CCC</td>
<td>2.9</td>
<td>0.441</td>
<td>1033</td>
<td>58.90</td>
<td>42.6</td>
<td>72.30</td>
<td>1.58</td>
</tr>
<tr>
<td>46% Pt₃Cu₁/CCC</td>
<td>3.3</td>
<td>0.35</td>
<td>1565</td>
<td>64.38</td>
<td>22.36</td>
<td>34.73</td>
<td>1.83</td>
</tr>
<tr>
<td>46% Pt₂Ni₁/C</td>
<td>3.5</td>
<td>0.45</td>
<td>1036</td>
<td>56.77</td>
<td>43.43</td>
<td>76.52</td>
<td>2.25</td>
</tr>
</tbody>
</table>

**HIGHLIGHT:**

- 30% and 46% USC catalysts show particle sizes in the range between 2.9 and 3.6 nm.
- The ECSA ranges from 34.6 – 72.9 m²/g and mass activities in the range from 0.35 to 0.45 A mgPt⁻¹.
- The open circuit potential depends on the initial catalyst loading. 30% USC catalysts showed OCP of ~1 V and 46% USC catalysts showed OCP of ~ 0.97 V.
Technical Accomplishments and Progress

Comparison of H₂-Air Fuel Cell Performance

**H₂-air fuel cell performance (DOE)**

- H₂/air (1.5/1.8 stoic.)
  - 80 °C, 40% RH, 150 kPa abs.
  - Anode: 46% Pt/C (0.1 mg/cm²)
  - Cathode: USC catalysts (0.125 mgPt/cm²)
  - Membrane: Nafion NRE 212

**Effect of Cathode Stoic.**

- H₂/air (1.5/1.8 stoic.)
  - 80 °C, 40% RH, 150 kPa abs.
  - Anode: 46% Pt/C (0.1 mg/cm²)
  - Cathode: USC catalysts (0.125 mgPt/cm²)
  - Membrane: Nafion NRE 212

**HIGHLIGHT:**

- 30% Pt₃Ni₁/CCC USC catalyst shows ~1.0 V OCP under H₂-air operating conditions.
- USC Pt₂Ni₁/C shows 1.25 A/cm² at 0.58 V_{ir-free}.

**HIGHLIGHT:**

- The cathode stoic. significantly increases the H₂-air fuel cell performance and USC Pt₂Ni₁/C catalyst shows 1.4 A at 0.58 V_{ir-free} when 1.5/2.0 stoic is used.
- Currently the catalyst layer structure is being optimized to achieve high current density performance under DOE suggested H₂-air operating conditions.
Graphitic Carbon Modification

- Surface modification of graphitic carbon with a non-covalent π-π interaction using (i) Pyrenyl and (ii) Carboxylic acid groups
- Process optimization

Synthesis of Pt/CNC Catalyst

- Deposition of Pt on functionalized CNC using in-house deposition process
- Control of Pt particle size and Pt dispersion on surface modified CNF

Synthesis of Pt-alloy on Surface Modified CNC

- Inhibition of Pt sintering at alloying temperature using in-house developed heat-treatment procedure.
- Impregnation of transition metal precursor.
- Leaching of the catalyst to remove non-alloyed transition metal.

Technical Accomplishments and Progress
Synthesis and Characterization of Pt$_2$Ni$_1$/CNC Alloy Catalyst

Objective: Develop Pt and Pt-alloy catalysts deposited on carbon nano cage (CNC)

Shape Controlled Pt
Technical Accomplishments and Progress
Electrochemical Performance Evaluation* of Pt$_2$Ni$_1$/CNC Catalyst (Effect of atomic Pt/Ni ratio)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size in XRD (nm)</th>
<th>Mass activity (A/mg$_{Pt}$)</th>
<th>ECSA (m$^2$g$^{-1}$)</th>
<th>Utilization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yonsei U. 50wt% Pt$_x$Ni$_y$/CNC</td>
<td>3.4</td>
<td>0.44</td>
<td>33.2</td>
<td>74</td>
</tr>
<tr>
<td>Yonsei U. 50wt% Pt$_x$Ni$_y$/CNC</td>
<td>3.3</td>
<td>0.43</td>
<td>34.5</td>
<td>76</td>
</tr>
<tr>
<td>Yonsei U. 50wt% Pt$_x$Ni$_y$/CNC</td>
<td>3.3</td>
<td>0.37</td>
<td>33.7</td>
<td>77</td>
</tr>
</tbody>
</table>

Condition: 150kPa, 80°C, 100% RH, H$_2$/air 2/9.5 stoic, 25 cm$^2$, 0.1mg$_{metal}$/cm$^2$

Catalyst: Yonsei U. Pt$_2$Ni$_1$/CNC, TKK 46 Pt/C

HIGHLIGHT:
- YU Pt$_x$Ni$_y$/CNC catalysts show particle sizes of ~3.3 nm.
- The mass activity of Pt$_x$Ni$_y$/CNC catalysts increases with the increase in the Ni content.
- The catalyst utilization for the Pt$_x$Ni$_y$/CNC catalysts are between 74 and 77%.

