

Engineering a Membrane Electrode Assembly

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One quickly realizes that a polymer electrolyte membrane fuel cell (PEMFC) unit powered by hydrogen or methanol is more than just a stack of cells. Rather, it is a tightly integrated system of pumps, valves, flow meters, sensors, and heat exchangers that must work reliably for thousands of hours. This requires the expertise of a wide range of scientists and engineers to design, fabricate, and test an efficient, low cost unit that can compete in the marketplace with other energy producing devices.

What is less obvious is that the heart and soul of the PEM fuel cell, the membrane electrode assembly (MEA), is also a highly integrated system requiring the expertise of polymer chemists, electrochemists, chemical and mechanical engineers, mathematical modelers, and statisticians to design, fabricate and test an efficient, low cost unit that can compete in the marketplace.

In the most complete form, a MEA consists of seven layers: a proton exchange membrane, three-phase anode and cathode catalyst layers, two gas diffusion layers (GDLs), and two sets of sealing gaskets, as shown in Fig. 1. Each layer of the MEA performs a unique role, which is described below. However, the MEA is more than a simple collection of these layers because a change in one has an impact on the performance of the others. Rather, the MEA is truly a highly integrated system.

Membranes such as DuPont's Nafion consist of a polytetrafluoroethylene (PTFE) backbone with perfluorinated-vinyl-polyether side chains containing sulphonic acid end groups.¹ When these membranes become hydrated, the protons become highly mobile. These perfluorosulfonic-acid membranes were originally developed for the chlor-alkali industry and so the fuel cell environment is relatively mild. However, the need for high power densities has led to much thinner membranes than those developed for the chlor-alkali industry. For example, Nafion 117 has a thickness of 175 μm (the 7 in 117 refers to a membrane seven thousandths of an inch thick). Now the standard for fuel cells is Nafion 112, which is 50 μm , and a newer Nafion 111 coming in at a scant 25 μm . These thinner membranes have less mechanical strength, which has lead other companies such as W. L. Gore to develop composite membranes to reinforce Nafion.²

Another consequence of using thinner membranes is the resulting increase in reactant crossover, which decreases fuel utilization. This is especially problematic in a direct methanol fuel cell (DMFC) because methanol has similar properties to water. Thicker membranes reduce reactant crossover but at the expense of higher resistance and hence lower power density. Another approach is to develop composite membranes with the dual properties of high proton conductivity and low methanol crossover.

For example, Libby *et al.*³ developed a membrane made of polyvinylalcohol and loaded with mordenite, a proton conducting, methanol impermeable zeolite. Even in these new membranes, however, there is a tradeoff between efficiency and power.

Although Nafion has been the standard for PEM fuel cells, the market is demanding alternative operating conditions, which is driving the search for new membranes. For example, the automobile companies would prefer operating temperatures well above 100 $^{\circ}\text{C}$ because this would dramatically reduce the size of the radiator. However, it is not possible to maintain adequate membrane water content, and hence acceptable proton conductivity, at these temperatures without operating at

