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Executive Summary: The research performed at BASF from 2003 to 2009 relating to recovery of platinum group metals from fuel cell electrode membrane electrode assemblies (MEA) has been successful in inventing a single approach for processing fuel cells of differing architecture and materials of construction. The scope of the proposed process includes MEA's incorporating both catalyst-coated membranes and gas diffusion electrodes. The process is equally applicable to MEA's with membranes of both Nafion® and non-fluoropolymeric composition. This achievement has been recognized by all involved as a necessary requirement for a commercially-viable recycling process. In addition to this accomplishment, two other project objectives, high (>98%) Pt yield and minimal environmental impact, have also been met. As currently conceived, the only waste streams are a dilute, fluorine-free, salt solution from an alkaline scrubber and the non-hazardous leached MEA residue, although value-added use of the leach residue has been provisionally proposed; emission of hydrogen fluoride and carbon dioxide are eliminated. The process diagram is shown below:

Based on a leach with 10% solids, the cost of reagents, energy and waste disposal are only one-third of 1% of the estimated platinum value of the MEA's.

Accomplishment versus Objectives: When the project was initiated in 2003, there were two primary objectives:

1. Achieve high platinum group metal recovery (e.g. Pt) from used fuel cell membrane electrode assemblies
2. Avoid release of hydrogen fluoride into the environment

These objectives were fairly easy to understand. Platinum, the main catalytic component in the fuel cell MEA, is an expensive material that is in limited supply. In fact, the cost of

platinum, which fluctuates with economic cycles, peaked at almost five-fold of the Pt price when the DOE Hydrogen Program guidelines were first issued. In 2009, it was estimated that Pt would still contribute 37% of the cost of the catalyst stack in 2015 if 500,000 fuel cell powered cars would be produced, assuming a Pt cost of \$1100/T.O.¹

Therefore, recycling the Pt in a fuel cell is an enabling technology for the fuel cell industry as it stabilizes the supply of this metal. The standard approach for recovery of platinum from an organic material is combustion. However, this technique liberates the fluorine incorporated in fluoropolymers as hydrogen fluoride, a toxic and highly corrosive gas. It is common sense that eliminating HF release would be positive for society. Similarly, release of carbon dioxide is avoided by eliminating the need for combustion of the carbon-rich MEA.

There were two other minor objectives:

1. Recycle ruthenium used in the fuel cell anode.
2. Recover the Nafion® dispersion for re-use.

Ruthenium, which is also a platinum group metal, is added to the electrocatalyst in the fuel cell anode to mitigate the negative impact of carbon monoxide on the ability of platinum to dissociate hydrogen molecules, a phenomenon that occurs in a reformat-fueled fuel cell. As the project proceeded, automotive on-board reforming was rejected and replaced with direct hydrogen fueling, so the importance of ruthenium recovery was limited to the stationary reformer market, which is predominantly reformat-fueled. Ru is also present as an anode component in direct methanol fuel cells.

Nafion® re-use was an objective added to the project in April 2004 at the request of USCAR. The auto industry consortium was interested in achieving maximum value from the components in the vehicle, and envisioned Nafion® re-use as a way to offset raw material costs.

As the project stands at its conclusion, the goals have been met and/or addressed to the satisfaction of interested parties. The originally undefined goal of high Pt recovery was formalized as the ability to recover >98%, which is an industry guideline for reclamation of metal from common organic matrices. This level of Pt recovery has been achieved, using a single oxidizing leach step and a rinse. By replacing the standard practice of combustion with acid leaching, the platinum is liberated without thermal decomposition of either Nafion® or PTFE in the MEA, so HF liberation is minimized (Discussion below will address polymer decay during oxidative leaching.). Release of SO₂, the decomposition product of the sulfonic acid group of Nafion®, is also avoided. After leaching, the neutralized MEA residue can be land-filled, since the fluorine content is immobile.

An understanding of the behavior of ruthenium in the overall process was achieved. The mobility of ruthenium is determined by the leachate used. When chlorine, derived from the reaction of HCl and hydrogen peroxide, was the oxidizing agent, the ruthenium was

solubilized and recovered along with the platinum in fairly good yield. To a large degree, ruthenium volatilized, presumably as ruthenium tetroxide, when other oxidants, such as sodium chlorate or nitric acid, were used with HCl. However, in experiments using sub-stoichiometric amounts of HNO₃ added to HCl, the retention of Ru in the excess HCl was high. Depending on the future usage of ruthenium in fuel cell anodes, the selection of oxidant may, in part, be based on the volatility of ruthenium, since platinum and ruthenium need to be separated during the metal purification process.

The issue of Nafion® re-use has been addressed. There are several obstacles in re-using Nafion®. First of all, it has been shown that the polymer degrades with use, depending on the method of MEA construction and the aging cycle. This degradation, illustrated by the change in the polymer response to solvent, demonstrates that the polymer has not retained its original properties, so re-use as a membrane would be questionable. The degraded polymer may be used as a solid acid catalyst, but there is a list of issues, including cost, right-to-practice and commercial volume, that pose a problem for this outlet. Furthermore, there is recognition that Nafion® may only be an interim material of choice for fuel cell membranes. Devoting additional effort to Nafion® re-use was deemed to be non-productive, and our customer, USCAR, agreed that this was no longer a BASF objective.

Introduction to MEA's

Fuel cell membrane electrode assemblies are composed of multiple layers, including the following:

- Core membrane
- Anode and cathode electrocatalyst layers in contact with the membrane
- External gas diffusion layers (GDL's)
- Gaskets

The laminate of membrane, catalyst layers and GDL's are referred to as a 5-layer MEA. When the GDL's are stripped off, the result is a 3-layer MEA.

When the electrocatalyst is applied directly to the membrane, the product is referred to as a catalyst-coated membrane, or CCM. The alternate construction is a gas diffusion electrode (GDE), where the electrocatalyst is directly applied to the GDL. The membrane is then sandwiched between two GDE's

Project Summary:

Initial Approach - There were three hypotheses proposed at the project kick-off in 2003. They are listed below with the accompanying research approach:

1. **PGM is recoverable through direct leaching of the MEA strips.**
 - a. Intact 5-layer MEA pieces were leached in an oxidizing acid and material balance obtained.

2. **The MEA needed to be combusted to recover Pt. Liberated HF fumes would be sequestered.**
 - a. The 3- and 5-layer MEA were placed in a microwave oven and heated to determine combustion conditions based on the property of carbon as a microwave absorber (susceptor)
 - b. An adsorbent was tested for HF capacity
3. **PGM can be separated from the Nafion® membrane by dispersing the polymer using supercritical fluids (SCF).**
 - a. The 3-layer CCM from an MEA was exposed to supercritical CO₂ and co-solvents to disperse the polymer

Direct MEA Leaching - To some degree, all three original hypotheses were rejected. Because of the small edge to surface area ratio, leaching, of 5-layer MEA's, which was done using microwave heating at 200°C at 10 bar pressure, was inefficient. Also, because of the hydrophobic nature of the MEA, the intact pieces of MEA tended to float in the oxidizing medium. Table I shows the poor recovery for direct leaching of the MEA compared to quantitative recovery when the membrane is exposed to the leaching acid by GDL stripping (CCM).

Table I. Comparison of Pt Yields from CCM MEAS Leached W/WO GDLs

Results of Microwave-Assisted Acid Leaching using HCl/H ₂ O ₂			
Sample	GDL present?	Temperature / Pressure	% Pt removal (based on membrane residue)
3-layer MEA	no	200 / 10 bar	100, 100
5-layer MEA	yes	200 /10 bar	82, 65

While increased recovery could be achieved by decreasing the size of MEA pieces to increase the edge to surface area ratio (see below), the practice of direct leaching was discontinued. Stripping the GDL's off the CCM's to expose the catalyst layers would be labor intensive and could incur Pt losses that would be unacceptable. Similar arguments apply to the GDE architecture of MEA's. Experiments with GDE's are discussed below.

Microwave Combustion/ HF Sequestration – At the onset of the program, success of unconventional methods for Pt recovery was difficult to predict, so a variation of the conventional process was funded. It was decided to pursue a combustion method that would also include capture of the undesirable HF, analogous to CO₂ sequestration at a coal-fired power plant. Professor David Clark, at Virginia Polytechnic Institute, had been chosen for the microwave combustion technology development because of prior experience with integration of combustion and waste gas remediation using microwave energy as an efficient source of heat.

Several problems were encountered using microwave combustion. First of all, while the 3-layer CCM easily combusted in the microwave oven, the presence of graphite-based

gas diffusion layers in a 5-layer MEA acted to diffuse the electrical field; the MEA temperature stayed around 300°C, below the combustion temperature of the MEA layers. This is shown in Figure 1. Therefore the process was initially only useful for CCM-type MEA's that had the GDL pre-removed.

