

V.A.12 Non-Precious Metal Fuel Cell Cathodes: Catalyst Development and Electrode Structure Design

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Project Start Date: April 1, 2013
 Project End Date: March 31, 2016

Overall Objectives

Advance non-platinum-group metal (non-PGM) cathode technology through the development and implementation of novel materials and concepts for oxygen reduction catalysts and electrode layers with:

- Oxygen reduction reaction (ORR) activity viable for practical fuel cell systems
- Much improved durability
- Sufficient ionic/electronic conductivity within the catalyst layer
- Adequate oxygen mass transport
- Effective removal of the product water

Fiscal Year (FY) 2013 Objectives

- Optimize the most active LANL catalysts by the heat-treatment approach for maximum hydrogen-air performance
- Synthesize non-pyrolyzed phthalocyanine-derived catalysts
- Develop testing protocols for the evaluation of the performance durability of non-PGM catalysts

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 [1]:

- (A) Durability (catalysts, electrode layers)
- (B) Cost (catalyst, membrane electrode assemblies [MEAs])
- (C) Performance (catalysts, electrodes, MEAs)

Technical Targets

Non-PGM fuel cell catalyst research in this project focuses on the DOE technical targets in Table 3.4.13 in Section 3.4.4 (Technical Challenges) of the Multi-Year Research, Development, and Demonstration Plan [1]. The main DOE performance target for non-Pt (more precisely, non-PGM) ORR catalysts is listed in Table 1.

The ultimate technical targets of the project are:

- Volumetric catalyst activity in MEA at 0.80 V (i_{R-free}), 80°C: $\geq 300 \text{ A cm}^{-3}$
- Four-electron selectivity (rotating ring-disk electrode): $\geq 99\%$; $\text{H}_2\text{O}_2 \leq 1\%$
- MEA maximum power density at 80°C: $\geq 1.0 \text{ W cm}^{-2}$
- Performance loss at 0.80 A cm^{-2} after 30,000 cycles in N_2 : $\leq 30 \text{ mV}$

TABLE 1. Project Technical Targets

Table 3.4.13 Technical Targets: Electrocatalysts for Transportation Applications				
Characteristic	Unit	2011 Status	Targets	
			2017	2020
Non-Pt catalyst activity per volume of supported catalyst	$\text{A/cm}^3 @ 800 \text{ mV}_{IR-free}$	60 (measured at 0.8 V) 165 (extrapolated from >0.85 V)	300	300

IR-free – internal resistance free



APPROACH

Materials development, which represents the core of this research effort, focuses on the following four groups of catalysts and supports: (1) heat-treated catalysts obtained using multiple nitrogen precursors; (2) alternative supports for heat-treated catalysts; (3) non-pyrolyzed phthalocyanine-derived catalysts; and (4) metal-free catalysts based on nitrogen-doped nanostructures.

In FY 2013, we have concentrated on the optimization of heat-treated metal-nitrogen-carbon catalysts. A new Fe-based catalyst derived from polyaniline (PANI) has been synthesized and characterized (Figure 1). The surface area of this catalyst is ca. 1,100 m²/g, significantly more than