*Catalyst performance evaluation is under progress at USC
Technical Accomplishments and Progress

Pt$_2$Ni$_1$/CNC Catalyst Durability Studies*

Effect of Potential Cycling on the Mass Activity

**HIGHLIGHT:**
- YU Pt$_2$Ni$_1$/CNC catalyst shows 31.8% mass activity loss and 26.3% ECSA loss after 30k cycles.
- The catalyst durability satisfies the DOE target of ≤ 40% after 30K cycles.

**Effect of Potential Cycling**

<table>
<thead>
<tr>
<th>After 30,000 cycles</th>
<th>Mass activity at 0.9V</th>
<th>ECSA in MEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE target</td>
<td>≤ 40% loss</td>
<td>≤ 40% loss</td>
</tr>
<tr>
<td>Yonsei U. 50wt%</td>
<td>31.8 % loss</td>
<td>26.3 % loss</td>
</tr>
<tr>
<td>Pt$_2$Ni$_1$/CNC</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**DOE Accelerated Protocol**

0.6 ~ 1.0 V, 50mV/s, 30,000 cycle, H$_2$/N$_2$

80°C, 100 % RH, single cell 25cm$^2$

Catalyst : Yonsei U. Pt$_2$Ni$_1$/CNC, 0.1mg$\text{metal}$/cm$^2$

Pt mass activity : H$_2$/O$_2$, 2.0/9.5 stoic, 100% RH, 80°C, 150 kPa

*Catalyst cycling performance evaluation is under progress at USC*
Technical Accomplishments and Progress
Pt$_2$Ni$_1$/CNC Support Durability Studies (Potential hold at 1.2 V)

Effect of 1.2 V Potential Hold on the Mass Activity

- **HIGHLIGHT:**
  - YU Pt$_2$Ni$_1$/CNC catalyst shows 47.7% mass activity loss and 42.7% ECSA loss after 400 h potential holding.
  - The support durability of YU Pt$_2$Ni$_1$/CNC does not satisfy the DOE target of ≤ 40% after 400 h.

**Discussion**

**DOE Accelerated Protocol**

Hold at 1.2V for 24 h, H$_2$/N$_2$

80°C, 150 kPa, 100 % RH, single cell 25cm$^2$

Catalyst : Yonsei U. Pt$_2$Ni$_1$/C, 0.1mg$_{metal}$/cm$^2$

Pt mass activity : H$_2$/O$_2$, 2.0/9.5 stoic, 100% RH, 80°C, 150 kPa
Technical Accomplishments and Progress

H₂-Air Fuel Cell Performance and Mass Activity Comparison

**HIGHLIGHT:**

- YU Pt₂Ni₁/CNC catalyst shows 1.03 A/cm² at 0.7 V_{ir-free}.
- Very thin (~2 µm) uniform catalyst layer can be deposited directly on the membrane.

**HIGHLIGHT:**

YU PtₓCoᵧ/CNC PtₓNiᵧ/CNC catalysts show mass activities in the range between 0.33 and 0.44 A/mg_{Pt}.  

**H₂-air fuel cell performance (DOE)**

- GDL 10 BB Nafion 211 membrane, Nafion 20% (H₂/air, 1.5/1.8, RH 40%, 80°C, 150 kPa)
- Anode: 46% TKK Pt/C, 0.1 mg_{Pt} cm⁻²
- Cathode: Pt₂Ni/CNC, 46% TKK Pt/C 0.1 mg_{metal} cm⁻²

