

V.A.4 Tailored High-Performance Low-PGM Alloy Cathode Catalysts

Vojislav R. Stamenkovic and Nenad M. Markovic
Argonne National Laboratory (ANL)
9700 Cass Ave.
Argonne, IL 60439
Phone: (630) 252-8946
Email: vrstamenkovic@anl.gov

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

Subcontractors:

- Karren More, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN
- Rod Borup, Los Alamos National Laboratory, Los Alamos, NM
- Peidong Yang, Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA

Project Start Date: October 2015
Project End Date: September 2018

Overall Objectives

- Develop and deliver advanced low-PGM (platinum group metal) cathode catalysts for use in polymer electrolyte membrane fuel cells (PEMFCs) with increased mass activity at high electrode potentials, enhance performance at high current density.
- Improve durability while reducing the total loading of PGM and cost.
- Reduce PGM loading in the catalyst through alloying of Pt with other transition metals.
- The low-PGM materials will be in form of nanomaterials deployed on high surface area supports.
- Rational development and evaluation of durable high surface area supports for tailored nanomaterials.
- Development and implementation of scalable chemistry that would allow synthesis of tailored nanomaterials at the gram scale.
- Insight on the differences and similarities between the rotating disk electrode (RDE) and membrane electrode assembly (MEA) performance.
- Ionomer catalyst interaction and optimization of catalyst layers.
- The MEA will have a total PGM loading of <0.125 mg PGM/cm² and 0.125 g PGM/kW with mass activity higher than 0.44 A/mg PGM.

- Total loss of electrochemically mass activity will be less than 40% after 30,000 voltage cycles.

Fiscal Year (FY) 2017 Objectives

- Development of active and durable catalysts for fuel cell cathodic reaction.
- Synthesis, structural, and electrochemical evaluation of Pt-alloy nanoparticles with controlled physical parameters such as size, compositional profile and topmost surface.
- Development of scalable process to produce larger quantities of catalysts.
- Integration and evaluation of novel carbon supports with tailored Pt-alloy nanoparticles.
- Reproducibility of performance measured in MEA for tailored Pt-alloy catalysts with total PGM loading of <0.125 mg PGM/cm² and mass activity >0.44 A/mg PGM.

Technical Barriers

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

(A) Durability

Develop improved catalysts:

- Reduce precious metal loading of catalysts.
- Increase the specific and mass activities of catalysts.
- Increase the durability and stability of catalysts with cycling.
- Test and characterize catalysts.

Technical Targets

The project is aimed at developing nanoparticles with tailored architectures and composition based on Pt-alloys with transition metals PtM (M = Ni, Co, Cr, V, Ti, etc.), including alloys with Au, to improve performance for the fuel cell cathodic oxygen reduction reaction. The design principles will be focused to produce systems with low content of PGMs while exhibiting highly active and durable electrochemical properties evaluated in MEAs that will meet and/or exceed the DOE 2020 targets (Table 1).

TABLE 1. Progress towards Meeting DOE 2020 Technical Targets for Electrocatalysts

	Unit	2020 DOE Targets	Project Status
PGM Total Loading	mg _{PGM} /cm ²	0.125	0.120
Mass Activity	A/mg _{PGM} @ 900 mV	0.44	0.60
Mass Activity Loss	%	<40	<20

FY 2017 Accomplishments

- Established relationship between surface morphology and dissolution rates for Pt surfaces by implementing RDE-inductively coupled plasma with mass spectrometer (ICP/MS).
- Established relationship between the thickness of Pt overlayer and dissolution rates for Pt-based thin films by implementing RDE-ICP/MS.
- Established relationship between the particle size and dissolution rates for Pt/C catalysts by implementing RDE-ICP/MS.
- Improved durability and established stabilization mechanism for Pt thin films and nanoparticles by different metal subsurfaces.
- Established optimal, highly active and durable Pt:Ni ratio to be 1:1.
- Discovered and synthesized novel Pt-alloy nanoscale architectures that are highly active and durable: nanopinwheels, nanocages, nanoframes with radial joists and excavated nanoframes.
- Established scalable chemistry to produce 3 g and 5 g amount of PtNi catalyst with multilayered Pt-skin surfaces in a single batch.
- Exceeded mass activity 2020 DOE technical targets for PtNi catalyst in MEA; mass activity = 0.5 A/mg_{PGM}.
- Delivered gram-scale quantities of Pt-alloy catalysts to collaborators and stakeholders and performed electrochemical evaluations of the catalysts in MEA.



