V.E.5 Advanced Cathode Catalysts



Project Start Date: March 2007 Project End Date: 2011

Objectives

The main objective of this project is to:

• Develop oxygen reduction reaction (ORR) catalysts, alternative to pure Pt, capable of fulfilling cost, performance and durability requirements established by DOE for the polymer electrolyte fuel cell (PEFC) cathode; assure path to large-scale fabrication of successful compositions.

Individual objectives of this research are as follows:

• Design, synthesize and characterize new catalyst supports and electrode structures for new-generation ORR catalysts.

- Determine ORR mechanism on newly developed catalysts via extensive physicochemical characterization and electrochemical and fuel cell testing.
- Optimize electrodes with new catalysts and structures for maximum performance.
- Evaluate catalyst stability; minimize performance loss over time.
- Assure path forward for the fabrication and scale up of viable catalysts.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability (of catalysts and electrode layers)
- (B) Cost (of catalysts and membrane electrode assemblies [MEAs])
- (C) Performance (of electrodes, including (i) ORR overpotential and (ii) O₂ mass-transport rates)

Technical Targets

Non-platinum cathode catalysis research in this project focuses on DOE's 2010 technical targets specified in Table 3.4.12 (Electrocatalysts for Transportation Applications) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan. The 2010 targets relevant to this research project together with the current status (where applicable) are shown in Table 1.

Accomplishments

- Significantly advanced knowledge of factors affecting ORR activity of the Pt monolayer-type catalysts (facet, shape, particle size, high coordination number).
- Specific and mass activity of ultra-low Pt-content core-shell catalysts significantly improved, up to 1,200 µA/cm² and 1.1 A/mg_{PGM} (2.4 A/mg_{Pt}) at 0.90 V, respectively (rotating disk electrode [RDE] testing); DOE performance targets met and substantially exceeded.
- Excellent stability demonstrated with several platinum group metal (PGM) catalysts, including hollow-Pt nanoparticle catalyst (less than 17 mV performance loss at E_{ν_2} after 20,000 scans) and $Pt_{ML}/Pd_2AuNi/C$ nanoparticles (ΔE_{ν_2} limited to 6 mV after 10,000 potential cycles).

TABLE 1. Targets and Current Status

Characteristics	Units	2010 Stack Target (Anode + Cathode)	2010 Status (Cathode)
PGM total loading (50 cm ² fuel cell)	mg _{PGM} /cm ² electrode area	0.3	0.28 ¹
Mass activity	A/mg _{PGM} @ 900 mV _{iR-free}	0.44	1.1 ² 2.4 ³
Non-Pt catalyst activity per volume of supported catalyst	A/cm ³ @ 800 mV _{iR-free}	>130	165 ⁴
Durability with cycling	5,000 hours at T ≤80°C	2,000 hours at T >80°C	see results ⁵

¹ $Pt_{M/}$ Pd/C catalyst from scaled-up synthesis by Cabot Fuel Cells, tested in 50-cm² single fuel cell at 80°C; cathode - 0.28 mg_{PGM} cm² (0.06 mg_{Pt} cm⁻² + 0.22 mg_{Pd} cm⁻²); anode - 0.05 mg_{Pt} cm⁻² Pt/C; MEA not optimized.

² Mass activity per mg_{PGM} in Pt/Au/Pd Co catalyst in RDE testing at 0.90 V.

³ Mass activity per mg_{Pt} in Pt/Au/Pd Co catalyst in RDE testing at 0.90 V.

⁴ Current per electrode (not catalyst) volume, obtained from extrapolation to 0.80 V from log-plot of currents at higher voltages to remove mass-transport losses; CM-Fe-C catalyst tested in 5-cm² single fuel cell at 80°C; cathode - 3.5 mg cm²; anode - 0.25 mg_{Pt} cm² Pt/C; MEA not optimized.

⁵ Most catalysts tested using DOE electrocatalyst accelerated stress test protocol of cycling from 0.6 V to 1.0 V at 50 mV s⁻¹ for 30,000 cycles under N₂ gas flow.

