

V.F.1 Platinum Group Metal Recycling Technology Development

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Consultant:
Ceralink, Troy, NY

Start Date: October 1, 2003
Projected End Date: October 31, 2009

- Cost - \$7/kW (based on \$1,100/troy ounce of platinum)
- Total Pt catalyst loading – 0.20 g /kW

Accomplishments

The following tasks related to development of the process for precious metal recovery from fuel cell MEAs were performed in the past year:

- Identified two competitive material preparation technologies, granulation and cryo-milling/agglomeration, that are compatible with the process of leaching Pt from used MEAs.
- Determined critical elements of leaching chemistry, resulting in 98% Pt yield in a single leach.
- Performed corrosion studies of titanium, a potential reactor material, under modified leach conditions, and demonstrated the potential for a 10-fold increase in corrosion resistance using a copper additive.
- Refined the original process flow diagram and the economic analysis based on the technical improvements made over the last year, including 85% reduction in acid consumption.
- Validated a technology for near-quantitative removal (>99%) of phosphoric acid from polybenzylimidazole (PBI)-based MEAs.

Objectives

Develop a new process for precious metal recovery from polymer electrolyte membrane electrode assemblies (MEAs), while eliminating hydrogen fluoride emission, a disadvantage of the current combustion-based recycling process.

Technical Barriers

This project addresses the following technical barriers from Section 3.4.4 (Technical plan/Barriers) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) High Cost of Catalyst Materials

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:



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 overtake freshly-mined Pt as the dominant source of metal for the fuel cell market [1].

Over the last year, the leaching process proposed in 2008 to recover Pt has been radically improved, resulting in a simpler process that requires a single leach and rinse cycle that is carried out in one vessel.

Approach

Last year, a two-stage leach was proposed to achieve 98% recovery of the Pt contained in MEAs. Over the last year, an effort was made to improve the yield of the process, with an objective of requiring only one leach, with investigations into reagent selection and

usage. Also, work was performed to simplify material handling and safety issues, as well as to investigate the potential for corrosion of a titanium-lined reactor. Process improvements noted in bench scale testing were validated in scaled-up testing.

Results

Cryo-milling had previously been validated as a mechanism to prepare MEAs as a powder that could be sampled in-line, but the resultant hydrophobic product required wetting with an aqueous surfactant to leach Pt successfully. Alternatives to this process were identified over the last year. It was found that the milled MEA powder could be agglomerated using a hot melt process. The resulting coarse powder was hydrophilic and porous enough for efficient leaching. Pt recoveries of >99% were reported in a single leach. However, an alternative was desirable because of the complexity and cost of using liquid nitrogen for MEA pre-embrittlement and mill cooling. Granulation was identified as a viable, room temperature alternative to cryo-milling. In one trial, 5-layer MEAs made with gas diffusion layers (GDLs) of either carbon cloth (gas diffusion electrode, GDE) or carbon paper (catalyst-coated membrane, CCM) were granulated with a Press Side Granulator (Hosokawa Polymer Systems). The fluffy products were leached with efficiency of ~98% in a single step. In a second, scaled-up trial with MEAs made with carbon cloth (GDE), a denser product was achieved. Leaching of this material resulted in Pt recovery in excess of 99%.

The high Pt yield reported above was far better than project results previously reported for a single leach

step. This improvement was achieved, in some degree, by successive changes in the leaching process. First, the amount of surfactant decreased; for the granulated MEA, the surfactant was reduced 5- to 10-fold by using sonication to stimulate material dispersion. Next, the amount of nitric acid used for the leaching was decreased from the amount required for reaction with hydrochloric acid (HCl) to yield aqua regia to ~15% of the stoichiometric amount required to react with HCl. Third, the order of acid addition was studied. Dosing with concentrated HCl and then limiting HNO₃ usage resulted in consistently high Pt yields, whereas lower yields were achieved when HNO₃ was added first. For agglomerated powders, 99% of Pt was recovered and, for granulated MEAs, the results ranged from 97 to 99% for carbon fiber GDEs and 98% for CCMs with carbon paper GDLs, respectively. When azeotropic HCl was used in place of concentrated HCl, Pt yields decreased 3-5% for the agglomerated samples. The conclusion from the various experiments was that high chloride concentration promoted Pt recovery. A result of decreased HNO₃ usage is that >80% of the HCl initially added can be recycled. Since concentrated HCl optimizes Pt recovery, the HCl/water azeotrope generated during HCl distillation will have to be treated using an azeotrope breaker to recycle HCl as the concentrated acid. Figure 1 shows a representation of the overall Pt recycling process with the granulation option.

