The Investigation and Development of Low Cost Hardware Components for Proton-Exchange Membrane Fuel Cells

Final Report

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Executive Summary

Fuel cells, particularly those utilizing a proton-exchange membrane ("PEM" fuel cells), offer a realistic opportunity for the replacement of combustion-type, energy production technologies in many facets of the United States economy. As is well known, combustion technologies contribute significantly to the degradation of the environment through the release of atmospheric pollutants, including uncombusted hydrocarbon particulates, carbon monoxide, oxides of nitrogen and sulfur and greenhouse gases, such as carbon dioxide. PEM fuel cells, operating on hydrogen or a hydrogen-rich gas, produce electricity with little or no atmospheric pollution. These fuel cells electrochemically convert hydrogen and the oxygen in air directly into electricity without combustion. The only by-products of the reaction are heat and pure water. While the principle of fuel cell operation was discovered over a century ago, practical fuel cells are a relatively recent phenomenon, dating back to the United States space program.

For the United States to embark on the path toward a "hydrogen economy", there are many obstacles to be overcome with respect to hydrogen production, distribution and storage. Other Department of Energy-funded programs are in progress to address these complex and difficult issues. However, assuming that reliable hydrogen supplies can be made available in a cost-effective manner, the mechanism for converting the hydrogen to useful energy will be the fuel cell. For example, PEM fuel cells are currently being evaluated by the auto industry for zero emission vehicles ("ZEV's") to replace the internal combustion engine and by utilities as a means to establish a distributed power generation system.[1]

The basic component parts of a PEM fuel cell stack or battery are: (1) a proton-exchange membrane; (2) catalyzed electrodes; (3) bipolar plates; (4) gaskets; and (5) endplates. Currently, PEM fuel cells are not economically viable alternatives to standard combustion technologies. A recent study by Arthur Little and Associates for the Department quantified the cost dilemma posed by PEM fuel cell technology. Even in mass production, the basic components of the PEM fuel cell alone would cost over US$240 per kilowatt. To be cost-competitive with the internal combustion engine, the cost per kilowatt must be reduced to about US$50 per kilowatt for vehicle applications. See, Appendix 1.

The present investigation was begun in order to determine whether significant cost reductions could be achieved with respect to the hardware components of the PEM fuel cell stack. The project was performed with the financial assistance of the United States Department of Energy/Energy-Related Inventions Program under Grant No. DE-FG01-97EE15679, whose financial and marketing support have been greatly appreciated.

Electrode Design

The initial phase of the project focused upon potential cost reduction with respect to the catalyzed fuel cell electrodes used in PEM fuel cells. Fuel cell electrodes are comprised of a platinum catalyst and a substrate for catalytic support. It has been known for several years that the portion of the catalyst which is most directly adjacent to the membrane is responsible for the majority of power produced by the cell (a "front-loaded catalyst")[2]. State-of-the-art PEM fuel cell electrodes require distribution of the catalyst throughout the body of the electrode and front-loading is not normally employed. If all of the catalyst could be front-loaded onto a different type of electrode substrate, however, the amount of precious metal catalyst required for each cell could be substantially reduced. Since platinum sells on the open market for about US$400 per ounce, any reduction in the amount of platinum needed for PEM fuel cells can lead to significant cost savings when fuel cells reach the mass production stage of development.

The electrode substrate which was utilized in this project was a commercially available, flexible graphitic material commonly known as "grafoil" (Alfa-Aesar Product No. 10832). The platinum catalyst was front-loaded onto the substrate by means of sputtering. Sputtering is a well-established commercial technique for depositing thin layers of a material onto a surface. Sputtered material has excellent adherence to the substrate, which is of crucial importance for extended operation of an electrode in the electrochemical environment of a fuel cell.

