

V.A.10 Development of Ultra-Low Platinum Alloy Cathode Catalysts for PEM Fuel Cells

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(≤ 30 mV loss at 0.8 A cm^{-2}) under H_2/air using DOE potential cycling (0.6-1.0 V, 30k cycles, potential cycling (1.0-1.5 V), and potential holding tests (1.2 V, 400 h).

- Scale up synthesis of supports (CCC and A-CCC) and catalysts (Pt/CCC, doped-Pt/CCC, Pt/A-CCC, and doped-Pt/A-CCC).

Fiscal Year (FY) 2014 Objectives

- Synthesis and performance evaluation of Co-doped Pt/CCC catalyst using partially graphitized CCC support having Brunauer-Emmett-Teller (BET) surface area of $400 \text{ m}^2 \text{ g}^{-1}$ and well-defined pore-size and pore-size distribution.
 - Initial high kinetic mass activity under $\text{H}_2\text{-O}_2$
 - Initial high current density performance under $\text{H}_2\text{-air}$
 - Catalyst durability under potential cycling experimental conditions
- Synthesis and performance evaluation of Pt/A-CCC catalyst using graphitized A-CCC support having BET surface area $200 \text{ m}^2 \text{ g}^{-1}$ and well-defined pore-size and pore-size distribution.
 - Initial high kinetic mass activity under $\text{H}_2\text{-O}_2$
 - Initial high current density performance under $\text{H}_2\text{-air}$
 - Catalyst durability and support stability under potential cycling and potential holding experimental conditions, respectively

Overall Objectives

- Develop a cost-effective, high-volume synthesis procedure to manufacture highly stable and catalytically active partially graphitized carbon composite catalyst (CCC) and graphitized activated carbon composite catalyst (A-CCC) supports.
 - Achieve onset potential close to 0.9 V vs. the reference hydrogen electrode (RHE) for oxygen reduction reaction (ORR) with well-defined kinetic and mass transfer regions for CCC and A-CCC supports.
 - Achieve ≤ 30 mV loss at 0.8 A cm^{-2} in H_2/air fuel cell 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 non-metallic catalytic sites from the support and compressive Pt-lattice catalyst.
 - Demonstrate mass activity of $\geq 0.44 \text{ A mg}_{\text{PGM}}^{-1}$ in H_2/O_2 fuel cell, initial high current performance under H_2/air ($< 0.125 \text{ g}_{\text{PGM}} \text{ kW}^{-1}$ rated power density) and stability of mass activity ($\leq 40\%$ loss) and stability of high current density performance

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 PEM fuel cells. The catalysts developed in this project are

Pt/CCC, doped-Pt/CCC, Pt/A-CCC, and doped-Pt/A-CCC using procedures developed at USC. These catalysts have the potential to meet the 2017 DOE technical target for electrocatalysts for automotive applications as shown in Table 1.

- Accomplished 32% ECSA loss (2017 DOE target is $\leq 40\%$ loss) and 40 mV loss (iR-corrected) after 30k cycles (0.6-1.0 V) for the doped-Pt/CCC catalyst (2017 DOE target is ≤ 30 mV loss at 0.8 A cm^{-2}). (BET surface area of the CCC support is $400 \text{ m}^2 \text{ g}^{-1}$.)

FY 2014 Accomplishments

- For the first time, USC has reported the development of Pt/A-CCC catalyst which shows high support stability both under 1.2 V potential holding and under 1.0-1.5 V potential cycling conditions. (BET surface area of the A-CCC support is $200 \text{ m}^2 \text{ g}^{-1}$.)
- Advances have been made in approaching the DOE 2017 power density (rated) target of $0.125 \text{ g}_{\text{PGM}} \text{ kW}^{-1}$ with a Pt/A-CCC catalyst ($0.196 \text{ g}_{\text{PGM}} \text{ kW}^{-1}$).
- Achieved 24 mV loss at 1.5 A cm^{-2} after 5k cycles between 1.0 V and 1.5 V for the Pt/A-CCC catalyst which satisfies the 2017 DOE target for support stability (≤ 30 mV loss at 1.5 A cm^{-2}).
- Accomplished 32% mass activity loss and 30% ECSA loss, and 27 mV loss at 0.8 A cm^{-2} after 400 h potential holding (1.2 V) for the Pt/A-CCC catalyst. These values meet the 2017 DOE targets for support stability ($\leq 40\%$ loss of initial mass activity and $< 40\%$ loss of initial ECSA after 400 h).
- Achieved initial mass activity of $0.44 \text{ A mg}_{\text{PGM}}^{-1}$ (2017 DOE target is $0.44 \text{ A mg}_{\text{PGM}}^{-1}$) and $0.25 \text{ A mg}_{\text{PGM}}^{-1}$ (2017 DOE target is $0.26 \text{ A mg}_{\text{PGM}}^{-1}$) after 30k cycles (0.6-1.0 V) for the doped-Pt/CCC catalyst. (BET surface area of the CCC support is $400 \text{ m}^2 \text{ g}^{-1}$.)



