

V.A.3 Nanosegregated Cathode Alloy Catalysts with Ultra-Low Platinum Loading

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Project Start Date: September 2009

Project End Date: September 2014

Overall Objectives

- Fundamental understanding of the oxygen reduction reaction (ORR) 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-active 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 nanomaterials in rotating disk electrodes (RDEs) and membrane electrode assemblies (MEAs).
- 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.

- Develop and synthesize highly active and durable practical catalyst with ultra-low content of precious metals.

Fiscal Year (FY) 2014 Objectives

- Optimization of synthesis methods to produce larger volumes of catalysts in a single batch.
- Implementation of the advanced protocols for surfactant removal for different classes of nanomaterials.
- Synthesis and characterization of the most active and durable PtM₁N₂ alloy nanoparticles with controlled particle size and elemental distribution.
- Evaluation of the nanosegregated compositional profile in the most active and durable systems.
- Employment of high crystallinity in nanoscale materials.
- Design and synthesis of multimetallic three-dimensional (3-D) nanowire-based material with controlled length, width and composition.
- Evaluation of catalyst properties in an MEA.

Technical Barriers

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

- (A) Durability
- 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 ORR on Pt-based PtM (M= Ni, Co, Fe, Cr, V, and Ti) binary and PtM₁N₂ (nanomaterials = 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 following DOE 2015 targets:

- Specific activity @ 0.9 V (iR-free): 720 mA/cm²
- Mass activity @ 0.9 V: 0.44 A/mg_{Pt}
- Catalyst support loss: <30% over 30,000 potential cycles
- Platinum group metal total content: 0.2 g/kW
- Total loading: 0.2 mg/cm²
- Durability with/cycling (80°C): 5,000 hrs

FY 2014 Accomplishments

- Developed experimental protocol to synthesize novel class of core/interlayer/bi-metallic-shell nanoparticles with Pt-“pseudo-skin” and established concentration profile for core/interlayer/shell.
- Evaluated surface Au vs. subsurface Au effect in multimetallic systems.
- Synthesis and characterization of the core/shell Au/CoPt₃ nanoparticles.
- Optimized compositional profile of the Ni-core/Au-interlayer/NiPt-shell nanoparticles for the maximal catalytic activity, superior durability and minimal loading of precious metals.
- Performed 10,000 potential cycles by RDE for activity/durability evaluations of core-interlayer/shell nanoparticles.
- Developed protocols for synthesis of highly crystalline multimetallic nanoframes with 3-D network of catalytically active surfaces, well-defined size, shape, composition, and surface structure.
- Performed detailed in situ and ex situ structural characterization of nanoframes and established compositional profile of nanoframes and tuned their surface composition towards multi-layered Pt-skin.
- Demonstrated high thermal stability of nanoframes. Established electrochemical pretreatment for nanoframe particles and optimized catalyst loading into high-surface-area carbon and performed detailed electrochemical characterization by establishing the activity/stability signature for nanoframe catalysts before and after 10,000 potential cycles.
- Implemented ionic-liquid approach into the nanoframe catalyst and performed detailed structural and electrochemical evaluations by high-resolution transmission electron (TEM) microscope and RDE.
- PtNi nanoframe catalyst achieved the highest specific and mass activity for the ORR ever measured for practical nanoscale electrocatalysts.



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 ORR and minimize dissolution of the cathode catalysts. Here, we report on progress for FY 2014 in experimental and theoretical studies to addressing the importance of alloying Pt with 3-D elements (M= Ni, Co, Fe, etc.) 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 with 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 Hydrogen and Fuel Cells Program we rely on our materials-by-design approach [1-8]. This involves four major steps: (i) advanced chemical and physical methods for synthesis of novel nano/mesoscale materials, which enables control of their size, composition, morphology and structure; (ii) characterization of atomic and electronic properties by ex situ and in situ surface specific tools 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 practical catalysts, which are guided by the fundamental understanding of structure-function relationships.

