

## V.D.5 Nanosegregated Cathode Alloy Catalysts with Ultra-Low Platinum Loading

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### Fiscal Year (FY) 2012 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.
- Develop highly-active and durable Au/PtM<sub>3</sub> nanoparticles with ultra-low Pt content.
- Find relationships between activity/stability of well-characterized bulk alloys and real nanoparticles.
- Develop novel chemical and physical methods for synthesis of monodispersed PtM and PtM<sub>1</sub>N<sub>2</sub> alloy nanoparticles 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 nanoparticles in rotating disk electrode (RDE) and membrane electrode assembly (MEA).
- Use computational methods as the basis to form any predictive ability in tailor making binary and ternary systems to have desirable reactivity and durability properties.

### Technical Barriers

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

- (A) Durability
- (B) Cost
- (C) Performance

### Technical Targets

ANL is conducting fundamental studies of the oxygen reduction reaction on Pt-based PtM (M= Ni, Co, Fe, Cr, V, and Ti) binary and PtM<sub>1</sub>N<sub>2</sub> (NM = Fe, Co, and/or Ni) catalysts as well as on Au/Pt<sub>3</sub>M ternary nanoparticles. 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:

• Specific activity @ 0.9 V iR-free: 720 mA/cm <sup>2</sup>	• Platinum group metal total content: 0.2 g/kW
• Mass activity @ 0.9 V: 0.44 A/mg <sub>Pt</sub>	• Total loading: 0.2 mg/cm <sup>2</sup>
• Catalyst support loss: <30%	• Durability w/cycling (80°C): 5,000 hrs

iR - internal resistance

### FY 2012 Accomplishments

- Synthesized wide range of bi/multi metallic nanoparticles with controlled size and composition by colloidal organic solvo-thermal approach.
- Developed vapor deposition/annealing methods to make stable and active Pt thin metal film (1-7 atomic layers) on Pt<sub>3</sub>Ni substrate.
- Established relationships between the morphology/thickness of Pt atoms in skeleton structure and stability/activity of the catalysts: Pt film can both effectively protect Ni from dissolution and provide superior catalytic activity (x6 vs. Pt).
- Developed experimental protocol to synthesize PtNi/C nanoparticles with Pt multilayered "skin" (2-3 ML) that are mimicking stability/activity of thin metal film systems.
- In MEA, for PtNi/C multilayered skin confirmed:
  - (i) three times higher specific (surface area ~0.8 mA/cm<sup>2</sup>) than benchmark Pt/C catalysts and mass

activity of  $\sim 0.35 \text{ A/mg}_{\text{Pt}}$ ; (ii) high durability, e.g., after 20,000 cycles activity, surface area loss was only 12% compared to  $\sim 40\%$  for Pt/C.

- Established accurate surface area determination for the nanoscale catalyst with Pt-skin surfaces.
- Performed extended X-ray absorption fine structure analysis characterization in an MEA on PtNi multilayered skin catalysts, which revealed that catalyst did not suffer structural/composition changes after 20,000 cycles in the MEA.
- Developed magnetron sputtering deposition methods and annealing protocol to make reproducible ternary Pt-alloy thin metal films.
- Performed composition optimization of ternary  $\text{Pt}_3\text{M}_1\text{N}_2$  catalysts.
- Developed synthetic routes and characterized monodisperse, highly homogeneous ternary alloy nanoparticles.
- Performed modeling related to the existence of Pt-skin structure in ternary alloy catalysts for extended and nanoscale systems.
- Establish activity trend for ternary  $\text{Pt}_3\text{MN}$  nanoparticles.
- Synthesis and characterization of the core/shell Au/CoPt<sub>3</sub> nanoparticles
- Demonstrated that ternary alloys could provide additional activity gain vs. binaries (4-fold vs. Pt-poly).



## Introduction

In the quest to make the polymer electrolyte membrane fuel cell 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 FY 2012 in experimental and theoretical studies to addressing the importance of alloying Pt with 3d elements (M= Ni, Co, Fe etc.) and making a novel tailored nanostructure of Au/Pt<sub>3</sub>M in order to form catalytically active materials with so-called *nanosegregated profile* [1]. In our previous work we have identified that the nanosegregated surfaces are superior in both: exceptional catalytic activity for the ORR and improved stability of Pt surface atoms.