INTRODUCTION

Novel methodologies were developed at USC to synthesize A-CCC and CCC [1-14] supports. Highly active and stable Pt/CCC, Pt/A-CCC, doped-Pt/CCC, and doped-Pt/A-CCC catalysts are developed that show higher performance than the commercial Pt/C at low loadings ($\leq 0.1 \text{ mg cm}^{-2}$) [1-5]. These catalysts are a combination of non-metallic active site containing CCC and platinum or compressive Pt lattice catalyst, which shows higher activity for the ORR through synergistic effect. Pt catalyst deposited on CCC and A-CCC supports with high activity towards ORR was synthesized and its catalytic activity and stability were evaluated using potential cycling (0.6-1.0 V for 30k cycles) and potential holding (1.2 V for 400 h) experiments.

APPROACH

In order to develop ultra-low Pt loading catalyst for automotive applications, the research at USC was aimed at developing catalytically active and stable supports having $200\text{-}400 \text{ m}^2 \text{ g}^{-1}$ BET surface area with well-defined pore-size and pore-size distribution to sustain potential cycling and potential holding experiments. The CCC support was synthesized through (i) surface modification with acids and

TABLE 1. Progress towards Meeting Technical Targets for Electrocatalysts for Automotive Applications.

Characteristic	Units	2017 Targets	FY 2014 Status
PGM total content	g kW^{-1} (rated)	0.125	0.196 (Pt/A-CCC) 0.241 (Doped-Pt/CCC)
PGM total loading	mg cm^{-2}	0.125	0.2
Mass activity (H_2/O_2 (2/9.5 stoic.) 80°C , 100% RH, $150 \text{ kPa}_{\text{abs}}$)	$\text{A mg}_{\text{Pt}}^{-1}$ @ $0.9 \text{ V}_{\text{iR-free}}$	0.44	0.44 (Doped-Pt/CCC)
Catalyst durability (30k cycles, 0.6-1.0 V, 50 mV/s, 80°C , H_2/N_2 , 100% RH, No back press.)	% Mass activity (MA) loss % ECSA loss mV loss @ 0.8 A cm^{-2}	$\leq 40\%$ $\leq 40\%$ $\leq 30 \text{ mV}$	Catalyst 1: Pt/A-CCC 50% loss (MA) 41% loss (ECSA) 72 mV loss (H_2 -air)
			Catalyst 2: Doped-Pt/CCC 43% loss (MA) 32% loss (ECSA) 40 mV loss (H_2 -air)
Support stability (1.2 V for 400 h 80°C , H_2/N_2 , 100% RH, $150 \text{ kPa}_{\text{abs}}$)	% Mass activity (MA) loss % ECSA loss mV loss @ 0.8 A cm^{-2}	$\leq 40\%$ $\leq 40\%$ $\leq 30 \text{ mV}$	Catalyst 1: Pt/A-CCC 32% loss (MA) 30% loss (ECSA) 27 mV loss (H_2 -air)

RH – relative humidity

inclusion of oxygen groups, (ii) metal catalyzed pyrolysis, and (iii) chemical leaching to remove excess metal used to dope the support. The A-CCC support was synthesized through a stabilization process to remove electrochemically unstable amorphous carbon from the support. A novel surface modification process was developed to achieve uniform Pt deposition on the CCC and A-CCC supports. Pt deposition was carried out using a modified polyol process to synthesize Pt/CCC and Pt/A-CCC catalysts with particle size in the range 3-5 nm. A protective coating method was also developed to inhibit particle growth during heat treatment for the synthesis of doped-Pt/CCC and dope-Pt/A-CCC catalysts. The novelty of the method is that the doping metal is present within the CCC or A-CCC supports which diffuses during controlled heat treatment to form doped-Pt catalysts having compressive Pt lattices. A schematic of USC methodology of preparing Pt and doped-Pt catalysts is shown in Figure 1.

RESULTS

Our approach in FY 2013 was to synthesize ultra-low Pt loading catalysts by optimizing the properties of the support. Based on our previous experience in synthesizing various CCC supports, our target in FY 2014 was to synthesize A-CCC support with optimized BET surface area, pore size and pore-size distribution to sustain potential cycling and potential holding experiments.