Different sputtering techniques were tested over the course of the project. High surface area catalytic structures were fabricated using an extremely low catalyst loading of less than 0.15 mg/cm^2 of platinum. By comparison, typical state-of-the-art carbon cloth fuel cell electrodes use platinum loadings of 0.35 to 0.4 mg/cm^2. Despite a ~60% reduction in the catalyst loading in the graphite electrode, the data indicates that the current generated at a given voltage was only reduced by ~50%. Consequently, there was a significant **increase in the activity of the platinum catalyst per unit weight**. For example, the inventor's sputtered graphite electrode produced 0.6 volts at 200ma/cm^2 and a carbon cloth electrode (purchased from BCS Technology of Bryan, Texas) produced 400ma/cm^2 at the same voltage and under similar operating conditions. In principle, therefore, if the catalytic surface area of the sputtered graphite electrode could be doubled, its performance would approach that of the carbon cloth electrode but with just one-half to two-thirds(or less) the precious metal content. Unfortunately, the inventor was unable to achieve the necessary doubling of the catalytic roughness factor during the course of this investigation. While numerous sputtering techniques were employed which resulted in very unique, front-loaded catalytic microstructures, none of the microstructures was capable of supplying the same amount of current per unit area of electrode surface as the high platinum loading carbon cloth electrodes. However, continued work with platinum and/or platinum alloy microstructures is clearly justified. If extremely rough, high surface area catalytic microstructures can be fabricated, a significant reduction in precious metal loadings could be achieved, using front-loaded graphite electrodes, without a reduction in overall fuel cell performance.

Bipolar Plates and Gasket Assemblies

Until recently, the state-of-the-art PEM bipolar plate was made from graphite, into which flow-field channels were machined. Flow-fields allow the reactant gases (e.g., hydrogen and air) to enter the catalyzed fuel cell electrodes. Flow-fields also allow venting of the oxygen-depleted air supply and of the product water produced by the electrochemical reaction. Graphite is an excellent material for use in PEM fuel cells because it is extremely non-corrosive in the electrochemical cell environment. However, machined graphite plates are very expensive to manufacture and they are bulky. Recent research for an alternative to machined graphite bipolar plates has focused primarily on substituting other materials for graphite. For example, treated titanium plates, stainless steel plates and carbon/polymer composite plates have been developed. While the main advantage to carbon/polymer plates is that they can be molded rather than machined, the metal plates often have other advantages over machined graphite plates. Metal plates can be lighter weight. In addition, they usually have higher "cell stacking density" (i.e., the number of cells that can be stacked together per lineal inch).

The second phase of the investigation was begun in order to determine whether flexible graphite sheet could be combined with a unitized gasket to make a cost-effective PEM bipolar plate and gasket assembly (a "PGA"). The PGA was used primarily for establishing baseline data for the carbon cloth electrodes referred to above. The PGA's combine the benefits of machined graphite bipolar plates (excellent corrosion resistance and low material costs) with the benefits of metal plates (light-weight, high cell stacking density and low mass production costs). The PGA's are comprised of inexpensive and light-weight materials. The plate portion is made of flexible graphite. A flow-field may be stamped or embossed into one surface of the flexible graphite, the graphite surface may be left unprocessed, or a carbon cloth flow-field may be added as discussed below. The costs formerly associated with machining are thereby eliminated in any case. Internal manifolds can be cut from the plate, also by routine stamping processes.

At least one of the flow-fields for the plate is carbon cloth. The cloth allows for an ample flow of gas to reach the fuel cell electrodes. The carbon cloth also serves as a "spring" type electrical contact in the connection of individual PEM fuel cells in the stack. The graphite/carbon cloth structure of the plate component of the PGA provides a low-resistance electronic pathway for the electricity generated by the fuel cells in a stacked series arrangement.

