V.A.11 Development of Ultra-Low Platinum Alloy Cathode Catalysts for Polymer Electrolyte Membrane Fuel Cells

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Overall Objectives

- Synthesize carbon composite catalyst (CCC) support and optimize the parameters that control the number of catalytic sites.
- Develop low cost and durable hybrid cathode catalyst (HCC).
- Develop Pt and Pt-alloy/activated graphitic carbon catalyst.
- Optimize the procedures for the formation of more active Pt-alloy catalysts.
- Develop facile scale up catalyst synthesis procedure (at least 100 g).
- Demonstrate kinetic mass activity in H_2/O_2 fuel cell higher than DOE target of 0.44 A mg_{PGM}⁻¹ and durability of the mass activity (\leq 40% loss of initial mass activity).
- Demonstrate high current performance in H_2/air fuel cell that meets DOE targets and durability of high current performance in H_2/air under potential cycling (0.6-1.0 V)

and potential holding (1.2 V) experimental conditions (\leq 30 mV loss at 0.8 A cm⁻²).

• Construct short stack (50 cm² up to 10 cells) and evaluate the performance under simulated automotive conditions.

Fiscal Year (FY) 2013 Objectives

- Evaluation of different strategies for the optimization of HCC with total loadings of 0.2 mg_{Pt} cm⁻² /membrane electrode assembly (MEA):
 - Initial and durability of kinetic mass activities.
 - Catalyst and support durability under potential cycling and potential holding experimental conditions, respectively.
- Synthesis and performance evaluation of Pt/USCactivated graphitic carbon (AGC) catalyst with total loadings of 0.2 mg_p cm⁻²/MEA:
 - Initial and durability of kinetic mass activities.
 - Catalyst and support durability under potential cycling and potential holding experimental conditions, respectively.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

In this project, studies are being conducted to develop highly active and stable ultra-low Pt loading cathode catalysts for polymer electrolyte membrane fuel cells. This includes HCC and Pt/USC-AGC catalysts using procedures developed at USC. These catalysts have the potential to meet the 2017 DOE technical target for electrocatalysts for transport applications as shown in Table 1.

FY 2013 Accomplishments

Achieved initial mass activity of 0.38 A mg_{Pt}⁻¹ and 0.2 A mg_{Pt}⁻¹ after 30k cycles, and 0.19 A mg_{Pt}⁻¹ (after 400 h potential holding) for the HCC catalyst.

| Characteristic | Units | 2017 Targets | Status |
|---------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|-------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| PGM total content | g/kW (rated) | 0.125 | 0.32 <u>Pt/USC-AGC</u> 0.34 <u>Pt/CCC</u> |
| PGM total loading | mg cm ⁻² | 0.125 | 0.2 |
| Mass activity (80°C, 100% RH, 150 kPa _{abs} .) | A/mg _{Pt} @ 0.9 V _{iR-free} | 0.44 | 0.38 A/mg _{Pt} <u>HCC</u> 0.25 A/mg _{Pt} <u>Pt/USC-AGC</u> |
| Catalyst durability (30,000 cycles, 0.6-1.0 V, 50 mV/s, 80/80/80, 100 kPa _{abs} ., H ₂ /N ₂) | % Mass activity loss % ECSA loss mV loss @ 0.8 A cm ⁻² | ≤40% ≤40% ≤30 @ 0.8 A cm² | $\label{eq:HCC} \frac{\text{HCC}}{47\% \text{ loss (MA)}} \\ 15\% \text{ loss (ECSA)} \\ 46 \text{ mV loss (H_2-air)} \\ \frac{\text{Pt/USC-AGC}}{52\% \text{ loss (MA)}} \\ 51\% \text{ loss (ECSA)} \\ 78 \text{ mV loss (H_2-air)} \\ \end{array}$ |
| Support durability (1.2 V for 400 h at 80°C, H ₂ -N _{2, 150} kPa _{abs.} 100% RH) | % Mass activity loss % ECSA loss | ≤40% ≤40% ≤30 mV @ 0.8 A cm ⁻² | $\begin{tabular}{lllllllllllllllllllllllllllllllllll$ |

