2014 DOE Hydrogen and Fuel Cells Program Review

Development of Ultra-low Doped-Pt Cathode Catalysts for PEM Fuel Cells

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Project ID # FC088

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Overview

Timeline

- Start date: June 2010
- End date: May 2015
- Percent complete: 85%

Budget

- Total Funding Spent as of 3/31/2014: \$2,660,608.22
- Total Project Value: \$4,750,000
- Cost Share Percentage: 20.0

Barriers

A. Durability

Retain kinetic activity and high current density performance in H₂/air after potential holding (support durability) and potential cycling (catalyst durability) experiments.

B. Cost

- Decrease in PGM content
- Cost effective synthesis procedures

C. Performance

 Obtain high current density performance in H₂/air and maintain the power density

DOE Technical Targets

Electrocatalyst/MEA	2017 Targets
PGM Loading (mg/cm ²)	0.125
Mass Activity (A/mg _{PGM})	≥0.44
Mass activity and ECSA Loss after 30k Cycles (Catalyst Stability) (%)	≤ 40
Mass activity and ECSA Loss after 400 h (Support Stability) (%)	≤ 40
Potential loss after 30 k cycles (Catalyst Stability)	≤30 mV
Potential loss after 400 h (Support Stability)	≤30 mV

Project Lead

University of South Carolina (USC)

Additional Interactions

- Rudiger Laufhutte (UIUC)
- Dr. Lax Saraf (Clemson University)
- Dr. Alan Nicholls (UIC)
- Electron Microscopy Center, USC

Relevance

Develop cost effective high volume synthesis procedure to manufacture highly stable activated carbon composite catalyst (A-CCC) support.

- Achieve onset potential of 0.9 V vs. SHE for ORR.
- Achieve $\leq 30 \text{ mV}$ loss in H₂/air 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 pyridinic-nitrogen catalytic sites from the support and suppressed Pt-lattice catalyst.
 - Demonstrate mass activity of ≥0.44 A/mg_{PGM} in H₂/O₂ fuel cell, initial high current performance under H₂/air (<0.125 g_{PGM}/kW rated power density) and stability of mass activity (≤ 40% loss) and stability of high current density performance under H₂/air using DOE potential cycling and potential holding tests.

Develop a low cost catalyst with optimized average mass activity, stability of mass activity, initial high current performance under H_2/air (power density), catalyst and support stability able to meet 2017 DOE targets.

Approach

Develop doped Pt/A-CCC catalyst with high activity for ORR through synergistic effect of pyridinic nitrogen containing A-CCC support and suppressed Pt-lattice catalyst.

Support Development

- Develop a corrosion resistant support with desired BET surface area to sustain potential cycling and potential holding experiments.
 - Surface modification with acid and inclusion of oxygen groups.
 - Metal-catalyzed pyrolysis with N-containing compounds to (i) dope the support, (ii) include pyridinic nitrogen active sites and (iii) increase graphitization.
 - Chemical leaching to remove excess metal used to dope the support.

Catalyst Development

- ✓ Development of doped Pt/A-CCC catalyst.
- Two in-house developed procedures contribute to the high activity of the catalyst with the following electrocatalytic properties:
 - Enhanced activity due to synergistic effect of pyridinic nitrogen containing A-CCC support and Pt towards oxygen reduction reaction.
 - Suppressed Pt-lattice catalyst having Pt-shell/doped-metal core structure (with different doping metal content from 0 to 50%).
- ✓ In order to synthesize doped Pt/A-CCC catalyst with high activity and stability:
 - Modified polyol process was developed for uniform Pt deposition.
 - Heat treatment process was optimized to control the particle size between 3 and 5 nm.

Approach

Synthesis of Metal-doped HCC Catalyst (Doped Pt/A-CCC)



Project Timeline (According to Revised SOPO Dated 01/23/2014)





From 2013 AMR Presentation

- Development of three generations of carbon composite catalyst supports with increasing graphitization and support stability.
- Two methodologies were used at USC to synthesize ultra-low Pt loading catalysts:
 - Metal impregnation followed by high temperature pyrolysis and leaching (<u>Details are given in Reviewer Only</u> <u>Slides 46-51</u>).
 - Metal doped Pt catalyst by diffusing the metal previously embedded in the support (<u>USC method This</u> <u>presentation</u>)
- Synthesis of catalysts with initial high kinetic activity (0.38 0.44 A/mg_{PGM}) and good stability of mass activity (32 50% loss in mass activity) after 30k cycles.
 - However, high mass activity does not translate into ORR activity in high current performance under H₂-air operating conditions.