**Condition:** 80°C, 40% RH, H₂/air, 1.5/1.8 stoic, 25 cm², 0.1 mg_{metal} cm⁻², 150 kPa abs.

**Catalysts:** Yonsei U. Pt₂Ni₁/CNC & TKK 46 Pt/C

**Mass Activity Comparison of YU Catalysts**

- Pt₂Ni₁/CNC: 0.44 A mg_{Pt}⁻¹
- TKK 46: 0.37 A mg_{Pt}⁻¹
- DOE: 0.13 A mg_{Pt}⁻¹
- Pt: 0.34 A mg_{Pt}⁻¹
- Pt₂Co₁/CNC: 0.41 A mg_{Pt}⁻¹
- Pt₃Co₁/CNC: 0.34 A mg_{Pt}⁻¹
- Pt₄Co₁/CNC: 0.33 A mg_{Pt}⁻¹
- Pt₂Ni₁/CNC: 0.44 A mg_{Pt}⁻¹
- Pt₃Ni₁/CNC: 0.43 A mg_{Pt}⁻¹
- Pt₄Ni₁/CNC: 0.37 A mg_{Pt}⁻¹

**MEA Cross-sectional Analysis**

- Catalyst layer: 1.7 ~ 1.9 µm
- Membrane
Collaborations

Subcontractors:

- **Yonsei University**
  - Activation procedure to deposit Pt on graphitic carbon support.
  - Pt-alloy/CNC catalyst development with high mass activity, specific activity and durability.
  - Process to control the particle size at high temperature treatment.
  - Evaluation of high current density performance under H2-air.
  - Support corrosion mechanism studies.

- **Hyundai Motor Company** (Funding ended Dec. 2011 and will resume in Feb 2013)
  - Pt-Pd catalyst development and performance evaluation.
  - Flow-field design optimization.
  - Short-stack design and construction.
  - Performance evaluation of Pt/C catalyst under short-stack conditions.
  - Construction and delivery of short-stack (10 cells, 50 cm²) to University of South Carolina. HMC delivered a short-stack (50 cm²) in Nov 2011.

Additional Interactions:

- Rudiger Laufhutte (University of Illinois, Urbana Champagne): ICP analysis of Pt-alloy catalysts.
- JoAn Hudson & Haijun Qian (Clemson University): Transmission Electron Microscopy analysis.
- Soumitra Goshroy (EM Center, USC): HR-TEM analysis
- Scribner Associates: Design and construction of fuel cell test station according to USC requirements.
- Fuel Cell Technologies: Design and construction of 25 and 50 cm² single cells according to USC specifications.
Future Work

**USC:**

**Milestone 3: June 2012**
- Develop support which will increase the catalyst utilization and eliminate the loss of electrochemical surface area through performance optimization of carbon composite support (CCS).
- Accomplish durability of kinetic mass activity of at least 0.24 A mg$_{\text{Pt}}^{-1}$ after 30 K cycles tested according to DOE protocol (cycling between 0.6-1.0 V) or less than 40% loss of mass activity at 0.9 V and ECSA loss less than 40%.
- Accomplish durability of catalyst support according to DOE target: hold at 1.2 V (400h) with less than 40% loss of mass activity at 0.9 V and less than 40% loss of ECSA.

**Milestone 4 & 5: December 2012**
- Accomplish high current density performance and durability in H$_2$/air fuel cells (80 °C, 100% / 40% RH, 150 kP$_{\text{abs.}}$ outlet pressure, 1.5/1.8 stoic) to meet the DOE targets.
- Demonstrate facile scale-up synthesis of the catalyst.

**Yonsei University**

**Specific Objectives to Accomplish Milestone 3 and Milestone 4**
- Support durability optimization studies of Pt$_2$Ni$_1$/CNC catalyst.
- Modification of protecting coating method to improve the durability of Pt-Ni catalyst.
- Modification of synthesis method to reduce particle size of Pt/CNC-S catalyst.
- Durability test for Pt/CNC-S catalyst.
- Additional research for physical characterization of Pt/CNC-S catalyst.
Summary: Status Against DOE Targets (As of March 2012)