The BET surface area, pore-size, and pore-size distribution of the partially graphitized CCC support was tailored using various procedures developed at USC. The CCC support showed BET surface area of $400 \text{ m}^2 \text{ g}^{-1}$ with pore-size distribution in the range between 4 nm and 7 nm. Furthermore, the CCC support showed very high activity with an onset potential of 0.87 V vs. RHE for ORR and well-defined kinetic and mass transfer regions (Results were reported in FY 2012 annual report).

Doped-Pt/CCC with an average particle size of $\sim 4.0 \text{ nm}$ was synthesized through a controlled heat-treatment procedure developed at USC. The catalyst durability of doped-Pt/CCC catalyst was evaluated using a potential

cycling protocol (cycling between 0.6 V and 1.0 V). Figures 2a and 2b present the durability of mass activity and durability of H_2 -air fuel cell performance of doped-Pt/CCC catalyst subjected to potential cycling in a 25 cm^2 membrane electrode assembly. The doped-Pt/CCC catalyst showed initial mass activity of $0.44 \text{ A mg}_{\text{PGM}}^{-1}$ and $0.25 \text{ A mg}_{\text{PGM}}^{-1}$ after 30k cycles corresponding to 43% loss. The ECSA decreased from $74 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ to $50 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ after 30k cycles (32% loss). The H_2 -air fuel cell polarization test showed initial current density of 1.4 A cm^{-2} at $0.6 \text{ V}_{\text{iR-free}}$. The potential loss at 0.8 A cm^{-2} was used as a metric to evaluate the stability of the catalyst under potential cycling. Initially, the cell exhibited a cell voltage of $0.706 \text{ V}_{\text{iR-free}}$ and after 30k cycles, it decreased to $0.666 \text{ V}_{\text{iR-free}}$ at 0.8 A cm^{-2} with a cell potential loss of 40 mV. The cell potential loss is very close to that of 2017 DOE target ($\leq 30 \text{ mV}$ loss after 30k cycles). In the case of commercial Pt/C (46.7% Pt supported on high-surface-area carbon, Tanaka Kikinokogyo [TKK] Corporation, Japan), the mass activity loss and ECSA loss are 56% and 83%, respectively. The commercial Pt/C showed iR-corrected cell voltage loss of 284 mV at 0.7 A cm^{-2} after 30k cycles, since the polarization curve did not show any activity beyond 0.7 A cm^{-2} after 30k cycles. The catalyst durability study results of doped-Pt/CCC and commercial Pt/C catalysts are summarized in Table 2.

Based on our studies using the CCC support with BET surface area of $400 \text{ m}^2 \text{ g}^{-1}$, the following observation is made: In order to dope the Pt catalyst with transition metals, it is necessary to use high surface area carbon support which results in catalysts with very good catalyst stability under potential cycling conditions (0.6-1.0 V). The doped-Pt/CCC catalyst showed 100-120 mV loss in potential holding experiment and further optimization studies are in progress to improve the support stability at 1.2 V.

In order to further improve the support stability at high potentials, a novel process was developed to stabilize and activate the support through various treatments including a first heat treatment, leaching, and a second heat treatment to remove the electrochemically unstable amorphous carbon. The resulting graphitized A-CCC with a BET surface area

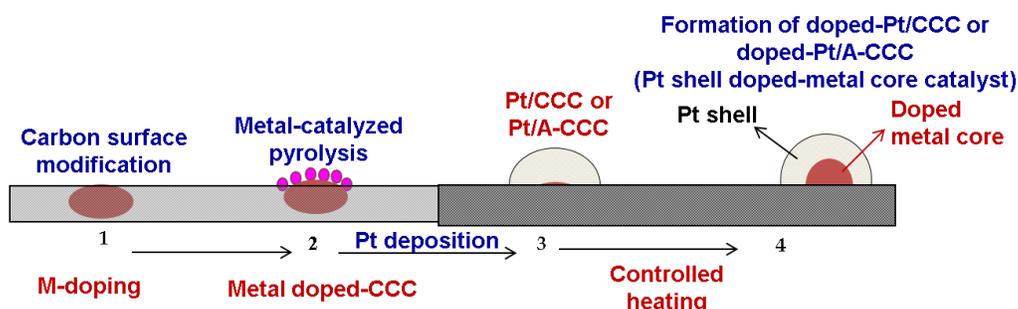


FIGURE 1. Schematic of synthesis procedure for Pt/CCC, Pt/A-CCC, doped-Pt/CCC, and doped-Pt/A-CCC catalysts developed at USC.

