

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

Nenad M. Markovic (Primary Contact) and
Vojislav R. Stamenkovic
Argonne National Laboratory
Argonne, IL 60439
Phone: (630) 252-5181
Email: nmmarkovic@anl.gov; vrstamenkovic@anl.gov

DOE Manager
Nancy Garland
Phone: (202) 586-5673
Email: Nancy.Garland@ee.doe.gov

Contributors:

- Karren More, Oak Ridge National Laboratory
- Shuoheng Sun, Brown University, Rhode Island
- Guofeng Wang, University of Pittsburgh
- Charles Hays, Jet Propulsion Laboratory
- Radoslav Atanasoski, 3M Company

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Overall 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-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 nanoparticles in rotating disk electrodes 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) 2013 Objectives

- Optimization of synthesis methods to produce larger volumes of catalysts in a single batch.
- Evaluation of the existing protocols for surfactant removal after colloidal synthesis.
- Synthesis and characterization of the PtM₁N₂ ternary alloy nanoparticles with controlled particle size and elemental distribution.
- Evaluation of the nanosegregated compositional profile in ternary systems.
- Utilization of highly crystalline practical catalysts in the form of nanowires and thin metal films.
- Design and synthesis of multimetallic nanowires with controlled length, width, and composition.
- Utilization of highly crystalline thin metal films as practical catalysts.
- Evaluation of catalyst properties in 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
- (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 (NM = 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 at 0.9 V _{iR-free} : 720 mA/cm ²	PGM total content: 0.2 g/kW
Mass activity at 0.9 V: 0.44 A/mg _{Pt}	Total loading: 0.2 mg/cm ²
Catalyst support loss: <30%	Durability w/cycling (80°C): 5,000 hrs

PGM – precious-grade metal

FY 2013 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 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 ML) that are mimicking stability/activity of thin metal film systems.
- In MEAs, for PtNi/C multilayered skin confirmed: (i) three times higher specific activity (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 20K cycles activity, surface area loss was only 12% compared to ~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 MEAs on PtNi multilayered skin catalysts, which revealed that catalyst did not suffer structural/composition changes after 20K 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 Pt₃M₁N₂ 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 Pt₃MN nanoparticles.

- Synthesis and characterization of the core/shell Au/CoPt₃ nanoparticles
- Demonstrated that ternary alloys could provide additional activity gain vs. binaries (4-fold vs. Pt-poly).
- Established procedure for efficient removal of surfactants after colloidal synthesis.
- Developed synthetic routes and characterized monodisperse, highly homogeneous multimetallic nanoparticles with inner gold shell.
- Developed synthetic routes and characterized highly homogeneous multimetallic nanowires.
- Developed annealing protocols for multimetallic nanowires with Pt-skin surfaces.
- Developed thin-film-based mesoscale electrocatalysts with tunable composition and surface structure.
- Mesoscale thin-film-based materials achieved the highest specific activity for the oxygen reduction reaction (ORR) ever measured for practical electrocatalysts.



INTRODUCTION

In the quest to make the polymer electrolyte membrane 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 a progress for FY 2013 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]. 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 Hydrogen and Fuel Cells Program we rely on our materials-by-design approach [1-9]. 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