INTRODUCTION

The major obstacle for broad utilization of PEMFCs in transportation is cost, performance, and durability of Pt catalysts that are employed in each individual cell of a fuel cell stack. Considering that Pt is the best known catalyst for both hydrogen oxidation and oxygen reduction reaction (ORR), it is of paramount importance to develop practical catalysts that will exhibit optimal performance through high specific activity (current per electrochemical surface

area of catalyst), with minimal content of PGMs that will ensure high mass activity (current per mass unit of PGM). The cathode in PEMFCs suffers from substantial kinetic limitations and degradation of catalyst for the ORR, and for that reason the main focus in catalyst development is to create a highly efficient, durable cathode with low content of PGM. Therefore, this project will aim to develop and deliver advanced low-PGM cathode catalysts for PEMFCs that will increase mass activity at high electrode potentials, enhance performance at high current density, and improve durability while decreasing the cost. The decrease of the total loading of PGM in the fuel cell will be accomplished by improving activity and durability of Pt-based catalysts through alloying with other transition metals [1]. These PGMs in the form of nanomaterials will be deployed on high surface area supports in the cathode of the MEA with total PGM loading less than the DOE 2020 target of 0.125 mg_{PGM}/cm² and 0.125 mg_{PGM}/kW with mass activity higher than 0.44 A/mg_{PGM}.

APPROACH

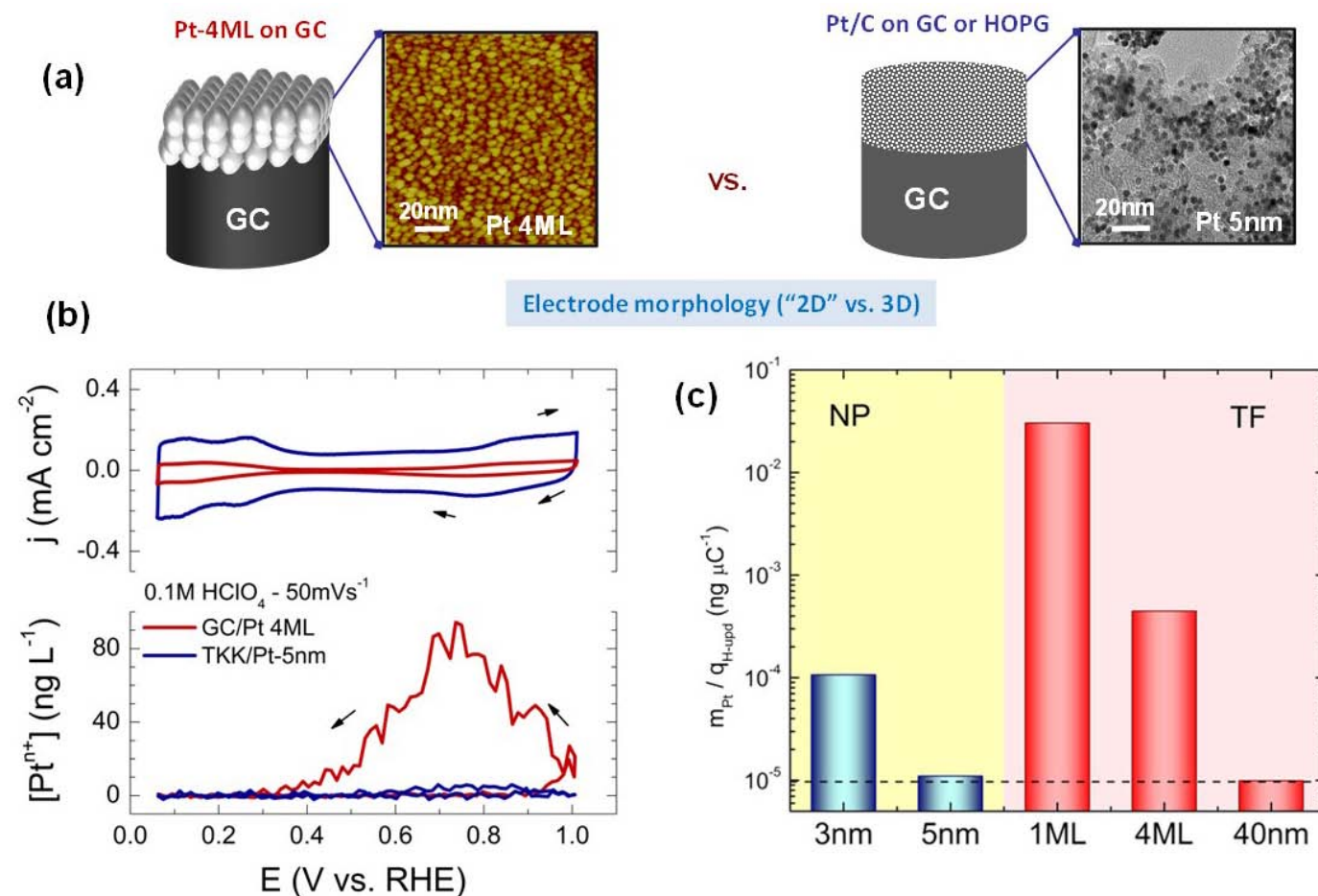
This is a multi-performer project led by ANL and supported by inter-lab collaborations with LBNL, Los Alamos National Laboratory, and ORNL. ANL leads and coordinates this applied research effort with other national laboratories, defines project scope, topics, milestones, and is responsible for deliverables as well as quarterly and annual reports to the Fuel Cell Technologies Office. LBNL is involved in chemical synthesis of advanced nanoscale structures and development of scaling-up protocols of the most promising catalytic systems. Los Alamos National Laboratory fabricates and tests the MEAs and provides alternative carbon-based supports to conventional high surface area carbon. ORNL characterizes synthesized materials and catalysts deployed in an MEA before and after testing protocols by electron microscopy. The approach of this project is based on the knowledge obtained from well-defined systems that will be used to tailor functional properties of corresponding nanoscale materials, with desired shape, size, structure and compositional profile. Integration of engineered nanomaterials in electrochemical systems requires integration of a broad range of scientific disciplines such as solid state physics, surface science, physical chemistry and electrochemistry. This effort also includes a combination of highly diverse experimental tools supported by state-of-the-art synthesis and characterization strategies, together with the fabrication and testing capabilities. The project is executed simultaneously in five tasks throughout duration of the project: Task 1 – Well-Defined Systems, Task 2 – Synthesis of Nanoscale Materials, Task 3 – Electrochemical and Structural Characterization of Catalyst, Task 4 – Advanced Supports for Novel Catalysts, and Task 5 – Scaling Up of Catalysts.

