

# **A New Membrane Electrode Assembly for Low-Temperature PEM Fuel Cells Having a Nanocomposite Catalyst Layer .**

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Studies are currently underway to manufacture a novel membrane electrode assembly (MEA) for polymer electrolyte fuel cells. This MEA will be designed to incorporate a nanocomposite catalyst layer comprising a functionally graded distribution of Platinum nano particles chemically embedded near boundaries and surfaces of the polyelectrolytic membrane. The process involved is called a REDOX operation in which first the ionic polymer membrane is oxidized with a catalyst metal. After oxidation, the ionic polymer is reduced to create functionally-graded conductor composite and near boundary porous electrodes. Initial performance tests of fuel cells incorporating these membranes show promising results which will serve as a baseline for further process optimization.

## **Introduction**

Fuel cells show exceptional promise as energy conversion devices due to their intrinsically high efficiency and effective fuel utilization. They are electrochemical devices that convert the chemical energy of fuel directly into electrical power without first requiring the generation of shaft horsepower in a heat engine. Unlike conventional power plants, which require the mechanical manipulation of a “working fluid” to convert the heat of a combustion reaction into useful work, fuel cells rely on the ability of an electrolyte to convey charged species between two electrodes – separating the oxidation and reduction half reactions of a fuel conversion through the transport of ions and electrons.

The successful commercialization of fuel cells begins with identifying marketable applications where the characteristics of each fuel cell type are carefully matched with the specific conditions and power requirements. Once target markets have been identified, the next step to high-volume commercialization is to reduce product costs and improve performance to the point where the cells are economically competitive with other existing products. For low-temperature fuel cells, the key technology issues slowing commercialization include materials costs (including the cost of the precious metal catalysts), transition to high-volume manufacturing, durability of the polymer electrolyte membrane, and catalyst degradation. Wheeler (1) identifies several manufacturing “technology gaps” associated specifically with the catalyst deposition within the MEA, including registration of components during assembly, low catalyst loading, and the thickness and uniformity of the catalyst layers. In addition, long term studies have identified several catalyst degradation mechanisms (2) including the oxidation of the carbon catalyst support (3).

The heart of a low-temperature fuel cell is the membrane electrode assembly (MEA) that generally consists of the following components: an ion-conducting membrane between two porous electrodes, a gas diffusion layer (GDL) to distribute and remove gaseous or liquid products or reactants, which may also contain some catalyst material and also polymer ionomer. This assembly is then sandwiched between gas-channel plates (“bipolar plates” in a multi-cell stack) that supply fuel and oxidant (air) to the fuel cell and provide mechanical stability. The MEA plus the two gas channel plates comprise a 7 layer fuel cell, as shown in Figure 1.

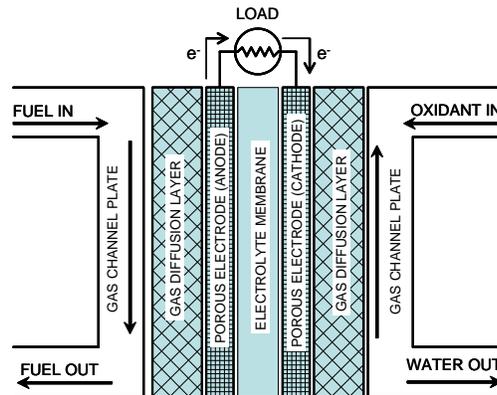


Figure 1. Seven-Layer Fuel Cell Assembly.

Over the past two decades of focused PEM fuel cell development, several different electrode design strategies have been explored (4) and techniques have been researched for reducing platinum loadings and increasing utilization (5). These methods include sputter deposition (6) and pulsed electrodeposition (7) of catalyst as well as the use of innovative carbon support structures such as nanotubes (8).

