

V.A.2 Nanosegregated Cathode Alloy Catalysts with Ultra-Low Platinum Loading

Vojislav R. Stamenkovic (Primary Contact) and
Nenad M. Markovic

Argonne National Laboratory
Argonne, IL 60439
Phone: (630) 252-8946
Email: vrstamenkovic@anl.gov

DOE Manager

Nancy Garland
Phone: 202-586-5673
Email: Nancy.Garland@ee.doe.gov

Subcontractors

- Karren More, Oak Ridge National Laboratory, Oak Ridge, TN
- Deborah Myers, Argonne National Laboratory, Argonne, IL

Project Start Date: September 2009

Project End Date: September 2015

Overall Objectives

- Establish the parameters that control kinetics of the oxygen reduction reaction on multimetallic PtM (M = Co, Ni, Fe, and Ti) and PtM₁N₂ (M₁ = Co/Ni; N₂ = TM) alloys
- Develop highly efficient, durable, nanosegregated Pt-skin PtM and PtM₁N₂ catalysts with ultra-low Pt content
- Develop highly active and durable Au/PtM₃ nanoparticles (NPs) with ultra-low Pt content
- Find relationships between activity/stability of well characterized bulk alloys and NPs
- Develop novel chemical and physical methods for synthesis of monodispersed PtM and PtM₁N₂ alloy NPs 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 NPs in rotating disk electrodes (RDEs) and membrane electrode assemblies (MEAs)
- Use computational tools as the basis to form any predictive ability in making binary and ternary systems with desirable reactivity and durability properties

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

Fiscal Year (FY) 2015 Objectives

- Development of synthesis routes to produce larger volumes of catalysts in a single batch
- Synthesis and characterization of the most active and durable Pt-alloy NPs with controlled size, compositional profile, and Pt-skin surface
- Electrochemical characterization of the nanosegregated catalysts by RDE
- Reproducibility of performance for large scale batches of highly active catalysts
- Integration of highly active catalyst into MEA, fabrication and characterization

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.5) of the Fuel Cell Technologies Office (FCTO) Multi-Year Research, Development, and Demonstration Plan of 2012:

- Durability
- Cost
- Performance

Technical Targets

This project is conducting research related to Pt-based binary PtM (M= Ni, Co, Fe, Cr, V, and Ti), ternary PtM₁N₂ (NM = Fe, Co, and/or Ni) and core/shell Au/Pt₃M multimetallic NPs for the oxygen reduction reaction. The design and synthesis of highly efficient, durable, nanosegregated Pt-skin catalysts with ultra-low Pt content are targeted to meet or exceed the DOE 2015 targets shown in Table 1.

TABLE 1. Progress towards Meeting DOE 2015 Technical Targets for Electrocatalysts

	Unit	2015 DOE Targets	Project Status
PGM Total Loading	mg _{PGM} /cm ²	0.200	0.035
Mass Activity	A/mg _{Pt} @ 900 mV	0.44	0.76
Specific Activity	μA/cm ² _{Pt} @ 900 mV	720	2,600

PGM – precious group metal

FY 2015 Accomplishments

- Synthesized novel bi/multi-metallic NPs with controlled size and composition by colloidal organic solvothermal approach
- Increased the amount of a single batch for synthesis of highly active nanoframe catalyst from 5 mg to 30 mg per batch
- Established a relationship between the mass of single batch and performance
- Established structure–composition–function relationship for a novel class of core/interlayer/bimetallic shell NPs
- Optimized the thickness of the subsurface Au-interlayer in the Ni-core/Au-interlayer/NiPt-shell NPs for the maximal catalytic activity, superior durability, and minimal loading of PGMs
- Verified 20,000 cycle activity/durability performance for core-interlayer/shell NPs
- Employed nanoframe catalyst in MEA
- Established structural properties of nanoframes in MEA before and after testing
- Established compositional properties of nanoframes in MEA before and after testing
- Evaluated catalyst/ionomer ratio for nanoframe particles in MEA suspension
- Established oxygen reduction reaction (ORR) performance for nanoframes by RDE and MEA for the ORR
- Implemented ionic-liquid approach into the nanoframe catalyst and performed detailed structural and electrochemical evaluations by high resolution transmission electron microscopy (HR-TEM) and MEA
- Achieved three-fold improvement in specific activity and two-fold improvement in mass activity vs. 2015 DOE technical targets for PtNi nanoframe catalyst in MEA



