

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

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Objectives

- Develop low-cost and durable hybrid cathode catalyst (HCC).
- Develop Pt alloy/activated graphitic carbon catalyst.
- Develop corrosion resistant supports.
- Develop facile scale-up catalyst synthesis procedure (at least 100 g).
- Optimize the parameters which control the number of catalytic sites on carbon composite catalyst (CCC).
- Optimize the procedure for the formation of more active Pt alloy catalysts.
- Demonstrate kinetic mass activity in H_2/O_2 fuel cell higher than DOE target of $0.44 \text{ A mg}_{\text{PGM}}^{-1}$ and durability of the mass activity.
- Demonstrate high current performance in H_2 /air fuel cell to meet DOE targets.
- Construct short stack (50 cm^2 up to 10 cells) and evaluate the performance under simulated automotive conditions.

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 $0.2 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ /membrane electrode assembly (MEA).
 - Initial and durability of kinetic mass activities.
 - Initial high current density performance in H_2 -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

Characteristic	Units	2017 Targets	Status
Power Density	g/kW	0.125	
Precious group metal (PGM) total loading	mg/cm ²	0.125	0.1-0.2 mg _{metal} cm ⁻² with HCC and 0.1 mg _{metal} cm ⁻² with Pt ₂ Ni ₁ /CNC catalysts
Mass activity (80°C, 100% relative humidity (RH), 150 kPa _{abs})	A mg _{Pt} ⁻¹ @ 0.9 V _{IR-free}	0.44	0.45 A mg _{Pt} ⁻¹ for Pt ₂ Ni ₁ /CCC ^(A) (0.1 mg cm ⁻²) 0.33 A mg _{Pt} ⁻¹ for Pt ₂ Ni ₁ /CCC ^(B) (0.15 mg cm ⁻²) 0.37 A mg _{Pt} ⁻¹ for Pt ₁ Co ₁ /CCC ^(C) (0.2 mg cm ⁻²) 0.41 A mg _{Pt} ⁻¹ for Pt _{1.3} Co ₁ /CCC ^(D) (0.1 mg cm ⁻²) 0.44 A mg _{Pt} ⁻¹ for Pt ₂ Ni ₁ /CNC (0.1 mg _{metal} cm ⁻²)
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	30.3% mass activity loss (Pt ₂ Ni ₁ /CCC ^(B)) 46-49.3% mass activity loss and 27.8% ECSA loss (Pt ₁ Co ₁ /CCC ^(C)) 31.8% mass activity loss and 26.3% ECSA loss (Pt ₂ Ni ₁ /CNC)
Support durability (1.2 V for 400 h at 80°C, H ₂ -N ₂ , 150 kPa _{abs} , 100% RH)	% Mass activity loss	<10%	47.7% mass activity loss for Pt ₂ Ni ₁ /CNC.
High current density performance [H ₂ /air (1.5/1.8), 80°C, 40% RH, 150 kPa _{abs}]	A cm ⁻² @ 0.58 V _{IR-free}	-	1.25 (1.5/1.8) and 1.4 (1.5/2.0) for Pt ₂ Ni ₁ /CCC ^(A) (0.1 mg cm ⁻²)

CCC^(A) – Brunauer-Emmett-Teller (BET) surface area higher than 600 m² g⁻¹; CCC^(B) – BET surface area = 250 m² g⁻¹; CCC^(C) – BET surface area = 380 m² g⁻¹;
CCC^(D) – BET surface area = 350 m² g⁻¹.

