

**An Environmentally-Friendly Process for Fuel Cell Electrode Reclamation**  
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If society is to meet its objective of sustainable growth, then issues relating to energy conservation and environmental stewardship need to be in the forefront of engineering concerns. It has been proposed that both energy efficiency and the environment can be improved by switching to hydrogen as an energy carrier in our economy. While production of hydrogen introduces some environmental and cost issues, the overall impact on air pollution should be positive because of the lack of emissions at point-of-use during combustion of the fuel; the only by-product is water. By comparison, elaborate pollution control strategies, both in engine design and operation and in exhaust clean-up via catalytic removal of unburned hydrocarbons, carbon monoxide and oxides of nitrogen, and particulate matter in the case of diesel, are needed to enable us to use liquid fossil fuels for transportation.

One of the promising ways to utilize hydrogen is to release its chemical energy in a fuel cell. Theoretically, a fuel cell, where chemical energy is directly converted to electrical energy, can achieve higher efficiency than a heat engine, which is limited by the Carnot cycle. In stationary applications, even greater efficiency is achieved by capturing waste heat, which is useful to supply residential hot water. While fuel cells have been actively under development for the last 40 years, the last decade has seen widespread international interest in this technology because of its potential for gains in energy efficiency and reduced air pollution. Japan leads the world in both support and development of early-generation distributed fuel cells for stationary (residential) applications, but most industrialized nations are pursuing this technology. These stationary installations are either directly fueled by hydrogen or reform a hydrocarbon fuel, such as natural gas or LPG, into a hydrogen-rich reformat. Of course, major automotive manufacturers worldwide are interested in the development of fuel cell-powered vehicles. For the most part, they have decided to concentrate on 'engines' fueled by high-purity hydrogen; on-board reforming introduces a high level of complexity in system design and issues like rapid start-up are difficult to address and, therefore, this approach has been mostly eliminated from consideration..

The bulk of work relating to fuel cells driven with hydrogen is based on the proton exchange membrane fuel cell design, otherwise known as PEMFC. At the heart of a PEM fuel cell is a membrane electrode assembly, or MEA. That is a laminate composed of a membrane in contact on one side with an electrode layer that acts as the anode and, on the second side, a layer that serves as the cathode. The sandwich is completed by placement of gas diffusion layers on the exterior of the laminate. The construction either has the electrode layers directly applied to the membrane, which is referred to as the 'CCM' design, or has the catalyst layers applied to the gas diffusion layers, which is referred to as the 'GDE' design.

The mechanism of a PEM fuel cell is fairly simple. Molecular hydrogen diffuses to the anode and dissociates, and electrons are stripped off. The resultant protons diffuse across a membrane, commonly composed of negatively charged sulfonate groups attached to a

perfluoropolymeric backbone: the most common material used is Nafion<sup>®</sup>, a polymer made by DuPont Corporation. (There are other commercial membrane compositions, such as polybenzimidazole, sold by Pemeas.) The protons react with oxygen at the cathode to form water, while the electrons pass through an external load and neutralize the positive charge at the cathode.

A drawback in the current design of the PEM fuel cell is the cost of materials of construction. Nafion<sup>®</sup> is a high-cost polymer; although its cost is expected to decline significantly as demand for the polymer increases; current demand is almost exclusively for membrane-based chlor-alkali production. Of greater import is the need to use platinum as the catalyst in both the anode and cathode layers. Platinum is dispersed on special grades of activated carbon, and is present at high level (~40% wt/wt.) As of July 13, 2006, platinum was at ~\$1250/troy ounce, or \$17,500/lb. Besides its relatively high price, the source of platinum is limited. Newly refined platinum is almost exclusively obtained from deposits in South Africa. At the same time, a substantial amount of platinum is obtained by refining spent automotive exhaust catalysts and recycling the precious metal present. Recovery of precious metal is element and substrate specific, but yields in excess of 95% are achievable.

As part of its program to support the Hydrogen Economy, the U.S. Department of Energy awarded Engelhard Corporation ( now BASF Catalysts LLC) a cost-shared project to recover precious metals from PEM fuel cells. The project, which has an 80:20 cost share, began in 2003 and is scheduled to run to 2008. The primary objective of the project is to develop a commercially-viable process for recovering precious metals from fuel cells without releasing hydrogen fluoride. In addition to the Nafion<sup>®</sup> membrane, Nafion<sup>®</sup> ionomer is usually incorporated into the electrode layer, and PTFE is present in the gas diffusion layer to add hydrophobicity. The first step in routine refining of a carbon-containing material such as Pt/C catalyst is to combust the material. Dupont has reported that HF, which is a corrosive and hazardous gas, is a major product of thermal degradation of Nafion<sup>®</sup>. In addition, another by-product, carbonyl fluoride, is also highly hazardous. As understanding of the materials increases, the possibility of recovery of the perfluorosulfonic acid for non-fuel cell related applications should be explored.

