

V.E.1 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).
- 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 of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

- (B) Cost
- (C) 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:

TABLE 1. 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 durability of over 1,000 hours with practically no irreversible performance losses (testing stopped; cell still fully operational)
 - Activity comparable to state-of-the-art NPM catalysts as reported in the literature.
 - Tested at 0.65 V under hydrogen-air in 50-cm² fuel cell.
- Reached catalytic activity of 0.1 A/cm² at 0.77 V, approaching Interim Milestone #5 (0.1 A/cm² at 0.8 V).
- Fabricated higher surface area, thermally stable substrates for use with the vacuum approach.
- Achieved activity surpassing the best previous result by a factor of four.
- Made advances in testing, characterization, and modeling that provide valuable feedback for materials development.



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: (1) exhibit high inherent catalytic activity for oxygen reduction; (2) have high volumetric concentration of active catalyst centers at the catalyst/membrane interface; (3) demonstrate high stability with respect to reversible and irreversible processes such as corrosion; (4) be fabricated by processes compatible with high-volume manufacturability; and (5) 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) electrocatalysts [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 and, in the latest phase of the project, non-carbon supports. The two synthetic methods work interactively—insights from one method are extended to the other. Catalysts are then assembled 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 on exploration of new materials and synthetic routes to produce high performing, high durability NPM catalysts. Electrochemical characterization continued to be performed in a 50-cm² fuel cell (FC), but the effort was mainly directed towards durability testing in the FC environment.

Over 100 catalysts were synthesized, characterized and tested as 50-cm² FCs during the past year. Last year we reported on the high performance obtained by making dispersed NPM catalysts on high surface area, high stability carbon supports as part of the nanotechnology approach. The high performance of these materials was achieved by using two structurally related isomers, 2- and 4- nitroaniline as precursors. The polarization curves under oxygen of the catalyst obtained from 4- nitroaniline were superior and therefore this precursor was used as the starting point for the synthesis of an entire family of catalysts. These NPM catalysts 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), with an open circuit voltage of the best-performing catalysts greater than 0.9 V and a Tafel slope similar to that of Pt (~70 mV/decade).

However, being supported on carbon, all these catalysts suffered a lack of durability; in a matter of several tens of hours of testing under air, the performance of the catalysts falls to below 10% of the original. While changes to the catalyst loading and certain additives were found to increase durability, the improvements were not sufficient. Therefore, materials different than dispersed carbon, conducting and electrochemically stable in a fuel cell environment, were introduced as catalyst supports. Additional considerations for the substrate materials were their cost and availability. The classes of materials we have considered fall in the category of carbides, silicides, nitrides and their combinations, representative examples of which are the carbides and the silicides of titanium.

Figure 1 presents the 1,000+ hour durability test of a catalyst derived from a 4- nitroaniline as precursor and applied on titanium carbide as a substrate. No irreversible loss of performance during the test was noticed. To our knowledge, this is the longest durability test of a non-precious metal catalyst performed in a real PEM FC to date. Note that the durability test was run under air and at 0.65 V, which is within the useful voltage range for PEM FCs. The test procedure was standardized as follows:

- Testing conditions: 75°C cell, 500 sccm H₂/500 sccm air (30/30 psig), 100%/100% relative humidity (RH).
- Potentiostatic polarization at 0.65 V for 5 hours.
- After 5 hours at 0.65 V, polarization curves were measured under the same conditions as above.
- The previous two steps were continuously repeated.
- Periodically, testing was stopped for recording baseline cyclic voltammograms (CVs) under nitrogen and for AC impedance measurement.

In Figure 2 the performance characteristics of the TiC supported catalyst after the 1,000 hours of testing