RESULTS

The effect of surface Au vs. subsurface Au on the ORR electrocatalysis. In Pt-alloy nanoparticle electrocatalysts, Au can have both catalytic and durability roles owing to its high redox potential. Its effectiveness for both is greatly affected by the nanoparticle structure as well as compositional profile, and therefore, proper electrocatalyst design requires a fundamental understanding of the structure-function relationship, specifically how Au placement can affect the catalytic properties of Pt-alloys. Two different cases were considered, one in which Au is deposited on the surface of PtNi nanoparticles, PtNi-Au, and the other one in which Au is located beneath the surface, Au@PtNi. The ORR activity trend associated with Au placement results in lower specific activity where 10% surface coverage of Au leads to a decrease in half-wave by 40 mV while 50% surface coverage leads to a loss of over 100 mV in the half-wave potential and a significant decrease in the diffusion limited current, suggesting a partial shift from 4-electron toward 2-electron oxygen reduction mechanism. From these results it is clear that the beneficial effects of Au are best realized in Pt-Au-Ni ternary system when Au is located beneath the

surface, not directly being exposed to the reactive species. In principle, core-shell transition metal@Pt catalysts can minimize the mass of buried, electrocatalytically inactive Pt; however, if the core itself is high in precious metal content, such as Au, it fails to effectively address the cost per kW in polymer electrolyte membrane fuel cells. All of the above points towards a unique multilayered compositional profile where the core is entirely composed of an inexpensive transition metal while the interface between the core and Pt alloy shell contains an optimal amount of Au to enhance durability and limit the total mass of precious metals within the catalyst. Nanomaterials with such distinct compositional profile are termed as core/interlayer/shell nanoparticles.

Synthesis and characterization of Ni-Core, Au-interlayer, NiPt-shell nanoparticles. Through a controlled layer-by-layer growth mechanism, we add Au to the interface between the nanoscale core and shell. In brief, 3.1 nm ($\sigma < 5\%$) Ni nanoparticles are synthesized and used as core, Figure 1, to deposit Au in a desired quantity, forming an intermediate Ni@Au core/shell nanostructure. The final step is deposition of a PtNi shell with the thickness of approximately 1 nm (~ 6 MLs) which forms the desirable nanosegregated Ni@Au@PtNi nanoparticles with a diameter of 5.0 nm ($\sigma = 6\%$), as shown in Figure 1. The scanning transmission electron microscopy (STEM) images (Figure 1c and d) show that after exposure to acidic electrolyte, the core-shell structure and the Ni core are preserved, and the line scan of energy-dispersive X-ray spectroscopy (EDX) confirms the formation of the Pt-skeleton surface (Figure 1e). In our previous study, the durability enhancement in Au/FePt ternary core/shell electrocatalyst was ascribed to the hindered place-exchange mechanism [7]. Subsurface Au

content equivalent to 0.25 ML in the underlying atomic layer of a Pt surface reduce the adsorption strength of subsurface oxygen at all relevant potentials for the ORR. The presence of subsurface oxygen drives the place-exchange mechanism which is responsible for bringing transition metals to the surface as well as being the dominant mechanism by which Pt is dissolved. Therefore, placement of Au atoms with higher redox potential in the near-surface region lowers the probability for both transition metal (Fe, Co and/or Ni) and Pt dissolution. We determined that the amount of interlayered Au that surrounds the Ni core can be successfully controlled from a complete monolayer down to 0.25 ML. Detailed electrochemical evaluation revealed that after 10,000 potential cycles in 0.1 M HClO₄ between 0.6 and 1.1 V vs. RHE, there is a negligible loss in activity for all of the nanoparticles containing some quantity of subsurface Au, as revealed in Figure 2. The amount of Au was varied from a solid Au core where Au makes up 47 at% of the nanoparticle, to an equivalent of ~ 1 ML over the Ni core where Au is 28 at% of the crystal down to a Au content of 5 at% which is close to 0.25 ML on the Ni core. The ORR activity of Ni@Au@PtNi/C electrocatalysts is tested and compared with commercial Pt/C and PtNi/C electrocatalysts. As shown in Figure 2, the Ni@Au@PtNi/C electrocatalysts possess great durability towards the ORR without noticeable loss in either electrochemically active surface area (ECSA) or specific activity. The specific and mass activity enhancement of Ni@Au@PtNi/C is over 8-fold versus the Pt/C and outperforms multilayered Pt-skin PtNi/C due to the Ni replacement of expensive Pt in the core. Figure 2d shows TEM images of Pt/C, PtNi-Skeleton/C, and Ni@Au@PtNi/C nanoparticles before and after 10,000 cycles. After potential cycling, the