- 2010 DOE activity target for non-PGM catalysts reached; open circuit voltage (OCV) of 1.04 V and volumetric ORR activity of 165 A/cm³_{electrode} (after mass-transport correction) achieved with cyanamide (CM)-Fe-C catalyst in fuel cell testing; rapid improvement in fuel cell performance of several other non-precious metal catalysts shown.
- High durability accomplished with polyaniline (PANI)-based catalysts to potential holding at OCV as well as to potential (RDE) and voltage (fuel cell) cycling, up to 30,000 cycles (DOE protocols followed).
- ORR activity of PANI-derived catalysts correlated to microporosity and Fe-N coordination; improved durability linked to graphene sheet formation (results of advanced spectroscopic and microscopic characterization).
- Synthesis of BNL's Pt_{ML}/Pd/C core-shell catalyst scaled up to 20 g per batch.

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Introduction

This multitask and multi-partner project focuses on the development of new oxygen reduction catalysts and electrode structures for the PEFC cathode, with either greatly reduced precious-metal content relative to that presently used by stack developers, or entirely preciousmetal-free. The main objective of this effort is to lower the catalyst cost in the fuel cell power system through improvements in ORR performance in terms of both electrocatalysis and oxygen transport to the reaction site.

Approach

The primary research goal of this project is the development of new oxygen reduction catalysts, in two different classes: (i) catalysts with ultra-low platinum content (stable metals or alloys as cores; non-preciousmetal core catalysts; mixed metal shells for higher ORR activity) and (ii) non-precious metal catalysts obtained by high-temperature treatment of various precursors of carbon, nitrogen and transition metals. Understanding of the key factors impacting ORR activity and performance durability of catalysts in both classes is pursued through a major characterization effort including X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (TEM), among other techniques.

Development of new catalysts is closely tied to novel electrode structures, tailored to maximize either catalyst utilization in the case of precious metal-based ORR catalysts (e.g. core-shell Pt-based catalysts) or the loading of non-precious metal catalysts with intrinsically lower than platinum volumetric ORR activity. The electrode-structure component of the effort concentrates on two groups of materials: (i) carbon- and non-carbonbased nanostructures for efficient mass transport, improved durability, and maximum catalyst utilization, and (ii) open-frame catalyst structures obtained using microemulsion/reverse emulsion techniques.

In addition to short-term testing and initial performance assessment, catalysts, supports, electrode structures, and membrane-electrode assemblies developed in this project are subject to long-term performance (durability) testing. Performance degradation mechanisms are being identified and, if possible, addressed. Fabrication and scale up of viable catalysts and supports is also being tackled through collaboration between partners in this project.

Results

Catalysts with Ultra-Low Pt Content — A variety of strategies were implemented in the past year to generate PGM-containing catalysts with high activity and stability. Three major ideas were applied:

(1) inducing proper degree of lattice contraction in the Pt surface layer to increase ORR activity, (2) removing low-coordination surface atoms that decrease activity and durability, and (3) partially substituting PGM with non-precious metals into the cores of the catalysts. A more flexible synthesis approach using Prussian blue analogs for the latter type of catalyst was also developed. Scale-up efforts on the more mature PtPd/C catalyst were also continued.

Several catalysts based on applying Pt monolayers to Pd cores were prepared. In general, depositing Pt onto Pd results in higher ORR activity because of the Pt lattice contraction (Figure 1a) and beneficial electronic interaction. The addition of an Ir layer onto the Pd core followed by annealing to bring Pd to the surface generates a contracted Pd layer. When the Pt monolayer is deposited, the additional lattice contraction due to the presence of subsurface Ir results in even higher ORR activity = Pt_{ML}PdIr/C specific ORR activity: 938 μ A/cm² (3× that of Pt/C); mass activity: 2.17 A/mg_{Pt} (more than 20× that of Pt/C) (Figures 1b and 1c). Pt₈₀Ir₂₀/Pd/C showed good fuel cell performance (0.53 A/mg_{Pt}), and the E_{u_2} of Pt_{ML}Pd/C gained 27 mV (to 0.903 V) after a Br treatment that removed low coordination atoms.