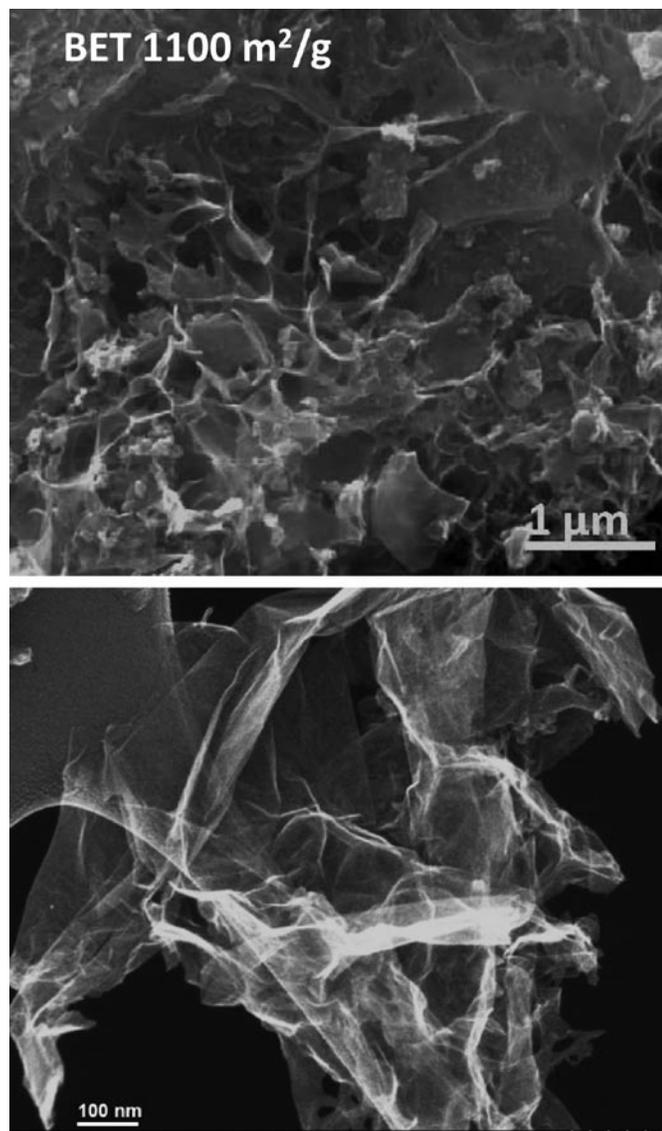


FIGURE 1. Morphology of the high surface-area PANI-Fe-C catalyst.

the surface area of non-PGM catalysts prepared previously. This new catalyst exhibits improved fuel cell performance, reaching a current density of more than 100 mA/cm² at 0.8 V (*i*R-free) in fuel cell testing (Figure 2). The latter performance already matches the state of the art in non-PGM electrocatalysis of oxygen reduction in an operating MEA.

In another part of the catalyst development effort, nitrogen-doped carbon nanotubes were prepared with strictly controlled tube diameter and nitrogen functionalities by varying transition metals precursors (Figure 3). Given the commonly accepted hypothesis that ORR active sites species are embedded into the graphitized carbon structures [2], the highly graphitic nanotubes can offer a potentially attractive host for the ORR active sites in non-PGM catalysts under the development in this project by enhancing catalytic activity. Improvements to the catalyst performance durability and even mass transfer are also possible.

Extensive catalyst characterization effort has begun with the purpose of evaluating the performance and understanding the nature of the ORR active site(s). In particular, a new characterization technique of nuclear resonance vibrational spectroscopy (NRVS) is being combined with density functional theory (DFT) to study the surface active Fe species and to elucidate the nature of active site(s) (Figure 4, left). In the part of the project that concentrates on the electrode layer design and characterization, microstructured electrode scaffold (MES) diagnostics has been used to measure spatiotemporal, through-plane distribution of potential, conductivity, and reaction rate (Figure 4, right). The ultramicroelectrode measurements of O₂ concentration in the electrode have been realized by flux-interrupt method. The newly developed in situ current-probe technique allows for accurate conductivity determination.

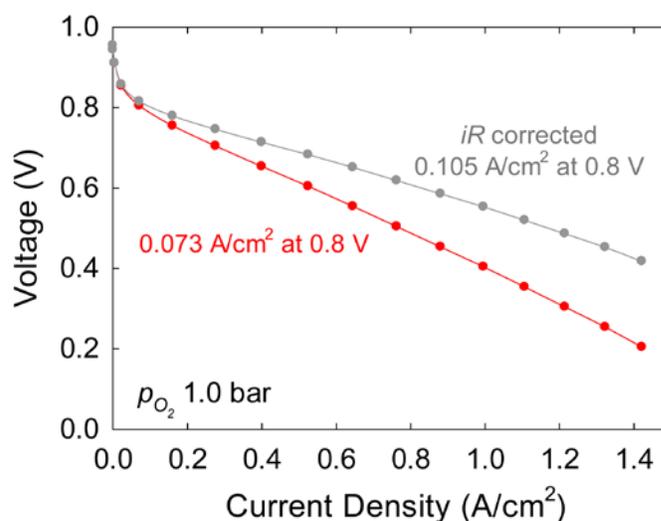


FIGURE 2. Fuel cell performance of the high surface-area PANI-Fe-C catalyst. Anode: 2.0 mg/cm² Pt; cathode: 4.1 mg/cm²; cell temperature: 80°C; 100% relative humidity; membrane: two Nafion® 212 layers.