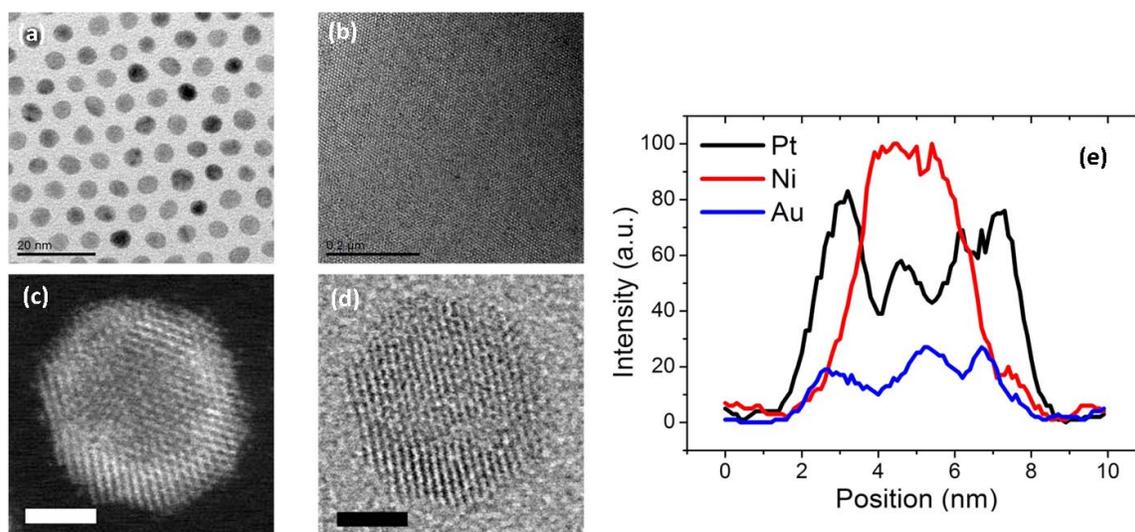


FIGURE 1. TEM images of (a-b) as-synthesized Ni nanoparticles (c) Ni@Au@PtNi core/interlayer/shell nanoparticle bright-field STEM images; (d) dark-field STEM images, (e) EDX data clearly show the core-shell structure; and (f) the EDX line profile shows a Pt-rich skeleton structure over the Au-coated Ni core. Scale bars: a) 0.2 μ m, b) 20 nm, c, d) 2 nm.