Cotolyst	Particle	Mass activity (A/mg _{PGM})			
Catalyst	size (nm)	Initial	30 k*	400h**	
НСС	4.0	0.38	0.2 (<u>47% loss</u>)	0.19 (<u>50% loss</u>)	
Pt-alloy/CNC	3.5	0.44	0.3 (<u>32% loss</u>)	0.23 (<u>48% loss</u>)	

*30,000 cycles between 0.6 and 1.0V with rates of 50mV/s

1. Support Development

Development of Activated Carbon Composite Catalyst (A-CCC) Support



HIGHLIGHT:

BET&BJH: The surface areas for A-CCC (fresh) and A-CCC (stabilized) are 80 and 200 m²/g. BET shows presence of mesopores after stabilization step.

HRTEM: Graphitic carbon containing carbon nano fibers/tubes are formed during metal catalyzed pyrolysis.

ADVANTAGE: The BET surface area and the pore-size of the A-CCC support can be tailored to achieve uniform Pt deposition (3-5 nm).

1. Support Development Metal inclusion and Estimation of Metal Content in A-CCC Support





ICP analysis	Co amount (wt%)	BET surface area (m²/g)
A-CCC H800	4.76%	137
A-CCC H900	6.84%	131
A-CCC H1000	8.13%	125
A-CCC H1100	10.69%	85

HIGHLIGHT

- Cobalt amount in the support increased with the increase in heat treatment temperature.
- BET surface area decreased at temperatures >900 °C.

1. Support Development Metal inclusion and Estimation of Metal Content in A-CCC Support



- Graphitic carbon formation through metal-catalyzed pyrolysis.
- Co particles are embedded in the bulk of the carbon during pyrolysis in the presence of Co-N chelate compound.
- Carbon nano fiber can be formed in the presence of Co at relatively low temperature (~800°C) which is more stable than amorphous carbon.
- The A-CCC catalyst showed an onset potential of 0.9 V vs. RHE and well-defined kinetic and mass transfer regions.

1. Support Development

Support Stability-1.2 V Potential Holding



	Pt/A-CCC		Pt/C
	Initial	400h	Loss
Mass activity (A/mg _{PGM})	0.25	0.17 <u>(32% loss)</u>	<u>72% loss</u>
ECSA (m²/g)	31.4	29.5 <u>(6% loss)</u>	<u>71% loss</u>
V _{iR-free} loss @ 0.8A/cm ² (mV) (2.0/2.0 stoic.)	689	662 (27 mV loss)	<u>No Activity</u>

HIGHLIGHT:
(Status against 2017 DOE targets)
 The mass activity decreases from 0.25 to
0.17A/mg _{PGM} (<u>32% mass activity loss</u>) after 400
h.
•The potential loss is 27mV after 400 h
potential holding against the 2017 DOE target
of 30 mV loss after 400 h, respectively.
 The rated power density is <u>0.18g_{PGM}/kW.</u>
 Commercial Pt showed 72% mass activity
loss, 71% ECSA loss and no activity after 400 h.

2. Catalyst Development (Pt Deposition)



Polarization : H₂/O₂, 750/750 sccm, 100% RH, 80°C

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Technical Accomplishments 2. Catalyst Development Doped Pt Catalyst Development

Development of a Process to Control the Particle Size During High Temperature Pyrolysis



2. Catalyst Development

Doped Pt Catalyst Development





Heat treatment time (h)	Pt peak (deg)	PtCo peak (deg)	Particle size (nm)
0	67.3		2.5
0.5	67.9	69.4	2.8
1	67.8	69.5	3.9
2		69.4	3.9
4		69.5	4.5

Co doped Pt Composition	Pt _{1.3} Co ₁ /C
Co amount in the CCC (wt%)	10.32%
Pt amount (wt%)	30
Support(C+Co) amount (%)	70
Carbon amount (wt%)	62.776
Cobalt amount (wt%)	7.224
Pt amount (mol ratio)	0.154
Co amount (mol ratio)	0.123
Pt/Co mol ratio	1.3

- XRD shows the
- presence of Pt and PtCo phases after 0.5
- h heat treatment.
- Single-phase **Co-doped Pt is** formed after 2 h.
- The shift in 2θ can be varied by adjusting the heat treatment time.

