

## IV.E.2 Platinum Group Metal Recycling Technology Development

*Lawrence Shore (Primary Contact), Bruce Robertson*

*Engelhard Corporation*

*101 Wood Avenue*

*Iselin, NJ 08830*

*Phone: (732) 205-5447; Fax: (732) 205-5300; E-mail: larry.shore@engelhard.com*

*DOE Technology Development Manager: Arlene Anderson*

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

*Technical Advisor: Robert D. Sutton*

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

*Subcontractors: Virginia Polytechnic Institute, Blacksburg, VA; University of Kansas, Lawrence, KS*

*Consultant: Ceralink, Alfred, NY*

### Objectives

- Develop a new process for precious metal recovery from proton exchange membrane (PEM) membrane electrode assemblies (MEAs)
- Eliminate HF release, a downside of the current recycling process
- Evaluate the feasibility of recycling the fluoropolymer (Nafion<sup>®</sup>) membrane
- Develop a process for recycling of 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:

- N. Cost
- O. Stack Material and Manufacturing Cost

### Approach

- Evaluate the application of a tandem microwave oven for sequential decomposition of the MEA and sequestration of the liberated fluorine (HF)
- Evaluate the liberation of the precious metals from an MEA using mineral acids in a microwave oven
- Determine the solubility of Nafion using supercritical CO<sub>2</sub>
- Evaluate the process of MEA delamination
- Investigate washcoat delamination from a metal monolith substrate

### Accomplishments

- Separated the precious metal electrode catalysts from the fluoropolymeric membrane using a non-destructive method
- Demonstrated the rapid decomposition of a 3-layer MEA using microwave heating

- Constructed apparatus for screening supercritical CO<sub>2</sub> mixtures for treating Nafion<sup>®</sup> and began screening co-solvents for disruption of the membrane

### **Future Directions**

- Explore the issue of universality for the MEA delamination process and optimize the process conditions
- Determine precious metal recovery from the 3- and 5-layer MEAs using the microwave decomposition and construct the emissions capture stage
- Evaluate the recovery of precious metals from MEAs using closed-vessel microwave-assisted solubilization
- Perform experiments using supercritical carbon dioxide to define the process for catalyst separation from Nafion<sup>®</sup>

---

### **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 limited 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 recycling of precious metal from the fuel cell membranes. A secondary objective involves the investigation of a process for precious metal recovery from metal monoliths.

The current process for Pt recovery from a fuel cell membrane combusts the organic component of the MEA. Besides destroying the intrinsically valuable fluoropolymer, the combustion results in the evolution of copious amounts of HF, a corrosive and toxic gas. While the bulk of the HF can be removed from the exhaust using a wet scrubber, it is preferable to develop a process that eliminates HF formation.

### **Approach**

Engelhard has recognized the complexity in developing an environmentally friendly commercial process for recycling MEAs. There is uncertainty relating to logistics for materials collection and segregation prior to recycling and the advisability of trying to reuse materials that may be technologically out of date. Therefore, a series of approaches are under investigation for the recycling of the MEA components.

The primary approach involves microwave treatment. In one line of research, microwave energy

is used to decompose the layered MEA, leaving a precious metal-rich ash. The exhaust would be treated in a second chamber to capture HF. Conversely, microwaves can be used to efficiently heat mineral acids in a vessel containing the MEAs, thereby achieving solubilization of the precious metals. The impact of the acids on the Nafion<sup>®</sup> membrane would have to be determined.

Other experiments are designed specifically to recycle both the precious metals and the fluoropolymer membrane. Solubilization of the Nafion<sup>®</sup> is being investigated using supercritical carbon dioxide. Because of the polarity of the membrane polymer, co-solvents that will act to form an emulsion with the Nafion<sup>®</sup> are also being evaluated. In a parallel experiment, the delamination of the MEA is being investigated. In practice, it has been shown that the catalyzed carbon layers can be removed from the membrane, leaving the latter intact and available for recycling.

In a separate study, the recovery of precious metals from catalysts made with metal monoliths will be pursued. The metal monolith supports are not amenable to either hydro- or pyro-metallurgical techniques. Delamination of the washcoat layer from the catalyst channels will be investigated.