TABLE1. Progress towards Meeting Technical Targets for Electrocatalysts for Transport Applications

PGM – platinum-group metal; iR – internal resistance; RH – relative humidity; ECSA – electrochemical surface area; MA – mass activity

- Accomplished potential losses (iR-corrected) of 46 and 29 mV after 30k cycles and 400 h potential holding, respectively for the HCC catalyst.
- Achieved initial mass activity of 0.25 A mg_{Pt}⁻¹ and 0.12 A mg_{Pt}⁻¹ after 30k cycles, and 0.17 A mg_{Pt}⁻¹ (after 400 h potential holding) for the Pt/USC-AGC catalyst.
- Accomplished potential losses (iR-corrected) of 78 mV and 18 mV after 30 k cycles and 400 h potential holding, respectively for the Pt/USC-AGC catalyst.

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INTRODUCTION

Stable, highly active Pt/CCC and HCCs were developed that show higher performance than the commercial Pt/C at low loadings ($\leq 0.1 \text{ mg cm}^{-2}$). The hybrid cathode catalyst is a combination of nitrogen-containing CCC and platinum, which shows higher activity for the oxygen reduction reaction (ORR) [1-12]. Pt catalyst deposited on USC activated graphitic carbon (Pt/USC-AGC) support with high activity towards oxygen reduction was synthesized and its catalytic activity was evaluated.

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 hybrid cathode catalyst through a patented process. In brief, in-house developed procedures were used for the HCC synthesis including (a) CCC support synthesis using transition metal-assisted low temperature graphitization process, (b) surface modification of the CCC support for uniform Pt deposition, (c) platinum deposition on CCC support (Pt/CCC) using a modified polyol process, and (d) high temperature annealing process to control the catalyst particles size of the HCC catalyst. The goal of our second strategy is the synthesis of Pt catalyst deposited on activated graphitic carbon support developed at USC (Pt/USC-AGC).

RESULTS

In this reporting period (FY 2013), procedures for the synthesis of CCC and USC-AGC were optimized and used as catalyst supports for the preparation of Pt/CCC, HCC and Pt/USC-AGC catalysts. The performance of these catalysts was studied in 25-cm² single fuel cells according to the testing protocol suggested by the U.S. DRIVE Partnership/ Fuel Cell Technical Team. The catalyst durability was evaluated by cycling the cathode potential between 0.6 and 1.0 V under H_2/N_2 (200/75 cc min⁻¹) in the anode and cathode compartments, respectively at a cell temperature of 80°C and 100% RH. The support durability was evaluated by holding the potential at 1.2 V (vs. anode) under H_2/N_2 in the anode and cathode compartments, respectively at a cell temperature of 80°C, 100% RH and 150 kPa back pressure. The mass activity was evaluated under the following conditions: H_2/O_2 (stoic. 2/9.5); 100% RH; 80°C; and 150 kPa_{abs} back pressure. The H₂/air fuel cell performance was evaluated under the following conditions: H₂/air (stoic. 1.5/1.8); 40% RH; 80°C; and 150 kPa_{abs} back pressure.

Platinum was deposited on CCC support by a polyol method [13]. The initial fuel cell performances of 35 and 40% Pt/CCC under H_2/O_2 (constant flow, 750/750 sccm) and H_2/air (40% RH, 80°C, and 150 kPa_{abs} back pressure) are shown in Figure 1(a) and Figure 1(b), respectively. Figure 1(a) shows that both 35% and 40% Pt/CCC catalysts exhibit ~2.1 A cm⁻² at 0.7 V_{iR-free}. The H_2/air fuel cell testing (Figure 1b) shows 1.25 A cm⁻² for both the catalysts at 0.58 V_{iR-free} (1.5/1.8 stoic.) and 1.35 A cm⁻² at 0.58 V_{iR-free} (1.5/2.0 stoichiometry). This high fuel cell performance is due to the synergistic effect between the Pt and CCC support, which itself possesses catalytic active sites for ORR.

