VII.E Platinum Recycling

VII.E.1 Platinum Recycling Technology Development

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Objectives

- Develop a cost-effective and environmentally friendly technology for the recycling and re-manufacture of catalyst coated membranes that are used in proton exchange membrane (PEM) fuel cell systems.
- Improve Nafion®-catalyst separation efficiency.
- Achieve high platinum/Nafion® catalyst recovery rate.
- Identify catalyst coated membrane (CCM) material degradation mechanisms by characterizing end-of-life separated materials.
- Develop a low-cost re-manufactured catalyst coated membrane process.

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:

- A. Durability
- B. Cost

Technical Targets

This project is conducting studies of end-of-life membrane electrode assemblies (MEAs) in a new approach. The project is attempting to demonstrate the vitality of the separated materials for re-use, namely the platinum catalyst and membrane ionomer materials. Understandings gained here will elucidate the failure modes of the materials and allow us to design better starting materials that have the target durability. Furthermore, recovery and re-use of the end-of-life materials will offset the total life-cycle costs of fuel cell systems; in particular, the membrane re-use could demonstrate a source of high-quality, low-cost membrane material.

Approach

- Dissolve used CCMs by using an autoclaving process.
- Separate Nafion®-catalyst mixture by using centrifugation or other appropriate methods.
- Characterize recovered catalyst and Nafion®.
- Re-manufacture CCMs with recycled Pt catalyst.
- Re-manufacture CCMs with recycled Pt catalyst and recovered Nafion®.
- Use 1 – 5 kW commercial fuel cell systems as source for CCM materials.

Accomplishments

- Demonstrated world's first fuel cell operating with a re-manufactured membrane made from recovered end-of-life fuel cell membranes.
- Completed scale-up of developed processes; operating on a commercial volume (18 pounds) of end-of-life material.
- Demonstrated new end-of-life catalyst evaluation tool.
- Developed framework of an economic model; used model to assess commercial stacks for ease of recyclability.
- Demonstrated recycling processes on end-of-life direct methanol fuel cell (DMFC) MEAs.
- Demonstrated that recovered end-of-life Nafion® has properties similar to fresh Nafion®; however, further demonstration work and study are required.

Future Directions

- Further scale up the process to demonstrate a stack operating on recycled membrane material.
- Conduct additional detailed evaluation of recovered Nafion® materials.
- Improve the method to characterize the activity of recovered catalyst, especially for the oxygen reduction reaction (ORR).
- Incorporate additional process improvements for suitability to all types of MEAs.
- Conduct additional fuel cell tests to evaluate re-manufactured CCMs.
- Develop additional used/aged CCM sources.

Introduction

The platinum catalyst has been identified as one of the major cost contributors to the PEM fuel cell material cost structure. Currently, platinum is the most viable catalyst for PEM fuel cell systems. The catalyst is composed of Pt-carbon-ionomer mixture coated onto the Nafion® membrane to form a catalyst-coated-membrane (CCM), or so-called membrane electrode assembly (MEA). The commercialization of fuel cell systems will result in an increasing demand for platinum group metals (PGMs). Obviously, without the recycling of PGM, not only does the high cost issue remain, but also the long-term availability of platinum becomes a serious limitation. Hence, platinum recycling is critical to the long-term economic sustainability of PEM fuel cells. Unfortunately, conventional platinum recovery processing is ill-suited for the fuel cell components due to (1) low recovery rate of acid solvent method because the platinum particles are covered by the ionomer, and (2) the presence of the Nafion® fluorine-containing polymer, which decomposes at high temperature, resulting in toxic and corrosive hydrogen fluoride (HF) gas being released. Thus, an advanced process that enables the extraction and re-use of both the precious metal and the ionomer in current fuel cell components is under development in this project.

Approach

Ion Power researchers are developing a process that allows for the manufacture of new catalyst coated membranes from used CCMs extracted from failed fuel cell stacks. This will be accomplished by first removing the CCMs from the disassembled stacks, decontaminating the CCMs to remove impurities, and dissolving the CCMs in an autoclave reactor to form a slurry of dissolved Nafion® together with the carbon-supported platinum catalyst particles. The second step is to develop a technology that separates these two valuable ingredients and allows the Nafion®-containing solution to be re-processed into a new fuel cell membrane. Ideally, the recovered platinum catalyst will be re-deposited on the re-manufactured membrane so that a completely re-manufactured CCM is the final product. In order to do this, recovered catalyst and Nafion ® are characterized to examine the changes of properties and structures during the component's life. The proper manufacturing process will be developed based on the properties and structures of recovered materials to realize a completely re-manufactured CCM. The characterization of aged CCM material will also provide very important information to help the investigation of CCM decay and failure mechanisms that are currently hampering the performance of state-of-the-art catalyst coated membranes.

