

V.P.2 Platinum Group Metal Recycling Technology Development

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Objectives

Develop a new process for precious metal 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.

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 precious metal (PM) catalyst loading – 0.20 g/kW

Accomplishments

- Developed a simple recycling process, equally applicable to catalyst coated membrane (CCM) and gas diffusion electrode (GDE)-style MEAs, having the following advantages over prior approaches:
 - Increased access to Pt in the MEA by preliminary grinding with liquid nitrogen embrittlement.
 - Eliminated combustion of the MEA or its components, so HF scrubbing is no longer required.
 - Avoided MEA delamination, thereby eliminating the need for solvents.
 - Facilitated recovery of Pt that migrated from the cathode and deposited within the membrane during aging.
- Terminated the microwave combustion studies at Virginia Tech because of the low capacity utilization of the recommended adsorbent and the progress made in direct leaching of the MEA.
- Demonstrated high Pt recovery via acid leaching of next generation base-metal alloyed electrocatalysts.



Introduction

PMs 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 PMs 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 HF, a corrosive and hazardous gas. The fluoropolymer in the membranes may be recoverable and recycled into a non-fuel cell application.

Approach

In 2006, discrete processes that incorporated solvent delamination were proposed to recycle GDEs and CCMs. Based on the recognition that both GDE and CCM MEA architectures could be commercialized and that recycled MEAs could include a mixture of different materials, the Pt recovery processes described in 2006 were universalized. The focus was placed on Pt recovery, while Nafion® recycling was de-emphasized. The latter decision was based on recognition that replacements for Nafion® are being developed, as well as the technical and economic issues related to placement of recycled Nafion® in non-fuel cell applications.

The ‘universal’ process includes the following steps:

1. Shred the MEA sheets to facilitate handling.
2. Embrittle the MEAs with liquid nitrogen then grind in the presence of LN₂.
3. Blend the lot; remove a sub-sample for analysis.
4. Leach the lot with an oxidizing mineral acid mixture at elevated temperature (and pressure). Separate the phases. Repeat this step to maximize Pt yield.
5. Filter and wash the residue, which can be processed to liberate Nafion®.
6. Using conventional chemistry, process the liquid phase to produce refined precious metals.

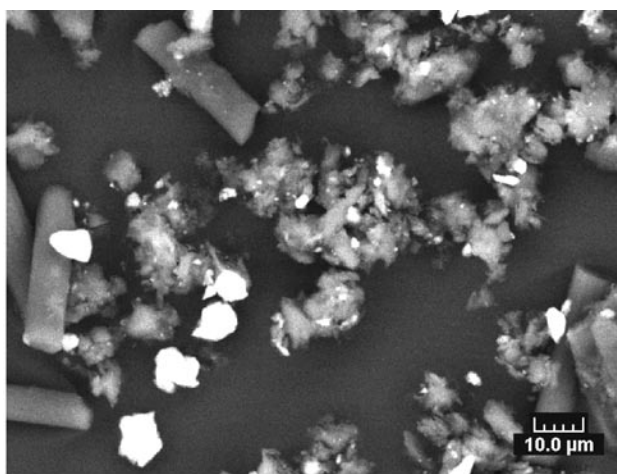
Results

In 2006, BASF Catalysts LLC, formerly Engelhard Corporation, reported Pt recoveries using processes optimized for GDE and CCM-type MEAs, respectively. Based on the favorable results obtained using solvents to delaminate the MEAs, assembly of a pilot plant was initiated. Concurrent to that activity, it was recognized that a single process for all types of MEAs was more desirable than the approach of using customized methods, and that the process should concentrate on Pt yield at the expense of Nafion® recycling. Furthermore, it was recognized that a portion of the Pt on the cathode could migrate into the membrane and deposit in a finely-dispersed form [2,3]. Solvent delamination of CCM membranes, followed by polymer re-dispersion, would mobilize the Pt crystallites, but these particles were small enough to pass through the filter intended to separate the electrode catalyst from the polymer dispersion, resulting in a loss of platinum. In addition, the option of combustion of harvested electrode catalyst was downgraded because of low capacity utilization of the adsorbent recommended for HF removal, the sintering of the Pt particles and the potential for Ru loss.

