IV.C.5 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 (Pt)
- Perform as well as conventional precious metal catalysts currently in use in membrane electrode assemblies (MEAs)
- Cost 50% less than a catalyst with Pt loading 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 Multi-Year Research, Development and Demonstration Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability
- Q. Electrode Performance

Approach

- Use 3M's unique nanostructured thin film substrate [1].
- Utilize processes compatible with high-volume manufacturability, including catalyst vacuum deposition processes.
- Produce precursors suitable for forming transition metal (TM) catalysts, including carbon-based materials.
- Explore and expand to alternative catalyst combinations and processes.
- Scale up selected catalysts for stack testing.

Accomplishments

The initial work was directed at reproducing Fe-N-C as a model catalytic site.

• Produced highly nitrogenated carbon by processes compatible with high-volume production, mostly in pyridinic form.

- Demonstrated one-step synthesis process for producing the targeted chemical structure.
- Formed and characterized 50-cm² MEAs from the new materials.
- Modeled the incorporation of nitrogen and iron in the graphene layers.

Future Directions

- Assess appropriateness of nitrogenated carbon precursor for transformation into catalyst.
- Thermally apply TM to achieve TM-N-C_x model catalyst.
- Identify the nature of the most active sites.
 - Intensify and expand the use of physicochemical methods (x-ray photoelectron spectroscopy, x-ray fluorescent spectroscopy, etc.).
- Continue modeling leading to promising NPM catalyst systems.
- Explore boundaries of the NPM catalyst space.
 - Broaden the range of processes and key synthesis parameters.
 - Use fast screening methods (subcontract with Dalhousie University).

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 [2], producing an oxide layer that inhibits its catalytic activity in the oxygen reduction reaction (ORR). Therefore, replacing platinum could contribute significantly to fuel cells becoming widely accepted in the transportation area.

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 current performance or durability. To achieve these objectives, the NPM catalysts have to exhibit high inherent catalytic activity for oxygen reduction. The catalysts should also have a high volumetric concentration of active catalyst centers at the catalyst/membrane interface, exhibit high stability with respect to reversible and irreversible processes such as corrosion, and be fabricated by processes compatible with high-volume manufacturability. The project is directed at meeting these objectives while taking 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, vacuumdeposited, 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 TM/low-Pt catalysts, 3M's unique nanostructured thin film substrate [1], and processes compatible with highvolume manufacturability. Efforts in the initial phase have been directed at reproducing Fe-N-C moieties as "model catalyst" for non-Pt-based ORR catalysts for PEM fuel cells. Thermally converted macrocyclic TM-N-C moieties have been reported in the literature [3,4], but they are produced at high temperature, ~700°C - 900°C, and by high-cost processes. The approach in this project uses recent advances and knowledge relating to vacuum-deposited precursors suitable for forming TM catalysts, including a variety of carbon-based materials.

Results

The intent in this initial phase, both experimentally and theoretically (modeling), was to produce baseline, state-of-the-art catalyst entities using vacuum processing. The focus was on reproducing Fe-N₂-C_x as a model active center, as described in papers by J.-P. Dodelet [3,4]. His main postulate for achieving high catalytic activity has been that all three elements must be present and high

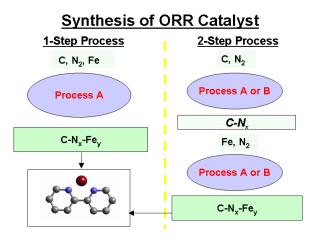


Figure 1. Schematic Presentation of the Two Synthesis Paths

nitrogen concentration must be achieved on the surface of the carbon support, where nitrogen would preferably be in pyridinic form [4].

In order to synthesize the NPM catalytic sites, two different sets of vacuum equipment and processes, A and B, have been used, both capable of continuous high-rate deposition appropriate for highvolume production. Process A was used to produce the catalyst in one single step. Alternatively, the same equipment was used to produce highly nitrogenated carbon as a precursor for subsequent deposition of transition metals and conversion in catalytic sites in process B (two-step process; see Figure 1). Over 50 carbon coatings were produced, 35 of which were subsequently used as substrates for additional deposition of transition metals. In addition, more than ten C-N-Fe materials were produced via one-step synthesis. Highly nitrogenated carbon was successfully prepared by these processes, mostly in "pyridinic" form. The carbon that was produced contains 10-12% nitrogen, five times the amount reported in the model system. The N1s x-ray photoelectron spectroscopy (XPS) peak has a twocomponent peak structure similar to that reported for the model NPM catalysts. The higher binding energy component at about 400 eV is attributed to nitrogen substituting into sp²-bonded graphene rings. However, there is some disagreement in the literature regarding the lower binding energy component at about 398.5 eV. Some researchers attribute this peak to nitrogen bonded to sp³ carbon while others attribute it to "pyridinic" nitrogen.

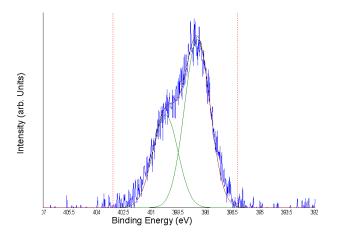
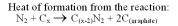


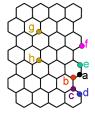
Figure 2. High-Resolution XPS of the Nitrogen Region for the 1-Step Sample (Note: 15-20% higher pyridinic nitrogen than in model catalyst.)

