

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

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Fiscal Year (FY) 2011 Objectives

- Fundamental understanding of the oxygen reduction reaction on multimetallic PtM (M = Co, Ni, Fe, Mn, Cr, V, and Ti) and PtM₁N₂ (M₁ = Co or Ni; N₂ = Fe, Mn, Cr, V, and Ti) materials.
- Develop highly-efficient, durable, nanosegregated Pt-skin PtM and PtM₁N₂ catalysts with ultra-low Pt content.
- Develop highly-efficient and durable Au/PtM₃ 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 PtM₁N₂ alloy nanoparticles and thin metal films.
- Resolve electronic/atomic structure and segregation profile of PtM and PtM₁N₂ systems.
- Resolve composition effects of PtM and PtM₁N₂ systems.
- Demonstrate mass activity and stability improvement of PtM and PtM₁N₂ alloy nanoparticles.
- 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 the Fuel Cells section (3.4.5) of the Hydrogen, Fuel

Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

This project is conducting fundamental studies of the oxygen reduction reaction on Pt-based PtM (M = Ni, Co, Fe, Cr, V, and Ti) binary and PtM₁N₂ (N, M = Fe, Co, and/or Ni) catalysts as well as on Au/Pt₃M 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 DOE 2015 targets (Table 1).

TABLE 1. DOE 2015 Targets

Specific activity @ 0.9 V _{iR} -free: 720 mA/cm ²	PGM total content: 0.2 g/kW
Mass activity @ 0.9 V: 0.44 A/mgPt	Total loading: 0.2 mg/cm ²
Catalyst support loss: <30%	Durability w/cycling (80°C): 5,000 hrs

V_{iR} – volt internal resistance; PGM – precious group metal

FY 2011 Accomplishments

- Synthesized wide range of bi/multimetallic 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 Pt₃Ni 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 monolayers, ML) that are mimicking stability/activity of thin metal film systems.
- In a membrane electrode assembly (MEA), for PtNi/C multilayered skin confirmed: (i) three times higher specific amperage (SA ~0.8 mA/cm²) than benchmark Pt/C catalysts and mass activity of ~0.35 A/mg_{Pt}; (ii) high durability, e.g., after 20,000 cycles activity, surface area loss was only 12% compared to ~40% for Pt/C.
- Performed composition optimization of ternary PtM₁N₂ catalysts.

- Established activity (stability) trends for bimetallic nanoparticles (NPs).
- Demonstrated 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 progress for FY 2011 in experimental and theoretical studies to addressing the importance of alloying Pt with *3d* elements ($M = \text{Ni, Co, Fe}$ etc.) and making a novel tailored nanostructure of Au/Pt_3M in order to form catalytically active materials with so-called nanosegregated profile [1]. 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 Cell Technologies 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, structure 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 (scale up) of the highly efficient nanoscale materials, which are guided by the fundamental understanding of structure-function relationships.

Results

From Model Thin Films to Real Pt-Skin PtNi Nanoparticles. The term Pt-skeleton has been coined to describe unique Pt structure that remains on the surface of bi(multi)-metallic alloys after dissolution of non-Pt atoms from the near-surface region in acidic environments [3]. On the other hand, the term Pt-skin has been used to describe another unique formation of Pt surface atoms that is formed after thermal treatment of bimetallic alloys due to tendency of Pt to have complete segregation over Pt_3M systems. In some cases, 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 for the ORR [1]. Particularly,