Surfactant Removal from Nanoparticles Prepared by Solvo-Thermal Synthesis

During the solvo-thermal synthesis, Pt and Pt-alloy surfaces of nanoparticles have been covered by surfactant molecules, oleylamine and oleic acid. If not removed, these molecules can tremendously affect catalytic properties by blocking active sites for adsorption of reactants. Pt and Pt-alloy nanoparticles were subject to different treatments in order to evaluate their efficiency in removing the surfactant molecules that are strongly attached to the Pt surface atoms. The surface cleanliness of differently treated particles was characterized by thermogravimetric analysis, infrared absorption spectroscopy and cyclic voltammetry. Obtained results revealed that thermal annealing is the most effective method to clean the surface of the Pt-based nanoparticles. In addition, these findings provide a direct correlation between the surface cleanliness and functional properties of differently treated Pt nanoparticles, and point out the importance of efficient surfactant removal in catalytic applications. Figure 1a displays transmission electron microscope (TEM) images of as-synthesized Pt nanoparticles with surfactant molecules, in which the average particle size is around 3 nm. Figure 1b and 1c illustrate that after the nanoparticles were loaded on a high surface area carbon support and subsequently annealed at 185°C, no significant change of particle size and/or shape was observed. Other surfactant removal treatments of Pt nanoparticles with carbon were detailed in a full article ACS Catalysis, 2(2012)1358. Briefly, the results display the order of activity as: annealed > HAC > UV-O₃ > untreated > TMAOH. Based on the shape of cyclic voltammograms and the ORR current densities, thermal annealing method is established to be the most effective approach in cleaning the surface of the catalysts.

Highly Homogeneous and Efficient Ternary Alloy Nanoparticles

In order to approach multimetallic electrocatalysts at nanoscale and to have surface chemistry under control [8], it is of paramount importance to have highly homogeneous distribution of constituents among the entire volume of a single nanoparticle. Our focus in the previous report has been on Pt-skin formation over ternary alloys by annealing treatment only. Here, we proceed towards monodisperse nanoparticles with homogeneous elemental distribution and hence surface chemistry that can lead to formation of multilayered Pt-skin surfaces. Our solvo-thermal approach was used to obtain nanoparticles that went through a mild annealing treatment in order to remove surfactants. Figure 2 summarizes structural and electrochemical characterizations of ternary alloy nanoparticles. TEM images in Figure 2 confirm that nanoparticles are monodisperse particles with an average particle size of ~6 nm, which is close to the optimal

size for Pt-alloy catalysts established before [5]. Distribution of elements in the ternary nanoparticles was mapped by energy dispersive X-rays based on high angle annular dark field–scanning transmission electron microscopy. Figures 2b-e show overlapped and separate maps of the elements in a typical Pt₃(CoNi)₁ particle. It is obvious that all of the constituents, Pt, Co and Ni, are uniformly distributed across the particle, and well intermixed in the overlapping map (Figure 2b). The observations here are consistent with our recent findings on Pt-bimetallic nanoparticles prepared by similar approach [9], confirming the highly homogeneous nature of the ternary alloy nanoparticles obtained by organic solution synthesis. Previously established protocol for thermal treatment was applied to remove the surfactants and induce beneficial surface segregation for best catalytic performance. TEM images in Figures 2f and 2g show that no significant size or morphology change happened after these treatments. A catalyst suspension was prepared by sonication of the catalyst in deionized water, and a drop of that suspension was deposited on a polished glassy carbon disk (6 mm in diameter) electrode. The content of Pt in the catalyst was adjusted to ~25%, and the loading of Pt on the glassy carbon electrode was ~12 μg/cm²_{disk}. Figures 2 h, i, and j summarizes electrochemical results for the Pt₃(CoNi)₁ nanocatalysts and commercial Pt/carbon of a similar size (6 nm, Tanaka), that was used as a reference. The measured cyclic voltammograms (CVs) have H_{upd} peaks at E < 0.4 V and Pt oxidation/reduction peaks at 0.8 ~ 0.9 V. The onset of Pt-OH_{ad} on the ternary catalyst shifted positively for >25 mV vs. Pt/C (Figure 2h), confirming altered electronic structures and surface adsorption properties of ternary alloy nanoparticles. Consequently, corresponding polarization curves exhibit similar shifts in half-wave potentials, and show substantially enhanced catalytic activities (Figure 2j). At 0.95 V, the as-prepared and annealed Pt₃(CoNi)₁/C catalysts have achieved improvement factors of 2.3 and 4.2 in specific activity versus Pt/C, with the annealed catalyst reaching 0.55 mA/cm² (versus 0.13 mA/cm² for Pt/C). The level of catalytic activity improvement is consistent with the trend established on extended thin-film surfaces reported previously. Similar improvement factors were also present in mass activity, with the annealed Pt₃(CoNi)₁/C achieving 183 A/g in comparison to 49 A/g for Pt/C.