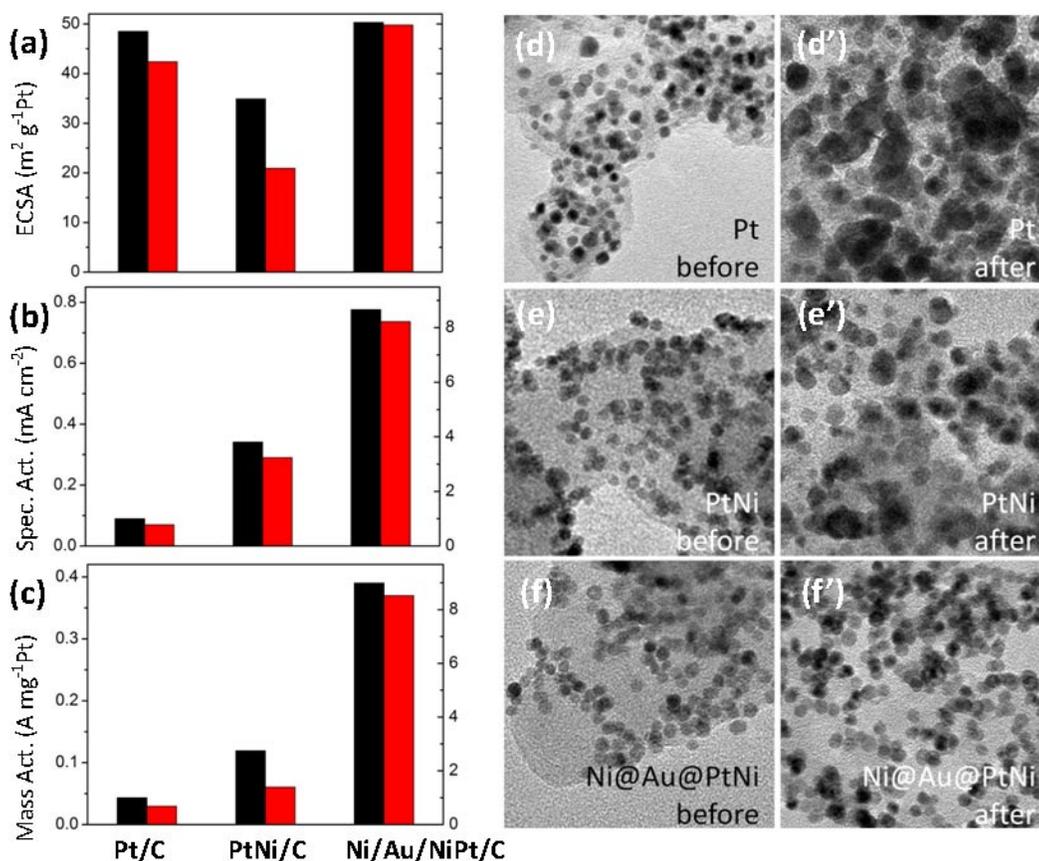


FIGURE 2. Bar charts showing a) electrochemically active surface areas, b) specific activities, and c) mass activities of Pt/C, PtNi/C (with Pt-Skeleton), and Ni@Au@PtNi/C (with pseudo Pt-Skin) electrocatalysts before and after 10,000 cycles of electrochemical cycling up to 1.1 V. The activity is normalized kinetic current density measured at 0.95 V. The specific activity is the activity normalized to the ECSA measured by CO-stripping. (d-f) TEM images of Pt, PtNi, and Ni@Au@PtNi nanoparticles before and (d'-f') after 10,000 cycles up to 1.1 V. All the images are at size of 100 nm \times 100 nm.

sizes of Pt and PtNi nanoparticles are significantly changed: big particles (>10 nm) and small particles (<5 nm) are observed instead of the initial ~ 5 nm size, indicating that Pt and PtNi are affected by the well-known Ostwald ripening process under the potential cycling. However, such change in size and shape is not observed on Ni@Au@PtNi, again demonstrating the synergy between high activity and high durability of Ni@Au@PtNi/C electrocatalysts.

Highly crystalline multimetallic nanoframes as electrocatalysts. An entirely new class of catalysts was synthesized from PtNi₃ polyhedra in oleylamine that had a uniform rhombic dodecahedron morphology and size (20.1 ± 1.9 nm), as observed in Figure 3. Initially, the oleylamine-capped PtNi₃ polyhedra were dispersed in nonpolar solvents, during which time they transformed into Pt₃Ni nanoframes, with unchanged symmetry and size. Solid nanostructures gradually eroded into hollow frames, and the bulk composition changed from PtNi₃ to PtNi and eventually Pt₃Ni, as evidenced by X-ray diffraction and EDX spectra. After dispersion of nanoframes onto a high-surface-

area carbon support (VULCAN[®] XC72) and subsequent thermal treatment in inert gas (Ar) atmosphere between 370 and 400°C, most nanoframes developed the smooth Pt-skin type of structure. The electrocatalytic properties of Pt₃Ni nanoframes were evaluated and compared to PtNi/C and commercial state-of-the-art Pt/C nanoscale electrocatalysts (Figure 3). The polarization curves shown in Figure 3b show an increase in ORR activity in the following order: Pt/C < PtNi/C \ll Pt₃Ni nanoframes. The ratio between ECSA values determined by integrated charge from CO-stripping and underpotentially deposited hydrogen (H_{upd}) was 1.52 for the Pt₃Ni nanoframes, strongly suggesting formation of a Pt-skin terminated (111)-like surface structure. Moreover, EDX line profiles confirmed the presence of Pt-skin on the nanoframe surfaces with a thickness of at least two Pt monolayers. As a result, the specific activity of Pt₃Ni nanoframes at 0.95 V exhibited an improvement factor of over 16 versus commercial Pt/C electrocatalyst (Figure 3c). The synergy between specific activity and the open architecture of the Pt₃Ni nanoframes that enables access of reactants to both the

