

V.A.6 Development of Ultra-Low Platinum Alloy Cathode Catalysts for PEM Fuel Cells

Branko N. Popov
University of South Carolina
301 Main Street
Columbia, SC 29208
Phone: (803) 777-7314; Fax: (803) 777-8265
Email: popov@cec.sc.edu

DOE Manager
Donna Ho
Phone: (202) 586-8000
Email: Donna.Ho@ee.doe.gov

Technical Advisor
Thomas Benjamin
Phone: (630) 252-1632
Email: benjamin@anl.gov

Contract Number: DE-EE0000460

Project Start Date: September 1, 2010
Project End Date: December 31, 2015

Overall Objectives

- Develop a unique hybrid cathode catalyst (HCC) through the interaction of a highly active and stable compressive Pt-lattice catalyst (Pt*) with an activated carbon composite support (A-CCS) having high activity for the oxygen reduction reaction (ORR)
- Enhance the activity of HCC by increasing the synergistic effect of catalytic active sites present on the supports and those on the Pt* catalyst
- Specific objectives are to:
 - Perform optimization studies to develop a catalyst support with high kinetic activity and stability.
 - Estimate the role of Brunauer-Emmett-Teller (BET) surface area, porosity, pore size and distribution, and hydrophilic/hydrophobic properties on the support stability.
 - Synthesize a low-platinum group metal (PGM) cathode catalyst for automotive application by decreasing the PGM loading while simultaneously increasing the catalytic activity and stability of both A-CCS and Pt*.
 - Develop low-cost procedures to synthesize A-CCS and Pt*/A-CCS.

Specific Objectives for Fiscal Year (FY) 2015

- Development of an A-CCS with desired BET surface area, porosity, pore-size distribution, and hydrophilic/hydrophobic properties
- Synthesis and performance evaluation of Pt*/A-CCS catalyst using optimized A-CCS
 - Initial mass activity under H₂-O₂
 - Initial high current density performance under H₂-air
 - Catalyst durability under 0.6–1.0 V potential cycling experimental conditions
 - Support stability under 1.0–1.5 V potential cycling experimental conditions

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 proton exchange membrane (PEM) fuel cells. In FY 2015, a Pt*/A-CCS catalyst was synthesized using procedures developed at the University of South Carolina (USC). Our results showed that the Pt*/A-CCS catalyst has the potential to meet the 2017 DOE technical targets for electrocatalysts for automotive applications as shown in Table 1.

FY 2015 Accomplishments

The following results were accomplished for the Pt*/A-CCS catalyst:

- Achieved an initial mass activity of 0.41 A/mg_{PGM} and loss of mass activity of 46% after 30,000 cycles (0.6–1.0 V)
- Measured a potential loss of 35 mV (iR-free) at 0.8 A/cm² after 30,000 cycles (0.6–1.0 V)
- Accomplished 25% ECSA loss after 30,000 cycles (0.6–1.0 V)

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

Characteristic	Units	2017 DOE Targets	FY 2015 Status at USC (Pt*/A-CCS)
PGM total content	g/kW (rated)	0.125	0.19
PGM total loading	mg _{PGM} /cm ²	0.125	0.2
Mass activity (H ₂ /O ₂ (2/9.5 stoic.) 80 °C, 100% RH, 150 kPa _{abs})	A/mg _{Pt} @ 0.9 V _{IR-free}	0.44	0.41
Catalyst durability (30,000 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	≤40% ≤40% ≤30 mV @ 0.8 A/cm ²	46% loss (MA) 25% loss (ECSA) 35 mV loss (H ₂ -air)
Support stability (5,000 cycles, 1.0–1.5 V, 500 mV/s, 80 °C, H ₂ /N ₂ , 100% RH, no back press.)	% mass activity (MA) loss % ECSA loss mV loss @ 1.5 A/cm ²	≤40% ≤40% ≤30 mV @ 1.5 A/cm ²	53% loss (MA) 24% loss (ECSA) 10 mV gain (H ₂ -air)