Technical Accomplishments 2. Catalyst Development **Doped Pt Catalyst Development** HRTEM and XEDS Analysis of Doped Pt/A-CCC Catalyst

<u>XEDS Mapping</u>



Pt L series





25nm

60-

50

40-

30-20-10-

High resolution line-scanning

All Flement

0.012

0.016

0.02

0.024



Pt shell thickness: 0.8nm

- Co is present within the A-CCC support and diffuses during controlled annealing in the presence of a protective coating to form Codoped Pt catalyst.
- Line scan confirms the existence of Co in the core and a Pt-shell thickness of 0.5-0.8nm (Core-shell structure). 15



3. Catalyst Durability Catalyst Durability Studies of Doped Pt/A-CCC (<u>0.6-1.0 V Cycling</u>)



Mass Activity Loss of Doped Pt/A-CCC



DOE Accelerated Stress Test Protocol $0.6 \sim 1.0 \text{ V}, 50 \text{mV/s}, 30,000 \text{ cycle},$ $\text{H}_2/\text{N}_2, 80^{\circ}\text{C}, 100 \% \text{ RH}, \text{ single cell}$ 25cm² Polarization : H₂/O₂, 750/750 sccm, 100% RH, 80°C Pt mass activity : H₂/O₂, 2/9.5 stoic, 100% RH, 80°C, 150kPa backpressure

HIGHLIGHT: (Status against 2017 DOE targets)

•<u>H₂-O₂</u>: The initial cell potential at 2 A/cm² current density is 0.701 V_{iR-corr} initially and 0.669 V_{iR-corr} after 30k potential cycling corresponding to a loss of 32 mV. •<u>Mass Activity</u>: The initial mass activity of the Co-doped Pt/A-CCC catalyst is 0.408 A/mg_{PGM} After 30k cycles, the mass activity decreased to 0.23 A/mg_{PGM} which corresponds to 43.6% decay from the initial value.

3. Catalyst Durability Catalyst Durability Studies of Doped Pt/A-CCC (<u>0.6-1.0 V Cycling</u>)



Fresh Catalyst HRTEM (<u>Scale = 10 nm</u>)



HRTEM After 30k (Scale = 10 nm)

HIGHLIGHT:

- The doped Pt/A-CCC catalyst exhibits potential loss of 79 mV (from 0.700 V_{iR-free} to 0.621 V_{iR-free}) after 30k cycles at 0.8 A/cm².
- Pt/C showed no activity after 30k cycles.

DOE Accelerated Stress Test Protocol

0.6 ~ 1.0 V, 50mV/s, 30,000 cycle, H_2/N_2 , 80°C, 100 % RH, single cell 25cm² H₂/air: 2.0/2.0 stoic, 40% RH, 80°C, 170 kPa



 The particle size increased from ~3.4 nm to 5-7 nm after 30k cycles

2~3 3~4 4~5 5~6 6~7 7~8 8~9 9~1010~1111~1212~1313~14

Particle size (nm)

Technical Accomplishments Catalyst Development Doped Pt Catalyst Development Formation of doped Pt/A-CCC₁ catalyst-Effect of leaching



HIGHLIGHT:

XRD shows after high temperature pyrolysis, Co present within the A-CCC₁ support diffused to the surface and doped into Pt lattice which is confirmed by the Pt peak shift in the XRD from 39.7 for pure Pt to 41.2° for the Co-doped Pt.

■ XRF & ICP analysis show that <u>37% Co was removed from the</u> catalyst after 0.5 h. Further leaching for 12h did not leach out all the transition metal (only 18% more Co is leached out). 45% Co remains in the catalyst corresponding to a <u>Pt to Co ratio of 1 to</u> 0.43. The Co dissolution rate in the first half an hour is 49 times higher than the remaining 11.5 hours.

□ <u>HRTEM</u> shows 3 to 6 nm doped Pt catalyst particles after controlled heat treatment process.

