V.E.1 Platinum Recycling Technology Development

Dr. Stephen Grot (Primary Contact),
Walther Grot

Ion Power, Inc.
720 Governor Lea Rd.
New Castle, DE 19720
Phone: (302) 832-9550; Fax: (302) 832-9551
E-mail: s.grot@ion-power.com

DOE Technology Development Manager:
Arlene Anderson

Phone: (202) 586-3818; Fax: (202) 586-9811
E-mail: Arlene.Anderson@ee.doe.gov

DOE Project Officer: Reg Tyler

Phone: (303) 275-4929; Fax: (303) 275-4753
E-mail: Reginald.Tyler@go.doe.gov

Technical Advisor: Bob Sutton

Phone: (630) 252-4321; Fax: (630) 252-4176
E-mail: sutton@cmt.anl.gov

Contract Number: DE-FC36-03GO13105

Subcontractors:

DuPont Fuel Cells, Wilmington, DE
Delaware State University, Dover, DE

Start Date: August 2003
Projected End Date: August 2008

Objectives

- Develop a cost effective and environmentally friendly technology for the recycling and remanufacture of catalyst coated membranes that are used in polymer electrolyte 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 remanufactured catalyst coated membrane process.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R, D&D Plan:

(A) Durability

(B) Cost

Technical Targets

This project is conducting studies of end-of-life membrane electrode assemblies (MEAs) using a new approach. The project is attempting to demonstrate the viability 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 reuse of the end-of-life materials will offset the total life-cycle costs of fuel cell systems, and in particular, membrane reuse could demonstrate a source of high-quality low-cost membrane material.

Accomplishments

- Examined batch materials from actual end-of-life systems from four different original equipment manufacturers (OEMs).
- Identified significant amounts of contamination in end-of-life membranes, such as ammonia, sodium, metals, and platinum group metals (PGMs).
- Identified in situ methods for removing foreign cations during fuel cell operation.
- Demonstrated the end-of-life Nafion® membrane retains much of its original properties.
- Scaled-up the separation equipment, providing materials and information for cost analysis.
- Improved catalyst vitality test to work in the presence of small amounts of Nafion®.

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 MEA. The commercialization of fuel cell systems will result in an increasing demand of PGMs. Obviously, without the recycling of PGMs 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 fuel cell components

due to (1) low recovery rate of the acid solvent method because the platinum particles are covered by the ionomer, and (2) the presence of the Nafion® fluorine-containing polymer decomposition at high temperature 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 CCMs made from used CCMs extracted from failed fuel cell stacks. This will be first accomplished by removing the CCMs from the disassembled stacks, decontaminating the CCMs to remove impurities, and then dissolving the CCMs in an autoclave reactor to form a slurry of dissolved Nafion® together with the carbon supported platinum catalyst particles (see Figure 1). 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 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 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 costs of fuel cell systems.

Results

During the past year, we have procured additional commercial quantities (10s of kilograms) of end-of-life MEAs, both hydrogen-based and direct methanol-based. These materials had varying amounts of cation contamination, some up to 30% of their original capacity lost, as measured by ion exchange capacity. This contamination would have a significant negative impact on the cell performance and was likely the cause of performance degradation that resulted in stack failure.

Several of the batches of recovered ionomer were analyzed via inductively coupled plasma (ICP) to determine the types of cation contamination in the membrane. Table 1 shows the results from MEAs removed from an end-of-life direct methanol fuel cell (DMFC) system. Fresh, un-used MEAs were also available and were compared to the used MEAs in order to quantify the amount of contamination that the MEAs received during operation. As one can see, the significant contaminations absorbed were calcium and nickel (shown in bold). Sources of this contamination were likely the system components, and the system integrator is can identify components in their systems that are the source for these contaminations, thereby increasing the system lifetime.
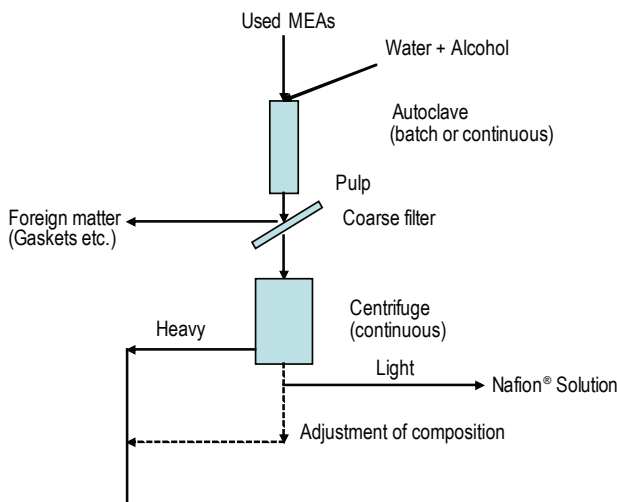
Large Scale Recycling of used MEAs