RESULTS

Pt Dissolution Rates and the Mechanism of Catalyst Degradation

In the development of superior low-PGM catalysts it is of paramount importance to address the stability of Pt-based catalysts by establishing stability range dissolution rates and mechanism. In the previous period, we combined efforts between Tasks 1, 2, and 3 to reveal trends in dissolution of Pt surfaces. As reported last year [2], dissolution trends from Pt single crystals are clearly indicating that the topmost surface atoms with the highest coordination number are less sensitive to dissolution processes. For that reason, the most stable surface was found to be Pt(111). Linking the properties between well-defined single crystalline surfaces and a real world catalyst would ultimately lead towards design of advanced systems with high durability. The most recent efforts aimed at exploring different Pt thin film surfaces and nanoparticles. In all cases, a glassy carbon electrode

was used as a substrate either to deposit a thin metal film or thin catalyst layer. In each case, the experiments were executed in ultra clean environments to ensure high purity of electrochemically active constituents. Depositions of thin metal films were done in a magnetron sputtering chamber with the ability to vary the thickness from 1 ML (monolayer) to multilayers of Pt. These films were transferred either to an electrochemical cell for evaluation or to an ex situ scanning tunneling microscope (STM) to determine the surface morphology. Figure 1a depicts a STM image of 4 ML Pt film over glassy carbon. From the STM image, it is obvious that the surface has highly corrugated morphology with well-defined average cluster size distribution, which was found to be 5 nm in diameter. On the other electrode, monodisperse 5 nm Pt/C catalyst was deposited and characterized by high transmission electron microscopy. Each sample was characterized by cyclic voltammetry in RDE, which was followed by on line ICP/MS. It is important to note that thin film clusters and the 5 nm Pt/C catalyst have identical cluster-particle size. However, the main difference