The development of a process to recover precious metals, primarily platinum, from fuel cell MEAs has progressed along a slightly misaligned path. It has been found that the provenance of the MEA is very critical. Parameters of importance include MEA type, degree of usage (new vs. aged) and fabricator. Although 3M has submitted a patent<sup>1</sup> for direct recovery of platinum from an intact fuel cell, the business model predicted for fuel cell recycling will involve collection and disassembly of stacks at a centralized facility, with the fuel cell MEA being sent to a refiner. This is the model currently used for automobiles, and is how automotive catalysts are returned for processing.

The obvious approach to recycling would be to disassemble the stack, which is composed of multiple MEAs, and to contact the MEAs with an oxidizing acid. Using 1" x 1" sections of aged CCM-style MEAs, this approach was tried using aqua regia, which is a 3:1 mixture of HCl and HNO<sub>3</sub>. The results were disappointing; yields of 62 and 85% of

total Pt were obtained. The low yield and poor precision of the trial demonstrates the need to expose the electrode catalyst layer to direct contact with the oxidizing acid.

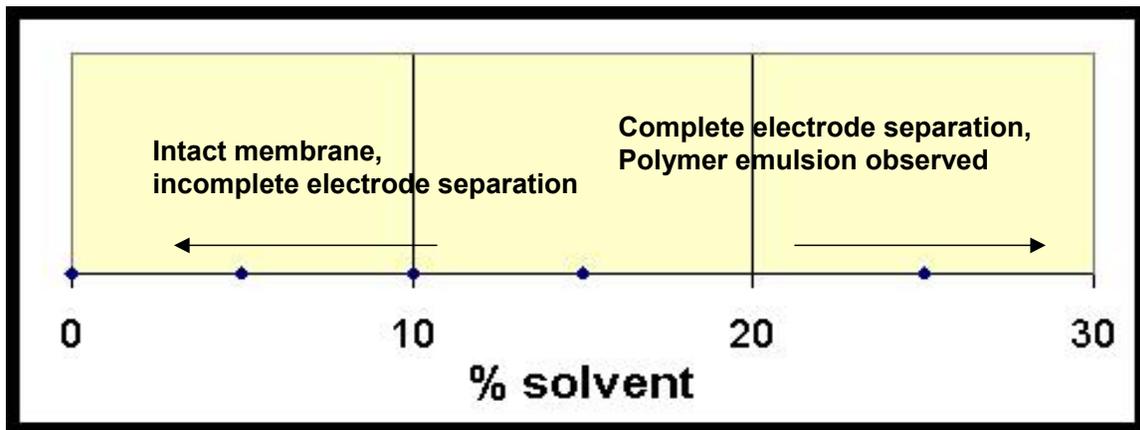
To improve platinum leachability, the electrode-covered membrane of an aged MEA from a commercial supplier was exposed to acid by manually separating the external gas diffusion layer from the core 3-layer MEA (anode/membrane/cathode). While the retrieval of platinum from the 3-layer MEA was very high, with <1% of the platinum remaining on the membrane after the acid leach, as determined by analysis of membrane ash after combustion, it was found that a significant amount of platinum remained on the to-be discarded gas diffusion layer that had initially been removed from the MEA.

Based on these results, it was obvious that a more efficient mechanism for separation of the layers of the membrane electrode assembly was required because of the co-mingling of MEAs with different sources during the recycling collection process. Experience had shown that boiling the MEAs in hot water was useful, but this was not universally true. Table 1 describes the degree of separation between the GDL and the inner layers of the MEA.

| Vendor/ usage  | Boiling water | Solvent delamination |
|----------------|---------------|----------------------|
| Vendor A/ new  | Good          | Good                 |
| Vendor A/ aged | No effect     | Good                 |
| Vendor B/ new  | Good          | Good                 |
| Vendor B/ aged | Good          | Good                 |

Another approach is to expose the MEAs to a mixture of lower alkyl alcohols and water. Nafion<sup>®</sup> is unique in its properties, and it is shown to swell in a solvent containing both water and alcohol<sup>2</sup>. In actual practice, the polymer layer swells in contact with this solvent mixture, causing the gas diffusion layers to separate immediately from the rest of the MEA. The fate of the catalysts layers and membrane is dependent on the MEA history. In the case of an unused MEA, the electrode layers come off the membrane, which is minimally affected by the solvent; there may be some swelling of the polymer. In the case of an aged MEA, the electrode catalyst layers then come off the membrane and start to break apart into fine particles. However, depending on the supplier and the solvent selected, the membrane itself disintegrates. Control of this disintegration is difficult to achieve and makes filtration tedious. Figure 1 shows a representation of the effect of solvent concentration on the dismemberment of an aged MEA.