RH - relative humidity; ECSA - electrochemical active surface area

- Pt*/A-CCS showed excellent support stability after 5,000 cycles (0.6–1.0 V)
 - Potential gain of ~10 mV (cell potential) was accomplished at 1.5 A/cm² after 5,000 cycles
- Accomplished 53% mass activity loss and 24% ECSA loss after 5,000 cycles (1.0–1.5 V)
- Accomplished (rated) initial power density of 0.19 g_{PGM}/kW



INTRODUCTION

Novel methodologies were developed at USC to synthesize catalytically active and highly stable carbon-based supports [1–19]. Pt/A-CCS and Pt*/A-CCS catalysts with enhanced ORR kinetics were developed that showed higher performance than commercial Pt/C at low loadings (≤0.1 mg/cm²) [17–19]. In FY 2015, a Pt*/A-CCS catalyst with high activity towards ORR was synthesized and its support stability (1.0–1.5 V potential cycling, 5,000 cycles) and catalyst durability (0.6–1.0 V potential cycling, 30,000 cycles) were evaluated.

APPROACH

The HCC technology developed at USC is based on a two-step patented process to synthesize highly active and stable ultra-low-PGM HCC. The research at USC was aimed at developing catalytically active and stable supports to sustain load cycling and startup/shutdown conditions. In the first step, the following major constraints directed our development of cathode catalyst supports: (1) the support should be chemically and electrochemically stable at high potentials, low pH, and high temperature; and (2) the support

should have an onset potential and kinetic activity for ORR similar to that of the platinum catalyst. To accomplish these requirements, an A-CCS was synthesized with optimized (1) BET surface area, porosity, pore size, and pore size distribution; (2) hydrophilic/hydrophobic ratio; (3) structural properties (amorphous/crystalline ratio); (4) number of catalytic active sites through metal catalyzed pyrolysis; (5) Pt/Pt*-support interaction by inclusion of active surface functional groups; and (6) with cobalt incorporated into its structure, necessary for the formation of Pt*.

In the second step, a compressive Pt-lattice catalyst (Pt*) was synthesized through a USC-developed annealing procedure that controls the particle size during annealing. Monolayers of Pt* were formed by diffusing Co atoms present in the support into Pt which is deposited on the A-CCS. A mathematical model developed at USC was used to optimize the Co diffusion time, annealing temperature, and Pt/Co stoichiometric ratio.

RESULTS

Synthesis, support stability, and catalyst durability of the Pt/A-CCS catalyst were reported in the FY 2014 annual report. In FY 2015, the A-CCS with optimized physical properties was used for the synthesis of Pt*/A-CCS to meet the DOE 2017 technical targets for electrocatalysts and catalyst support. Initially, Pt/A-CCS was prepared by depositing Pt nanoparticles on A-CCS using a modified polyol reduction procedure developed at USC [17–19]. Then, a Pt*/A-CCS catalyst having a particle size distribution of 4–5 nm was synthesized through the controlled annealing of the Pt/A-CCS catalyst. The novel annealing procedure developed at USC inhibited the Pt particle growth at high temperature. The compressive Pt-lattice is formed by the diffusion of cobalt, which is present in the A-CCS, into Pt during the annealing process. The support stability and catalyst durability of the Pt*/A-CCS catalysts were evaluated

using 1.0–1.5 V potential cycling and 0.6–1.0 V potential cycling protocols, respectively.

Figure 1 shows the initial mass activity and stability of mass activity after 30,000 potential cycles (0.6–1.0 V) for the 30% Pt*/A-CCS catalyst. At 0.9 V_{ir-free}, the catalyst showed an initial mass activity of 0.41 A/mg_{Pt} and 46% loss after 30,000 cycles. The commercial 30% Pt/C catalyst showed a 68% loss (Table 2) after 30,000 cycles. The ECSA loss for the Pt*/A-CCS catalyst is 25% (decreased from 24.1 m²/g_{Pt} to 18 m²/g_{Pt}) while the commercial 30% Pt/C catalyst showed an 80% loss after 30,000 cycles.

