

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

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Dalhousie University, Halifax, N.S., Canada

Collaborators:

Brookhaven National Laboratory

University of Missouri, Kansas City, MO

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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 (Pt)
- 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
- Demonstrate durability of >2000 hours with <10% power degradation

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section 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. The 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, by 2015 the new catalyst should

- Substantially reduce the dependence of PEM fuel cells on platinum
- Cost 50% less than Pt-based catalysts at the DOE target loading of 0.2 g Pt/peak kW

Approach

- Synthesize NPM catalysts using two complementary approaches amenable to high-volume manufacturability:
 - Vacuum process technologies
 - Nanotechnology: Dispersed catalyst on high-stability carbon substrate
- Guide and verify synthetic efforts with modeling work.
- Analyze materials via physicochemical methods both at 3M and in collaboration with National Laboratories and universities.
- Form catalysts into MEAs and evaluate as 50-cm² fuel cells.
- Scale up selected catalysts for stack testing.

Accomplishments

- Implemented new nanotechnology-based synthesis approach and demonstrated that it has significant potential for this application.
- Achieved catalytic activity orders of magnitude higher than previously reported on this project.
- Gained new insights into catalytic sites from modeling and state-of-the-art characterization/analytical techniques.
- Identified most thermodynamically favorable CN_xFe sites by modeling.
- Addressed and developed understanding of catalyst high impedance issue.
- Established compositional areas of stability of vacuum-deposited CN_xFe catalyst.

Future Directions

- Direct the synthetic effort towards achieving the project's interim milestone performance of 0.1 A/cm² at 0.6 V.
- Implement the most recent findings by combining the two synthetic processes to reduce the high impedance and achieve a synergetic effect.
- In the nanotechnology process, combine the most promising nanoparticle precursors, pretreated substrates, application procedures, and thermal treatment processes.
- In the vacuum processes, utilize the advanced instrumental techniques and modeling effort for process parameter optimization.
- On the fundamental level, identify with more certainty the possible active sites via modeling. Continue and expand the effort to experimentally confirm/identify the nature of the new oxygen reduction reaction (ORR) catalysts.
- Characterize the best-performing catalysts for stability and peroxide generation.
- Downselect the catalyst for scale-up and 1- to 2-kW stack testing by March 2006.

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 either 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 a 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 synthesis methods. The synthesis methods include a wide variety of vacuum deposition techniques on a range of substrates and a new nanotechnology-based technique, which involves making dispersed catalysts on high-stability carbon supports. Catalysts are then transformed 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

The effort during the past year included the exploration of new materials as NPM catalysts and of post-treatments to enhance activity and stability under both the vacuum and the new nanotechnology synthetic methods. It also included a continuation of the modeling work. Besides the physicochemical and electrochemical techniques and testing procedures already in place [4], new techniques such as ellipsometry, X-ray adsorption spectroscopy (XAS), secondary ion emission spectroscopy (SIMS), and ultraviolet photoelectron spectroscopy (UPS) were utilized. Over 150 catalysts were synthesized, characterized, and tested in 50-cm² fuel cells during the past year.

Higher performance was observed with the samples made via the *nanotechnology* effort. Much of the work in this area has focused on adding new materials and post-treatment procedures to enhance the activity and the stability of the CN_xFe model system. The samples are made on a carbon substrate in fabric or particle form on which catalyst precursors are deposited and nitrogen sources are introduced, followed by a variety of thermal treatment procedures. An example is given here to illustrate this approach: the synthesis of catalysts based on two components, Fe and a second component denoted as S2. Electrochemically, the cyclic voltammograms (CVs) for the combination Fe/S2/C catalyst appear additive of the individual components as if no interaction between the two has taken place (Figure 1A). However, careful UPS studies reveal some interaction between the components in the form of mixed S2/Fe d-states and p-states (Figure 1B).

