

## IV.E Platinum Recycling

### IV.E.1 Platinum Recycling Technology Development

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#### *Subcontractors:*

*DuPont, Wilmington, DE*  
*Delaware State University, Dover, DE*

### 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<sup>®</sup>-catalyst separation efficiency.
- Achieve high platinum/Nafion<sup>®</sup> catalyst recovery rate.
- Identify catalyst-coated membrane (CCM) material degradation mechanisms by characterizing aged 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:

- O. Stack Material and Manufacturing Cost
- P. Durability

### Approach

- Dissolve used CCMs by using an autoclaving process.
- Separate Nafion<sup>®</sup>-catalyst mixture by using centrifugation method.
- Characterize recovered platinum and Nafion<sup>®</sup>.
- Re-manufacture CCMs with recycled Pt catalyst.
- Re-manufacture CCMs with recycled Pt catalyst and recovered Nafion<sup>®</sup>.
- Use 1-5 kW commercial fuel cell systems as source for CCM materials.

### Accomplishments

- Achieved satisfactory CCM dissolution rate.
- Demonstrated a high Nafion<sup>®</sup>/catalyst separation rate by centrifugation method.

- Selected test methods for recovered catalyst characterization.
- Selected test methods for recovered Nafion<sup>®</sup> characterization.
- Building a fuel cell mobile office unit for CCM lifetime test.

### Future Directions

- Optimize autoclave operating conditions to facilitate separation/re-manufacture.
- Investigate Nafion<sup>®</sup> nanophase structure.
- Improve the method to characterize the activity of recovered catalyst.
- Develop the re-manufacturing CCM process.
- Conduct fuel cell tests to evaluate re-manufactured CCMs.
- Analyze recovered platinum catalyst and Nafion<sup>®</sup> structure for CCM decay mechanisms study.
- Conduct fuel cell endurance test to investigate the CCM decay mechanisms.
- Develop the used/aged CCM sources.

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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. The catalyst is in the form of Pt-carbon-ionomer mixture coated onto the Nafion<sup>®</sup> membrane to form a catalyst-coated-membrane (CCM), or so-called membrane electrode assembly (MEA). The platinum loading ranges from 0.1 ~ 0.8 mg/cm<sup>2</sup>, depending on the type of fuel. The commercialization of fuel cell systems will result in an increasing demand of the platinum group metals (PGM). Obviously, without the recycling of PGM, not only the high cost issue remains, 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 platinum with the acid solvent method because the platinum particles are covered by the ionomer and (2) the decomposition of the Nafion<sup>®</sup> fluorine-containing polymer at high temperature, resulting in the release of toxic and corrosive HF gas.

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. Major progress has been made in two areas. The first area is CCM dissolution in a water-

solvent mixture using an autoclaving process. Ionomer (both from membrane and catalyst mixture) dissolves into the solution under pressure and temperature without decomposition. The second area is a very high separation efficiency of Nafion<sup>®</sup>/catalyst mixture separation achieved by using centrifugation method. Two valuable materials without structural damage are obtained and potentially suitable for reuse. Test methods for characterization of recovered platinum and Nafion<sup>®</sup> ionomer are under development.

### Approach

Ion Power researchers are developing a process that allows for the re-manufacture of new catalyst-coated membranes 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<sup>®</sup> together with the carbon-supported platinum catalyst particles. The next step is to develop a technology that separates these two valuable ingredients and allows Nafion<sup>®</sup> 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<sup>®</sup> should be characterized to examine the changes of properties and structures. The proper manufacturing process will be developed based