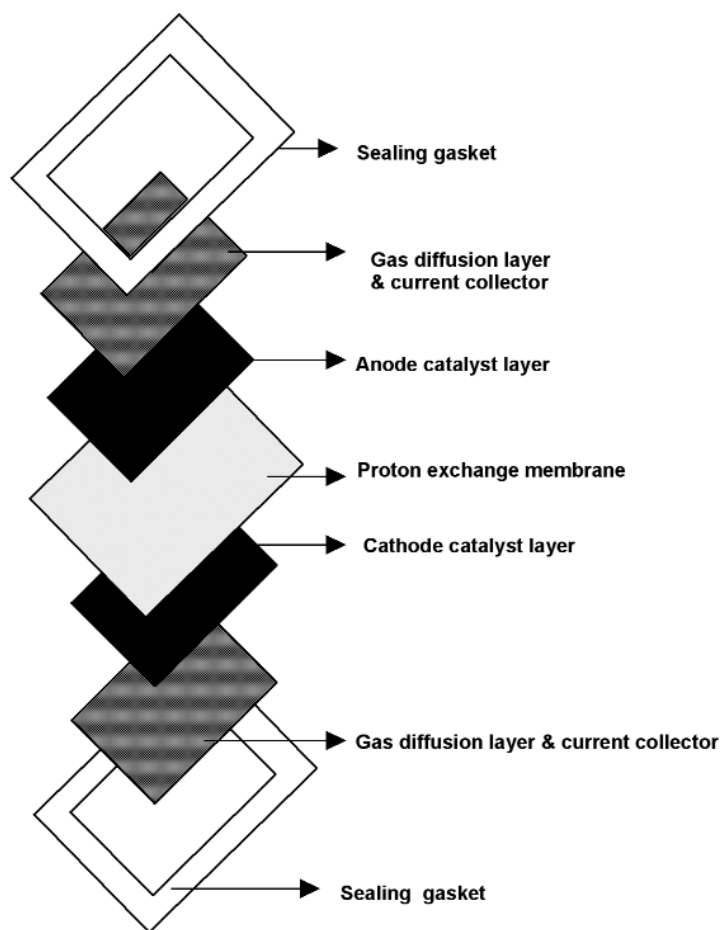


FIG. 1. A seven layer MEA consists of a proton exchange membrane, three-phase anode and cathode catalyst layers, two gas diffusion layers, and two sealing gaskets.

elevated pressures. Elevated pressure introduces its own set of problems, such as a need for an energy consuming compressor. In addition, the glass transition temperature of Nafion is 111 °C⁴ and therefore the mechanical stability is compromised at elevated temperatures.

The catalyst layers on the anode and cathode are composite structures consisting of the proton conducting polymer (*e.g.*, Nafion) and a carbon supported metal catalyst. Catalyst layer thicknesses vary between 10 and 20 μm depending on catalyst loading levels. Platinum is by far the best catalyst for both the anode and the cathode. However, the choice of the anode catalyst and loading levels also depends on the fuel source. When operating on pure hydrogen relatively little Pt is needed since the hydrogen oxidation reaction is facile and the resulting overpotential is small. If the fuel is a reformat (*i.e.*, a mixture of H₂, CO₂, N₂, and impurities such as CO) or methanol, then catalysts such as a PtRu, PtRh, or PtNi alloys can be used to minimize the adverse affect of CO poisoning.⁵

The oxygen reduction reaction (ORR) is the more limiting reaction in a well performing fuel cell. Therefore, reducing the activation overpotential for ORR is a crucial factor in improving the fuel cell performance. Increasing the cell temperature and pressure, increasing the reactant concentration (*i.e.* operating on pure oxygen), increasing the electrode roughness and the catalyst loading are some of the ways to deal with the performance loss due to the sluggish ORR kinetics. For example, for a PEM fuel cell fueled by hydrogen and oxygen operating at 80 °C and 1 atmosphere, the loss due to the ORR at 0.5 A/cm² is 160 mV.⁶

Currently the catalyst loading levels on the cathode side are between 0.1 and 0.2 mg/cm². This is a dramatic improvement over loadings in the 1960s which were about 28 mg/cm². At current prices, this translates into a Pt cost about \$1,000 for a 1 kW stack. The two-fold decrease in loading levels since then brings Pt costs down to \$10 for a similar unit. This is relatively insignificant for an estimated cost of a mass-produced fuel cell subsystem of \$325/kW.⁷ However, the DOE goal of \$45/kW⁷ will require further reduction or elimination in the amount of precious metals.

Though the details vary, the basic structure of the electrode in different PEMFCs is similar. The catalyst particles, approximately 5-20 nm, are dispersed onto a carbon support (*e.g.*, Vulcan XC72 Cabot). Smaller particle sizes lead to a larger active area and a better performance per mg of catalyst loading. However, smaller particles are less stable and so agglomeration of particles can occur over time. Two methods are currently practiced in the fabrication of the catalyst layer. In the first method,⁸ the carbon supported catalyst is sprayed or electrodeposited onto a porous and conductive material such as carbon cloth or carbon paper. The catalyst loaded electrodes are then put onto each side of a proton exchange membrane and hot pressed at 132 °C at 500 psig for 2-3 minutes. The second method involves building the electrodes directly on the proton exchange membrane. The platinum on carbon catalyst is applied to the electrolyte membrane using rolling methods, by spraying or through a process similar to screen-printing.⁹ Each processing step imparts known and unknown characteristics to the membrane, catalyst layer, and interfaces. Therefore, variations in the processing steps can play as big of a role in performance as variations in materials themselves.

