V.D.13 Development of Ultra-Low Platinum Alloy Cathode Catalysts for PEM Fuel Cells

Specific Objectives for Fiscal Year (FY) 2012

- Evaluate the oxygen reduction reaction (ORR) kinetics of the CCC support.
- Evaluate the synergistic effect of CCC support and Pt or Pt-alloy catalysts.
- Evaluation of different strategies for the optimization of HCC and Pt-alloy/carbon nanocage (CNC) catalysts with total loadings of 0.2 mg cm⁻²/membrane electrode assembly (MEA).
  - Initial and durability of kinetic mass activities.
  - Initial high current density performance in H₂-air.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:
(A) Durability
(B) Cost
(C) Performance

Technical Targets

The technical targets for the year FY 2012 are to:
(i) study the effect of various surface modifications on USC CCC, (ii) evaluate the oxygen reduction reaction (ORR) kinetics of the CCC support, and (iii) evaluate the synergistic effect of CCC support, Pt and Pt alloy catalyst.

To increase the catalyst performance and durability, the following new procedures were developed during the reporting period.
- A new low temperature method was developed to synthesize partially graphitized carbon composite catalyst (support) based on catalyzed pyrolysis in presence of transition metals.
- 1-pyrene carboxylic acid was used to modify and functionalize the partially graphitized CCC and CNC supports.
- A high temperature alloying process was developed to synthesize uniformly distributed platinum alloy particles with an average particle of 3.3 nm deposited on functionalized partially graphitized CCC and CNC supports.
TABLE1. Progress towards Meeting Technical Targets for Electrocatalysts

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2017 Targets</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Density</td>
<td>g/kW</td>
<td>0.125</td>
<td>0.1-0.2 mg&lt;sub&gt;cat&lt;/sub&gt;/cm&lt;sup&gt;2&lt;/sup&gt; with HCC and 0.1 mg&lt;sub&gt;cat&lt;/sub&gt;/cm&lt;sup&gt;2&lt;/sup&gt; with Pt&lt;sub&gt;2&lt;/sub&gt;Ni/CNC catalysts</td>
</tr>
<tr>
<td>Precious group metal (PGM) total loading</td>
<td>mg/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.125</td>
<td></td>
</tr>
<tr>
<td>Mass activity (80°C, 100% relative humidity (RH), 150 kPa&lt;sub&gt;abs&lt;/sub&gt;)</td>
<td>A mg&lt;sub&gt;Pt&lt;/sub&gt;&lt;sup&gt;-1&lt;/sup&gt; @ 0.9 ViR-free</td>
<td>0.44</td>
<td>0.45 A mg&lt;sub&gt;Pt&lt;/sub&gt;&lt;sup&gt;-1&lt;/sup&gt; for Pt&lt;sub&gt;2&lt;/sub&gt;Ni/CNC&lt;sub&gt;(a)&lt;/sub&gt; (0.1 mg cm&lt;sup&gt;-2&lt;/sup&gt;)</td>
</tr>
<tr>
<td>Catalyst durability (30,000 cycles, 0.6-1.0 V, 50 mV/s, 80/80/80, 100 kPa&lt;sub&gt;abs&lt;/sub&gt;, H&lt;sub&gt;2&lt;/sub&gt;/N&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>% Mass activity loss</td>
<td>≤40%</td>
<td>30.3% mass activity loss (Pt&lt;sub&gt;2&lt;/sub&gt;Ni/CNC&lt;sub&gt;(b)&lt;/sub&gt;)</td>
</tr>
<tr>
<td>Support durability (1.2 V for 400 h at 60°C, H&lt;sub&gt;2&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt;, 100% RH)</td>
<td>% Mass activity loss</td>
<td>&lt;10%</td>
<td>47.7% mass activity loss for Pt&lt;sub&gt;1&lt;/sub&gt;C&lt;sub&gt;0&lt;/sub&gt;/CNC.</td>
</tr>
<tr>
<td>High current density performance [H&lt;sub&gt;2&lt;/sub&gt;/air (1.5/1.8), 80°C, 40% RH, 150 kPa&lt;sub&gt;abs&lt;/sub&gt;]</td>
<td>A cm&lt;sup&gt;-2&lt;/sup&gt; @ 0.58 ViR-free</td>
<td>-</td>
<td>1.25 (1.5/1.8) and 1.4 (1.5/2.0) for Pt&lt;sub&gt;2&lt;/sub&gt;Ni/CNC&lt;sub&gt;(a)&lt;/sub&gt; (0.1 mg cm&lt;sup&gt;-2&lt;/sup&gt;)</td>
</tr>
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</table>