### **Results**

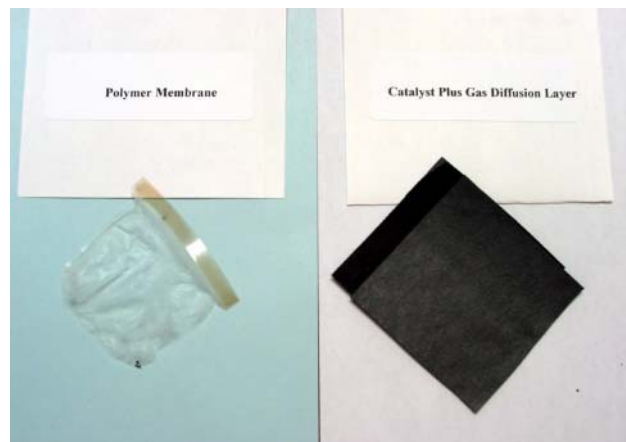
The research plan involves a multi-faceted approach to the recycling of precious metals from MEAs that recognizes the current uncertainties regarding both the value of the non-precious metal components of the MEA and the method of collection and pre-processing of the MEAs prior to

actual recovery. For example, a major accomplishment has been reached in membrane recycling. A proprietary process has been developed to recover the membrane intact; the mixed precious metal electrode catalysts can be recovered with or without the gas diffusion layer, depending on pre-processing steps. Evidence of the delamination process is shown in Figure 1. While this process eliminates release of fluorine, it is unknown whether the polymer can be re-used. Furthermore, segregation of polymer by a fabricator would become necessary if the membrane composition starts to be differentiated (compared to Nafion<sup>®</sup>).

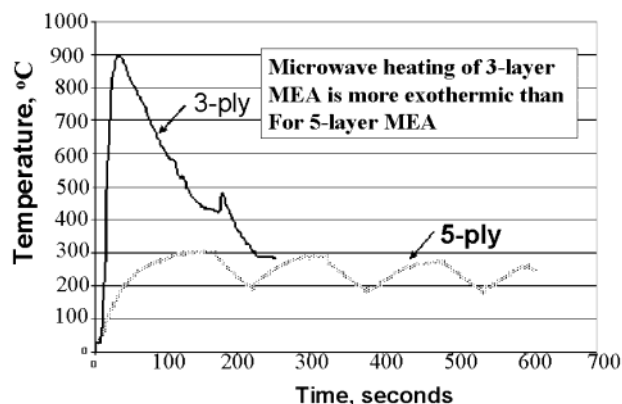
Research at Virginia Tech has concentrated on the environmental concerns of the project rather than the recovery of the membrane. Figure 2 shows that both 3- and 5-layer MEAs absorb microwave energy, although the temperature rise associated with the 3-layer MEA is meteoric. Figure 3 shows that the microwave combustion approach is efficient in removal of polytetrafluoroethylene (PTFE) (white material) from the carbon fibers of a gas diffusion layer. It is obvious that the merits of the microwave decomposition approach will be weighed against the reclamation value of the polymeric membrane and the carbon fibers of the gas diffusion layer (GDL). By contrast, Ceralink has initiated closed-vessel microwave digestion experiments using mineral acids to liberate precious metal from the membrane. Figure 4 shows a temperature vs. time curve using aqua regia. Because of the pressure build-up, the reaction can be run at 190°C, far above the normal boiling point of the acid mixture.

Initial supercritical CO<sub>2</sub> experiments have been performed at the University of Kansas. The supercritical testing is being performed using the apparatus shown in Figure 5. Testing with CO<sub>2</sub> with and without added ethanol has failed to dissolve the membrane, but conditions have been observed for liberation of the carbon particles from the surface of the Nafion<sup>®</sup>.

Engelhard has decided that, in the near term, the stationary market for fuel cells is more important than the automotive market. Therefore, effort has been devoted to working with MEAs that have a Pt/Ru/C anode (applications that use hydrogen-rich reformat). Analytical method development was



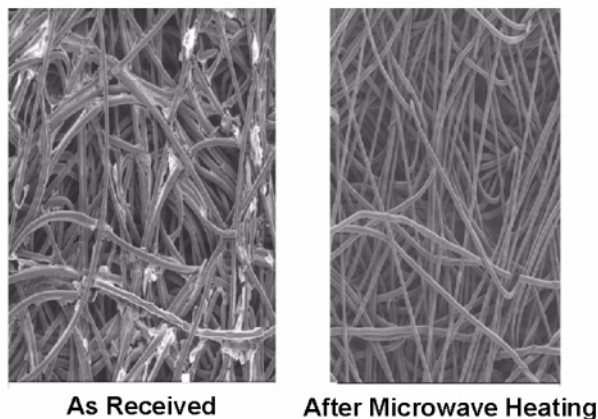
**Figure 1.** Delamination of PEM Membrane Assembly - Carbon Electrode Layers Separated from Nafion<sup>®</sup> Membrane