## Approach

In order to address the challenges that are listed as the DOE targets for the Fuel Cell Technologies Program we rely on our materials-by-design approach [1-9]. This involves four major steps: (i) synthesis of novel nanoscale materials, with controlled size, structure and composition; (ii) establishing atomic and electronic properties by utilizing ex situ and

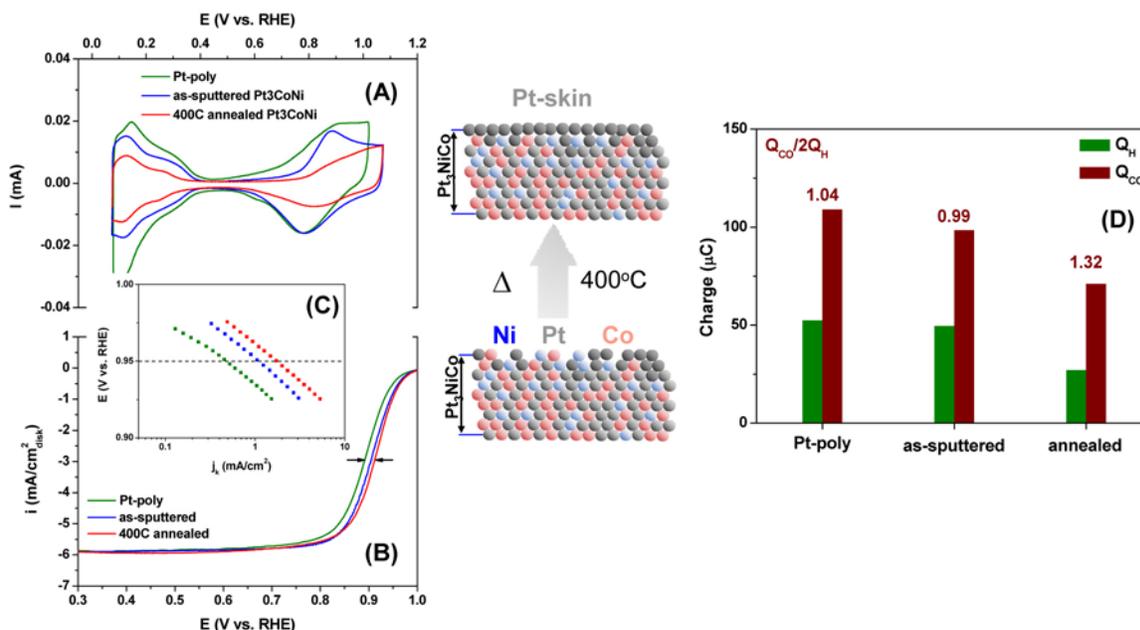
in situ surface characterization techniques and theoretical methods; (iii) resolving the surface electronic and crystal structures at atomic/molecular level that govern efficient kinetics of the ORR; and (iv) synthesis/fabrication (scale up) of the highly efficient nanoscale materials.