FY 2012 Accomplishments

- 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_{Pt}⁻¹ for Pt₂Ni₁/CCC^(A), Pt₂Ni₁/CCC^(B) (0.15 mg_{Pt} cm⁻²), Pt₁Co₁/CCC^(C) (0.2 mg_{Pt} cm⁻²) and Pt_{1.3}Co₁/CCC^(D) catalysts, respectively.
- Accomplished mass activity loss of 30.3% and 46-49.3% for Pt₂Ni₁/CCC^(B), Pt₁Co₁/CCC^(C) catalysts, respectively.
- Accomplished ECSA loss of 27.8% for the Pt₁Co₁/CCC^(C) catalyst.
- Accomplished mass activity of 0.44 A mg_{Pt}⁻¹ for Pt₂Ni₁/CNC catalyst.
- Achieved 0.3 A mg_{Pt}⁻¹ after 30 k cycles for Pt₂Ni₁/CNC catalyst.
- Achieved 1.25 A cm⁻² and 1.4 A cm⁻² at 0.58 V_{IR-free} for the Pt₂Ni₁/CCC^(A) catalyst at 1.5/1.8 and 1.5/2.0 stoichiometry, respectively under H₂-air operating conditions (80 °C, 40% RH, 150 kPa_{abs}).



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⁻²). 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 Pt₂Ni₁/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 cm² 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 HNO₃ and incorporation of nitrogen and

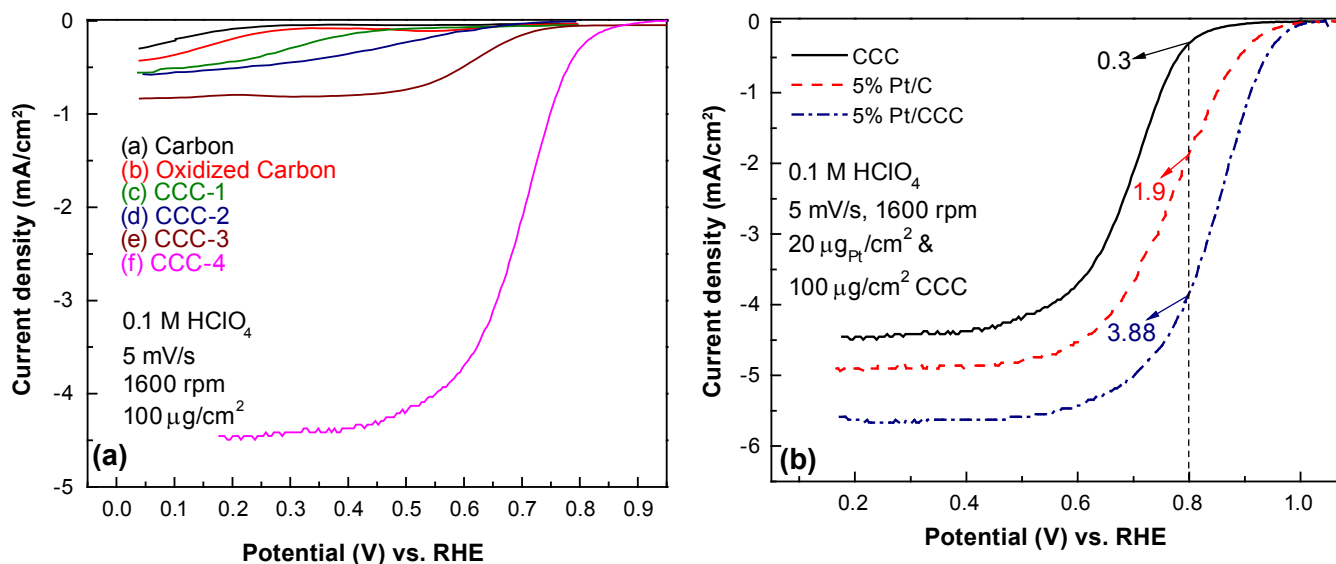


FIGURE 1(A). Comparison of ORR performances of carbon (Ketjen black) and surface modified carbons. Polarization curves: (a) as received Ketjen black carbon, (b) HNO₃-oxidized carbon, (c) oxidized carbon with nitrogen and transition metal (CCC-1), (d) oxidized carbon with nitrogen and transition metal (CCC-2), (e) oxidized carbon with nitrogen and transition metal (CCC-3) and (f) low temperature graphitized oxidized carbon with nitrogen and transition metal (CCC-4).
FIGURE 1(B). Comparison of ORR activities of carbon composite catalyst, 5% Pt/C and 5% Pt/CCC in rotating ring disk electrode (RRDE).

