

V.C.9 Novel Approach to Non-Precious Metal Catalysts

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Objectives

Develop new, lower-cost non-precious metal (NPM) cathode catalysts for replacement of Pt in proton exchange membrane (PEM) fuel cells that will:

- Reduce dependence on precious metals,
- Perform as well as conventional precious metal catalysts currently in use in membrane electrode assemblies (MEAs), and
- Cost 50% less compared to a target of 0.2 g Pt/peak kW.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Cost
- (C) Electrode Performance

Technical Targets

This project is directed at the development of NPM catalysts synthesized by processes that are amenable to scale-up. This project will develop a solid fundamental knowledge necessary for the synthetic effort while at the same time providing a platform for scale-up of the most promising new catalysts. If successful, the project will address the following DOE technical targets as outlined in the HFCIT Multi-Year RD&D Plan:

3M Progress Toward Meeting DOE Targets for Non-Precious Metal Catalysts

Parameter	DOE 2010 Target	3M Status (50 cm ² FC)
Non-Pt Catalyst Activity per volume of supported catalyst at 800 mV _{IR-free} (A/cm ³)	> 130	19

Accomplishments

- Achieved performance exceeding state-of-the-art NPM catalyst activity reported in the literature with 50-cm² samples made by scalable processes.
 - Volumetric current density of 19 A/cm³ surpasses 2004 status value reported by DOE (8 A/cm³ at 0.8 V).
 - Met interim performance milestone #2 (0.08 A/cm² at 0.6 V) and #3 (0.1 A/cm² at 0.7 V).
- Fabricated new higher surface area, thermally stable substrates for use with the vacuum approach. Achieved activity surpassing the best previous result by over an order of magnitude.
- Started integration of the two synthetic approaches—vacuum processes and nanotechnology.
- Made advances in testing, characterization, and modeling that provide valuable feedback for materials development.
 - Introduced rotating-ring disk electrode (RRDE) studies and routine durability testing.
 - Expanded ultraviolet photoelectron spectroscopy (UPS)/x-ray adsorption spectroscopy (XAS) catalyst characterization to include the “model” catalyst.
 - Modeled catalytic site in more realistic synthesis environment.

Introduction

Replacing platinum as a catalyst in fuel cells in general and in PEM fuel cells in particular has long been an industry goal. Well-known drawbacks of using platinum as a catalyst are its price and scarcity. An additional, fundamental limitation is that the use of platinum makes the fuel cell operation energy inefficient. At high voltages, platinum reacts with water or with oxygen [1], producing an oxide layer that inhibits its catalytic activity in the oxygen reduction reaction (ORR). Developing a suitable replacement could contribute significantly to fuel cells becoming widely accepted.

This project is directed at reducing the dependence of PEM fuel cell catalysts on precious metals in order to reduce the cost of the fuel cell stack as well as the overall system cost without loss of performance or durability. To achieve these objectives, the project has been focused on developing NPM catalysts that should: exhibit high inherent catalytic activity for oxygen reduction; have high volumetric concentration of active catalyst centers at the catalyst/membrane interface; demonstrate high stability with respect to reversible and irreversible processes such as corrosion; be fabricated by processes compatible with high-volume manufacturability; and take into account that the total cost of the catalysts includes the processing costs for their synthesis and integration into an MEA.

Approach

To achieve the project objectives, new NPM catalysts are being developed by utilizing the infrastructure for, and understanding of, catalysts generated by previous and concurrent 3M/DOE cooperative agreements and 3M's commercial program. This includes, in particular, high transition metal (TM)/low Pt catalysts, 3M's unique nanostructured thin film (NSTF) substrate [2], 3M nanotechnologies, and processes compatible with high-volume manufacturability. Initial efforts were focused on exploring new ways of fabricating Fe-N-C moieties as "model catalysts" [3]. Once sufficient understanding was gained on the model catalysts, the effort was expanded to the development of new catalyst constructions and synthetic methods. The synthesis methods include a wide variety of vacuum deposition techniques on a range of substrates and a nanotechnology-based technique, which involves making dispersed catalysts on high-stability carbon supports. The two synthetic methods work interactively—insights from one method are extended to the other. Catalysts are then integrated into MEAs and tested as 50-cm² fuel cells. Extensive physicochemical analytical characterization is performed while, simultaneously, modeling guides and verifies the synthetic effort.