## Results

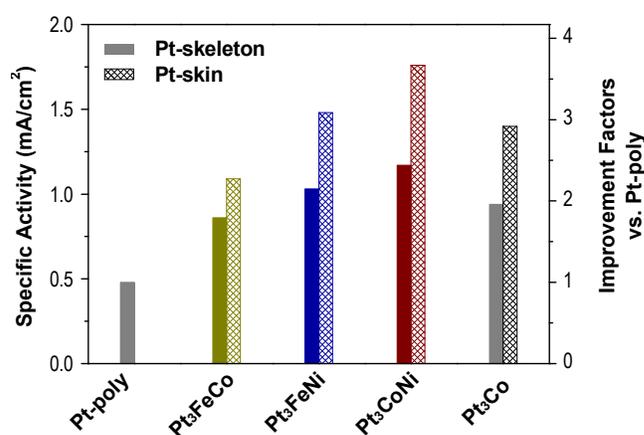
**Real surface area of the catalysts with Pt-skin surfaces.** The term Pt-skin has been used to describe unique arrangement of Pt surface atoms that is formed after thermal-induced segregation profile of bimetallic Pt<sub>3</sub>M alloys. An oscillatory concentration profile with 100% Pt in the first layer is counterbalanced by depletion of Pt in the second layer, which is followed by enrichment of Pt in the third layer. Alloys with such segregation profile in near surface region we term nanosegregated systems, and they have been found to have superior catalytic properties [1]. For the extended Pt<sub>3</sub>M electrodes we found that the Pt-skin surfaces are more active for the ORR than the corresponding Pt-skeleton structures [8]. In the FY 2011 report, we emphasized the feasibility to form Pt-skin-like surfaces at the nanoscale. In addition to numerous characterization techniques to confirm Pt-skin surface profile, we developed strategy for fast electrochemical screening of Pt-alloy catalysts in order to reveal the existence of Pt-skin formation on the catalyst surface. In the case of Pt<sub>3</sub>Ni(111)-skin, we found that the formation of H<sub>upd</sub> adlayer is substantially suppressed (up to 50%) when compared to Pt(111) with the same geometric surface area. In turn, for the Pt-skin type catalysts, it is not possible to establish electrochemically active surface area (ECSA) solely on the surface coverage by H<sub>upd</sub>. For that reason, it is important to use the CO stripping methodology because we found that surface coverage of adsorbed CO is the same on Pt and Pt-skin surfaces. The latter approach, therefore, eliminates errors originated by underestimation of ECSA, and hence, overestimation of specific activity. Moreover, the observed discrepancy between surface area estimations based on H<sub>upd</sub> and CO stripping can serve as descriptor for the formation of a skin-type nanocatalyst alloy, as acid leached skeleton-type surfaces and nanoparticles do not show such behavior. Specifically, the ECSA of the multilayered PtNi-skin catalyst [9] obtained from integrated H<sub>upd</sub> region was over 30% lower than that from CO stripping, which confirms the formation of Pt-skin type of surface in the nanocatalyst. All of results related to PtNi catalysts include surface area revealed from CO stripping experiments.

**Formation of Pt-skin surfaces in ternary alloys.** Since the last report our focus has been placed on possibility to form Pt-Skin surfaces over ternary alloys. We first studied the ternary systems on extended surfaces of polycrystalline thin films to establish the trend of electrocatalytic activities, and then applied this knowledge to synthesize ternary alloy nanocatalysts prepared by solvo thermal approach. Polycrystalline 50-nm thick ternary films were prepared

by confocal magnetron sputtering. Different targets of pure metals were used for sputtering over mirror polished glassy carbon substrate with 6 mm in diameter. The obtained films were subjected to annealing to induce homogeneous elemental distribution and subsequent surface analyses in order to explore existence of Pt-skin formation in ternary systems (see the Methods). Figure 1 summarizes the results of electrochemical studies for these thin films acquired by RDE. Compared to polycrystalline Pt (Pt-poly), cyclic voltammetry (CV, Figure 1A) of the as-sputtered films have similar features for underpotentially deposited hydrogen ( $H_{\text{upd}}$ ) regions ( $E < 0.4$  V) with slightly suppressed peaks. In the ORR-relevant regions ( $E > 0.6$  V), the ternary alloy surfaces exhibit positive shifts for the onset of  $\text{Pt-OH}_{\text{ad}}$  formation, which occurs at  $\sim 0.9$  V on the alloys, compared to Pt-poly, indicating weaker chemisorptions of oxygenated species on these surfaces. After annealing at  $400^\circ\text{C}$  the  $H_{\text{upd}}$  peaks of ternary systems are additionally suppressed, while the onset of  $\text{Pt-OH}_{\text{ad}}$  formation is shifted to even more positive potentials. Even though both effects could be mistaken by altered surface morphology upon thermal annealing, we proved by applying CO stripping methodology that they are associated with the formation of Pt-skin structure due to Pt segregation, see models in Figure 1. Compared to the Pt-poly surface, the as-sputtered and annealed  $\text{Pt}_3(\text{CoNi})_1$  surfaces show positive shifts of half-wave potentials by 12 and 22 mV, respectively. The specific activity at 0.95 V of the annealed surface reaches  $1.75 \text{ mA/cm}^2$ , whereas the as-sputtered surface achieves  $1.12 \text{ mA/cm}^2$  (Figure 1C). These values correspond to improvement factors of 4 and 2.5 compared to Pt-poly ( $0.45 \text{ mA/cm}^2$ ), respectively. The same strategy