<u></u>	HRTEM
^{20 nm} 20 nm scale	2 nm scale 18

	Pt (wt%)	Co (wt%)	Molar ratio (XRF)	Molar ratio (ICP)
Fresh	78.4	21.6	Pt : Co = 1:0.93	Pt : Co = 1:1
HT800°C	78.4	21.6	Pt : Co = 1:0.93	Pt : Co = 1:0.85
Leach 0.5h	85.1	14.9	Pt : Co = 1:0.59	Pt : Co = 1:0.59
Leach 12h	88.8	11.2	Pt : Co = 1:0.42	Pt : Co = 1:0.43

Mass Activity and High Current Density Performance Improvement Effect of leaching on doped Pt/A-CCC₁ Formation





HIGHLIGHT:

□ <u>Mass activity</u> increased from 0.22 to 0.35 A/mg_{PGM} after Co-doping. leaching leads to better catalytic activity at 0.9 V $(0.47 \text{ A/mg}_{PGM})$.

□ <u>H₂/air performance</u>: At 0.6 V_{iR-free}, the current densities are 0.68, 1.00, 1.45 and 1.70 A/cm² for fresh, heat-treated, leached for 0.5h and leached for 12h catalysts, respectively. The 12 h leached catalyst showed initial power density of 0.196 g_{PGM}/kW (rated power).

□ <u>Catalyst stability</u>: Doped Pt/A-CCC₁ (12 h leached) catalyst showed 7 mV potential loss after 10k cycles. 19

Collaborations

Characterization and Interactions

- <u>Rudiger Laufhutte</u> (University of Illinois, Urbana-Champaign): ICP analysis of doped Pt catalysts.
- Alan Nicholls (University of Illinois, Chicago): HRTEM & XEDS mapping.
- Lax Saraf & Haijun Qian (Clemson University): Transmission Electron Microscopy analysis.
- <u>EM Center</u> (University of South Carolina): HR-TEM analysis
- Scribner Associates: Design and construction of fuel cell test stations according to USC requirements.
- Fuel Cell Technologies: Design and construction of 25 and 50 cm² single cells according to USC specifications.

Summary of Accomplishment of Doped Pt/A-CCC Cathode Catalyst

Metric	Units	Status (FY2014)	Commercial Pt/C	2017 DOE target	
	Initial Mass Activ	ity			
Initial Mass activity	A/mg _{PGM} @ 900 mV _{iR-free}	0.25~0.47	0.18	≥0.44	
	Catalyst Stability (0.6-1.0	V cycling)			
Loss in catalyst activity	% loss after 30k cycles	43%	68%	≤40%	
Loss in ECSA	% loss after 30k cycles	15%	80%	≤40%	
Potential loss @ 800 mA/cm ²	mV loss after 30k cycles	79 mV	No Activity	≤30 mV	
	Support Stability (1.2 V	holding)			
Loss in catalyst activity	% loss after 400 h	32%	72%	≤40%	
Loss in ECSA	% loss after 400 h	6%	71%	≤40%	
Potential loss @ 800 mA/cm ²	mV loss after 400 h	27 mV	No Activity	≤30 mV	
PGM Content and PGM Loading					
PGM total content (Power Density)	g _{PGM} /kW (rated)	0.18~0.24	0.3	≤0.125	
PGM total loading	mg _{PGM} /cm ² _{geo}	0.2	0.2	≤0.125 2 1	

Future Work

Task 1: Synthesis of metal doped Pt/A-CCC (HCC) catalysts

Task 2. Optimization studies of selected catalysts

- Initial and durability of mass activity and high current performance under H₂-air under potential cycling condition (0.6-1.0 V, 30k cycles).
- Increase the performance of Pt-M/A-CCC catalysts as a function of concentration of doped metal in the A-CCC support and pyrolysis temperature.
- **Task 3**. Optimization of high volume production procedures for the A-CCC support and doped Pt/A-CCC catalysts.

Task 4. Performance evaluation of two selected catalysts

- a) Durability of high current performance under H₂-air
- b) Catalyst down selection

The goal is to select a best performing catalyst to demonstrate the following characteristics in single cells: (According to Revised SOPO Dated 01/23/2014)

- (i) initial mass activity of 0.3 A/mg_{PGM} and stability of mass activity of at least 0.26 A/mg_{PGM} after 30k cycles
- (ii) initial high current density performance of at least 1.5 A/cm² at 0.6 $V_{iR-free}$
- (iii) stability of high current density of only 30-60 mV loss at 0.8 A/cm² following accelerated stress testing.
- (iv) Evaluation of reproducibility of support and catalyst performance.

Deliverables:

Supply of <u>a most promising catalyst</u> for independent evaluation. The amount to be determined by the DOE.