GC – glassy carbon; HOPG – highly oriented pyrolytic graphite; RHE – reference hydrogen electrode; NP – nanoparticle; TF – thin film

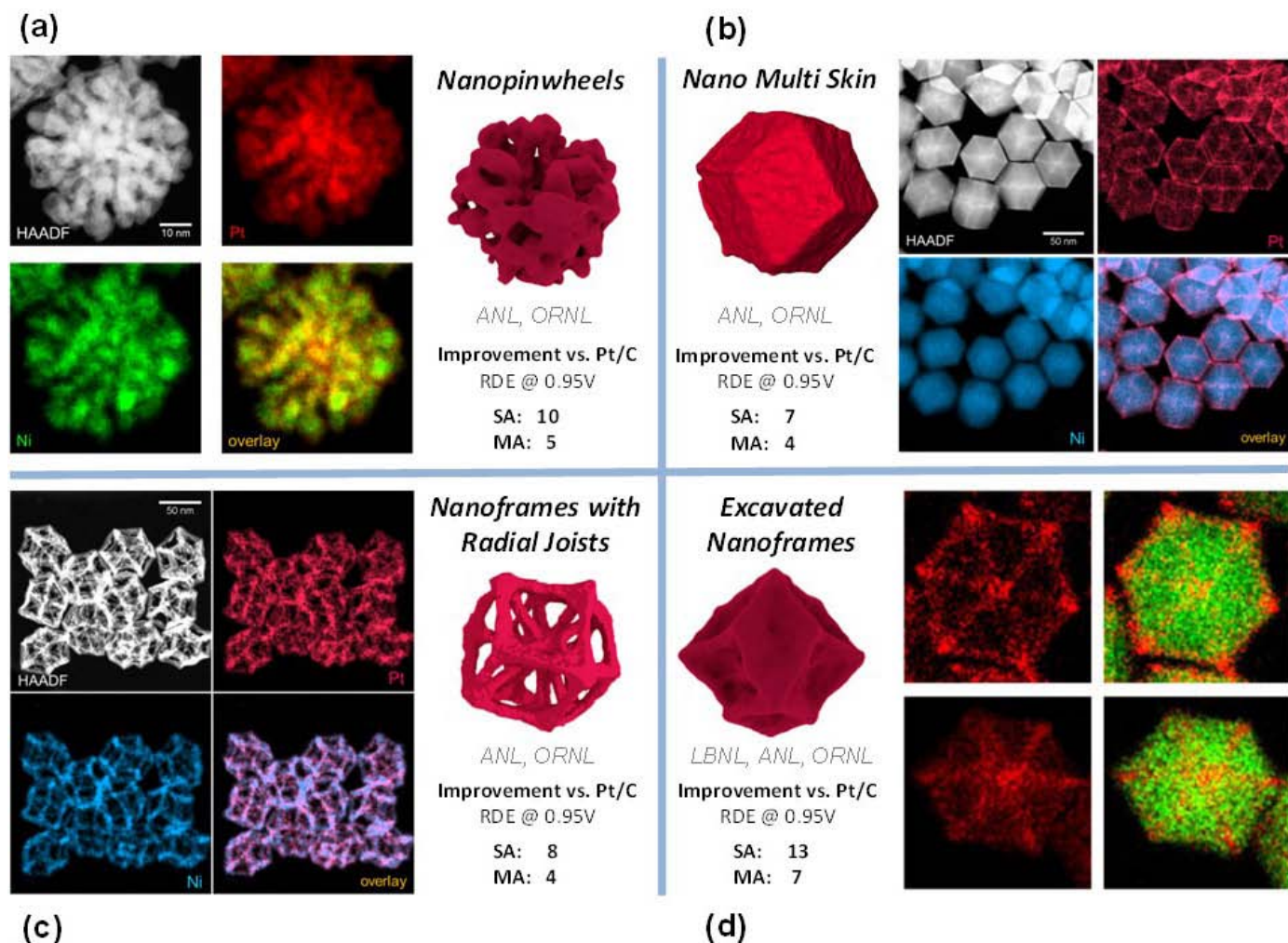
FIGURE 1. Structural and electrochemical characterization of Pt thin film surfaces and Pt nanoparticles deposited over the glassy carbon electrode by (a) STM and high resolution transmission electron microscope, (b) RDE-ICP/MS, and (c) dissolution rates from during single potential cycle between 0.6 V and 1.0 V from different Pt nanoparticles and Pt thin films with various thicknesses.