Figure 1. Comparison of Measured Temperature of MEA Samples Heated Using Microwave Energy

Using the experimental model of removal of the gas diffusion layer prior to combustion (an extra processing step that carries the risk of loss of electrocatalyst layer with the GDL), VT personnel constructed a stacked microwave furnace assembly to combust the 3-layer MEA and to capture the HF vapors. The microwave ovens were modified to have variable power. The apparatus set-up is shown in Figure 2. In the upper chamber, a tube was filled with adsorbent. The effluent of the tube was sampled by an FT-IR to determine the concentration of gases. It was shown that small amounts of HF were completely removed when the adsorbent tube was filled with activated alumina.

Based on these results, a simulated scale-up test was performed. Activated alumina was washcoated onto a silicon carbide support. The dispersed adsorbent was then loaded into a reactor in a tube made of Monel, since this alloy is resistant to HF attack. A stream of HF gas in nitrogen was then passed through the tube and the HF in the effluent was measured using FT-IR.

The FT-IR data showed that the adsorbent proposed for HF remediation did not have sufficient capacity. While the initial data from Virginia Tech reported 99% HF removal during short-duration combustion runs, passing a continuous gas stream containing 500ppm HF through a bed of alumina coated on silicon carbide demonstrated that the

active capacity of the adsorbent was very low, as HF breakthrough occurred almost immediately. The mechanism of fluoride capture was chemical adsorption:

The process data is shown below in Figure 3. The breakthrough curve rose less sharply at 200°C compared to 100°C, a phenomenon expected for a chemical reaction.

Figure 2. Representation of a double microwave furnace for combustion and pollutant removal from the effluent stream

Figure 3. Breakthrough of a 500ppm HF gas stream passing through an alumina adsorbent

Super-critical Fluid Processing

The proposed supercritical fluid work, carried out at Professor Bala Subramaniam at the University of Kansas, proved to be a failure. Nafion® re-dispersion was not achieved in the non-polar medium selected. For informational purposes, the experimental apparatus was used to replicate work in the literature for dispersing Nafion® polymer using high pressure water; the result is shown in the tableau below (Figure 4) for a sample of 3-layer CCM MEA:

Figure 4. Stepwise Results for Aqueous Re-dispersion of Nafion® in a 3-layer MEA

Vacuum filtration of product from 3-layer MEA experiment conducted at 270 °C, 690 psi, 2000 rpm for five hours, starting with ~1 g sample.

1. Vacuum filtration apparatus, after filtration
2. Filtrate is in the flask at right, distilled water is in the flask at left, for color comparison
3. Solid retentate collected on the 0.4 micron Isopore membrane filter

1.

2

3

However, commercial obstacles existed to the use of that technology and the cost of capital required for scale-up of the lengthy dispersion process was difficult to justify. An interesting aspect of the experiment was the measurement of HF in the aqueous Nafion® dispersion. Even though the Nafion® had been exposed to a temperature of >250°C, ion chromatography showed that the free HF level was roughly 100 ppm. This implies that low temperature processing of Nafion®-containing MEA's should liberate only low levels (ppm) of HF.

Alternative Processes

Solvent re-dispersion - Obviously, another approach was required to move forward. Working with CCM-style MEAs from W.L. Gore, it was observed at Ceralink that MEA layers would delaminate when the MEA was placed in a beaker containing lower alcohols. This process was predicated on the tendency of Nafion® to swell in alcohol/water mixtures^{2,3}. When a 5-layer CCM MEA was placed in an alcohol/water solution, it was observed that the gas diffusion layers would drop off, followed by the sloughing off of the electrocatalyst layers. [In 2005, a patent application, US 2006/0237034, was filed to cover a process that facilitated the recovery of fuel cell electrocatalyst separated from 5-layer MEA's using a solvent based swelling process.] It was further noticed that this process was severely limited in application. First of all, GDE-style MEA's did not delaminate under the conditions used in the patent application. Of greater significance was the behavior of aged CCM-style MEA's during solvent delamination. It was observed that the polymer disintegrated in the solvent and tended to form an emulsion that trapped the liberated electrocatalyst particles. The degree of disintegration was related to the solvent composition. This is represented in Figure 5 below:

Figure 5. Representation of Nafion® emulsion formation of Aged MEA's based on solvent concentration

It was shown that the polymer component of the emulsion could be re-dispersed with heat, enabling the electrocatalyst particles to be filtered off. An example of a particle size distribution of re-dispersed Nafion® is shown below in Figure 6: This was demonstrated using a commercially available microwave reactor called the FlowSYNTH, manufactured by Milestone Scientific. A patent application for the modified process was submitted in 2006 (US 2007/0292745). After discussion with W.L. Gore, an obstacle to using this

methodology was identified. The literature demonstrated that Pt from the cathode electrocatalyst can oxidize and migrate into the membrane, then deposit within the membrane as nano-particulates. The Pt crystallites are smaller than the re-dispersed Nafion® and would remain in the filtrate when the filtered electrocatalyst particles are separated from the polymer dispersion. Evidence of this migration phenomenon is shown in Figure 7⁴. Electrochemical measurements were found to corroborate the microscopic findings.⁵

Figure 6. Particle Size Distribution for a Nafion® Dispersion Obtained from Heat Treating a Nafion® emulsion

Figure 7. Example of Pt nanostructure after migration into a Nafion® membrane⁴

Furthermore, it was recognized that the re-dispersion process may be limited to CCM-style MEA's since the aged GDE's tested did not delaminate with exposure to solvent. At this point in time, processing of GDE's was aided by the observation that the electrocatalyst layer of a GDE could be exposed to leaching medium if the MEA was manually delaminated immediately after exposure to hot water or steam. Figures 8 and 9 demonstrate the importance of wet stripping. If the layers are dry during separation, then the electrode layers partially adhere to the membrane.

Figure 8. Dry-stripping of a 5 layer GDE-style MEA

When the MEA is kept wet, stripping resulted in the electrode layers staying fixed on the gas diffusion layers.

Figure 9. Wet-stripping of a 5 layer GDE-style MEA

After this information was compiled, it was decided that sample handling procedures dependent on the method of MEA construction (CCM vs. GDL) was impractical as the basis for a recycling business. Furthermore, this did not include the behavior of MEA's made with polybenzylimidazole (PBI). Studies with PBI-based MEA's showed that the distribution of electrocatalyst layer was dependent on the handling method. If the outer layers of the phosphoric acid laden MEA was removed by hand-stripping, the catalyst layers stayed almost exclusively on the membrane. However, handling phosphoric acid is undesirable. The acid can be removed using a hot water treatment of the 5-layer MEA; if the MEA was then hand-stripped while still wet, the catalyst layer once again stayed attached to the membrane. (The PBI-based MEA did not delaminate on contact with alcohol-water mixtures.) However, if the washed MEAs dried out, then the catalyst layer recovery was non-quantitative and irreproducible. The results for the three PBI process options are shown in Table II.

Table II. Pt yields for different PBI Treatment Approaches

Process Variation	% Pt yield
Hand-strip GDL from membrane with H ₃ PO ₄ present	98
Boil MEA in water, hand strip while wet	97
Boil MEA in water, dry MEA then hand-strip	82

Because of the variations in processing MEA's of differing architecture that resulted from a piecemeal approach to process development, it was decided that an all-inclusive, or consolidated, method of sample preparation was mandatory.

Consolidated Process - It was recognized that leaching was a viable mechanism to liberate Pt from the electrocatalyst particles if enough surface area was available for the acid to contact the precious metal sites. Conventional milling was challenging because of the elastic properties of the polymeric membrane. It was shown that milling could be accomplished if carried out at reduced temperature. Cut up MEA's were reduced to a fine, free-flowing powder when embrittled and milled at liquid nitrogen (-197°C) temperature. This is shown below in Figure 10.

The milling was performed using the SPEX 6850 cryogenic mill, an impact mill operating in a chamber filled with liquid nitrogen. The powder product was assayed before and after blending. The materials were determined to be homogenous after blending based on the reduction in analytical variance, as expressed by the relative standard deviation (% RSD). The data is shown below in Table III.

