

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

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## Fiscal Year (FY) 2011 Objectives

- Develop low cost and durable hybrid cathode catalyst (HCC).
- Develop Pt alloy/activated graphitic carbon (AGC) 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  $0.44 \text{ A/mg}_{\text{PGM}}$  and durability of the mass activity.
- Demonstrate high current performance in  $H_2/\text{air}$  fuel cell to meet DOE targets.
- Construct short-stack (50  $\text{cm}^2$  up to 10 cells) and evaluate the performance under simulated automotive conditions.

## 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:

- Durability
- Cost
- Performance

## Technical Targets

The expected outcome of the project is the fabrication of catalysts, fully integrated into a proton exchange membrane electrode assembly (MEA), with the following performance characteristics:

- PGM loading of  $0.1 \text{ mg/cm}^2$ .
- Mass activity of  $0.44 \text{ A/mg}_{\text{Pt}}$  at  $0.9 \text{ V}_{\text{iR-free}}$ .
- Specific activity of  $720 \mu\text{A/cm}^2$  at  $0.9 \text{ V}_{\text{iR-free}}$ .
- Mass activity of at least  $0.24 \text{ A/mg}_{\text{Pt}}$  after 30,000 cycles, DOE protocol (0.6-0.9 V).
- Initial high current density performance of  $1.5 \text{ A/cm}^2$  at  $0.56 \text{ V}_{\text{iR-free}}$  in  $H_2$ -air.
- Electrochemical surface area (ECSA) loss less than 40% of initial catalytic activity after 30,000 cycles.
- Short-stack specific power density of  $0.1 \text{ g/KW}$  at rated power.
- Durability under cycling transportation conditions at  $\geq 80^\circ\text{C}$  for 2,000 hours and at  $\leq 80^\circ\text{C}$  for 5,000 hours.
- High volume production (manufacturability).

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

Characteristic	Units	Target 2015	USC 2011 status (25 $\text{cm}^2$ cell)
PGM Total Content	g/kW rated	$\leq 0.125$	To be determined
PGM Total Loading	mg PGM/ $\text{cm}^2$ electrode area	$\leq 0.125$	0.1 (anode)/ 0.1 (cathode)
Loss in Catalytic (mass) Activity	percentage	<40% loss of initial	34%
Current Density Performance in $H_2/\text{Air}$	$\text{A/cm}^2$ at $0.56 \text{ V}_{\text{iR-free}}$	$1.5 \text{ A/cm}^2$	1.45 ( $\text{Pt}_3\text{M}_1/\text{AGC}$ )
Mass Activity	$\text{A/mg PGM @ } 900 \text{ mV}_{\text{iR-free}}$	$\geq 0.44$	0.43 ( $\text{PtM}_2/\text{C}$ ) 0.42 ( $\text{Pt}/\text{CCC}$ [HCC]) 0.41 ( $\text{Pt}_3\text{M}_1/\text{AGC}$ )
Specific Activity	$\mu\text{A/cm}^2 @ 900 \text{ mV}_{\text{iR-free}}$	720	1135 ( $\text{Pt}_3\text{M}_1/\text{AGC}$ )

## FY 2011 Accomplishments

- Accomplished onset potential for oxygen reduction on CCC close to 0.9 V and less than 2.5% of peroxide production.
- Accomplished mass activity of 0.43 A/mg<sub>Pt</sub>, 0.42 A/mg<sub>Pt</sub> and 0.41 A/mg<sub>Pt</sub> for PtM<sub>2</sub>/C, Pt/CCC (HCC) and Pt<sub>3</sub>M/AGC catalysts, respectively.
- Achieved durability of kinetic mass activity of 0.27 A/mg<sub>Pt</sub> after 30,000 cycles for Pt<sub>3</sub>M<sub>1</sub>/AGC catalyst in 25 cm<sup>2</sup> cell.
- Accomplished initial high current density of 1.45 A/cm<sup>2</sup> at 0.56 V<sub>ir-free</sub> in H<sub>2</sub>-air for Pt<sub>3</sub>M<sub>1</sub>/AGC catalyst.