Samples fabricated with a one-step process had a small amount of iron. High-resolution XPS showed that nitrogen bonding had not changed significantly compared to the material without iron, since the characteristic double peak was present (see Figure 2). The binding energies of the two N1s components had also not changed significantly. The Fe 3p core level binding energy is usually at about 710 eV, which is significantly shifted relative to the value for metallic iron (707 eV). These data indicate that the iron is not clustering to form metallic regions that would be unstable in fuel cells. The carbon 1s peak was also studied, and the spectra were found to be similar to those published for model catalyst materials.

XPS analyses of materials from the two-step process show that about 10% transition metal is added to the near-surface region. However, after the second step, the near-surface region had significant oxygen content, usually between 30 and 40%. The high oxygen content detected in these samples may be caused by the transfer of the samples between systems. To address this issue, equipment capable of carrying out both process steps in the same vacuum deposition system is being adapted for use in this project.

The modeling effort provides guidance as to what are the possible combinations of the three constituent elements in the model system. Unlike the model system where carbon is used as a substrate and, as such, has its own structure, the carbon





atoms	substitution (eV)	(eV)
a-b	-2.89	0.0
a-c	-3.26	-0.37
a-d (model)	-4.78	-1.89
a-e	-4.65	-1.76
a-f	-4.78	-1.89
g-h (bulk)	1.55	

Figure 3. Model of Nitrogen Incorporation in the Graphene Layer

produced in this work is deposited along with nitrogen or nitrogen + iron on a dissimilar substrate and, therefore, its structure and chemistry are not known. So far, the modeling effort has dealt with thermodynamic calculations of the possibility for substitution of two nitrogen atoms in the graphene sheets (Figure 3). Calculation of the heat of substitution has shown that substituting two nitrogen atoms in the bulk of the graphene layer is thermodynamically unfavorable. In contrast, the substitution of two nitrogen atoms on the edge of the graphene layer is thermodynamically favorable. Moreover, in the latter case, the heat of substitution is more negative the farther apart the two nitrogen atoms are, indicating that the phenantroline configuration (indicated as a-d in Figure 3) is thermodynamically favorable.

Both fundamental electrochemical characterization and practical evaluation of the NPM catalyst were conducted in a "real" fuel cell environment. The catalyst coatings were successfully transformed into MEAs and tested in 50-cm² single cells. The testing procedure addressed the three basic properties of the NPM catalysts:

- 1. AC (alternating current) impedance for coating resistance,
- 2. Cyclic voltammetry under nitrogen to measure stability in a voltage window for fuel cells and to serve as a baseline for oxygen activity, and
- 3. Current–voltage measurements under oxygen for catalytic activity.

Over 50 MEAs have been assembled and tested. Most of the samples exhibited good electrochemical stability as measured by the (lack of a) current response under inert gas (nitrogen) on the cathode

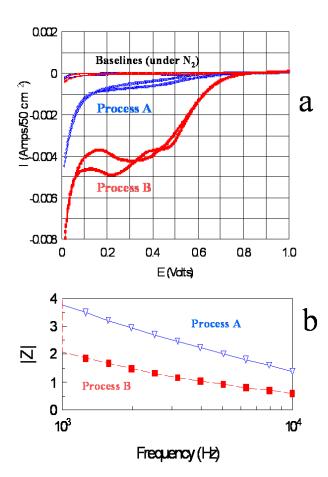


Figure 4. Electrochemical Characterization of Catalysts from Two Processes: a) Baselines (under nitrogen) and oxygen reduction polarization curves; b) High-frequency AC impedance. 50-cm² MEA, 75°C, full humidification. (Note: While both catalysts are stable (see baselines), TM coated on N-C exhibits better activity and lower impedance than one-step sample.)

side of the fuel cell. Samples having different behavior were identified, and the instability was related to the process conditions. The catalytic activity of the samples varied within an order of magnitude (Figure 4). In general, the catalytic activity was several orders of magnitude lower than for 3M samples with platinum catalyst. This phenomenon can be correlated with the impedance of the MEAs, which is two to three orders of magnitude higher for the NPM catalyst coatings compared to catalysts made of platinum alloys. Generally, within the group of NPM catalysts tested, the lower the impedance, the better the catalyst. For further

qualitative understanding of this phenomenon, measurements are underway to correlate the impedance as measured in the MEA configuration with the independently measured resistance of the coated materials.

Conclusions

In the initial phase of the project, novel vacuumbased processes for producing NPM catalyst were explored. The data were compared with the model state-of-the-art catalyst, as reported in the literature. The key ingredient for formation of the active site, pyridinic nitrogen, was produced in quantities as high as five times the reported values for the model catalysts. The catalytic coatings were successfully made into MEAs and tested in 50-cm² fuel cell arrangements. However, the catalytic films exhibited high resistance, via AC impedance measurements, that most probably is an indication of why the ORR was inhibited. Further studies, both in-depth and expanded, including alternative methods of activating and making the catalyst, are planned in the immediate future.

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FY 2004 Publications/Presentations

1. R. T. Atanasoski, 2004 DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review Meeting, May 24 - 27, 2004, Philadelphia, PA, Presentation FC17.