**Figure 1. Representation of sensitivity of aged membrane and electrode layer to exposure to solvent**

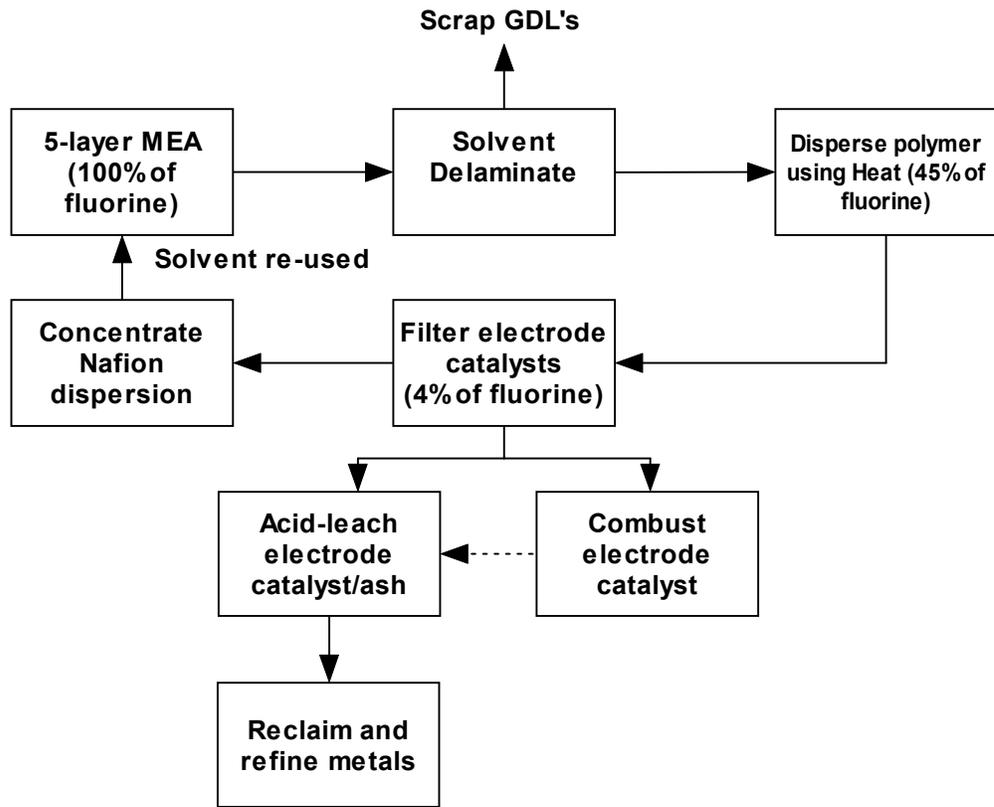


The decrease in stability of the membrane in solvent as a function of aging appears to be a result of loss of polymer molecular weight. The presence of peroxides within the fuel cell contributes to unzipping the polymer. This change in membrane properties would appear to be irreversible, and recovery of the polymer with the intent to recast membranes with properties equal to virgin Nafion<sup>®</sup> is certainly questionable. On top of that, the membrane formulation varies between vendors, and collection of MEAs to be recycled would result in mixing polymers, further reducing the possibility of a secondary market for recycled membranes. At the same time, it is expected that the sulfonic acid groups of Nafion<sup>®</sup> will be unaffected by aging. Therefore, reclamation of the polymer with the intent of producing a product benefiting from these acid sites is reasonable.

With the understanding that aged MEAs can be dismembered using a solvent mixture, attention was given to the separation of the phases. It was found that the polymer emulsion formed on contact of the membrane with the solvent would clarify as the polymer dispersed with the application of heat. Heating the solvent to <100°C resulted in a clear dispersion. Development of a practical process was investigated. It was decided that a continuous process had the best possibility of success while managing the hazards of solvent mixtures. Further investigation pointed to a continuous reactor that was heated using microwave energy. The apparatus, called the FlowSYNTH and sold by Milestone Inc., has the ability to directly heat the flowing solvent. Because microwave energy is directly adsorbed by the solvent, there is no need to heat container surfaces to an elevated temperature, as is normally the case with radial heating. This reduces the possibility of solvent vapor coming in contact with a surface above the solvent flash point.

Based on the ability to liberate electrode catalyst particles from both the membrane and gas diffusion layer of a CCM-style MEA, a process was proposed for the recovery of precious metals from a used MEA. This is shown in Figure 2.

**Figure 2. Schematic for Proposed Process for Fuel Cell MEA Recycling**



The proposed process addresses most of the concerns of the project, mainly achieving high yield of precious metal while avoiding evolution of HF.

#### References

1. Debe, M.K and C.V. Hamilton, US patent application 2006/0147791.
2. Yeo, R.S., *Polymer*, 1980, **21**, 432.