The catalytic activity per gram of precious metal was further increased in this class of catalysts by mixing Ni into the Pd core, removing reactive Ni atoms with exposure to Au, and finally depositing a Pt monolayer (Figure 2). The obtained Pt/Au/Pd_xNi catalyst shows remarkable activity (by RDE testing) far exceeding the DOE target specified above – 1.10 A/mg_{PGM} (2.41 A/mg_{Pt}). A synthesis involving Prussian blue analogs was developed allowing for surfactant-free synthesis of multi-metallic aggregates that include non-precious metals in the core (possibly convenient for further nanoparticle engineering). Using this approach, an active and durable Pt_{ML}/Pd₂Au₁Ni₁ catalyst was



FIGURE 2. Schematic depiction and ORR activity result (RDE) for Pt/Au/ Pd_Co core-shell catalyst.

prepared ($E_{u_2} = 0.865$ V). The catalyst loses only 6 mV in E_{u_2} after 10,000 potential cycles.

In an alternative approach, a Pt/Ni core shell catalyst was synthesized and the Ni was subsequently removed, resulting in a hollow Pt sphere with 1.2% Pt lattice contraction (Figures 3a and 3b). The hollow-sphere catalyst exhibits good durability, losing only 17 mV in E_{v_2} after 10,000 potential cycles and 10,000 potential pulse sequences (see figure caption for details) and maintaining a high activity of 0.62 A/mg_{PGM} (Figure 3d).

Scale-Up Synthesis of Catalysts with Ultra-Low Pt Content — The synthesis of the $Pt_{ML}/Pd/C$ catalyst was scaled up further to 20 g by Cabot Fuel Cells using a spray-pyrolysis approach. The catalyst delivered very good performance in fuel cell testing, matching mass-



FIGURE 1. Effect of Pd core on Pt_{ML} activity: (a) depiction of Pt lattice contraction that occurs on Pd core; (b) ORR activity vs. Pt surface area (A/cm²) of Pt_{ML} Pdlr/C as measured by RDE compared to Pt/C and Pt_{ML} Pd/C; activity after 1,000 potential cycles also shown; (c) ORR activity per gram Pt (A/g_{Pt}) of Pt_{ML} Pdlr/C with same comparisons as in (b).



FIGURE 3. Pt hollow spheres: (a) hollow-spheres synthesis scheme; (b) TEM images showing hollow core and demonstrating 1.2% lattice contraction; (c) ORR activity curve from RDE experiment; (d) bar graph of ORR activity before and after 10,000 potential cycles followed by 3,000 + 7,000 potential pulse sequences; potential cycle: 0.60-1.05 V scan at 50 mV/s; potential pulse sequence: 0.60 V then 1.05 V, 30 s at each potential.

activity of previous smaller batches (0.55 $A/mg_{\rm Pt}$ and 0.12 $A/mg_{\rm PGM}$ at 0.90 V).

Precious Metal-Free Catalysts — The focus of research in this catalyst category continued to be on materials obtained by heat-treating carbon supported

precursors in the presence of transition metal salts (Fe and Co), with the scope now limited to CM-derived and PANI-derived catalysts. The ORR activity of both types of catalyst greatly increased over the Fiscal Year (FY) 2009 versions as shown in Table 2, with a nine-fold

TABLE 2. Progress in volumetric ORR activity as measured by RDE and fuel cell testing for CM-derived and PANI-derived catalysts according to project year.