## Introduction

Stable and highly active HCC was developed at USC 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, developed at USC, and platinum for oxygen reduction reaction [1-10]. Yonsei University developed a procedure for the synthesis of leached Pt-alloy catalysts deposited on AGC. Furthermore, Pt dendrites with controlled size have been developed for oxygen reduction reactions (ORR) [11-13]. The dendrites show superior activity for ORR and better selectivity when compared to the commercial Pt/C catalyst. HMC optimizes the design of 50 cm<sup>2</sup> active area bipolar plates and short stack assembly.

## 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 USC's patented process. The synergetic effect present in HCC results from contribution of the active sites present in CCC which improve the catalyst performance at low potentials, while implementation of Pt or leached Pt-alloy active sites increase the mass activity at high potentials. The goal of our second strategy is the synthesis of Pt-alloy catalysts deposited on AGC. To overcome the drawbacks associated with carbon corrosion under automotive operating conditions, corrosion-resistant catalyst support based on TiO<sub>2</sub> and corrosion-resistant hybrid TiO<sub>2</sub>-CCC are under development at USC. HMC optimizes the design of 50 cm<sup>2</sup> active area bipolar plates and short stack assembly.

## Results

In this reporting period, Pt/CCC (HCC) and PtM<sub>2</sub>/C alloy catalysts were synthesized at USC. Pt and Pt-alloy catalysts deposited on AGC were developed at Yonsei

University. HMC optimized the flow-field design of 50 cm<sup>2</sup> active area bipolar plates and short stack assembly. The performance of the catalysts including ECSA, kinetic mass activity, catalyst durability after 30,000 cycles, specific activity and initial high current performance were evaluated using rotating ring disc electrode and in a proton exchange membrane fuel cell (PEMFC).

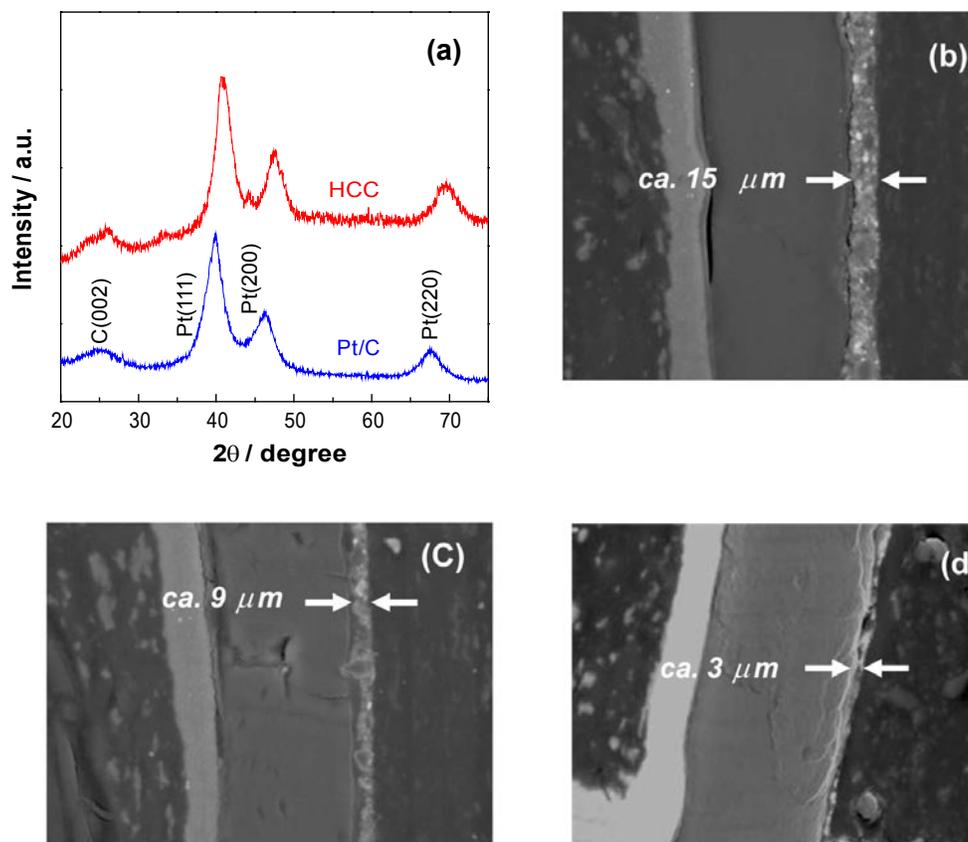
Figure 1 shows the X-ray diffraction (XRD) of HCC catalyst and the cross-sectional analysis of MEAs utilizing different loadings of HCC catalyst. Shift of the diffraction peaks to higher Bragg angles indicates a decrease in the lattice constant due to alloy formation during the heat treatment. The ECSAs of the HCC catalyst and Pt/C catalyst were calculated to be 102 and 97.2 m<sup>2</sup>/g, respectively.

