

## V.E.8 Nanosegregated Cathode Alloy Catalysts with Ultra-Low Platinum Loading

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### Objectives

- Fundamental understanding of the oxygen reduction reaction on multimetallic PtM (M = Co, Ni, Fe, Mn, Cr, V, and Ti) and PtM<sub>1</sub>N<sub>2</sub> (M<sub>1</sub> = Co or Ni; N<sub>2</sub> = Fe, Mn, Cr, V, and Ti) materials.
- Develop highly-efficient, durable, nanosegregated Pt-skin PtM and PtM<sub>1</sub>N<sub>2</sub> catalysts with ultra-low Pt content.
- Find relationships between activity/stability of well-characterized bulk alloys and real nanoparticles (NPs).
- Develop novel chemical and physical methods for synthesis of monodispersed PtM and PtM<sub>1</sub>N<sub>2</sub> alloy NPs and thin metal films.
- Resolve electronic/atomic structure and segregation profile of PtM and PtM<sub>1</sub>N<sub>2</sub> systems.
- Resolve composition effects of PtM and PtM<sub>1</sub>N<sub>2</sub> systems.
- Demonstrate mass activity and stability improvement of PtM and PtM<sub>1</sub>N<sub>2</sub> alloy NPs.
- Use computational methods as the basis to form any predictive ability for tailoring binary and ternary systems to have desirable reactivity and durability properties.

### 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:

#### (B) Cost

- Reduce precious metal loading of catalysts.
- Increase the specific and mass activities of catalysts.
- Increase the durability/stability of catalysts with cycling.
- Test and characterize catalysts.

### Technical Targets

This project is conducting fundamental studies of the oxygen reduction reaction on Pt-based PtM binary and PtM<sub>1</sub>N<sub>2</sub> catalysts. Insights gained from these studies will be applied toward the design and synthesis of highly-efficient, durable, nanosegregated Pt-skin catalysts with ultra low Pt content that meet or exceed the following DOE 2015 targets:

<ul style="list-style-type: none"><li>• Specific activity @0.9 V<sub>R</sub>-free: 720 mA/cm<sup>2</sup></li><li>• Mass activity @0.9 V: 0.44 A/mgPt</li><li>• Catalyst support loss: &lt;30%</li></ul>	<ul style="list-style-type: none"><li>• Platinum group metal total content: 0.2 g/kW</li><li>• Total loading: 0.2 mg/cm<sup>2</sup></li><li>• Durability with cycling (80°C): 5,000 hrs</li></ul>
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### Accomplishments

- Synthesized wide range of bi/multi-metallic NPs with controlled size and composition by colloidal organic solvo-thermal approach.
- Resolved particle size effect for bimetallic NPs: optimal size is found to be 5 nm with activity (1.5 A/mg<sub>Pt</sub>) that exceeds the DOE 2015 targets.
- Established post-synthesis routes for altering surface/adsorption and catalytic properties:
- Acid treatment for removal of non-precious metal atoms and optimal annealing temperature to create the most active (1.4 A/mg<sub>Pt</sub>) segregation profiles for bimetallic PtM NPs.
- Performed composition optimization of bimetallic PtM catalysts.
- Established activity (stability) trends for bimetallic NPs.
- Confirmed that ternary alloys could provide additional tunability towards activity and stability.