Figure 10 – Disintegrated MEA following Cryogenic Milling

**Ground CCM MEA, 1000x
Magnification (BASF Microscopy)**

**Intact GDL from a CCM MEA,
500x
Magnification (Virginia Tech)**

Table III –Improvement in MEA powder homogeneity with mixing

Run	CCM –1 (unblended)	CCM-2 (blended)	GDE-1 (unblended)	GDE-2 (blended)
1	2.644	2.494	2.160	1.984
2	2.786	2.491	2.047	2.010
3	2.628	2.501	2.109	1.998
Mean	2.686	2.496	2.105	1.998
RSD	3.2%	0.22%	2.7%	0.64%

Leaching of the powder proved more challenging than expected. Samples of milled CCM and GDE MEA's were respectively contacted with an oxidizing medium. Because of the hydrophobic nature of the MEA, imparted in part by the presence of PTFE, the sample powder floated on the surface of the acid and tended to creep up the walls of the beaker. The results of this leach process were very unsatisfactory. Only 72% of the Pt in a CCM-style MEA was liberated by the acid. (The corresponding GDE yield was 93%.) It was decided to investigate the use of surfactants to wet the sample, allowing the acid to better contact the particles. When the MEA powder was wetted using an aqueous surfactant in a mortar and pestle, the MEA powder granulated and became submerged in the beaker containing acid. Using the surfactant, the previous leaching experiment was repeated. The yield from the CCM sample jumped to 94%, while the yield from the GDE rose marginally. These results formed the basis of a 2007 patent application (US 2009/0049954) showing the efficacy of cryogenic-temperature grinding in combination with surfactant wetting for preparing a sample for leaching

Milling experiments included MEA's with phosphoric acid-saturated PBI. Milling was performed as is and with a sample that had been leached with hot water (~80% of the

H₃PO₄ was removed from the MEA's that had been cut into strips.) After milling, the leached sample yielded a free-flowing powder, while the product of milling the unleached sample was clumpy. Even so, after correction for H₃PO₄ dilution, assay of both powders showed equal Pt content and equivalent leachability. On the other hand, handling phosphoric acid introduces safety and maintenance concerns, and the non-volatile acid would concentrate in the leach bottoms during HCl distillation. In the presence of base metals, insoluble base metal phosphates may precipitate and would have to be filtered off prior to platinum reclamation. Leaching the acid from PBI membranes and treatment of PBI-based MEA wash water is discussed below.

Base metal-alloyed electrocatalysts - The statistics gathered for MEA leaching was based on electrocatalysts composed of either Pt only or Pt/Ru. However, as a means of improving cathode efficiency while reducing Pt content, the industry was developing a variety of base metal-alloyed catalyst compositions. Samples of these experimental materials were received from several industry sources, as well as the Naval Research Lab, with the understanding that the actual compositions were confidential. Small portions of these powders were leached using the standard acid approach, although surfactant was not needed. Because of their high precious metal content, the powders were very dense. It was observed that the yields from leaching using the microwave vessels, which had a concave bottom that acted as a well for the catalyst powder, were normally lower than those obtained with open beakers. Table IV below summarizes the % Pt recovery from the electrocatalyst powders tested.

Table IV Pt Yield from Leaching of Base-Metal Alloyed electrocatalysts

Material	% Pt yield, open beaker	% RSD, open beaker	% Pt yield, sealed microwave vessel	% RSD, sealed microwave vessel
Pt-TaPO			95	1.3
Pt/Fe/C	95	2.0	90	2.6
Pt/Co/C	97	0.1	89	3.0
Pt/Cr/C	97	0.9	94	0.5
Pt/C	92.6	1.1	83	
Pt/Ru/C	95.8	0.4	90	
Pt/Ni/Cu/C	95.9	1.0	82	
Pt/Co/Cu/C	96.6	0.4	87	
Pt/Co/Mn NSTF (3M MEA milled)	98.2	0.7	92.2	1.2
		Second leach	99.5	0.3

Process Integration - Following identification of a process to liberate platinum from MEA's, it was necessary to specify the process steps required to prepare material for leaching, as well as the mechanism to recover the platinum for re-use. The responsibility for integration of the experimental data into a process flow diagram was assigned to BASF Engineering in Ludwigshafen, Germany, with the authorization of the DOE. Figure 11 shows the process block diagram for the projected process. The process includes two discrete leach steps.

Figure 11. Process Block Diagram For the Recovery of Pt from MEA's

Process improvement - Initial leaching experiments were performed by wetting the milled MEA with excess surfactant using a mortar and pestle. The mull was transferred to the reaction vessel using HCl, and nitric acid was added to initiate the leach. Tests were performed in either a beaker, with the hot plate surface temperature set at 125 or 150°C, or in the microwave oven, with reaction temperatures of 120-200°C. Both options were non-optimized. The beaker runs had no containment of oxidant, and reactant dissipated. However, the contents of the beaker could be stirred manually. The microwave bottles had a high L/D and had no stirring, so mixing depended on convection. There were two opposing forces in the vessel. Reaction rate increased with temperature, but chlorine solubility decreased with temperature. A curve of the leach yield as a function of temperature is shown in Figure 12. The data shown above indicates that ~150°C is more effective than 200°C in % Pt recovery. This information has a major impact on cycle time and rate of corrosion of vessel materials.

Figure 12. Pt Recovery from CCM MEA powder leached in a microwave oven , 120-200°C

Surfactant Usage - As mentioned above, surfactant was initially used in gross excess, with the principal objective being to fully wet the MEA powder. However, overdosing with surfactant is very expensive and may decrease leachability because of micelle formation, which would prevent contact of the oxidant with the MEA material. Using two surfactants and milled GDE powder (made with carbon cloth GDL), the effect of surfactant usage was studied. Surfactant was used at three levels: 5%, 1% and 0.25%. (Wetting with 0.25% was very difficult and the data was non-reproducible.) The leaching results were very dramatic. The Pt leach yield increased roughly 5% for both surfactants when the surfactant concentration was decreased from 5 to 1%. This is shown in Table V. (Plurafac LF 120 is a surfactant manufactured by BASF, while Strodex PK90 is a surfactant made by Ashland Chemicals (formerly Dexter Chemicals)).

Table V. Influence of Surfactant Concentration on % Pt yield			
Surfactant	% surfactant	Sample, g	% Pt yield
Plurafac LF 120	5.0	0.527	83.1
		0.529	81.3
	1.0	0.509	88.4
		0.506	88.7
	0.25	0.518	88.4
		0.532	84.6
Strodex PK90	5.0	0.534	88.6
		0.530	85.3
	1.0	0.527	93.0
		0.514	90.6

Agglomeration – During a trip to BASF in Ludwigshafen, Germany in 2007, I discussed the surfactant issue with process experts. It was suggested that the surfactant is also acting as an agglomerating agent, and the agglomerated particles tend to sink in the aqueous medium. Portions of milled GDE powder were sent to Germany and were agglomerated in a Somakon mixer using a hot melt technique, with a mixture containing a waxy, high MW surfactant and an aqueous surfactant in a 9:1 ratio. The surfactant cocktail was added using either a syringe (4 minutes) or a funnel (14 minutes). These samples are identified as NE-17-08 and NE-18-08, respectively. Initial testing of the leachability of these agglomerated products was very positive. When aqua regia was added to the materials, at a hot plate setting of either 125 or 150°C, a yield of 97.5% was achieved in a single leach step. This compares very favorably with the analysis of the precursor non-agglomerated GDE powder, which had Pt yields of 86 and 90%, respectively for open beaker and microwave bottle leaching using aqueous surfactant wetting in a mortar and pestle. These samples were further studied during process optimization and the data included in Table VI below.

HNO₃ consumption - Using the agglomerated powders, a study of the relationship between Pt yield and HNO₃ usage was made. The reason for this study is that limiting HNO₃ usage has many advantages, including the following:

1. Decrease NO_x (and excess chlorine) production to reduce vessel pressure, reduce scrubber requirements and reduce cost.
2. Increase HCl recycle to reduce waste neutralization and reduce reagent cost.

Agglomerated samples were leached with aqua regia and with HCl and substoichiometric additions of HNO₃. In this test, the nitric acid was used to wet the agglomerated powders before the HCl was added, except for the standard aqua regia trial where the acids were added as the mixture. The results of the study were unexpected. By decreasing the addition of the nitric acid oxidant precursor, the Pt yield increased. This is displayed below in Figure 13.

The ability to decrease HNO₃ usage was validated in an extensive study. Using the agglomerated GDE materials, a less-than-standard amount of HNO₃ was used to leach the agglomerated powders, starting with adding either HNO₃ or HCl first, allowing the acid to saturate the particles, followed by addition of the second acid. In addition, azeotropic HCl, the normal product of HCl distillation, was also used in place of concentrated HCl. The leach was also modified by starting the process at a hot plate setting of 150°C for 15 minutes, then increasing to 175°C and holding for 30 minutes. The data is shown in Table VI. For the runs where concentrated HCl was added first, 99% Pt yield was consistently achieved with one leach. Lower yields were observed when HNO₃ was added directly to the agglomerated materials. An important observation was a decrease of Pt yield of roughly 4% when azeotropic HCl was used instead of concentrated HCl. There is a commonality in this data. Using either excess HNO₃ or reduced-concentration HCl lowers Pt yield, as does the use of HNO₃ as the first acid added. It can be postulated that Pt removal is promoted by increasing the concentration of free HCl at the Pt sites within the agglomerated material.