- Carbon composite support was synthesized with onset potential for oxygen reduction closer to 0.9 V vs. SHE and less than 2.5% H₂O₂ production. **Project Milestone 1.**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2017 Targets</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGM total loading</td>
<td>mgPt/cm²</td>
<td>0.125</td>
<td>0.1-0.15 mgcatalyst/cm² with <strong>USC Pt₂Ni₁/C</strong> and 0.1 mgcatalyst/cm² with <strong>YU Pt₂Ni₁/CNC</strong></td>
</tr>
<tr>
<td>Mass activity (80 °C, 100% RH, 150 kPa_{abs.})</td>
<td>A/mgPt @ 0.9 V_{ir-free}</td>
<td>0.44</td>
<td>0.45 A/mgPt with <strong>USC Pt₂Ni₁/C</strong> and 0.44 A/mgPt <strong>YU Pt₂Ni₁/CNC</strong> (Milestone 2)</td>
</tr>
<tr>
<td>Catalyst durability (30,000 cycles 0.6-1.0 V, 50 mV/s, 80/80/80, 100 kPa_{abs.}, H₂/N₂)</td>
<td>% Mass activity loss</td>
<td>≤40%</td>
<td>31.8% mass activity loss</td>
</tr>
<tr>
<td></td>
<td>% ECSA loss</td>
<td>≤40%</td>
<td>26.3% ECSA loss</td>
</tr>
<tr>
<td></td>
<td>mV loss @ 0.8 A/cm²</td>
<td>≤30</td>
<td>For <strong>YU Pt₂Ni₁/CNC</strong> (Milestone 3)</td>
</tr>
<tr>
<td>Support durability (1.2 V for 400 h at 80 °C, H₂-N₂, 150 kPa_{abs.} 100% RH)</td>
<td>% Mass activity loss</td>
<td>≤40%</td>
<td>47.7% mass activity loss</td>
</tr>
<tr>
<td></td>
<td>% ECSA loss</td>
<td>≤40%</td>
<td>42.7% ECSA loss</td>
</tr>
<tr>
<td></td>
<td>mV @ 0.8 A/cm²</td>
<td>≤30</td>
<td>For <strong>YU Pt₂Ni₁/CNC</strong></td>
</tr>
</tbody>
</table>

- Corrosion resistant Pt/TiO₂ catalyst was developed with Pt particle size d_{pt}= 3-6 nm which showed high stability under potential holding at 1.2 V.
Team Members who contributed to this presentation

University of South Carolina
Branko N. Popov, Tae-keun Kim, Won-suk Jung, Xie Tianyuan, Xuguang Li, Gang Liu, Akos Kriston and Prabhu Ganesan

Yonsei University (S. Korea)
Hansung Kim
Acknowledgement

U.S. Department of Energy
Technical Backup Slides
Developed methodologies to increase the open circuit potential (OCP) and mass activities of catalysts synthesized at USC. For e.g. a gain of 66 mV (from 0.943 to 1.009 V) can be achieved for the USC catalyst by optimizing the catalyst particle size, surface area and porosity of the catalyst support.

Polarization curves obtained at different Pt loadings in H₂-O₂ indicated that the mass activity depends up on the utilized Pt surface area (ECSA).

The ECSA is found to depend on the Pt loading. The ECSA increased from 41.08 m²/g (Pt loading = 0.4 mg/cm²) to 70.18 m²/g (Pt loading = 0.05 mg/cm²).

An increase in mass activity up to 0.24 A/mgₚt (for USC Pt/C catalyst) was observed for a Pt loading of 0.05 mg/cm² compared to 0.08/5 A/mgₚt for 0.4 mgₚt/cm². The observed increase is due to the increase of Pt utilization from 48.33% (Pt loading = 0.4 mg/cm²) to 82.56% (Pt loading = 0.05 mg/cm²).

The current density under H₂-air measured at 0.6 V_iR-free increased from 700 mA/cm² to 1300 mA/cm² as the Pt loading increased from 0.05 to 0.4 mg/cm².

Identified and optimized an appropriate membrane to increase the high current density performance under H₂-air. The optimized proprietary membrane (PM) increased the current density of the MEA containing 0.15 mgₚt/cm² by 500 mA/cm² at 0.7 V_iR-free when compared to the Nafion® NRE 212 having 0.4 mgₚt/cm² under H₂-O₂.
Major Technical Accomplishments since Last Review (06/10/11)

- Developed TiO₂-based non-carbon support which showed OCP close to 1.0 V and low mass transfer loss.
- Corrosion studies on Pt/TiO₂ indicated only 20% ECSA loss compared to 93% ECSA loss for conventional Pt/C catalyst. No potential loss was observed at 0.5 A/cm² after 200 h support corrosion test whereas, Pt/C showed 100 mV loss after 40 h.
- Validated a new process for the synthesis of Pt-alloy catalysts which does not increase the particles size after heat treatment.
- The BET surface area of the catalyst support has an important role on the stability of the catalysts. Low surface area supports drastically increased the catalyst stability.
- New methodology was developed at USC to decrease the BET surface area and partial graphitization of different carbon supports from 800 m²/g up to 100-150 m²/g using low heat treatment temperatures.
- Novel technique was developed to increase the hydrophilic character of the graphitic carbon which enabled uniform Pt deposition having particles sizes between 2 and 3.5 nm.
- New process was developed to synthesize Pt-rich alloy having particles size ~3.5 nm by interacting Pt nanoparticles and transition metals, which were previously embedded in the bulk of the carbon, at high temperature.
- Studies performed on 30% Pt/C and 30% HCC indicated that the OCP depends on the reactants' partial pressure, H₂ crossover, and the porosity of the catalyst layer.
- The lower OCP results from the presence of trace amounts of mixed oxides of Pt and alloying metals formed during high temperature treatment.
Technical Accomplishments and Progress
Synthesis of HCC Catalysts