The processes will be demonstrated on the 0.1 to 1 kg scale, which represents the quantity of material required to result in enough recovered material to be introduced into the re-manufacturing process. This represents a 5 kW to 50 kW quantity of state-of-the-art MEAs. We will search the marketplace for this quantity of materials and work with the key stakeholders in the industry to demonstrate the advantages of our new approach in terms of reducing the complete life-cycle cost of fuel cell systems.

Results

During the past year, we have procured commercial quantities (10's of kilograms) of end-of-life MEAs, both hydrogen based and direct methanol based. In order to process this material, we scaled up some of our processes for the separation of catalyst from the end-of-life membrane electrode assemblies. The result of this work was the recovery of enough end-of-life material to form a Nafion®-containing dispersion that allowed the film casting of a re-manufactured fuel cell membrane. This membrane was tested in a single-cell fuel cell and benchmarked against a similar fresh membrane.

In an attempt to answer the question about the suitability for re-use of Nafion® that has reached its end-of-life in an actual commercial fuel cell system, we received 18 pounds of end-of-life MEAs from a commercial fuel cell system integrator. The MEAs were based on Nafion® membranes, typically the N115 or N112 membrane, and had typical Pt/C based electrodes with ~1 mg PGM/cm^2 loading. The membranes were on the order of 6 inches square and were returned to the manufacturer as a complete stack when the end-of life condition was achieved, typically after several thousand hours of use. We developed a procedure (see Figure 1) that allowed us to extract the membrane in its original form so that a more complete analysis of the membrane can be made, including, for example, visual analysis, infrared spectroscopy, and in-plane conductivity. We made the following measurements on the recovered membrane (see Figure 2):

- Acid Capacity: 1233 equivalent weight (EW; grams/mole) as received, 1171 EW after acid exchange
- Thickness: 6 mils versus 5 mils for the new membrane N115
- Conductivity: 10.3 Ohm-cm as-received; 9.9 Ohm-cm after acid exchange
- Fenton Test: similar stability as compared to virgin Nafion® (0.011 meq F/gram)
- Infrared: No carboxylic acid groups found

Thus, the polymer after recovery has close to the reported specifications for acid capacity and conductivity of fresh material; however, it likely has contaminates, as indicated by color staining and improvements in conductivity observed by subsequent acid washing. The Fenton test shows fluoride ion release rates similar to those of new Nafion® membranes.

The above process involved an initial manual separation process which was done simply in an attempt to recover the membrane "intact" for a good