Mesostructured Thin Films as Electrocatalysts

We developed a new class of catalysts based on mesostructured multimetallic thin films with adjustable structure and composition, which have been tailored to emulate the distinctive properties of the Pt(111)-skin. We aimed towards materials that can bridge the world of extended surfaces with superior activity and nanoscale systems with high utilization of precious metals. Such synergy is present at the mesoscale, which does not only imply a specific length scale, but also a principle of operating “in between” different physical regimes that exhibit

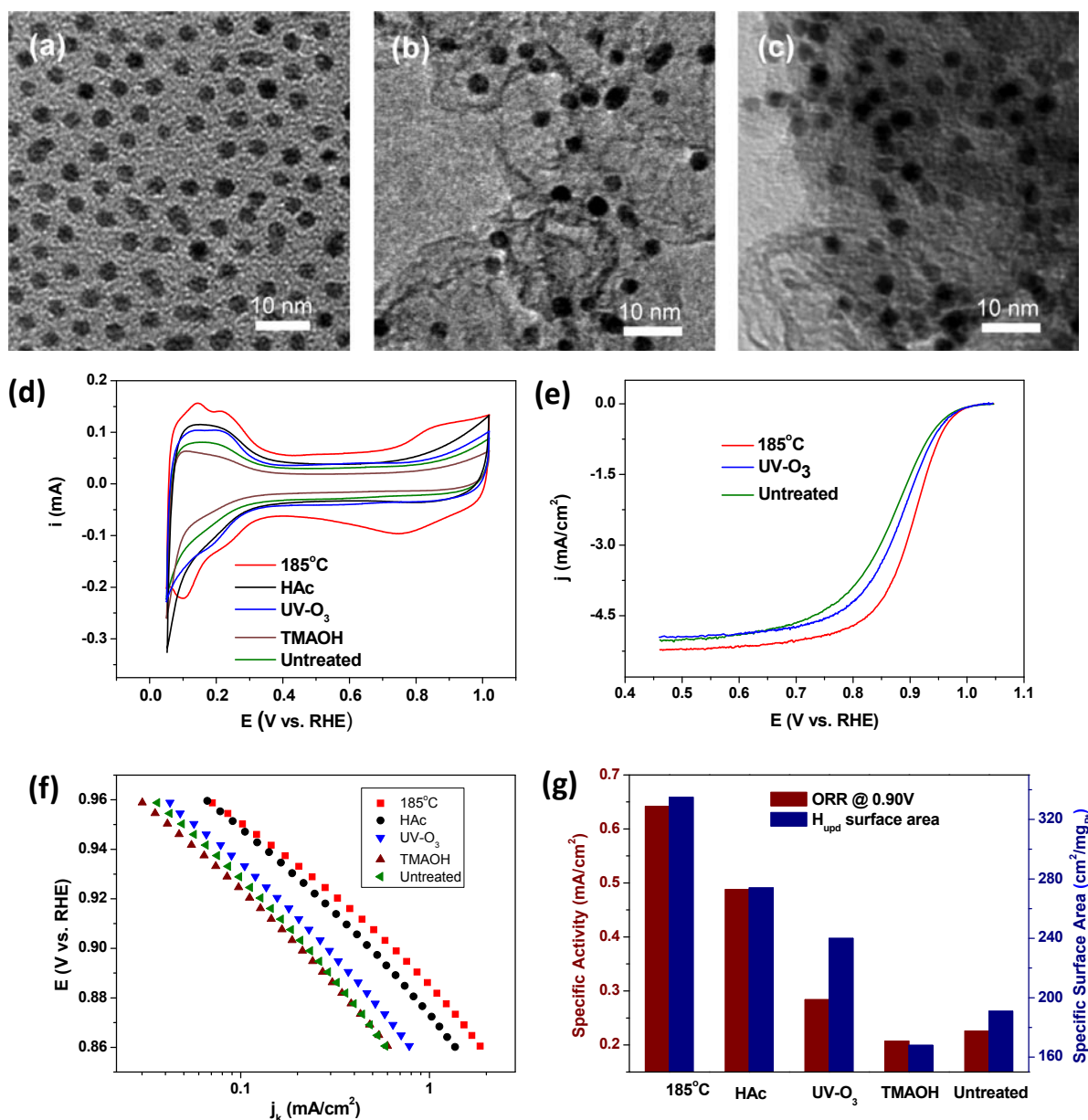


FIGURE 1. TEM images of (a) as-synthesized Pt nanoparticles, (b) Pt nanoparticles loaded on carbon black after annealing, (c) Pt nanoparticles on carbon black after UV-O₃ treatment, (d) cyclic voltammograms of Pt/C after different treatments with respect to the untreated sample, (e) ORR polarization curves of annealed, ultraviolet ozone treated versus untreated sample, (f) Tafel plots of Pt/C at 20 mVs⁻¹, 1,600 rpm, 20°C, and (g) specific activity at 0.90 V and specific surface area.

distinct functional behavior. Continuous Pt and Pt-alloy nanostructured thin films (NSTF) [9] were deposited by planar magnetron sputter deposition. It is well known that NSTF catalysts provide good surface area utilization and eliminate issues related to carbon support corrosion and contact resistance at the carbon-metal interface that lead to poor utilization and degradation of the catalyst. Ability to control the deposition rate, as well as the combination and order of constituents, established sputter deposition as an effective tool to form thin films with desirable thickness, composition profile and surface roughness. However, the

surface structure of a thin film, an important catalytic parameter, cannot be altered by this method to match those established on single crystalline systems. For that reason, we attempted a thorough examination of thin film properties on extended, flat, non-crystalline and chemically-inert substrates such as a mirror polished glassy carbon surface. This approach brings an additional level of control in terms of defined geometric surface area and surface roughness factor that is unattainable in the case of nanoscale substrates. Consequently, our efforts have been directed toward exploring structural transitions in polycrystalline thin films,