Unitized plates and gaskets are uncommon in PEM fuel cell architecture. Normally, a fluoroelastomer gasket (e.g., teflon or Viton) is placed on either side of the bipolar plate without bonding. The structure of the PGA's, however, does not allow for the use of the normal type of gasket. Instead, a rigid/compressible gasket is employed. The rigid/compressible gasket seals the adjacent fuel cells but allows the reactant gases (and product water) to enter and exit either the fuel flow-field side or the oxidant flow-field side of the plate via the manifolds. The gasket must be bonded to the plate to perform these functions. Consequently, the plate and gasket comprise a unitized assembly. For stack cooling purposes, the graphite can be extended beyond the edges of the gasket to comprise a "cooling fin" for each cell. Adjacent fins are separated by an electronic insulator to prevent short circuits. The PEM's membrane and electrode assembly is inserted into adjacent PGA's and sealed, thereby completing an individual fuel cell and further simplifying stack construction.

The PGA's allow a cell stacking density of 20 cells per lineal inch, which is about 50% higher than metal bipolar plates and 250% higher than machined graphite or carbon/polymer plates. The PGA's are extremely light-weight. The most costly materials used in the fabrication of a PGA are the carbon cloth and flexible graphite, which are relatively inexpensive, commercially-available materials. Because the PGA's are fabricated by routinized stamping, cutting and joining steps, production costs can also be minimized. PGA's thereby combine the best features of machined graphite bipolar plates with the best features of metal and/or carbon/polymer plates in a cost-effective manner. In mass production, PGA's could only cost pennies a copy to manufacture.

Electrode Commercialization

Several United States patents have been issued in recent months for the sputtered graphite electrodes. See, United States Patent Nos. 5,869,201, 5,869,202 and 5,885,729; see also, Appendix 2. There are currently two obstacles to commercialization of these electrodes. First, the surface area roughness of the catalytic microstructures must either (i) be doubled so that the current generated by the front-loaded electrodes per unit area is comparable to high platinum loading carbon cloth electrodes or (ii) a catalyst must be developed that is more active for the oxygen reduction portion of the fuel cell reaction. Recent work by Dr. Watanabe in Japan indicates that a sputtered platinum/nickel catalyst may be considerably more active in oxygen reduction than platinum alone. Further work will be necessary, however, in order to determine whether comparable power levels can be achieved under either proposed approach.

Second, a thinner graphite precursor material is necessary. The graphite sheet used for the test electrodes is initially 0.25mm thick. It is then processed to reduce the thickness to ca. 40-50 microns, at which point the graphite is rendered sufficiently gas-permeable for PEM fuel cell operation. Unfortunately, as it turned out, processing increases the complexity and costs of manufacture dramatically. Reduction in the thickness of the graphite precursor material will probably be essential to commercialization of this unique variety of fuel cell electrodes.

Bipolar Separator Plate Commercialization

A United States patent application is currently pending for the PGA. The PGA performs all of the essential functions of the bipolar plate and gasket in a PEM fuel cell at a fraction of the cost of other plates. We have approached the Institute for Gas Technology (IGT) with a version of the PGA designed for pressurized fuel cell stack operation. While the IGT fuel cell group was very impressed with the technology, IGT is committed to non-pressurized fuel cell stacks using its own molded carbon/polymer technology. We have also met with the automotive fuel cell group at Argonne National Laboratory to discuss possible independent testing of the PGA to confirm our data. Argonne has a fuel cell testing program, but it is limited to large pressurized fuel cell stacks. Discussions are currently in progress with H Power of Canada to design PGA's for their fuel cell stacks. The inventor met representatives of H Power of Canada at a fuel cell conference held in Montreal, Canada in July, 1999. The inventor presented his PGA's at the conference exhibition of new fuel cell technologies.

Commercialization may be delayed, however, by virtue of a recent agreement between Ballard Power Systems and UCAR. Under this agreement, UCAR has agreed that it will not sell flexible graphite (UCAR's product is commonly known as "Grafoil") to any fuel cell manufacturers except Ballard. Consequently, another source for flexible graphite will have to be identified by the inventor before further commercialization efforts can be undertaken.

Future commercialization efforts will focus on presenting the invention at fuel cell conferences, publishing reports in scientific journals, approaching other fuel cell testing groups and seeking additional funding for development.

I.