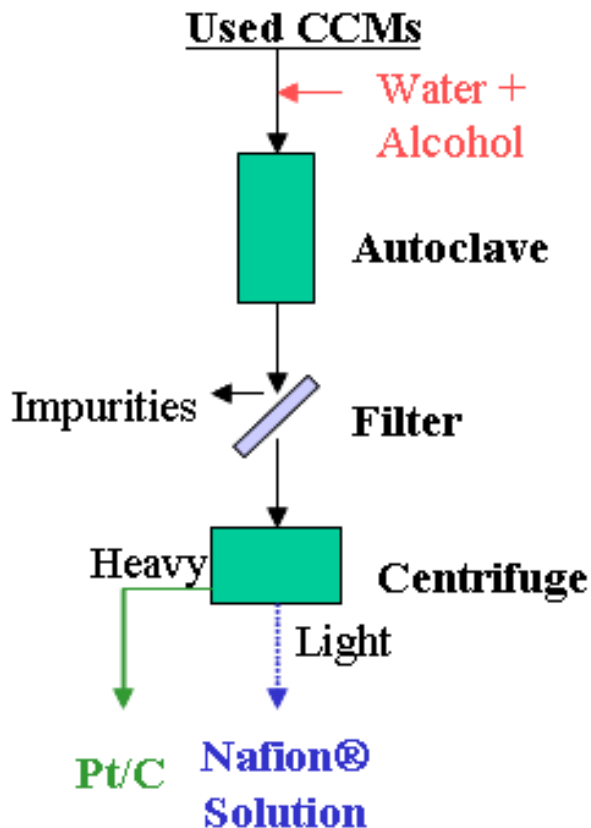
on the properties and structures of recovered materials to realize a completely re-manufactured CCM. The research and development on the characterization of aged CCM material will also provide very important information to help the investigation of CCM decay and failure mechanisms that are currently hampering the performance of state-of-the-art catalyst-coated membranes.

Unused CCM samples were recycled and characterized per above processes to confirm the suitability of the processes and create recycling base lines. Aged CCMs will be processed once they are available. Ion Power will extend its fuel cell test facilities to be capable of endurance testing in different scales. The re-manufactured CCM performance, measured both in terms of power density as well as durability, will be compared with that of original built CCMs.

## Results

A schematic of the used CCM recycling process is shown in Figure 1. A one-liter autoclave reactor running at pressure and at a temperature greater than 200°C achieves complete ionomer dissolution. The intention is to discover the baseline procedures to dissolve and separate catalyst-coated membranes into their constituent materials. One of Ion Power's standard solution-making procedures is adapted that results in low-viscosity solutions. Kapton frame material removal is an example of the decontamination step by a coarse filter. The operation results in a mixture that behaves like a typical catalyst/Nafion® solution ink that we use in our manufacturing processes. The catalyst/Nafion® mixture discharged from the autoclave is centrifuged. Centrifugation is seen as the most promising method to separate the catalyst particles from Nafion® solution. A Sorvall SS-3 automatic super-speed centrifuge with rated speed of 18,000 rpm generates centrifugal forces of about 40,000g. Twice centrifugation achieves a 98.9% Nafion® separation efficiency (from the light stream). The platinum content of the recovered Nafion® solution is approximately 135 ppm. Only 1.1% of original Nafion® remains in the wet catalyst pigment cake.

Characterization techniques and methods are under development and evaluation to characterize recovered platinum and Nafion® materials. DuPont

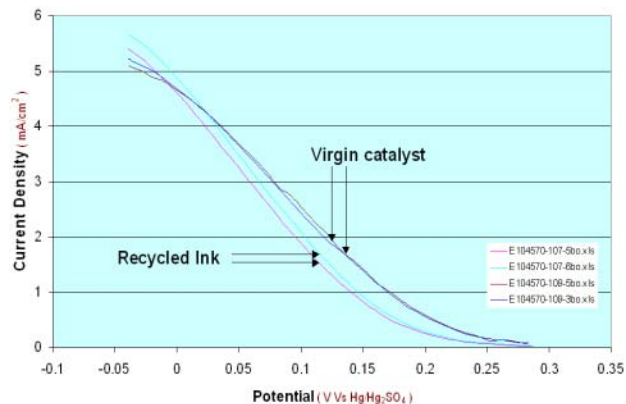


**Figure 1.** Process of Used CCM Recycle

(subcontractor) conducted two tests to characterize the recovered catalyst powder samples from the centrifuge: (1) inductively coupled plasma adsorption (ICP) to determine platinum content and (2) thermo-gravimetric analysis (TGA) to determine Nafion® content. The results from these two tests are shown in Table 1. DuPont also conducted half-cell testing to compare the activity of the recovered catalyst to that of fresh catalyst. From the result shown in Figure 2, the recovered catalyst is only.