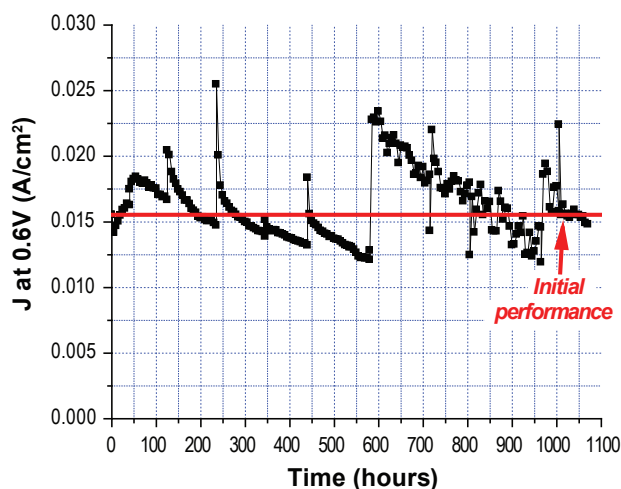


FIGURE 1. Durability test (1,000-hour) of NPM catalyst on TiC support: 50-cm² FC, 75°C; 500 sccm H₂/500 sccm air, 100%/100%. Current measured at 0.6 V after 5 hour hold at 0.65 V. Note that the test was stopped while cell was still fully operational.

is presented. This performance is exactly the same as at the beginning of the durability test. In addition, the polarization curve coincides with the recently published data for state-of-the-art performance and durability by non-precious metal catalysts [4]. However, this performance is a factor of four lower than the best achieved by the catalysts we have produced from the same precursor on carbon substrate indicating that the surface area of TiC substrate and/or the number of catalytic active sites on the surface of the TiC substrate have to be improved.

In order to elucidate the role and potentially the contribution of the TiC itself to the catalytic activity towards the ORR, a sample of TiC underwent the same preparation procedure and thermal treatment as used for making the catalyst, however, without the catalyst precursor. The results are presented in Figure 3. The cyclic voltammograms obtained while the catalyst side was under nitrogen (Figure 3A) indicate that the surface area of the catalyst covered TiC is a factor of four larger than bare TiC. However, while TiC has a rather appreciable catalytic activity towards the ORR, its activity contributes approximately less than 1% to the total activity of catalyst coated TiC, which is three to four orders of magnitude higher (Figure 3B).

In addition to the long-term durability testing under normal operational FC conditions, both the substrate materials and the catalyst coated substrates were exposed to voltages up to 1.5 V. No appreciable changes were observed in the CVs (recorded under nitrogen) or in the AC impedance spectra (recorded under hydrogen) after the high voltage exposures on any of the substrates or the catalysts. The FC polarization curves recorded before and after the exposure were also identical.

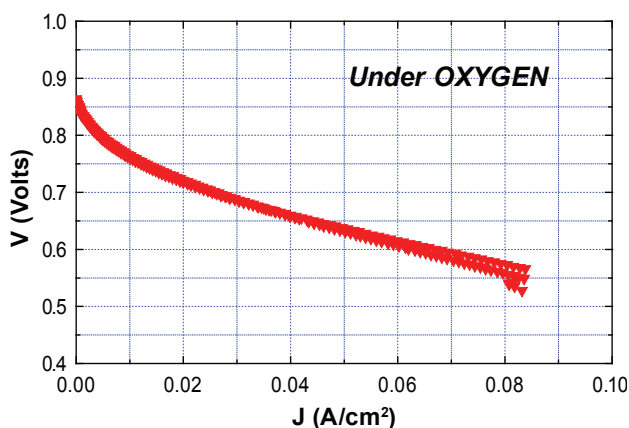


FIGURE 2. Performance of NPM catalyst on TiC support after 1,000-hour durability test: 50-cm² FC, 80°C, 30/30 psig, 560 sccm H₂/1000 sccm O₂, CDP 90°C/CDP 80°C.