INTRODUCTION

In the quest to make the polymer electrolyte membrane fuel cells a competitive force, one of the major challenges is to reduce the significant overpotential for the ORR and minimize dissolution of the cathode catalysts. Here, we report progress for FY 2015 in experimental studies to address the importance of alloying Pt with 3d metals 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, which make them capable to address DOE technical targets for application of fuel cells in transportation.

APPROACH

In order to address the challenges that are listed as the DOE targets for FCTO, we rely on our materials-by-design approach [1-11]. This approach involves five major steps: (i) advanced chemical and physical methods for synthesis of novel nano/mesoscale materials, which enables control of material 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; (iv) synthesis/fabrication (scale-up) of the highly efficient practical catalysts, which are guided by the fundamental understanding of structure-function relationships; and (v) electrochemical evaluation of catalyst properties by RDE and MEA.

RESULTS

Non-PGM Core/Au-Interlayer/with Pt-Based Overlayers

These unique nanostructures were introduced last year through a synthesis that produced an intentional concentration profile that warrants catalytic performance of Pt-bimetallic alloys with substantially improved durability due to presence of subsurface Au atoms. The initial step in synthesis was to produce monodisperse Ni particles with narrow size distribution of 3.1 nm ($\sigma < 5\%$) Ni NPs and to coat them with optimized quantity of Au, forming an intermediate Ni@Au core/shell nanostructure. The final step in chemical synthesis was to deposit a desirably thick PtNi shell of approximately 1 nm. Ni@Au@PtNi nanoparticles with a diameter of 5.0 nm ($\sigma = 6\%$) were formed and characterized to confirm compositional profile and reveal electrochemical properties. The scanning transmission electron microscopy analysis showed that after exposure to 0.1 M HClO₄ electrolyte, the core/shell structure and the Ni core are preserved, while the line-scan of energy dispersive X-ray spectroscopy depicts the formation of the Pt-skeleton surface due to dissolution of surface Ni atoms that are present on the as-prepared NP surfaces. Electrochemical evaluation after 10,000 potential cycles between 0.6 V and 1.1 V vs. reference hydrogen electrode (RHE) showed a negligible loss in activity of the NPs with core/interlayer/shell structures (Figure 1). Our initial report on the role of subsurface Au explained that placement of Au atoms with higher redox potential in the near-surface region lowers the probability for both Ni and Pt dissolution through the hindered place-

