

VII.E.2 Platinum Group Metal Recycling Technology Development

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Subcontractors:

Virginia Polytechnic Institute, Blacksburg, VA

University of Kansas, Lawrence, KS

Consultant:

Ceralink, Troy, NY

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Projected End Date: September 30, 2008

Objectives

- Develop a new process for precious metal (PM) recovery from proton exchange membrane (PEM) membrane electrode assemblies (MEAs):
 - Eliminate hydrogen fluoride (HF) release, a downside of the current recycling process
 - Evaluate the feasibility of recycling the fluoropolymer (i.e. Nafion[®]) membrane
- Develop a process for recycling precious metals in metal monolithic catalysts used in fuel reformers for hydrogen production

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:

- B. Cost

Technical Targets

The cost of the fuel cell stack will depend on the cost of precious metals, which will be impacted both by the amount of precious metals used in the stack and by the development of a cost-effective recycling process. The 2015 targets for precious metal content and cost for transportation applications are as follows:

- Cost - \$6/kW (based on \$450/troy ounce of platinum)
- Total PM catalyst loading – 0.20 g/kW

Approach

- Evaluate the application of a tandem microwave oven for sequential decomposition of the MEA and sequestration of the liberated HF.
- Develop a microwave-assisted acid digestion process for the liberation of the precious metals from an MEA using mineral acids.
- Determine the solubility of Nafion[®] using supercritical solvents (CO₂ and co-solvents, and high-pressure water).
- Develop a solvent delamination process for separation of electrode catalysts from the fluoropolymer membrane.
- Investigate precious metal recovery from a metal monolith substrate.

Accomplishments

- Developed a microwave-assisted acid digestion process capable of decomposing electrode catalyst particulates while dissolving the precious metals on the fuel cell membrane and leaving the membrane intact.
- Installed a Fourier transform – infrared (FT-IR) instrument and began capturing time-resolved data for gases released with combustion of a Nafion[®]-based MEA. This is useful in understanding the difference in gases released from conventional and microwave-induced combustion.
- Found a method to re-disperse Nafion[®] membranes using water.
- Observed significant differences, depending on source and history of the MEA, in recovery of electrode catalyst using solvent delamination.
- Reached the halfway point in a 2000-hr aging study in a 16-cell stack to generate real-world samples for validation of recycling processes, with samples harvested at 500-hour intervals.

Future Directions

- Complete the 2000-hour MEA aging study, and use recovered samples to certify validity of prior experimental results.
- Evaluate applicability of recovery methods for MEAs that have precious metals coated onto the gas diffusion layer (i.e., gas diffusion electrodes, GDEs).
- Scale up microwave-assisted acid digestion process and optimize process variables.
- Continue to work on identification of gases produced during combustion of Nafion[®] and identify remediation solutions.
- Evaluate recoverable Nafion[®] for use in non-fuel cell applications.
- Estimate economics for each recycling process.
- Begin study of unique pyrometallurgical approach to recover precious metal from metal monoliths.

Introduction

Precious metals are enabling materials in the fuel cell, both for the fuel reformer that generates hydrogen and the fuel cell itself, where the hydrogen is consumed. The precious metals used—Pt, Pd, Rh and Ru—are found in limited quantities in nature, and recycling is required to ensure that market forces do not make the fuel cell economically unattractive.

This project will primarily concentrate on cost-effective recycling of precious metal from the fuel cell membranes without the release of hydrogen fluoride, a corrosive and hazardous gas. The fluoropolymer membranes may be recovered and recycled into a non-fuel cell application, assuming the precious metal recycling process avoids a combustion step. A secondary objective involves the investigation of a process for precious metal recovery from metal monoliths, which are a favored catalyst platform for distributed production of hydrogen.

Approach

Developing an environmentally friendly commercial process for recycling MEAs is a complex problem because of the variability of the fuel cells in use. To address this problem, Engelhard is investigating a series of approaches for recycling MEA components. Both polymer non-destructive and polymer destructive processes are being evaluated, both for technical feasibility and economic rationality.

Polymer non-destructive:

- Microwave-promoted acid digestion dissolves the precious metal without attacking the membrane.
- Solvent delamination separates the carbon catalyst particles from the membranes.
- High-pressure treatment re-disperses the polymeric membrane, which facilitates fluoropolymer recycling, while liberating the carbon catalyst particles.

Polymer destructive:

- The MEA is combusted using microwave energy and hazardous vapors are sequestered.

Results

Independent research activities were carried out at Virginia Polytechnic Institute, the University of Kansas and Ceralink. Generally speaking, the work this year is a continuation of research started last year.