between them is due to the two-dimensional (2D) nature of the thin film surface versus a three-dimensional (3D) catalyst overlayer. Accordingly, dissolution rates measured from these samples exhibit remarkably different values. Pt dissolution from thin film surfaces is higher by more than one order of magnitude compared to the Pt/C catalyst. The main reason is due to the 3D nature of the catalyst layer where high surface area carbon matrix acts as a scavenger of dissolved Pt atoms. Based on this finding, thin metal films can be used to magnify the real dissolution effect in order to resolve the dissolution mechanism and propose more stable systems. Along those lines, a subsurface made of different metals including Au was used to evaluate influence on the topmost Pt dissolution. Thin metal films of various precious metals (Pd, Re, Au, Ir, Ag, etc.) were deposited over a glassy carbon electrode and then 4 ML of Pt has been added to the topmost surface layer (not shown here). It was confirmed that subsurface Au has the most beneficial properties for

preventing Pt dissolution. As reported before [3], a rather high dissolution rate of 4 ML Pt on glassy carbon can be completely suppressed by Au subsurface. This has been used [4,5] and will be implemented in novel nanoscale systems.

Novel Nanoscale Architectures of Pt-Alloy Catalysts

A series of monodispersed nanoparticles with novel architectures have been synthesized and characterized to determine particle size, composition, morphology, and electrochemical performance in RDE. The most promising systems are summarized in Figure 2 together with high-angle annular dark-field and elemental mapping images. Nanopinwheels depict highly porous morphology, rather large particle size (~50 nm) and homogeneous elemental distribution between Pt and Ni. The synthesis protocol allows formation of highly dealloyed structures with high roughness factor that creates sufficient number of active sites and hence,



SA – specific activity; MA – mass activity

FIGURE 2. High-angle annular dark-field micrographs and elemental distribution of synthesized monodisperse PtNi NPs with novel architecture along with their performance for the ORR measured in 0.1M HClO₄ by RDE: (a) nanopinwheels, (b) octahedrons with multilayered Pt-skin surfaces, (c) nanoframes with radial joists, and (d) excavated nanoframes.

high specific and mass activities. Figure 2b shows PtNi alloy particles that are highly monodisperse cuboctahedrons with multilayered Pt-skin surfaces with well-defined compositional profile. In addition to previously reported PtNi nanoframes [6], we report here two novel architectures: nanoframes with radial joists as additional active sites within the nanoframe structure and excavated nanoframes. Based on the RDE screening of these catalysts dispersed in high surface area carbon, the increase in specific activity is up 13-fold, and mass activity up 7-fold when compared to Pt/C. Each of these nanoarchitectures will be evaluated for scale-up protocol.