transition metals. The carbon composite catalyst (curve f in Figure 1a) showed an onset potential of 0.9 V_{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

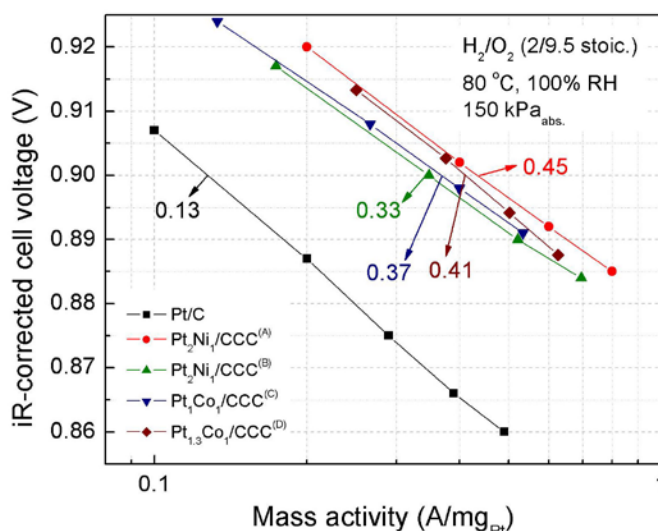


FIGURE 2. Comparison of mass activities of conventional Pt/C and various HCC (Pt-alloy deposited on CCC support) catalysts.

CCC and Pt or Pt-alloy in the USC developed Hybrid Cathode Catalyst. Pt₂Ni₁/CCC^(A) catalyst showed mass activities of 0.45 A mg_{Pt}⁻¹. The mass activities of Pt/C, Pt₂Ni₁/CCC^(B), Pt₁Co₁/CCC^(C) and Pt_{1.3}Co₁/CCC^(D) are 0.13, 0.33, 0.37 and 0.41 A mg_{Pt}⁻¹, 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 Pt₂Ni₁/CCC^(B) and Pt₁Co₁/CCC^(C) catalysts indicated mass activity loss of 46–49.3% and 30.3% after 30 k cycles, respectively. Furthermore, the Pt₁Co₁/CCC^(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/CCC^(D), and 1.25 A cm⁻² for 46% Pt₂Ni₁/CCC^(A) at 1.5/1.8 stoichiometry. The Pt₂Ni₁/CCC^(A) 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_{Pt}⁻¹ for Pt₂Ni₁/CCC^(A), Pt₂Ni₁/CCC^(B), Pt₁Co₁/CCC^(C) and Pt_{1.3}Co₁/CCC^(D) catalysts, respectively.
- Accomplished initial mass activity of 0.44 A mg_{Pt}⁻¹ for the Pt₂Ni₁/CNC catalyst.
- Accomplished mass activity loss of 30.3% and 46–49.3% after 30 k cycles for Pt₂Ni₁/CCC^(B), Pt₁Co₁/CCC^(C) catalysts, respectively.