extended Pt_3M electrodes with Pt-skin surfaces are more active for the ORR than the corresponding Pt-skeleton structures [4]. In the previous FY 2010 report, we pointed out that the skeleton-like structure of $\text{Pt}_{50}\text{Ni}_{50}/\text{C}$ catalyst, formed by dissolution of the surface/subsurface Ni atoms, has the highest specific (4.0 mA/cm^2) and mass ($1.5 \text{ A/mg}_{\text{Pt}}$) activities for the ORR compared to the other $\text{Pt}_x\text{Ni}_{1-x}$ NPs. In the mean time, we have revealed that the concentration profile formed after leaching out of *3d* element from $\text{Pt}_x\text{Ni}_{1-x}$ catalysts indicated skeleton type of surface structure, whose thickness depends on the ratio between Pt and Ni [1]. In this report, we summarize the results that are providing both fundamental insights required for efficient transformation of the Pt-skeleton to more active Pt-skin morphology, which we used as guiding principles that have led to the synthesis of an advanced PtNi nanocatalyst with the optimized Pt-skin type of surfaces. In order to evaluate correlation between the thickness of Pt-skeleton overlayer and catalytic properties we used physical vapor deposition method to prepare well characterized Pt-skeleton surfaces over the $\text{Pt}_{50}\text{Ni}_{50}$ substrate, which was found to be the most active bimetallic catalyst. As depicted in Figure 1, the as-sputtered Pt films consisted of randomly distributed Pt atoms, which simulate the Ni-depleted Pt-skeleton overlayers. Figure 1 also shows that the optimal activity for the ORR (improvement factor 2.5) is observed on the surface covered by ca. 3 MLs of Pt, which is in line with the previous results on polycrystalline Pt_3M bulk alloys with the skeleton type of surfaces. Reduced enhancement was observed for thicker Pt films, e.g., improvement factor of 1.7 for 5 ML of Pt, while the specific activity measured for the 7 ML film was close to that of poly-Pt. In order to transform the Pt-skeleton morphology to more active Pt-skin, we applied a moderate thermal treatment at 400°C , which was previously optimized for bimetallic NPs [5]. Such treatment induced relaxation of low-coordinated Pt surface atoms and formation of energetically favorable adlayer with higher coordination of surface atoms. Electrocatalytic properties and structural characterization of such adlayer revealed the formation of Pt-skin, which was verified by the suppressed H_{upd} region and substantial positive shift of the Pt-OH_{ad} peak as well as by ~5-times increased in specific activity of the ORR (Figure 1).

The knowledge obtained from the well-defined systems is then used to optimize the catalytic properties of the $\text{Pt}_{50}\text{Ni}_{50}$ NPs with skeleton type of surfaces mentioned above [FY 2011 Ref. 3]. Further modification of near-surface morphology was obtained by a subsequent annealing of the skeleton-type of NPs at 400°C . This treatment has facilitated relaxation of low-coordinated surface atoms and transition of the particle surface morphology into Pt-skin type. Combined scanning transmission electron microscopy (STEM) and energy dispersive X-ray (EDAX) analyses revealed a concentration profile and the thickness of the Pt overlayer. It has been found that the particle core has