Regardless of the composition of the catalyst, these porous layers not only contain the sites for charge transfer, but they also must have a dual conduction mechanism. That is, they must conduct protons through the polymer to complete the ionic path and electrons through the carbon to complete the electronic path. In addition, gases and water must move easily through these layers. Finally, one must guard against the case of cell reversal when one of the cells in the fuel cell stack gets starved of fuel. When fuel starvation occurs at the anode, the local anode potential increases causing water electrolysis or carbon oxidation. One way to protect the carbon-based components is to incorporate an additional electrocatalyst in the anode catalyst layer to sustain the water electrolysis.

The gas diffusion layers might play the most critical and least appreciated role of all. As the name implies, the main purpose of the GDL is to distribute the reactants from the gas flow channels uniformly along the active surface of the catalyst layer. In addition, the GDL has to ensure proper transport of product water, electrons, and heat of reaction. It also forms a protective layer over the very thin layer of the catalyst. The GDLs are either carbon paper (*e.g.*, Toray paper) or conductivity and PTFE for hydrophobicity. The in-plane and the through-plane resistivities of the commercial GDLs are in the range of 25-100 mΩ cm and 6-20 mΩ cm² respectively. The in-plane and the through-plane resistances depend on the microstructure of the GDL. The through-plane resistance dictates the cell resistance and the in-plane resistance affects the reaction uniformity.

Finally, the role of the GDL on the anode is not identical to its role on the cathode. For example, water formed on the cathode must be easily repelled from the catalyst surface to prevent flooding (*i.e.*, liquid water formation). This liquid water blocks catalyst site and prevents oxygen from getting through the catalyst layer. In contrast, the anode must retain some water to keep the membrane from drying out. This is especially true if the anode gas stream is dry.

The integrated seals and gaskets provide for a compact design while performing its primary function of eliminating leaks and over-compression. The thickness and the compressibility of these gaskets dictate compression levels on the GDLs. Also, contaminants from the seals can poison the catalysts or degrade over time. So far, there has been little detailed accounting on the effects of various gaskets in the literature.

All MEA producers strive to provide high power density, long and dependable lifetime, low cost, consistent and reliable performance, simplicity of use, and operational flexibility. Unfortunately these are not mutually exclusive and so there is a continuous tradeoff among these goals while continuing to drive down cost. Where that optimum lies depends on the end use of the product as defined by the customer. For example, for stationary applications durability is the key attribute. These units must run continuously for tens of thousands of hours without fail. Because they are stationary, power density is not as important as lifetime and reliability. Also, these units are large so the incremental size and cost of additional auxiliary units (*e.g.*, humidifiers, heat exchangers, pumps, and controllers) can be justified if they extend life and minimize maintenance.

For transportation, high power density (*i.e.*, size of the unit) is critical because these units are moving with the load. Therefore, the efficiency of the load plus the fuel cell must be optimized. In addition, durability and flexible operation are also critical design constraints. For example, the load and temperature on these units fluctuate, especially during cold starts or prolonged operation. They must also perform well whether they are being used in the hot, dry Arizona desert or in the middle of a Wisconsin winter.

For portable applications, size and simplicity must be achieved with dry rather than humidified gas streams. Auxiliary units that can help optimize performance by controlling operating conditions are often not practical. Like fuel cells used for transportation, portable applications have varying loads or even no loads for extended periods of time. Therefore, fuel and water management must be maintained even when the cell is not operating. A membrane cannot be allowed to dry out when the fuel cell is not in use or it will not deliver power when power is demanded. And although cost is always an issue, there are some applications where the consumer will pay premium price for the unique attributes of a fuel cell. For example, the military is willing to pay more than a typical consumer for a device that is quiet, dependable, and has a small thermal signature.