PtM<sub>2</sub>/C alloy catalyst was synthesized by depositing a protective layer on the surface of Pt/C to inhibit Pt particle agglomeration during high temperature alloying process. XRD showed slight shift of the diffraction peaks towards higher angle which confirms the lattice contraction even after chemical leaching procedure. With the protecting layer, there is no change of the Pt peak width and intensity suggesting the small change of the Pt particle size after high temperature alloying procedure. The average Pt particle sizes of Pt/C, Pt/C heated at 800°C, and de-alloyed PtM<sub>2</sub>/C catalysts are 3, 22.2 and 3.3 nm, respectively. The results show that the Pt particles agglomerated during high temperature heat treatment in the absence of protecting layer. The ECSAs of the 60% Pt/C and 60% PtM<sub>2</sub>/C catalysts are calculated to be 56.6 and 40.7 m<sup>2</sup>/g, respectively.

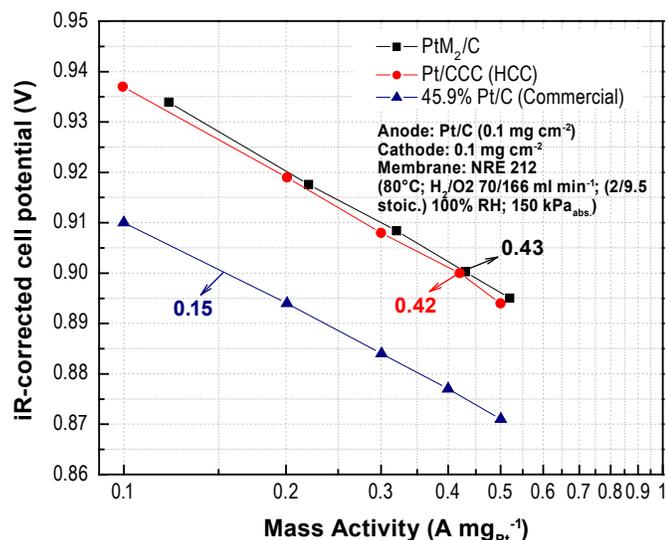
Figure 2 compares the mass activities of HCC, PtM<sub>2</sub>/C and commercial Pt/C catalysts. The cathode catalyst loadings were maintained at 0.1 mg/cm<sup>2</sup>. Nafion<sup>®</sup> NRE 212 membrane was used for making the MEAs. As shown in Figure 2, the kinetic mass activities of 0.43 A/mg<sub>Pt</sub> and 0.42 A/mg<sub>Pt</sub> were estimated for 60% PtM<sub>2</sub>/C and 40% HCC catalyst, respectively. The mass activity of 45.9% commercial Pt/C catalyst is 0.154 A/mg<sub>Pt</sub>.

A new method was developed to functionalize the graphitic carbon through the non-covalent  $\pi$ - $\pi$  interaction using a bifunctional molecule namely, 1-pyrenecarboxylic acid (1-PCA). The results indicated that this molecule irreversibly adsorbs on the inherently hydrophobic surfaces of carbon nanofibers (PCA-CNFs). The results revealed that the Pt nanoparticles deposited on PCA-CNF are uniformly distributed on the CNFs, with no agglomeration. The average Pt particle size was 2.0 ± 0.2 nm which is smaller than the particle size observed on the raw CNF. The Pt content loaded on 1-PCA treated CNF was 38 wt%, which is much higher than the raw CNF (18 wt%).