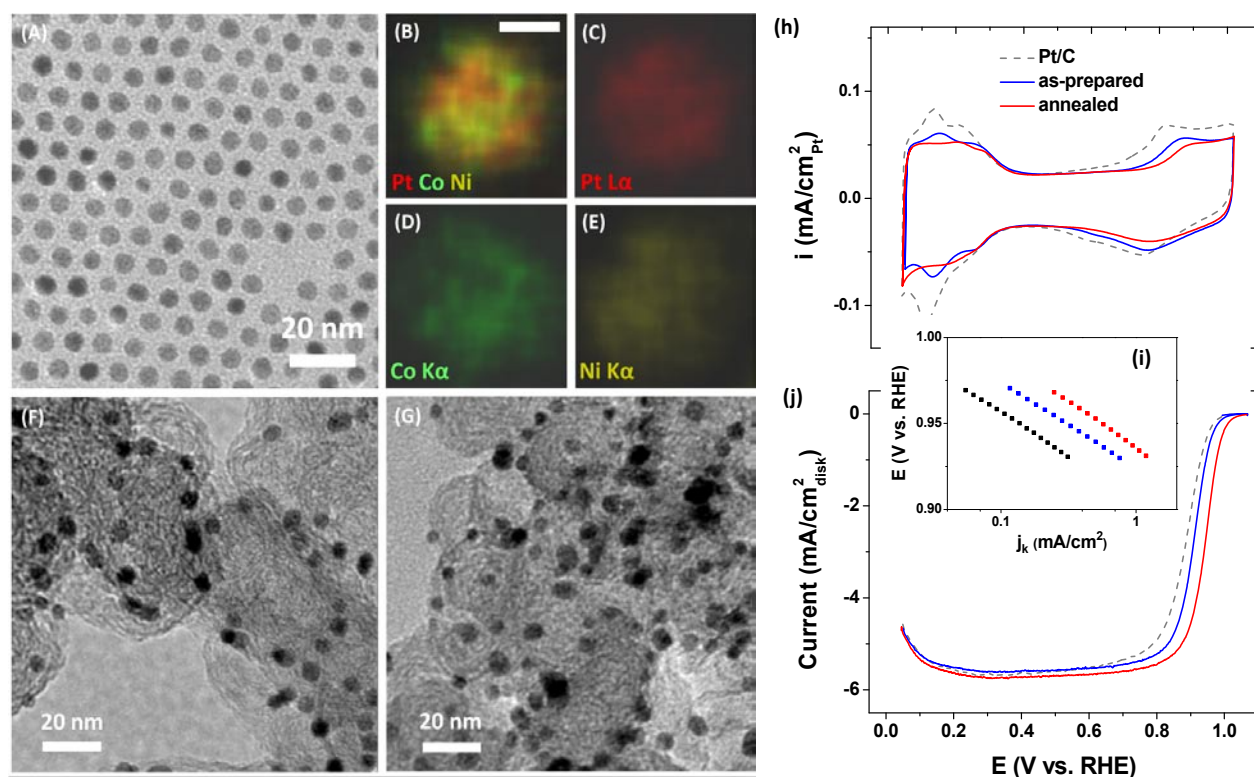


FIGURE 2. TEM image of (a) as-synthesized $\text{Pt}_3(\text{CoNi})_1$ alloy nanoparticles; (b-e) representative elemental maps from energy dispersive X-ray spectroscopy analysis based on scanning transmission electron microscopy for (b) overlapping of Pt, Co and Ni, (c) Pt, (d) Co, and (e) Ni; the scale bar in (b) is equal to 2 nm and it also applies for (c) – (e); (f) and (g) show TEM images of the ternary catalyst before (f) and after (g) surfactant removal and thermal treatment; (h) CVs recorded at 50 mV/s in Ar saturated 0.1 M HClO_4 ; (i) Tafel plots of the kinetic current densities depending on electrode potentials; (j) polarization curves for the ORR with iR drop correction recorded in O_2 saturated 0.1 M HClO_4 .

and we found that as-deposited Pt film with corrugated nanostructured three-dimensional surface morphology has been transformed into a smooth two-dimensional surface with large 20×100 nm (111) facets. The characteristic surface features are confirmed by both scanning tunneling microscopy and electrochemical cyclic voltammetry to be predominantly (111) facets encompassing the entire surface. The synergy between the surface structure, domain size, and functionality defines that the thin-film surface has a distinct mesostructured morphology. These findings clearly demonstrate the feasibility of controlling surface ordering of extended Pt thin films deposited over a non-crystalline substrate, i.e., without use of templates for epitaxial growth. Instead of building the crystal lattice from a seed or underlying crystalline substrate, individual randomly oriented nanoscale grains coalesce and form large well-ordered (111) facets. All of that greatly expands the potential for utilization of thin-film materials and introduces thermal annealing in a controlled atmosphere as a compelling tool in the fine tuning of a thin film's structure and hence electrocatalytic properties. Figure 3 depicts this thermodynamically driven transition that releases stress and strain of the as-deposited thin film and leads towards the state with minimum surface energy without compromising