Results

In the past year, the main focus remained exploration of new materials and synthetic routes to produce candidate NPM catalysts. Electrochemical characterization continued to be performed in a 50-cm² fuel cell (FC), but the effort was expanded to durability testing in the FC environment as well as fundamental characterization of the catalyst using the rotating-ring disk electrode (RRDE). Advanced physicochemical characterization, including UPS and XAS, continued and was expanded to the model catalyst prepared by Dodelet's group (INRS-Energie, Matériaux et Télécommunications, Varennes, Quebec, Canada). The modeling effort focused on mimicking the spectra obtained from UPS.

Approximately 160 catalysts were synthesized, characterized and tested as 50-cm² FCs during the past year. Higher performance continued to be obtained by making dispersed catalysts on high surface area, high stability carbon supports as part of the nanotechnology approach. Performance on these materials has improved around an order of magnitude at 0.6 V in the past year. As an example of the work that has been done, Figure 1A shows the cyclic voltammograms (CVs) under nitrogen for catalysts derived from two structurally related isomers, precursors X and Y, and a mixture of the two (X + Y). The polarization curves under oxygen are shown in Figure 1B. The performance scales with the apparent surface area determined from the charge of the CVs recorded under nitrogen and the content of the more active component.

Precursor Y was used as the starting point for the synthesis of an entire family of catalysts. The ORR activity of this family is presented in Figure 2. The different markers represent variations in the chemistry used to synthesize the catalyst. The open markers have been subjected to a physical post-treatment. Iron content of the post-treated catalysts was approximately 10 micrograms/cm². Note that the open circuit voltage of the best-performing catalyst is greater than 0.9 V and the Tafel slope is similar to that of Pt (~70 mV/decade). This family showed the highest performance on the project to date and several samples fulfilled the project's interim performance milestone (0.1 A/cm² at 0.7 V) indicating a large processing window.

Durability testing under air was routinely carried out on better performing catalysts. Many of the higher performing catalysts were not very robust. However, changes to the catalyst loading and certain additives were found to improve durability. These insights will be exploited to try to further increase durability.

In the area of vacuum synthesized catalysts, performance increased substantially with the introduction of new, higher surface area substrates. Several new substrates have been fabricated. One