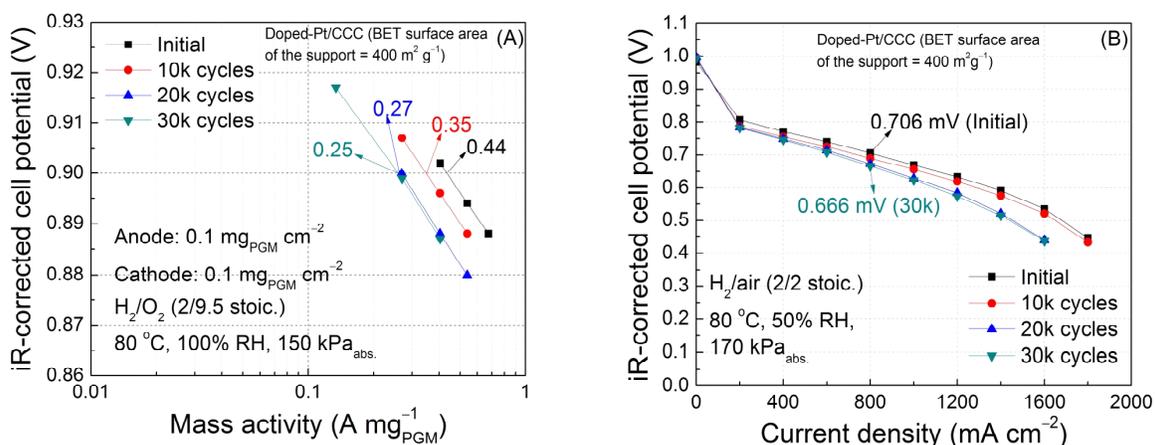


FIGURE 2. (A) Comparison of mass activities of doped-Pt/CCC catalyst before and after 30k potential cycling between 0.6 and 1.0 V. The catalyst loading is $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ on both the anode and cathode electrodes. The fuel cell operating conditions are: H_2/O_2 (2.0/9.5), 80°C , 100% RH, $150 \text{ kPa}_{\text{abs}}$ back pressure. Nafion® NRE 212 membrane is used as the electrolyte. (B) H_2/air fuel cell performance of doped Pt/CCC catalyst subjected to 30k potential cycling between 0.6 V and 1.0 V. The catalyst loading is $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ on both the anode and cathode electrodes. The fuel cell operating conditions are: H_2/air (2/2 stoic.), 80°C , 50% RH, $170 \text{ kPa}_{\text{abs}}$ back pressure. Nafion® NRE 212 membrane is used as the electrolyte.

TABLE 2. Summary of Catalyst Durability Test (30k potential cycling between 0.6 V and 1.0 V) for Doped-Pt/CCC and Commercial Pt/C Catalysts

Catalyst	Particle size (nm)	Mass activity ($\text{A mg}_{\text{Pt}}^{-1}$)		ECSA ($\text{m}^2 \text{ g}^{-1}$)		Cell voltage loss at 0.8 A cm^{-2} (mV)	
		Initial	Final	Initial	Final	ΔV_{Cell}	$\Delta V_{\text{iR-free}}$
Doped-Pt/CCC	4.0	0.44	0.25 (43% loss) (30k cycles)	74	50 (32% loss) (30k cycles)	36 (30k cycles)	40 (30k cycles)
Pt/C	2.2	0.18	0.08 (56% loss) (30k cycles)	68	12 (83% loss) (30k cycles)	No activity (30k cycles)	No activity (30k cycles)

of $200 \text{ m}^2 \text{ g}^{-1}$, high degree of graphitization, and improved hydrophobicity was used to synthesize Pt/A-CCC catalyst having an average Pt particle size of 3.1 nm.

The catalyst durability of Pt/A-CCC catalyst was evaluated using a potential cycling protocol (cycling between 0.6 and 1.0 V). Upon cycling, the catalyst showed mass activity loss and ECSA loss of 50% and 41%, respectively after 30k cycles. Initially, the single cell with Pt/A-CCC catalyst exhibited a cell voltage of $0.715 \text{ V}_{\text{iR-free}}$ at 0.8 A cm^{-2} which decreased to $0.643 \text{ V}_{\text{iR-free}}$ after 30k potential cycles corresponding to a loss of 72 mV (Figure 3).

The support stability of Pt/A-CCC catalyst was evaluated by applying a constant potential of 1.2 V for 400 h. The Pt/A-CCC catalyst showed mass activity loss of 32% and ECSA loss of 30% after 400 h. The initial H_2 -air polarization curve and polarization curves obtained after 100 h, 200 h, and 400 h potential holding at 1.2 V for the Pt/A-CCC catalysts are compared in Figure 4. Figure 4 shows an initial potential of 689 mV at 0.8 A cm^{-2} and 662 mV at 0.8 A cm^{-2} after 400 h

potential holding with a potential loss of 27 mV. The observed potential loss is less than the 2017 DOE target for support stability ($\leq 30 \text{ mV}$ loss after 400 h). Furthermore, the initial peak power density was $1,098 \text{ mW cm}^{-2}$ which decreased to 958 mW cm^{-2} after 400 h stability tests corresponding to a loss of only 13%. The catalyst durability and support stability test results of Pt/A-CCC catalyst are summarized and compared with that of commercial Pt/C catalyst in Table 3.