the overall shape and dimension of the whisker. Similar to Pt thin films on glassy carbon, the initial nanostructured surface morphology that originated from the closely bonded whiskerettes' tips is transformed into a smooth continuous film with large crystalline domains (20–40 nm). Specifically, randomly oriented nanoscale grains coalesce and give rise to a mesostructured thin film with unique physiochemical properties, therefore, the materials after this treatment will be referred to as mesostructured thin films (MSTF). Close inspection of high-resolution TEM micrographs after applied thermal treatment confirms that emerged facets with (111) structure prevail on the surface while under-coordinated sites are diminished, which also has important implications towards improved stability. Figure 3 also summarizes the electrochemical signature and compares adsorption and catalytic properties between different classes of thin-film materials and state-of-the-art Pt/C by rotating disk electrode. From CV it is obvious that the onset of surface oxide formation is shifted positively in the following order: Pt-NSTF < PtNi-NSTF < PtNi Meso-TF and consequently, the ORR polarization curves, follow the same trend in activity. Figures 3d and 3f summarize kinetic current densities (specific activities per electrochemically active surface area of Pt) as Tafel plots and a bar graph. Usually we report values

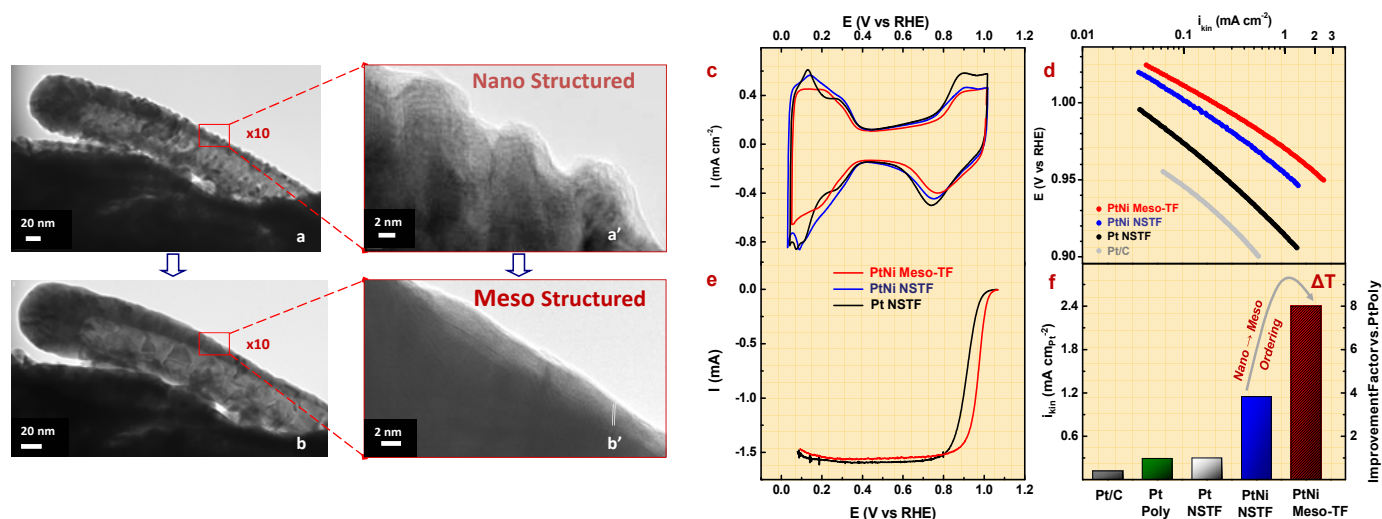


FIGURE 3. In situ TEM transition from nanostructured into mesostructured thin film: (a)–(b) annealing between room temperature and 400°C on a single whisker that induce the ordering from randomly oriented to a homogeneous structure with crystalline domains; cyclic voltammetry on the thin-film-based catalysts: (c) Pt-NSTF, PtNi-NSTF and PtNi-MSTF; (e) the ORR polarization curves; (d) Tafel plots and (f) specific activities at 0.95 V and improvement factor versus Pt-Poly (and Pt-NSTF).

