
V.E.2 Platinum Group Metal Recycling Technology Development

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Objectives

- Develop a new process for precious metal (PM) recovery from proton exchange membrane (PEM) membrane electrode assemblies.
 - 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 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 (3.4.4.2) 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 price 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

Accomplishments

- Completed 2,000-hour aging study of catalyst coated membrane (CCM)-style membrane electrode assemblies (MEAs), and harvested the MEAs for project feedstock.
- Demonstrated the ability to separate electrode catalyst particles from the rest of the aged membrane electrode assembly using an alcohol-water mixture. The process was accelerated using a continuous microwave-heated reactor. Less than 2% of the Pt was left on the gas diffusion layer (GDL) and membrane remnants.
- Developed a two-stage filtration process for electrode catalyst recovery, polymer dispersion re-concentration, and solvent recycling.
- Absorbed >99% of HF and carbonyl fluoride liberated during combustion of a 3-layer MEA using a proprietary adsorbent.
- Integrated unit operations into a 'green' process for precious metal recovery and potential reuse of the perfluoropolymer dispersion.

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. A study by TIAX has shown that by 2050, recycled Pt will eclipse mine-derived Pt as the dominant source of metal for the fuel cell market [1].

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 in the

membranes may be recoverable and recycled into a non-fuel cell application.

Approach

Because of the wide variation of methods of construction and materials, as well as the expectation for product degradation and evolution, Engelhard has concentrated on recycling of fuel cell MEA components, rather than their reuse. Separate approaches are applied to CCM-style MEAs and gas diffusion electrode (GDE)-style MEAs.

CCMs

1. Decompose an aged MEA using an alcohol/water mixture to form a suspension of electrode catalyst within a polymer emulsion.
2. Disperse the emulsion using heat.
3. Using a two-stage proprietary filtration process, harvest the electrode catalyst, reconcentrate the dilute emulsion for secondary applications and purify the solvent for reuse.
4. The precious metal will be recovered by acid digestion of the electrode catalyst, either directly or after combustion of the electrode catalyst to yield a high-grade ash. The combustion process will feature minimal release of fluorine-containing gases.

GDEs

1. The layers of the MEA are separated using either hot water or an alcohol-water solvent; the electrode catalyst remains almost exclusively on the GDE.
2. The precious metal is recovered from the GDE using microwave-assisted acid digestion.

Results

During the past year, we had access to aged membrane electrode assemblies and these samples drove our work. The bulk of the work has been performed on CCM-style MEAs that had been acquired from W.L. Gore and aged at Greenlight Power/Hydrogenics. We were surprised by two observations when handling the aged MEAs. First of all, the layers of the aged samples did not separate when heated in hot water as was previously observed with samples from other vendors. Second, while membranes from virgin MEAs were unaffected by the solvent, the membrane from the aged membrane disintegrated in the solvent mixtures used in the study.

Originally, it was expected that acid digestion of 3-layer MEAs would be acceptable; ~98% of the Pt was recovered using microwave-assisted acid digestion after the gas diffusion layer had been removed. However, a variable and significant amount of platinum (2-10%) was

left on the hand-stripped GDL. It was realized that an effective method was needed to remove the GDL from the rest of the MEA without retention of the electrode catalysts on the GDL. It was shown that the membrane would delaminate in the appropriate solvent and, after heating, the electrode catalyst could be separated from the GDL and the dispersion of the membrane polymer. Over 98% of the platinum was recovered using this approach. Typical data is shown in Table 1. The data shows that solvent selection and concentration is more critical than the temperature for polymer dispersion.

From a commercial perspective, there is an advantage to combust the recovered electrode catalyst as part of the metal recovery process. By achieving separation of the electrode catalyst from the rest of the MEA, fluorine emissions (primarily HF and carbonyl fluoride, COF₂) are reduced by a factor of ~25x compared to complete MEA combustion. Virginia Tech has been working on the adsorption of the fluorine gases using a proprietary adsorber package. Figure 1 shows the reduction in peak HF during combustion of a 3-layer MEA, a fairly rapid event that is monitored using fourier transform infrared (FT-IR). Twenty runs were made with and without the adsorber, and >99% of the HF was removed by the adsorber. Analogous results were obtained when COF₂ emission data were plotted.

Up to December 2005, the University of Kansas was part of the research team, working on a supercritical water process for Nafion[®] dispersion as part of a process for fuel cell recycling. Besides technical issues related to the project, the commercial viability of the process was questionable because of the requirement for large capital investment and the uncertainty in the resale value of the polymer dispersion. The work at the University of Kansas was terminated but the concept of membrane dispersion and electrode catalyst liberation was merged with the prior experience in solvent delamination to create the process shown in Figure 2. This process incorporates the delamination required to shed the gas diffusion layer, and substitutes a lower temperature and

TABLE 1. Data for Recovery of Platinum from CCM MEAs using Solvent Delamination

Solvent/Temp for heating membrane	% Pt recovered	% of Pt left on membrane residue	% of Pt left on GDL
10% Solvent A @100°C	80.3	0.4	19.3
10% Solvent A @150°C	90.5	0.9	8.6
25% Solvent A @100°C	95.1	0.3	4.5
10% Solvent B @100°C	97.4	0	2.5
10% Solvent B @150°C	98.5	0.2	1.3
10% Solvent C @100°C	97.45	0.5	2.1
10% Solvent C @150°C	98.6	0.6	0.8