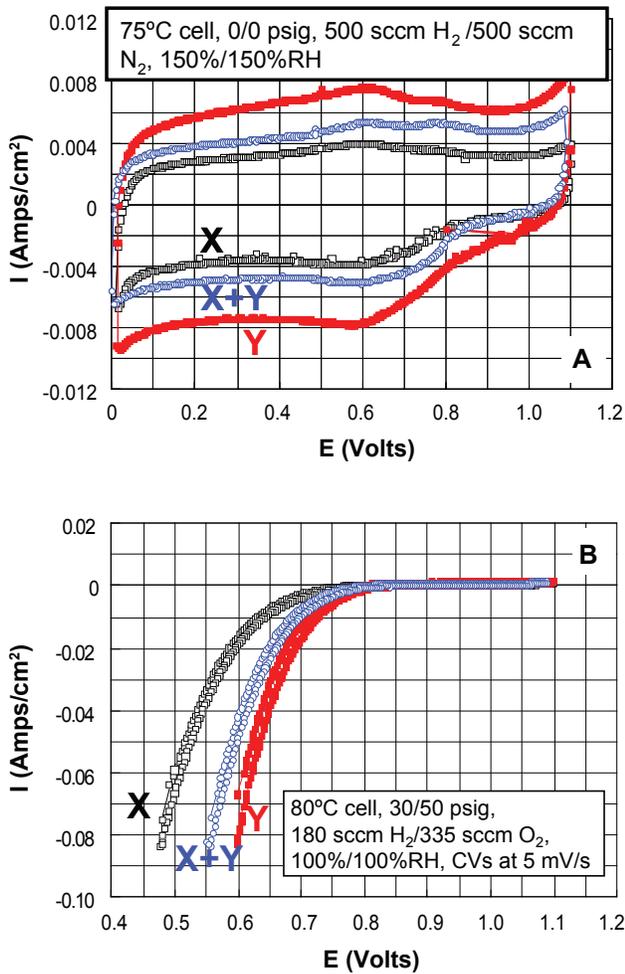


FIGURE 1. Characterization of catalyst derived from two structurally related isomers, precursors X and Y, and a mixture of the two (X + Y). A) CVs under nitrogen at 50 mV/s and B) polarization curves under oxygen. Note that the activity of the catalyst follows the content of precursor Y.

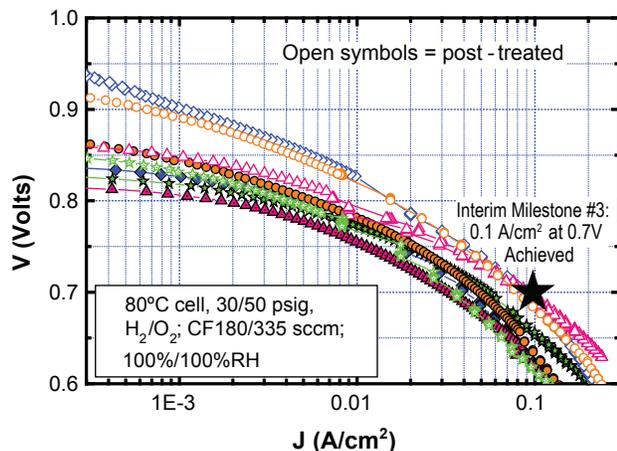


FIGURE 2. Performance of a family of catalysts derived from precursor Y. The open markers represent catalysts that have been subjected to a further post-treatment.

example of the characteristics of these new substrates is depicted in Figure 3. Figure 3A shows CVs under nitrogen for an unmodified carbon fabric substrate and this same material after modifications (new substrate A). Substrate A exhibits a surface area enhancement of several orders of magnitude relative to the unmodified substrate. Polarization curves of performance under oxygen at various points in the synthetic process (bare substrate A, substrate A modified with iron) and the finished catalyst (substrate A modified with iron and subsequently thermally treated) are presented in Figure 3B. Performance of the finished catalyst is over an order of magnitude better than the previous best vacuum sample.

Multiple series of vacuum deposited Fe-C-N compositions were produced and tested using a high-throughput approach in collaboration with Dalhousie University. As reported last year, the area of stability