Figure 13. Relationship between HNO₃ added for an aqua regia leach and Pt yield.

Table VI. Pt yields from leached agglomerated GDE – HNO₃ and HCl as variables

Sample	Acid Priority	g HNO ₃	Azeotrope?	% HCl excess	g sample	% Pt	% yield
Ne-17-08	HNO ₃	0.98	No	85	0.532	2.11	98.2
	HNO ₃	2.96	No	54	0.522	2.05	92.8
	HCl	1.01	No	84	0.511	2.07	99.1
	HCl	3.04	No	53	0.534	2.09	98.9
	HNO ₃	1.03	No	84	1.000	2.04	99.1
	HNO ₃	1.07	No	83	1.509	2.04	99.0
	HCl	1.02	No	84	1.003	2.04	99.2
	HCl	1.03	No	84	1.531	2.05	99.2
	HNO ₃	1.00	Yes	85	0.999	2.06	92.1
	HNO ₃	1.02	Yes	84	1.517	2.05	92.4
	HCl	1.05	Yes	84	1.034	2.05	95.8
	HCl	1.05	Yes	84	1.520	2.06	97.1
Ne-18-08	HNO ₃	0.96	No	85	0.514	1.90	97.9
	HNO ₃	2.98	No	54	0.537	1.88	91.7
	HCl	1.04	No	84	0.518	1.88	98.9
	HCl	3.06	No	53	0.534	1.89	98.3
	HNO ₃	1.02	No	84	1.022	1.88	98.9
	HNO ₃	1.08	No	83	1.532	1.87	98.9
	HCl	1.14	No	82	1.043	1.90	99.2
	HCl	1.12	No	83	1.546	1.89	99.1
	HNO ₃	1.08	Yes	83	1.005	1.9	95.4
	HNO ₃	1.07	Yes	83	1.547	1.88	94.6
	HCl	1.07	Yes	83	1.012	1.90	97.3
	HCl	1.30	Yes	80	1.530	1.88	96.5

Granulation- In attempt to automate the cryogenic milling of MEA's, use of a pre-embrittlement cryo-tunnel was evaluated at Pulva Corporation (Valencia, PA). The feedstock was simulated MEA, made from Gore 3-layer CCM and either carbon cloth or carbon paper GDL's. The individual materials were shredded into 1/4" x 5/8" pieces, then mixed in a 1-to-2 CCM:GDL ratio. This demo was very unsuccessful as the shredded MEA's, the feed expected for the mill, matted together between the outlet of the cryo-tunnel and the inlet of the mill; the movement of the feeder screw was insufficient to push the mass forward. To continue the milling part of the experiment, the vendor first granulated the shredded MEA materials at room temperature. The granulator is a cutting mill that works well with flexible material, such as an MEA membrane. Most of the granulated product was then milled at LN₂ temperature.

Both the granulated and mill materials were then assayed. Although the same % Pt yield was achieved for all samples, the test data, shown in Table VII, indicates a significant loss of Pt during the cryo-milling step; the granulated material had 1.5% Pt compared to only 1.3% Pt for the granulated and milled materials. It can be surmised that the finely divided Pt was carried off by the volume of nitrogen gas liberated through the gasification of the liquid nitrogen. These results may exaggerate the effect because the starting materials were not laminated. However, there is cause for concern that cryo-milling will require extra care to ensure collection of Pt-rich fines.

Table VII. Statistics for Leaching of Granulated and Milled Simulated MEAs (dry basis)

Material	Run	% Pt	% yield
CCM/cloth GDL, granulated	1	1.56	91.4
	2	1.49	92.4
CCM/cloth GDL, granulated & milled	1	1.34	91.3
	2	1.36	91.2
CCM/paper GDL, granulated	1	1.57	91.2
	2	1.57	91.8
CCM/paper GDL, granulated & milled	1	1.39	91.8
	2	1.38	91.7

Because of the potential for loss and the ease of granulation (no shredding or coolant required), an investigation into using granulation without downstream milling was initiated. Granulation of used CCM MEA's and unused GDE MEA's was performed at Hosokawa Polymer Systems (Berlin, CT) using a press-side granulator. After the granulation, portions of each product were milled using the SPEX 6850 mill to determine if milling increased the Pt yield. The milled portions were manually wetted with surfactant and otherwise leached as before, first adding HCl and using limited HNO₃. This procedure was not applicable to the granulated mass, as the material was downy and would be difficult to wet with surfactant by hand. A new technology was employed to wet the granulated MEA. The material was added to a beaker with HCl, and a small

amount of surfactant was weighed into the beaker. Then the mixture was agitated using a sonicator. Within one minute, the granulated material was fully dispersed. Nitric acid was added appropriately and the leaching carried out. The results from the study were very positive. First of all, yields of 97.5 and 98.5% were determined for the GDE and CCM MEA's, respectively. Second, equivalent results were obtained for both the granulated and the milled materials, indicating that the granulation sufficiently disintegrates the MEA laminate structure to expose the electrocatalyst layer to the leaching medium.

Table VIII. Leaching of Granulated CCM and GDE MEA's

GDE MEA's				
1g Sonicated with trace surfactant			0.5g of granulated and milled MEA wet manually	
Run	Surfactant usage, wt/wt	% Pt yield	Surfactant usage, wt/wt	% Pt yield
A	0.0058	97.3	0.05	97.6
B	0.0109	97.5	0.05	97.8
C	0.0157	97.5	0.02	97.1
D			0.02	97.2

Aged CCM MEA's				
1g Sonicated with trace surfactant			0.5g of granulated and milled MEA wet manually	
Run	Surfactant usage, wt/wt	% Pt yield	Surfactant usage, wt/wt	% Pt yield
A	0.0062	98.4	0.05	98.5
B	0.0022	98.1	0.05	98.6
C	0.0009	98.4	0.02	98.4
D			0.02	98.5

Scale-up Results

During the first four years of the project, all developmental work was done on a small scale using non-optimized apparatus. The bulk of the work was performed in open beakers, which were prone to loss of active ingredients through evaporation. Pressurized testing was performed in microwave heated vessels that had a high L/D design with conical bottoms, and mixing was limited to convection; loss of oxidant to the vessel head-space was also a problem. Based on the progress using this equipment, a decision was made to scale up the testing using an agitated reactor. Since there was uncertainty in the operating conditions of the reactor (chemistry, temperature and pressure), flexibility in its operation was required. Working with Parr Company (Moline, IL), it was decided that the reactor would be constructed out of titanium. Parr does not offer a glass liner and the titanium construction offers tolerance to 600 psi. Recognizing the possibility of corrosion, the surfaces of the reactor were toughened by applying a silicon barrier layer (Silco Tek., Bellafonte, PA). Titanium tubing was used for high pressure, and the pressure release disc was fabricated out of tantalum. Hosing for reagent transfer was made using perfluoroalkoxy (PFA) copolymer and polytetrafluoroethylene (PTFE). The schematic of the reactor and process flow are shown in Figures 14 and 15, respectively. Besides having higher capacity than the previous apparatus, the autoclave has two additional features. First of all, it has variable speed agitation, so that the influence of

stirring can be determined. Second, the reagents are pumped into the reactor, so the volatiles are contained; when using the microwave vessels, the reagents are added before sealing, and loss of oxidant has occurred, particularly when using a mixture of HCl and hydrogen peroxide.

Figure 14. - Parr Autoclave Apparatus

Figure 15. Process flow using the Parr autoclave

An example of the run conditions is shown in Figure 16. In this particular experiment, the leaching was performed at 100°C, with stirring at 350 rpm, and the pressure in the vessel reached a maximum value of 200 psi. Table IX lists the run conditions and the Pt yields recorded for representative runs.