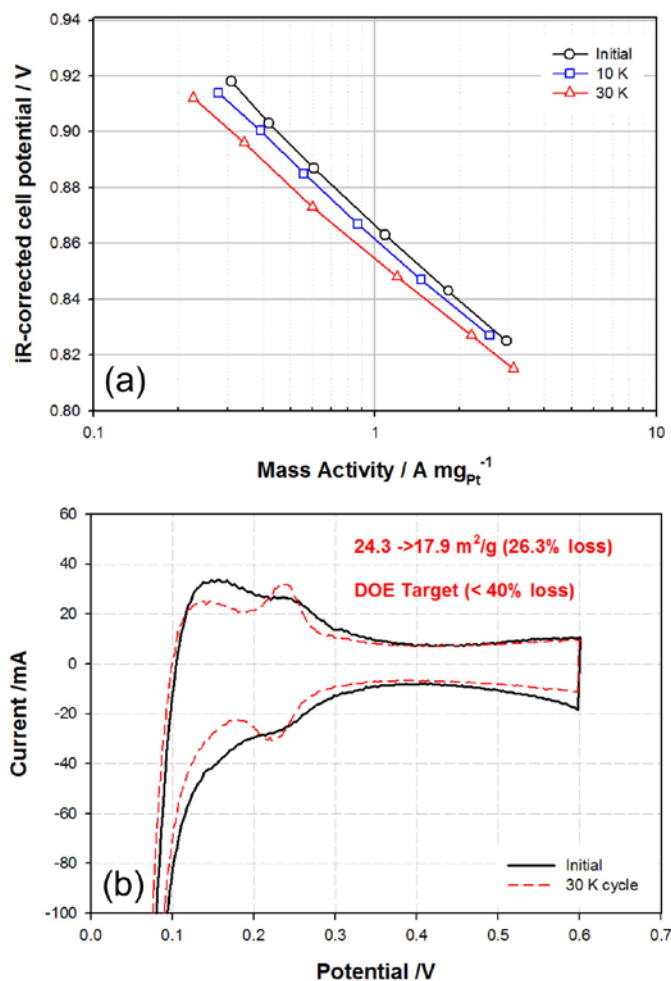


FIGURE 3(A). Catalytic oxygen reduction activities of the 50 wt% Pt₂Ni₁/CNC-NA catalysts (0.1 mg_{metal} cm⁻²) during accelerated stress test (AST) by cycling protocol.

FIGURE 3(B). Cyclic voltammogram of the 50wt% Pt₂Ni₁/CNC-NA catalyst (0.1 mg_{metal} cm⁻²) before and after the accelerated stress test.

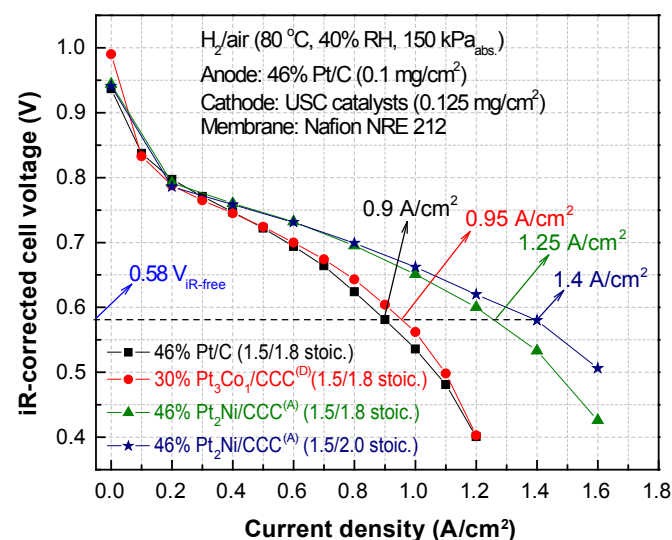


FIGURE 4. Comparison of H₂-air fuel cell performances of Pt/C and HCC catalysts (Pt-alloy deposited on CCC support). The fuel cell was operated at 80°C, 40% RH, 150 kPa_{abs} back pressure and 1.5/1.8 H₂/air stoichiometry. The anode and cathode Pt loadings were 0.1 and 0.125 mg cm⁻², respectively, and Nafion® 212 membrane was used as the electrolyte.

- Accomplished ECSA loss of 27.8% for the Pt₁Co₁/CCC^(C) catalyst.
- Accomplished 0.3 A mg_{Pt}⁻¹ after 30 k cycles for the Pt₂Ni₁/CNC catalyst.
- Achieved 1.25 A cm⁻² and 1.4 A cm⁻² at 0.58 V_{iR-free} for the Pt₂Ni/CCC^(A) catalyst at 1.5/1.8 and 1.5/2.0 stoichiometry, respectively, under H₂-air operating conditions (80°C, 40% RH, 150 kP_{abs.} outlet pressure).