Scaling the Amounts Synthesized Pt-Alloy Catalysts to Gram Levels

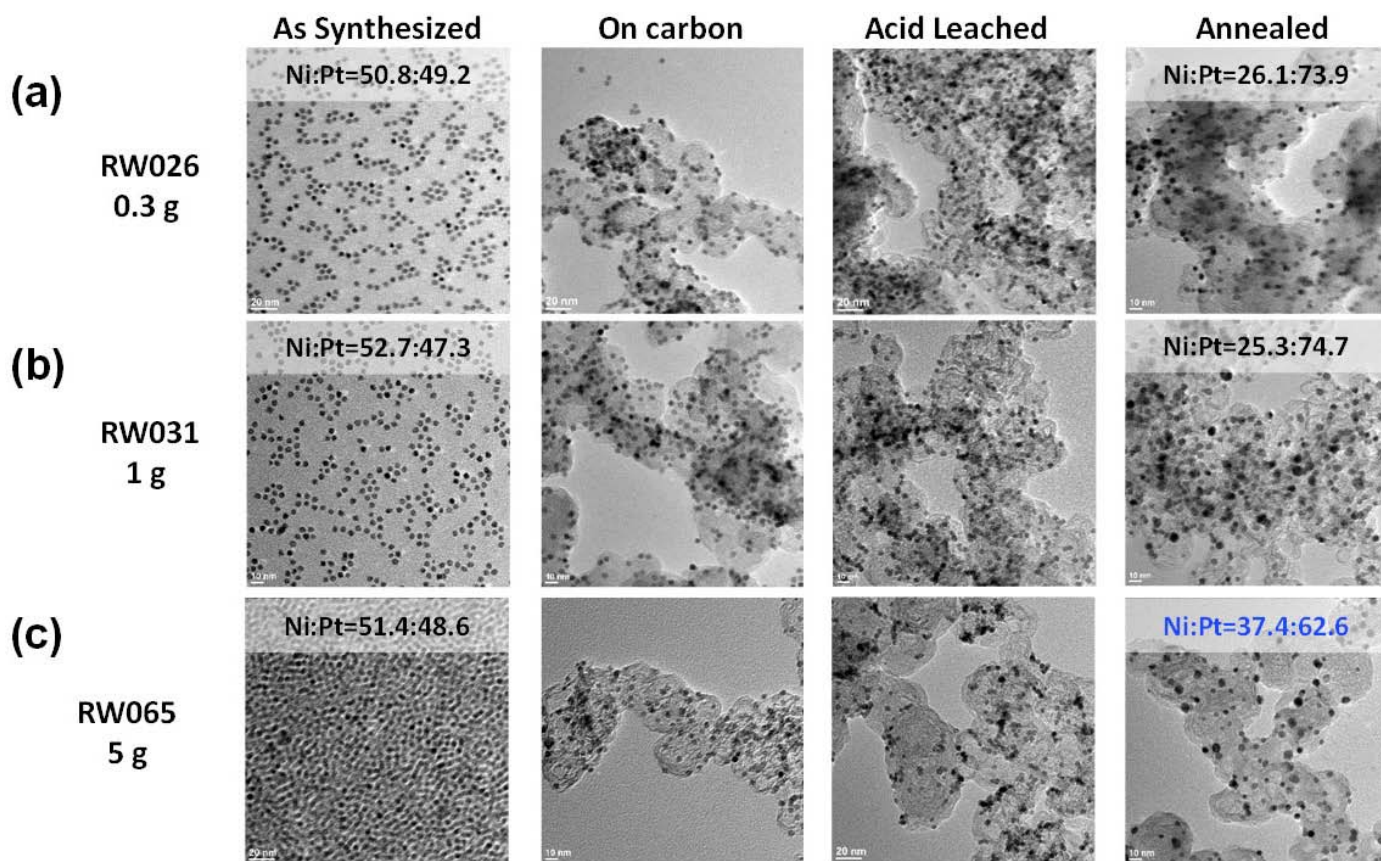
A new procedure which is capable of making 5 g catalyst per batch with similar or higher RDE activity was developed by modifying several steps of the original small batch synthesis process (Figure 3).

In the original procedure [7], Pt precursor dissolved in 1,2-dichlorobenzene (boiling point 180°C) was preheated to 80°C and injected into Ni precursor solution at 200°C. This

process is not operationally practical and may not be safe for large-scale synthesis because of the pressure change and possibility of introducing oxygen during injection.

The new scale-up procedure utilizes one-pot synthesis that avoids the injection of the hot Pt precursor. This makes the scale-up of the monodispersed PtNi nanoparticles feasible at least to a gram-scale. In the loading PtNi nanoparticles onto carbon step of the original procedure, nanoparticles were dispersed in hexane or chloroform solvent and then mixed with carbon black (Tanaka, KK), which was followed by evaporation of the solvent. Evaporation of the large amount of flammable and/or toxic solvents is both prohibited by regulations and not operationally safe. In addition, loading of the significant amount of nanoparticles in hexane, usually results in non-uniform dispersion of nanoparticles on carbon support. Although the loading of nanoparticles on carbon in chloroform is uniform, some particles will come off the carbon support if a centrifuge is used to separate them from the solvent.

In the new procedure, PtNi nanoparticles are dispersed in chloroform and then mixed with carbon black which was already dispersed in chloroform. After mixing, hexane is



SA – specific activity; MA – mass activity

FIGURE 3. Progress and evolution of the scaling-up synthesis protocol for PtNi/C nanoparticles with multilayered Pt-skin surfaces.