### Catalysts and Particle Size

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30% Pt$_{1.3}$Co$_1$/CCC</td>
<td>3.6</td>
</tr>
<tr>
<td>30% Pt$_3$Ni$_1$/CCC</td>
<td>2.9</td>
</tr>
<tr>
<td>46% Pt$_3$Cu$_1$/CCC</td>
<td>3.3</td>
</tr>
<tr>
<td>46% Pt$_2$Ni$_1$/C (USC)</td>
<td>3.5</td>
</tr>
</tbody>
</table>

**HIGHLIGHT:**
- Alloy formation is confirmed by the shift in the $2\theta$ values of all the USC catalysts thus decreasing the Pt-Pt interatomic distance.
- Complete alloying process since no peaks corresponding to the alloying metals are observed.
- The particle size can be controlled within the range between 3 and 4 nm using the proprietary coating and heating procedures developed at USC.

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**Technical Accomplishments and Progress**

**Synthesis of HCC Catalysts**

- **30% Pt$_{1.3}$Co$_1$/CCC**: 4.3 nm, 3.6 nm, 2.6 nm
- **30% Pt$_3$Ni$_1$/CCC**: 3.6 nm
- **46% Pt$_3$Cu$_1$/CCC**: 3.3 nm
- **46% Pt$_2$Ni$_1$/C (USC)**: 3.5 nm

**HIGHLIGHT:**
- Alloy formation is confirmed by the shift in the $2\theta$ values of all the USC catalysts thus decreasing the Pt-Pt interatomic distance.
- Complete alloying process since no peaks corresponding to the alloying metals are observed.
- The particle size can be controlled within the range between 3 and 4 nm using the proprietary coating and heating procedures developed at USC.

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**Technical Accomplishments and Progress**

**Synthesis of HCC Catalysts**

- **30% Pt$_3$Ni$_1$/CCC**: Fresh, Heat-treated
- **Pt (111)**
- **Pt (220)**

**HIGHLIGHT:**
- Alloy formation is confirmed by the shift in the $2\theta$ values of all the USC catalysts thus decreasing the Pt-Pt interatomic distance.
- Complete alloying process since no peaks corresponding to the alloying metals are observed.
- The particle size can be controlled within the range between 3 and 4 nm using the proprietary coating and heating procedures developed at USC.
Technical Accomplishments and Progress
Mass Balance of HCC Catalyst

Sample Calculation for the Final HCC Catalyst Composition

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co amount in the CCC (g)</td>
<td>0.0516</td>
</tr>
<tr>
<td>Co amount in the CCC (wt%)</td>
<td>10.32%</td>
</tr>
<tr>
<td>Pt amount (wt%)</td>
<td>30</td>
</tr>
<tr>
<td>Support(C+Co) amount (%)</td>
<td>70</td>
</tr>
<tr>
<td>Carbon amount (wt%)</td>
<td>62.776</td>
</tr>
<tr>
<td>Cobalt amount (wt%)</td>
<td>7.224</td>
</tr>
<tr>
<td>Pt MW (g/mol)</td>
<td>195.084</td>
</tr>
<tr>
<td>Co MW (g/mol)</td>
<td>58.933</td>
</tr>
<tr>
<td>Pt amount (mol ratio)</td>
<td>0.154</td>
</tr>
<tr>
<td>Co amount (mol ratio)</td>
<td>0.123</td>
</tr>
<tr>
<td>Pt/Co mol ratio</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Final catalyst composition (assuming that all the cobalt were formed Pt-Co alloy)

Pt$_{1.3}$Co$_1$/C

HIGHLIGHT:

• New method was developed to synthesize Pt-alloy catalysts by interacting Pt and transition metal previously embedded in the bulk of the carbon support at high temperature

• The Co content stabilizes after 30 minutes leaching in 0.5 M H$_2$SO$_4$