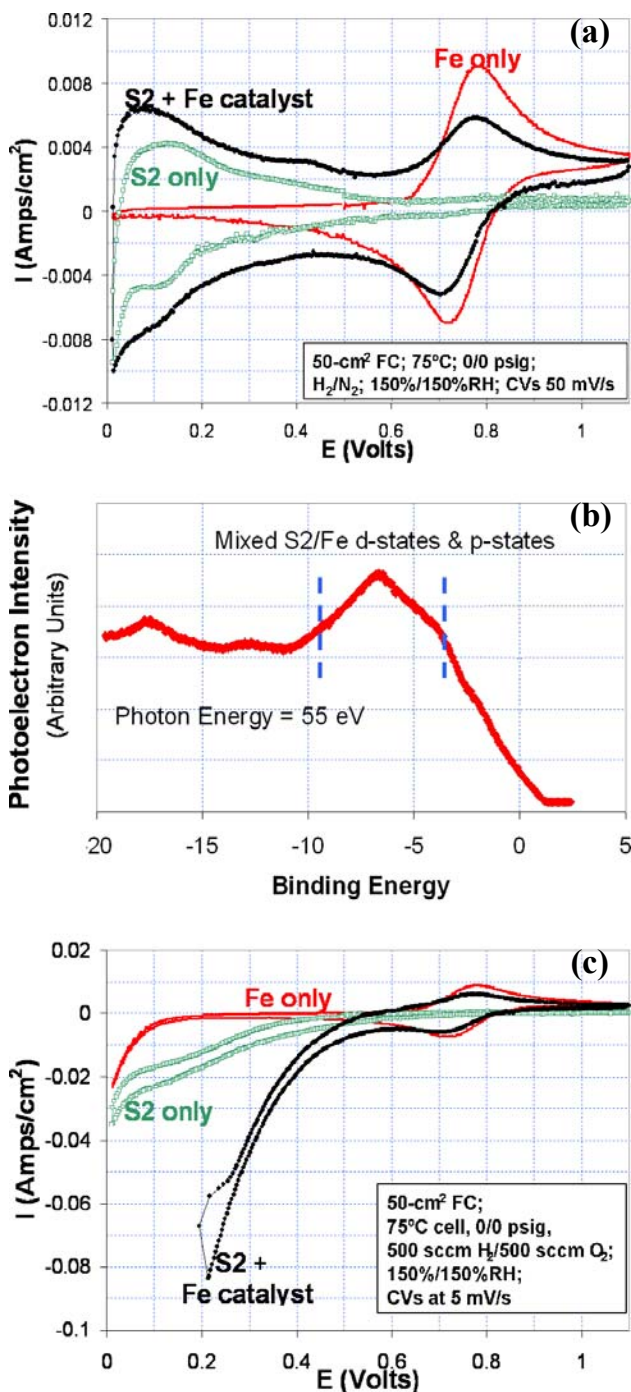


Figure 1. Characterization of Two-Component Catalyst Made via Nanotechnology Approach; Example Given for Fe and Substance S2 as Second Component: A) CVs (under nitrogen); B) UPS Spectra; C) Oxygen Reduction Polarization Curves

This interaction of Fe with S2 manifested itself in the oxygen performance measurements. The oxygen

reduction current of the Fe/S2/C catalyst is orders of magnitude enhanced relative to the single component baselines (Figure 1C).

The effect of catalyst loading for the Fe/S2/C system was also investigated. A linear relationship was found between the loading of catalyst, determined both by weight basis and X-ray fluorescent spectroscopy (XRF) measurements, and current density at 0.6 V. Evidence of increased loading was seen both by the CVs under nitrogen and the impedance under hydrogen. As expected, the high-frequency component of the impedance increased while the polarization resistance decreased with increased catalyst loading.

The performance of the *vacuum synthesized catalysts* has improved by an order of magnitude compared to the best results from a year ago [4]. The impedance also improved by a factor of 2.5, but remains high. Therefore, efforts have been taken to better understand the cause of the high impedance and to find methods to overcome it. Impedance values were found to depend on the type of substrate. A carbon cloth substrate gave lower impedance values than NSTF whiskers for an identical coating. Certain post-process treatments of the coated carbon substrates decreased the impedance further (Figure 2A). Oxygen response increased as the impedance decreased (Figure 2B). However, the decrease in impedance cannot fully account for the increase in activity. To better understand this phenomenon, synchrotron UPS and extended X-ray adsorption fine structure (EXAFS) were employed. These techniques revealed electronic and structural changes from post-treatment of the catalyst. Specifically, the Fe d-state intensity at the Fermi level is reduced. The Fe nearest neighbor distance decreases approximately 0.15 Angstroms, and the atomic order of the catalysts is increased.

In collaboration with Dalhousie University, multiple series of CN_xFe compositions were produced, effectively mapping the entire C-N-Fe material space. Stability of these materials was assessed using a test in liquid acid, revealing the regions of high stability [5].

The *modeling work* continued by using both semiempirical (AM1) and ab initio (VASP)

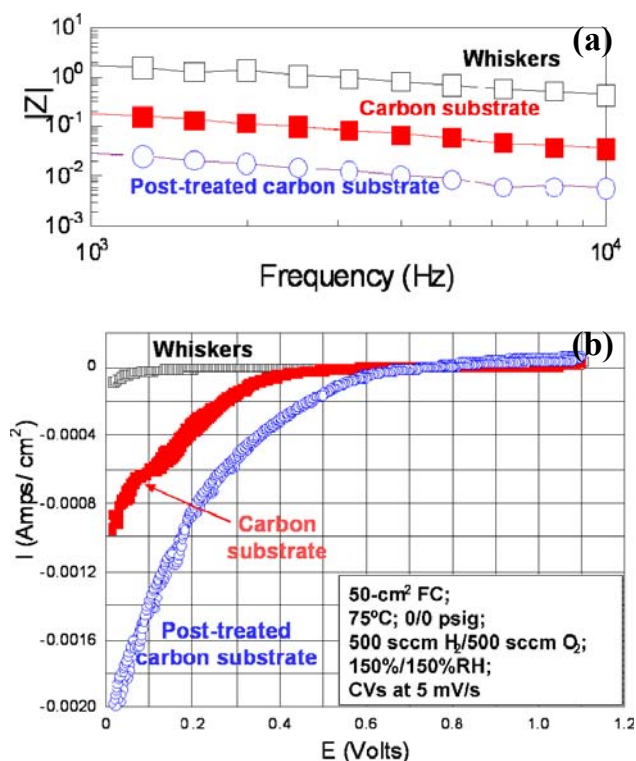


Figure 2. Effect of Substrate and Post-Treatment of Vacuum-Synthesized Catalyst on A) AC Impedance and B) Oxygen Polarization Curves