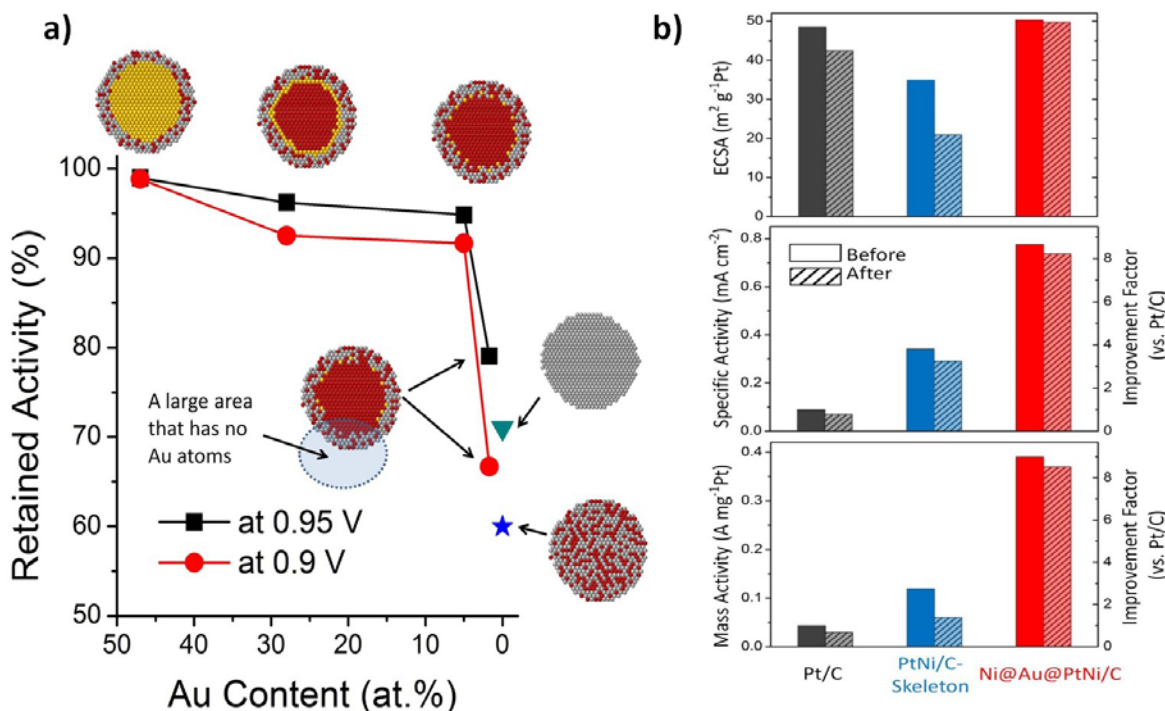


FIGURE 1. Core/interlayer/shell NPs. a) Retained activity after 10,000 potential cycles between 0.6 V and 1.1 V for NPs with different content of Au. b) Electrochemical evaluations by RDE of Ni@Au@NiPt/C, PtNi/C, and Pt/C before and after potential cycling.

exchange mechanism. Moreover, we found that minimal amount of subsurface Au could be around 5 at%, which is close to 0.25 ML, in order to induce high durability in designated potential region. The specific and mass activity enhancement of Ni@Au@PtNi/C is over eight-fold versus the Pt/C and outperforms multilayered Pt-skin PtNi/C [8] due to the replacement of expensive Pt by Ni in the core. Structural characterization of Pt/C, PtNi-Skeleton/C, and Ni@Au@PtNi/C nanoparticles before and after 10,000 cycles revealed that the size of Pt and PtNi NP was significantly changed, while the size and shape of Ni@Au@PtNi was not affected, demonstrating high durability of this system.

In the most recent period, we extended our focus on the possibility to further enhance catalytic activity by achieving a favorable nanosegregated subsurface concentration profile with Pt-skin as the topmost surface layer. Our initial attempts to induce Pt-skin formation by thermal annealing were spoiled due to the strong tendency of Au to segregate over Pt in a given multimetallic system. For that reason, we have changed the strategy by introducing another component in the system that might prevent Au from migrating to the surface. Initial results obtained with sputtered thin films are shown in Figure 2, which illustrates the effect of thermal annealing and confirms feasibility of Pt-skin formation over PtNi shell for the systems that contain subsurface Au. Such fine tuning of the near surface composition profile allows

synergy between maximal utilization of precious metals and maximal catalytic and durability performance.

Synthesis Scale-up of the PtNi Nanoframe Catalyst

Nanoframe Pt_3Ni catalyst exhibits 16-fold improvement in specific activity for the ORR at 0.95 V vs. commercial Pt/C electrocatalyst. The open architecture of the Pt_3Ni nanoframes enables access of reactants to both the internal and external surfaces and leads to 22-fold enhancement in the mass activity vs. Pt/C in RDE measurements. The mass activity at 0.9 V was measured to be $5.7 \text{ A mg}^{-1} \text{ Pt}$ and is over one order of magnitude higher than $0.44 \text{ A mg}^{-1} \text{ Pt}$, the DOE 2017 target, which makes the Pt_3Ni nanoframes the most efficient electrocatalyst for the ORR [12]. In addition, nanoframes exhibited remarkable durability due to the nanosegregated composition profile that has at least two atomic layer thick Pt surface. Our initial synthesis effort was focused to produce quantities that would be sufficient for RDE evaluations, which was in the order of 5 mg of catalyst per single batch. Considering that MEA evaluation was our main target, we have optimized synthesis protocol to produce higher amounts of nanoframes. Figure 3 displays the outcome of our efforts expressed as performance measured for different batch quantities over a wide time frame. As of now, we managed to establish a synthesis protocol that yields about 30 mg of catalyst with performances that match the lower quantities reported last year. From Figure 3, it is