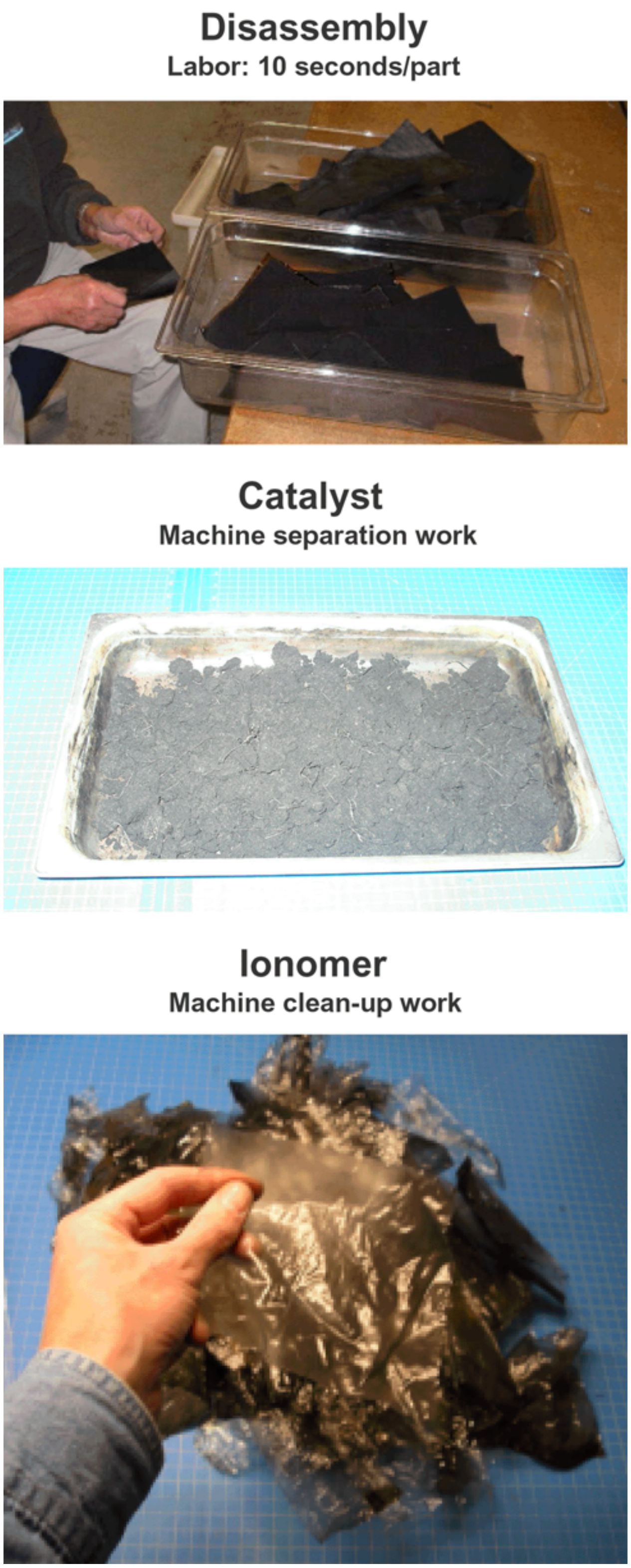

Figure 1. Scale-Up in the Recovery and Separation of Catalyst from Membrane

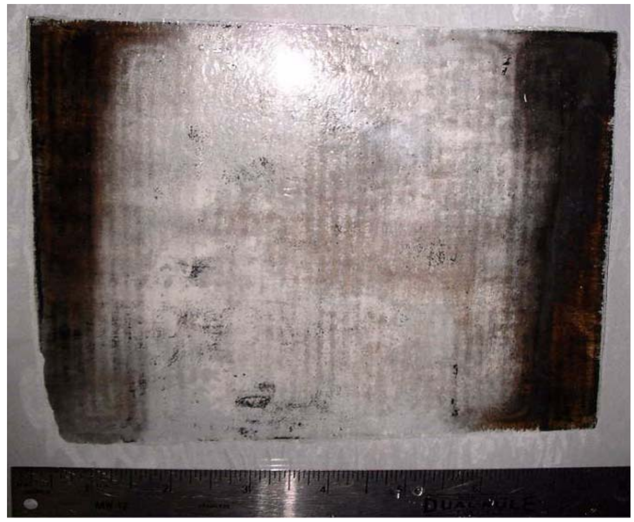

Figure 2. Close-Up of End-of-Life Membrane Showing Potential Contamination in the Membrane at Reactant Gas Inlets

comparison of properties. An advancement in the process allowed us to process the complete MEA in one step to separate the materials. We therefore performed a separation experiment by processing 106 g of small 50 cm^2 MEAs with gas diffusion media still attached. Complete separation occurred, and three components were recovered in a process that could be automated: membranes, carbon cloth gas diffusions and catalyst "mud". The Nafion® and the carbon cloth were removed from the catalyst "mud" and rinsed. The rest was filtered and the mud dried. The recovery was:

77.3 g	gas diffusion matl	=	72.9%
17.2 g	Nafion®	=	16.2%
8.6 g	dried catalyst mud	=	8.1%
====	====	====	====
103.1 g	total	=	97.3% recovery of starting materials

Even in this relatively small batch size, a good yield of recovered materials was obtained. A further advantage of recovery and separation using this advanced method was that the carbon cloth recovered from this experiment still retained the carbon black/ TEFLON® gas diffusion coating typical of commercial gas diffusers. In the manual peeling step described earlier, most of this layer stayed with the membrane and thus further diluted the PGM content of the catalyst "mud" recovered.

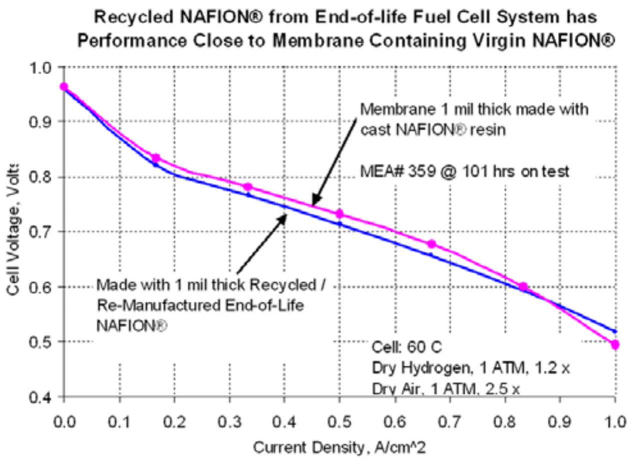

Figure 3. Performance of Fuel Cell Made with Fresh Nafion® as Compared to Recovered End-of-Life Nafion® Re-Manufactured into a New Fuel Cell Membrane