The H₂-air fuel cell performance of the 30% Pt*/A-CCS catalyst subjected to 0.6–1.0 V potential cycles (30,000 cycles) is shown in Figure 2A (iR-corrected cell voltage vs. current) and Figure 2B (cell voltage vs. current). In H₂-air, the fuel cell exhibited an initial current density of 1.55 A/cm² at 0.6 V_{ir-free} with a rated power density of 0.19 g_{Pt}/kW. The catalyst showed 35 mV (iR-free) loss and 32 mV (cell voltage) loss at 0.8 A/cm² after 30,000 cycles (0.6–1.0 V). The commercial Pt/C catalyst showed no activity at 0.8 A/cm² after 30,000 potential cycles between 0.6 V and 1.0 V. The catalyst durability results of the 30% Pt*/A-CCS and commercial Pt/C catalysts are compared in Table 2.

Figure 3A (iR-corrected cell voltage vs. current) and Figure 3B (cell voltage vs. current) show the H₂-air fuel cell performance of 30% Pt*/A-CCS catalyst subjected to 1.0–1.5 V potential cycles (5,000 cycles). The 30% Pt*/A-CCS catalyst exhibited an initial mass activity of 0.41 A/mg_{Pt} and 53% loss after 5,000 cycles. The H₂-air fuel cell performance showed an initial current density of 1.4 A/cm² at 0.6 V_{ir-free} and 1.45 A/cm² after 5,000 cycles. The catalyst showed 10 mV gain (iR-free) and 29 mV gain (cell voltage) at 1.5 A/cm² after 5,000 cycles (1.0–1.5 V). The ECSA loss is 24% (decreased from 21 m²/g_{Pt} to 16 m²/g_{Pt}). The commercial

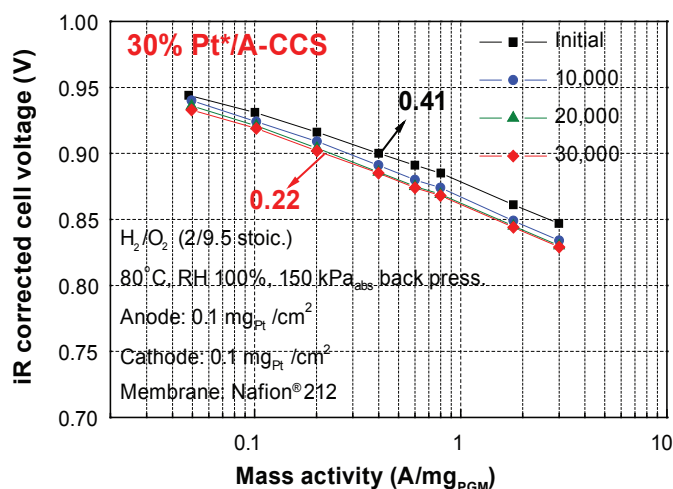


FIGURE 1. Stability of mass activity of Pt*/A-CCS catalyst subjected to 30,000 potential cycles between 0.6 V and 1.0 V at 50 mV/s. The catalyst loading is 0.1 mg_{Pt}/cm² on both the anode and cathode electrodes. The fuel cell operating conditions are: H₂/O₂ (2/9.5 stoic.), 80°C, 100% relative humidity (RH), 150 kPa_{abs} back pressure. Nafion® NRE 212 membrane is used as the electrolyte.

Pt/C catalyst showed very high mass activity loss (74%), 92% ECSA loss, and no activity at 1.5 A/cm² after 5,000 potential cycles between 1.0 V and 1.5 V. The support stability test results for the 30% Pt*/A-CCS and commercial Pt/C catalysts are summarized in Table 2. According to Reiser et al. [20], the cathode interfacial potential difference can reach ~1.5 V due to the H₂-air front in the anode compartment during startup/shutdown and carbon corrosion is an inevitable parasitic reaction at these high potentials. However, the 1.0–1.5 V potential cycling experimental results of the 30% Pt*/A-CCS catalyst show that the USC-developed A-CCS

TABLE 2. Summary of Support Stability Test (5,000 Potential Cycles between 1.0 V and 1.5 V) and Catalyst Durability Test (30,000 Potential Cycles between 0.6 V and 1.0 V) for Pt*/A-CCS and Commercial Pt/C Catalysts