The HCC catalyst was prepared by impregnating a transition metal salt in Pt/CCC, followed by the application of a protective coating and high temperature pyrolysis developed at USC. The protective coating prevented the Pt-alloy particle growth and uniform Pt-alloy particles of ~4.0 nm could be distributed on the CCC support. The HCC catalyst was subjected to both catalyst and support durability studies in a 25-cm² area MEA and the results are summarized and compared with that of a commercial 46% Pt/C catalyst in Table 2. The stability of mass activity of HCC and commercial 46% Pt/C catalysts are compared in Figure 2 which shows an initial mass activity of 0.38 A mg_{Pt}^{-1} and mass activity of 0.20 A mg_{Pt}^{-1} after 30k cycles in H_2/O_2 , corresponding to a loss of 47% for the HCC catalyst. The commercial 46% Pt/C catalyst showed an initial and final (after 30k cycles) mass activities of 0.18 and 0.06 A $mg_{p_{t}}^{-1}$, respectively (67% loss). The ECSA of HCC

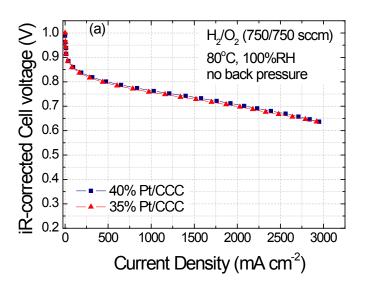


FIGURE 1(a). H₂/O₂ fuel cell performance of 35% and 40% Pt/CCC catalysts. The fuel cell operating conditions are: H₂/O₂ (750/750 sccm), 80°C, 100% RH, no back pressure. Nafion[®] NRE 212 membrane was used as the electrolyte.

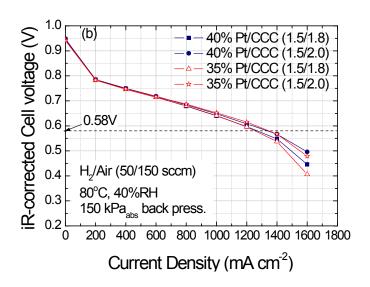


FIGURE 1(b). H₂/air fuel cell performance of 35% and 40% Pt/CCC catalysts. The fuel cell operating conditions are: H₂/air (1.5/1.8), 59°C, 40% RH, 150 kPa back pressure. Nafion[®] NRE 212 membrane was used as the electrolyte.

catalyst decreased from 23.2 to 19.8 m² g⁻¹ after 30k cycles (15% loss). The H₂/air fuel cell polarization curves showed an initial H₂/air performance of 800 mA cm⁻² at 0.607 V_{iR-free} and 0.561 V_{iR-free} after 30k cycles (iR-corrected voltage loss is 46 mV). The corresponding cell potential loss is 53 mV after 30k cycles. The loss in cell voltage is slightly higher than the 2017 DOE target (\leq 30 mV loss after 30k cycles). The cell potential loss of 53 mV after 30k cycles is much lower than that observed for the commercial 46% Pt/C catalyst (149 mV loss after 30k cycles) as shown in Table 2.

The results of support durability for the HCC catalyst are summarized in Table 2. The HCC catalyst showed an initial mass activity of 0.38 A mg_{pt}⁻¹, which decreased to 0.19 A mg_{pt}⁻¹ after 400 h potential holding at 1.2 V. The HCC catalyst exhibited an initial H₂/air performance of 800 mA cm⁻² at 0.644 V_{iR-free} and decreased to 0.615 V_{iR-free} after 400 h (iR-correcetd voltage loss is 29 mV). The cell voltage loss is also 29 mV after 400 h holding. The DOE 2017 target is \leq 30 mV loss after 400 h potential holding. The ECSA decreased from 21.3 to 16.2 m² g⁻¹ after 400 h (24% loss). These results indicate that the HCC catalyst is stable at high potentials due to the highly graphitized nature of the CCC support.