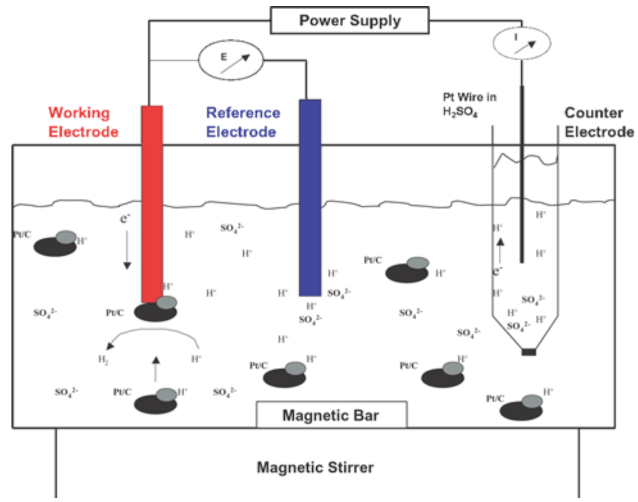

Figure 4. Schematic of a New and Simple Catalyst Activity Test Used to Measure Vitality of End-Of-Life Pt/C Catalyst

We have repeated these procedures on numerous batches of materials, including fresh and aged DMFC components and additional commercial fuel cell systems with unknown membrane manufacturer. We were able to recover high-quality ionomer from all of these sources, and the processes that we have developed here are repeatable.

After recovery of the membrane material as described above, the ionomer was fully acid exchanged and further cleaned and processed in an autoclave reactor to form a solution suitable for our standard film casting procedure used in the manufacture of commercial fuel cell catalyst coated membranes. We applied a catalyst coating made from fresh Pt/C catalyst material to the re-manufactured membrane so as to demonstrate a comparison of only the re-manufactured membrane with a fresh membrane made from new Nafion® resin. Both tests were carried out in a 60 cm^2 single cell in Ion Power test labs and are shown in Figure 3.

Research at Delaware State University was aimed at developing a catalyst activity test that was able to give meaningful measurements of the catalyst activity in the presence of small amounts of Nafion®. In the process of recovering the catalyst material, some small amounts of Nafion® remain (<1%) that can effect sensitive tests for catalyst activity such as CO chemisorption. Furthermore, attempts to process the recovered catalyst "mud" back to an ink and make electrodes has resulted in irreproducible half-cell characterizations.

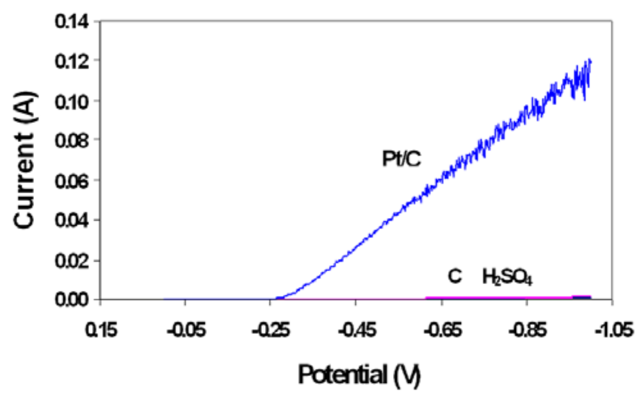

Figure 5. Measurements Show That the Test is Sensitive to the Presence of Pt

The schematic of the new test being developed at Delaware State University is shown in Figure 4. The catalyst material is dispersed in a dilute sulfuric acid and a potientiostat is used to measure current on the working electrode as a function of applied voltage. The hydrogen evolution reaction can be sustained only at low voltages (<0.4 V) when a catalytic behavior of the dispersed particles is present. For example, when just carbon black is used, no signal is measured; however, when the same amount of Pt/C is dispersed in the solution, orders-of-magnitude greater current is detected (see Figure 5).

Conclusions

- The properties of end-of-life Nafion® polymer in our tests to date show similar performance as compared to fresh polymer.
- The Nafion® polymer can be recovered from an end-of-life fuel cell and re-used to make a new fuel cell.
- Additional work is needed to demonstrate the vitality of recovered catalyst material for re-manufacture.
- Excellent processes have been developed to refine and separate the valuable materials from end-of-life MEAs.

FY 2005 Publications/Presentations

1. Stephen Grot, "Platinum Recycle Technology Development"; presented at the DOE review meeting, Arlington, VA, May 24, 2005.
2. March 24, 2005 filing US Patent Application S.N. 11/089,547 "Recycling of Used Perfluorosulfonic Acid Membranes"; patent pending
3. J. E. Trower, A. O. Amoako, B. Workie, A. Goudy, H. P. Hayward, S.A. Grot, W.G Grot, "Simple Electrochemical Procedure to Test the Catalytic Activity of Platinum Supported on Carbon"; presented at the HBC UUP 2005 National Research Conference, Park Plaza Hotel, New Orleans, LA, February 10 – 13, 2005.