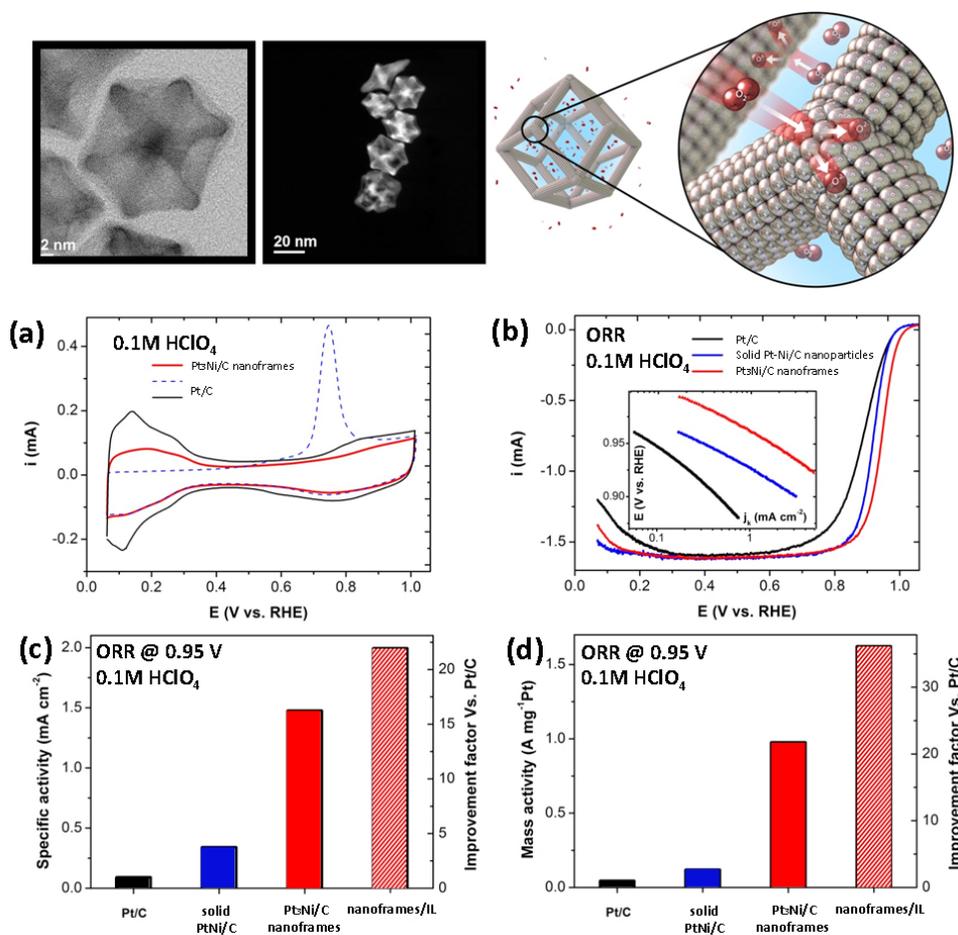


FIGURE 3. High-resolution TEM images of Pt₃Ni nanoframes. (a) cyclic voltammograms of Pt/C and Pt₃Ni nanoframes signify the difference in surface coverage by H_{upd} and OH_{ad}. ECSA of the nanoframes is determined by integrated charge of adsorbed CO electrooxidation curve; (b) The ORR polarization curves and corresponding Tafel plots; (c) specific activities and (d) mass activities measured at 0.95 V and improvement factors versus Pt/C catalysts. Because of the high intrinsic activity of the Pt₃Ni nanoframes the ORR activity values are given at 0.95 V in order to avoid the extensive error margin introduced by the close proximity of current values at 0.9 V to the diffusion limited current.