**FIGURE 1.** Electrochemical characterization of the extended  $\text{Pt}_3(\text{CoNi})_1$  thin-film surfaces. (A) Cyclic voltammograms, (B) polarization curves and (C) Tafel plots. Specific activities for the ternary systems were presented as kinetic currents normalized by ECSAs obtained from  $\text{CO}_{\text{ad}}$  stripping curves. (D)  $H_{\text{upd}}$  ( $Q_{\text{H}}$ ) and CO stripping ( $Q_{\text{CO}}$ ) integrated charges assessed under the hydrogen adsorption/desorption peaks and a CO stripping peak.



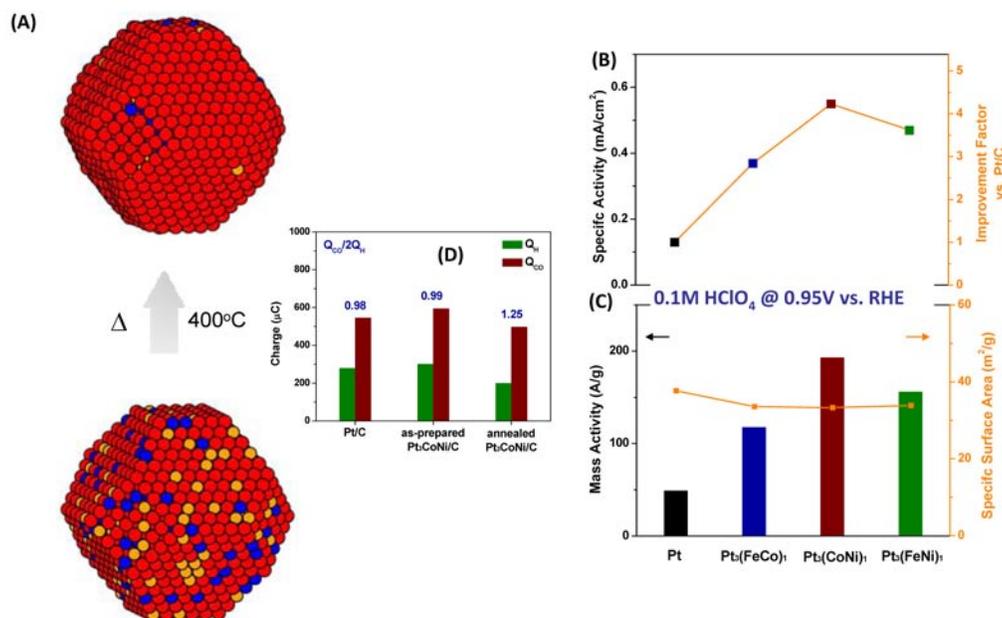
**FIGURE 2.** Summary of the ORR catalytic activities for the Pt-bimetallic and Pt-ternary alloy thin films compared to Pt-poly. Activities of both as-sputtered (Pt-skeleton) and annealed (Pt-skin) surfaces are presented.

was employed to investigate other ternary alloys, and hence a trend in the ORR activity has been established. Figure 2 shows a summary of the catalytic activities of the ternary alloys for the ORR in comparison with Pt-poly and  $\text{Pt}_3\text{Co}$ . All the as-sputtered alloy surfaces show higher activity than Pt-poly, with the improvement factors ranging from 1.7 to 2.5. Further improvement was consistently achieved by thermal annealing for each alloy. For the annealed surfaces,  $\text{Pt}_3(\text{CoNi})_1$  shows an improvement factor of  $\sim 4$  vs. Pt-poly, vs.  $\sim 2.2$  and  $\sim 3.0$  for  $\text{Pt}_3(\text{FeCo})_1$  and  $\text{Pt}_3(\text{FeNi})_1$ , respectively. We used these findings to approach corresponding nanoscale