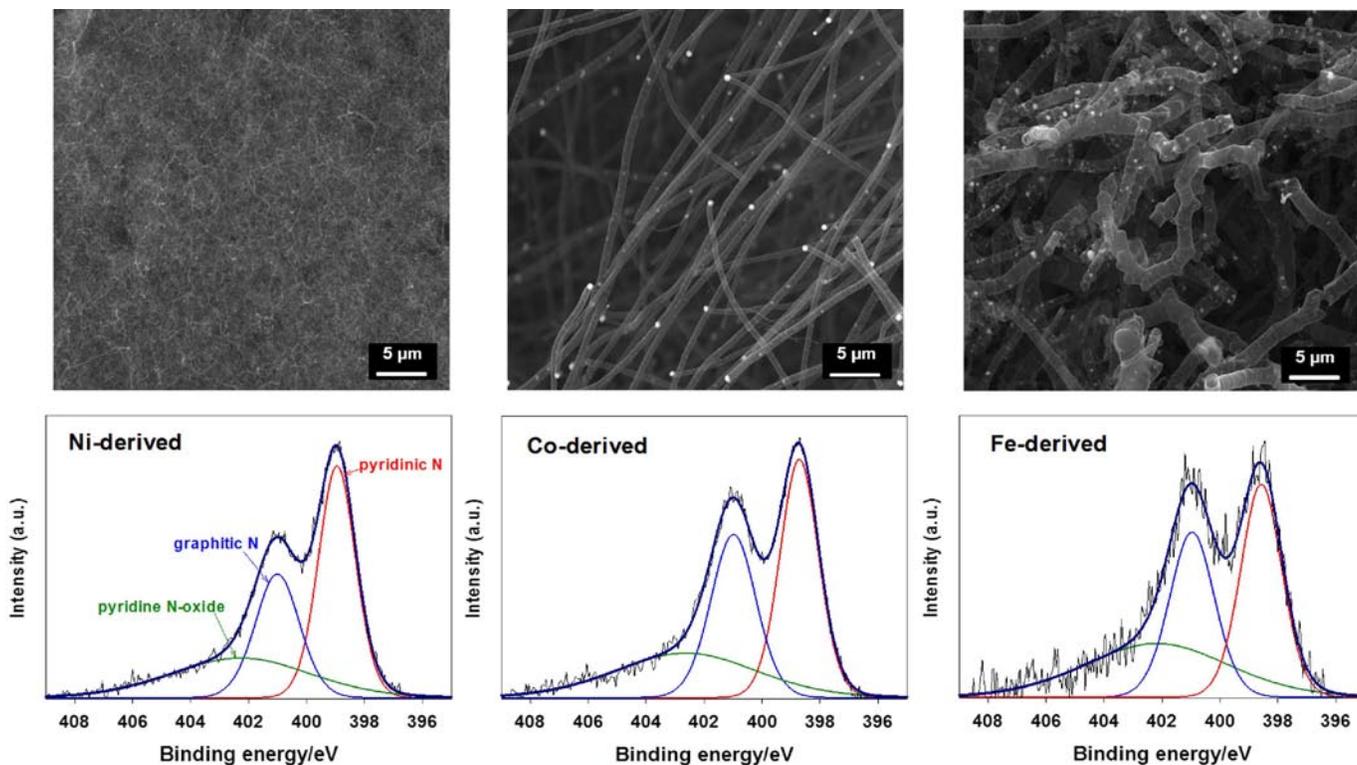
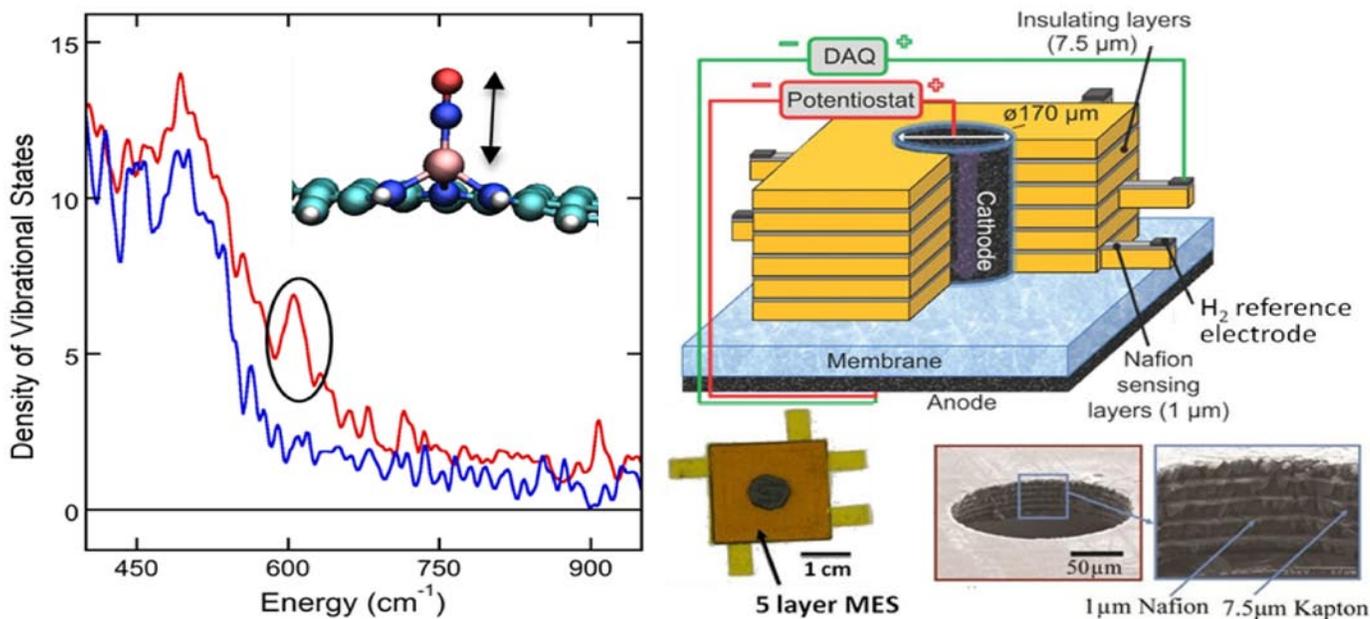