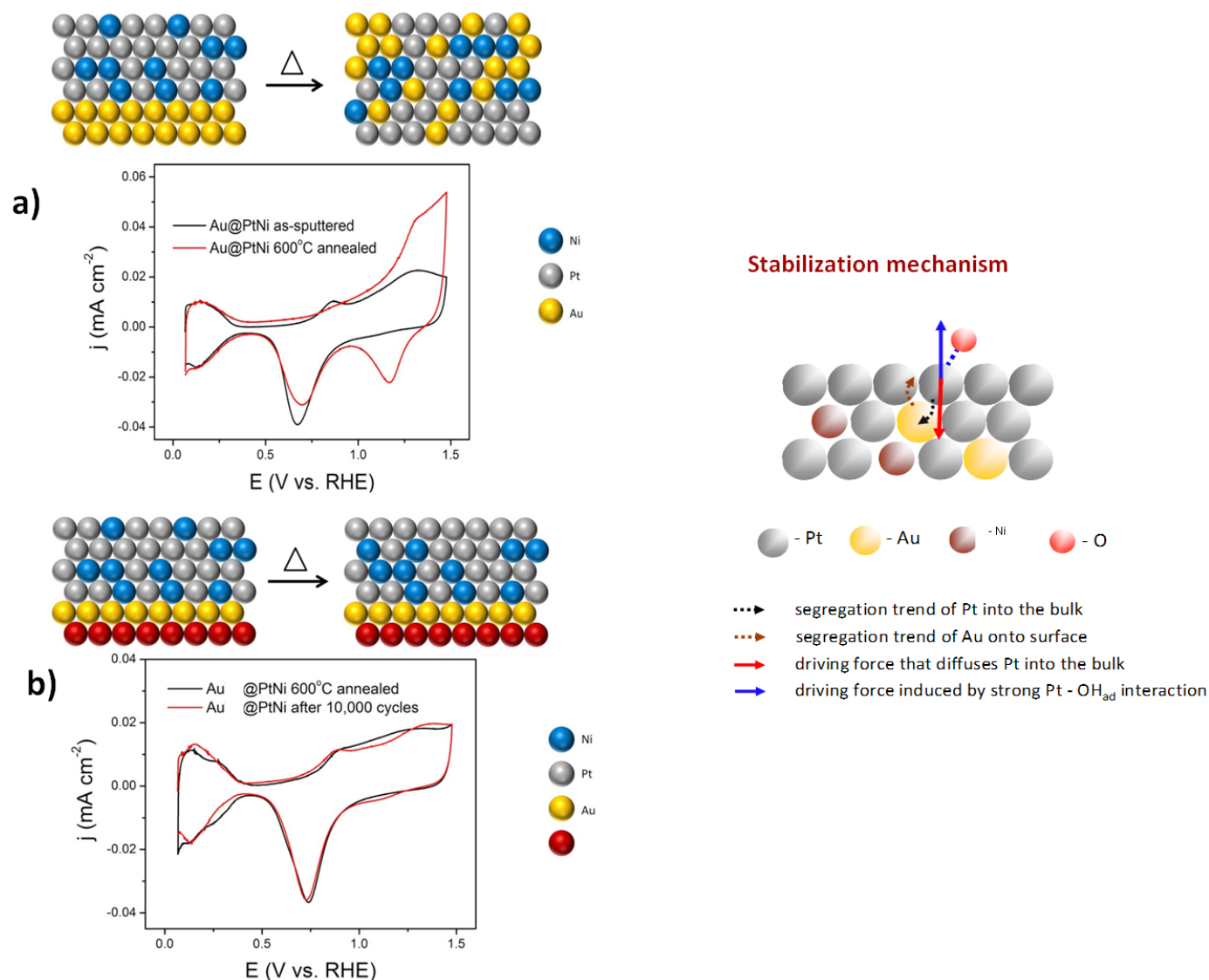


FIGURE 2. RDE characterization of sputtered thin films with distinct segregation profiles. a) Typical cyclic voltammetry after thermal annealing that shows redox Au peaks confirming the existence of surface Au atoms that lowers the number of Pt active sites atoms and specific activity for the ORR. b) Altered core composition prevents segregation of Au atoms after thermal annealing and allows Pt-skin formation with superior specific activity.