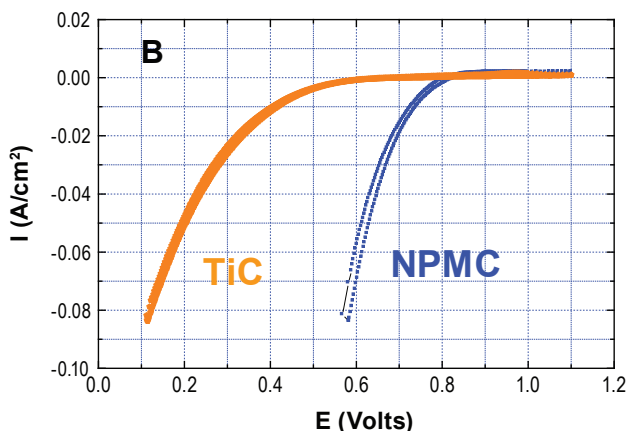
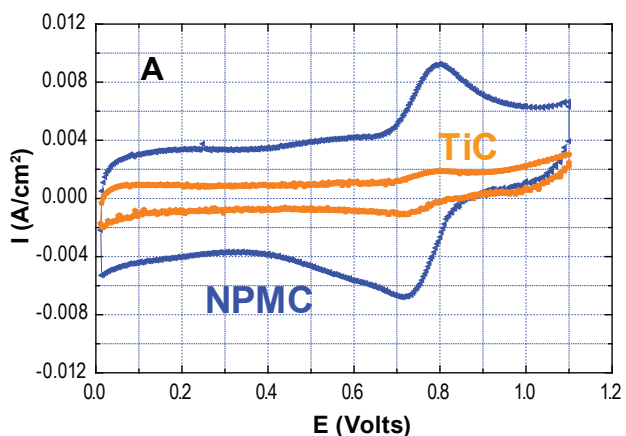


FIGURE 3. The influence of TiC as a catalyst support on the performance of the NPM catalyst. A) Cyclic voltammograms (50 mV/s) under nitrogen for TiC substrate (inner curve) and NPMC covered TiC. B) FC polarization curves under oxygen.

The strategy in the area of vacuum synthesized catalysts was to increase the performance further by introducing new, higher surface area substrates [5]. In Figure 4 the improvements achieved during this year are presented. Figure 4A shows CVs under nitrogen for the best performing vacuum produced catalyst in 2006 and in 2007. Under the assumption that the nature of the two surfaces is the same, the new substrate shows an increase in surface by a factor of seven. This is reflected in the polarization curves recorded under oxygen where an improvement of approximately an order of magnitude was observed (Figure 4B).

The nature of the activity of vacuum deposited catalyst was addressed by the high-throughput approach in collaboration with Dalhousie University. The thermal treatment step that is necessary in order to activate the as-deposited catalyst material induces a reduction in nitrogen content. The loss of nitrogen is at the same time accompanied by a transition from homogeneity to heterogeneity in the material structure which is reflected

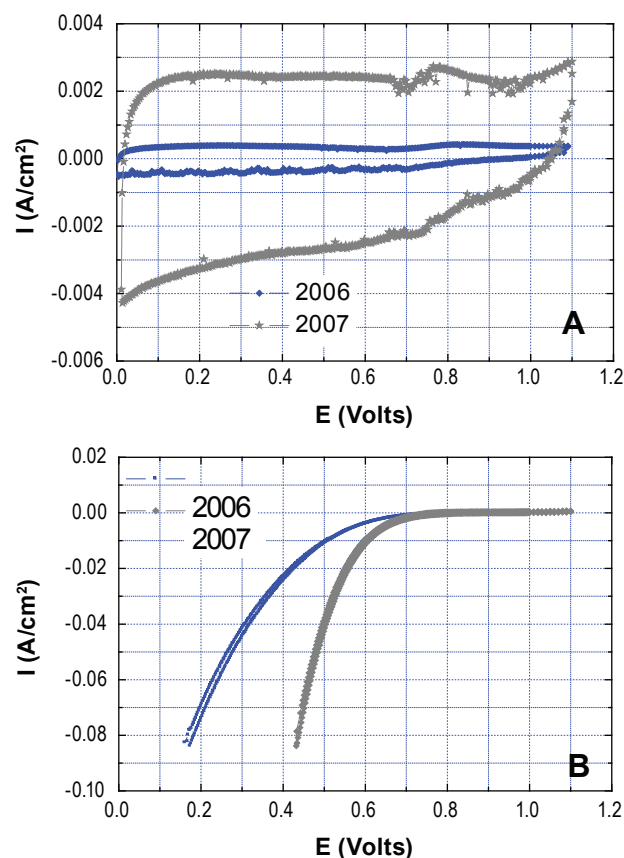


FIGURE 4. The influence of the surface area of the substrate (A) on the performance of the vacuum-deposited NPM catalyst (B). A) Cyclic voltammograms (50 mV/s) under nitrogen for substrates (inner curve: 2006 status). B) FC polarization curves under oxygen (left curve: 2006 status); 50-cm² FC, 80°C, 30/50 psig, 180 sccm H₂/335 sccm O₂, CDP 80°C/CDP 80°C.

by the ORR activity as measured by rotating disk electrodes [6].