FIGURE 3. Nitrogen-doped carbon micro- and nano-tubes with the diameter and nitrogen functionalities controlled by the transition metal used in the synthesis. Top: scanning electron microscopy images; bottom: corresponding N1s X-ray photoelectron spectroscopy data.



Nafion is a registered trademark of E. I. du Pont de Nemours and Company

FIGURE 4. Selected catalyst and electrode characterization methods. Left: NRVS spectra with DFT-assigned vibrational mode of the NO probe molecule; right: MES diagnostics.

A careful cathode design is required to (1) enhance the mass transport of oxygen, (2) assure sufficient protonic conductivity, (3) prevent catalyst layer flooding, and (4) make non-PGM catalysts potentially viable for automotive applications. Once optimized, the cathodes will undergo a scale-up, necessary for obtaining the project deliverable, a 50-cm² MEA (Figure 5).

FY 2013 ACCOMPLISHMENTS

- High-surface-area, graphene-rich, PANI-derived catalyst was synthesized and tested in a fuel cell, reaching current density in excess of 0.1 A/cm² at 0.8 V (already matching the state of the art in non-PGM cathode performance).
- Carbon nano/micro tubes were synthesized using a one-step, simple synthesis method that assures high yields and requires no further purification; the control over the tube diameter and the nature of nitrogen functionalities was achieved via proper selection of a transition metal.
- Three-dimensional graphene-based nanostructures were synthesized in order to enhance non-PGM catalyst utilization while maintaining high electron conductivity; methodology possibly adaptable to heat-treated non-PGM ORR catalysts under development at LANL.