apparent that higher amounts of catalyst produced under laboratory conditions did coincide with the same structural, and hence catalytic, properties. For that reason we optimized the synthesis protocol for amounts lower than 30 mg of catalyst per single batch.

MEA Evaluation of PtNi Nanoframe Catalyst

A number of nanoframe catalyst evaluations were carried out in 5 cm² MEAs. The results for the best performing MEAs are shown in Figure 4, and they are compared to an MEA with a commercial Tanaka Kikinokogyo (TKK) 20 wt% Pt/C catalyst on the cathode. The same loading of the catalyst was applied for the results shown below. The MEAs were fabricated by the decal method with the ionomer

and membrane in the proton form and hot-pressing of the decals to the membrane at 130°C. The ionomer to carbon ratio was set to 0.8, and it is important to emphasize that the ionomer was found to be detrimental to the activity of this catalyst in RDE testing. Below is the summary of the MEA characteristics.

- Cathode: PtNi nanoframe, 0.0346 mg-Pt/cm²
- Cathode electrochemically active surface area (ECSA): 49 cm² H_{upd}
- Cathode ionomer to carbon ratio: 0.8
- Anode: 0.2 mg-Pt/cm² TKK 46 wt% Pt/HSC
- Nafion[®] XL membrane

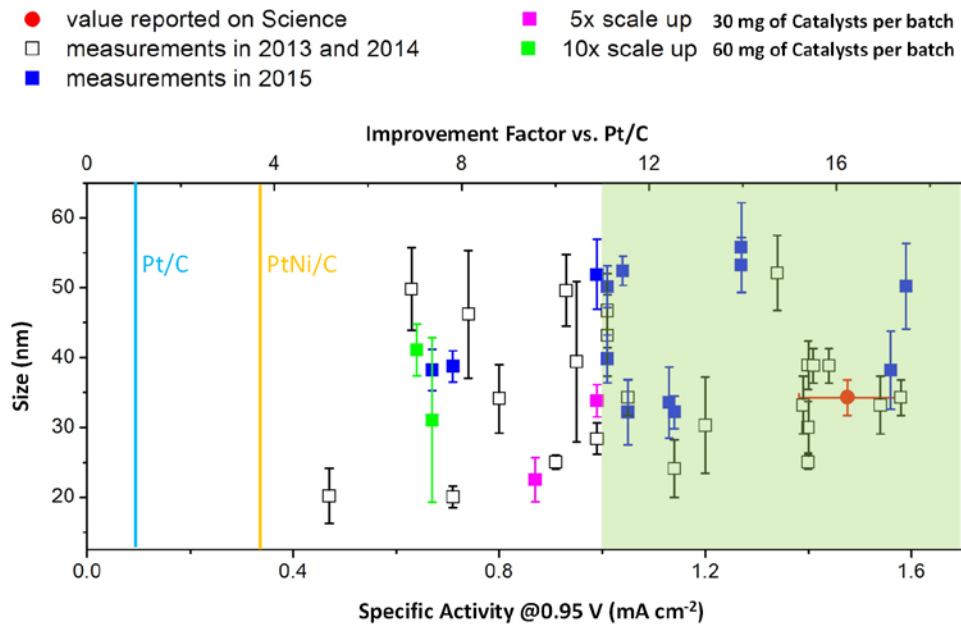
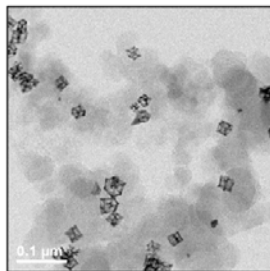
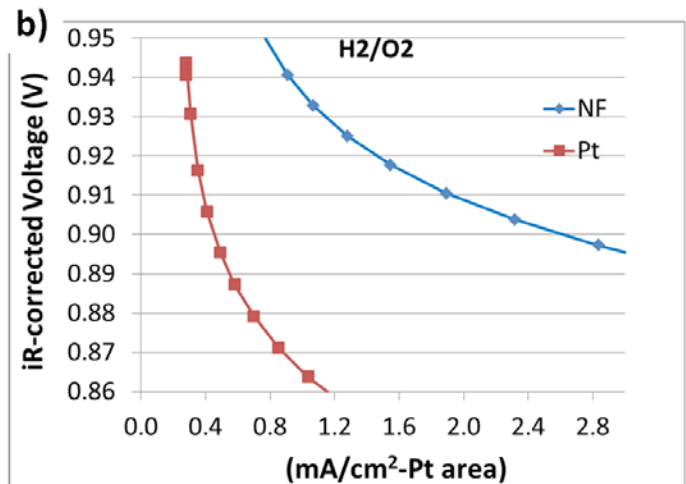
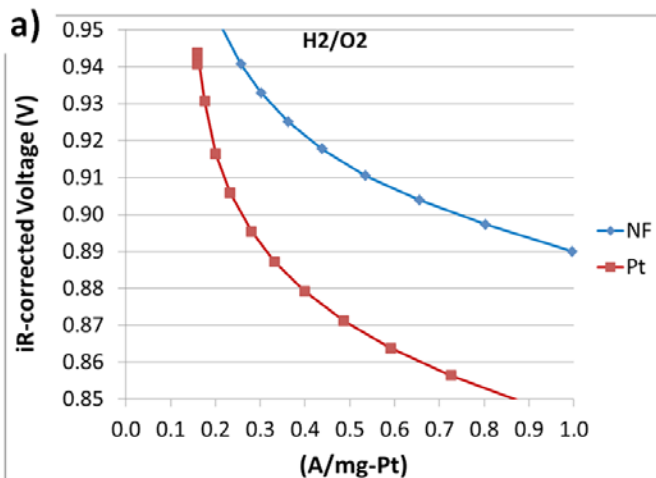