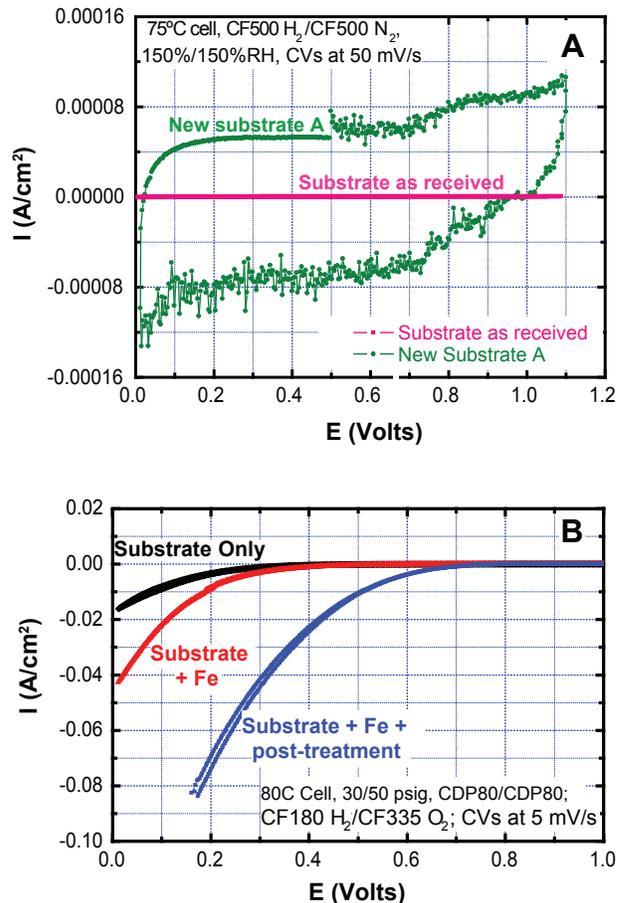


FIGURE 3. A) Cyclic voltammograms under nitrogen for an unmodified carbon fabric substrate and new substrate A made by modifying the same carbon fabric. B) Polarization curves obtained at various points in the synthetic process (substrate A and substrate A modified with Fe) and the finished catalyst (substrate A modified with Fe and thermally post-treated).

had been assessed by a test in liquid acid. In order to activate the material, a thermal treatment step was added to the synthetic process. RRDE studies were performed to assess ORR activity. The area of the Fe-C-N phase diagram that is both stable in acid and ORR active was defined [4].

On the modeling effort, work continued using both semiempirical (Austin Model 1) and ab initio (Vienna ab initio simulation package, VASP) techniques to establish the most thermodynamically stable Fe-C-N configuration. As reported last year, NC-Fe-NC was found to be the lowest energy in the absence of hydrogen. However, the Dodelet model catalyst

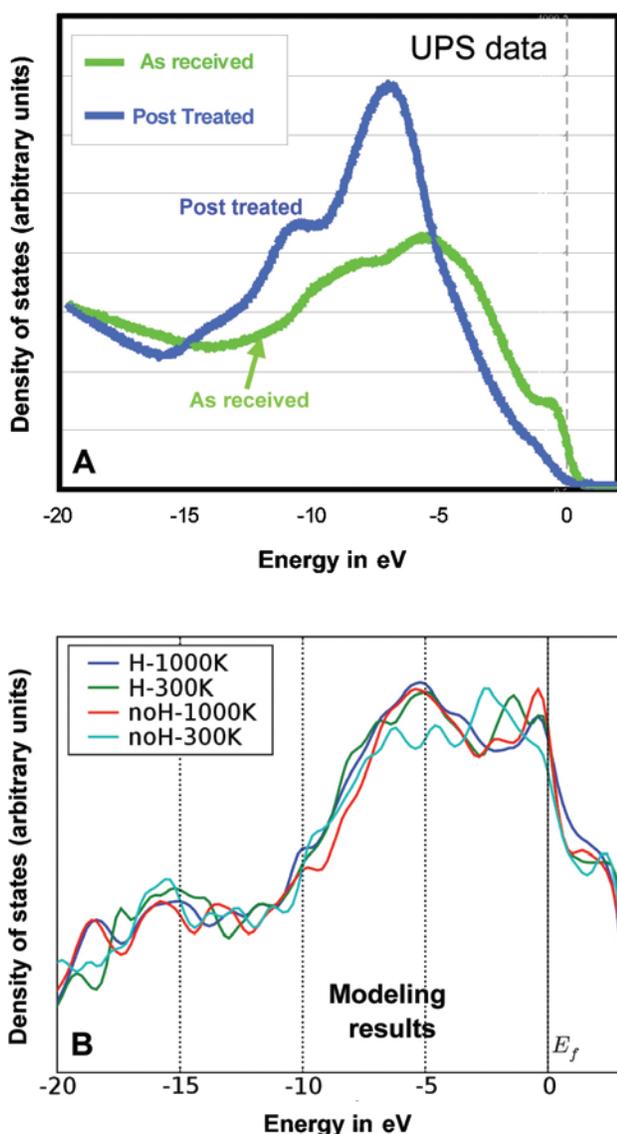


FIGURE 4. A) Ultraviolet photoelectron spectra for a vacuum deposited catalyst as received and after thermal post-treatment. B) Calculated modeling results assuming hydrogen present (H) or hydrogen absent (no H) in the structure and the atoms quenched to two different temperatures (300K and 1000K).