Experiment	Test Conditions	Measured Volumetric Activity per Electrode Volume at 0.8 V (A cm ⁻³)			Improvement Eactor
		2008	2009	2010	(2008→2010)
RDE at 25°C	900 rpm 0.5 M H ₂ SO ₄ mass-transport corrected	0.22 EDA-FeCo-C	1.0 PANI-FeCo(3:1)-C	5.4 PANI-Fe/EDA-Co-C	25
H ₂ -O ₂ fuel 30 psig (11 psig) cell at 80°C 100% RH	1.0 EDA-FeCo-C	6.8 PANI-FeCo(3:1)-C	36 (20) PANI-Fe/EDA-Co-C	36	
		14 CM-Fe-C	127 (60) CM-Fe-C (v2)	127	

Average electrode density assumed as 0.4 g/cm³ (Neyerlin et al., J. Electrochem. Soc. **153**, A1955, 2006; Lefèvre et al., Science **324**, 71, 2009)

increase observed for CM-type catalysts and a five-fold increase observed for PANI-derived catalysts.

The activity of CM-derived catalyst was enhanced by (1) the use of a different carbon support, and (2) the addition of a second sulfur-containing precursor. With these changes, the activity of the catalyst was determined to be 165 A cm⁻³ (per *electrode* volume) at 0.80 V in fuel cell testing, using extrapolation to compensate for mass-transport losses (see Figure 4b). This value is comparable to the DOE 2010 performance target (see targets table above). The PANI-derived catalysts were improved through the design of a two-step synthesis that was intended to maximize the benefits of using both Co and Fe precursors. Based on our previous results, Co has been shown to increase the presence of graphene-type structures (perhaps connected to durability) and pyridinic nitrogen content, whereas Fe has been shown to generate more active catalysts and perhaps to form more bonds with nitrogen. Introducing the metals in two separate steps indeed increases the catalytic activity as shown in Figure 5a with $E_{t_2} = 0.82$ V, gaining 20 mV versus PANI-Fe-C and 40 mV versus PANI-FeCo(3:1)-C. The latter catalyst showed the best combination of activity



FIGURE 4. Fuel cell performance of CM-Fe-C catalysts: (a) polarization plots comparing FY 2009 and FY 2010 versions of the catalyst; (b) plot showing extrapolation used to calculate the catalyst activity at 0.80 V in the fuel cell test (extrapolation allows for removal of mass-transport losses, and determination of the intrinsic activity). Anode – 0.25 mg cm² Pt (E-TEK); cathode – 3.5 mg cm² CM-Fe-C; membrane – Nafion[®]117; cell temperature – 80°C.



FIGURE 5. Performance of PANI-derived catalysts at 25°C: (a) ORR activity curves from RDE tests; (b) fuel cell polarization plots. Anode -0.25 mg cm⁻² Pt (E-TEK); cathode -4.0 mg cm⁻² PANI-derived catalyst; membrane - Nafion[®]212; cell temperature -80° C.

and durability in FY 2009; the two-step PANI-Fe/ EDA-Co-C catalyst exhibits higher activity at kineticallycontrolled voltages (~100 A/cm³_{catalvst}/~ 20 A/cm³_{electrode} at 0.80 V, Figure 5b) and similar durability in fuel cell testing. Durability testing at 0.60 V was performed, and the performance degradation is greatly accelerated versus testing at 0.40 V (see the Annual Merit Review presentation file). However, switching between different humidification levels during testing recovers much of the performance loss, highlighting the need for better electrode design for non-precious catalysts. The durability of PANI-derived catalysts (specifically PANI-Fe-C) to potential cycling was also examined. After 30,000 potential cycles (0.60 V to 1.0 V, 50 mV/s) in the fuel cell, a performance increase occurs with the PANI-Fe-C cathode in a H₂-O₂ cell at lower voltages than 0.65 V; only ~25% loss in current density was observed at 0.80 V (kinetic range).

The effect of carbon support type on PANI-derived catalysts was assessed as shown in Figure 6a, and it was discovered that the selection of multi-walled nanotubes (MWNTs) for the support material creates a durable catalyst without the use of a cobalt precursor. All previous durable PANI-derived catalysts have contained cobalt, which generates an abundance of graphene-sheet structures. Upon TEM analysis of the PANI-Fe-MWNT sample, it was noted that (1) a similar abundance of graphene-sheet structures is present (Figure 6b), (2) these structures are associated with Fe_xS_y clusters, and (3) residual Ni catalyst from the MWNT preparation is also present (could affect the formation of graphene sheets). Although the details of graphene-sheet formation remain unclear, a strong association between graphene-sheet structures and fuel cell durability has been observed in two distinct catalyst types.