Studies at Ceralink of delamination of 3-layer MEAs have shown a wide disparity in effectiveness depending on the source of the material, the degree of aging and the method of gas diffusion layer (GDL) removal. New membranes needed a relatively high solvent concentration to separate the catalyst layer from the membrane, and recovery decreased when the MEA was exposed to hot water prior to hand-stripping (a useful method for GDL removal). Table 1 gives examples of catalyst removal efficiency under certain conditions. Recent experiments have shown improved process efficiency using elevated temperature and we are further exploring this process parameter. A patent application was filed for an MEA recycling process that incorporates a solvent delamination step.

Table 1. Platinum Recovery from a New 5-layer MEA Following Solvent Delamination – GDL Handstripped w/wo Boiling

| Treatment | Solvent | % Pt released from MEA |
|-------------------------|---------|------------------------|
| Boiled and Handstripped | 70% A | 67 |
| | 70% B | 68 |
| | 70% C | 79 |
| Hand-stripped only | 70% A | 99 |
| | 70% B | 96 |
| | 70% C | 95 |

Very promising results have been obtained at Ceralink using a microwave-assisted acid digestion process. The process is shown in Figure 1. In a single step, the carbon catalyst on a 3-layer MEA is decomposed and the precious metals are solubilized. Figure 2 illustrates that the Nafion[®] membrane, in this case almost transparent, can be recovered. While dissolution of the precious metals is achievable under a range of conditions, temperature and pressure play

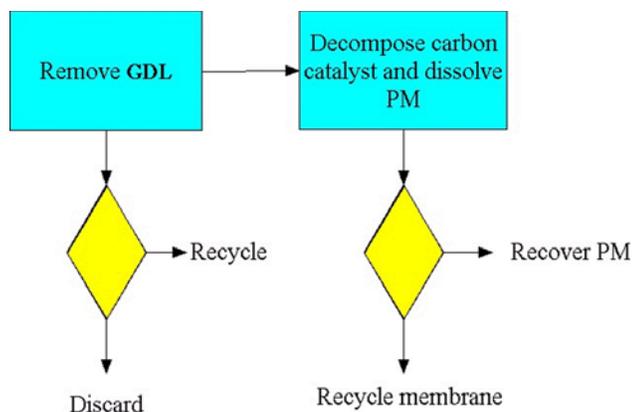


Figure 1. Process for MEA Recycling Using Microwave-Assisted Acid Digestion

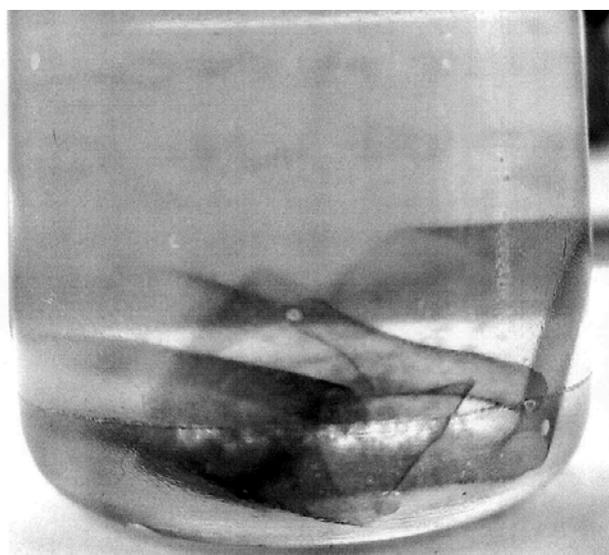


Figure 2. Results of an Acid Digestion Run – Clear Solution and Transparent Membrane

a large part in the effectiveness of the destruction of the carbon catalyst support. Engelhard has identified a potential application for a product made using the recovered membrane. We plan to further investigate the economic viability of this application.

Virginia Tech has concentrated on microwave-induced combustion of 3-layer MEAs. Since the objective of the project is to avoid discharge of HF, work has concentrated on designing an emission control system. An FT-IR instrument has been installed at Virginia Tech to identify gases produced during combustion of MEAs upstream of the emission control chamber. It has been observed that MEA combustion starts immediately on application

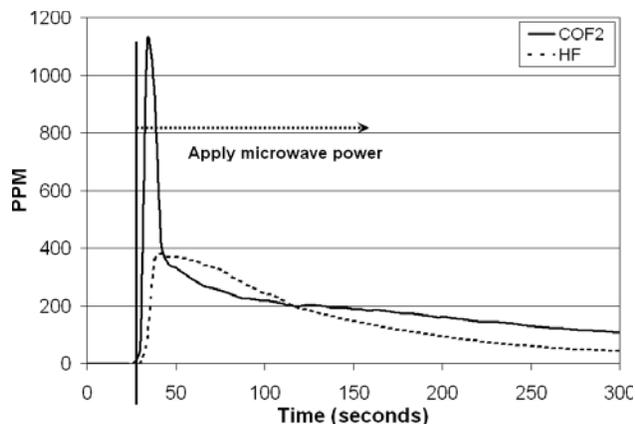


Figure 3. Emission of HF and COF₂ versus Time for Microwave-Induced Combustion of a 3-Layer MEA