State-of-the-Art Proton Exchange Membrane Fuel Cell Electrodes

In the late 1980's, scientists at Los Alamos National Laboratories ("LANL") developed the first practical fuel cell electrode for use with proton exchange membranes ("PEM's"). The LANL electrode structure consists of catalyzed carbon particles in a sintered fluoroelastomer binder (the "catalytic carbon/teflon layer") which is affixed to a carbon cloth backing. The catalyst is platinum. By impregnating the catalytic carbon/teflon layer with a liquid ionomer, such as a liquid form of Nafion, LANL was able to extend the three-phase electrochemical reaction boundary and thereby achieve relatively high power densities with this particular electrode structure. The **three-phase boundary** is the junction where the membrane, the catalyzed electrode and the reactant gases meet. By increasing the surface area, i.e., the roughness, of the three-phase boundary, the power per unit area of the fuel cell's membrane and electrode assembly ("MEA") can be increased signficantly, as LANL found.[3]

In order to achieve the desired higher roughness factors per unit area, LANL extended the three-phase boundary into the body of the electode. This **interior extension of the three-phase boundary** served to increase the effective surface area of the catalyst available for the electrochemical reaction. The LANL-type of fuel cell electrode is available commercially from such companies as E-Tek of Natrick, Massachusetts and BCS Technology of Bryan, Texas.

A second important aspect of the LANL work was the discovery that, by sputtering a thin layer of platinum onto the surface of the electrode as a **front-loaded catalyst**, additional power could be produced per unit area of electrode surface.[2] LANL did not pursue sputtering any further, however. LANL reported that its sputtered catalyst layer was insufficient to produce reasonable power densities in and of itself.

In addition to catalytic surface area, the power density of a PEM fuel cell is also affected by the internal temperature of the cell, the pressures of the reactant gases and cell water management. The power generated by the cell increases significantly with temperature up to about 50°C without external humidification of the cell. Temperatures of up to 80°C can be employed with external humidification. In addition, pressurization of the reactant gases can double the current produced at a given voltage. Water management is extremely important for proper cell operation because (1) too little water will dry out the membrane (thereby inhibiting the ion transfer across the membrane and so reducing power) and (2) too much water can flood the electrode (thereby inhibiting gas flow to the catalyst surface and so reducing power). These three **operating parameters**, i.e., cell temperature, gas pressures and water management, act like the proverbial "three-legged stool". When one parameter is changed, the other parameters must also be adjusted to maintain optimum power conditions.

Finally, the power density of the PEM fuel cell is dependent on the type of proton exchange membrane utilized. Although a wide variety of membranes have been described in the literature, few are commercially available. The Nafion series of membranes has been made commercially available by Du Pont and these membranes were used in the project. Nafion membranes come in varying thicknesses from 50 microns to 175 microns.

II.
Project Objectives

The principal project objective was to increase the surface area of a front-loaded catalyst layer at the three-phase boundary of the PEM fuel cell's membrane and electrode assembly by (i) transforming the normal two dimensional nature of the electrode/membrane juncture into a three dimensional interface and (ii) employing catalytic microstructures. If the front-loaded catalyst layer could be made sufficiently rough through these techniques, then, even with low platinum loadings, power characteristics similar to high platinum loading state-of-the-art fuel cell electrodes would be achievable.

III.
Electrode Structure

The electrode structure employed in the first phase of the project is radically different from the LANL design. The basic LANL electrode structure consists of catalyzed carbon particles in a sintered fluoroelastomer binder, which is then compressed into a carbon cloth backing. The three-phase boundary of electrochemical reaction is extended into a third spatial dimension by impregnating the catalytic binder layer with a liquid ionomer. The electrodes are then hot-pressed to the membrane and sandwiched between bipolar plates to complete the basic fuel cell unit. In subsequent years, refinements have been made to the basic LANL structure. Despite these refinements, the basic state-of-the-art PEMFC electrode continues to employ a relatively thick catalytic binder layer. The rationale for employing a thick catalytic binder layer is that more catalyst can be made available for the electrochemical fuel cell reaction by extending the three-phase boundary into the third spatial dimension formed by the catalytic binder layer. Increasing the available catalytic surface is particularly important on the **oxidant** side of the electrochemical reaction because of oxygen's or air's much lower electrochemical activity. Typically, the amount of catalyst incorporated into the catalytic binder layer will be about 0.35-0.4mg/cm^2 using the LANL electrode structure.