## Introduction

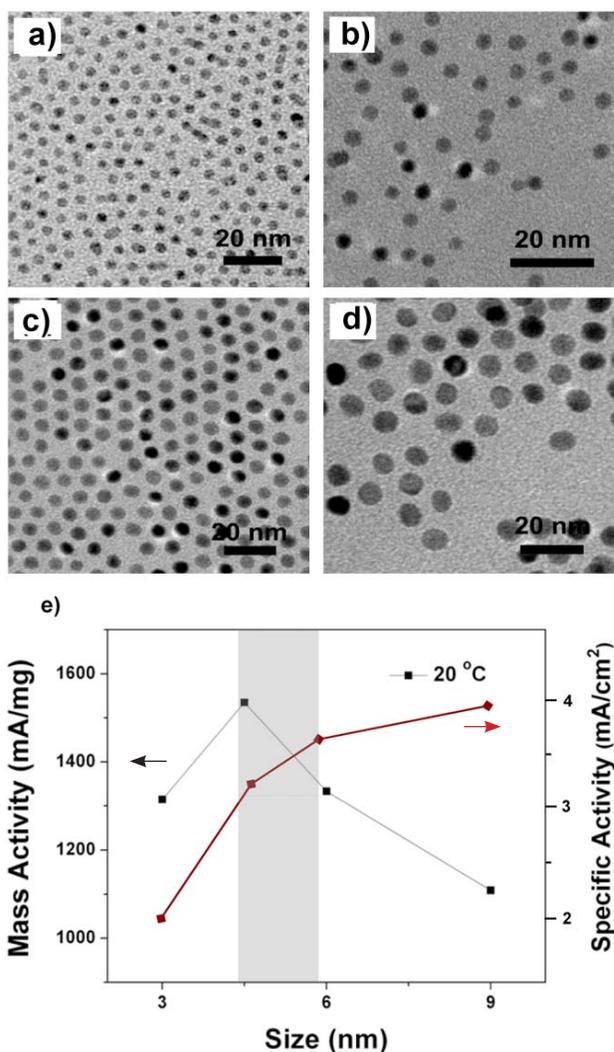
In the quest to make the proton exchange membrane fuel cell (PEMFC) a competitive force, one of the major limitations is to reduce the significant overpotential for the oxygen reduction reaction (ORR) and minimize dissolution of the cathode catalysts. Here, we report a progress for Fiscal Year (FY) 2010 in experimental and theoretical studies to addressing the importance of alloying Pt with 3d elements (M= Ni, Co, Fe etc.) in order to form catalytically active materials with so-called *nanosegregated profile* [1] and to minimize the amount of Pt. We have demonstrated that the nanosegregated surfaces are superior in both: exceptional catalytic activity for the ORR and higher stability of Pt surface atoms.

## Approach

To address the challenges that are listed as the DOE targets for the Fuel Cells sub-program we rely on our materials-by-design approach [2,3]. This involves four major steps: (i) advanced synthesis of novel nanoscale materials, which enables control of their size and composition; (ii) characterization of atomic and electronic properties by ex situ and in situ surface characterization techniques and theoretical methods; (iii) resolving the surface electronic and crystal structures at atomic/molecular level that govern efficient kinetics of the ORR; and (iv) synthesis/fabrication of the highly efficient nanoscale materials, which are guided by the fundamental understanding of structure-function relationships.

## Results

**The Crystallite Size Effect for Pt<sub>3</sub>M Catalysts:** The crystallite/particle size effect is the variation in reaction rate or selectivity with characteristic dimension of metallic catalysts, while the structure sensitivity refers to the dependence of reaction rate or selectivity on the geometry of the surface. Hence a structure sensitive reaction is expected to exhibit a crystallite size effect. This has been confirmed for the ORR on Pt, i.e., the ORR is strongly affected by the particle size of Pt NPs supported on carbon [4]. In order to systematically explore this effect for Pt alloys we have established novel colloidal organic solvo-thermal routes for synthesis of monodisperse PtM NPs with controlled size ranging from 3 to 9 nm in diameter. We have found that the particle size effect also applies for the ORR on Pt<sub>3</sub>M NPs [5]. As summarized in Figure 1 for 3-9 nm Pt<sub>3</sub>Co NPs, while specific activity increases with the particle size, i.e., from 2-4 mA/cm<sup>2</sup>, respectively, the optimal mass activity is obtained for ~5 nm NPs. Both the specific activity



**FIGURE 1.** Particle size effect for bimetallic particles: transmission electron microscope (TEM) images of monodisperse Pt<sub>3</sub>Co nanoparticles with various particle size a) 3 nm, b) 4.5 nm, c) 6 nm, and d) 9 nm; e) corresponding specific and mass activity dependence for various particle size measured by rotating disk electrode (RDE) in 0.1M HClO<sub>4</sub> at 20°C.