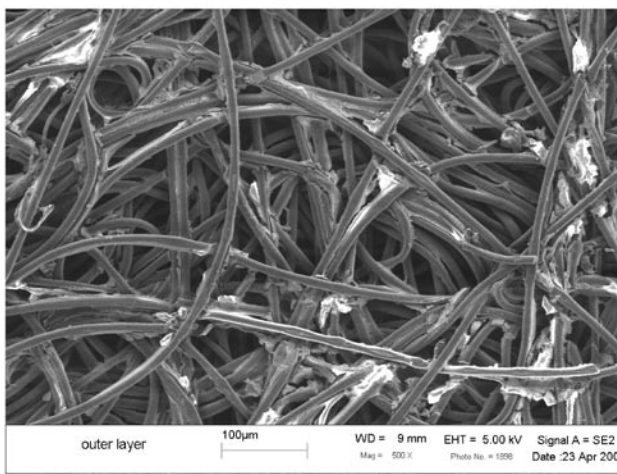
A new approach to sample preparation was investigated. Grinding of the MEAs was demonstrated on a trial basis by embrittling the MEA at liquid nitrogen temperature then shattering the MEA layers using an impact method (SPEX CertiPrep 6850 Mill).

Figure 1 compares a milled CCM MEA with the intact gas diffusion layer removed from a CCM. Besides particle size reduction, the grinding process, followed by blending, achieved a nearly homogenous sample that could be used to quantify the value of the lot based on Pt content. The grinding process was tested on a larger scale using the Hosokawa Micron ‘Mikro Bantam’, which is a cryo-mill having a centrifugal design. Figure 2, which compares the particle size distribution for an MEA sample containing gasket material ground with and without external embrittlement, demonstrates the improvement in particle size reduction when the material is embrittled upstream of the actual milling; mill throughput also increased with external embrittlement. However, the data in Table 1 show that Pt availability (as expressed as % yield in a single leach step) does not increase with a smaller particle size distribution (PSD).

After the MEA was ground, the PM content could be recovered using acid leaching. Tests were performed in a sealed vessel with microwave heating and an acid

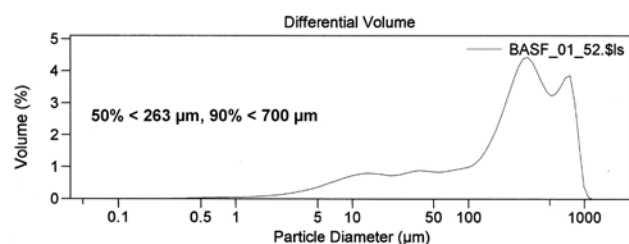


Ground CCM MEA, 1000x magnification

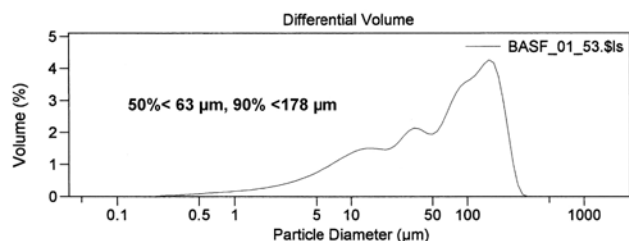


Intact GDL from a CCM MEA, 500x magnification

FIGURE 1. Cryo-Grinding Dismembers the MEA Structure



A. MEA w/ gasket milled with LN₂.



B. MEA w/ gasket chilled in LN₂ bath, then milled with liquid nitrogen

FIGURE 2. Reduced MEA PSD Achieved using External Embrittlement in Liquid Nitrogen

TABLE 1. External MEA Embrittlement Does Not Increase Pt Leachability after Cryo-Milling (First Yield with Acid 'C')

Run	Portion	wt.	% Pt yield
6	1	0.543	93.00
	2	0.594	94.14
7	1	0.52	94.23
	2	0.518	92.87

MEA stock contained rigid gasket material, which made milling difficult. Run 7 had both external embrittlement and cryo-cooling of the mill; run 6 milled with only cryo-cooling of the mill.

mixture specified acid 'A', as well as in an open vessel with an acid mixture specified acid 'C'. Working with virgin MEAs, it was found that the MEA powder was fairly hydrophobic, so contact with the acid mixture was inefficient. A series of surfactants were tested with different order of reagent addition. A surfactant was identified that wetted the MEA powder, was compatible with acid and had no deleterious decomposition products. Table 2 lists the experimental results for the leaching study.

The next step in the process development was to determine the factors controlling the leach yields using the microwave-assisted leaching process. Variables that were tested included run time and mass of sample; successive leaches were performed to determine conditions required for maximum Pt recovery. Reaction temperature and leachate were held constant. Table 3, which lists the results from the process evaluation

TABLE 2. Improving the Yield of Pt Leached from Ground MEAs with a Surfactant

Material	Surfactant	% Pt yield
CCM	No	72.5
	Yes	94
GDE	No	93
	Yes	95

Samples of 0.5 g with 25 mL of Acid 'C' at ~100°C, ambient pressure.