During MEA manufacturing, the catalyst is deposited on a carbon particle support. The carbon particles are either deposited on the GDL, resulting in a gas diffusion electrode (GDE), or on the membrane, resulting in a catalyst coated membrane (CCM) (9). Perfluorinated sulfonic acid (PSA) ionomer (usually in an alcohol solution) is then infused into the catalyst layer. This ionomer infusion is necessary because the carbon catalyst support is a poor conductor of ions. Once the MEA is assembled, either by the GDL or CCM approach, the MEA is hot-pressed to cure the ionomer and bind the layers together. In order for the catalyst material to be effective, it must be physically located within the MEA at locations where it is accessible to the gas molecules, and also to the electrodes (which conduct electrons) and the electrolyte (which conducts ions). These two regions (of finite thickness) occur at the triple phase boundaries (TPBs) at the “front” of the porous electrodes, that is, the side of the electrode in contact with the electrolyte.

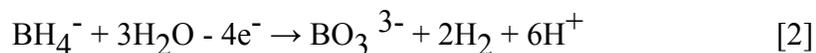
This project proposes the study of an innovative catalyst application technique that uses electroless plating to imbed catalyst material and other metals within the polymer electrolyte molecular network, thereby improving the distribution and utilization of catalyst, and ionic conduction through the polymer membrane. This technique may also allow a wider range of high-volume manufacturing strategies and improve the durability of the membrane electrode assembly.

## Experimental

The processing of the ion-conducting membrane is the same as that used by Shahinpoor to fabricate ionic polymer metal composite (IPMC) distributed nanosensors, nanoactuators and artificial muscles [10, 11]. Modifying the perfluorinated sulfonic acid membrane (PSM) will involve in-depth molecular metallization/catalyzation to disperse a discrete phase of a catalyst metal such as Platinum nanoparticles as catalysts into the ionic polymeric network. The Platinum nanoparticles are produced by reducing the oxidized membrane with sodium or lithium borohydride or tetrahydroborate to create molecular plating right around the 3-5 nm clusters within the molecular network.

The REDOX manufacturing technique incorporates two distinct processes:

1. Initial process of oxidizing the ionic polymer with solutions of platinum anions, such as chloroplatinate ( $\text{PtCl}_6^{2-}$ ),
2. Subsequent exposure to a reducing agent, typically tetrahydroborate ion ( $\text{BH}_4^-$ ), to create a functionally-graded conductor composite and near-boundary porous electrodes.



to give the overall process:



This membrane-catalyst layer nanocomposite is then sandwiched between two porous carbon gas diffusion layers. The whole assembly is then sandwiched between two flow-field or bi-polar plates in a standard fashion, thus giving rise to a 5-layer fuel cell rather than the currently standard 7-layer fuel cells. Fuel cell testing was performed at constant temperature and pressure using single cells of  $25\text{cm}^2$  and  $5\text{cm}^2$  active area on an Electrochem MTS-150 test station with humidified hydrogen and oxygen. Reactant gasses were humidified to 100% relative humidity at  $25^\circ\text{C}$ .

## Results

Chemical treatment causes penetration of metallic nanoparticles into the membrane molecular network near boundary, while creating surface porosity which extends into the metalized layer. Figure 2 shows surface features which increase effective surface area and create gas porous microchannels extending into the membrane. The catalyst nanoparticles form open clusters, seen in Figure 2a. Upon reduction of the catalyst metal a typical PSM will have a fractal distribution of catalyst metal particles on both sides, as shown in Figure 2b. Figure 3 shows additional details of the surface and outer layers of the treated membrane. Figures 4a and 4b are SEM images of the surface, illustrating the complex, highly-featured texture of the surface, while Figures 4c, 4d, and 4e illustrate the penetration of the metalized layer into the membrane. Preliminary steady-state performance of a fuel cell incorporating one of these membranes is shown in figure 5.