Future anticipated accomplishments are to:

- Confirm durability of kinetic mass activity of at least 0.24 A mg_{Pt}⁻¹ after 30 k cycles or less than 40% loss of mass activity at 0.9 V_{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_{iR-free} and less than 40% loss of ECSA.
- Accomplish high current density performance and durability in H₂/air fuel cells (80°C, 40% RH, 150 kP_{abs.} 1.5/1.8 stoichiometry).
- Reproducibility of catalyst performance evaluation in at least three MEAs in two laboratories using 25 and 50 cm² cells.
- Demonstrate facile scale-up synthesis of the catalysts.

Special Recognitions & Awards/Patents Issued

1. Carbon-based composite electrocatalysts for low temperature fuel cells, *US 7,629,285*, 2009.
2. Composite catalysts supported on modified carbon substrates and methods of making the same, *US 7,618,915*, 2009.

FY 2012 Publications/Presentations

Publications

1. Sheng-Yang Huang, Prabhu Ganesan, and Branko N. Popov, "Electrocatalytic Activity and Stability of Titania Supported Platinum-Palladium Catalysts for Polymer Electrolyte Membrane Fuel Cell" *ACS Catalysis*, 2 (2012) 825-831.
2. Sheng-Yang Huang, Prabhu Ganesan, Ho-Young Jung and Branko N. Popov, "Development of supported bifunctional oxygen electrocatalysts and corrosion-resistant gas diffusion layer for unitized regenerative fuel cell applications", *J. Power Sources*, 198 (2012) 23-29.
3. Sehkyu Park, Branko N. Popov, Effect of a GDL based on carbon paper or carbon cloth on PEM fuel cell performance, *Fuel*, 90, (2011) 436-440.
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, *Journal of 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 Carbo-based catalyst for Oxygen Reduction at USC, *Catalysis Science & Technology*, 1, (2011) 207-217.
6. Sheng-Yang Huang, Prabhu Ganesan, Branko N. Popov, Titania supported platinum catalyst with high electrocatalytic activity and stability for polymer electrolyte membrane fuel cell, *Appl. Catal. B: Environmental*, 102 (2011) 71-77.
7. Xuguang Li, Gang Liu, Prabhu Ganesan, Hansung Kim, Bumwook Roh, and Inchul Hwang, Development of Ultra-Low Pt Alloy Cathode Catalyst for PEM Fuel Cells, Branko N. Popov, *ECS Transactions*, 2011, 41 (1), 955-969.
8. S.Y. Huang, P. Ganesan, and B.N. Popov, Titanium dioxide-supported platinum catalysts, *ECS Transactions*, 41, 2255-2268 (2011).

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, *220th ECS Meeting*, Boston, MA, October 9–14, 2011.
2. S. Huang, P. Ganesan, and B.N. Popov, Titanium Dioxide-Supported Platinum Catalysts, *220th ECS Meeting*, Boston, MA, October 9–14, 2011.
3. X. Li, G. Liu, T. Kim, S. Ganesan, P. Ganesan, and B.N. Popov, Development of Non-Precious Metal Catalysts for Oxygen Reduction Reaction in Fuel Cells with High Activity and Stability, *220th ECS Meeting*, Boston, MA, October 9–14, 2011.

References

1. 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.
2. 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.
3. 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.
4. 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.
5. 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.

6. 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, *Appl. Catal. B: Environmental*, **93** (2009) 156-165.
7. 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.
8. 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.
9. 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.
10. 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.
11. 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, *Journal of Power Sources*, 196 (2011), 1717-1722.
12. 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.
13. K.H Lim, H-S Oh, H. Kim, Use of a carbon nanocage as a catalyst support in polymer electrolyte membrane fuel cells *Electrochem. Commun.*, **11** (2009) 1131-1134.
14. K.H Lim, H-S Oh, S-E Jang, Y-J Ko, H-J Kim, H. Kim, Effect of operating conditions on carbon corrosion in polymer electrolyte membrane fuel cells, *J. Power Sources*, **193** (2009) 575-579.
15. H-S Oh, K.H. Lim, B. Roh, I. Hwang, H. Kim, Corrosion resistance and sintering effect of carbon supports in polymer electrolyte membrane fuel cells, *Electrochim. Acta*, **54** (2009) 6515-6521.