structure (CN-Fe-NC) was found to be the lowest in energy in the presence of hydrogen [5].

A liquid quench method using VASP was used to simulate the experimentally measured UPS spectra. Structures formed by liquid-quenching are known to be similar to the ones obtained using vacuum deposition processes [6]. Figure 4A shows experimentally determined UPS spectra for a vacuum deposited Fe-C-N catalyst with and without a thermal post-treatment. The calculated modeling results from this system are presented in Figure 4B. While the overall density-of-state curves obtained via modeling look similar, there are differences in the states around the Fermi level depending on the presence of hydrogen and the quench temperature. Both the high (1000K) and low (300K) temperature quench in Figure 4B correspond well with the as-received experimental data in Figure 4A. The high temperature quench (Figure 4B) does not yield a spectrum similar to that experimentally obtained with a high temperature post-treatment (Figure 4A).

Conclusions and Future Directions

Performance has improved an order of magnitude in the past year on both vacuum and nanotechnology approaches and interim performance milestones have been achieved. Figure 5 summarizes the best NPM activity achieved on this project in relation to state-of-the-art Pt [7] and the DOE non-platinum activity targets. Ink formulation or coating optimization may make the NPM electrode layer thinner, leading to further gains in volumetric current density.

While performance has improved substantially, further gains must be made in durability. Performance and durability will be worked on in parallel with a goal of better performing, more durable catalysts.

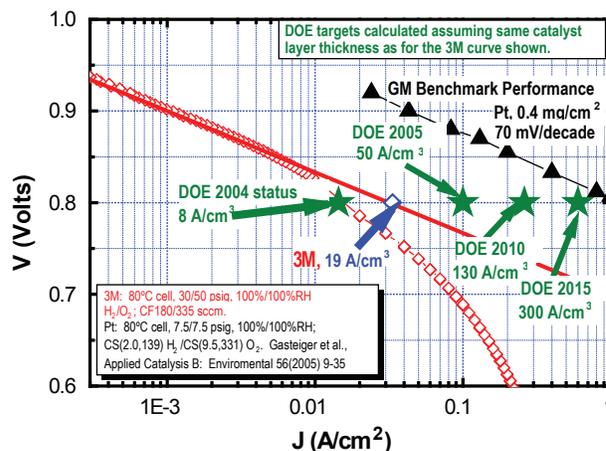


FIGURE 5. Polarization curve from the best performing nanotechnology catalyst as compared to state-of-the-art Pt [7]. DOE targets for non-platinum catalyst activity are calculated assuming an electrode layer thickness equal to that of the NPM catalyst presented in the figure.

Strong, fully-integrated collaborations supplement 3M expertise in advanced characterization and modeling leading to fundamental understanding of the catalyst. This work will continue with an aim of identifying the active site.