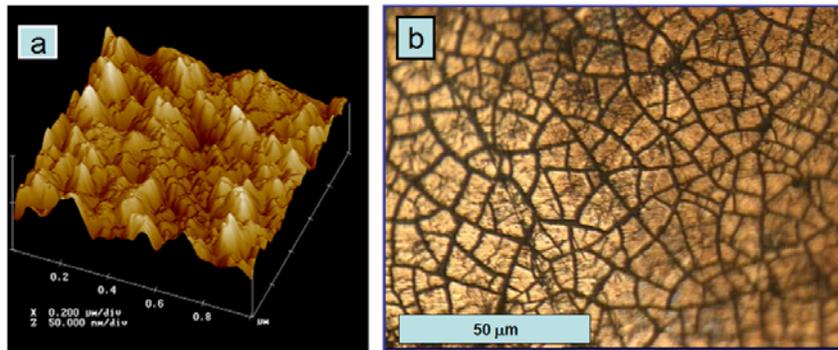


Figure 2. Surface features of the treated membrane. (a) AFM image of roughened membrane. (b) Optical micrograph of the membrane surface, showing gas penetration channels.

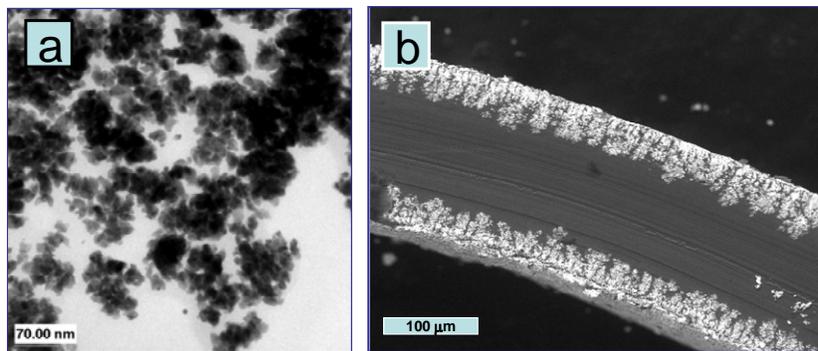


Figure 3. Metallic structure formation inside the membrane. (a) TEM image of particle clusters. (b) Fractal distribution of nanoparticles of the catalyst metal within the membrane.

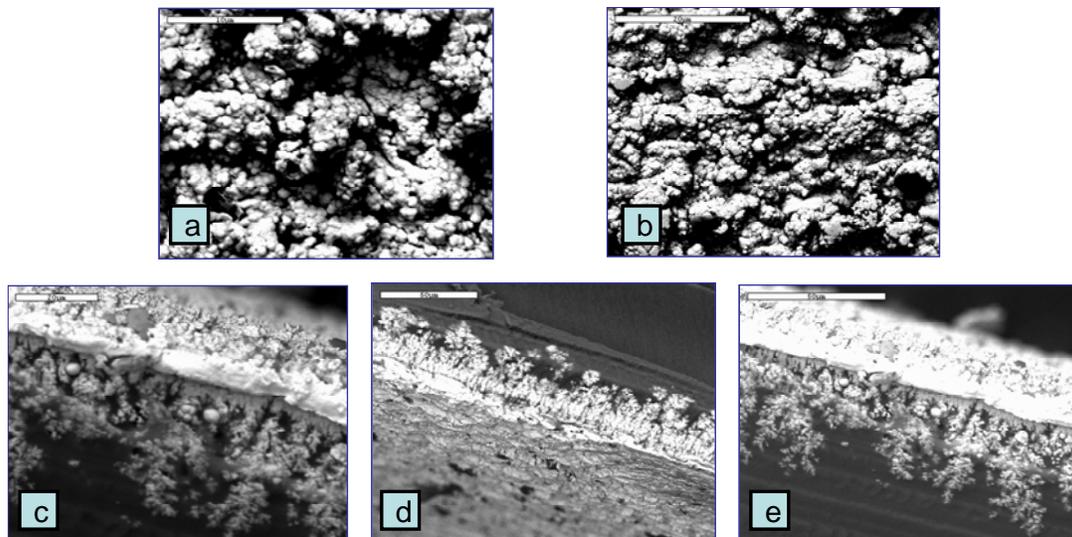


Figure 4. SEM images of treated membranes. (a) and (b) Surface roughness and porosity after treatment. (c), (d) and (e) Cross sectional views of catalyst penetration into membrane.