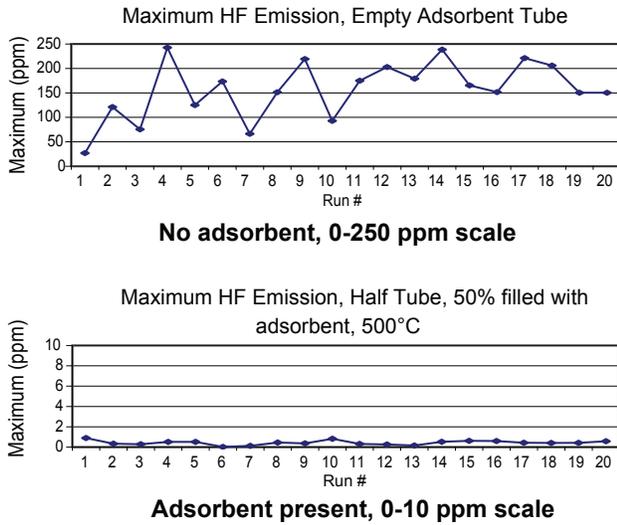


FIGURE 1. Reduction in Concentration of HF Vapor from MEA Combustion using Proprietary Adsorbent

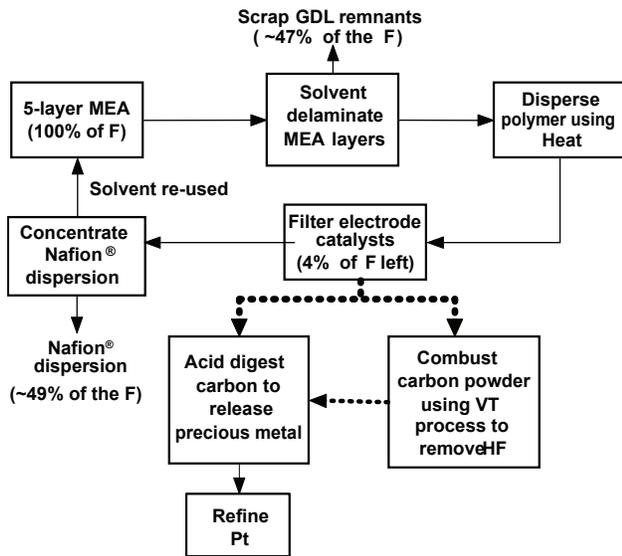


FIGURE 2. Proposed Process for Platinum Recovery and Membrane Re-Dispersion for CCM-style MEAs

pressure solvent dispersion step for the high temperature and pressure aqueous process. The filtration steps were validated at Pall Corporation.

A parallel project was directed towards recycling of GDE-style MEAs; aged GDEs were obtained from ETEK. When the GDE was separated from the dry membrane by mechanical means, 75% of the electrode catalyst remained with the membrane. When the MEA was first boiled in water, the GDEs separated from the membrane and almost all the electrode catalyst remained on the GDE; similar results were obtained immediately after immersion of the GDE in aqueous solvents. Results using boiling water are shown in

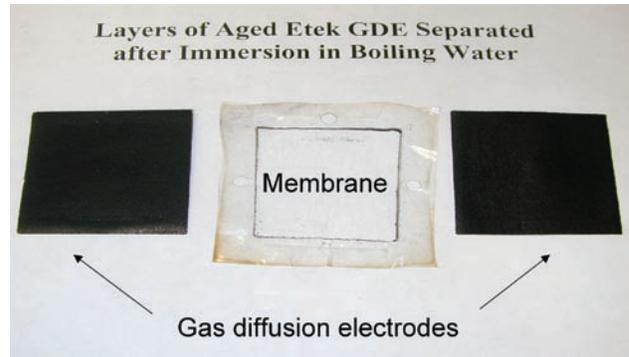


FIGURE 3. Quantitative Recovery of Electrode Catalyst on Exterior Layer after Boiling an Aged GDE-style MEA

Figure 3. Pt was recovered using acid leaching of the outer layers. While 90% of the Pt was recovered using conventional acid treatment, the yield increased to 98% using microwave-assisted acid digestion. The data obtained in the GDE study is summarized in Table 2.

TABLE 2. Distribution of Platinum between Layers Based on Treatment of Aged GDE-style MEAs

Process	% Pt on Membrane Acid-leachable	% Pt on Membrane Non-leachable	% Pt on GDE Acid-leachable	% Pt on GDE Non-leachable
Handstripped, dry	72.7	3.1	22.1	2.1
Handstripped, wet with conv. heating	0.2	0.2	86.4	13.2
Handstripped, wet with microwave heating		0.3	~98	~2

Conclusions and Future Directions

- The platinum content of fuel cells can be recovered with high yield using a process that has low emissions and operates under moderate conditions. The recovery process may vary depending on the MEA type: CCM vs. GDE.
- The ability to scale up the recovery of platinum from electrode catalyst using microwave-assisted acid digestion will be tested using a custom autoclave built at Autoclave Engineers and fitted with microwave heating at Microwave Materials Technology.
- A determination needs to be made whether to combust the electrode catalysts or directly acid leach to dissolve the platinum. One of the critical criteria will be the capacity of the adsorber for fluorine gases, which still needs to be determined.

Special Recognitions & Awards/Patents Issued

1. In June, 2006, Engelhard submitted a patent application for a process for precious metal recovery from aged MEAs.

References

1. TIAX LLC: D0034, DOE: DE-FC04-01AL67601