Trying to reach quantitative Pt recovery is desirable because of the high cost of Pt; a 1% Pt loss was estimated to be equivalent to a revenue loss of about \$3.50/kg of MEA, assuming 1% wt/wt Pt and a cost of \$1,100 per troy ounce of Pt. It was shown that the

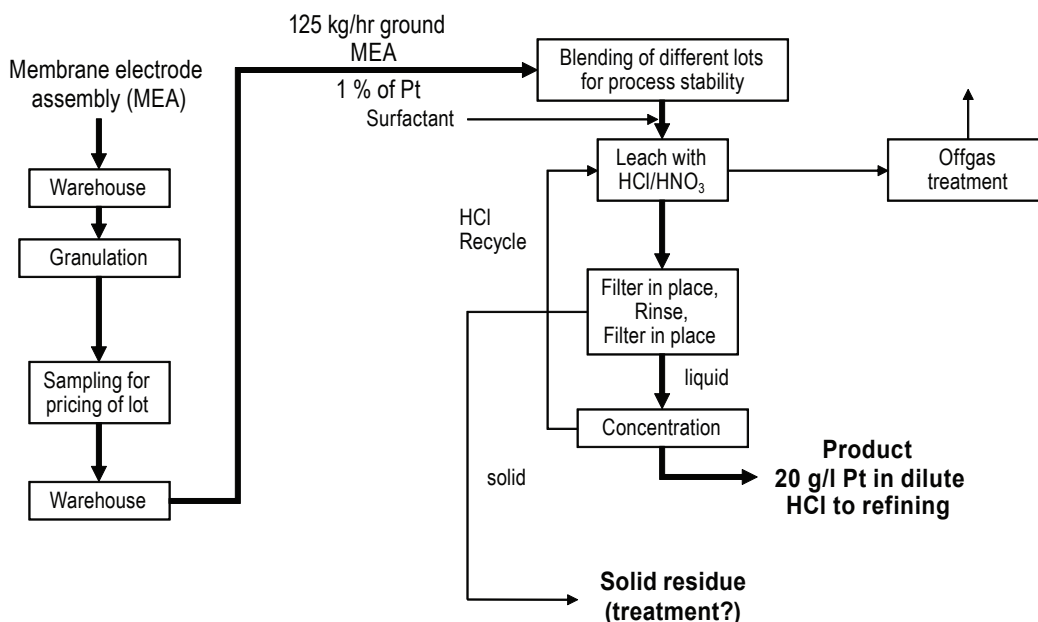


FIGURE 1. Revised Process Flow Diagram

Pt yield from the granulated GDE could be increased by 1% if the residue was sonicated in an alkaline rinse, a medium that also neutralizes the residue prior to disposal. Sonication adds almost no cost to the process and more effectively rinses the MEA residue than conventional methods. Similarly, very high Pt recovery is achieved using the agglomeration approach, at a slight increase in processing cost. For example, the combination of cryomilling and agglomeration increases the process cost by an estimated \$0.60/per kg MEA (<20% of the value of the increased Pt yield) compared to the granulation and surfactant wetting process alternative. The cost differential is based on LN₂ cost and higher reagent usage.

Data for the optimized leaching process, including both lab runs with sonification-intensified rinsing and scale-up data, are shown in Table 1. The scale-up of the leaching process, using a stirred titanium Parr reactor, successfully demonstrated near quantitative Pt yield when the experiment was run at 100°C, independent of nitric acid usage (15 or 100% of aqua regia stoichiometry). Minimizing HNO₃ added is highly preferred economically and environmentally, but affects the corrosion resistance of titanium. The impact of temperature, oxidant and corrosion inhibitors on a titanium vessel is shown in Figure 2. Operating at 100°C

TABLE 1. Data for Optimized Leaching Process

A. Representative Leach Data for Granulated/sonicated GDEs

Rinse	mg F	mg rinse	mg R	mg T	% Pt yield
NaOH	49.10	0.37	0.36	49.83	99.28
NaOH	54.63	0.42	0.30	55.35	99.46
Water	51.70	0.25	0.39	52.34	99.25
Water	54.60	0.24	0.40	55.24	99.28

mg F - mg of Pt in filtrate; mg rinse - mg Pt in the sonicated rinse;
mg R - mg Pt in the residue; mg T - total mg Pt

