Interim Report Re: Component Parts for
Proton-exchange Membrane Fuel Cells--October, 1999
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Fuel Cell Electrode Modeling

I. State-of-the-Art Fuel Cell Electrodes

The purpose of the first phase of the grant project is to design, develop and test a simplified fuel cell electrode structure for use in proton-exchange membrane fuel cells ("PEMFC"). By simplifying the structure of the electrode, mass production manufacturing efficiencies can be brought into play which will result in significant cost reductions for this fuel cell component. With a reduction in the cost of this key fuel cell component, overall costs for PEMFC's can be brought within the commercialization target range of about US$100 per kilowatt for the fuel cell stack.

Fuel cell electrodes are necessarily "multi-layered" composites. Multi-layers are required because of the several functions that the electrode must be able to perform in the working PEM fuel cell. The current generation of state-of-the-art porous fuel cell electrodes for PEMFC's is comprised of three primary layers.

The first layer is the catalyst layer. Since hydrogen is the fuel used in this project and air is used as the oxidant, the catalyst must be capable of adsorbing hydrogen and oxygen from the air. While work is constantly on-going with respect to new hydrogen or oxygen catalysts, the best available catalyst at present for both of the reactant gases is platinum. To be effective, the catalyst (1) must be exposed to a constant flow of the respective reactant gas; (2) must be in intimate contact with the proton-exchange membrane; and (3) must be a finely divided catalyst and have a large specific surface area, especially on the oxidant side where the electrochemical reaction is slower by several orders of magnitude.

The second layer is the substrate layer. The substrate layer provides structural support for the finely divided catalyst. It also functions as an electronic junction for conducting electricity produced by the electrochemical reaction from the catalyst layer to the bipolar plate of the fuel cell. In state-of-the-art PEMFC's, this layer is comprised of carbon particles (onto which the catalyst has been deposited) and a binder material. In Dr. Mahlon Wilson's fuel cell electrode design, the binder material is liquid Nafion. By using liquid Nafion, the membrane is effectively extended into a third spatial dimension. This extension of the membrane serves to

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increase the effective catalyst surface area per real geometric unit of fuel cell area, which is quite important for the reasons discussed above.

In the more traditional Los Alamos design, the binder is liquid Teflon, which is mixed with the catalyzed carbon particles and then sintered to create hydrophobic gas pores in the substrate layer. In order to extend the membrane into a third spatial dimension with this type of electrode, liquid Nafion is then applied to the substrate and allowed to seep through the sintered Teflon pores into the substrate/catalyst layer.

The third layer is the backing layer. The backing layer is normally comprised of either carbon cloth or porous carbon paper. The purpose of the backing layer is (1) to conduct electricity generated by the electrochemical reaction; (2) to provide structural support for the substrate layer; and (3) to allow the reactant gases to enter and leave the sustrate/catalyst layers.

Thus, in state-of-the-art fuel cell electrode design, the electrode is a "triple layer composite", consisting of the catalyst layer, the substrate layer and the backing layer. The triple layer composite electrode, when hot-pressed to the proton-exchange membrane, is strong enough to prevent the membrane from expanding in the localized area of the fuel cell electrode. This strength is significant because **membrane expansion** could otherwise damage the electrode and adversely affect its electronic conductivity.

While triple layer composite electrodes function well, their structure does not readily lend itself to mass production. Consequently, fuel cell electrodes are extremely expensive to manufacture. For example, E-Tek of Natrick, Massachusetts, the leading manufacturer of fuel cell electrodes in this country, has quoted a **mass production price** of $0.30 per square centimeter[1] for its fuel cell electrode. Since two electrodes (anode and cathode) are required for the fuel cell, the cost of the electrodes alone for a PEMFC would be about $6000 per square meter. Except in specialized applications where cost is not a significant factor, the projected cost of fuel cell electrodes remains too high for most commercial applications.