Platinum was deposited on USC-AGC support by a polyol method [13] with a particle size of ~3.1 nm. The catalyst durability test was performed by cycling the cathode between 0.6 and 1.0 V under H_2/N_2 and the results are summarized in Table 3. The Pt/USC-AGC catalyst shows an initial mass activity of 0.25 A mg_{Pt}⁻¹, which decreased to 0.12 A mg_{Pt}⁻¹ after 30k cycles (52% loss). The ECSA decreased from 31.4 m² g⁻¹ to 15.3 m² g⁻¹, corresponding to a loss of 51% after 30k cycles.

TABLE 2. Summary of Catalyst Stability Test (30k Potential Cycling between 0.6 and 1.0 V) and Support Stability Test (Potential Holding at 1.2 V for 400 h) for the HCC Catalyst

| нсс | Particle size (nm) | Mass activity (A mg _{Pt} ⁻¹) | | ECSA (m² g⁻¹) | | Cell voltage loss at 800 mA cm ⁻² (mV) | |
|-------------------------------------------------|-----------------------|------------------------------------------------------|--------------------------------------------------------------------------------------|---------------|---------------------------------------------------------------------------------------|------------------------------------------------------|--------------------------------------------|
| | | Initial | Final | Initial | Final | V _{Cell} | V _{iR-free} |
| Catalyst Durability Support Durability | 4.0 | <u>0.38</u> 0.38 | 0.2 (<u>47% loss</u>) (30k cycles) 0.19 (<u>50% loss</u>) (400 h) | 23.2 21.3 | 19.8 (15% loss) (30k cycles) 16.2 (<u>24% loss</u>) (400 h) | 53 (30k cycles) 29 (400 h) | 46 (30k cycles) 29 (400 h) |
| Pt/C Catalyst Durability | 2.2 | <u>0.18</u> | 0.06 (<u>67% loss</u>) (30k cycles) | 67.8 | 11.8 (<u>82.6% loss</u>) (30k cycles) | <u>149</u> (30k cycles) | <u>142</u> (30k cycles) |

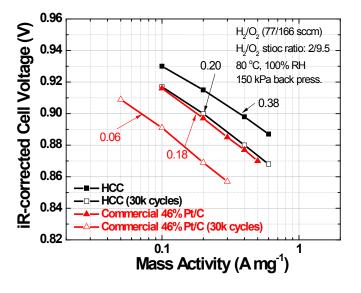


FIGURE 2. Comparison of mass activities of HCC and commercial 46% Pt/C catalysts before and after 30k potential cycling between 0.6 and 1.0 V. The fuel cell operating conditions are: H_2/O_2 (2.0/9.5), 80°C, 100% RH, 150 kPa_{abs} back pressure. Nafion[®] NRE 212 membrane was used as the electrolyte.

Table 3 also shows that the Pt/USC-AGC catalyst exhibits an initial H₂/air performance of 800 mA cm⁻² at 0.668 V_{iR-free} which decreased to 0.590 V_{iR-free} after 30k cycles. The Pt/USC-AGC catalyst showed iR-corrected voltage loss of 78 mV and cell voltage loss of 82 mV after 30k cycles which are higher than the 2017 DOE targets (\leq 30 mV loss after 30k cycles). The cell potential loss of 82 mV after 30k cycles is much lower than that observed for the commercial 46% Pt/C catalyst (149 mV loss after 30k cycles) as shown in Table 2.