- Electrospinning was successfully used in the preparation of three-dimensional non-PGM electrodes.
- NRVS was demonstrated to be a surface-specific technique, of considerable value to the ORR active site studies with Fe-based non-PGM catalysts.

FUTURE DIRECTIONS

Catalyst Development:

- Development and optimization of multi-nitrogen-precursor, heat-treated ORR catalysts with high activity and four-electron selectivity.
- Synthesis of non-PGM catalysts supported on highly-graphitic carbon(s) as a way of enhancing active-site density and improving performance durability.
- Validation of the metal-free approach in ORR electrocatalysis.
- Development of the durability and stress-test cycling protocols specific to non-PGM catalysts, (including a realistic potential/voltage window under specific environmental conditions of humidity, reagent stoichiometry, etc.).

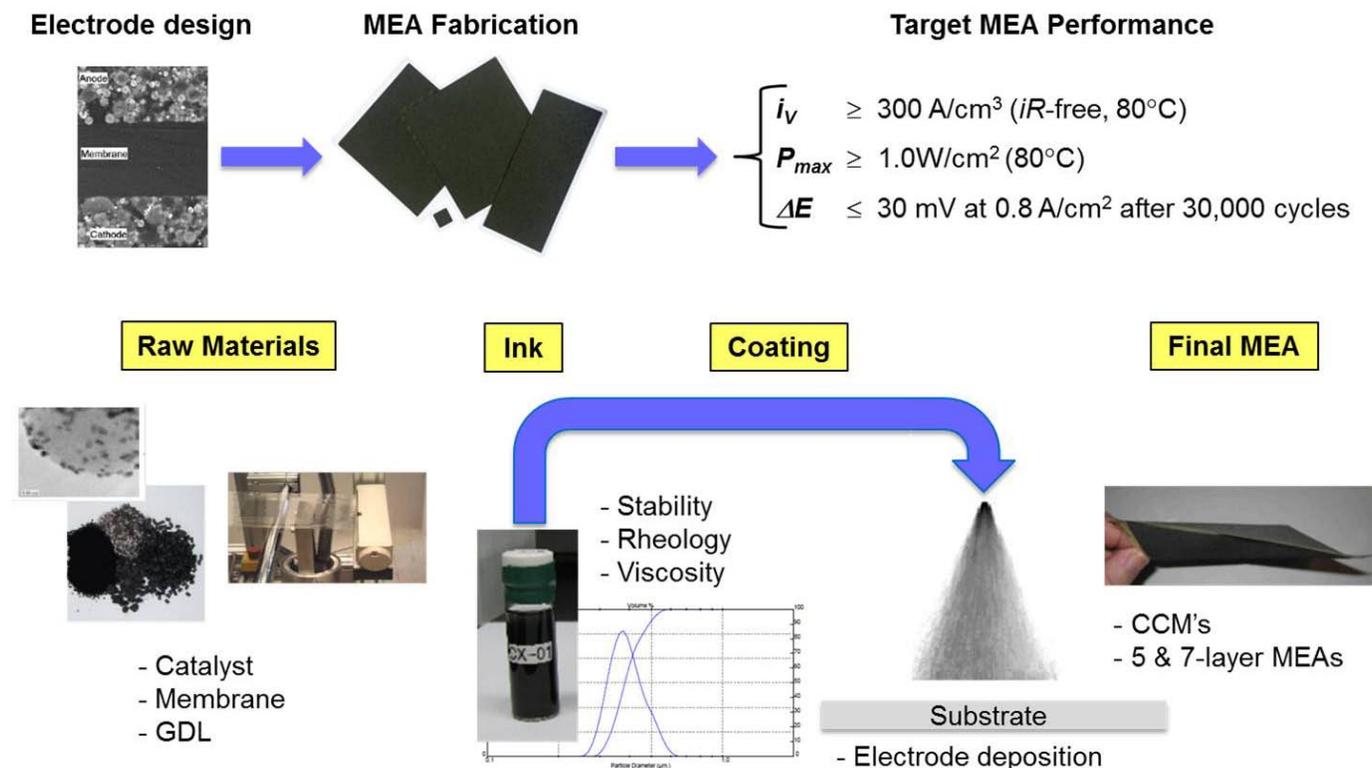


FIGURE 5. A scheme of MEA fabrication with targets.