A comprehensive characterization effort has continued with a special focus on PANI-Fe-C catalysts prepared at different heat-treatment temperatures and having very different ORR activities. These samples have been thoroughly analyzed ex situ using spectroscopic and structural methods to gain insight into the nature of the active site. XAS, XPS, and pore-distribution results have been combined using the principal component analysis (PCA) method as shown in Figure 7 in an attempt to identify the strongest correlations between observations and catalyst activity. Fe-N-type coordination, as identified by XAS and XPS, remains strongly associated with oxygen reduction activity in ORR-active samples (900°C, 850°C, 800°C), and thus continues to be a primary candidate for the active site. The most active, 900°C catalyst has the highest Brunauer-Emmett-Teller (BET) surface and microporous surface area (in agreement with Dodelet group results), a bimodal pore distribution, and high initial contents of Fe carbide. Fe in oxidelike coordination, and Fe in phthalocyanine-like coordination.

Conclusions and Future Directions

 Core-shell and core-less catalysts with greatly reduced Pt loading have been developed that offer much better ORR performance in aqueous electrolytes and in hydrogen-air fuel cells than standard carbon-supported Pt catalysts; based on measured RDE activity in FY 2010, the best of these catalysts can lose up to a factor of 3 activity (see Table 1) upon incorporation into stacks and still meet 2010 DOE stack performance targets, provided de-alloying and catalyst agglomeration can be avoided; FY 2010 RDE durability data



FIGURE 6. PANI-Fe-C catalysts prepared with different support materials: (a) 500-hour fuel cell life tests; (b) TEM images showing the presence of graphene-sheet "bubbles" in PANI-Fe-MWNT; "bubbles" (\rightarrow) are co-located with the FeS_x regions/particles (\rightarrow); MWNTs are still present (\rightarrow) after catalyst preparation.



FIGURE 7. PCA plot showing correlation between experimental observations (XAS, XPS, BET surface area, and pore distribution) and ORR activity. Samples and variables with mean composition, activity, BET or pore size would lie on the intersection of axes on this biplot. The further the variables or samples from the intersection in any direction (vertical, horizontal or diagonal), the more different they are from the average values. As-synthesized powders were examined ex situ by XAS and XPS.

from catalysts containing Ni in the core are very encouraging in that regard, but the stability challenge is not yet fully overcome; catalyst scale up makes the generation of "perfect" shell structures more difficult and needs further optimization.

- Two types of non-precious metal catalysts were further advanced in terms of ORR activity and fuel cell performance – CM-derived and PANIderived; 9-fold and 5-fold increases in activity vs. FY 2009 were obtained, respectively; following these achievements in activity, the durability challenge has become more pressing; making the distinction between recoverable (flooding) and non-recoverable (active-site degradation) performance losses has become increasingly important, but both types of degradation must be addressed.
- Characterization efforts have led to the identification of strong correlations between ORR activity and (1) high overall surface area and high microporous surface area (confirming Dodelet group results) and (2) Fe-N type species as identified by XAS and XPS; future work involving chemical probes will be pursued to distinguish ORR active from ORR inactive sites; high catalyst durability has been linked to the presence of graphene-sheet structures in at least two distinct catalyst types; a clearer relationship between synthesis steps and graphene sheet formation, and in turn to durability, should be established.

 Susceptibility of carbon-rich non-precious metal catalysts to flooding continues to be a major performance issue for non-precious catalysts, especially at high current densities; based on FY 2010 results, apparent durability is also impacted by water management in the electrodes; future research efforts must focus on designing electrode structures that allow for more efficient water management than traditional MEA designs.

Special Recognitions & Awards/Patents Issued

1. P. Zelenay; DOE Hydrogen Program R&D Award in Recognition of Outstanding Contributions to Fuel Cell Technologies, Washington, D.C., June 2010.