The support stability test of Pt/A-CCC and commercial Pt/C (Pt deposited on high surface area carbon) catalysts was performed using “U.S DRIVE Fuel Cell Tech Team Cell Component Accelerated Stress Test and Polarization curve Protocols for PEM Fuel Cells” revised on January 14, 2013. Support durability test was carried out using triangular sweep cycles between 1.0 V and 1.5 V at 500 mV s^{-1} sweep rate for 5,000 cycles under H_2/N_2 . The H_2 -air polarization results after 0 and 5k cycles for the Pt/A-CCC catalyst is compared in Figure 5. The Pt/A-CCC catalyst showed $0.587 \text{ V}_{\text{iR-free}}$ at 1.5 A cm^{-2} which decreased to $0.563 \text{ V}_{\text{iR-free}}$ after 5k cycles

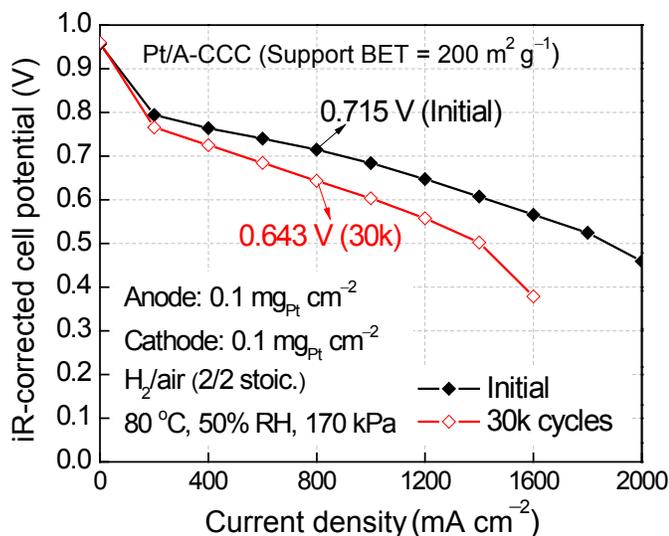


FIGURE 3. H₂/air fuel cell performance of Pt/A-CCC catalyst subjected to 30k potential cycling between 0.6 V and 1.0 V. The catalyst loading is 0.1 mg_{Pt} cm⁻² on both the anode and cathode electrodes. The fuel cell operating conditions are: H₂/air (2/2 stoic.), 80 °C, 50% RH, 170 kPa_{abs.} back pressure. Nafion[®] NRE 212 membrane is used as the electrolyte.

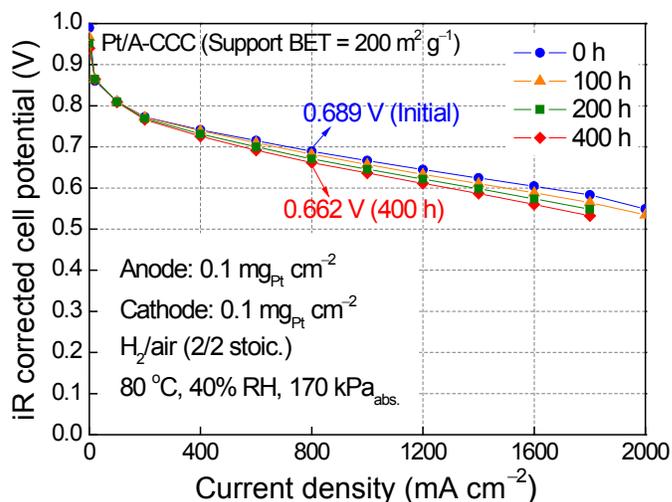


FIGURE 4. H₂/air fuel cell performance of Pt/A-CCC catalyst subjected to potential holding at 1.2 V for 400 h. The catalyst loading is 0.1 mg_{Pt} cm⁻² on both the anode and cathode electrodes. The fuel cell operating conditions are: H₂/air (2/2 stoic.), 80 °C, 40% RH, 170 kPa_{abs.} back pressure. Nafion[®] NRE 212 membrane is used as the electrolyte.