To inhibit the agglomeration of Pt particles during the high temperature alloying process, a new impregnation method was developed at Yonsei University to synthesize platinum alloy particles to be uniformly distributed on the support. The Pt-alloy particle size was calculated from the XRD. The normal heat-treatment of commercial



**FIGURE 1.** (a) XRD of HCC Catalyst — Cross-sectional Images of MEAs Utilizing HCC Catalysts (b) 0.2 mg/cm<sup>2</sup>, (c) 0.1 mg/cm<sup>2</sup> and (d) 0.04 mg/cm<sup>2</sup>



**FIGURE 2.** Mass Activity Comparison of Pt/CCC (HCC), PtM<sub>2</sub>/C and Commercial Pt/C Catalysts

50% Pt<sub>3</sub>M<sub>1</sub>/C resulted in 10.8 nm particles while the 50% Pt<sub>3</sub>M<sub>1</sub>/AGC synthesized in this study resulted in 3.4 nm

particles. The aggregation of Pt particles was restrained by the protective film used in this study.

The performance of commercial Tanaka Kikinzo Kogyo K. K. (TKK) 40% Pt/C, 46% Pt/C, and 50% Pt<sub>3</sub>M<sub>1</sub>/AGC as cathode catalysts was investigated in a PEMFC. The ECSA measured in a three electrode system and fuel cell was used to estimate the catalyst utilization. The utilization ratio for Pt<sub>3</sub>M<sub>1</sub>/AGC catalyst was estimated to be 88% which is higher than that of TKK 40 wt% Pt/C (76%) and TKK 46 wt% Pt/C (56%). The utilization of 88% observed for the in-house synthesized catalyst is due to better Pt-alloy particle distribution on PCA modified graphitic carbon nanocage which was used as a catalyst support.

To optimize the protecting coating process, Pt<sub>3</sub>M<sub>1</sub>/AGC catalyst was synthesized with different mass ratio (25, 50 and 60% on a carbon support). XRD was used to determine the alloy particle size. No extra peaks assigned to M<sub>1</sub> or M<sub>1</sub>-oxides were identified. The results indicated that a high degree of alloying is present for Pt<sub>3</sub>M<sub>1</sub>/AGC catalysts. The particle sizes of the Pt<sub>3</sub>M<sub>1</sub>/AGC catalysts were calculated to be 3.2, 3.4 and 4.1 nm at catalyst loading of 25%, 50% and 60% on the carbon support, respectively.

The performance of the catalysts was estimated from the polarization curves and evaluated based on the mass activity

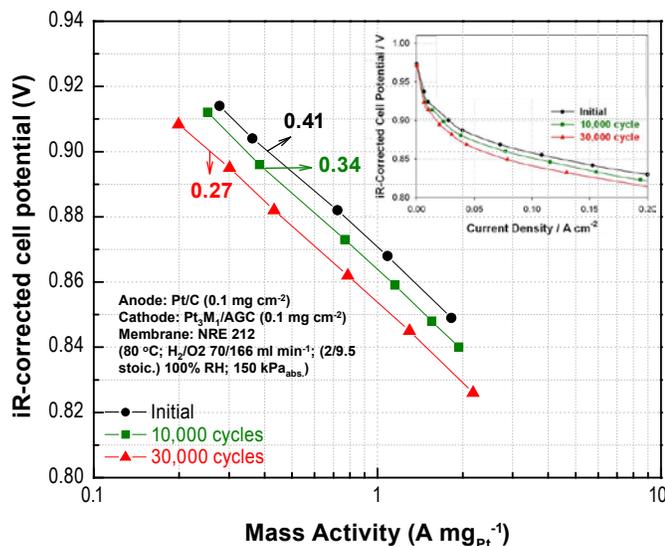
( $A/mg_{PGM}$  @  $900\text{ mV}_{iR-free}$ ) and the specific activity ( $\mu A/cm^2$  @  $900\text{ mV}_{iR-free}$ ). The specific activity of 50%  $Pt_3M_1/AGC$  is  $1,023\ \mu A/cm^2$ , which is higher than the DOE target ( $720\ \mu A/cm^2$ ). The ECSA of the catalyst used to calculate the specific activity was obtained from the MEA.