CCC<sub>(a)</sub> – Brunauer-Emmett-Teller (BET) surface area higher than 600 m<sup>2</sup>/g; CCC<sub>(b)</sub> – BET surface area = 250 m<sup>2</sup>/g; CCC<sub>(c)</sub> – BET surface area = 380 m<sup>2</sup>/g; CCC<sub>(d)</sub> – BET surface area = 350 m<sup>2</sup>/g.

FY 2012 Accomplishments

- Accomplished onset potential for oxygen reduction reaction close to 0.9 V<sub>RHE</sub> and <2.5% H<sub>2</sub>O<sub>2</sub> production for the CCC support.
- Accomplished initial mass activities of 0.45, 0.33, 0.37, and 0.41 A mg<sub>Pt</sub><sup>-1</sup> for Pt<sub>2</sub>Ni<sub>1</sub>/CCC<sub>(a)</sub>, Pt<sub>2</sub>Ni<sub>1</sub>/CCC<sub>(b)</sub> (0.15 mg<sub>Pt</sub> cm<sup>-2</sup>), Pt<sub>2</sub>C<sub>0</sub>/CCC<sub>(c)</sub> (0.2 mg<sub>Pt</sub> cm<sup>-2</sup>) and Pt<sub>2</sub>C<sub>0</sub>/CCC<sub>(d)</sub> catalysts, respectively.
- Accomplished mass activity loss of 30.3% and 46-49.3% for Pt<sub>2</sub>Ni<sub>1</sub>/CCC<sub>(b)</sub>, Pt<sub>1</sub>C<sub>0</sub>/CCC<sub>(c)</sub> catalysts, respectively.
- Accomplished ECSA loss of 27.8% for the Pt<sub>1</sub>C<sub>0</sub>/CCC<sub>(c)</sub> catalyst.
- Accomplished mass activity of 0.44 A mg<sub>Pt</sub><sup>-1</sup> for Pt<sub>2</sub>Ni<sub>1</sub>/CNC catalyst.
- Achieved 0.3 A mg<sub>Pt</sub><sup>-1</sup> after 30 k cycles for Pt<sub>2</sub>Ni<sub>1</sub>/CNC catalyst.
- Achieved 1.25 A cm<sup>-2</sup> and 1.4 A cm<sup>-2</sup> at 0.58 V<sub>iR-free</sub> for the Pt<sub>2</sub>Ni<sub>1</sub>/CCC<sub>(c)</sub> catalyst at 1.5/1.8 and 1.5/2.0 stoichiometry, respectively under H<sub>2</sub>-air operating conditions (80°C, 40% RH, 150 kPa<sub>abs</sub>).

Introduction

Stable and highly active HCC was developed which shows higher performance than the commercial Pt/C at low loadings (between 0.04 and 0.4 mg cm<sup>-2</sup>). The hybrid cathode catalyst is a combination of nitrogen-containing CCC and platinum for oxygen reduction reaction [1-12]. Pt-alloy catalyst deposited on activated graphitic carbon support with high activity towards oxygen reduction was synthesized and its catalytic activity was evaluated [13-15].

Approach

Currently, the main strategies to decrease the platinum loading in cathode electrodes are based on the optimization of electrode structures and implementation of more active Pt alloy catalysts. The new approach used in this work consists of development of a HCC through a patented process. The goal of our second strategy is the synthesis of Pt-alloy catalysts deposited on activated graphitic carbon support.