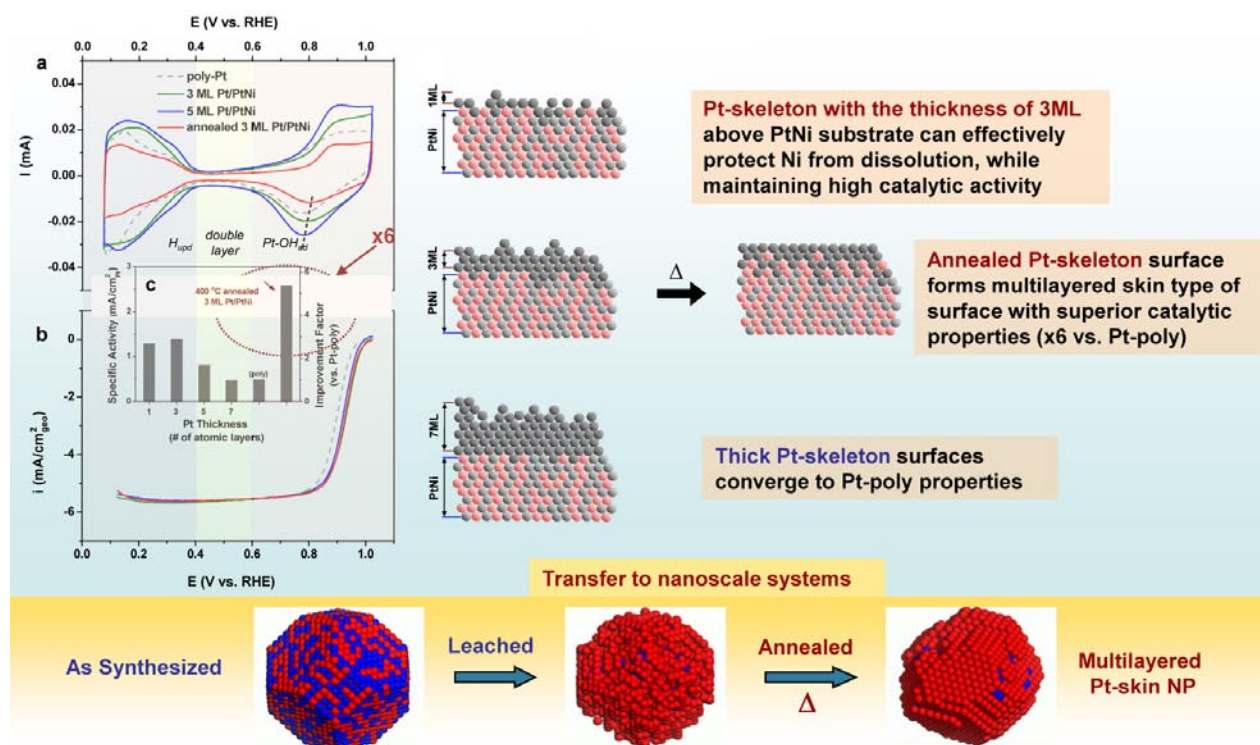


FIGURE 1. Electrochemical studies on the Pt thin films deposited over PtNi substrate by rotating disk electrode (RDE): (a) cyclic voltammograms, (b) polarization curves and (c) summary of specific activities and corresponding improvement factors (vs. polycrystalline Pt surface) for the Pt films of various thicknesses. Cyclic voltammograms were recorded in Ar saturated 0.1 M HClO₄ electrolyte with a sweeping rate of 20 mV/s. Polarization curves were recorded in the same electrolyte under O₂ saturation with a sweep rate of 20 mV/s. Specific activities were presented as kinetic currents normalized by electrochemical surface areas obtained from integrated H_{up,d}, except that for the annealed 3 ML Pt/PtNi surface it was based on CO_{ad} stripping polarization curve. Schematic representation of surface morphology transformations for PtNi NP.

Pt₅₀Ni₅₀ composition, while the thickness of the Pt overlayer is about 2-3 ML; schematic representation is depicted in Figure 1. Based on electrochemical characteristics we concluded that these nanoparticles have typical Pt-skin properties, i.e., suppressed H_{up,d} region and superior catalytic activity towards the ORR: SA=1 mA/cm² at 0.95 V. In addition, PtNi NPs with multilayered skin surfaces are found to have excellent durability after 30,000 cycles between 0.5 to 1.1 V [1].

Finally, catalytic activity and stability of these NPs were tested in an MEA (General Motors R&D facilities). It is found that PtNi/C NPs with Pt multilayer skin surfaces have 3x higher specific activity (0.8 mA/cm²) than benchmark Pt/C and mass activity of 0.35A/mg_{Pt}. Furthermore, after 20,000 cycles the activity loss was only 12%, while commercially available Pt/C and bimetallic catalysts suffer loss of 30-50%. Therefore, we concluded, that Pt₅₀Ni₅₀/C NPs with multilayered Pt skin meet DOE 2015 targets for specific activities and exceed anticipated targets for stability.

Characterization, Activity and Stability of Ternary Systems. Organic colloidal solvo-thermal approach was developed to synthesize Pt₃MN (N,M = Fe, Co, and/

or Ni) ternary alloys that potentially could be used as the cathode materials in PEMFC systems. Although many types of catalysts have been synthesized, for our purposes here we present only the results for the most promising ternary catalysts. As summarized in Figure 2, the transmission electron microscope (TEM) image depicts highly uniform particle size of the Pt₃NiCo NPs, with the average particle size of ~6 nm. On the other hand, the analysis of high angle annular dark field (HAADF) and STEM data indicated homogenous distribution of the alloying elements. The X-ray diffraction analysis showed single crystal phase for all NPs, confirming the homogeneous alloy composition. It is obvious, therefore, the solvo-thermal synthesis brings high level of control of the crucial parameters such as homogenous distribution of particle size and composition profiles. We demonstrate further that these types of NPs may possess desirable catalytic activity for the ORR. For example, Figure 3 shows that acid-leached Pt₃CoNi NPs have the highest specific (0.85 mA/cm²) and mass (0.3 A/mg_{Pt}) activity at 0.95 V. These results strongly suggest that alloying Pt with the 3d elements can provide additional tunability towards the activity of Pt-based alloy catalysts. We anticipate that catalytic activity of the PtMN NPs with skeleton type of