FIGURE 1. Schematic of the proposed MEA recycling process being developed in this project.

TABLE 1. Contaminants from Used MEAs

CATION	Fresh MEA	Used MEA #1	Used MEA #2	Units	% of IEC
K	170	303	348	ppm	0.8%
Na	170	331	341	ppm	1.6%
Ca	**92.7**	**680**	**694**	**ppm**	**3.8%**
Ni	**10.2**	**352**	**353**	**ppm**	**1.3%**
Fe	53.4	97.2	103	ppm	0.6%
Cr	9.8	15.6	15.5	ppm	0.1%
					TOTAL: 8.2%

We performed similar analysis of hydrogen- or reformate-fed PEM systems. However, in almost all samples we discovered a significant difference between the total cation contamination (as determined via a titration) and the specific cations detected via ICP. Typically, the titration method suggested an additional 10% of the total available ion sites were contaminated, whereas the ICP identified common cations like K, Na, Fe, Ca, Ni, Cr. We puzzled as to the cause of the difference and then thought to test the membranes for ammonium cation contamination. Since ammonia is a gas it can not be detected via the ICP test. We detected and quantified it by taking the cleaned end-of-life membranes and exposing them to NaOH. The contact with NaOH releases the ammonia from the membrane and distilled it into a known quantity of HCl acid with a pH indicator. Back titration of the receiver vessel determined the quantity of ammonia released. A qualitative but more sensitive method was also demonstrated where damp pH paper was suspended in the vapor space above a membrane that was being exchanged with NaOH. The pH paper turned blue indicating the release of ammonia. We tested a blank, i.e. a fresh piece of Nafion® and found that the pH paper did not indicate the presence of any ammonia or other base type of vapors. The ammonia present in the different OEM samples ranged from approx 12% of the ion exchange to detectable but not quantifiable (<0.1% of the ion exchange capacity, IEC). The lower range came from a supplier that did not have significant run hours on the MEAs. The obvious source of the ammonia would be contamination in the hydrogen gas used in the fuel cell. Other researchers have reported on the effects of ammonia gas contamination in the hydrogen on the performance of PEM fuel cells and their findings are consistent with contamination of the membrane ion exchange sites rather than a poisoning effect of the catalyst [1,2]. These two reports disagree on the degree of permanence of the contamination.

In an attempt to clarify the degree of persistence of the ammonium cation in a fuel cell membrane, we performed an in situ procedure to remove cations from the membrane. The method involves high current draws during low cell voltage operation, resulting in a large flux of "cleansing" protons passing from the anode to the cathode, as well as a strong electric field that sweeps foreign cations out to the cathode. At the cathode the cations that form water soluble compounds like ammonium and sodium can be carried out of the cell with the product water. Figure 2 shows the procedure applied to a membrane that was intentionally placed entirely in the sodium cation form, and as a result has very poor initial performance.