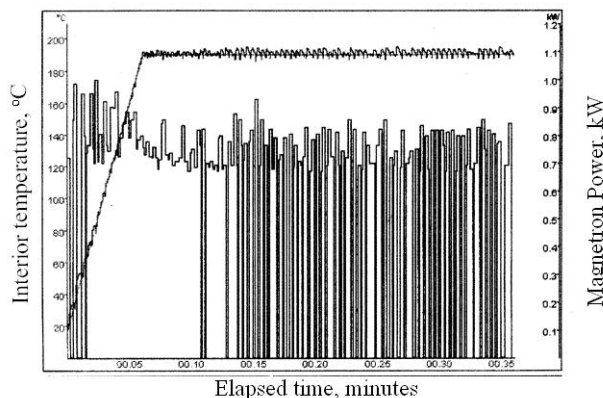
**Figure 2.** Application of Microwave Combustion Technique to MEAs with (5-layer) and without (3-layer) the Gas Diffusion Layer Attached

designed around the use of small samples, a situation where gravimetric methods are impractical. Based on their high precision and low cost of implementation, colorimetric methods were selected for process validation. Because of the difficulty of measuring Pt in the presence of Ru, a sample of Pt/C was used as the benchmark material. Using a SnCl<sub>2</sub> colorimetric method, anode catalyst containing Pt can be analyzed with a relative standard deviation of <0.5%. Initial work has pointed to a bleaching method that permits the determination of Pt in the presence of Ru using the SnCl<sub>2</sub> method; normally, the overlap of the spectra of the complexes formed by these two precious metals makes quantification of the mixture difficult. While additional testing is

### Micrographs of a Gas Diffusion Layer



**Figure 3.** Microwave Removal of PTFE from the Gas Diffusion Layer



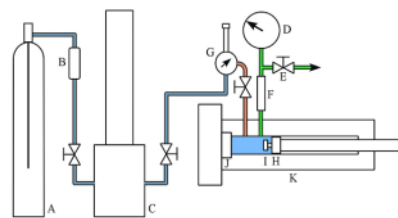
**Figure 4.** Temperature vs. Time for Microwave-Assisted Digestion Using Aqua Regia

required, good results have been achieved for Ru measurement using a thiourea method<sup>1</sup>. This method does not suffer from Pt interference.

### Conclusions

Progress has been made in discovering discrete operations that support recycling of components from fluorine-containing MEAs. Approaches include the following:

- Separation of the Nafion membrane from other MEA components



A. CO<sub>2</sub> (industrial grade) cylinder with dip tube  
 B. 0.5 micron filter  
 C. Syringe pump  
 D. Pressure gauge (Heise 0–10,000 psig)  
 E. Shutoff valve (HiP 15–11AF2)  
 F. High pressure filter, 2 micron  
 G. Valco 4UW valve with syringe adapter  
 H. Plunger  
 I. Magnetic stirrer  
 J. Sapphire window  
 K. Vessel

**Figure 5.** Thar Technologies Phase Equilibrium Analyzer in Use at the University of Kansas for Supercritical CO<sub>2</sub> Studies

- Efficient MEA processing using microwave energy, including upgrading the recycling value of the GDL
- Development of supporting analytical methodology

Although the project is in its first year, the direction for recycling processes is being identified. As the exploratory activities continue in the coming year, the project will be matched up with societal approaches to the collection and dismantling of the fuel cells and, potentially, the dismemberment of the MEAs as part of the plan for precious metal recycling. In the coming year, the technological approaches under consideration will be measured by the recycle value of the components and the environmental impact of the process.

### References

1. M. Balcerzak, E. Swiecicka and D. Bystronska, *Analytical Letters*, **32**, 1799-1805, 1999.

### FY 2004 Publications/Presentations

1. L. Shore, "Precious Metal Recovery from Fuel Cell MEA's", 2004 AIChE Spring Meeting, New Orleans, LA (2004).