Figure 16. An example of a Parr autoclave run

Table IX. Listing of Experimental Data from Parr Autoclave Runs

Run #	Sample ID	Prep Method	Acid	RPM	Temp, °C/ min	% yield
8	HM #9	3.651g Milled	Aqua Regia	350	100	98.6
9	NE-17-08	3.654g Agglom.	Aqua Regia	350	100	99.5
10	NE-18-08	3.660g Agglom	Aqua Regia	350	100	99.5
11	NE-17-08	7.303g Agglom	Aqua Regia	600	100	99.5
12	NE-17-08	3.645g Agglom	Aqua Regia	350	100	99.3
13	NE-17-8	3.656g Agglom	'Reduced' aqua regia	300	100	99.5
14	NE-17-08	3.652g Agglom				
15	NE-18-08	3.653g Agglom	Aqua Regia	?	90	96.5
16	NE-17-08	3.651g Agglom	Aqua Regia	60	100/ 30	99.6
17	NE-17-08	3.659g Agglom	Aqua Regia	120	100/ 30	99.5
18	HPS #2	3.660g Gran.	Aqua Regia	360	100/ 30	99.3
19	HPS #2	3.651g Gran.	Aqua Regia	360	100/ 30	99.5
20	HPS #2	3.665g Gran.	Aqua Regia	80	100/ 30	99.5
21	HPS #2	3.607g Gran.	Aqua Regia	300	100/ 30	99.6
22	HPS #2	3.656g Gran.	Aqua Regia	300	100/ 30	99.5

23	HPS #2	3.659g Gran.	Aqua Regia	300	80/ 30	99.2
24	HPS #2	3.657g Gran.	Aqua Regia	300	100 /30	99.4
25	HPS #2	3.651g Gran.	Aqua Regia	60	80/ 30	99.1
26	HPS #2	7.324g Gran.	Aqua Regia	300	100/ 30	99.6
27	HPS #2	10.96g Gran.	Aqua Regia	300	100/ 30	99.4
28	HPS #2	14.63gGran.	Aqua Regia	300	100/ 30	99.4
29	HPS #2	3.674g Gran.	Aqua Regia	300	100/ 10	99.7
30	HPS #2	3.659g Gran.	Aqua Regia	300	100/ 20	98.4
31	NE-17-08	3.646g Agglom.	Aqua Regia	300	100/ 20	99.5
32	NE-17-08	3.653g Agglom.	Aqua Regia	300	100/ 10	99.3
33	HPS #2	14.65g Gran.	Aqua Regia	300	100 10	99.6
34	HPS #2	14.63g Gran	Aqua Regia	300	100/20	99.4
35	HPS #2	3.674g Gran	Aqua Regia	300	100/5	99.0
36	NE-17-08	10.96g Agglom	Aqua Regia	300	100/10	99.3
37	HPS #2	7.426g Gran	'Reduced' aqua regia	300	100/10	99.2
38	HPS #2	14.63g Gran	'Reduced' aqua regia	300	100/10	99.3
39	HPS #2	14.63g Gran, no surfactant	'Reduced' aqua regia	300	100/10	99.0
40	HPS #2	14.63g Gran, no surfactant, no sonication	'Reduced' aqua regia	300	100/10	98.5

Only a limited number of runs were performed using the 'Reduced aqua regia' recipe. However, enough runs were completed using the granulated GDE material to demonstrate the robustness of the leach. Even under the worse case, with no surfactant added or sonication for dispersion, a yield of 98.5 % was achieved, which included 1.4% of the Pt coming from the sonicated rinse. Although this is the preferred leach mixture, the HCL-rich medium is relatively reductive and the titanium Parr vessel is susceptible to attack, even with the silicon barrier coating. This condition is discussed further below in the Materials of Construction section.

Because of the success demonstrated in scale-up, the process of Pt recovery has been simplified by using only one leach stage. This is shown in Figure 17, using the granulation option of material preparation.

Figure 17. Simplified process for Pt leaching of MEA's

Analytical validation - The analytical data reported for % Pt yield is based on the assumption of 100% material balance by determining the Pt content of the leachate and residue. The latter value is made following partial combustion of the residue, treatment with hydrazine and re-leaching with aqua regia. Of course, Pt that resisted the first leach could, in principle, be resistant to a second leach. To validate the material balance, the residues from the sonicated runs of granulated MEA's were subjected to a destructive method known as fire assay. In this process, the residue is heated at high temperature in a vessel containing a lead mixture. The reduced lead acts as a collector for traces of precious metal. Subsequently, the Pt is concentrated in a small bead of gold. When this method was applied to MEA residues, the quantity of Pt recovered was roughly 0.04 mg. This in turn corresponded to roughly 0.2% of the original Pt mass. Therefore, the analytical methodology accounted for roughly 99.8% of the Pt in the original MEA. The data for the fire assay study is in Table X.

Table X. Impact of Non-leached Pt on Material balance

Run	mg Pt by Fire Assay	Total mg Pt	% Bias
CCM A	0.03	24.41	-0.1
B	0.03	25.92	-0.1
C	0.03	24.32	-0.1
GDE A	0.04	20.51	-0.2
B	0.03	22.35	-0.1
C	0.05	22.70	-0.2

Materials of Construction - Based on the block diagram, it was possible to identify capital equipment for a plant sized for processing 1000 MT/year. That corresponds to fuel cell MEA's from ~500,000 cars/year. With 1% by weight Pt content and a 98% projected yield, the plant would yield 9800 kg Pt/year. An important issue in the plant design is the materials of construction. Of greatest concern are the wetted surfaces of the leaching vessel, which would be operated at elevated temperature and pressure with a corrosive environment. The decision on the decomposition medium is complex, with different results obtained depending on the mixture of reagents used. Table XI gives a summarized comparison of oxidants studied.

Table XI. Comparison of Oxidizing Agents in Combination with HCl

	Nitric Acid	Sodium Chlorate	Hydrogen Peroxide	Chlorine (extrapolated from behavior of H₂O₂)
Oxidant	NOCl, Cl ₂	ClO ₂	Cl ₂	Cl ₂
HCL consumption	3:1		2:1	none
PM dissolution	Good	Average	Good	Good
Carbon oxidation	Poor	Good	Poor	poor
Ru retention	Poor	Poor	Good	Good
Process compatibility	Good	Sodium salt build-up during distillation step	Good	Good (delivery pressure issue)
Safety Hazard potential	Safe	Runaway reaction possible	Strong Exotherm Observed	Gas Leak
Comments	Oxidant should be metered in under controlled conditions			

An extensive corrosion study was performed in the sealed microwave bottles with conditions that simulated operating of a sealed reactor. Metal coupons were submerged in an oxidizing medium, then heated to and held at a given temperature. The coupon was weighed before and after the acid exposure, and the dissolved metal was checked by ICP analysis of the acid solution.

Metal samples included stainless steel, Hastelloy[®], titanium and tantalum. Some of the coupons were also treated with a passivating layer of silicon prior to corrosion testing. The results of the study were very dramatic. Stainless steel and, to a lesser extent, Hastelloy[®] were attacked rapidly, but the presence of the silicon layer did afford some corrosion resistance; weight loss decreased 10 to 20-fold compared to the untreated metal coupons. Titanium was far superior to Hastelloy[®] and performance further improved following the application of the silicon layer. The most resistant metal was tantalum, which had almost no loss of mass. Representative data using HCl/peroxide reagent is shown in Figure 18

Figure 18. Corrosion Resistance Study for Reactor Materials of Construction

The experiment was expanded to determine the effect of free fluoride on the metal coupons and the extent of fluoride liberation during leaching. Initial experiments were made by adding NaF solution to the leach medium. There was an observation that the corrosion increased significantly. The leaching experiments were then performed with addition of 0.5g of MEA powder. Tests were done at 125, 150 and 200°C. A dramatic increase in corrosion was observed for the Si-coated titanium coupon as leach temperature increased. In fact, the Ti coupon dramatically lost half its weight during the 200°C trial using HCl and hydrogen peroxide, a mixture that liberates chlorine, as an exothermic event was observed. Table XII lists data for differing temperature and time for corrosion studies.

Table XII. Comparison of Corrosion for Si-coated Ti Coupons with MEA's present

Metal	Acid	Fluorine Present	Temp, °C	Time, min	% wt loss
Uncoated Ti-	HCl/H ₂ O ₂	No	125	10	0.0070
Coated Ti	HCl/H ₂ O ₂	No	125	10	0.00027
Coated Ti	HCl/H ₂ O ₂	No	150	30	0.00039
Coated Ti	Aqua Regia	No	125	10	0.00046
Coated Ti	HCl/H ₂ O ₂	CCM	125	10	0.013
Coated Ti	HCl/H ₂ O ₂	CCM	150	30	0.70
Coated Ti	HCl/H ₂ O ₂	CCM	200	30	>50%
Coated Ti	Aqua Regia	GDE only	125	10	0
Coated Ti	Aqua Regia	GDE only	150	30	0.012
Coated Ti	Aqua Regia	GDE only	200	30	0.084

Based on this work and the results obtained for leaching in both the Milestone microwave apparatus and the agitated Parr reactor, it was observed that a commercial process for Pt

recovery could be run at 100°C. Therefore, an extensive study was performed using uncoated Ti coupons exposed to a variety of acidic media along with MEA sample to act as a potential source of HF. Figure 19 shows the comparison for corrosion rate at 100 and 150°C. It can be seen that Ti corrosion is highest in a reducing environment. Addition of copper sulfate inhibits corrosion. Using a sub-stoichiometric aqua regia mixture (HNO₃-deficient) increases the corrosion of Ti, but the copper reduces the corrosion rate to that of standard aqua regia. Also, running at 100°C reduces corrosion by a factor of 10 compared to 150°C.