The durability of 50%  $Pt_3M_1/AGC$  catalyst was evaluated using DOE cycling protocol. The active area of the MEA was  $25\text{ cm}^2$ . The cathode was cycled under  $N_2$  (relative to the anode under  $H_2$ ) 30,000 times between 0.6 and 1.0 V at a sweep rate of 50 mV/s. Cell diagnostics of the cathode catalyst such as ECSA, ORR mass activity, and oxygen polarization curves were performed after 3,000, 10,000, 20,000, and 30,000 cycles. The activity of the catalyst was evaluated based on its mass activity. Figure 3 shows the  $iR$ -corrected polarization curves under  $H_2O_2$  and 100% relative humidity. The fuel cell operating conditions are given in the graph. The initial mass activity and the mass activity loss after 10,000 and 30,000 cycles are also presented in Figure 3 (inset). The mass activity loss of 50%  $Pt_3M_1/AGC$  is 34% which is lower than the DOE target (40% loss). The ECSA loss is only 30% (decreased from 29.5 to 20.8  $m^2/g$  after 30,000 cycles). The DOE target is less than 40%. Comparison of  $H_2/air$  fuel cell performance at high current densities of commercial Pt/C and  $Pt_3M_1/AGC$  catalyst is shown in Figure 4. Fuel cell operating conditions are shown in the figure.

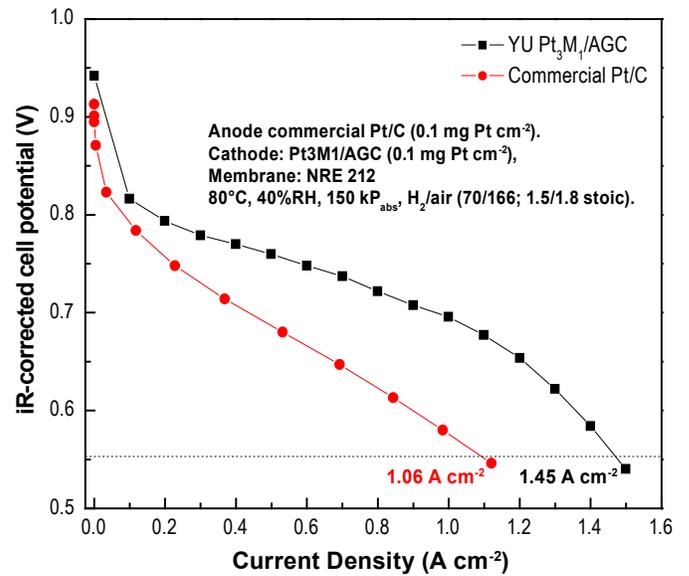
### Conclusions and Future Directions

Accomplishments in the reporting period:

- Achieved onset potential for oxygen reduction close to 0.9 V and less than 2.5% peroxide formation for CCC.



**FIGURE 3.** Mass Activities of 50%  $Pt_3M_1/AGC$  Catalysts as a Function of Number of Cycles (The  $iR$ -corrected polarization curves obtained for 50%  $Pt_3M_1/AGC$  as function of number of cycles is shown in the inset.)