FY 2006 Publications/Presentations

1. M. Jain, S.-H. Chou, A. Siedle, "In Search for Structure of Active Site in Iron-Based Oxygen Reduction Electrocatalysts," *J. Phys. Chem. B*, 110 (2006) 4179-4185.
2. E. B. Easton, D. A. Stevens, T. Buhrmester, D.G. O'Neill, R.T. Atanasoski and J. R. Dahn, "A Study of Vacuum Deposited Fe-C-N Based Catalysts For Oxygen Reduction," 208th Meeting of The Electrochemical Society, Los Angeles, CA, Oct. 16-21, 2005.
3. M. Jain, "Non-Precious Metal Catalysts for PEM Fuel Cells" (*Invited*), Workshop on Computational Materials and Molecular Electronics, Austin, TX, Oct. 20-22, 2005.
4. R. Atanasoski, "Recent Advances in the 3M MEA Technology for PEMFC: The Catalysts: Low Platinum and Non-Precious Metal Catalysts" (*Invited*), Keynote Lecture at the International Conference on "New Proton Conducting Membranes and Electrodes for PEMFCs," in Honor of Prof. G. Alberti, Assisi, Italy, Oct. 22-26, 2005.
5. D. G. O'Neill, A. Schmoeckel, G. Vernstrom, D. O'Brien, M. Jain, R. Atanasoski, E. B. Easton, T. Buhrmester, J. Dahn and D. Wieliczka, "Vacuum Deposited Non-Precious Metal Catalysts for PEM Fuel Cells" (*Invited*), MRS Meeting, Session A3: Fuel Cells, Electrodes and Solid Oxide Fuel Cells, Boston, MA, Nov. 28-Dec. 02, 2005.
6. M. Jain, S.-H. Chou, A. Siedle and D. G. O'Neill, "Theoretical Modeling of Non-Precious Metal Catalysts for PEM Fuel Cells," MRS Meeting, Session A3: Fuel Cells, Electrodes and Solid Oxide Fuel Cells, Boston, MA, Nov. 28-Dec. 02, 2005.
7. E. B. Easton, A. Bonakdarpour, J. R. Dahn, "Sputtered Fe-C-N Oxygen Reduction Catalysts," *Electrochem. Solid-State Lett.* (accepted).
8. R. Yang, A. Bonakdarpour, J. R. Dahn, "Investigation of Sputtered Ta-Ni-C as an Electrocatalyst for the Oxygen Reduction Reaction," submitted to *J. Electrochem. Soc.*
9. E. B. Easton, R. Yang, A. Bonakdarpour, J. R. Dahn, "Thermal Evolution of the Structure and Activity of Magnetron Sputtered TM-C-N (TM = Fe, Co) Oxygen Reduction Catalysts," submitted to *Electrochem. Solid-State Lett.*
10. E. B. Easton, A. Bonakdarpour, D. A. Stevens, J. R. Dahn, "Sputtered Fe-C-N Based Oxygen Reduction Catalysts," 89th Canadian Chemistry Conference and Exhibition, Halifax, NS, May 2006.
11. R. Yang, A. Bonakdarpour, J. R. Dahn, "Investigation of Sputtered Ta-Ni-C as an Electrocatalyst for the Oxygen Reduction Reaction," 89th Canadian Chemistry Conference and Exhibition, Halifax, NS, May 2006.
12. 2006 DOE Hydrogen Program Review, Washington, D.C., May 16-19, 2006.

References

1. C. H. Paik, T. D. Jarvi, W. E. O'Grady, *Electrochem. Solid-State Lett.*, 7 (2004) A82.
2. M. K. Debe, "Novel catalysts, catalyst support and catalyst coated membrane methods," in Handbook of Fuel Cells, Fundamentals, Technology and Applications, Vol. 3, eds. W. Vielstich, A. Lamm and H. Gasteiger, John Wiley and Sons (2003), p. 576.
3. M. Lefevre, J. P. Dodelet, *J. Phys. Chem. B*, 104 (2000) 11238.
4. E. B. Easton, A. Bonakdarpour, J. R. Dahn, *Electrochem. Solid-State Lett.* (accepted).
5. M. Jain, S.-H. Chou, A. Siedle, *J. Phys. Chem. B*, 110 (2006) 4179.
6. A.R. Merchant, D. R. McKenzie, D. G. McCulloch, *Phys. Rev. B*, 65 (2001) 024208.
7. H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, *Applied Cat. B: Environ.*, 56 (2005) 9.