B. Representative Leaching Data from 600-mL Parr Reactor Runs

Sample ID	HNO ₃ , % of aqua regia stoichiometry	Temperature	% Pt yield
Milled GDE	100	100	98.6
Agglomerate A	100	100	99.5
Agglomerate B	100	100	99.5
Agglomerate A	100	100	99.5
Agglomerate A	100	100	99.3
Agglomerate A	10	100	99.5
Agglomerate B	100	90	96.5

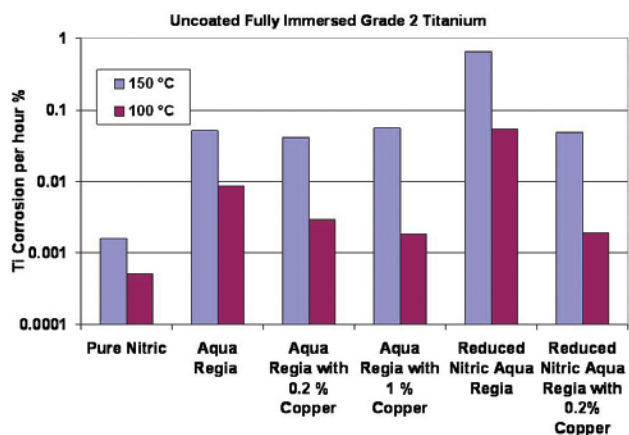


FIGURE 2. Comparison of Corrosion Rates for Titanium at 100 and 150°C

reduces corrosion by an order of magnitude compared to 150°C, and the loss of passivation of titanium as a result of using less nitric acid in the leach can be offset by addition of copper sulfate.

Whereas Nafion[®] is used as the membrane for low-temperature fuel cells, high-temperature (180°C) fuel cells, which are relatively immune to CO poisoning, are constructed using phosphoric acid-saturated PBI membranes. Removing the H₃PO₄ prior to acid leaching is desirable; otherwise, phosphorus will enter the precious metal purification process. Water leaching of the PBI membranes is only partially effective; roughly 80% of the acid is removed using water leaching and this is not improved using sonication. An extended sonication study was performed in conjunction with MEC Chemicals. Half inch wide strips of MEAs were treated at room temperature with either water only, a single proprietary reagent, or successive treatments with two proprietary reagents. The impact of treatment time and use of a cold water rinse were also studied. During the study, all virgin MEA samples delaminated, while the strips of aged MEAs stayed laminated. The residual H₃PO₄ in the strips was determined using inductively coupled plasma after an acidic extraction was performed. The achievement of 99% H₃PO₄ removal from both virgin and aged MEAs is remarkable, particularly since the membranes of the aged MEAs were not in direct contact with the extractant. The validity of the test results was checked by milling the extracted samples and checking for residual acid. The re-extraction of the milled samples showed an insignificant amount of acid remaining. The comparison of the different sonication-activated H₃PO₄ extraction processes is shown in Figure 3.

Based on unit operations testing, a revision was made to the pilot plant proposed in 2008. The new estimate is roughly \$1.5MM. The plant is sized to process 1 kg batches of MEAs.

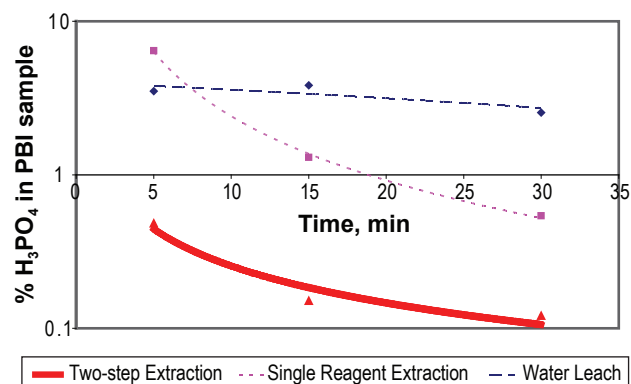


FIGURE 3. Improvement in H_3PO_4 Leaching using Proprietary Extraction Agents

Conclusions and Future Directions

- Using a semi-optimized process, up to 99% Pt recovery from MEAs in a single leach has been demonstrated under lab conditions. Changes in the process conditions contribute to increasing free HCl concentration.

- Alternative technology, including granulation and agglomeration, has been evaluated to improve wetting of the hydrophobic MEA powder prior to leaching. For example, sonication improves MEA dispersion while reducing the amount of surfactant required roughly 10-fold.
- A 600-mL Si-passivated titanium-lined high-pressure reactor is being used to optimize process conditions (temperature, pressure, agitation). >99% Pt recovery has been achieved in a single leach.
- Ultrasonic pre-treatment to remove phosphoric acid from PBI-based MEAs results in almost quantitative removal of the acid.

References

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