**FIGURE 4.** Comparison of  $H_2/air$  Fuel Cell Performance of Commercial Pt/C and  $Pt_3M_1/AGC$  Catalysts

- The kinetic mass activities of  $0.43\ A/mg_{Pt}$ ,  $0.42\ A/mg_{Pt}$  and  $0.41\ A/mg_{Pt}$  were estimated for 60%  $PtM_2/CCC$ , 40% HCC catalyst and 50%  $Pt_3M_1/AGC$  catalyst, respectively compared with mass activity of 45.9 % commercial Pt/C catalyst is  $0.154\ A/mg_{Pt}$ .
- The specific activity of 50%  $Pt_3M_1/AGC$  synthesized at Yonsei University is  $1,023\ \mu A/cm^2$ , which is higher than the DOE target ( $720\ \mu A/cm^2$ ).
- The mass activity loss after 30,000 cycles, DOE protocol (0.6-0.9 V) of 50%  $Pt_3M_1/AGC$  is 34% is lower than that the DOE target (40% loss).
- The ECSA loss for the same catalyst is only 30% (decreases from 29.5 to 20.8  $m^2/g$ ) after 30,000 cycles. The DOE target is less than 40%.

Future anticipated accomplishments are to:

- Achieve ultra-low Pt HCC catalysts for oxygen reduction reaction with mass activity larger than  $0.44\ A/mg_{Pt}$  and durability of  $0.24\ A/mg_{Pt}$  after DOE suggested potential cycling (0.6 to 1 V) (USC).
- Develop activated high surface area Pt catalyst through synthesis of Pt-alloy catalyst using in-house developed procedures (Yonsei University and USC).
- Accomplish high current density performance and durability in  $H_2/air$  fuel cells to meet the DOE targets (USC and Yonsei University).
- Develop support which will increase the catalyst utilization and eliminate the loss of ESCA through: performance optimization of CCC, stable conductive  $TiO_2$  and CCC- $TiO_2$  hybrid supports developed at USC and modified graphitic carbon developed at Yonsei University. (USC, Yonsei University and HMC)

- Evaluation of MEA and fuel cell stack: To perform accelerated durability tests of MEAs with commercial catalyst to optimize the design of 50 cm<sup>2</sup> active area bipolar plate flow field and short stack assembly (HMC).

## 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 2011 Publications/Presentations

### Publications

1. 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.
2. 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.
3. 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.
4. 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.
5. Xuguang Li, Sheng-Yang Huang, Branko Popov, "Development of Low Pt Loading Cathode Catalysts for Polymer Electrolyte Membrane Fuel Cells", *ECS Trans.* 2010, **33**, 239-246.
6. Sheng-Yang Huang, Prabhu Ganesan, Won Suk Jung, Nicholas Cadirov, Branko Popov, "Titania Supported Platinum Catalyst with High Electrocatalytic Activity and Stability for Polymer Electrolyte Membrane Fuel Cell", *ECS Trans.* 2010, **33**, 483-491.
7. Sheng-Yang Huang, Prabhu Ganesan, Won Suk Jung, Nicholas Cadirov, Branko Popov, "Development of Supported Bifunctional Oxygen Electrocatalysts with High Performance for Unitized Regenerative Fuel Cell Applications", *ECS Trans.* 2010, **33**, 1979-1987.

### Presentations

1. B.N. Popov, Li Xuguang, T. Kawahara, H. Yanagi, "Development of Low Platinum Loading Cathode Catalysts for Polymer Electrolyte Membrane Fuel Cells," 218<sup>th</sup> ECS Meeting, Las Vegas, Nevada, October 13, 2010. Contributed.
2. B.N. Popov "Recent Advances in Non-Precious Metal Catalyst for Oxygen Reduction Reaction in Fuel Cells," 218<sup>th</sup> ECS Meeting, Las Vegas, Nevada, October 13, 2010. Contributed.

3. B.N. Popov, S.-Y. Huang, "Titania Supported Platinum Catalyst with High Electrocatalytic Activity and Stability for Polymer Electrolyte Membrane Fuel Cell," 218<sup>th</sup> ECS Meeting, Las Vegas, Nevada, October 13, 2010. Contributed.
4. B.N. Popov, S.-Y. Huang, "Development of Supported Bifunctional Oxygen Electrocatalysts with High Performance for Unitized Regenerative Fuel Cell Applications," 218<sup>th</sup> ECS Meeting, Las Vegas, Nevada, October 13, 2010. Contributed.

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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.
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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.
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