If all of the catalyst is front-loaded, however, the thick catalytic binder layer is rendered completely unnecessary. The front-loaded catalytic layer is not significantly extended into a third spatial dimension. Consequently, a much more simplified electrode structure is possible. All that is theoretically necessary is a gas-permeable, electronically conductive substrate onto which the front-loaded catalytic layer is then deposited. The catalyst layer and the gas-permeable, electronically conductive substrate comprise the PEM **fuel cell electrode**. When two fuel cell electrodes are hot-pressed or otherwise affixed to the proton exchange membrane a membrane and electrode assembly or ("**MEA**") is fabricated.

A. The Modified Electrode Structure

One of the principal structural drawbacks to the use of proton exchange membranes is the fact that they expand with water uptake and contract as they dry out. The expansion/contraction of the membrane is a normal part of the PEM fuel cell's operation. The expansion/contraction is quite significant and can actually result in the **delamination** of the hot-pressed electrode from the membrane under some circumstances. It was found during the course of this work that an inexpensive graphitic material, commercially known as "grafoil" could be successfully hot-pressed to the proton exchange membrane. The grafoil used in the project is 10 mils (0.25mm) thick and is sold by Alfa/Aesar as their product number 10832. At its "as-received" thickness, the grafoil is not gas-permeable and it can delaminate from the membrane. However, the bulk of the grafoil material can be stripped away using a rotary press after the grafoil has been hot-pressed to the proton exchange membrane. By stripping away the majority of the grafoil, an extremely thin (ca. 40-50 microns), gas-permeable, electronically conductive substrate results. The substrate is affixed to the membrane and does not delaminate. The substrate is thin enough that it may, to some degree, expand and contract with the membrane, thereby preventing delamination.

The grafoil substrate is rendered gas-permeable by virtue of micropores and mesopores which are exposed as the material is thinned to the 50 micron level. In contrast to the "hydrophobic" gas pores created by sintered teflon in the LANL electrode design, there is no teflon in this electrode. Since this electrode has no hydrophobic teflon, its pores are essentially hydrophilic and allow for the ready passage of both reactant gases and water into and out of the electrode.

B. Deposition of the Front-Loaded Catalytic Layer

With an appropriate substrate for the fuel cell electrode having been identified, the next task was to find a means to deposit an adherent catalyst layer onto the grafoil substrate. Sputtering was selected as the means to deposit an extremely thin catalyst layer onto the substrate. Sputtering allows for precisely controlled and repeatable catalyst depositions. In addition, it is a well-developed commercial technique that is also used in semi-conductor fabrication processes.

C. Catalyzed Electrode Structure

Thus, the basic electrode structure is a radically simple one. A very thin catalyst layer is sputtered onto a grafoil substrate. Two catalyzed substrates are then hot-pressed to opposite sides of a proton exchange membrane. The hot-pressing step is performed at about 275^0F. The hot-pressed assembly is then run through a rotary press, which strips away the bulk of the substrate material. What is left are very thin, catalyzed electrodes comprised of gas-permeable grafoil hot-pressed to a proton exchange membrane. Together these components comprise an MEA for a PEM fuel cell.

IV.

Increasing The Surface Area of the Three-Phase Boundary

In a fuel cell, as previously stated, the three-phase boundary is the juncture of the electrolyte, the solid electronic conductor (i.e., the fuel cell electrode) and the reactant gas. Proton exchange membranes are essentially two dimensional materials. Because the two dimensional surface area is quite limited, the membrane itself presents an inherent obstacle to increasing the real geometric surface area of the three-phase boundary. Consequently, one of the major technical tasks was to increase the **real geometric surface area** of the three-phase boundary.

