

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: March 31, 2009

- Cost - \$3/kW (based on \$450/troy ounce [T.O.] of platinum)
- Total PM catalyst loading – 0.20 g/kW

Accomplishments

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

- Generated process flow diagrams for both preparation (milling, sampling, etc.) and leaching phases of the process.
- Selected key process equipment (i.e. reactors) and evaluated materials of construction.
- Prepared an economic analysis of the process.
- Designed and completed a cost estimate for a process pilot plant.
- Evaluated cost-savings measures related to energy usage, reagent consumption and waste generation using absorptive resins and advanced distillation methods.
- Developed a unique technology for process control of the leaching step.



Objectives

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

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) (Technical plan/Barriers) 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 PMs, which will be impacted both by the amount of PMs used in the stack and by the development of a cost-effective recycling process. The 2015 targets for PM content and cost for transportation applications are as follows:

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].

Last year, the two essential project objectives, high Pt recovery and the avoidance of HF emission, were achieved by acid-leaching milled MEAs.

Approach

Progress was made over the last year by concurrently performing both process validation of unit operations and underlying engineering studies. The latter included a process design phase followed by an in-depth economic analysis. Based on the engineering study, a proposal was made for a pilot plant to demonstrate practical scale-up of the Pt recovery technology.

Results

The block diagram for the proposed process for Pt recovery from fuel cells is shown in Figure 1. The process involves leaching the Pt from the milled MEA and concentrating the leachate 20 to 40-fold using distillation; the platinum, which remains in the distillation bottoms, is then refined. The leaching step is performed in a highly corrosive environment, with chlorine present in any process variation. Use of glass-lined vessels and reactors made from corrosion-resistant alloys has been investigated. The latter operate at higher pressure but are more expensive. (A third reactor liner material, perfluoroalkoxy [PFA[®]], is also under consideration.) A study was performed at Ceralink using metal coupons placed in a sealed chamber with leach media; some of the coupons were coated by Restek Corporation with a silicon barrier layer. Even with the silicon coating, nickel-based alloys like Hastelloy[®] displayed unacceptable rates of corrosion. Specialty metals like tantalum and, to a lesser extent, titanium, were resistant to corrosion under the test conditions. Representative data are shown in Figure 2. When the corrosion resistance testing of Si-coated titanium was repeated with the addition of MEA powder, the corrosion rate increased exponentially as a function of temperature, demonstrating that the Nafion[®] is liberating HF under the strong oxidizing conditions during the acid leaching. This information is useful in determining practical leaching conditions.

In the process design, attempts were made to minimize the environmental footprint. Three areas under investigation were reduction of water and HCl usage and minimized waste treatment. The use of resins was investigated for Pt recovery from dilute streams. Resin treatment of Pt-containing wash water would optimize Pt yield while reducing the volume of liquid to be distilled. Using resins selective for platinum group metals, it was found that Pt could be almost quantitatively removed from 0.2 M chloride solutions, simulating wash liquor obtained after leaching and harvesting the primary leachate. The experiments were performed in batch and demonstrated a small impact of residence time; minimal decrease in Pt removal was observed when equilibration was reduced from 60 minutes to 15 minutes for three successive volumes of Pt-containing solution treated by a resin sample.

Because of the large amount of HCl distilled during leachate concentration, recycling the unconsumed acid would avoid the need to neutralize the acid and save on acid consumption. The properties of HCl/water impact the distillation of process leachate. HCl and water form an azeotrope with a boiling point of 109°C and a composition of 21% HCl; concentrated HCl is 37% HCl. With this limitation, there is merit to perform the leaches in an HCl/water solution near the azeotrope composition. Experiments showed that using 18% HCl decreased Pt yield by about 3% compared to tests with 37% HCl; the lower yield is acceptable assuming a two-stage leach is used. However, hydrochloric acid at its