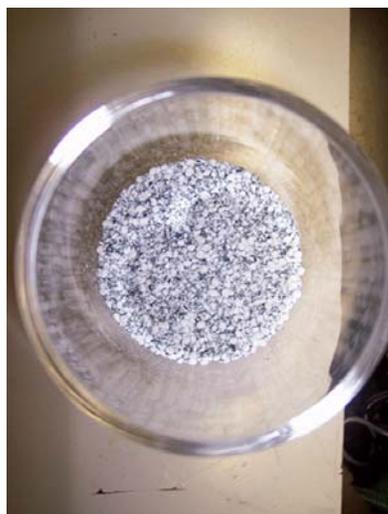


Figure 4. Example of Adsorbent Cartridge for Remediation of Hazardous Vapors from Microwave-Induced Combustion

of microwave energy, while standard combustion requires that the MEA heat up before burning. An example of the emission profile is shown in Figure 3. The sharp peak associated with carbonyl fluoride is highly correlated (>99% probability) with the release of carbon monoxide (not shown) and is probably formed from the reaction between CO and HF. (Combustion conditions are being modified to suppress CO formation.) The gases evolved are swept into a separate chamber for remediation. Figure 4 shows an example of a cartridge to be used for emissions capture.

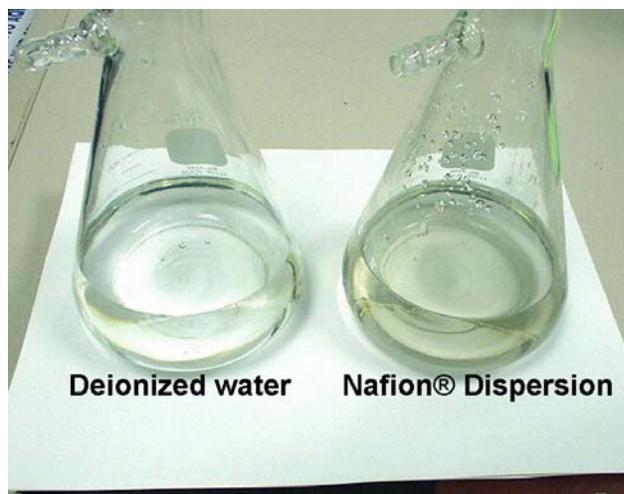


Figure 5. Nearly-Colorless Nafion[®] Dispersion Derived from High-Pressure Treatment of 3-Layer Membrane (flask of deionized water on left for color comparison)

Activity at the University of Kansas has concentrated on determining if the fluoropolymer can be converted to a dispersion. Experiments using supercritical CO₂ and co-solvents were unsuccessful in re-dispersing the fluoropolymer. Furthermore, using neutron activation analysis to determine fluorine content, the catalyst particles separated from the membrane were shown to contain a significant amount of ionomer, with 7-17% fluorine measured. The fluoropolymer membrane was successfully converted to a dispersion by exposing it to high-pressure water. The product of this procedure is shown in Figure 5. Applications of this technology will be investigated.

Conclusions

- By pursuing independent approaches to PM recovery from MEAs, opportunities have arisen for combining technologies to obtain a process for recovering both precious metals and fluoropolymer.
- Microwave-assisted acid digestion appears to be favored because of the ability to recover precious metal while decomposing the carbon (electrode catalyst) particles supporting the PM. An added advantage of this process is that the fluoropolymer is left intact and can be recovered.
- Since scale-up of the microwave-assisted acid digestion process needs to be demonstrated, efforts continue on microwave-induced combustion, a very energy-efficient process that needs to be better understood. Since HF is evolved during combustion, a viable process for HF sequestration still needs to be developed.
- The work on supercritical fluid (CO₂) dissolution was unsuccessful. The work has evolved into a process for Nafion[®] re-dispersion using water at elevated temperature and pressure, and may be useful in developing a cost-effective outlet for recycled Nafion[®].
- Because the bulk of work to date has been performed using fresh MEAs with membranes coated with electrode catalysts, the key challenge ahead is the validation of recycling processes using aged MEAs, as well as MEAs having the electrode catalysts coated on the GDL.

Special Recognitions & Awards/Patents Issued

1. In June, 2005, Engelhard submitted a patent application for a process for precious metal recovery from MEAs.