2. P. Atanassov and T. Olson; "Self Supporting-Structurally Engineered Non-Platinum Electrocatalyst for Oxygen Reduction in Fuel Cells;" US Patent No. 7,678,728, issued March 16, 2010.

3. P. Zelenay, J.-H. Choi, N. Alonso-Vante, A. Wieckowski, and D. Cao; "Chalcogen catalysts for polymer electrolyte fuel cell;" U.S. Patent No. 7,588,857, issued September 15, 2009.

4. Y.S. Kim, J.-H. Choi, and P. Zelenay; "Method for improving fuel cell performance by removing at least one metal oxide contaminant from a fuel cell electrode;" U.S. Patent No. 7,575,824, issued August 18, 2009.

5. P. Zelenay and R. Bashyam; "Method of making metalpolymer composite catalysts;" U.S. Patent No. 7,550,223, issued June 23, 2009. **6.** "Platinum Monolayer Electrocatalysts for Oxygen Reduction;" B. Vukmirovic J. Zhang, K. Sasaki, F. Uribe, M. Mavrikakis, and R.R. Adzic, *Electrochim. Acta*, **52** 2257 (2007) – *Publication recognized in 2010 as the most cited Electrochimica Acta paper of 2007.*

FY 2010 Publications

 "Advanced Cathode Catalysts;" P. Zelenay, J. Bradley, J. Chlistunoff, H. Chung, S. Conradson, F. Garzon, C. Johnston, P. Mukherjee, M. Nelson, G. Purdy, G. Wu, D. Myers, M. Ferrandon, J. Kropf, X. Wang, R. Adzic, K. Gong, K. Sasaki, M. Vukmirovic, J. Wang, W. Zhou, P. Atanassova, Y. Sun, K. More, Y. Yan, S. Alia, K. Jensen, A. Wieckowski (PI), C. Delacôte, S. Goubert-Renaudin, X. Zhu, P. Atanassov, K. Artyushkova, D. Petsev, S. Pylypenko; US Department of Energy, Hydrogen, Fuel Cells & Infrastructure Technologies Program; 2009 Annual Progress Report; pp. 1092-1099. http://www.hydrogen. energy.gov/pdfs/progress09/v_e_5_zelenay.pdf

2. "Recent Advances in Non-Precious Metal Catalysis for Oxygen-Reduction Reaction in Polymer Electrolyte Fuel Cells;" F. Jaouen, E. Proietti, M. Lefèvre, R. Chenitz, J.P. Dodelet, G. Wu, H.T. Chung, C.M. Johnston, and P. Zelenay, Energy Environ. Sci., submitted.

3. "The effect of diluting ruthenium by iron in Ru_xSe_y catalyst for oxygen reduction;" C. Delacôte, A. Lewera, M. Pisarek, P.J. Kulesza, P. Zelenay, and N. Alonso-Vante, *Electrochim. Acta*, in press (available online January 18, 2010).

4. "Templated Platinum/Carbon Oxygen Reduction Fuel Cell Electrocatalysts;" S. Pylypenko, T.S. Olson, N.J. Carroll, D.N. Petsev, and P. Atanassov, *J. Phys. Chem. C.*, 114 4200–4207 (2010).

5. "Bifunctional Oxygen Reduction Reaction Mechanism on Non-Platinum Catalysts Derived from Pyrolyzed Porphyrins;" T.S. Olson, S. Pylypenko, J.E. Fulghum, and P. Atanassov;" *J. Electrochem. Soc.*, 157 (2010) B54-B63.

6. "Synthesis and Evaluation of Heat-treated, Cyanamidederived Non-precious Catalysts for Oxygen Reduction;" H.T. Chung, C.M. Johnston, and P. Zelenay, *ECS Trans.*, 25 (1), 485 (2009).

7. "Performance Durability of Polyaniline-derived Non-Precious Cathode Catalysts;" G. Wu, K. Artyushkova,
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12. "Transition Metal/Polymer Catalysts for O2 Reduction;" C.M. Johnston, P. Piela, and P. Zelenay, in *Handbook of Fuel Cells: Fundamentals, Techology, and Applications*; vol. 5; Chapter 4, pp. 48-70, W. Vielstich, H. A. Gasteiger, H. Yokokawa, Eds., Wiley & Sons; Chichester, United Kingdom, 2009.