Characterization:

- Validation of the surface-probe approach for the ORR active-site identification.
- Full implementation of advanced catalyst characterization methods (NRVS, magnetic circular dichroism, Mößbauer, MES, low-voltage aberration-corrected scanning transmission electron microscopy, high-resolution scanning electron microscopy/scanning transmission electron microscopy, inductively coupled plasma, X-ray fluorescence, nano-X-ray computer tomography, X-ray absorption, thermogravimetric analysis, porosimetry, etc.) in non-PGM catalysis studies.

Electrode Design and Modeling:

- Initiation of the predictive model for non-PGM catalyst layers (ORR activity, conductivity, and O₂ transport); validation of the preliminary model.
- Adoption of the agglomerate model to non-PGM cathodes.
- Complete implementation of the pore-scale model.
- Fabrication of MEAs with optimized microstructure and morphology.
- Demonstration of Generation-1 spray-coated MEA with non-PGM cathode.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Piotr Zelenay, The Electrochemical Society Energy Technology Division Research Award, The Electrochemical Society Meeting, Toronto, Canada, May 2013.

FY 2013 PUBLICATIONS (SINCE APRIL 2013)

1. G. Wu, K.L. More, P. Xu, H.-L.Wang, M. Ferrandon, A.J. Kropf, D.J. Myers, S. Ma, C.M. Johnston, P. Zelenay, A Carbon-Nanotube-Supported Graphene-Rich Non-Precious Metal Oxygen Reduction Catalyst with Enhanced Performance Durability, *Chem. Commun.*, **49**, 3291-3293, 2013.
2. G. Wu, P. Zelenay, Nanostructured Non-Precious Metal Catalysts for Oxygen Reduction Reaction., *Acc. Chem. Res.*, doi:10.1021/ar400011z, 2013.
3. H.T. Chung, J.H. Won, P. Zelenay, Active and Stable Carbon Nanotube/Nanoparticle Composite Electrocatalyst for Oxygen Reduction. *Nat. Commun.*, doi:10.1038/ncomms2944, 2013.

FY 2013 PRESENTATIONS (SINCE APRIL 2013)

1. Hydrogen and Fuel Cells Zing Conference 2013, Silverado Resort and Spa, Napa, California, July 12–15, 2013. Title: “Nanostructure vs. Reactivity of Non-Precious Metal Oxygen Reduction Catalysts;” H. T. Chung, G. Wu and P. Zelenay (invited lecture).
2. First International Conference on Electrochemical Materials and Technologies for Clean Sustainable Energy, Guangzhou, China, July 5–9, 2013. Title: “The Effect of Carbon Derived from Different Nitrogen Precursors on Oxygen Reduction Activity of Non-Precious Metal ORR Catalysts;” P. Zelenay, G. Wu, Q. Li, H.T. Chung (invited keynote lecture).
3. U.S. Department of Energy, Energy Efficiency and Renewable Energy, Fuel Cell Technologies Program, 2013 Merit Review and Peer Evaluation Meeting, Arlington, VA, May 13–17, 2013. Title: “Non-Precious Metal Fuel Cell Cathodes: Catalyst Development and Electrode Structure Design;” P. Zelenay (delivered by R. Borup) (DOE invited poster presentation).

REFERENCES

1. *Multi-Year Research, Development and Demonstration Plan: Section 3.4 Fuel Cells*, Fuel Cell Technologies Program, 2011. http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf
2. G. Wu, P. Zelenay, Nanostructured Non-Precious Metal Catalysts for Oxygen Reduction Reaction, *Acc. Chem. Res.*, doi:10.1021/ar400011z, 2013.