A. Roughening the Substrate Surface

In order to increase the real geometric surface area of the three-phase boundary, the grafoil substrate was roughened to create shallow channels. The shallow channels provided a significant increase in the real geometric surface area available for front-loaded catalyst deposition. Because the proton exchange membrane, when hot-pressed, will be plasticized, the membrane can be compressed **into** the shallow channels of the grafoil substrate.

A wide variety of methods of substrate roughening were tried during the course of the investigation. Some methods resulted in channels which were too shallow. Other methods resulted in channels which were too deep. If the channels were too deep, the membrane, despite being plasticized in the hot press, could not be compressed fully into the channel bed.

It was finally determined that roughening with 320 grit sandpaper was the most effective means to fabricate the shallow channels needed to increase the real geometric surface area of the three-phase boundary. The channels were formed by hand-sanding the substrate ten times in one direction and then five times in a direction which was perpendicular to the initial direction. This technique resulted in MEA's which had the desired increase in real geometric surface area and which further allowed the membrane to be compressed completely into the substrate channel beds. Unlike the LANL electrode composition (discussed above), no liquid Nafion was needed to extend the three-phase boundary. The three-phase boundary was extended by virtue of hot-pressing the membrane itself into the shallow channels of the electrode surface.

In this way, the two dimensional nature of the proton exchange membrane was modified and the membrane assumed a three dimensional structure at the interface with the fuel cell electrodes.

B. Increasing the Roughness of the Front-Loaded Catalyst

It has long been recognized that catalysis is a surface phenomenon. Therefore, as the **roughness** of the catalytic surface increases, power per unit area of the fuel cell also increases. Even with an electrode substrate that has been pre-roughened, however, such as the grafoil substrate used in the project, there are inherent limitations of available **catalyst deposition sites** on the surface of the electrode when the catalyst is entirely **front-loaded**. Because the number of catalyst deposition sites are limited, increasing the amount of platinum catalyst beyond a certain point actually results in less power being generated because the catalyst layer begins to thicken and roughness is thereby decreased.

Different catalyst deposition techniques were tested in an attempt to identify a method which would create an extremely rough catalytic surface on the limited number of catalyst depostion sites available.

(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. The sputtering technique is described in more detail in Appendix 3. Power density results using this type of low-platinum-loading sputtered platinum electrode are discussed in more detail below.

(4) *Platinum black sputtering*

In an attempt to improve upon the results obtained with the sputtered platinum electrode, the inventor and the inventor's contractor (BP Vacuum Analysis of Evanston, Illinois) developed a unique sputtering technique. This technique enabled the inventor to sputter platinum black directly onto the electrode surface. Interestingly, unlike the standard electroplating method for depositing platinum black, the sputtered platinum black was quite adherent to the graphite electrode surface. The technique is described in more detail in Appendix 4.

The platinum black catalytic layer was approximately the same thickness as the low-platinum-loading sputtered electrode. It was hypothesized that since the platinum black had a higher roughness factor than the room temperature sputtered platinum, the power density of the fuel cell would increase. Unfortunately, the hypothesis proved to be incorrect.

Apparently, the increase in catalytic roughness had a detrimental side effect. The sputtered platinum black particles did not have very good particle/particle and particle/electrode electrical contact. Consequently, there was increased internal electronic resistance at the catalytic layer and the power density levels of this particular structure, although promising theoretically, failed to meet those of the sputtered platinum electrode.

V.

Experimental Conditions and Test Results

The membrane and electrode assemblies (MEA's) used in the project were fabricated by hot-pressing the low-platinum-loading sputtered graphite electrodes into a proton exchange membrane. The test electrodes were generally 3 cm^2 in area. The proton exchange membranes used were commercially available membranes manufactured by Du Pont. The membranes are known as the Nafion series of perfluorinated membranes. The primary Nafion membrane used in the testing program was Nafion 117.