13. "Recent Developments in the Electrocatalysis of the O₂ Reduction Reaction;" Y. Xu, M. Shao, M. Mavrikakis, and R.R. Adzic, in *Fuel Cell Catalysis: A Surface Science Approach*, Ed. M. Koper, pp 271-315, J. Wiley & Sons, New York, 2009.

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15. "Intrinsic Kinetic Equation for Oxygen Reduction Reaction in Acidic Media: The double Tafel slope and fuel cell applications;" J.X. Wang, F. Uribe, T.E. Springer, J. Zhang, R.R. Adzic, *Faraday Discuss.* **140**, 347-362 (2009).

16. "XAS of Platinum Monolayer Fuel Cell Electrocatalysts – Unambiguous, Direct Correlation of Spectroscopy Data with Catalytic Properties;" K. Sasaki, R.R. Adzic, *Synchrotron Radiation News*, **22**(1), 17-21 (2009).

17. "Microparticles with Bidisperse Nano-Porosity Derived by Microemulsion Templating;" N.J. Carroll, S. Pylypenko, P. Atanassov, and D.N. Petsev, *Langmuir*, **25**, 13540-13544 (2009).

18. "Improving Electrocatalysts for O₂ Reduction by Fine-Tuning the Pt-Support Interaction: Pt Monolayer on the Surfaces of a Pd₃Fe(111) Single-Crystal Alloy;" W-P. Zhou, X. Yang, M.B. Vukmirovic, B.E. Koel, J. Jiao, G. Peng, M. Mavrikakis, R.R. Adzic, *J. Am. Chem. Soc.*, **131**, 12755– 12762 (2009).

19. "Oxygen Reduction on Well-Defined Core-Shell Nanoparticles: Size, Facet, and Pt Shell Thickness Effects;" J.X. Wang, H. Inada, L. Wu, Y. Zhu, Y. Choi, P. Liu, W-P. Zhou, R.R. Adzic, J. Am. Chem. Soc., 131, 17298
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FY 2010 Presentations

 217th Meeting of The Electrochemical Society, Vancouver, Canada, April 25–30, 2010. Title: "Effect of Synthesis Conditions on ORR Activity of Polyaniline-Fe-C Catalysts;"
 G. Wu, K. Artyushkova, C. Johnston, and P. Zelenay*. **2.** 217th Meeting of The Electrochemical Society, Vancouver, Canada, April 25–30, 2010. Title: "A Quantum Mechanical and Experimental Study of Cobalt/Polypyrrole Catalysts: Investigation of Oxygen Reduction Active Site;" Z. Shi*, H. Liu, K. Lee, J. Zhang, Z. Liu, J. Chlistunoff, M. Blair, and P. Zelenay.

3. 217th Meeting of The Electrochemical Society, Vancouver, Canada, April 25–30, 2010. Title: "A New Two-Step Synthesis of CoFe-Based Non-precious Metal ORR Catalysts;" G. Wu, M. Nelson, C. Johnston, and P. Zelenay*.

4. 239th American Chemical Society National Meeting & Exposition, San Francisco, California, USA, March 21–25, 2010. Title "RRDE Study of Oxygen reduction on Pyrolyzed Polyaniline-Iron Catalyst;" J. Chlistunoff*, G. Wu, and P. Zelenay.

5. International Battery Association & Pacific Power Source Symposium 2010, Waikoloa, Hawaii, USA, January 11–15, 2010. Title: "Novel Non-Precious Metal Oxygen Reduction Catalysts for the Polymer Electrolyte Fuel Cell Cathode;" P. Zelenay*, H.T. Chung, G. Wu, J. Chlistunoff, and C.M. Johnston - *invited lecture*.

6. 2009 Fuel Cell Seminar & Exposition, Palm Springs, California, USA, November 16-19, 2009. Title: "Non-Precious Cathode Catalysts for Polymer Electrolyte Fuel Cells;" G. Wu*, C.M. Johnston, and P. Zelenay.