Results

In this reporting period, procedures for CCC synthesis were optimized and the synergistic effect of CCC support and low Pt (5%) was studied. Furthermore, HCCs using various CCC with different BET surface areas as supports and Pt<sub>1</sub>Ni<sub>1</sub>/CNC catalysts were synthesized. The performance of the synthesized catalysts including ECSA, kinetic mass activity, catalyst durability after 30 k cycles, specific activity and initial high current performance were evaluated in a 25 cm<sup>2</sup> polymer electrolyte membrane fuel cell (PEMFC) under DOE suggested fuel cell operating conditions.

Carbon composite catalysts were prepared according to the procedures developed previously and used as catalyst supports. The ORR kinetics of as-received carbon (Ketjen black) and Ketjen black subjected to various surface modification steps is compared in Figure 1(a). The onset potential for ORR increases when the as-received carbon is subjected to various surface modifications including oxidation in HNO<sub>3</sub> and incorporation of nitrogen and
transition metals. The carbon composite catalyst (curve f in Figure 1a) showed an onset potential of 0.9 V vs. RHE and well-defined kinetic and mass transfer regions in 0.1 M HClO₄ electrolyte at room temperature. The H₂O₂ production for CCC was in the range between 2-3% (figure not shown).

The synergistic effect of CCC carbon composite catalyst used as the catalyst support and Pt catalyst was evaluated by depositing 5 wt% Pt on CCC and Ketjen black supports. The results are compared in Figure 1(b). As can be seen from the figure, the onset potential for ORR for CCC, 5% Pt/C and 5% Pt/CCC are 0.97 V and 1.01 V, respectively. The current density at 0.8 V (vs. the reversible hydrogen electrode, RHE) for the CCC, 5% Pt/C and 5% Pt/CCC catalysts are 0.3, 1.9 and 3.88 mA cm⁻², respectively. The highest open circuit potential of 1.01 V and current density measured at 0.8 V of 5% Pt/CCC clearly indicated the presence of the synergistic effect between CCC and Pt. The diffusion currents of CCC, 5% Pt/C and 5% Pt/CCC catalysts are 4.5, 4.9 and 5.6 mA cm⁻², respectively.

During the reporting period, we developed a new methodology to functionalize partially graphitized CCC and CNC supports through non-covalent π-π interaction using a bifunctional molecule, 1-pyrenecarboxylic acid (1-PCA). The functionalization resulted in an average Pt particle size of 2.5 ± 0.2 nm as measured by the X-ray diffraction studies using the Scherrer equation. A new coating and impregnation method was also developed to inhibit the Pt-alloy particle sintering during high temperature alloying process. The normal heat-treatment procedure resulted in an average Pt-alloy particle size of 10.8 nm while the new protective coating methodology resulted in 3.4 nm particles. The aggregation of Pt particles was restrained by the protective film used in this study.

Comparison of mass activities of various HCC catalysts (Pt-alloy deposited on CCC support) and conventional Pt/C catalyst is shown in Figure 2. As shown in the figure, the mass activities of HCC Pt/C catalyst, are nearly 3-4 times higher than that of conventional Pt/C, which confirms our initial studies for presence of a synergistic effect between
CCC and Pt or Pt-alloy in the USC developed Hybrid Cathode Catalyst. Pt₃Ni/CNC catalyst showed mass activities of 0.45 A mg⁻¹ Pt. The mass activities of Pt/C, Pt₃Ni/CNC(B), Pt₁Co₁/CNC(C) and Pt₁.₃Co₁/CNC(D) are 0.13, 0.33, 0.37 and 0.41 A mg⁻¹ Pt, respectively.

One of the primary challenges facing the development of PEMFCs for automotive and stationary power applications is the durability of the fuel cell catalyst and support. The DOE cycling protocol to evaluate the durability of the Pt₃Ni/CNC(B) and Pt₁Co₁/CNC(C) catalysts indicated mass activity loss of 46-49.3% and 30.3% after 30 k cycles, respectively. Furthermore, the Pt₁Co₁/CNC(C) catalysts showed ECSA loss of only 27.8% after 30 k cycles which is lower than the DOE target (40%) (Table 1). DOE cycling protocol was also performed to evaluate the durability of 50% Pt₂Ni₁/CNC-NA (NA-no acid treatment) catalysts. The ECSA, ORR mass activity, and H₂-air polarization curves were performed after 5,000, 10,000, 20,000, and 30,000 cycles. As shown in Figures 3 (a) and (b), the mass activity loss of 50% Pt₂Ni₁/CNC-NA is 31% and the ECSA loss of the Pt₂Ni₁/CNC-NA after 30 k cycles is only 26% which are lower than the 2017 DOE targets for mass activity and ECSA activity after 30 k cycles (40% loss).