As with all industries, the MEA manufacturer must work closely with their customers (*i.e.*, fuel cell manufacturers) and their suppliers (*i.e.*, manufacturers of membranes, catalysts, GDLs, seals) to engineer an MEA that meets the performance requirements and operating conditions of the fuel cell. This requires numerous iterations as MEAs are designed, fabricated, and tested. This process is shown in Fig. 2 and described on 3M's website.¹⁰

The process begins with the customer providing performance requirements, design specifications, and operating conditions to the MEA manufacturer. This will include such things as operating temperature, power requirements, size, application (*i.e.*, stationary, transportation, portable), target costs, and fuel and oxygen source. The MEA manufacturer must then choose a set of membranes, catalysts, GDLs, and seals that they feel will meet these specifications. In addition, they must determine how all these layers will be assembled and if there is a need for any interfacial coatings (*e.g.*, micro layer of a GDL). This requires close consultation with their suppliers

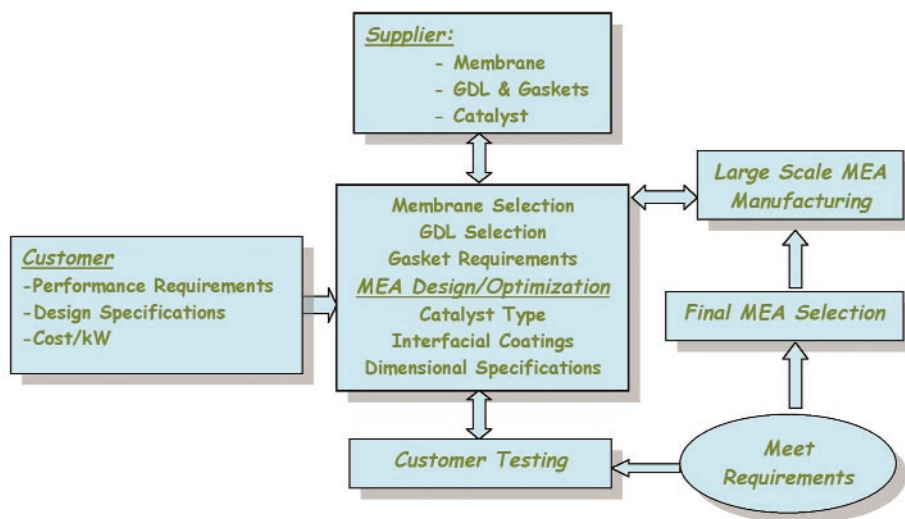


Fig. 2. A quality control flow sheet for selecting a proper MEA.

so they can get the components with the desired properties. While assessing material properties based on desired fuel cell performance, the MEA manufacturer must also try to drive down their costs by simplifying the manufacturing process without affecting quality. This in itself may affect the selection of materials. For example, a choice of carbon paper or carbon cloth may be dictated by which is more compatible for their assembly process.

Once the materials have been selected and the sequence in which layers are applied has been determined, the MEAs are fabricated, installed in a fuel cell, and tested under the specified operating conditions. These results are compared to the customer's specifications and new sets of materials, in consultation with suppliers, are selected for testing. This interactive process is continued until the customer's requirements are met. Large scale manufacturing of the MEA follows, and if problems arise here the iterative process could start over.

What makes this interactive process so involved is that a change in one layer, or operating condition, can affect the optimization of another. For example, super-saturation of the incoming gas streams result in a very high current density at the inlet but also the formation of liquid water (*i.e.*, flooding), which lowers the performance due to the increased film resistance for diffusion. In contrast, dry gas streams on either anode or cathode cause low membrane conductivity and low performance so components must be chosen to retain water. Because there are so many interacting parameters that need to be optimized, it is not possible to test all possible combinations within a reasonable amount of time. Therefore, the MEA manufacturer relies heavily on statistical analysis to test those combinations that have the highest probability for success.

Even statistical analysis has its limitations though, and costly testing can be minimized by using mathematical models to simulate fuel-cell performance. For example, a two-dimensional simulation for water and thermal management for the case of a single MEA was done by Fuller and Newman¹¹ and Nguyen and White.¹² More recently, computational fluid dynamics (CFD) technique has been used by researchers to simulate the performances of entire fuel cell stacks.¹³ On the other end of the size spectrum, a number of researchers are using molecular modeling to address such issues as the complex three-phase interface of the catalyst.¹⁴ All these modeling efforts help not only the MEA producer but also the stack manufacturer identify desirable MEA properties. That is, because a MEA has been optimized for a single cell does not mean it will perform well in a stack. Therefore, just like an optimal MEA for a particular application requires the MEA to be treated as a system and not a collection of layers, the optimal fuel cell will need to integrate the design of the MEA into the design of the stack, a truly wonderful engineering problem. ■

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