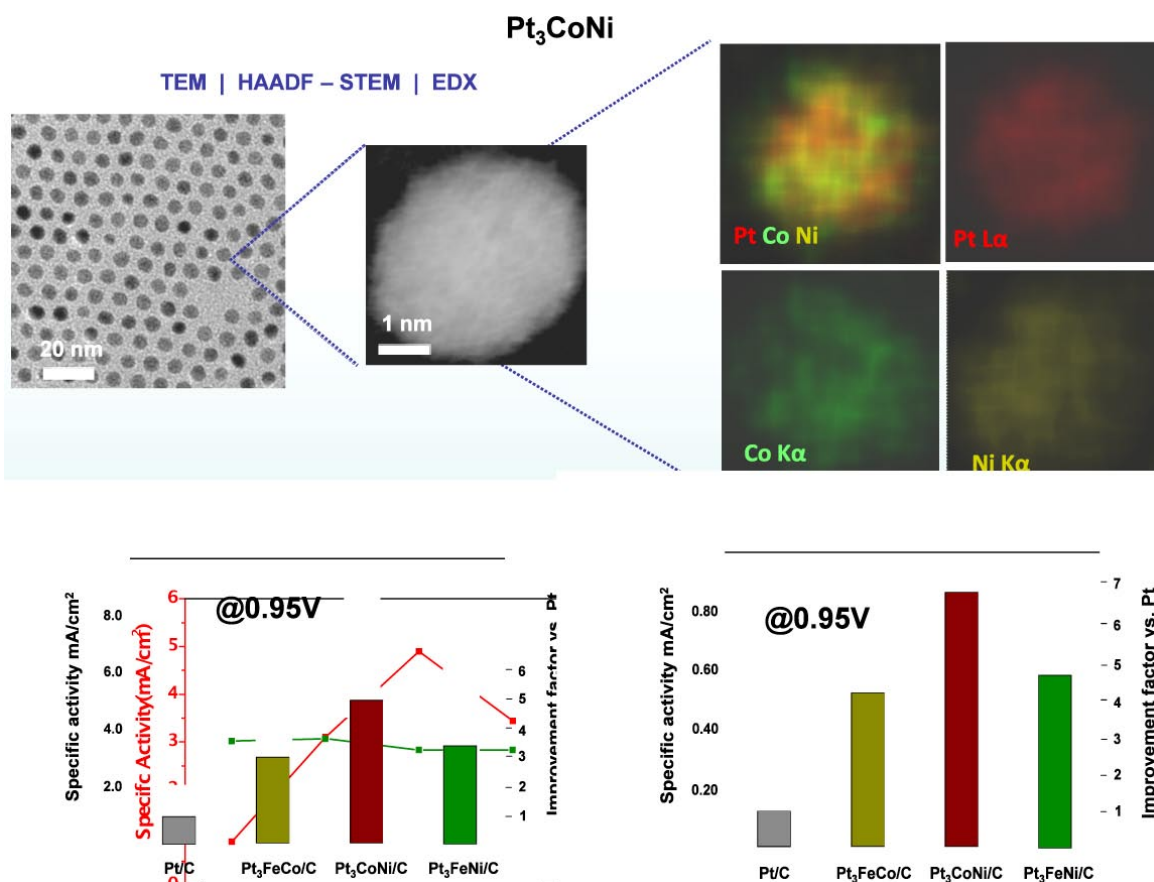


FIGURE 2. TEM, HAADF-STEM, EDAX and electrochemical characterization of Pt₃CoNi ternary alloy nanoparticles. Bar graphs: the summary of specific and mass activities of Pt₃MN NPs measured by rotating disk electrode in 0.1M HClO₄ at 0.95 V, 1,600 rpm and 20 mV/s.

surfaces could be further improved by the temperature-induced formation of the Pt-skin morphology.

Shape Controlled Core/Shell Ternary Nanoparticles.

In addition to ternary systems mentioned above we develop an approach toward design and synthesis of an advanced three component system with core/shell structure. A ternary catalyst with Au core and bimetallic Pt₃Fe shell is being developed for the ORR. Tailored Au/Pt₃Fe structure has been optimized through the studies of well-defined thin film surfaces and then synthesized by organic solvo-thermal method. The morphology control and preferred composition profile were achieved through epitaxial growth of Pt₃Fe over 7 nm Au seed. Figure 3 depicts the morphology, structure, and size of the Au/Pt₃Fe NPs with the average size of 10 nm. High resolution transmission electron microscopy (HRTEM) images reveal that while both Au NPs and Au/Pt₃Fe NPs possess an icosahedral-like shape, Pt₃Fe particles have a characteristic cubo-octahedral shape. The composition profile of multimetallic particles, established from HAADF-STEM imaging and elemental mapping, signify that the Au seed is surrounded by both Pt and Fe atoms. As shown in Figure 3, these multimetallic Au/Pt₃Fe NPs possess both the high catalytic activity and the superior