Catalyst/Test	Particle Size (nm)	Mass Activity (A/mg _{Pt})		ECSA (m ² /g _{Pt})		Cell Voltage Loss (mV)	
		Initial	Final	Initial	Final	ΔV _{Cell}	ΔV _{ir-free}
Pt*/A-CCC Support Stability	4–5	0.41	0.19 (53% loss) (5,000 cycles)	21	16 (24% loss) (5,000 cycles)	0 (29 mV gain) at 1.5 A/cm ² (5,000 cycles)	0 (10 mV gain) at 1.5 A/cm ² (5,000 cycles)
		Catalyst Durability	4–5	0.41	0.22 (46% loss) (30,000 cycles)	24	18 (25% loss) (30,000 cycles)
Commercial Pt/C Support Stability	2.2	0.18	0.047 (74% loss) (5,000 cycles)	68	5.4 (92% loss) (5,000 cycles)	No activity (5,000 cycles)	No activity (5,000 cycles)
		Catalyst Durability	2.2	0.18	0.057 (68% loss) (30,000 cycles)	68	13.6 (80% loss) (30,000 cycles)

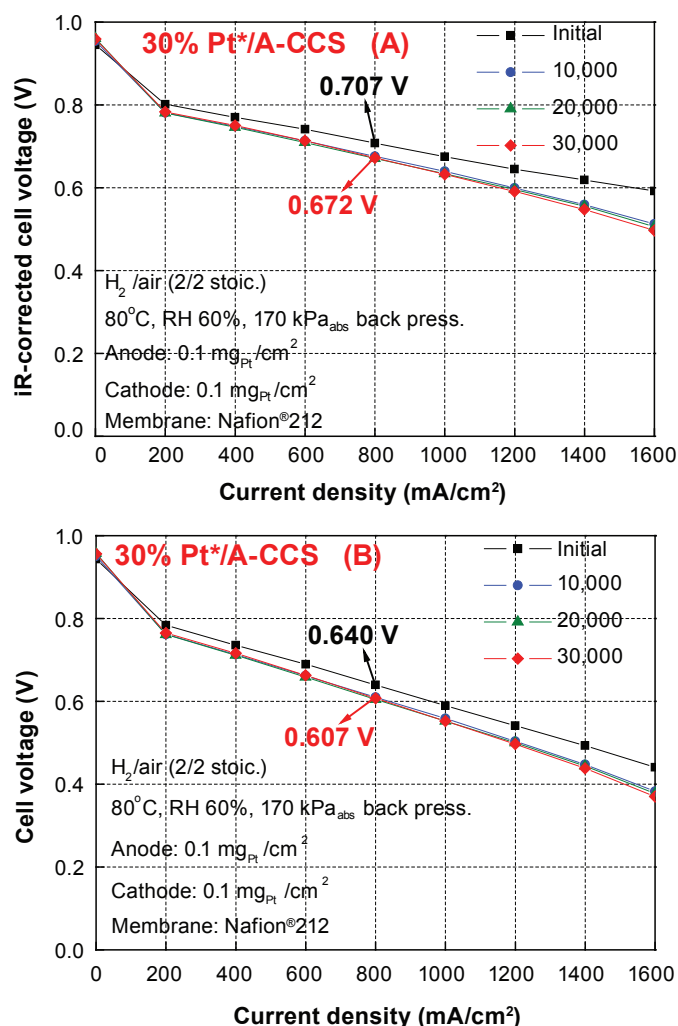


FIGURE 2. Comparison of H_2 -air fuel cell performance of 30% Pt*/A-CCS catalyst subjected to 30,000 potential cycles between 0.6 V and 1.0 V at 50 mV/s. (A) iR-corrected cell voltage vs. current and (B) cell voltage vs. current. The catalyst loading is 0.1 mg_{Pt}/cm² on both the anode and cathode electrodes. The fuel cell operating conditions are: H_2 -air (2/2 stoic.), 80°C, 60% RH, 170 kPa_{abs} back pressure. Nafion® NRE 212 membrane is used as the electrolyte.

support is highly stable at high potentials when compared to the carbon support used in commercial Pt/C catalyst. For the first time, by developing a breakthrough stable carbon-based composite at the Center for Electrochemical Engineering at USC, we have shown excellent support stability under 1.0–1.5 V potential cycling conditions for the Pt*/A-CCS catalyst.