In the modeling area, *ab initio* molecular dynamics studies using VASP were undertaken to further understand the effect of temperature on the structures formed during vacuum deposition. A liquid quench method was used [7] as discussed in the previous report [5]. Studies were done at three temperatures – 1,500 K, 1,000 K and 300 K. It was found that an increase in temperature decreases the Fe-C coordination number, while the presence of H in the system increases the coordination number. For Fe-N coordination neither temperature nor the presence of H has an effect on the coordination number [5].

Conclusions and Future Directions

Today, 3M's catalysts are among the best performing and most durable NPM catalysts tested in a real fuel cell:

- In 2007, a major breakthrough in durability was achieved.
- Overall, the project established new synthetic approaches and opened new avenues for further development in the NPM catalyst world.
- Strong interactive advanced characterization and modeling complement the synthetic effort.
- Strong, fully-integrated collaborations supplemented 3M expertise and lead to fundamental understanding of NPM catalysts.
- Thirteen publications and presentations, including four invited lectures were delivered.

For the remainder of the project, we will fulfill reporting obligations, most notably the final report, and prepare manuscripts for publication and conference presentations.

As for future directions, we will explore further the area of more durable catalyst substrates and more active catalytic sites. (This effort will continue at 3M after completion of the project.)

FY 2007 Publications/Presentations

1. 2007 DOE Hydrogen Program Review - Washington, D.C. - May, 2007. Presentation FC# 4.
2. V.C.9 - Non-Precious Metal Catalysts, DOE Hydrogen Program FY 2006 Progress Report.
3. E. B. Easton, A. Bonakdarpour, J. R. Dahn, "Sputtered Fe-C-N Oxygen Reduction Catalysts," *Electrochem. Solid-State Lett.* **9** (10) A463 – A467 (2006).
4. 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," *Electrochem. Solid-State Lett.* **10** (1) B6 – B10 (2007).

5. R. Yang, Arman Bonakdarpour and J.R. Dahn, "Investigation of Sputtered Ta-Ni-C as an Electrocatalyst for the Oxygen Reduction Reaction", *J. Electrochem. Soc.* 154, B1-B7 (2007).
6. E. B. Easton, A. Bonakdarpour, R. Yang, D. A. Stevens, D. G. O'Neill, G. Vernstrom, D. P. O'Brien, A. K. Schmoeckel, T. E. Wood, R. T. Atanasoski, J. R. Dahn, "Thermally Treated Fe-C-N Oxygen Reduction Catalysts Prepared by Vacuum Deposition," *ECS Transactions*, Vol. 3, 2006, Issue 1, 241 – 248.
7. R. Yang, J. R. Dahn, A. Bonakdarpour, E. B. Easton, "Co-C-N Oxygen Reduction Catalysts Prepared by Combinatorial Magnetron Sputter Deposition," *ECS Transactions*, Vol. 3, Issue 1, 2006, 221 – 230.
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9. R. Atanasoski: "Low platinum and non-precious metal catalysts for PEM fuel cell application", 233rd Am. Chem. Soc. Meeting, Nanoscale Inorganic Catalysis Session, Chicago, March 2007. (*Invited*)
10. R. Yang, K. Stevens, A. Bonakdarpour, and J.R. Dahn, "Dependence of the Activity of Sputtered Co-C-N ORR Catalysts on Heat-treatment Temperature", submitted to *J. Electrochem. Soc.* (2007).
11. R. Atanasoski: "Non-Precious Metal Catalysts for PEM Fuel Cell Application", XVIth International Symposium on the Reactivity of Solids, Minneapolis, USA, June 3–6, 2007. (*Invited*)
12. R. Atanasoski: "Can Platinum Be Replaced in PEM Fuel Cells? And When?", **International Conference on "Polymer Batteries-Fuel Cells, PBFC-2007"** in occasion of Professor Scrosati's 70th Birthday, Rome, Italy, June 11–15, 2007. (*Invited*)
13. R. Atanasoski: "High performance platinum and non-precious metal catalysts for PEM fuel cell application", Dept. Of Chemistry Seminar, Univ. of Padova, Italy, June 20, 2007.

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