Publications Resulted from the Current Project

- 1. 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.
- 2. 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.
- 3. 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.
- 4. 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," *ECS Transactions*, 58 (2013) 761-778.
- 5. 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, *ECS Transactions*, **50**, (2013) 1427-1438.
- 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.
- 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.
- 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.
- 9. Xuguang Li and Branko N. Popov, Development of Non-Precious Metal Catalysts for Oxygen Reduction Reaction in Fuel Cells with High Activity and Stability, *ECS Trans.* 2010, *33*, 2333-2339.
- 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.
- 11. 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.

Presentations from the Current Project

- 1. Development of Ultra-Low Loading Pt Hybrid Catalyst for PEM Fuel Cells, Tianyuan Xie, Taekeun Kim, Won Suk Jung, Prabhu Ganesan, and Branko N. Popov, *224th ECS Meeting*, San Francisco, CA, October 27-November 01, 2013.
- Development of Ultra-Low Loading Pt Alloy Cathode Catalyst for PEM Fuel Cells, Branko N. Popov, Tianyuan Xie, Taekeun Kim, Won Suk Jung, and Prabhu Ganesan, 224th ECS Meeting, San Francisco, CA, October 27-November 01, 2013.
- 3. Development of Ultra-Low Loading Pt/AGC Catalyst for PEM Fuel Cells, Taekeun Kim, Won Suk Jung, and Prabhu Ganesan, Tianyuan Xie, and Branko N. Popov, 224th ECS Meeting, San Francisco, CA, October 27-November 01, 2013.
- 4. Analyzing the effect of Ultra-Low Pt Loading on Mass and Specific Activity of PEM Fuel Cells, Akos Kriston, Tianyuan Xie, Taekeun Kim, Won Suk Jung, David Gamliel, Brian Murphy Prabhu Ganesan, Branko N. Popov, *222nd ECS Meeting*, Honolulu, HI, October 7-12, 2012.
- 5. Development of Ultra-Low Pt Alloy Cathode Catalyst for PEM Fuel Cells, Branko N. Popov, Tianyuan Xie, Taekeun Kim, Won-suk Jung, Akos Kriston Brian Murphy, David Gamliel and Prabhu Ganesan, *222nd ECS Meeting*, Honolulu, HI, October 7-12, 2012.
- Development of Highly Active Pt₂Ni/CCC Catalyst for PEM Fuel Cell, Tianyuan Xie, Won Suk Jung, Taekeun Kim, Kriston Akos Prabhu Ganesan and Branko N. Popov, 222nd ECS Meeting, Honolulu, HI, October 7-12, 2012.
- Development of Hybrid Cathode Catalyst for PEM Fuel Cells, Taekeun Kim, Won Suk Jung, Tianyuan Xie, Akos Kriston, Prabhu Ganesan, David Gamliel, Brian Murphy and Branko N. Popov, 222nd ECS Meeting, Honolulu, HI, October 7-12, 2012.
- 8. Development of ultra-low platinum alloy cathode catalyst for PEM fuel cells, Branko N. Popov, Tae-keun Kim, Xie Tianyuan, Prabhu Ganesan, and Hansung Kim, 220th ECS Meeting, Boston, MA, October 9-14, 2011.
- 9. Titanium Dioxide-Supported Platinum Catalysts, S. Huang, P. Ganesan, and B. N. Popov, 220th ECS Meeting, Boston, MA, October 9-14, 2011.
- Development of Non-Precious Metal Catalysts for Oxygen Reduction Reaction in Fuel Cells with High Activity and Stability, X. Li, G. Liu, T. Kim, S. Ganesan, P. Ganesan, and B. N. Popov, 220th ECS Meeting, Boston, MA, October 9-14, 2011.
- 11. Development of Low Platinum Loading Cathode Catalysts for Polymer Electrolyte Membrane Fuel Cells, X. Li, S. Huang, B.N. Popov, *218th Meeting of the Electrochem. Soc.*, Las Vegas, Nevada, October 13, 2010.
- 12. Recent Advances in Non-Precious Metal Catalyst for Oxygen Reduction Reaction in Fuel Cells," X. Li, B.N. Popov, T. Kawahara, H. Yanagi, 218th Meeting of the Electrochem. Soc., Nevada, October 13, 2010.

Team Members who contributed to this presentation

University of South Carolina

Branko N. Popov, Tae-keun Kim, Won-suk Jung, Xie Tianyuan, Joseph Rotchford, Akos Kriston and Prabhu Ganesan



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