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions for Pt*/A-CCS Catalyst

- Accomplished initial mass activity of 0.41 A/mg_{Pt} and loss of mass activity of 46% after 30,000 cycles (0.6–1.0 V)

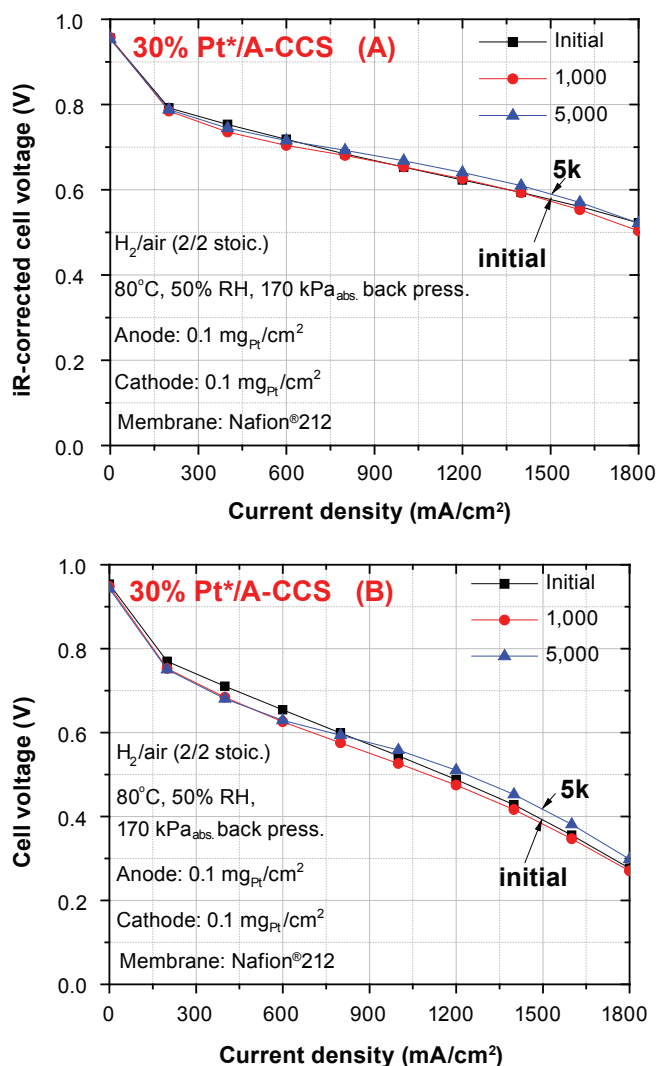


FIGURE 3. Comparison of H_2 -air fuel cell performance of 30% Pt*/A-CCS catalyst subjected to 5,000 potential cycles between 1.0 V and 1.5 V at 500 mV/s. (A) iR-corrected cell voltage vs. current and (B) cell voltage vs. current. The catalyst loading is 0.1 mg_{Pt}/cm² on both the anode and cathode electrodes. The fuel cell operating conditions are: H_2 -air (2/2 stoic.), 80°C, 50% RH, 170 kPa_{abs} back pressure. Nafion® NRE 212 membrane is used as the electrolyte.

- Accomplished potential loss of 35 mV (iR-free) and 32 mV (cell voltage) loss at 0.8 A/cm² after 30,000 cycles (0.6–1.0 V)
- Accomplished 25% ECSA loss after 30,000 cycles (0.6–1.0 V)
- The Pt*/A-CCS showed excellent support stability after 5,000 cycles (1.0–1.5 V)
 - Potential gain of ~10 mV (iR-corrected cell voltage) was accomplished at 1.5 A/cm² after 5,000 cycles

- Accomplished 53% mass activity loss and 24% ECSA loss after 5,000 cycles (1.0–1.5 V)
- Accomplished (rated) initial power density of 0.19 g_{PGM}/kW

