V.P.1 Platinum Recycling Technology Development

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Subcontractors:
- DuPont, Wilmington, DE
- Delaware State University, Dover, DE

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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 remanufactured 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

The cost target, as it relates to our project, is a recovery rate of over 95% of the platinum group metals (PGMs) originally deployed in the new fuel cell system. Our ability to demonstrate this will allow the PGM market price to maintain stability during the initial market penetration of PEM fuel cell systems. The durability target as it relates to our project is the demonstration of durable membranes manufactured with recovered end-of-life Nafion® membranes. This will also demonstrate the fundamental vitality of the Nafion® ionomer for durability and the nature of the impurities and failure modes of the membranes.

Accomplishments

- Identified significant amounts of contaminants in end-of-life membranes: ammonia, sodium, metals, and PGMs, while demonstrating the vitality of the recovered ionomer.
- Demonstrated a new purification method that effectively and efficiently removes the cation contamination found in the end-of-life membrane electrode assemblies (MEAs).
- Operated our recycling process on the 5 sq meter scale.
- Achieved >95% recovery of PGM material with our innovative process. This demonstrates that PGM is not lost in the exhaust of a fuel cell system over its life.
- Achieved >90% recovery of ionomer from end-of-life MEAs.
- Demonstrated the manufacture of the most durable 1 mil thick membrane in General Motor's membrane durability testing.
- Offered 10 gallons of solution to Dupont Team member for conversion to 80 m^2 of remanufactured membrane.

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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. It is in the form of Pt-carbon-ionomer mixture coated onto the Nafion® membrane to form a CCM, or so-called MEA. The commercialization of fuel cell systems will result in an increasing demand of the PGM. Obviously, without the recycling of PGM 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) the low recovery rate of acid solvent method because the platinum particles are covered by the ionomer; and (2) Nafion® fluorine-containing polymer decomposition at high temperature that results in toxic and corrosive hydrogen fluoride (HF) gas released. Thus, an advanced process that enables the extraction and reuse 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 remanufacture of new catalyst coated membranes made from used CCMs extracted from failed fuel cell stacks. This will be first accomplished by removing the CCMs from the disassembled stacks, then 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 reprocessed into a new fuel cell membrane. Ideally the recovered platinum catalyst will be re-deposited on the remanufactured membrane so that a completely remanufactured 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 remanufactured CCM. The research and development on 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 CCMs.

The processes will be demonstrated on the 0.1 to 10 kg scale, which represents the quantity of material required to result in enough recovered material to be introduced into the remanufacturing process. This represents a 5 kW to 500 kW quantity of state-of-the-art MEAs. We will search the marketplace for this quantity of material, and work with the key stakeholders in the industry to demonstrate the advantages of our new approach in terms of reducing the complete lifecycle costs of fuel cell systems.

Results

We have scaled-up the process by procuring a 40-gallon autoclave reactor. We have also scaled-up our separation process as shown in Figure 1. We have a 40-gallon mixing tank to receive the contents of the autoclave reactor, then the slurry of Nafion® solution with catalyst particles is pumped around through a continuous centrifuge where the heavier catalyst particles are deposited on the walls of the centrifuge bowl.

As a demonstration of our process, we summarize a recovery analysis from roughly 3 sq meters of MEAs from an end-of-life system. The MEAs were loaded into a 1 liter autoclave reactor and solubilized in de-ionized (DI) water. The 1 liter reactor was operated four times to process the entire 3 sq meter batch. We finished with 2.94 kg of Nafion® solution with the catalyst powder dispersed in the solution. This was pumped through the continuous centrifuge in 9 minutes time. The 300 ml of DI water was pumped through in order to clear the pump and container of the solution. The product was then separated from the starting batch: 2.94 kg solution + 0.3 kg rinse water = 3.24 kg as follows:

Processing Step Processing Step	Total Material	Total PGM Collected	Expressed as PGM Loading on MEA	% of PGM
Acid & DI Water Wash	1.5 liters acid	1.67 grams PGM	0.11 mg PGM/cm^2	5.5%
Centrifuge Top Discharge	2.04 kg liquid "tinted"	0.6 grams PGM	0.02 mg PGM/cm^2	2%
Centrifuge Bowl Solids	108 grams powder	27 grams PGM	0.90 mg PGM/cm^2	88.2%
Centrifuge Bowl Liquids	1.045 kg black liquid	0.75 grams PGM	0.025 mg PGM/cm^2	2.3%
Diffusion Media	0.64 kg carbon paper	0.6 grams PGM	0.02 mg PGM/cm^2	2%
TOTAL		**30.6 grams**	**1.075 mg PGM/cm^2**	**100%**

Thus, one can see the excellent recovery of the original 1 mg/cm^2 reported by the manufacturer of the MEAs. We can also conclude that there is not a significant amount of PGM lost in the exhaust of a fuel cell system over its life.

The recovered ionomer solution was purified and concentrated using a newly developed purification/enrichment system that allows reuse of the solvents used

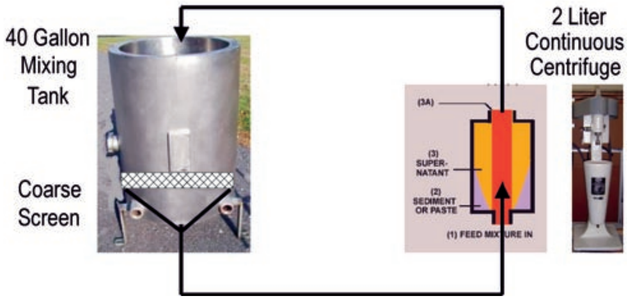

FIGURE 1. Schematic and Photo of Our Scaled-Up Separation Equipment

in the process. We delivered 10 gallons of this enriched and purified solution to Dupont for recasting into 1 mil thick membranes.

Conclusions and Future Directions

- The scale-up of our process continues to show good recovery of PGM and separation of the PGM and ionomer solution.
- We plan to make a significant amount of remanufactured MEAs and incorporate and test in commercial fuel cell systems.

Special Recognitions & Awards/Patents Issued

1. Patent filing for recycling process, March 2005, Notification of Allowance of Claims.

2. State of Delaware support of our project through a $250k "Green Energy Fund" Technology Demonstration Project.

FY 2007 Publications/Presentations

1. Stephen Grot, Platinum Recycle Technology Development, presentation has been given to DOE review meeting, Arlington, VA, May 18, 2007.

2. William Resende Presentation to University of Brazil, San Paulo, May 2006.

3. USCAR/DOE Tech-Team Meeting, February 2007, Detroit, MI, Grot, et al. "*Platinum Recycling Technology Development*".