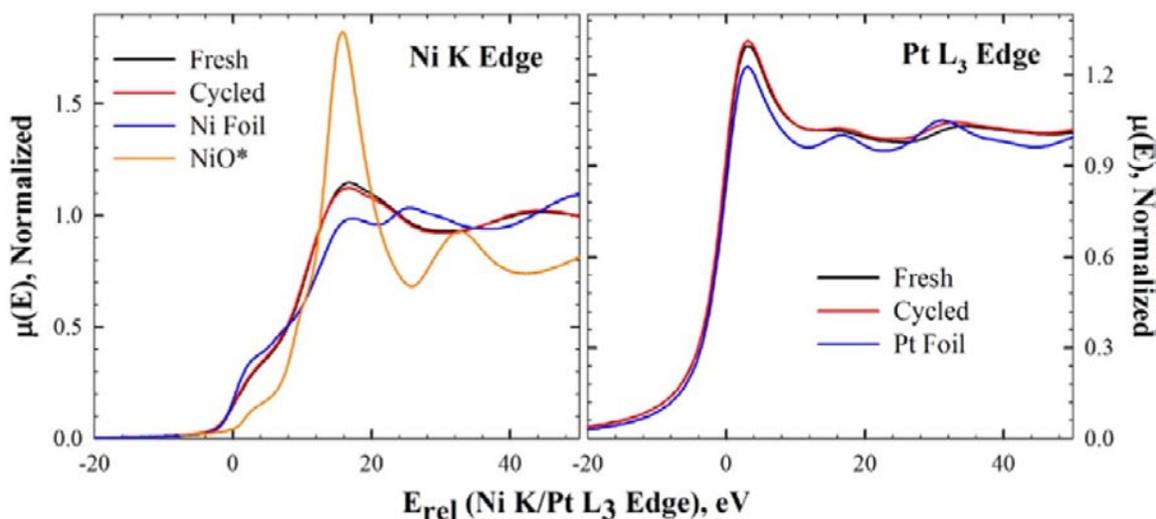
systems. As reported previously we used a solvo-thermal approach to obtain monodisperse and highly homogeneous Pt<sub>3</sub>MN nanoparticles. In addition to the previous year activities our focus lately has been focused on ability to form Pt-skin surfaces on ternary alloy NPs. Figure 3 summarizes results from electrochemical measurements of ternary alloys and confirms formation of Pt-skin. In accordance to extended surfaces results, the improvement factors show better performance when compared to Pt-bimetallic alloys. Our future efforts will be dedicated to increasing the content of non-precious metals, since our initial attempts were not successful. The main obstacle is different nucleation growth of Pt, which is much faster than Co, Ni and Fe and that induces formation of separate Pt NPs, Pt-rich core and inhomogeneous distribution elements across the nanoparticle.

**MEA durability studies.** For the most promising catalyst we performed detailed MEA characterization. Catalytic activity and stability of Pt-skin PtNi/C NPs were tested by the electrochemical potential cycling in 50-cm<sup>2</sup> fuel cells at General Motors. The electrodes were prepared by GM via a decal method. First, a catalyst ink with a targeted ionomer/carbon mass ratio of 0.8-1.0 was drawn down across an oversized (100-cm<sup>2</sup> frame) to coat the decal substrate. After drying, the decal was die-cut to 50 cm<sup>2</sup> and the electrode was laminated to a DuPont (25 μm) NRE 211 membrane in a hot press. The loadings on the cathodes were 0.13 mg<sub>Pt</sub>/cm<sup>2</sup>. X-ray absorption spectra were collected for the PtNi/C MEAs before and after the prolonged potential cycling. Figure 4 presents the normalized X-ray absorption near-edge spectroscopy (XANES) spectra at Ni K and Pt L<sub>3</sub>