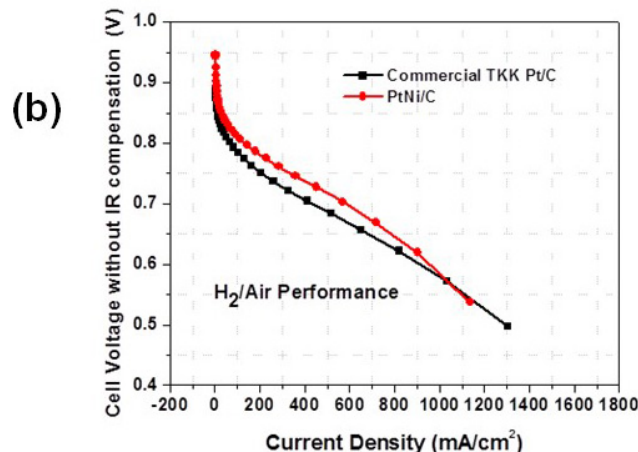
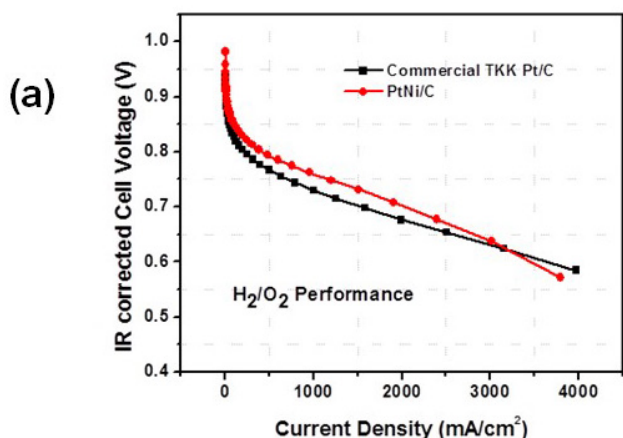
(a) Initial synthesis batch of about 0.3 g and was successfully scaled to (b) 1 g and (c) 5 g of catalyst, while particles maintained the same composition, particles size distribution, and multilayered Pt-skin surfaces.

introduced to precipitate PtNi/C from the solvent. Finally, PtNi/C could be separated from the solvent by filtration. In the acid leaching step of the original procedure, PtNi/C was assumed to be mixed with 0.1 M HClO₄ by brief sonication and further soaking in this solution was allowed. This process works well for a small amount of catalyst (typically milligram-scale). However, to disperse a large amount of PtNi/C, prolonged sonication is needed which results in severe loss of Ni from the nanoparticles. In the new procedure, PtNi/C was dispersed in water before mixing with 0.1 M HClO₄, and the leaching process was systematically investigated to give the best RDE activity. With all the modifications, the new procedure is capable of making 5 g catalyst per batch. Mass activity of the catalyst prepared with this procedure is 8–9 times higher than commercial Pt/C. The reproducibility of the process was confirmed with a second batch synthesis. Transmission electron microscopy

tomography confirms that all the PtNi particles are located on the surface of carbon which results in higher catalyst utilization at different humidification conditions in the MEA.

MEA Evaluation of Scaled Up Catalyst with Multilayered Pt-Skin Surfaces

The nanoparticle evaluations were made in RDE and 5 cm² MEA at ANL. The MEAs were made 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 0.8. The summary of the MEA test results is given in Figure 4. 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 and/or air on the cathode, with a relative humidity of 100%. The



	Units	PtNi Cathode	TKK Pt Cathode
Pt total loading	mg _{Pt} /cm ² _{geo}	~0.04	~0.04
Mass activity (H2-O2)	A/mg _{PGM} @0.9 V _{IR-free}	0.5	0.22
Specific activity (H2-O2)	mA/cm ² _{PGM} @0.9 V	1.01	0.39
MEA performance (H2-Air)	mA/cm ² @0.8 V	131.34	64.3
ECSA	m ² /g _{PGM}	50	52.5

IR – internal resistance; ECSA – electrochemically active surface area

FIGURE 4. MEA characterization of scaled 20 wt% PtNi/C catalyst with multilayered Pt-skin surfaces (red) and Pt/C TKK (black) obtained in 5 cm² cell: (a) hydrogen–oxygen polarization curves, (b) hydrogen–air polarization curves. The cathode Pt loading is 0.04 mg_{Pt}/cm², ionomer to carbon ratio = 0.8, 80°C, 150 kPa, 100% relative humidity. (c) Performance parameters of PtNi/C retrieved from MEA hydrogen–oxygen polarization curves.