durability, with mass activity enhancements of more than one order of magnitude over Pt catalysts. Furthermore, TEM images and electrochemical capacitance analysis of cyclic voltammograms acquired before and after durability testing (60,000 cycles in the potential range between 0.6 and 1.1 V in oxygen saturated electrolyte) unambiguously revealed that in contrast to Pt₃Fe/C and Pt/C no significant loss in electrochemically active surface area (360 vs. 340 cm²/mg_{Pt}) or specific activity (1.5 vs. 1.4 mA/cm²) before and after cycling was observed for Au/Pt₃Fe/C. The increased activity was explained based on electronic effects induced by alloying Pt with Fe, the enhanced durability was achieved by the tailored morphology of icosahedral NPs and unique compositional profile of three alloying components [2]. The reported result for the core-shell type of catalysts has opened new avenues for synthesis of highly active and stable cathode catalysts for the PEMFC applications.

Conclusions and Future Directions

- PtM and PtM₁N₂ NPs cathode catalysts obtained from the organic solvo-thermal synthesis exhibit superior activity and stability than those prepared by the

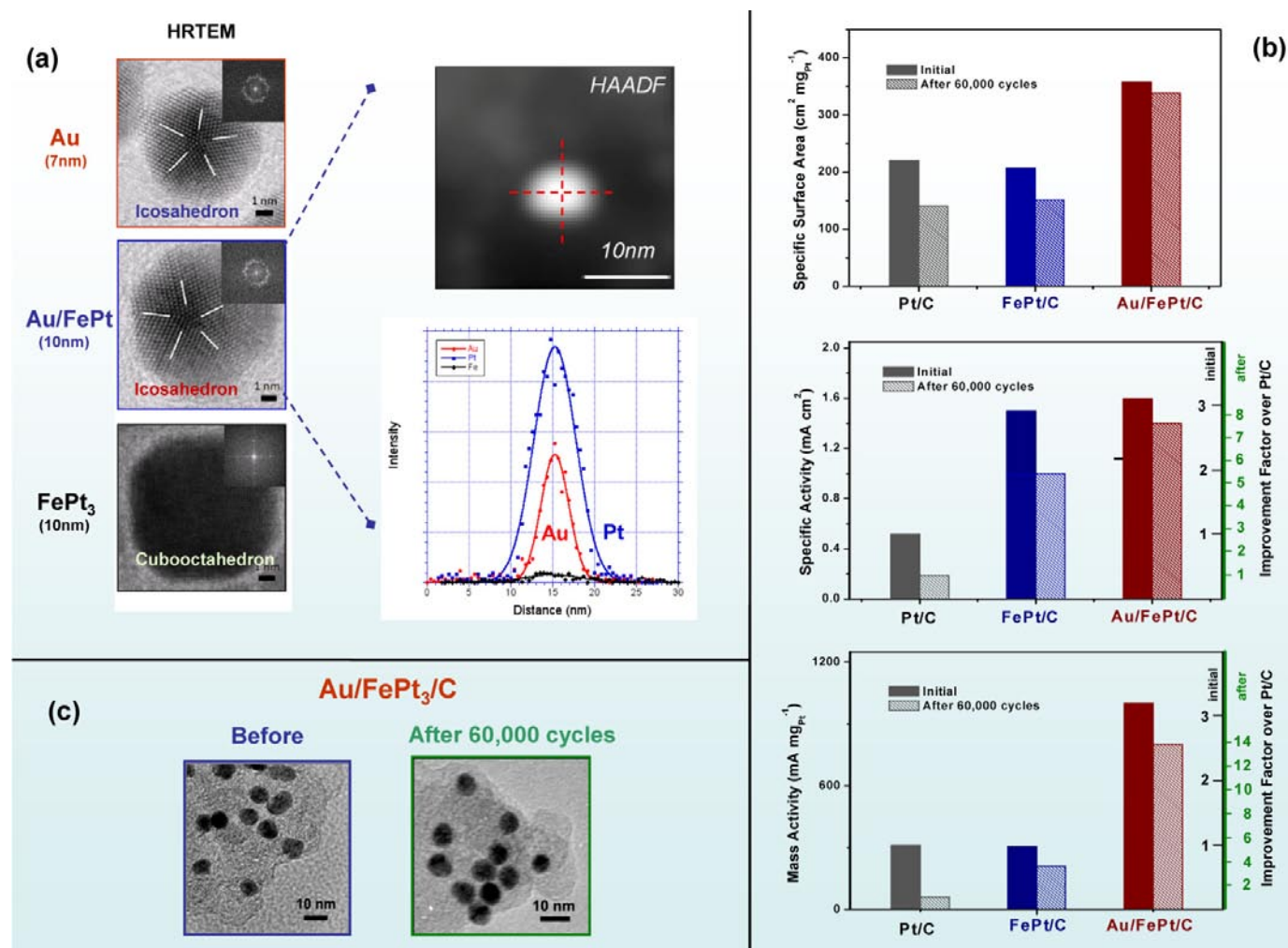


FIGURE 3. Ternary core shell Au/FePt catalyst: (a) HRTEM characterization of Au, Au/FePt and FePt₃ nanoparticles. HAADF and energy dispersive X-ray characterization of Au/FePt NP, which confirms core/shell structure. (b) Electrochemical characterization by RDE at 0.9 V in 0.1M HClO₄ for Pt/C, Pt₃Fe and Au/FePt catalysts. (c) Morphology studies by TEM before and after 60,000 potential cycles in 0.1 M HClO₄ between 0.6 to 1.1 V.

conventional methods. The methods of synthesis of PtNi NPs with highly active and stable Pt-skin morphology is developed.

- Significant mass activity and durability improvement are obtained for Pt-skin PtNi/C NPs with multilayered (2-3 atomic layers) Pt skin in both rotating disk electrode configuration and MEA. Advanced theoretical modeling methods are developed for resolving nanosegregated structures.
- Ternary systems possess high activity and stability but understanding the mode of action of two three-dimensional elements added to the Pt host has yet to be addressed.
- In collaboration with industrial partners, further testing in MEA of the most promising multimetallic catalysts is planned as well as scaling up synthesis methods for the larger scale production of the most active catalysts.