(3 mA/cm<sup>2</sup>) as well as the mass activity (1.6 A/mg<sub>Pt</sub>) of the ORR on 5 nm Pt<sub>3</sub>Co NPs significantly exceeds the DOE targets of 0.72 mA/cm<sup>2</sup> and 0.44 A/mg<sub>Pt</sub>.

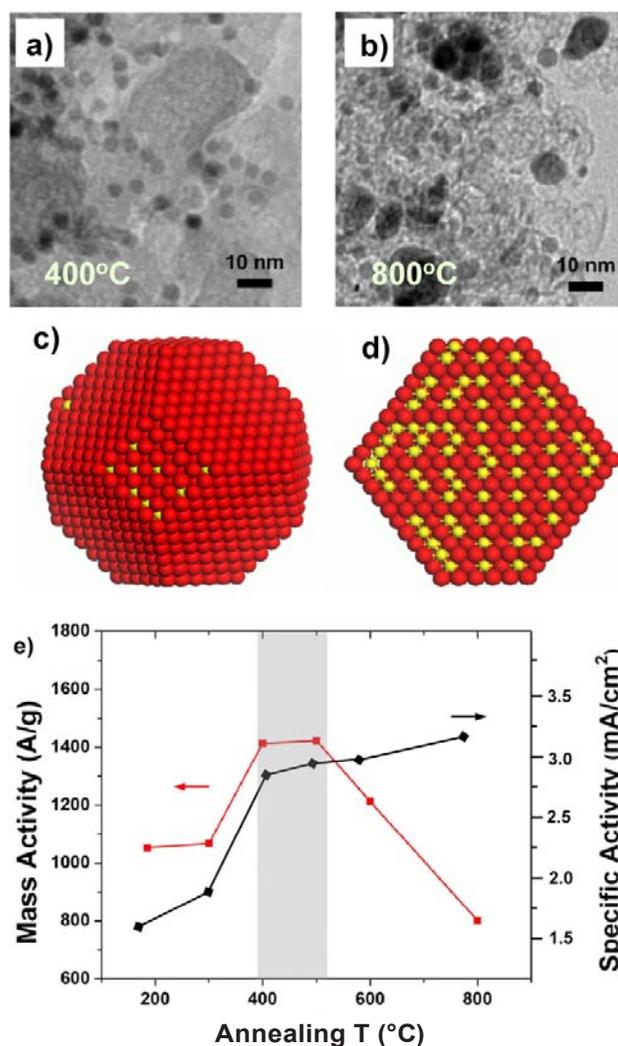
**Temperature-Induced Segregation towards the Nanosegregated Materials:** The term nanosegregated materials has been coined to describe the formation of oscillatory concentration profile with 100% Pt in the first layer, counterbalanced by depletion of Pt in the second layer, which is followed by enrichment of Pt in the third layer [1]. Surface segregation was confirmed experimentally and theoretically for the bulk Pt<sub>3</sub>M single and polycrystalline surfaces, but not for corresponding NPs. Given that the highest activity that has ever been observed on cathode catalyst was obtained on

Pt<sub>3</sub>Ni(111) electrode, with a specific activity 90-fold higher than the state-of-the-art Pt/C catalysts [1], it has been of paramount importance to develop preparation method that would allow the design of the PtM NPs with nanosegregated-like catalytic properties.