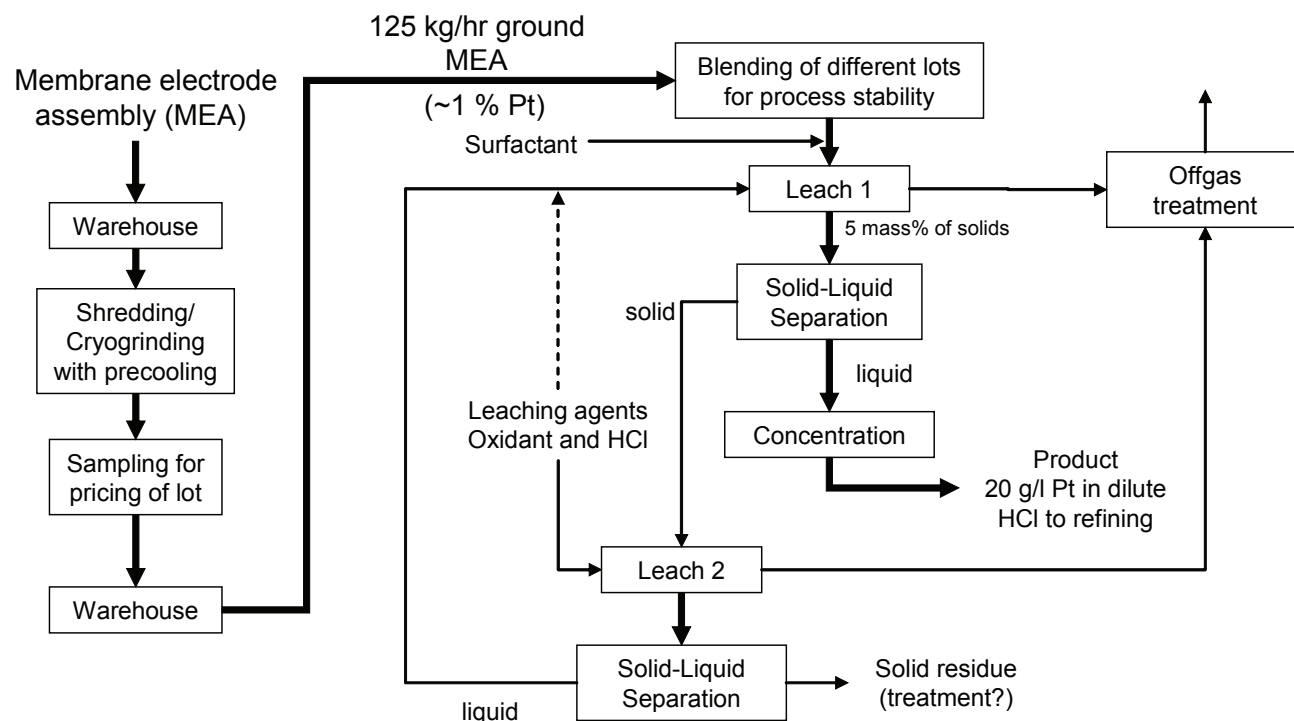


FIGURE 1. Process Flow Diagram for Precious Metal Recovery from MEAs

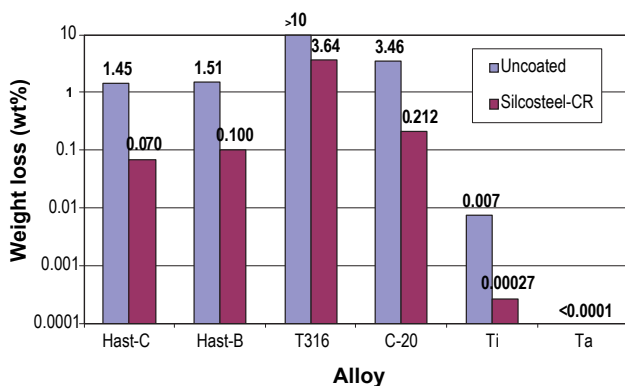


FIGURE 2. Comparison of Corrosion Rates for Selected Alloys in Leach Medium

azeotropic distillate has the highest corrosion rate for a glass-lined reactor; glass liner wear decreases as HCl concentration exceeds the azeotrope concentration. The HCL concentration in the distillate can be increased by using an azeotrope breaker. An example of an azeotrope breaker is the distillation of HCl/water mixtures in the presence of a recyclable desiccant, such as an alkaline earth chloride (e.g. CaCl_2). By using an azeotrope breaker, the residual HCl from the leach step would be distilled and returned to the process as concentrated HCl.

Another environmental issue is the disposal of phosphoric acid. Whereas attention is normally directed to Nafion[®]-based MEAs, a generic recycling plant should be capable of working with high-temperature MEAs that have a polybenzimidazole (PBI) membrane. The PBI membrane is normally saturated with phosphoric acid (H_3PO_4), a chemical that could have a negative impact on downstream refining chemistry. It was shown that the bulk of the H_3PO_4 could be removed from PBI-based MEAs using hot water. The phosphoric acid-rich leachate can be purified using Dowex[™] M-43 resin. Using batch experiments, the acid-adsorptive property of the resin resulted in near quantitative H_3PO_4 removal. This is shown in Figure 3. The treated water can be re-used, while the resin can be regenerated using NaOH solution; the eluted regenerant can be disposed of as waste. A patent application covering aspects of the process, including steps described above to reduce waste, was recently filed. In addition, consideration has been given to value-added use of the post-process leach residue. Rather than send the sludge to a landfill, a novel outlet for the material has been proposed and an invention record has been submitted.