FY 2011 Publications/Presentations

1. C. Wang, M. Chi, G. Wang, D. vanderVliet, D. Li, K.L. More, H. Wang, J.A. Schluter, N.M. Markovic, V.R. Stamenkovic, *Relationship between Surface Chemistry and Electrocatalytic Properties of Monodisperse Pt_xNi_{1-x} Nanoparticles*, *Advanced Functional Materials*, 21(2011)147, Cover Page 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, V.R. Stamenkovic, *Multimetallic Au/FePt₃ Nanoparticles as Highly Durable Electrocatalysts*, *Nano Letters*, 11(2011)919-928, Cover Page Article.
3. C. Wang, M. Chi, D. Li, D. Strmcnik, D. vanderVliet, G. Wang, V. Komanicky, K.-C. Chung, A.P. Paulikas, D. Tripkovic, J. Pearson, K.L. More, N.M. Markovic, V.R. Stamenkovic, *Design and Synthesis of Bimetallic Electrocatalyst with Multilayered Pt-Skin Surfaces*, *Journal of American Chemical Society*, In press.

5. C. Wang, S. Sun, N. Markovic and V. Stamenkovic, *Epitaxially Conjugated Composite Nanoparticles - Synthesis and Catalytical Applications*, Materials Research Society Spring Meeting, April 2010, San Francisco, CA.
6. C.Wang, D.Strmcnik, D.Tripkovic, K.L.More, N.M.Markovic and V.Stamenkovic, *The Role of Surface Structure and Surface Composition in Electrocatalysis* (Plenary Lecture) International Society of Electrochemistry Regional Meeting, June 2010, Belgrade, Serbia.
7. C.Wang, N.M.Markovic and V.Stamenkovic, *Morphology Controlled Synthesis of Composite Nanoparticles by Rational Designed Conditions*, American Chemical Society Fall Meeting, August 2010, Boston, MA.
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11. M. Chi, C. Wang, N. Markovic, K. More and V. Stamenkovic, *In-Situ Observation of Skin-layer Formation in Pt₃Ni Nanoparticles*, 2010 Materials Research Society Fall Meeting, November 2010, Boston, MA.
12. C. Wang, D. Strmcnik, D. Tripkovic, N. Markovic and V. Stamenkovic, *Advanced Nanoscale Electrocatalysts for Fuel Cells*, 2010 Materials Research Society Fall Meeting, November 2010, Boston, MA.

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6. C. Wang, D. van der Vliet, K.C. Chang, H. You, D. Strmcnik, J.A. Schlueter, N.M. Markovic, V.R. Stamenkovic, "Monodisperse Pt₃Co Nanoparticles as a Catalyst for the Oxygen Reduction Reaction: Size Dependent Activity", *J. Phys. Chem. C.*, **113**(2009)19365.