For that reason the temperature annealing effect on Pt-alloy NPs was explored. The results are summarized in Figure 2 for the monodisperse and homogeneous 4.5 nm Pt<sub>3</sub>Co/carbon catalyst synthesized by solvo-thermal route and then treated at various temperatures, ranging from 300 to 800°C. No obvious size or morphology change was observed for the catalysts annealed up to 400-500°C (Figure 2a). Particle sintering appeared for the catalyst annealed at the temperatures higher than 500°C, which is evident at 800°C (Figure 2b). The X-ray diffraction (XRD) analysis showed single crystal phase for all thermally annealed NPs, confirming the homogeneous alloy composition. This exclusion allowed exploration of the intrinsic effect of thermal annealing on the catalytic performance of the catalyst. Figure 2e and ref. [6] show that, without significant particle sintering, the specific activity increase of almost 1 mA/cm<sup>2</sup> was obtained for the nanoparticles pre-treated at 400°C. If compared to the state-of-the-art Pt/carbon catalyst, 3-fold activity enhancement for the ORR is reached on this catalyst. In turn, this may imply that the surface segregation may have happened with Pt<sub>3</sub>M NPs even at the moderate 400-500°C temperatures.

Due to experimental limitations in resolving the concentration profile of the very first atomic layers for nanoscale materials, we used Monte Carlo simulations to probe formation of the Pt-skin for 5 nm Pt<sub>3</sub>Co NP at the optimal temperature. Figures 2c and 2d reveal that the resultant Pt concentrations are 99 at% in the outermost surface layer, 44 at% in the second sub-surface layer, and 92 at% in the third sub-surface layer, suggesting that 400°C would induce formation of the nanosegregated structure. As shown in Figure 2e, the descending trend in specific surface area for different annealing temperatures is followed by ascending trend in specific activities. In turn, volcano-like shape is observed for mass activity vs. annealing temperature. It is important to point out that the activities presented here are much higher than those reported in the literature for PtCo alloy catalysts prepared by conventional co-precipitation or impregnation methods [7]. This suggests that the solvo-thermal synthesis brings high level of control of the crucial parameters such as homogenous distribution of particle size and composition profiles, which indeed lead to formation of nanosegregated-like properties.

**Composition Effects—Tailoring of Nanosegregated Layers:** Having established the optimal particle size of Pt<sub>3</sub>M NPs and the most favorable annealing temperature for the formation of nanosegregated-like materials, the next step was to establish the most favorable composition of PtM NPs. To unravel this complex issue we relied on the advanced solvo-thermal



**FIGURE 2.** Temperature-induced segregation of bimetallic particles: TEM images of 4.5 nm PtCo/C NPs annealed at a) 400°C and b) 800°C; c) and d) concentration profile for NPs annealed at 400°C obtained by Monte Carlo simulations; e) the summary of specific and mass activities vs. annealing temperature of 4.5 nm PtCo/C NPs measured by RDE in 0.1M HClO<sub>4</sub> at 20°C.

methods to synthesize Pt<sub>x</sub>Ni<sub>y</sub> NPs with altered 3:1, 1:1, 1:2 and 1:3 atomic ratios. In order to avoid the particle size effect, the size of all NPs was controlled to be 5 nm. Due to surface chemistry of the 3d elements under PEMFC-related conditions, the NPs were pretreated in acid solution to remove surface Ni atoms and to form the so-called skeleton-like surface structure (Figure 3). As summarized in ref. [8], the highest specific (4.0 mA/cm<sup>2</sup>) and mass (1.5 A/mg<sub>Pt</sub>) activities for the ORR are observed on NPs having 1:1 Pt to Ni atomic ratio. This result differs from the most active concentration profile (3:1 Pt/Ni atomic ratio) previously observed on the extended Pt<sub>3</sub>M surfaces [8]. The resolution of this disparity is obtained by utilizing energy-dispersive X-ray (EDX) spectroscopy; i.e. EDX

showed that acid pretreatment transforms PtNi NPs into Pt skeleton structure with ca. 25% Ni.

Further modification and altering of the activity and stability of PtNi NPs was obtained by subsequent annealing at 400°C. This treatment allowed relaxation of low-coordinated surface atoms and the formation of the core (PtNi)/shell (2 atomic Pt layers) structure depicted in Figure 3. The XRD analyses revealed that the core/shell-like NPs are homogenous having a face-centered cubic pattern with the decrease of lattice constant due to the alloying of Pt with Ni. The core/shell PtNi NPs have unique activity for the ORR, i.e., 1 mA/cm<sup>2</sup> at 0.95 V (!) as well as a promising stability (PtNi/Pt NPs do not suffer from the decay in activity or surface area after 30,000 cycles between 0.5 to 1.1 V).