The H₂-air fuel cell performance of Pt/C and HCC catalysts (Pt-alloy deposited on CCC support) is shown in Figure 4. The fuel cell operating conditions are given in the figure caption. The observed current densities are: 0.9 A cm⁻² for 46% Pt/C, 0.95 A cm⁻² for 30% Pt₃Co₁/CNC(B), and 1.25 A cm⁻² for 46% Pt₂Ni₁/CNC(C) at 1.5/1.8 stoichiometry. The Pt₂Ni₁/CNC(B) catalyst exhibited 1.4 A cm⁻² with an increased cathodic stoichiometry of 2.0.

Conclusions and Future Directions

Conclusions

- Accomplished onset potential for oxygen reduction reaction close to 0.9 V_{RHE} and <2.5% H₂O₂ production for the CCC support.
- Accomplished initial mass activities of 0.45, 0.33, 0.37, and 0.41 A mg⁻¹ Pt for Pt₂Ni₁/CNC(A), Pt₂Ni₁/CNC(B), Pt₁Co₁/CNC(C) and Pt₁.₃Co₁/CNC(D) catalysts, respectively.
- Accomplished initial mass activity of 0.44 A mg⁻¹ Pt for the Pt₂Ni₁/CNC catalyst.
- Accomplished mass activity loss of 30.3% and 46-49.3% after 30 k cycles for Pt₂Ni₁/CNC(B), Pt₁Co₁/CNC(C) catalysts, respectively.
Accomplished ECSA loss of 27.8% for the Pt\textsubscript{1}Co\textsubscript{1}/CCC\textsuperscript{(C)} catalyst.

Accomplished 0.3 A mg\textsubscript{Pt}\textsuperscript{-1} after 30 k cycles for the Pt\textsubscript{2}Ni\textsubscript{4}/CNC catalyst.

Achieved 1.25 A cm\textsuperscript{-2} and 1.4 A cm\textsuperscript{-2} at 0.58 V\textsubscript{iR-free} for the Pt\textsubscript{2}Ni/CCC\textsuperscript{(A)} catalyst at 1.5/1.8 and 1.5/2.0 stoichiometry, respectively, under H\textsubscript{2}-air operating conditions (80°C, 40% RH, 150 kP\textsubscript{abs} outlet pressure).

Future anticipated accomplishments are to:

- Confirm durability of kinetic mass activity of at least 0.24 A mg\textsubscript{Pt}\textsuperscript{-1} after 30 k cycles or less than 40% loss of mass activity at 0.9 V\textsubscript{iR-free} and ECSA loss less than 40% for the HCC catalysts.
- Accomplish durability of catalyst support according to DOE target of less than 40% loss of mass activity at 0.9 V\textsubscript{iR-free} and less than 40% loss of ECSA.
- Accomplish high current density performance and durability in H\textsubscript{2}/air fuel cells (80°C, 40% RH, 150 kP\textsubscript{abs} 1.5/1.8 stoichiometry).
- Reproducibility of catalyst performance evaluation in at least three MEAs in two laboratories using 25 and 50 cm\textsuperscript{2} cells.
- Demonstrate facile scale-up synthesis of the catalysts.

Special Recognitions & Awards/Patents Issued


FY 2012 Publications/Presentations

Publications


Presentations

1. Branko N. Popov, Tae-keun Kim, Xie Tianyuan, Prabhu Ganesan, and Hansung Kim, Development of ultra-low platinum alloy cathode catalyst for PEM fuel cells, 220\textsuperscript{th} ECS Meeting, Boston, MA, October 9–14, 2011.
2. S. Huang, P. Ganesan, and B.N. Popov, Titanium Dioxide-Supported Platinum Catalysts, 220\textsuperscript{th} ECS Meeting, Boston, MA, October 9–14, 2011.

References