TABLE 3. Summary of Catalyst Durability Test (30k Potential Cycling between 0.6 V and 1.0 V) and Support Stability Test (Potential Holding at 1.2 V for 400 h) for Pt/A-CCC and Commercial Pt/C Catalysts

Catalyst/Test	Particle size (nm)	Mass activity loss (%)	ECSA (m ² g _{Pt} ⁻¹)		Cell voltage loss at 0.8 A cm ⁻² (mV)	
			Initial	Final	ΔV _{Cell}	ΔV _{iR-free}
Pt/A-CCC						
Catalyst Durability	3.1	50	39	23 (41% loss) (30k cycles)	74 (30k cycles)	72 (30k cycles)
Support Durability	3.1	32	40	28 (30% loss) (400 h)	29 (400 h)	27 (400 h)
Pt/C						
Catalyst Durability	2.2	56	68	12 (83% loss) (30k cycles)	No activity (30k cycles)	No activity (30k cycles)
Support Stability	2.2	72	68	20 (71% loss) (48h)	No activity (48h)	No activity (48h)

with a potential loss of only 24 mV. The potential loss is less than the 2017 DOE target of ≤30 mV loss after 5k cycles (Figure 5). It has been reported that while high potentials effectively accelerate carbon corrosion, degradation of the catalyst due to Pt dissolution is minimized because of the oxide formation [15]. Drastic performance degradation was observed for the commercial Pt/C after 2k cycles due to severe carbon support corrosion at high potentials. The commercial Pt/C catalyst did not show any activity after 2k cycles.

Based on the studies carried out at USC for the past three years in developing various catalyst supports and catalysts, the following observations are made:

- Alloying Pt with transition metals helps increase the catalyst mass activity (measured under H₂/O₂). The enhanced mass activity does not translate to high current density performance of the catalyst under H₂-air. The effect of catalyst loading on catalyst mass activity has been previously studied at USC to understand the physical meaning of catalyst mass activity through

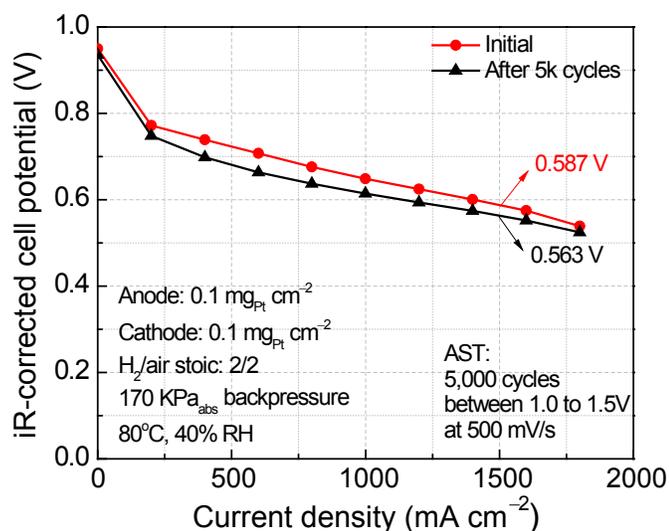


FIGURE 5. H₂/air fuel cell performance of Pt/A-CCC catalyst subjected to 5k potential cycling between 1.0 V and 1.5 V at 500 mV s⁻¹. The catalyst loading is 0.1 mg_{Pt} cm⁻² on both the anode and cathode electrodes. The fuel cell operating conditions are: H₂/air (2/2 stoichiometry), 80°C, 40% RH, 170 kPa_{abs} back pressure. Nafion[®] NRE 212 membrane is used as the electrolyte.

mathematical modeling [16-18]. Our studies showed that alloying Pt with transition metals may contribute to the catalyst durability under potential cycling.

- According to our studies, in order to increase the mass activity, it is necessary to introduce three additional steps in the synthesis procedure to synthesize Pt-alloy/C catalysts from Pt/C:
 - Impregnation of excess amount of transition metal salt into Pt/C
 - Heat treatment at elevated temperatures (800-900 °C) for the alloy formation
 - Prolonged leaching (~12 h) in strong acid solution to remove excess transition metal

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions

- Accomplished rated power density of 0.196 g_{Pt} kW⁻¹ for the Pt/A-CCC catalyst which is close to the 2017 DOE target of 0.125 g_{Pt} kW⁻¹.
- Accomplished 32% mass activity loss, 30% ECSA loss, and potential loss (iR-corrected) of 27 mV at 0.8 A cm⁻² after 400 h potential holding (1.2 V) for the Pt/A-CCC catalyst which satisfy the 2017 DOE targets for support stability. (BET surface area of the A-CCC support is 200 m² g⁻¹.)
- Achieved 24 mV loss at 1.5 A cm⁻² after 5k cycles between 1.0 V and 1.5 V for the Pt/A-CCC catalyst

which satisfies the 2017 DOE target of ≤30 mV loss at 1.5 A cm⁻². (BET surface area of the A-CCC support is 200 m² g⁻¹.)