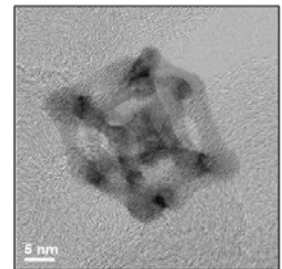


FIGURE 3. Scale-up synthesis of Pt₃Ni nanoframes: variation in performance of Pt₃Ni nanoframe catalyst for different batches of catalysts.



Cathode Loading: 0.035 mg-Pt/cm², I/C = 0.8
 H₂/O₂, 80°C, 150 kPa(abs), 100%RH

ORR Activity @ 0.9V: **Mass Activity x3.5** **Specific Activity x6.5**
 TKK 20 wt%Pt/C: 0.22 A/mg-Pt 0.39 mA/cm²-Pt
 PtNi Nanoframes: 0.76 A/mg-Pt 2.60 mA/cm²-Pt



RH – relative humidity

FIGURE 4. MEA evaluation of Pt₃Ni nanoframe catalyst: hydrogen-oxygen polarization curves from 5 cm² MEA obtained for PtNi nanoframes and Pt/C TKK catalysts. Note that the Pt loading is approximately three times lower than the DOE technical target yet the performance surpasses the DOE technical target for both mass activity (~two-fold) and specific activity (three-fold).

- Gas diffusion layer: Sigracet 25 BC

The MEAs were tested at temperatures ranging from room temperature to 80°C, with 150 kPa(abs) humidified hydrogen on the anode at 1 L/min and with 150 kPa(abs) humidified oxygen or air on the cathode, with a relative humidity of 100%. The hydrogen-oxygen mass activity results are provided for the MEAs with nanoframe cathode catalyst and the TKK Pt/C cathode catalyst.

The ECSA based on H_{upd} charge from the RDE results is approximately 60 m²/g Pt, while the H_{upd} based ECSA in MEA was found to be 49 m²/g Pt.