measured at 0.95 V to avoid diffusion-induced errors in kinetic current densities. The activity of PtNi MSTF exhibits an improvement factor of over 8 versus Pt-poly and Pt-NSTF, and when compared to the conventional Pt/C catalyst, the specific activity of the PtNi MSTF has 20-fold improvement. Even though optimal film thickness, alloy composition and total Pt loading will be extensively studied in the future, the measured improvement expressed in A/mg_{Pt} corresponds to a mass activity that is already three times higher than the DOE technical target. The CV curves, trend in specific activity, low Tafel slope, and the structural characterizations strongly suggest that the annealed PtNi Meso-TF has a nanosegregated Pt(111)-skin type of near-surface structure. The developed approach will be applied to generate a wide range of electrocatalysts with tailored structure/composition, ultra-low precious metal content as well as high activity and durability.

CONCLUSIONS AND FUTURE DIRECTIONS

- PtM and $Pt_3M_1N_2$ 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 Pt_3MN nanoparticles with highly active Pt-skin morphology is established.
- Specific and mass activity improvements are obtained for Pt-skin Pt_3MN/C nanoparticles in rotating disk electrode measurements. Advanced theoretical modeling 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 was not changed after 20K cycles.
- Future effort will be dedicated to the scale up synthesis of the most promising catalysts and MEA evaluation.
- Further decrease of the non-precious metal content will be pursued for different classes of catalysts based on thin films, nanowires and nanoparticles.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. D. Li, C. Wang, D. Tripkovic, S. Sun, N.M. Markovic, V.R. Stamenkovic *Surfactant Removal from Nanoparticles Prepared by Solvo Thermal Colloidal Synthesis* **ACS Catalysis**, **2(2012)1358**.
2. C. Wang, N.M. Markovic and V.R. Stamenkovic *Advanced Platinum Alloy Electrocatalysts for the Oxygen Reduction Reaction* **ACS Catalysis**, **2(2012)891**.
3. C. Wang, D. Li, M. Chi, J. Pearson, R.B. Rankin, J. Greeley, Z. Duan, G. Wang, D. van der Vliet, K.L. More, N.M. Markovic, V.R. Stamenkovic *Rational Development of Ternary Electrocatalysts* **Journal of Physical Chemistry Letters**, **3(2012)1668**.
4. D. van der Vliet, C. Wang, D. Tripkovic, D. Strmenik, X.F. Zhang, M.K. Debe, R.T. Atanasoski, N.M. Markovic, V.R. Stamenkovic *Mesostructured Thin Films as Electrocatalysts with Tunable Composition and Surface Morphology* **Nature Materials**, **11(2012)1051**.

5. C. Wang, D. Strmcnik, D. van der Vliet, N. Markovic, V. Stamenkovic *Materials for Energy Conversion at Solid-Liquid Interfaces* **2012 Materials Research Society Spring Meeting, April 2012, San Francisco, CA.**
6. D. van der Vliet, C. Wang, D. Li, N. Markovic, V. Stamenkovic *Towards Nano-engineered Pt-Skin High Surface Area Catalysts* **221th Int. Meeting of the Electrochemical Society, May 2012, Seattle, WA.**
7. D. van der Vliet, C. Wang, D. Li, N. Markovic, V. Stamenkovic *The Effect of Annealing on the Electrocatalytic Properties of Multimetallic Platinum Alloy Catalysts* **221th Int. Meeting of the Electrochemical Society, May 2012, Seattle, WA.**
8. C. Wang, D. van der Vliet, D. Tripkovic, D. Strmcnik, N. Markovic, V. Stamenkovic *Synthesis of Nanocatalysts with Tailored Structures* **244th American Chemical Society National Meeting, August 2012, Philadelphia, PA.**
9. C. Wang, D. van der Vliet, D. Tripkovic, D. Strmcnik, D. Li, N. Markovic, V. Stamenkovic *Advanced Electrocatalysts for PEM Fuel Cells* **222th Electrochemical Society Meeting, October 2012, Honolulu, HI.**

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