Practical experiments confirm the ability of HCl to attack titanium. The titanium Parr reactor vessel was used repeatedly using aqua regia runs. However, the reactor showed effects of corrosion with limited exposure to the leach medium where nitric acid was limited. In this medium, the vapor phase is rich in HCl and the reactor did not resist corrosion. Based on this experience and on the knowledge gained working at 100°C, future reactors will have to be constructed with liners of either glass or tantalum.

Figure 19. Corrosion rates for Titanium metal in various media

Process Efficiency - A major concern of the process is waste reduction. One specific example is disposal of HCl. Concentrated HCl is used as the basis of the leach medium. If the protocol of using minimal HNO₃ is accepted, >80% of the HCl will remain after the leach. It is expected that the concentration of Pt after leaching will be 1000 ppm wt/wt, based on an initial Pt content in the MEA of 1%, and a solids content of 10% during leaching. The targeted concentration for recovery of Pt is 20 g/L, which requires a 20-fold increase in Pt concentration in the leachate. This is achievable using distillation. Disposing of the distillate as waste creates two sets of problems. First of all, the acid would have to be neutralized, which will require a large amount of sodium hydroxide. There is cost for base storage and reagent usage. Also, the amount of salt formed during neutralization is problematic relative to a plant discharge permit. Obviously, the cost of replacement HCl for the next leach run is also an issue.

Rather than dispose of the distillate, the recovered HCl could be re-circulated to the leach vessel. This also represents a challenge. HCl/water mixtures distill as an azeotrope, with an azeotrope boiling point of 109°C and an HCl concentration of 21%. All leaching experiments performed using simulated azeotropic HCl resulted in a reduction of Pt yield, estimated to be roughly 3%. (In Barnes and Edwards, leaching of geologic materials was successfully achieved using 1:1 HCl and a stream of chlorine as oxidant.⁶) In later experiments, this yield reduction was the difference in the process between requiring one or two leaches. On the other hand, concentrated HCl can be produced from HCl distillation if an azeotrope breaker is used. There are several engineering approaches to distill HCl at a concentration above the azeotrope. A simple method is to distill HCl in the presence of a hygroscopic salt, such as an alkaline earth chloride, that can be thermally regenerated. The HCl rich distillate is then re-dissolved to yield concentrated HCl. The concentration of HCl in the reconstituted acid can be monitored using a high-precision density analyzer (DMA/DTR series), available from Anton Paar USA, Ashland, VA.

Other cost savings relate to disposal of waste streams. The first relates to the treatment of MEA wash streams (post-leach rinse). This liquid should be fairly low in acid but very low in Pt concentration. Distillation for Pt recovery work creates a bottleneck for this process. Rather than send the waste directly to a settling pond for neutralization and precipitation of heavy metals, the liquid can be treated using a resin to capture the Pt. Some experiments were performed using an isothiuronium resin, Sybron Ionac SR-3. It was shown that near quantitative recovery of trace Pt could be achieved using the resin and the capacity for Pt was very large. The recovery rate for successive batch runs of 50 mL solution with 1g of resin is shown below in Figure 20.

Figure 20. Removal of Pt from a solution with 200ppm Pt, 0.2N HCl using Ionac SR-3

The Pt can be recovered after resin capacity is consumed by ignition; the low-ash residue can be dissolved with aqua regia. In practice, the wash water could be recycled several times to increase the Pt content, then Pt recovered using the resin treatment. However, some degree of sensitivity to HCl concentration was observed. It was not determined whether the declining absorption of Pt was a function of chloride concentration or acidity. The acidity of the rinse water could be adjusted using NaOH if acidity is more important than chloride concentration in the resin removal of Pt.

PBI MEA's – Phosphoric acid management

Recovery of Pt from MEA's constructed using PBI in place of Nafion® introduces the challenge of handling the phosphoric acid-saturated MEA's. Leaching of the acid from the MEA upstream of other processing steps is advisable because of the corrosive nature of the acid and its non-volatility; when leached along with Pt, it would concentrate in the Pt concentrate and be carried as a contaminant into the refining process. A study was performed to determine if phosphoric acid can be simply removed from the MEA's. In an initial study using strips of PBI MEA's immersed in hot water, ~80% of the acid was removed. It was suggested that efficient acid stripping could be achieved using a sonication process. Using strips of both unused and aged PBI MEA's, three extraction media were evaluated, both with and without water rinses: cold water, a surfactant, and consecutive treatments of surfactant and base. The results of the study are tabulated in Table XIII.

Table XIII. Use of Sonication to Enhance Phosphoric Acid Removal from PBI-based, GDE-architecture MEAs		
Run	Sonication Conditions	% residual H₃PO₄, wt/wt
New		
A	Water/ 5 minutes, no rinse	1.85
B	Water/ 5 minutes, rinse	1.26
C	Water/ 15 minutes, no rinse	1.13
D	Water/ 15 minutes, rinse	1.22
E	Water/ 30 minutes, no rinse	0.97
F	Water/ 30 minutes, rinse	0.99
G	1:1 Surfactant/ 5 minutes, no rinse	4.33
H	1:1 Surfactant / 5 minutes, rinse	0.17
I	1:1 Surfactant / 15 minutes, rinse	3.08
J	1:1 Surfactant / 30 minutes, rinse	0.17
K	1:1 Surfactant /5 min, 1:1 Base/5 min, no rinse	3.19
L	1:1 Surfactant /5 min, rinse; 1:1 Base /5 min, rinse	0.28
M	1:1 Surfactant /15 min, rinse; 1:1 Base /5 min, rinse	0.21
N	1:1 Surfactant /30 min, rinse; 1:1 Base /5 min, rinse	0.22

Used		
O	Water/ 5 minutes, no rinse	6.39
P	Water/ 5 minutes, rinse	3.51
Q	Water/ 15 minutes, rinse	3.85
S	Water/ 30 minutes, rinse	2.54
U	1:1 Surfactant / 5 minutes, no rinse	8.88
V	1:1 Surfactant / 5 minutes, rinse	6.45
W	1:1 Surfactant / 15 minutes, rinse	1.31
X	1:1 Surfactant / 30 minutes, rinse	0.54
Y	1:1 Surfactant /5 min, 1:1 Base /5 min, no rinse	0.61
Z	1:1 Surfactant /5 min, rinse; 1:1 Base /5 min, rinse	0.48
AA	1:1 Surfactant /15 min, rinse; 1:1 Base /5 min, rinse	0.15
BB	1:1 Surfactant /30 min, rinse; 1:1 Base /5 min, rinse	0.12

It was shown that the two-step extraction could reduce the phosphoric acid level by 99%, with the bulk of the extraction performed in the first step using surfactant. This is displayed in Figure 21. The accuracy of the data was checked by milling the leached samples and re-leaching the resultant powder. The bias introduced by residual unleached H_3PO_4 was shown to be insignificant.

Figure 21. Comparison of Phosphoric Acid Residues in Sonicated Used MEA's (PBI)

Independent of the sonication study, the application of resin for removal of phosphate from the extraction medium was evaluated. A full-service recycling plant should be able to accommodate MEA's with PBI membranes. Based on the efficient acid removal demonstrated by sonication of MEA strips, it is expected that a high degree of H_3PO_4 can be removed from the PBI-based MEA's using a shredded sample. After leaching, the sample can be processed on a belt dryer to remove moisture upstream of the cryo-grinder. Disposal of the dilute acid solution is a concern. It was determined that most of the acid could be recovered using Dowex M-43 resin. Using batch experiments, 50 mL of solution was equilibrated with increasing amounts of resin. The results are shown below in Figure 22.

Figure 22. Removal of Phosphoric Acid from water using Dowex™ M-43 resin

Based on these results, it is easy to remove at least 95% of the phosphoric acid from the rinse water, which could be re-used. In turn, the resin can be regenerated using a sodium hydroxide eluant; the waste stream is a concentrated sodium phosphate solution. An example of the process, including a column for base metal removal, is shown in Figure 23.

Figure 23. Schematic of Process to Recycle PBI Wash Water

Process Control - A potential issue for process control is determination of the extent of leaching. Termination of the leach prematurely introduces the risk of precious metal loss, while continuation of leaching after the metal is mobilized results in unnecessary process delay and loss of throughput. Sampling of the MEA suspension during the leach would be helpful in determining when to terminate the Pt recovery process. Rapid analysis using some type of on-line or at-line assay is desirable. Analysis of the MEA/acid mixture is not practical because of the unknown distribution of metal between the two phases of the suspension; a practical assay will require separation of the leachate from the residue. While analysis of the leachate is straightforward, it introduces some degree of analytical error; a relative error of 2% would be unacceptable. The tolerance in error during the analysis of the residue is much greater. For example, 25% error at 2% residual Pt is an uncertainty of only 0.5% of original Pt content. Therefore, a rapid assay of the solid residue can include a relatively high level of error and still be meaningful.