On the topic of process cost analysis we made an estimation of a commercial size reactor that would be needed to operate a typical batch of 30 kg of MEAs. The solvents can be largely recycled in the process.
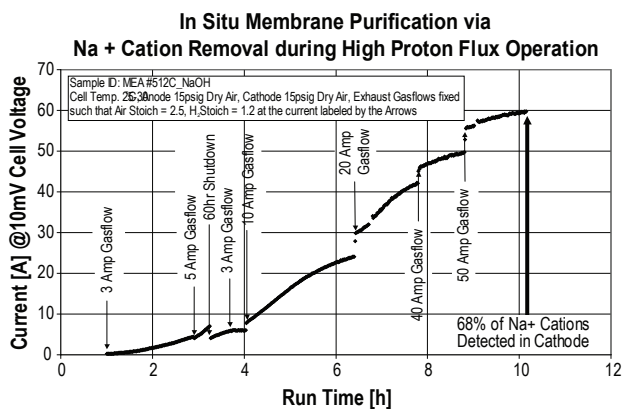

FIGURE 2. Start-up of a cell that had the membrane completely contaminated in the sodium form, shows that the cations can be removed using this procedure. The sodium was detected in the product water.

- Reactor size: 300 liters
  - 1,550 kg metal mass
  - Charge with 145 kg solvent, 30 kg MEAs (with GDL, typical lot)
  - Delta T: 250°C
  - 60 kW-hr required to heat metal and contents
  - Centrifuge: 1 kW for 1 hr (estimated)
- Output: $54,500/day; will need to reduce by 10x to meet the DOE 2015 goal of $5,400/day
  - Pt: typical of today's MEAs at 0.8 mg Pt/cm^2 total
  - 2-3% of MEA weight (0.75 kg) = $27,500 ($1,100/tr. oz.)
  - Nafion®: 30% of MEA weight (9 kg) = $27,000 ($300/sq meter)
  - GDL: 65% of MEA weight (20 kg) = No value
- Costs: Total: $656/day
  - Energy: $0.10/kW-hr = $6.10
  - Man-Power: Estimate 8 man-hours = $300
  - Solvents and acids can be reused: estimate = $100 cost
  - Capital equipment costs: ~ $500K; or $250/day (if used each day)

One can see that the energy costs are not significant as compared to the capital costs and the operator costs and even the value of the product recovered.

Conclusions and Future Directions

- 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 reused to make a new fuel cell.
- The durability of the recovered Nafion® needs still be demonstrated in an operating fuel cell.
- Excellent processes have been developed to refine and separate the valuable materials from end-of-life MEAs.

Special Recognitions & Awards/Patents Issued

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

FY 2006 Publications/Presentations

1. Stephen Grot, Platinum recycle Technology Development, presentation given at the DOE review meeting, Arlington, VA, May 18, 2006.

2. USCAR/DOE Tech-Team Meeting, February 2006, Detroit, MI, Grot, et al. *"Platinum Recycling Technology Development"*.

3. Fourteenth Annual Mid-Atlantic HBCU Science Research Conference, Princess Anne, MD, April 12, 2006, "Electrochemical Studies of the Suspension of Platinum Supported on Carbon (Pt/C) in H_2SO_4. Effects of the Amount of Pt/C, Sonication, and an Alcohol on the H+/H2 Reduction Current", D. Boucek, S. Lamar, A. Amoako, B. Workie, A. Goudy, H. P. Hayward, S. Grot, and W. Grot.

4. HBCU-UP 2006 National Research Conference, Baltimore, MD, February 9–12, 2006, "Electrochemical Studies of the Suspension of Platinum Supported on Carbon (Pt/C) in H_2SO_4. Effects of the Amount of Pt/C, Sonication, and an Alcohol on the H+/H2 Reduction Current", D. Boucek, S. Lamar, A. Amoako, B. Workie, A. Goudy, H. P. Hayward, S. Grot, and W. Grot.

5. "SANS Study of the Effects of Water Vapor Sorption on the Nanoscale Structure of Perfluorinated Sulfonic Acid (NAFION) Membranes" *Man-Ho Kim, Charles J. Glinka, Stephen Grot, and Walther Grot; to Macromolecules.*

References

1. H. J. Soto, W. Lee, J.W. Van Zee, and M. Murthy, Electrochem. Solid-State Lett., Volume 6, Issue 7, pp. A133-A135, July 2003.

2. F. A. Uribe, S. Gottesfeld, T.A. Zawodzinski, J. Electrochemical Soc., Vol 149, No.3, p. A293, March 2002.