internal and external surfaces led to an unprecedented 22-fold enhancement in the mass activity vs. Pt/C (Figure 3d). The mass activity calculated at 0.9 V (5.7 A mg⁻¹Pt) is over one order of magnitude higher than the DOE's 2017 target (0.44 A mg⁻¹Pt), making the Pt₃Ni nanoframes the most efficient electrocatalyst for the ORR. In addition to the high intrinsic and mass activities, the Pt₃Ni nanoframes exhibited remarkable durability throughout electrochemical operation, i.e., STEM (dark field and bright field) images confirmed that the frame structure was preserved while activity loss was negligible after 10,000 potential cycles. The enhanced durability is ascribed to the electronic structure of the Pt-skin surface resulting in a lower coverage of oxygenated intermediates because of the weaker oxygen binding strength, which diminishes the probability of Pt dissolution, plus, the optimized Pt-skin thickness of at least 2 MLs hinders the loss of subsurface transition metal through the place-exchange

mechanism during electrochemical operation consequently preserving the high intrinsic activity [8]. In addition, protic ionic liquids (ILs) were integrated into a porous nanoframe catalyst, where the high O₂ solubility of IL increases the O₂ concentration at the catalyst surface, resulting in higher attempt frequencies for the ORR and consequently higher activity. The [MTBD][NTf₂] protic-liquid was used that has an O₂ solubility ($C_{O_2, [MTBD][NTf_2]} = 2.28 \pm 0.12$ mM), approximately twice that of the common electrolyte HClO₄. Capillary forces exerted by the Pt₃Ni nanoframes pulled the IL inside the frames and prevented it from being washed away by electrolyte. The IL-encapsulated Pt₃Ni nanoframes showed sustained superior activity upon prolonged (10,000) potential cycling without noticeable decay in performance. As depicted in Figure 3, the IL-encapsulated Pt₃Ni nanoframes exhibited a 36-fold enhancement in mass activity and 22-fold enhancement in specific activity compared with

Pt/C, which is the highest activity ever measured for practical nanoscale catalysts.

CONCLUSIONS AND FUTURE DIRECTIONS

- PtM and Pt₃M₁N₂ nanoparticles 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 of Pt₃MN nanoparticles with highly active Pt-skin morphology is being further established.
- Ternary core-interlayer/shell systems operate through the same mode of action of improving the catalytic properties and durability as core/shell particles.
- Nanoframes with 3-D network of electrocatalytically active surface possess superior specific, mass activities with outstanding durability.
- Future effort will be dedicated to the scale up synthesis of the nanoframes and MEA evaluation.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. S. Guo, D.Li, H.Zhu, S.Zhang, N.M.Markovic, V.R.Stamenkovic, S.Sun *FePt and CoPt Nanowires as Efficient Catalysts for the Oxygen Reduction Reaction* Angewandte Chemie International Edition, 52(2013)3465.
2. C.Chen, Y.Kang, Ziyang Huo, Zhongwei Zhu, Wenyu Huang, Huolin L. Xin, Joshua D. Snyder, Dongguo Li, Jeffrey A. Herron, Manos Mavrikakis, Miaofang Chi, Karren L. More, Yadong Li, N.M.Markovic, G.Somorjai, Peidong Yang, V.R.Stamenkovic *Highly Crystalline Multimetallic Nanoframes with Three-Dimensional Electrocatalytic Surfaces* Science, 343(2014)1339.
3. D. Strmcnik, N. Markovic and V. Stamenkovic *Advanced Electrocatalysts* Fourth Regional ISE Symposium on Electrochemistry, May 2013, Ljubljana, Slovenia.
4. Y. Kang, D. Li, N.M.Markovic and V. Stamenkovic *Exploiting high activity and durability by tuning nanostructure for electrocatalytic applications* 245th American Chemical Society Spring Meeting, April 2013, New Orleans, LA.
5. C. Wang, N. Markovic and V. Stamenkovic *Design and Synthesis of Advanced Electrocatalysts* 246th American Chemical Society National Meeting, September 2013, Indianapolis, IN.
6. Yijin Kang, Dongguo Li, Nenad M. Markovic and V. Stamenkovic *Design of Highly Active and Durable Electrocatalysts by Tuning Nanostructure* 224th Electrochemical Society Meeting, October 2013, San Francisco, CA.
7. Joshua Snyder, Yijin Kang, Dongguo Li, Nenad M. Markovic and V. Stamenkovic *Mesostructured Multimetallic Thin Films as Electrocatalysts for Fuel Cells* 224th Electrochemical Society Meeting, October 2013, San Francisco, CA.
8. Joshua Snyder, Yijin Kang, Dongguo Li, Nenad M. Markovic and V. Stamenkovic *Advanced Electrocatalysts for Fuel Cells* 225th Electrochemical Society Meeting, May 2014, Orlando, FL.

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