Whereas X-ray fluorescence is frequently used for powder analysis, it is difficult to apply in this situation. The sample has a low average mass value and variable residual base metals. This will make calibration somewhat difficult. Also, the sample will have to be dry; otherwise, water vapor will collect on the sample holder window and skew the results. An alternative methodology, laser ablation-inductively coupled plasma (ICP), was proposed. The laser would ablate the sample surface, generating a fume that is carried to the ICP for vaporization and quantification. The measurement can be performed with an optical detector or by using a mass spectrometer; the latter approach is both more sensitive and more expensive.

In the preliminary evaluation, MEA powder was slurried and collected on a filter paper. It was observed that the laser energy blasted the powder off the filter. It was shown that the powder could be kept on the filter by using a lacquer spray, which served to hold the powder down adjacent to the path of the laser beam. An example of a laser track across a deposited layer of MEA powder is shown in Figure 24.

The solvent in the lacquer was not compatible with the polymeric filters used, so filtration was performed using glass filter discs. It was observed that the MEA powder was irregularly deposited on the surface of the filter. Moving the laser of the filter surface in a raster pattern resulted in temporal changes in the amount of fume in relation to the variable thickness of the MEA powder deposited on the filter. To compensate for the sample distribution problem, an internal standard was mixed with the sample powder. The internal standard needed to be equally distributed with the MEA powder and contain an element that satisfied three criteria:

1. Easily measurable
2. Absent from the sample and filter
3. No interference with the measurement of Pt.

Figure 24 Example of Laser track through MEA powder with lacquer fixative (213 nm laser, New Wave Corporation)

To address the most important issue, co-deposition of the internal standard and MEA powder, a set-up was devised using a dual syringe dispenser, a mixing 'T' and a syringe filter. Equal volumes of suspensions of MEA and internal standard flowed together in the

mixing 'T' and the mixture was deposited on the membrane filter. The internal standard selected was steatite, a refractory magnesium silicate. Because of the early use of glass fiber filters, Mg was originally used as the internal standard. The practicality of this methodology was tested using a suspension of alumina as a surrogate for MEA powder. The ratio of aluminum to magnesium was measured and compared to the direct measurement of aluminum. The statistics improved dramatically for the ratioed measurements. For example, the range of highest to lowest average counts for aluminum was roughly 8. The same statistic for Al/Mg was only 1.4. Similarly, the precision of the measurements improved, with a 90% reduction in the variance.

Experiments were then performed using 5% MEA suspension. Because of mechanical issues with the glass fiber filters, polymer filters were used. To avoid the use of lacquer fixative, a new approach was taken. The laser was used to sample the filtered material by shooting through the back of the filter. The powder adjacent to the laser path was shielded from the disruptive laser beam by the bulk of the filter. In this trial, silicon in the steatite was used as the internal standard, as the sensitivity of this element matched up better with the instrument's detection circuitry than magnesium and the filter was silicon-free. Unleached MEA powder was used for the trial. Two sets of eight runs were run using the back of the filter approach. The raw Pt counts varied, on average, by over 30% for the two runs, but the ratioed signal (Pt/Si), was almost unchanged. This held for the ratio of Pt 214.4 nm / Si 212.4 nm, as well as Pt 265.9 nm/ Si 251.6 nm. The intensity ratios for the two runs were 1.02 and 1.06, respectively, a reduction in run-to-run variability of almost 90% compared to the direct measurement of Pt.

The next step was to determine the linearity of the method. A sample of MEA powder was acid leached using aqua regia, filtered and rigorously washed to remove soluble Pt, then re-slurried. Based on assay of the filtrate and historical data, the MEA powder had 11% of the original Pt content. The suspension of Pt-depleted MEA was mixed on-line with steatite as described above and the resultant filter was sampled using the back of filter method. 11 runs, each with 10 repeats, were made. The data for the two MEA samples, as received and 89% depleted, are plotted in Figure 25. Both calibration lines show regression to the origin; the y-intercept for both lines is <1% of the signal for the original sample. Based on the success of the internal standard experiments with both alumina and MEA powder, a patent application covering the general use of laser-ablation-ICP for powder analysis was submitted in June 2008.

The utility of the laser ablation QC method could be compromised as the Pt loading of the MEA decreases by ~2/3 towards the DOE target of 0.20 mg/cm² and the requirement for analytical sensitivity increases proportionately. (This would correspond roughly to a 1% wt/wt loading of Pt in a prepared lot of MEA's.) Therefore, increasing the sensitivity of the method is desirable. The simplest way to increase analytical sensitivity is to increase the laser power and raster speed so that more sample is transferred to the ICP via the ablation process. In practice, this option has limitations as the moisture in the ablated sample tends to partially condense within the solenoid valve of the laser ablation system. After some time, wet sample powder accumulates in the solenoid valve and restricts the flow of sample to the ICP.

The second option is to increase the sensitivity of measurement. This can be achieved by substituting a mass spectrometer for the optical emission spectrometer attached to the ICP. In essence, ions formed in the hot plasma are counted in place of emitted light. ICP-MS is roughly 1000x more sensitive than ICP-OES, so the modified technique would have sufficient sensitivity for measuring highly Pt-depleted MEA powders. However, there are two technical issues using the mass spectrometer, both related to the internal standard. Internal standardization assumes that the reading of the sample and standard signals is simultaneous. This is achieved using the multi-channel detector of the ICP. While the mass spectrometer magnet scans over the mass region, the full-mass scan takes only 100 msec, so it is effectively a simultaneous measurement. More important is the selection of the internal standard. In the case of optical emission, the practice of using steatite (magnesium silicate) as the internal standard at a 1:10 ratio to the sample limited the internal standard to silicon; magnesium was much too sensitive an element for the system electronics.

With mass spectroscopy, both magnesium and silicon could be used as internal standard elements. However, the nominal unit mass resolution of the quadrupole mass analyzer introduces the potential for background interference. For example, the ion Si28 has the same m/e as N₂. Of interest was using Mg24, but there was concern that the dimer of C12 would represent a problem. Of course, carbon is the predominant element liberated from the ablated MEA (besides fluorine), so there is potential for spectral interference from the carbon dimer.

Figure 25 – Calibration of Laser Ablation-ICP-OES for MEA Pt content

Using a Peltier-cooled spray chamber and a Collision Reaction Cell, Thermo Scientific personnel, in a study prepared specifically for this project, demonstrated the near absence of spectral interference of carbon on magnesium at a ratio of 10⁷:1. Figure 26 shows the scans of 1 ppb Mg in the presence of increasing amounts of carbon (up to 1%).

Figure 26. Overlays of Scans of mass 24, 25 and 26 with 1 ppb Mg and increasing Carbon

In practical application, the carbon to magnesium ratio would not exceed $10^3:1$, so magnesium could be used as the internal standard using mass spectrometry.

Concluding Topics

Downstream operations – In conventional combustion of MEA's, a Pt-rich ash is obtained. The metal is impure and needs to be refined prior to re-use. After homogenization and sampling for analysis, the bulk of the lot is dissolved and the solution is processed to separate Pt sponge. The metal can then be re-dissolved and converted to the desired salt of Pt in the process of making a catalyst-containing ink. In the case of 3M's NSTF architecture, the pure Pt metal is sputtered onto the substrate whiskers.

The product of the 'consolidated' (leaching) process is a dilute Pt solution that is concentrated by distillation. This solution can directly be refined and Pt recovered as pure sponge using standard industry refining technology. Therefore, a large part of the refining cost of Pt recovered from MEA combustion is already included in the cost structure of the leaching process.

Environmental impact – Based on the use of HCl and 'minimal' HNO_3 during the leaching step, the leaching process ends up having a very small environmental footprint since 80% of the HCl added per cycle is recycled. [Based on 1% Pt content in the MEA, it is estimated that, even with reduction of nitric acid, there is still a 50:1 excess of chlorine. The large excess contributes to the elevated pressure in the reactor. Pilot plant practice can determine if additional reduction of HNO_3 usage can be achieved.] Using granulation and sonication, consumables per batch include 540 L of HCl, 135 kg of nitric acid and 1.5 to 3 kg of surfactant. Consequently, a scrubber system would use 240 kg of NaOH per batch for chlorine removal. The waste products of the process are 175 kg of NaCl and 250 kg of sodium hypochlorite. In addition, oxides of nitrogen can be removed either by scrubbing with a reducing agent such as sodium bisulfide or using selective catalytic oxidation to reduce NO_x to nitrogen using either ammonia or an ammonia precursor such as urea. In the latter case, roughly 20 kg of urea are consumed per batch.