Additionally, the initial and final (after 30k cycles) H_2/O_2 (750/750 sccm) fuel cell performances of Pt/USC-AGC are compared in Figure 3. The initial and final fuel cell performances are identical at high- and low-potential regions for the Pt/USC-AGC catalyst. This result indicates that the

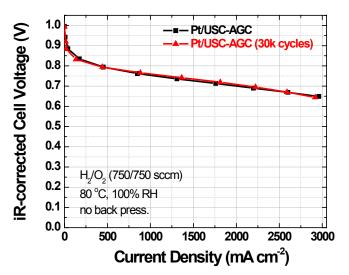


FIGURE 3. Comparison of H_2/O_2 fuel cell performance of Pt/USC-AGC catalyst before and after 30k potential cycling between 0.6 and 1.0 V. The fuel cell operating conditions are: H_2/O_2 (750/750 sccm), 80°C, 100% RH, no back pressure. Nafion[®] NRE 212 membrane was used as the electrolyte.

catalyst activity of Pt/USC-AGC catalyst is stable during the potential cycling experiment.

The support durability test for the Pt/USC-AGC catalyst was evaluated in 25-cm² area MEAs. The mass activity and H₂/air fuel cell performance was measured at regular intervals and the results are summarized in Table 3. The Pt/USC-AGC catalyst shows an initial mass activity of 0.25 A mg_{Pt}⁻¹, which decreased to 0.17 A mg_{Pt}⁻¹ after 400 h potential holding at 1.2 V. The observed mass activity loss of 32% and ECSA loss of 6% are much lower than the 2017 DOE target of \leq 40% loss after 400 h potential holding.

The initial and final (400 h) H₂/air fuel cell polarization curves are compared in Figure 4. The Pt/USC-AGC catalyst exhibits an initial H₂/air performance of 800 mA cm⁻² at 0.671 V_{iR-free} and decreased to 0.653 V_{iR-free} after 400 h potential holding at 1.2 V. The voltage losses are 18 (iR-free)

TABLE 3. Summary of Catalyst Stability Test (30k Potential Cycling between 0.6 and 1.0V) and Support Stability Test (Potential Holding at 1.2 V for 400 h) for the Pt/USC-AGC Catalyst

| Pt/AGC | Particle size (nm) | Mass activity (A mg _{Pt} ⁻¹) | | ECSA (m ² g ⁻¹) | | Cell voltage loss at 800 mA cm ⁻² (mV) | |
|------------------------|-----------------------|------------------------------------------------------|---------------------------------------------|----------------------------------------|---------------------------------------------|------------------------------------------------------|----------------------|
| | | Initial | Final | Initial | Final | V _{Cell} | V _{iR-free} |
| Catalyst Durability | 3.1 | 0.25 | 0.12 (<u>52% loss</u>) (30k cycles) | 31.4 | 15.3 (<u>51% loss</u>) (30k cycles) | 82 (30k cycles) | 78 (30k cycles) |
| Support Durability | 3.1 | 0.25 | 0.17 (<u>32% loss</u>) (400 h) | 31.4 | 29.5 (<u>6% loss</u>) (400 h) | 29 (400 h) | 18 (400 h) |

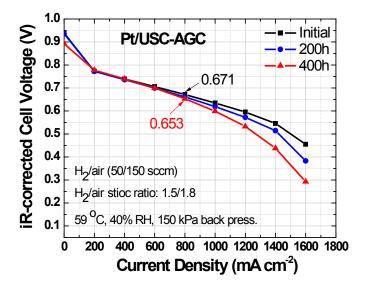


FIGURE 4. H₂/air fuel cell performance of Pt/AGC before and after 400 h potential holding at 1.2 V. The fuel cell operating conditions are: H₂/air (1.5/1.8), 59°C, 40% RH, 150 kPa back pressure. Nafion[®] NRE 212 membrane was used as the electrolyte.

and 29 mV (cell voltage) after 400 h cycles. The DOE 2017 target is \leq 30 mV loss after 400 h potential holding. These results indicate that the Pt/USC-AGC catalyst is stable at high potentials due to the highly graphitized nature of the USC-AGC support.

Further catalyst and MEA optimization studies are in progress in order to increase the high current density performance of the HCC and Pt/USC-AGC catalysts to meet the 2017 DOE targets.