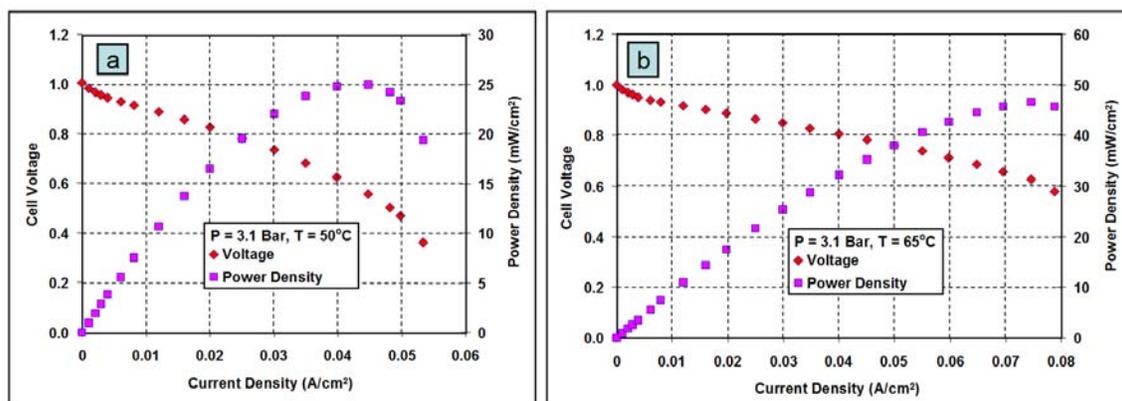


Figure 5. Fuel cell performance with new CCM membrane design. Cell pressure = 3.1 bar. (a) Cell temperature = 50°C. (b) Cell temperature = 65°C.

## Discussion

The proposed MEA design is composed of a polyelectrolytic membrane with an embedded nanocomposite catalyst layer comprising of a dispersed phase of Platinum nanoparticles distributed in a functionally graded manner near boundaries and surfaces of the ionic membrane.

This method of membrane manufacture offers promise to address a number of issues currently hindering high volume production of fuel cells. First, ease of assembly. The tests shown were performed using a catalyst coated membrane placed at assembly between two layers of carbon felt with serve as diffusion layers. No ionomer or catalyst was added to the GDLs, and no subsequent hot pressing was used in assembly.

The roughness and penetration of the metalized layer leads to a thicker electrode that is commonly associated with CCM designs, which can lead to a larger catalytically-active area, and improved water management at the cathode. The high surface area and porosity of the outer layers of the treated membrane yields triple phase boundary sites dispersed through a metalized layer that serves as a porous electrode. Note that additional catalyst materials can be applied concurrently, and non-catalytic metals can also be added to improve the electronic conductivity of the electrode.

Another area of promise is that the catalyst is supported by the membrane, not by carbon. This could lead to improved degradation resistance, leading to longer life. Also, hot pressing during assembly with sufficient temperature and duration to cure the ionomer can weaken the membrane; with the current CCM design, the need for hot pressing is reduced.

Initial tests, including the results presented in Figure 5, were performed on membranes optimized for use in sensor and actuator applications, as mentioned previously. The following process parameters may be used to optimize the CCM design for power density and membrane life:

- Catalyst loading and composition (anode and cathode)
- Non-catalyst metallization (anode and cathode)

- Membrane surface roughness/porosity
- Membrane thickness
- Metallization penetration
- Hot press parameters (pressure, temperature, duration).

## Conclusions

An innovative manufacturing technique, developed for use in PSM-based sensors and actuators, has been successfully applied to fuel cells. Initial fuel cell performance tests will serve as a baseline for optimization of process parameters. Currently in the early stages of development, this technology addresses issues that directly affect fuel cell commercialization, and shows promise for further development.

## References

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