Having a process that is NO_x-free would simplify the emission control required. Earlier studies showed that Pt could be recovered from MEA's using HCl and hydrogen peroxide, with chlorine liberated in-situ. Storage of hydrogen peroxide is challenging because of the potential for decomposition of the reagent, an event that would liberate heat and pressure. An alternative is to use direct chlorine injection. While storage of large quantities of chlorine should be avoided unless absolutely necessary, chlorine can be generated electrolytically on demand, at a cost equal to that of nitric acid. There are two restrictions with this approach. Charging the reactor with on-demand chlorine will extend the batch run time. The alternative is to convert the gas to a liquid by compressing the chlorine to 60 psi, which allows on-site storage; storage of batch-size quantities of liquid chlorine may be acceptable. This is an option that would be pursued in a pilot plant environment.

In addition to vapor emissions, there will be a residue of ~150 kg of MEA sludge (dry basis). Assuming a dilute caustic rinse was performed, the acidic exchange sites of Nafion[®] will have been neutralized and the carbon fiber-polymer mixture can be dried and disposed as non-hazardous solid waste.

Pre-treatment of PBI membranes to remove H₃PO₄ yields a dilute acidic waste stream. The H₃PO₄ can be concentrated using an ion exchange treatment and the resin regeneration solution elutes a phosphate rich solution. This can be disposed as a non-hazardous waste.

It should be remembered that by avoiding MEA combustion, emission of hydrogen fluoride and carbon dioxide is eliminated. For each kg of Nafion[®]-based MEA, roughly 400g of HF vapor would be liberated during combustion, along with 2 kg of CO₂; the latter value does not include the CO₂ liberated from natural gas used for the combustion process.

Process Economics – At the end of the day, the cost of recovering Pt using the technology detailed in this report must be competitive with other processes meeting minimal environmental standards and discharge permits. However, the complete economic analysis for this process is considered proprietary information and will be disclosed to the Department of Energy in a confidential addendum. The highlights of the economic analysis are that the process has the capability to recover 98% and the cost of recovering the Pt is a few per cent of the value of the metal, even at a Pt loading of 1% wt/wt. Obviously, the relative cost of MEA processing decreases if either the Pt content or the cost of Pt per T.O. increases

Within this report, the variable costs of the project will be discussed as a starting point for decision-making relating to process alternatives. The two principle options are using room temperature granulation vs. cryogenic milling and hot melt agglomeration. The cryogenic milling requires liquid nitrogen to embrittle the MEA and to cool the hammer mill. Agglomeration consumes a fairly large amount of inexpensive reagents and optimization of this step could result in substantial savings. The leaching chemistry is the same for both processing options and further reduction in nitric acid usage will reduce NaOH consumption, the single biggest reagent cost, as well as reduce the costs for HCl and HNO₃. Obviously, this is best determined in the pilot scale operation. Data in Table IX has demonstrated that granulated material can be leached successfully at a 10% solids content. The associated process costs for a batch of 300 kg of MEA are listed in Table XIV. It is estimated that the value of Pt per kg of MEA is \$350, assuming 1% Pt wt/wt and \$1100 per T.O. of platinum. Using the granulation option, cost of reagents, energy and waste disposal are only 0.34% of the estimated Pt value of the MEA.

The limited data acquired for leaching of granulated MEA showed that there was only a small decrease in Pt yield when surfactant-free granulate was dispersed using a sonicator. However, the minimal amount of surfactant used with sonication does not impact the economics sufficiently to justify running without surfactant at this time.

Table XIV. Variable Costs for the Recovery of Pt From a 300 kg Batch of MEA's

	Granulation		Agglomeration		
	cost/batch	cost/kg MEA	cost/batch	cost/kg MEA	Comments
Reagents					
HCl	91	0.30	91	0.30	\$130/MT
HNO ₃	34	0.11	34	0.11	\$250/MT
NaOH	144	0.48	144	0.48	\$600/MT
Urea	8	0.03	8	0.03	\$400/MT
Surfactant	10	0.03			0.02 g/g
			240	0.80	non-optimized
LN ₂		0.00	38	0.13	
Energy	51	0.17	51	0.17	
Solid waste	20	0.07	20	0.07	25% moisture
		0.00		0.00	
Total, \$	358	1.19	626	2.09	
% of Pt value		0.34		0.60	

Future Direction – Over the past five and one half years, this project has progressed to the point where near-quantitative recovery of platinum can be achieved using a simple process involving an oxidative acid leach, followed by material washing using alkaline and aqueous rinses. Although optimizing Pt extraction from the MEA's in the reactor is an engineering challenge, the depleted MEA material can be tested for residual Pt content in an at-line QC process. The next logical step in the project is to build a pilot plant.

Hammerhead Engineering of Flemington, NJ was commissioned to design a pilot plant. A layout of the plant is shown in Figure 27. The initial estimate for the plant was roughly \$1.5MM, but savings are anticipated if the granulation approach is adopted in place of cryo-milling. A reduction in the estimate for scrubber cost is also expected based on the decreased use of nitric acid.

There are major process questions that need to be answered during the pilot plant trials. These include the minimum amount of oxidant needed and the selection of oxidant. Certainly, the emissions treatment system can be simplified and cost savings achieved if chlorine can be used in place of nitric acid.

Figure 27. Proposed Pilot Plant for MEA Leaching

Outside Services- Almost all the testing performed for this project was completed at either Engelhard/BASF, Ceralink or one of the sub-contractors. However, an essential part of the project was the acquisition of large quantities of aged MEA's. This is not a simple task to achieve. A supply of 5-layer MEA's, having Pt/Ru anodes and Pt cathodes, were purchased from W.L. Gore. On two occasions, in 2004 and 2006, a series of MEA's were given to Green Light Power, a subsidiary of Hydrogenics, for aging in reformat. The first test set was aged for 2000 hours, with samples withdrawn every 500 hours. Based on the observation that the MEA has degraded during the first 500 hours, as evidenced by lower tolerance to solvent attack, the second set of samples were aged for

only 500 hours. The aged materials were used mostly for the solvent delamination studies, but were also used for acid leaching studies.

Also, combustion products produced by Virginia Tech were sent for neutron activation analysis to Becquerel Labs, of Mississauga, Ontario. This facilitated determination of fluorine in residues. This testing was also useful in determining the volatility of ruthenium during combustion.

Acronyms

Al	Aluminum
CCM	Catalyst coated membrane
Co	Cobalt
CO ₂	Carbon dioxide
Cr	Chromium
Fe	Iron
FT-IR	Fourier transform infrared
GDE	Gas diffusion electrode
GDL	Gas diffusion layer
H ₂ O ₂	Hydrogen peroxide
HCl	Hydrogen chloride, hydrochloric acid
HF	Hydrogen fluoride
HNO ₃	Nitric acid
H ₃ PO ₄	Phosphoric acid
ICP	Inductively coupled plasma
L/D	Length:diameter ratio
LA	Laser ablation
LN ₂	Liquid nitrogen
MEA	Membrane electrode assembly
Mg	Magnesium
Mn	Manganese
MS	Mass spectrometry
MW	Molecular weight
NaClO ₃	Sodium chlorate
NaHS	Sodium bisulfide
NaOH	Sodium hydroxide
Ni	Nickel
NO _x	Oxides of nitrogen
NSTF	Nano structured thin film
OES	Optical emission spectrometry
PBI	Polybenzylimidazole
PFA	Perfluoroalkoxy
Pt	Platinum
PTFE	Polytetrafluoroethylene
RSD	Relative standard deviation
Ru	Ruthenium
SCF	Super critical fluid
Si	Silicon

Ta	Tantalum
Ti	Titanium
Zr	Zirconium

Patent Applications

1. US Patent Application 2006/0237034, “Process for recycling components of a PEM fuel cell membrane electrode assembly”, filed April 20, 2005.
2. US Patent Application 2007/0292745, “Process for recycling components of a PEM fuel cell membrane electrode assembly”, filed June 20, 2006.
3. US Patent Application 2009/0049954, ‘ Simplified process for leaching precious metals from fuel cell membrane electrode assemblies”, filed August 24, 2007.
4. Unpublished US patent application, BASF Reference 5429/5439, “Method for On-line process control of fuel cell membrane electrode assembly leaching”, filed June 6, 2008.
5. Unpublished US patent application, BASF Reference 5477, “Method and apparatus for recovering catalytic elements from fuel cell membrane electrode assemblies”, filed June 6, 2008.
6. Unpublished US patent application, BASF Reference 5569, “Method for recovering catalytic elements from fuel cell membrane electrode assemblies”, filed May 15, 2009.

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