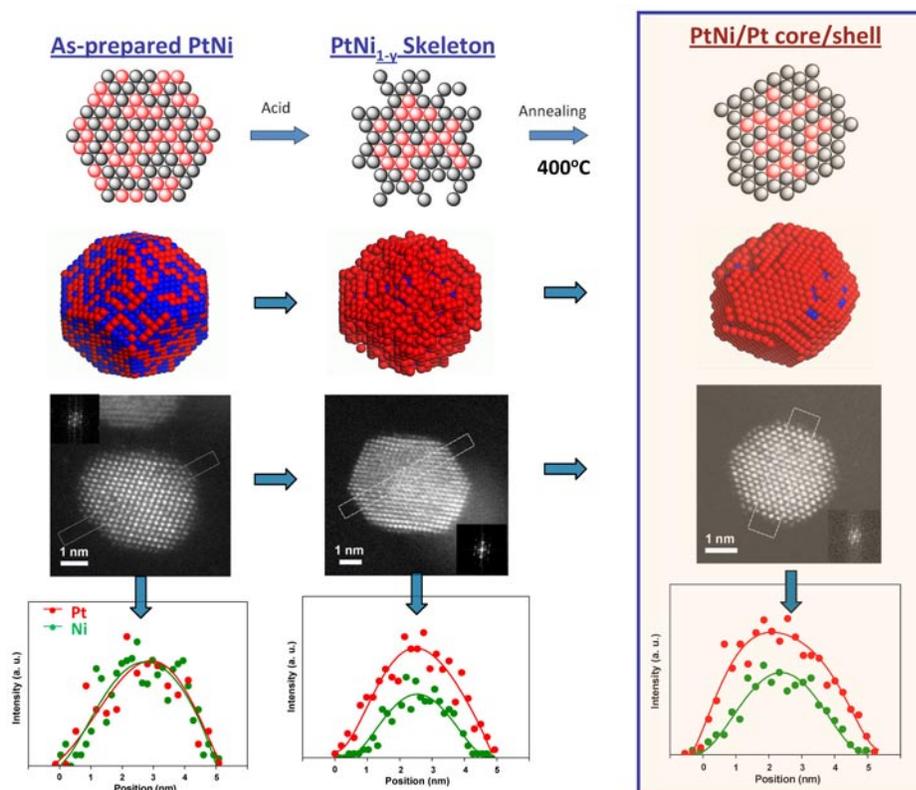
#### Electrocatalytic Trends for Ternary Systems:

Organic colloidal solvo-thermal approach was developed to synthesize Pt-based PtM<sub>1</sub>N<sub>2</sub> (NM = Fe, Co, and/or Ni) ternary alloys in order to understand fundamental differences between bimetallic and ternary systems, Figure 4. It is expected that addition of the third 3d element would induce additional level in altering of the catalytic activity for binary systems. Currently, there is