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions

Achieved initial mass activity of 0.38 A mg_{Pt}⁻¹ and 0.2 A mg_{Pt}⁻¹ after 30k cycles (47% loss) and 0.19 A mg_{Pt}⁻¹ (50% loss after 400 h potential holding) for the HCC catalyst.

- Accomplished iR-corrected potential losses of 46 mV and 29 mV after 30k cycles and 400 h potential holding experiments, respectively for the HCC catalyst.
- Accomplished ECSA losses of 15% and 24% after 30k cycles and 400 h potential holding experiments, respectively for the HCC catalyst.
- Achieved initial mass activity of 0.25 A mg_{Pt}⁻¹ and 0.12 A mg_{Pt}⁻¹ after 30k cycles (52% loss) and 0.17 A mg_{Pt}⁻¹ (32% loss after 400 h potential holding) for the Pt/USC-AGC catalyst.
- Accomplished iR-corrected potential losses of 78 mV and 18 mV after 30k cycles and 400 h potential holding, respectively for the Pt/USC-AGC catalyst.
- Accomplished ECSA losses of 51% and 6% after 30k cycles and 400 h potential holding experiments, respectively for the Pt/USC-AGC catalyst.

Future Anticipated Accomplishments

- Synthesis of highly stable and highly graphitized CCC and AGC supports with Brunauer-Emmett-Teller surface area of 150-200 m²/g.
- Transition metal content optimization studies and synthesis of HCC and Pt-alloy/USC-AGC catalysts containing low transition metal content (<8 wt%) in the alloy.
- Optimizing the procedures to purify the high temperature treated CCC and USC-AGC.

The goal is to select a best performing catalyst which satisfies the 2017 DOE requirements of $\leq 40\%$ loss of mass activity, $\leq 40\%$ loss of ECSA and ≤ 30 mV loss at 0.8 A/cm² under H₂-air after 30k potential cycling (between 0.6 and 1.0 V) and potential holding (at 1.2 V for 400 h) experiments.

FY 2013 PUBLICATIONS/PRESENTATIONS

Publications

1. Ákos Kriston, Tianyuan Xie, David Gamliel, Prabhu Ganesan, Branko N. Popov, "Effect of Ultra-Low Pt Loading on Mass Activity of PEM Fuel Cells," *J. Power Sources*, **243** (2013) 958-963.

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3. Branko N. Popov, Tianyuan Xie, Taekeun Kim, Won-suk Jung, Akos Kriston Brian Murphy and Prabhu Ganesan, "Development of Ultra-Low Pt Alloy Cathode Catalyst for PEM Fuel Cells," *ECS Transactions*, **50** (2) (2013) 773-785.

4. Tianyuan Xie, Taekeun Kim, Won Suk Jung, Kriston Akos Prabhu Ganesan and Branko N. Popov, "Development of Highly Active Pt₂Ni/C Catalyst for PEM Fuel Cell," *ECS Transactions*, **50** (2) (2013) 1615-1626.

5. Taekeun Kim, Won Suk Jung, Tianyuan Xie, Akos Kriston, Prabhu Ganesan, David Gamliel, Brian Murphy and Branko N. Popov, "Development of Hybrid Cathode Catalyst for PEM Fuel Cells," *ECS Transactions*, **50** (2) (2013) 1875-1885.

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Presentations

1. Akos Kriston, Tianyuan Xie, Taekeun Kim, Won Suk Jung, David Gamliel, Brian Murphy Prabhu Ganesan, Branko N. Popov, Analyzing the effect of Ultra-Low Pt Loading on Mass and Specific Activity of PEM Fuel Cells, *222nd ECS Meeting*, Honolulu, HI, October 7–12, 2012.

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3. Tianyuan Xie, Won Suk Jung, Taekeun Kim, Kriston Akos Prabhu Ganesan and Branko N. Popov, Development of Highly Active Pt₂Ni/CCC Catalyst for PEM Fuel Cell, *222nd ECS Meeting*, Honolulu, HI, October 7–12, 2012.

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

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