mass activities are shown in the table in Figure 4c. High performance PtNi/multilayered–Pt-skin nanoparticles have been evaluated by MEA and it has been confirmed that high durability originates from the protective multilayered Pt-skin surface that encapsulates the core that is Ni rich, as mentioned before. The multilayered Pt-skin catalyst was prepared by scaled-up protocol developed at ANL and its performance measured in MEA has achieved the DOE 2020 technical target. The Pt loading on the cathode was $0.04 \text{ mg}_{\text{PGM}}/\text{cm}^2$ and measured mass activity was found to be $0.50 \text{ A}/\text{mg}_{\text{PGM}}$ at 0.9 V. In addition to MEA evaluation at ANL, the same catalyst was distributed to our collaborators at Los Alamos National Laboratory, as well as to stakeholders. These characterizations are still undergoing.

CONCLUSIONS AND UPCOMING ACTIVITIES

New insights into dissolution mechanism of Pt have been obtained and it was confirmed that subsurface Au can indeed suppress dissolution of Pt. This will be further evolved and applied to nanoscale systems in the next phase of the project. Dissolution will continue to be strictly monitored for all promising nanoscale systems. A series of Pt-alloy nanoparticles with unique architectures were synthesized and have been employed in harvesting high catalytic performance. The next step will be to evaluate these systems for a scale-up protocol which would enable distribution of the catalyst among the network of collaborators and stakeholders. A number of carbon supports have been evaluated for the support that would lead to better utilization of Pt-alloy nanoparticles, however, most of these systems did not reach the performance of currently used carbon black. This effort will continue to be integral part of this project. MEA evaluation will be performed in 5 cm^2 to 50 cm^2 cells. The project will continue to explore novel architectures of Pt-alloy nanoparticles that would allow implementation of the scale-up protocol. All of these efforts are expected to generate new patents that would be readily available for licensing.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. V.R. Stamenkovic, P.P. Lopes, D. Strmcnik, and N.M. Markovic, *Energy and Fuels from Electrochemical Interface*, *Nature Materials*, 16 (2017) 57–69.
2. Y. Kang, P. Yang, N.M. Markovic, and V.R. Stamenkovic, *Shaping Electrocatalysis through Tailored Nanomaterials*, *Nano Today*, 11 (2016) 587–600.
3. H. Lv, D. Li, P.P. Lopes, D. Strmcnik, R. Wang, N. Markovic, and V. Stamenkovic, *From Fundamentals to PEMFC Systems*, 231st Electrochemical Society Meeting, May 2017, New Orleans, LA.
4. D. Strmcnik, D. Li, P.P. Lopes, E. Coleman, H. Lv, N.M. Markovic, and V. Stamenkovic, *Advanced Carbon Structures for PEMFC*, 231st Electrochemical Society Meeting, May 2017, New Orleans, LA.

5. D. Li, H. Lv, D. Strmcnik, N. Markovic, and V. Stamenkovic, *From Well-Defined Electrochemical Interfaces to Functional Nanoscale Materials*, 253rd American Chemical Society National Meeting, April 2017, San Francisco, CA.
6. D. Li, D. Strmcnik, N. Markovic, and V. Stamenkovic, *Design and Synthesis of Nanomaterials for Energy Applications*, Gordon Research Conference, February 2017, Ventura, CA.
7. V. Stamenkovic, *Tailored Electrocatalysts with Advanced Properties*, Fuel Cells Workshop, Bar Ilan University, November 2016, Tel Aviv, Israel.
8. P.P. Lopes, D. Li, D. Strmcnik, N. Markovic, and V. Stamenkovic, *Tuning of the ORR Performance-Durability for Pt-Based Electrocatalysts*, 230th Electrochemical Society Meeting, October 2016, Honolulu, HI.
9. D. Li, D. Strmcnik, N. Markovic, and V. Stamenkovic, *Novel High-Performance Low-PGM Catalysts*, Gordon Research Conference, August 2016, Easton, MA.
10. N. Markovic and V. Stamenkovic, *State of the Art and Challenges Facing Low-Temperature Fuel Cell Electrocatalysis*, DOE-EERE Catalysis Working Group Meeting, July 2016, Argonne, IL.

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3. V.R. Stamenkovic and N.M. Markovic, “Tailored High-Performance Low-PGM Alloy Cathode Catalysts,” FY 2016 Annual Progress Report, *DOE Hydrogen and Fuel Cells Program*.
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