II. Alternative Fuel Cell Electrode Structure

Any alternative to the triple layer composite fuel cell electrode structure must be able to perform the same essential functions described above. However, the structure must also be capable of being mass produced in a relatively efficient manner in order to reduce costs. In addition, it would be desirable if the amount of platinum catalyst could be reduced from the level currently associated with triple layer composite fuel cell structure.[2]

In addition to the basic electrode functions, several other parameters were developed. First, the binder material should be eliminated to reduce complexity. Second, the catalyst should be "front-loaded" onto the surface of the electrode. It has been noted in prior studies that the "front-loaded" portion of the catalyst is more electrochemically active than the catalyst that lies in the body of the electrode. Third, sputtering should be the method for depositing the "front-loaded" catalyst because it can be employed to produce thin layers of material in mass production. Fourth, the backing and substrate layers should be combined into a single, gas-permeable, electronically conductive layer.

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[1] Current E-Tek prices are considerably higher.

[2] Platinum loadings are about 0.4mg/cm^2 in the E-Tek electrode.

Thus, the alternative design only employs a catalyst layer and a substrate layer (a "dual layer composite"). The substrate material chosen for this project is a flexible graphite sheet sold commercially by Alfa Aesar as its product number 10832. Because the electrochemical environment of the fuel cell is quite corrosive, a non-corrosive material must be used. Graphite is a very stable material in a highly oxidizing environment.

The flexible graphite is a very good electronic conductor as well as being non-corrosive. But the as-received material is not gas-permeable and does not have a high specific surface area. The first several months of the project were spent in two tasks: investigating means to increase the gas permeability of the graphite and investigating means to increase the "front loading" surface area of the catalyst and substrate.

Alternative Fuel Cell Electrode Development

III. Gas permeability

The as-received graphite is about 10 mils thick (0.25 mm) and is not signficantly permeable to gases. Initially, the graphite was alternately punctured and rolled through a rotary press to decrease its thickness and to increase its gas permeability. While this method had some limited success, it was not found to be repeatable with any degree of quality assurance. It lacked a high specific "front-loading" surface area and, on occasion, did not adhere well to the membrane after hot-pressing.

The next method employed was to puncture the surface of graphite, hot-press the graphite to the proton-exchange membrane and then strip off the bulk of the graphite in a rotary press. This process resulted in the desired effect: a thin layer of graphite was affixed on either side of the membrane after the hot-press and stripping. The pressing, however, adversely affected gas flow by compressing the planar sheet structure of the graphite.

The next method employed was to sand the front surface of the graphite. The sanded graphite was then hot-pressed to the membrane. Many different sanding techniques and grits were tried using this method over several months. Some resulted in only a small increase in real "front loading" surface area. Others resulted in channels that were too deep for the membrane to be successfully hot-pressed. Still others could not be stripped successfully from the membrane to yield a very thin substrate. Finally, it was determined that an effective combination of depth and real surface area could be achieved by sanding the surface with 320 grit sandpaper. When graphite prepared in this manner was hot-pressed to the membrane, it adhered quite well. Stripping in the rotary press removed the bulk of the graphite material, leaving only a graphite "skin" of between 40 and 50 microns. These test electrodes were about 3 square centimeters in area. Because of the sanding, gas-permeable channels were formed in the back side of the thin electrodes when stripped. The electrodes adhered very well to the membrane, even when it expanded upon wetting.

Having accomplished this task, at least with respect to small electrode sizes, during the initial period of the grant, the next task was to address the front-loading of the catalyst.

IV. High surface area platinum front-loading

(1) *Electroplating*

The first technique that the inventor employed was to electroplate the electrode using established methods from the literature. The electroplating chemical bath was designed to produce "platinum black" on the pre-roughened electrode surface. Platinum black is an extremely powdery form of platinum with a very high roughness factor. Indeed, because of its roughness, the platinum visually appears to be black rather than its normal silver-gray color.

The inventor successfully electroplated platinum in its platinum black form onto the pre-roughened graphite substrate. Unfortunately, the platinum black thus formed was not very adherent to the graphite substrate and could be easily rubbed off. Adherence of the catalyst to the electrode is obviously crucial for fuel cell performance. Consequently, while the electroplated platinum black had the desired high roughness factor, its lack of adherence to the surface of the electrode eliminated it as a candidate for a front-loaded fuel cell catalyst.