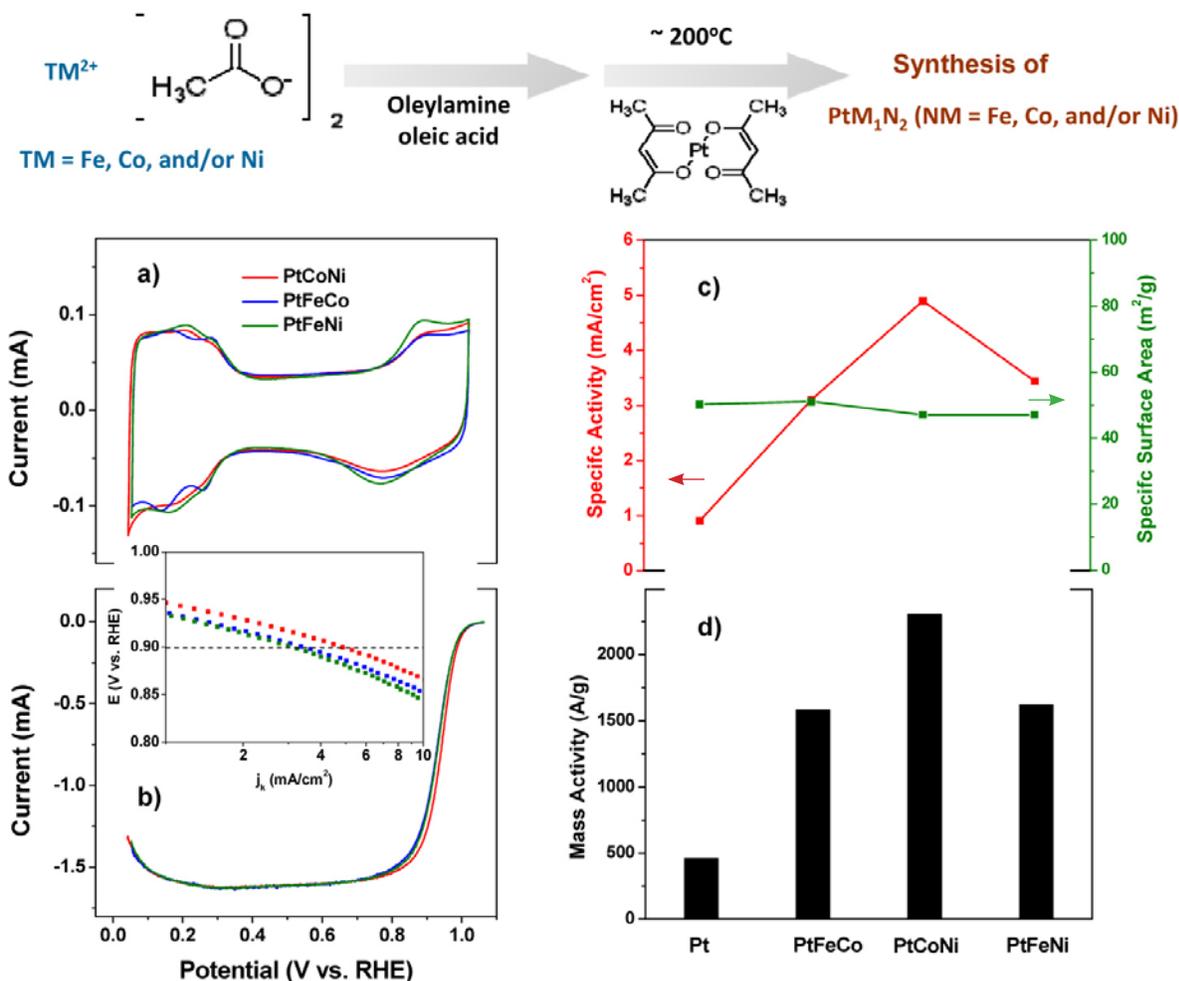
no fundamental correlation between the addition of *two* 3d elements and induced change of electronic/adsorption/catalytic properties of the nanosegregated materials. The preliminary results (summarized in Figures 4a-d) are encouraging, given that PtCoNi NPs show specific (5 mA/cm<sup>2</sup>) and mass (2 A/mg<sub>Pt</sub>) activity that exceed the corresponding bimetallic systems and the DOE 2015 targets. In turn, this indicates that ternary alloys could provide additional tunability towards the activity and stability of Pt-based alloys. We strongly believe, therefore, that our material-by-design approach will enable further enhancement of the catalytic properties with breakthrough performance for the cathode catalysts in PEMFCs.

#### Conclusions and Future Directions

- PtM and PtM<sub>1</sub>N<sub>2</sub> NP cathode catalysts obtained from the organic solvo-thermal synthesis exhibit superior activity and stability than those prepared by the conventional methods. The optimal particle size, annealing temperature, and alloy composition of the PtM NPs are determined.