TABLE 3. Effect of Time on MW-Assisted Leaching of Ground MEAs

Hold time	1 st yield, %
10	94.4
20	93.5
30	93.6
40	94.2

Leaching performed in a 100-mL fluoropolymer vessel @200°C with 0.25 g of sample, 1g of surfactant solution and 21 mL of acid 'A'.

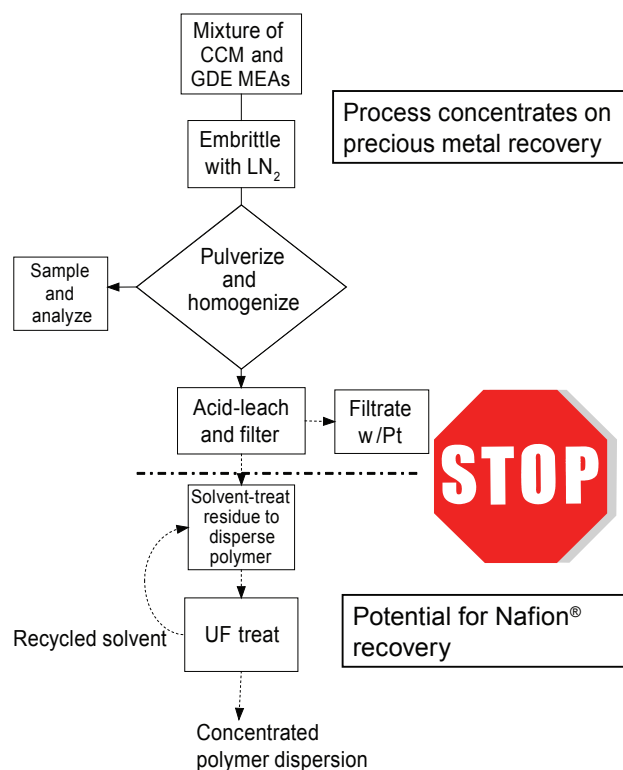


FIGURE 3. Simplified/Consolidated (CCM and GDE) Pt Recovery Process

runs, shows that the reaction is not kinetically-limited. Figure 3 gives a high-level block diagram of the proposed process.

A major concern was the robustness of the leaching process using advanced electrocatalyst formulations with base metal-alloyed Pt. Samples were received from the Naval Research Laboratory, Cabot Corporation and a Japanese catalyst supplier. When leaching was performed in an open beaker, the recovery of these binary and ternary materials was high, with roughly 95% Pt yield from a single leach. Table 4 lists the recoveries for a series of electrocatalysts. Analogous experiments were performed in sealed vessels in a microwave oven. The low yield observed relative to the open vessels was attributed to the high density of the electrocatalyst powders and the lack of agitation during a microwave-assisted leach; dispersion of the electrocatalysts on a MEA negates the density issue.

TABLE 4. Leachability of Base Metal-Alloyed Cathode Catalysts

Alloy Element(s)	% Pt Yield, 1st leach
Pure Pt/C	92.6
Ru	95.8
Ni and Co	95.8
Co and Cu	96.6
Fe	95.4
Co	96.3
Cr	96.8
TaPO (support)	95 (est)

Leaching performed in duplicate using Acid C.

Conclusions and Future Directions

- A single process has been proposed to recover Pt from MEAs with either GDE or CCM architecture. Because the process avoids the need for solvents and eliminates combustion, there are no hazardous emissions.
- The basis of the new process is cryogenic grinding of the MEAs. Tests have shown that external embrittlement is required to accommodate recycled MEAs with gaskets. Because of the friability of the electrode layers, Pt leachability is not directly related to overall particle size distribution following grinding.
- The ruggedness of the leaching process has been documented by the ability to recovery Pt from advanced, base metal-alloyed electrocatalysts.
- A detailed process design is being made and will be used to perform an economic analysis of the process.

References

1. TIAX LLC: D0034, DOE: DE-FC04-01AL67601.
2. Ferreira, P. J. et al, *Journal of The Electrochemical Society*, 152 (11), A2256-2271, 2005.
3. More, K. L., Bentley, J., Reeves, K. S., 'Microstructural Characterization of PEM Fuel Cell MEAs', 2006 DOE Hydrogen Review, FC27.