methodologies to provide insight as to the most thermodynamically stable configuration of the C-N-Fe systems. Relaxation of the layers of carbon in the presence of Fe had a large effect on the relative stability of the various structures. After relaxation, the literature-proposed CN-Fe-NC catalyst structure was found to be 0.99 eV higher in energy than a structure where Fe is connected to one nitrogen and one carbon, CN-Fe-CN (Figure 3).

Conclusions

- The tremendous activity during the past year has resulted in a large number of catalyst samples being synthesized, screened, characterized, and fully tested. This resulted in improved catalyst performance and is reflected in the quality and quantity of materials characterized by state-of-the-art techniques.
- Catalytic activity is nearing an interim milestone in the project, which was set to exceed the state-of-the-art NPM activity reported in the literature.
- The project has been greatly aided by the introduction of nanoparticle-based catalysts.

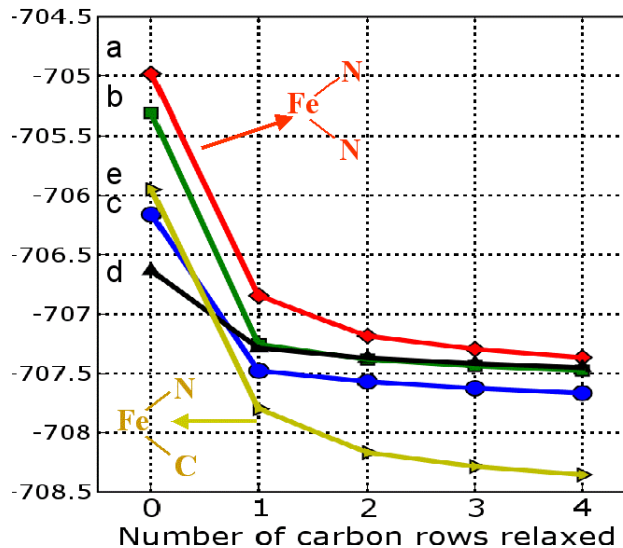
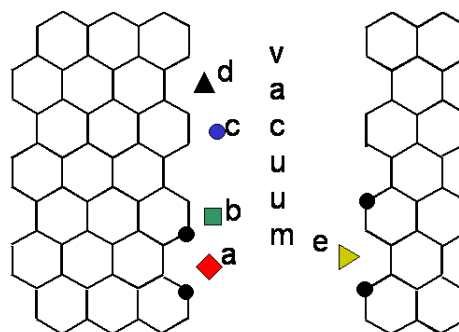


Figure 3. The Model Depicting Different Configurations of Fe (a – e) with Respect to the Graphene Edge Containing Two Nitrogen Atoms (upper) and the Corresponding Energies with the Effect of Relaxation of the Carbon Rows (lower)

- The modeling and characterization work has produced some unexpected results that could provide a lead to the synthetic effort, common to both the vacuum and the nanoparticle-based processes.
- The origin of the high coating impedance is well understood, and the catalysts' stability regions have been mapped.
- Task-oriented, interactive collaboration with universities and National Labs has been established.

FY 2005 Publications/Presentations

- E. B. Easton, T. Buhrmester, J. R. Dahn, "Preparation and Characterization of Sputter Fe(1-x)N(x) Films," *Thin Solid Films* (accepted).

2. M. Jain, S.-H. Chou, A. Siedle, "Structure of FeN₂C₄ Moiety from Quantum Mechanic Study," submitted to *J. Phys. Chem. B*.
3. R. Atanasoski, "Recent Advances in the 3M MEA Technology for PEMFC: The Catalysts," Departmental Seminar, Chemical Engineering Department, Univ. of South Carolina, Columbia, SC, April 21, 2005.

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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, p. 576.
3. M. Lefevre, J. P. Dodelet, *J. Phys. Chem. B*, 104 (2000) 11238.
4. R. T. Atanasoski, "Novel Approach to Non-Precious Metal Catalysts," DOE Hydrogen Program FY 2004 Progress Report (V.C.5).
5. A. Bonakdarpour, J. Wenzel, D. A. Stevens, S. Sheng, T. L. Monchesky, R. Löbel, R. T. Atanasoski, A. K. Schmoekkel, G. D. Vernstrom, M. K. Debe, and J. R. Dahn, *J. Electrochem. Soc.*, 152 A61 (2005).