The hydrogen-oxygen performance showed specific activity at 0.9 V_{IR-corr.} of 2,600 μA/cm² and mass activity of 0.76 A/mg Pt. Improved utilization of the PtNi nanoframes through optimization of the ionomer-carbon ratio allowed the PtNi nanoframe MEAs to surpass the DOE MEA performance targets by almost a factor of two, while specific activity was improved by factor of three. For comparison, the TKK Pt/C catalyst showed specific and mass activities at 0.9 V_{IR-corr.} of 326 μA/cm² and 0.24 mA/mg Pt.

The hydrogen-air performance for these two MEAs is shown in Figure 2. The performance of the nanoframe MEA surpasses that of the TKK Pt/C MEA. The current density at 0.8 V is 115 mA/cm². Given that the cathode catalyst loading in the nanoframe MEA was one third that of the DOE target cathode loading of 0.1 mg Pt/cm² (assuming an anode loading of 0.025 mg Pt/cm²), an MEA with a nanoframe catalyst loading of 0.1 mg Pt/cm² is expected to surpass the DOE target of 300 mA/cm² at 0.8 V.

CONCLUSIONS AND FUTURE DIRECTIONS

- Different classes of materials have been synthesized in the form of NPs, nanowires, and nanoframes and these materials have been characterized by transmission electron microscopy, high resolution scanning electron microscopy, in situ HR-TEM, X-ray diffraction, RDE, and MEA.
- Specific activity for the ORR measured in RDE of Pt-alloy vs. Pt/C electrocatalysts can be improved by 20-fold for nanoframes and mesostructured thin films (MSTF), 10-fold for core/shell NPs and seven-fold for nanowires.
- Mass activities improvements for the ORR measured in RDE vs. Pt/C are 36-fold for nanoframes, seven-fold for core/shell, six-fold for MSTF and four-fold for nanowires (RDE in 0.1 M HClO₄ at 0.95 V vs. RHE).
- Stability of nanoframes, MSTF, core/shell NPs and nanowires can be substantially improved compared to Pt/C.
- Two-fold power of annealing facilitates the formation of an energetically more favorable surface state rich in (111)

facets and distinct oscillatory segregation profile in core/shell NPs, nanowires, MSTF and nanoframes.

- Nanoframes are the first nanoscale catalyst with ORR bulk single crystal activity.
- Specific and mass activities of nanoframe catalysts measured in MEA surpass the 2015 DOE Technical Target by ~three-fold and two-fold, respectively.

This project is officially over in FY 2015; however, the performance of nanostructured catalysts in MEA will remain in focus in the next funding cycle.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. C. Chen, Y. Kang, N.M. Markovic, G. Somorjai, Peidong Yang and V.R. Stamenkovic, Patent Pending, “Highly Crystalline Pt₃Ni Nanoframes with Three-Dimensional Electrocatalytic Surfaces.”
2. R&D 100 Award Finalist Berkeley-Argonne Lab Nanoframe catalysts P. Yang and V. Stamenkovic.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Joshua Snyder, Yijin Kang, Dongguo Li, N. Markovic, and V. Stamenkovic, “Electrocatalysts with Tailored Properties,” 226th Electrochemical Society Meeting, October 2014, Cancun, Mexico.
2. Joshua Snyder, Yijin Kang, Dongguo Li, Dusan Strmcnik, N. Markovic, and V. Stamenkovic, “Novel Pathways for Improving the ORR Rate,” (KEY NOTE LECTURE), 226th Electrochemical Society Meeting, October 2014, Cancun, Mexico.
3. Y. Kang, N.M. Markovic, and V. Stamenkovic, “Electrochemical Energy Conversion,” (KEY NOTE LECTURE), International Conference on Electrochemical Science, October–November 2014, Shanghai, China.
4. Y. Kang, J. Snyder, D. Li, K. More, N.M. Markovic, and V.R. Stamenkovic, “Multimetallic Core/Interlayer/Shell Nanostructures as Advanced Electrocatalysts,” *Nano Letters*, 14(2014)6361–6367.

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