7. 2009 Fuel Cell Seminar & Exposition, Palm Springs, California, USA, November 16–19, 2009. Title: "Micro X-Ray Tomography as a Tool for Fuel Cells Materials Characterizations;" M.A. Nelson, R. Borup, R. Mukundan, J. Davey, G. Wu, P. Zelenay, and F. Garzon*.

8. 2009 Fuel Cell Seminar & Exposition, Palm Springs, California, USA, November 16–19, 2009. Title: "Nonprecious Oxygen Reduction Catalysts for PEFC Cathode;" P. Zelenay*, G. Wu, H.T. Chung, J. Chlistunoff, and C.M. Johnston - *invited lecture*.

9. 2009 AIChE Annual Meeting, Nashville, Tennessee, November 8-13, 2009. Title: "Fuel Cell Electrocatalysts Obtained from Bimodal Nano-porous Templates;" S. Pylypenko, T.S. Olson, D. Petsev, and P. Atanassov.

9. 2009 AIChE Annual Meeting, Nashville, Tennessee, November 8–13, 2009. Title: "Mechanism of Oxygen Reduction Reaction on Non-Platinum Catalysts Derived from Pyrolyzed Porphyrins;" T.S. Olson, S. Pylypenko, J.E. Fulghum, and P. Atanassov. **10.** Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany, October 19, 2009. Title: "Development, Performance, and Characterization of Novel Oxygen Reduction Catalysts for PEFC Cathode;" P. Zelenay *invited lecture*.

11. 216th Meeting of The Electrochemical Society, Vienna, Austria, October 4–9, 2009. Title: "Carbon Nanotubes as Support for Heteroatomic Polymer-derived Non-precious Metal Oxygen Reduction Catalysts;" G. Wu, L. Xie, T. Zhang, Y. Yan, and P. Zelenay^{*}.

12. 216th Meeting of The Electrochemical Society, Vienna, Austria, October 4–9, 2009. Title: "Performance Durability of Polyaniline-Derived Non-Precious Cathode Catalysts;" G. Wu, and P. Zelenay*.

13. 216th Meeting of The Electrochemical Society, Vienna, Austria, October 4–9, 2009. Title: "X-Ray Absorption Characterization of Polyaniline-Derived Polymer Electrolyte Fuel Cell Cathode Electrocatalysts;" M. Ferrandon*, D. Myers, A. Kropf, G. Wu and P. Zelenay.

14. 216th Meeting of The Electrochemical Society, Vienna, Austria, October 4–9, 2009. Title: "Oxygen Reduction on Se/Ru Electrodes;" P. Zelenay and A. Wieckowski*.

15. 216th Meeting of The Electrochemical Society, Vienna, Austria, October 4–9, 2009. Title: "Synthesis and Evaluation of Heat-treated, Polymer-derived Non-precious Catalysts for Oxygen Reduction;" H.T. Chung, C.M. Johnston, J. Chlistunoff and P. Zelenay*.

16. 3rd Sunrise Springs Workshop on Non-Platinum Group Metal Oxygen Reduction Electrocatalysts, Sunrise Springs Inn and Spa, Santa Fe, New Mexico, September 9–11, 2009. Title: "X-ray Absorption and Scattering Studies of Cathode Electrocatalysts;" D. Myers*, M. Smith, J. Gilbert, M. Ferrandon, and A.J. Kropf, G. Wu, H. Chung, J. Chlistunoff, C.M. Johnston, and P. Zelenay - *invited lecture*.

17. 3rd Sunrise Springs Workshop on Non-Platinum Group Metal Oxygen Reduction Electrocatalysts, Sunrise Springs Inn and Spa, Santa Fe, New Mexico, September 9–11, 2009. Title: "New Non-precious Metal Oxygen Reduction Catalysts;" G. Wu, H.T. Chung, C.M. Johnston, J. Chlistunoff, and P. Zelenay* - *invited lecture*.