**Table 1.** ICP and TGA Analysis

Sample ID	Pt/ICP	wt.% lost @			
		150°C (H <sub>2</sub> O)	150-390°C for original catalyst	150-390°C for sample	wt.% Nafion
11204	41.8	1.257	6.978	17.05	10.072
31704	33.9	4.203	7.496	16.06	8.564
31804		1.893	6.978	18.14	11.162



**Figure 2.** Half-Cell Comparison of Catalyst Activities

slightly inferior to the original catalyst. Delaware State University (DSU, subcontractor) characterized Nafion<sup>®</sup> samples with three methods. (1) Infrared spectroscopy was used to determine if polymer was degraded. The  $-\text{SO}_2\text{F}$  precursor form and the  $\text{Cs}^+$  form of fresh Nafion<sup>®</sup> were analyzed. The peak at approximately  $985\text{ cm}^{-1}$  in the  $\text{Cs}^+$  form contains a shoulder, whereas the same peak in the precursor does not. Information about the structure of the ether linkage can be deduced from this. (2) The Fenton's test was utilized for the determination of polymer stability. The result of the Fenton's test is shown in Table 2. The samples were first treated with ferrous

**Table 2.** Determination of Fluoride in Nafion by Fenton's Test

Mass of Nafion Before (mg)	178.8
Mass of Nafion After (mg)	171.8
Potential of 50 mL of Nafion Solution (mV)	142
Conc. of F- in the Nafion Solution (ppm)	1.35
mass of F- in the Nafion Solution (mg)	0.0677
meq of F- in the Nafion Solution	0.0036
meq of F- per gram of Nafion	0.02

sulfate and hydrogen peroxide. Then, the fluoride content was determined with an ion selective electrode. The amount of fluoride released was less than 0.1 milliequivalents per gram of Nafion<sup>®</sup>. This demonstrates that the ion-selective electrode is very sensitive and well suited for determination of low quantities of fluoride. (3) Ion exchange titration was used to determine the equivalent weight of Nafion<sup>®</sup>.

When analyses were performed on several fresh samples, the mean equivalent weight was found to be about 1055 grams mole equivalent, as expected. Ion Power has proposed an alternative method, so-called "suspended sample test". We believe that the proposed technique is more stable and reliable for the catalyst activity evaluation. Ion Power and DSU are jointly developing this technique. These methods should be quite suitable for analyzing aged catalyst and Nafion<sup>®</sup> samples extracted from fuel cells.

## Conclusions

An efficient CCM dissolution method has been developed, and a good dissolution yield has been achieved. The operation of the autoclave was excellent, and the measurement and control of operating parameters were good. Different dissolution procedures will be adapted to achieve different solution viscosities. Kapton framing material imbedded in the CCM has been successfully removed in the decontamination step. Centrifugation has been demonstrated as the most efficient method for the Nafion<sup>®</sup>/catalyst separation. High selectivity and good separation rate (98.9% Nafion<sup>®</sup> in the solution, 1.1% remaining with the catalyst) are achieved by twice centrifuge separations. Although this level of separation is more than adequate for the re-manufacture of new CCMs that we proposed in our project, we plan to be able to achieve higher levels of separation by modifying the dissolution techniques. To determine whether the recovered materials are in re-useable form is critical. Besides the test methods described above, more reliable techniques will be needed to define the structures of the recovered materials.

Future work will also focus on (1) development of the sources of used CCMs, (2) investigation and validation of the structure properties of recovered Nafion<sup>®</sup>, (3) re-manufactured CCM testing, and (4) establishment of a fuel cell aging facility able to test multi-kW fuel cells under real-world conditions.

## FY 2004 Publications/Presentations

1. Stephen Grot, Platinum Recycle Technology Development, presentation at the DOE Program Review Meeting, Philadelphia, PA, May 24, 2004