A single cell test station was constructed. The single cell unit utilized gold-plated copper endplates. Metal frits were attached to the endplates. These frits permitted the flow of reactant gases into and out of the electrodes of the MEA's. Teflon gaskets were used to seal the test cell. The membrane overlapped the gaskets, resulting in a gas-tight seal. Neat hydrogen was the fuel. Dry, tank-compressed air was generally employed as the oxidant, although oxygen was used in some tests. The test cell was normally run without external humidification. The air pressures were varied between 15psig and 60psig. Electrochemical activity increased with higher air pressures, as was expected. Hydrogen pressures were generally maintained at 10 to 15psig and no variance in electrochemical activity was detected at higher pressures, which again is consistent with the literature.

PEM fuel cells produce more power when heated because heat enhances the electrochemical activity of the platinum. With no external humidification, electrochemical activity increases up to about 50°C. Since the small test MEA's were incapable of generating much heat, the test station was provided with a separate heating unit by which internal cell temperature could be regulated. Temperature was measured with a thermocouple.

The anode and cathode of the test cell were in pressure contact with the endplates and were wired to resistors of known value and to a voltmeter. The voltage across a resistor was then determined. The current at a given voltage and resistance was then calculated using Ohm's Law: V/R=I.

As a control measure, pre-fabricated MEA's were purchased from BCS Technology of Bryan, Texas. Like the inventor's test MEA's, these BCS MEA's were also 3 cm^2 in active area. Using the test cell hardware, the BCS MEA's were capable of producing 0.6V across a 0.5 ohm resistor, or 1.2A. The current per square centimeter was, therefore, 400 milliamps at 0.6V for these MEA's. Power density was 240mW per square centimeter. The BCS MEA's utilize 0.4mg of platinum per square centimeter of active electrode area.

Typical test results for the inventor's MEA's are shown in Appendix 5. Sputtered platinum has a density of roughly one-half of the pure metal due to the particulate nature of sputtering. For the pure metal, a thickness of about 1000 angstroms yields 0.2 milligrams per square centimeter of the metal. So, the density of 600 angstroms of the sputtered metal is about 0.1 to 0.15 milligrams per square centimeter. Appendix 5 shows an increase in both voltage and current as the thickness of the front-loaded platinum catalyst layer is increased to the 600 angstrom level. Unfortunately, beyond 600 angstroms, no significant increase in voltage or current was noted. Apparently at that thickness, the roughness of the sputtered catalyst is at its maximum and further catalyst deposition does not serve to enhance the catalyst's electrochemical performance. The inventor's simplified electrode structure was capable of producing 0.6V across a 1 ohm resistor, or 0.6A, as shown in Appendix 5. The current per square centimeter was, therefore, 200 milliamps at 0.6V. The power density was 120mW per square centimeter, or one half the power density of the BCS MEA. See, Appendix 5, which is based on a 10 cm^2 electrode. Power per unit weight of catalyst, however, was higher with the inventor's electrodes than with the BCS electrodes:

(1) Power density of the BCS electrodes= 240mW/cm^2
Divided by 0.4mg/cm^2 of catalyst
Equals 600mW/mg of catalyst

(2) Power density of the inventor's electrodes= 120mW/cm^2
Divided by 0.15mg/cm^2 of catalyst
Equals 800mW/mg of catalyst

Given these test results, it is apparent that a sputtered, front-loaded electrode could be a viable alternative to the conventional electrode design **if the power per unit area could be doubled**. In principle, the reduction in the amount of platinum catalyst required per watt of power generated, coupled with the simplicity of a sputtered graphite electrode structure, could result in significant cost savings on a mass production basis.