Future Anticipated Accomplishments

- Our studies showed the formation of an ordered tetragonal Pt-Co phase, while the disorder to ordered Pt-Co phase ratio increased with increasing pyrolysis temperature. The catalyst performance was found to depend on the disordered/ordered Pt-Co structures (Pt*/A-CCS).
 - Detailed studies will be carried out to optimize the performance of Pt*/A-CCS with the structural properties of Co-doped Pt.
 - Structure-property performance relationships will be evaluated for different Pt-Co ratios which result in structures with different degrees of formation of compressive Pt-lattice structure.
 - A mathematical model developed at USC will be used to optimize the ratio of ordered and disordered Pt-Co phases.
- Further studies will be carried out to increase the H₂-air fuel cell performance of the Pt*/A-CCS catalyst by controlling the hydrophilic/hydrophobic properties of A-CCS. The goal is to eliminate the eventual flooding of the support during 1.0–1.5 V cycling.
- The catalyst which best achieves the 2017 DOE technical targets for electrocatalysts and catalyst supports will be selected.
- Reproducibility studies of the selected catalyst in 25 cm² and 50 cm² MEAs will be conducted.
- High-volume production procedures for the A-CCS support and Pt*/A-CCS catalyst will be optimized.
- Cost reduction will be achieved by:
 - Further decreasing the PGM loading.
 - Developing cost-effective synthesis procedures that eliminate the chemical leaching process during Pt*/A-CCS synthesis.
 - Optimizing of the Pt/Co ratio and decreasing the annealing temperature and reaction time.

Deliverables

1. Supply of 25 and 50 cm² MEAs for independent evaluation at NREL by the end of December 2015.

FY 2015 PUBLICATIONS

1. Wonsuk Jung, Tianyuan Xie, Taekeun Kim, Prabhu Ganesan, Branko N. Popov, “Highly Active and Durable Co-Doped Pt/CCC Cathode Catalyst for Polymer Electrolyte Membrane Fuel Cells,” *Electrochim. Acta*, **167**, (2015) 1–12.
2. T. Kim, T. Xie, W.S. Jung, F. Gadala-Maria, P. Ganesan, B.N. Popov, “Development of Catalytically Active and Highly Stable Catalyst Supports for Polymer Electrolyte Membrane Fuel Cells,” *J. Power Sources*, **273**, (2015) 761–774.
3. T. Xie, W.S. Jung, T. Kim, P. Ganesan, B.N. Popov, “Development of Highly Active and Durable Hybrid Cathode Catalysts for Polymer Electrolyte Membrane Fuel Cells,” *J. Electrochem. Soc.*, **161** (2014) F1489–F1501.

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, Vijayadurga; 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 ordered porous carbon,” *Appl. Catal. B: Environmental*, **93** (2009) 156–165.
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. 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," *J. 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. 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.
14. 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.
15. Ákos 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.
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. Wonsuk Jung, Tianyuan Xie, Taekeun Kim, Prabhu Ganesan, Branko N. Popov, "Highly Active and Durable Co-Doped Pt/CCC Cathode Catalyst for Polymer Electrolyte Membrane Fuel Cells," *Electrochim. Acta*, **167**, (2015) 1–12.
18. T. Kim, T. Xie, W.S. Jung, F. Gadala-Maria, P. Ganesan, B.N. Popov, "Development of Catalytically Active and Highly Stable Catalyst Supports for Polymer Electrolyte Membrane Fuel Cells," *J. Power Sources*, **273**, (2015) 761–774.
19. T. Xie, W.S. Jung, T. Kim, P. Ganesan, B.N. Popov, "Development of Highly Active and Durable Hybrid Cathode Catalysts for Polymer Electrolyte Membrane Fuel Cells," *J. Electrochem. Soc.*, **161** (2014) F1489–F1501.
20. C.A. Reiser, L. Bregoli, T.W. Patterson, J.S. Yi, J.D. Yang, M.L. Perry, T.D. Jarvi, "A Reverse-Current Decay Mechanism of Fuel Cells," *Electrochem. Solid-State Lett.* **8** (2005) A273–A276.