(2) *Co-sputtering*

A second technique that was employed during the course of the project was co-sputtering. In co-sputtering, a relatively thick layer of the platinum catalyst and a base metal are simultaneously sputtered onto the graphite surface of the electrode. The thickness of the co-sputtered catalyst layer was approximately 1000 angstroms. At a thickness of 2000 angstroms, the available catalyst deposition sites were overloaded and roughness was actually reduced. However, this was intentionally done.

To restore the catalytic roughness, the electrode was immersed in nitric acid. The nitric acid dissolved the base metal, which was copper, leaving platinum microstructures on the graphite surface. Neither the platinum nor the graphite were affected by nitric acid. The platinum microstructures were very adherent to the graphite substrate. A scanning electron microscope and auger analysis confirmed that platinum microstructures had been successfully formed on the surface and that the base metal had been dissolved.

It was hypothesized that the platinum microstructures thus formed would have an increased roughness factor because of the rough edges produced by the dissolution of the base metal and because of the "height" of the microstructures, being about 2000 angstroms. Many different percentages of base metal and platinum were tried using this technique, which had the effect of varying the size and shape of the platinum microstructures. While the fuel cell electrodes with platinum microstructures did produce some power, their power density fell short of that produced by platinum sputtering alone.

(3) *Platinum sputtering*

From a power density standpoint, the most successful technique proved to be room temperature sputtering. Much time and effort was spent in an attempt to quantify the optimum thickness for the front-loaded catalytic layer when the layer was formed by room temperature sputtering. It was finally determined that a platinum thickness of 600 angstroms produced the

maximum catalytic roughness and the highest power densities with the graphite electrodes used in the project. For comparison purposes, it should be noted that 600 angstroms of platinum is less than 0.15 mg/cm^2 or **only about 35-40% of the platinum loading** that is normally employed in state-of-the-art carbon cloth fuel cell electrodes. Power density results using this type of low-platinum- loading sputtered platinum electrode are discussed in more detail below.

Experimental Results

In order to establish a baseline measurement comparison for the "dual layer" fuel cell electrode, membrane and electrode assemblies ("MEA's) were purchased from BCS Technologies of Bryan, Texas and from E-Tek. The MEA's utilize a fuel cell electrode of the Los Alamos type. The active area of both the purchased MEA's and the inventor's MEA's were 3 square centimeters. The membranes were Nafion 117. A test fuel cell was constructed. Voltage was read across resistors of known value and the current was then extrapolated using Ohm's Law. Voltage values were logged by computer. After about 12 hours of operation in the fuel cell, the MEA's tend to reach their maximum power values. Reportedly, this occurs because the platinum needs time to be conditioned to the gases.

It was determined that the power produced by the E-Tek MEA's was 0.6 volts @ 0.5 ohms using hydrogen and air, both at 30psig. Current values were therefore about 400mA per square centimeter and power values were 240mW per square centimeter using this testing and measurement regime.[3] These tests were repeated with a second MEA set for confirmation of the results.

The inventor's MEA's were then tested in the same fuel cell. Under identical operating conditions, these MEA's using a front-loaded, sputtered platinum catalyst produced 0.6 volts @ one ohm. Current values were therefore about 200mA per square centimeter and power values were 120mW per square centimeter. These tests were repeated with other MEA's and the results were repeated and confirmed.

Perhaps the most interesting fact to arise from the testing at this juncture of the project is that the dual layer electrode structure, having only about 1/3 of the platinum loading, is capable of producing one half of the power of the state-of-the-art fuel cell electrode.

Future Investigations

The next phase of the work will continue investigations into increasing catalytic roughness factors and increasing the front-loading surface area of the electrode. Work will also begin on increasing electrode size from the present 3 cm^2 area to about 25 cm^2. Different hot-press techniques may be required to accomplish this task in a uniform and repeatable manner.

Work will also commence on building a larger fuel cell with bipolar plates in order to test multi-cell units.

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[3] Results in the literature are most often reported in terms of "current density". These measurements reflect the potential power production of the MEA set, not its actual measured power across a load of known value.