edges for the “fresh” and “cycled” PtNi/C catalysts overlaid with the appropriate Ni and Pt foil standards. No shift in the absorption edge energies ( $E_0$ ) was detected against the standards in either case, indicating that the bulk oxidation states of Ni and Pt are zero in the catalysts. The line shapes of the PtNi/C catalysts at the Ni K edge deviate from the Ni foil standard. In particular, the pre-edge features (-4 to +4 eV relative to  $E_0$ ) are slightly muted, and the magnitudes of the white line features (+5 to +25 relative to  $E_0$ ) are considerably larger than the bulk Ni foil, but neither signal approaches that of NiO. Both the pre-edge and white line features should arise from dipole-forbidden 1s to p and d transitions and are indicative of the oxidation and change of local symmetry of the Ni atoms in vicinity to Pt. At the Pt L<sub>3</sub> edge, the catalysts show a bulk Pt oxidation state of zero and an increase in the white line intensity compared to the Pt foil standard. This feature, and also the dampened post-edge oscillations (in comparison to the Pt foil), can be ascribed to the nanoscale nature of the catalysts. From both Ni and Pt edges it can be seen that negligible changes occurred to the PtNi/C catalyst after the extensive (but mild) potential cycling, suggesting that the outer Pt layers protected the subsurface Ni. That this catalyst is capable of preserving the nanostructure during electrochemical reactions is consistent with the findings from electrochemical studies. Therefore, in addition to high specific activity, multilayered PtNi-skin catalyst also exhibits high durability that is verified by high-resolution transmission electron microscopy, RDE [9], MEA, and XANES.



**FIGURE 3.** Pt<sub>3</sub>MN NPs (A) Monte Carlo simulation confirms Pt-skin formation (B) Specific activity and improvement factor vs. Pt/C (C) Mass activity and specific surface area (D) ( $Q_{H_2}$ ) and CO stripping ( $Q_{CO}$ ) integrated charges assessed under the hydrogen adsorption/desorption peaks and a CO stripping peak.



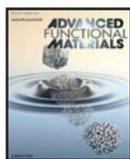
**FIGURE 4.** Ni K (left) and Pt  $L_3$  (right) edge XANES spectra of the fresh and cycled electrocatalyst cathode-side MEAs with the appropriate reference foils overlaid.

## Conclusions and Future Directions

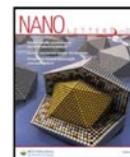
- PtM and  $Pt_3M_1N_2$  NPs cathode catalysts obtained from the organic solvo-thermal synthesis exhibit superior activity and stability than those prepared by the conventional methods. The method to synthesize  $Pt_3MN$  NPs with highly active Pt-skin morphology is established.
- Specific and mass activity improvements are obtained for Pt-skin  $Pt_3MN/C$  NPs in RDE measurements. Advanced theoretical modeling (density functional theory, Monte Carlo) methods predicted and confirmed Pt-skin type of nanosegregated structures in ternary alloys.
- Ternary systems operate through the same mode of action of improving the catalytic properties of the topmost Pt atoms as binary alloys.
- Ex situ characterization in MEA of the most promising nanoscale catalyst confirmed that the structure and composition of the catalyst were not changed after 20,000 cycles.
- Future effort will be dedicated to the scale-up synthesis of the most promising catalysts and MEA evaluation.
- Further increase of the non precious metal content will be pursued for ternary systems.

## FY 2012 Publications/Presentations

1. C. Wang, M. Chi, G. Wang, D. van derVliet, D. Li, K.L. More, H. Wang, J.A. Schluter, N.M. Markovic and V.R. Stamenkovic, *Relationship between Surface Chemistry and Electrocatalytic Properties of Monodisperse  $Pt_xNi_{1-x}$  Nanoparticles*, *Advanced Functional Materials*, 21 (2011) 147, Cover Article.



2. C. Wang, D. van derVliet, K.L. More, N.J. Zaluzec, S. Peng, S. Sun, H. Daimon, G. Wang, J. Greeley, J. Pearson, A.P. Paulikas, G. Karapetrov, D. Strmcnik, N.M. Markovic and V.R. Stamenkovic, *Multimetallic Au/FePt<sub>3</sub> Nanoparticles as Highly Durable Electrocatalysts*, *Nano Letters*, 11 (2011) 919-928, Cover Article.



3. C. Wang, M. Chi, D. Li, D. Strmcnik, D. van derVliet, G. Wang, V. Komanicky, K.-C. Chang, A.P. Paulikas, D. Tripkovic, J. Pearson, K.L. More, N.M. Markovic and V.R. Stamenkovic, *Design and Synthesis of Bimetallic Electrocatalyst with Multilayered Pt-Skin Surfaces*, *Journal of American Chemical Society*, 133 (2011) 14396.

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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.
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