- Achieved initial mass activity of 0.44 A mg_{Pt}⁻¹ and 0.25 A mg_{Pt}⁻¹ after 30k cycles (0.6-1.0 V) for the doped-Pt/CCC catalyst corresponding to a loss of 43%. The initial mass activity satisfies the 2017 DOE target for initial mass activity (0.44 A g_{Pt}⁻¹) and stability of mass activity after 30k cycles is very close to that of the 2017 DOE target (0.26 A g_{Pt}⁻¹). (BET surface area of the CCC support is 400 m² g⁻¹.)
- Achieved 32% ECSA loss and potential loss (iR-corrected) of 40 mV after 30k cycles (0.6-1.0 V) for the Pt/CCC catalyst. The ECSA loss satisfies the 2017 DOE target (≤40% loss of initial ECSA) and the potential loss at 0.8 A cm⁻² is very close to that of the 2017 DOE target (≤30 mV loss at 0.8 A cm⁻²). (BET surface area of the CCC support is 400 m² g⁻¹.)

Future Anticipated Accomplishments

- Synthesis of highly stable and highly graphitized A-CCC support with BET surface area of 200-300 m² g⁻¹ by optimizing the synthesis parameters such as heat treatment temperature and time.
- Study the structure-catalyst activity of doped-Pt/A-CCC catalysts through physical characterization studies such as high-resolution transmission electron microscopy and energy-dispersive X-ray spectroscopy, and fuel cell testing.
- Increase the performance of Pt-M/A-CCC catalysts by increasing the concentration of doped metal in the A-CCC support and pyrolysis conditions.
- Achieve stability of mass activity of ≤40% and stability of high current density (≤30 mV loss) after 30k potential cycling (between 0.6 and 1.0 V), potential holding (at 1.2 V for 400 h), and 5k potential cycling (between 1.0 and 1.5 V) experiments by optimizing the hydrophilic/hydrophobic properties of the support and introducing defects in the graphitic structure.
- The goal is to select a best performing catalyst which satisfies the 2017 DOE requirements of ≤40% loss of mass activity, ≤40% loss of ECSA and ≤30 mV loss at 0.8 A cm⁻² under H₂-air after 30k potential cycling (between 0.6 and 1.0 V), potential holding (at 1.2 V for 400 h), and potential cycling (between 1.0 and 1.5 V, total 5k cycles) experiments.

FY 2014 PUBLICATIONS/PRESENTATIONS

Publications

1. Taekeun Kim, Tianyuan Xie, Wonsuk Jung, Francis Gadala-Maria, Prabhu Ganesan, and Branko N. Popov, Development

of Catalytically Active and Highly Stable Catalyst Supports for Polymer Electrolyte Membrane (PEM) Fuel Cells, *J. Power Sources*, July 2014. Under Review.

2. Ákos Kriston, Tianyuan Xie and Branko N. Popov, Impact of Ultra-low Platinum loading on Mass Activity and Mass Transport in H₂-Oxygen and H₂-Air PEM Fuel Cells, *Electrochim. Acta*, **121** (2014) 116-127.

3. Branko N. Popov, Tianyuan Xie, Taekeun Kim, Won Suk Jung, Joseph C. Rotchford, Akos Kriston, and Prabhu Ganesan, Development of Ultra-Low Loading Pt Alloy Cathode Catalyst for PEM Fuel Cells, *ECS Trans.*, **58** (2013) 761-778.

4. 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.

5. Akos Kriston, Tianyuan Xie, Prabhu Ganesan, Branko N. Popov, "Effect of Pt Loading on Mass and Specific Activity in PEM Fuel Cells," *J. Electrochem. Soc.*, **160** (2013) F406-F412.

Presentations

1. Tianyuan Xie, Taekeun Kim, Won Suk Jung, Prabhu Ganesan, and Branko N. Popov, Development of Ultra-Low Loading Pt Hybrid Catalyst for PEM Fuel Cells, 224th ECS Meeting, San Francisco, CA, October 27 – November 01, 2013.

2. Branko N. Popov, Tianyuan Xie, Taekeun Kim, Won Suk Jung, and Prabhu Ganesan, Development of Ultra-Low Loading Pt Alloy Cathode Catalyst for PEM Fuel Cells, 224th ECS Meeting, San Francisco, CA, October 27 – November 01, 2013.

3. Taekeun Kim, Won Suk Jung, and Prabhu Ganesan, Tianyuan Xie, and Branko N. Popov, Development of Ultra-Low Loading Pt/AGC Catalyst for PEM Fuel Cells, 224th ECS Meeting, San Francisco, CA, October 27 – November 01, 2013.