Another process issue was determining the extent of Pt leaching. Process monitoring can be performed by extraction of a sample using a piston-based sampler (possibly limited to a reactor pressure of <10 bar), then mounting the sample as a thin film on a porous substrate. After the deposited slurry layer is washed to

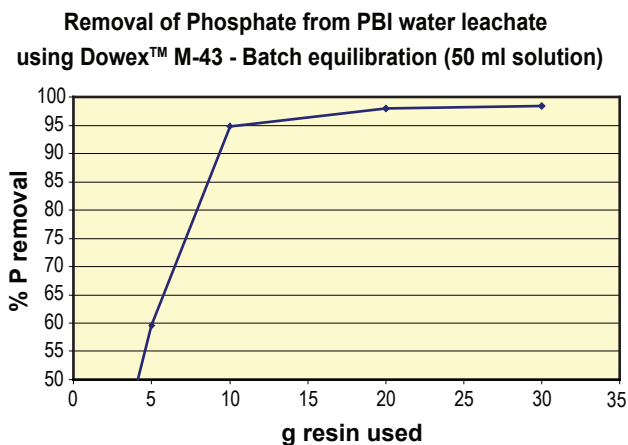


FIGURE 3. Removal of Phosphoric Acid using Dowex[™] M-43 Resin

remove entrained leachate, the solid is sampled using a laser ablation apparatus. The fume is transported to an inductively coupled plasma (ICP) instrument, where it is vaporized and quantified, using either optical emission or mass spectrometry. The analytical variability resulting from the uneven distribution of solids on the planar support can be improved using an internal standard. It was demonstrated that mixing the process suspension with a slurried internal standard resulted in improved run-to-run repeatability. For example, a suspension of steatite, a refractory magnesium silicate, was blended into the MEA suspension using a T-mixer, and the mixture deposited on a polymeric filter. The emission intensity was measured at the Pt lines of 214.4 and 265.9 nm, and the signal intensities ratioed to the emission of Si at 212.4 and Si 251.6 nm, respectively. Method calibration, based on the signal for unleached MEA powder and powder leached at ~89% efficiency, is shown in Figure 4. The extrapolated calibration lines nearly pass through the origin. The emission spectrometer used radial optics; the process sensitivity can be increased either using an emission spectrometer with axial optics or an ICP-mass spectrometer in place of the optical emission spectrometer. A patent application was filed to cover the use of laser-ablation with an internal standard for powder analysis.

Progress was made on the economic analysis of the process. For a plant with a capacity of 1,000 MT/year, which represents fuel cells powering ~500,000 cars/year, it was shown that 75% of the process cost was associated with depreciation, maintenance and overhead.

Compared to the legacy process, efficiency has improved because of the ability to composite customer lots after grinding, blending and sampling, instead of waiting for combustion of individual MEA lots. A pilot plant has been designed for process demonstration at a rate of 1 kg/day. The cost of the pilot plant is estimated to be \$1,000,000.

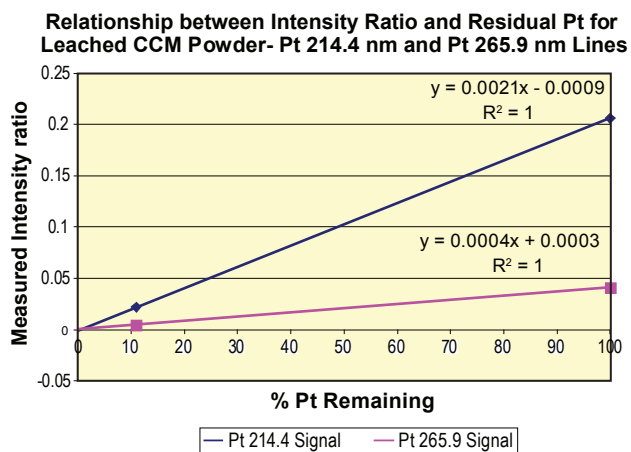


FIGURE 4. Calibration of the Laser-ablation ICP Emission Method using an Internal Standard

Conclusions and Future Directions

- Engineering resources devoted to the project have laid out a coherent commercial process for MEA preparation and sampling, followed by efficient leaching for high Pt yield.
- Except for a washing step to remove phosphoric acid, the processing of MEAs with PBI membranes is the same as the process for Nafion[®]-based MEAs.
- Alternative technology is being evaluated to improve wetting of the hydrophobic MEA powder prior to leaching.
- A 600-mL Si-passivated titanium-lined high-pressure reactor will be used to optimize process conditions (temperature, pressure, agitation).
- The current solution to avoid corrosion from fluoride would be to use a perfluoropolymer, such as PFA[®], as the reactor liner. Reagents capable of sequestering HF liberated from Nafion[®] during acid leaching will be evaluated.

References

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