**FIGURE 3.** Altering of the surface/adsorption/catalytic properties of the NPs by post-treatment protocols and schematic representation of surface morphology transformation from: 'as-prepared' to the skeleton-like structure (leaching out 3d elements in acidic solution) and finally to the core (PtNi)/shell (2 atomic Pt layers) structure after temperature annealing; corresponding models obtained from the Monte Carlo simulations, TEM micrographs, and the portrays of concentration profiles obtained from EDX scans.



**FIGURE 4.** Synthesis and electrochemical characterization of ternary PtMN NPs: a) and b) cyclic voltammetry and polarization curves for the ORR along with corresponding Tafel plots; c) and d) specific surface area, specific and mass activities of various 5 nm PtM<sub>1</sub>N<sub>2</sub> alloys measured by RDE in 0.1 M HClO<sub>4</sub> at 20°C.

- Significant mass activity and durability improvements are obtained for PtM and PtM<sub>1</sub>N<sub>2</sub> NPs. Advanced theoretical modeling (density functional theory, Monte Carlo) methods are developed for resolving nanosegregated structures.
- Understanding of the ternary alloy catalysts is yet to be addressed.
- In collaboration with industrial partners, fabrication and testing in a membrane electrode assembly of the most promising catalysts is planned as well as patenting of the novel synthetic routes developed in this project.

### FY 2010 Publications/Presentations

1. C. Wang, D. van der Vliet, K.C. Chang, H. You, D. Strmcnik, J.A. Schlueter, N.M. Markovic, V.R. Stamenkovic, "Monodisperse Pt<sub>3</sub>Co Nanoparticles as a Catalyst for the Oxygen Reduction Reaction: Size Dependent Activity", *J. Phys. Chem. C.*, **113**(2009)19365.
2. C. Wang, D. van der Vliet, K.C. Chang, N.M. Markovic, V.R. Stamenkovic, "Monodisperse Pt<sub>3</sub>Co Nanoparticles as Electrocatalyst: the Effect of Particle Size and Pretreatment on Electrocatalytic Reduction of Oxygen", *Phys.Chem.Chem. Phys.*, **12**(2010)6933-6939; **COVER Article**.
3. C. Wang, D. Strmcnik, P. Paulikas, D. Van der Vliet, C. Lucas, A. Brownrigg, N. Markovic and V. Stamenkovic, *The Role of Surface and Near-Surface Composition in Electrocatalysis*, Electrochemical Soc. 217<sup>th</sup> Meeting Vancouver, Canada, April 2010.
4. C. Wang, S. Sun, D. Strmcnik, P. Paulikas, D. Van der Vliet, N. Markovic and V. Stamenkovic, *Design and Synthesis of Advanced Nanoscale Electrocatalysts*,



Electrochemical Soc. 217<sup>th</sup> Meeting Vancouver, Canada, April 2010.

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6. C. Wang, D. van der Vliet, K.C. Chang, N.M. Markovic, V.R. Stamenkovic, "Monodisperse Pt<sub>3</sub>Co Nanoparticles as Electrocatalyst: the Effect of Particle Size and Pretreatment on Electrocatalytic Reduction of Oxygen," *Phys.Chem. Chem.Phys.*, **12**(2010)6933-6939; **COVER Article**.
7. N.M. Markovic, V. Radmilovic, P.N. Ross, "Physical and Electrochemical Characterization of Bimetallic Nanoparticle Electrocatalysis," in *Catalysis and Electrocatalysis at Nanoparticle Surfaces*, Edited by A. Wieckowski, E. Savinova and C. Vayenas, Marcel Dekker, Inc., Chapter 9, (2003) 311-342.
8. V. Stamenkovic, B.S. Mun, M. Arenz, K.J.J. Mayrhofer, C. lucas, G. Wang, P.N. Ross, and N.M. Markovic, "Trends in Electrocatalysis on Extended and Nanoscale Pt-bimetallic Alloy Surfaces," *Nature Materials.*, **6** (2007) 241-247.