REFERENCES

1. Taekeun Kim, Tianyuan Xie, Wonsuk Jung, Francis Gadala-Maria, Prabhu Ganesan, and Branko N. Popov, Development of Catalytically Active and Highly Stable Catalyst Supports for Polymer Electrolyte Membrane (PEM) Fuel Cells, *J. Power Sources*, July 2014. Under Review

2. Branko N. Popov, Tianyuan Xie, Taekeun Kim, Won Suk Jung, Joseph C. Rotchford, Akos Kriston, and Prabhu Ganesan, Development of Ultra-Low Loading Pt Alloy Cathode Catalyst for PEM Fuel Cells, *ECS Trans.*, **58** (2013) 761-778.

3. B.N. Popov, X. Li and J. W. Lee, "Power source research at USC: Development of advanced electrocatalysts for polymer electrolyte membrane fuel cells," *Int. J. Hyd. Energy*, **36** (2011) 1794-1802.

4. Xuguang Li, Branko N. Popov, Takeo Kawahara, Hiroyuki Yanagi, "Non-precious metal catalysts synthesized from precursors of carbon, nitrogen, and transition metal for oxygen reduction in alkaline fuel cells," *J. Power Sources*, **196** (2011), 1717-1722.

5. Gang Liu, Xuguang Li, Jong-Won Lee and Branko Popov, "A Review of the Development of Nitrogen Modified Carbon-based catalyst for Oxygen Reduction at USC," *Catalysis Science & Technology*, **1**, (2011) 207-217.

6. Xuguang Li, Gang Liu, Branko N. Popov, "Activity and stability of non-precious metal catalysts for oxygen reduction in acid and alkaline electrolytes," *J. Power Sources*, **195** (2010) 6373-6378.

7. Li, Xuguang, Park, Sehkyu, Popov, Branko N, "Highly stable Pt and PtPd hybrid catalysts supported on a nitrogen-modified carbon composite for fuel cell application," *J. Power Sources*, **195** (2010) 445-452.

8. Liu, Gang, Li, Xuguang, Ganesan, Prabhu, Popov, Branko N, "Studies of oxygen reduction reaction active sites and stability of nitrogen-modified carbon composite catalysts for PEM fuel cells," *Electrochim. Acta*, **55** (2010) 2853-2858.

9. Subramanian, Nalini P, Li, Xuguang, Nallathambi, Vijayadurda, Kumaraguru, Swaminatha P, Colon-Mercado, Hector, Wu, Gang, Lee, Jong-Won, Popov, Branko N, "Nitrogen-modified carbon-based catalysts for oxygen reduction reaction in polymer electrolyte membrane fuel cells," *J. Power Sources*, **188** (2009) 38-44.

10. Liu, Gang, Li, Xuguang, Ganesan, Prabhu, Popov, Branko N, Development of non-precious metal oxygen-reduction catalysts for PEM fuel cells based on N-doped ordered porous carbon," *Appl. Catal. B: Environmental*, **93** (2009) 156-165.

11. Nallathambi, Vijayadurga; Lee, Jong-Won; Kumaraguru, Swaminatha P, Wu, Gang; Popov, Branko N, "Development of high performance carbon composite catalyst for oxygen reduction reaction in PEM Proton Exchange Membrane fuel cells," *J. Power Sources*, **183** (2008) 34-42.

12. X. Li, H.R. Colon-Mercado, G. Wu, J.-W. Lee, B.N. Popov, "Development of Method for Synthesis of Pt-Co Cathode Catalysts for PEM Fuel Cells," *Electrochem. Solid-State Lett.*, **10** (2007) B201-B205.

13. N.P. Subramanian, S.P. Kumaraguru, H.R. Colon-Mercado, H. Kim, B.N. Popov, T. Black and D.A. Chen, "Studies on Co-Based Catalysts Supported on Modified Carbon Substrates for PEMFC Cathodes," *J. Power Sources*, **157** (2006) 56-63.

14. R.A. Sidik, A.B. Anderson, N.P. Subramanian, S.P. Kumaraguru and B.N. Popov, "O₂ Reduction on Graphite and Nitrogen-Doped Graphite: Experiment and Theory," *J. Phys. Chem. B*, **110** (2006) 1787-1793.

15. Inaba, Minoru, *ECS Trans.*, **25** (2009) 573-581.

16. Ákos Kriston, Tianyuan Xie and Branko N. Popov, Impact of Ultra-low Platinum loading on Mass Activity and Mass Transport in H₂-Oxygen and H₂-Air PEM Fuel Cells, *Electrochim. Acta*, **121** (2014) 116-127.

17. 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.

18. Akos Kriston, Tianyuan Xie, Prabhu Ganesan, Branko N. Popov, "Effect of Pt Loading on Mass and Specific Activity in PEM Fuel Cells," *J. Electrochem. Soc.*, **160** (2013) F406-F412.