Further work will be necessary to determine whether these potential cost savings can, in fact be realized with a front-loaded electrode structure. It would appear that one or more of the following improvements must be made to the inventor's front-loaded electrode design in order to realize the benefits of reduced platinum catalyst loadings: (1) the surface area of the three-phase boundary interface must be increased further; (2) the roughness of the sputtered catalyst must be maintained even when over 1000 angstroms of the catalyst is front-loaded onto the electrode; and/or (3) a sputtered catalyst that is more active than platinum alone must be identified. With respect to the last point, it is important to note that recent work by Professor Watanabe of Japan indicates that a co-sputtered nickel/platinum catalyst layer, in the ration of 60 atomic% platinum to 40 atomic% nickel, may be far more electrochemically active in the reduction of oxygen in a fuel cell than platinum alone.[4]

The primary electrochemical limitation in fuel cell power generation is the slow reactivity of the catalytic reduction of oxygen on pure platinum. Indeed, when compared with the catalytic oxidation of hydrogen, the reduction of oxygen on platinum is several **orders of magnitude** slower. Dr. Watanabe's work indicates that a co-sputtered nickel/platinum catalyst layer is several times more active than platinum alone for oxygen reduction. According to this study, a 600 angstrom layer of nickel/platinum catalyst reduced the oxygen overpotential of the test fuel cell by 150 millivolts. Interestingly, the 600 angstrom thickness of the Watanabe catalyst is identical to the preferred platinum catalyst thickness identified in this project. See, Appendix 5. A 150 millivolt improvement in the power output produced by front-loaded fuel cell electrodes would yield a power performance comparable to the conventional electrodes discussed above. Thus, an improvement in the electrochemical activity of the air or oxygen side sputtered catalytic layer could result in further increases in power density with front-loaded electrodes with little increase, or perhaps an actual decrease, in the total amount of platinum catalyst utilized per watt of power generated.

VI.
Conclusion

While the present work has resulted in several encouraging signs that a front-loaded catalyst type of electrode structure could eventually replace the more conventional PEM electrode structure, further work is obviously necessary on the prototype. While significant power was generated by the inventor's electrodes, the power density must be doubled for simplified, front-loaded electrodes to be considered as an alternative to the conventional PEM electrode structure.

Moreover, an alternative graphite or carbon substrate must be identified. While the inventor could successfully reduce the thickness of the graphite substrate in a stripping process to 40 to 50 microns, this proved to be both a labor-intensive task and less effective as larger substrate areas (e.g., beyond 10 square centimeters) were attempted. The identification of an alternate substrate, having the gas-permeability characteristics and the electronic conductivity of the graphite substrate but not requiring a stripping step, will also be necessary for the future commercialization of front-loaded PEM electrodes.

Footnotes

1. Lomax, et al., Directed Technologies, Inc. Arlington, Virginia, "Detailed Manufacturing Cost Estimates for Polymer Electrolyte Membrane (PEM) Fuel Cells for Light Duty Vehicles, prepared for Ford Motor Company under Prime Contract No. DE-AC02-94 CE 50389 with the United States Department of Energy, Office of Transportation Technologies (August 1998).
2. Ticianelli, et al., "Localization of platinum in low catalyst loading electrodes to attain high power densities in SPE fuel cells", Journal of Electroanalytical Chemistry, Vol. 251, No. 2, p. 275 (September 23, 1988).
3. See, footnote 2. See also, Ticianelli, et al., "Methods to Advance Technology of Proton Exchange Membrane Fuel Cells", Journal of the Electrochemical Society, Vol. 135, No. 9, p. 2210 (September 1988) and Srivivasan, "Fuel Cells for Extraterrestrial and Terrestrial Applications", Journal of the Electrochemical Society, Vol. 136, No. 2, p.41C (February, 1989).
4. Toda, Igarashi and Watanabe, "Role of Electronic Property of Pt and Pt Alloys on Electrocatalytic Reduction of Oxygen", Journal of the Electrochemical Society, Vol. 145. No. 12, p. 4185 (December 1998).

I.
State-of-the-Art Bipolar Plates for Proton-Exchange Membrane Fuel Cells

Fuel cells capture the imagination because they offer the promise of generating electrical power in a clean, highly efficient manner without the undesirable atmospheric pollution that is associated with twentieth century combustion technologies. Proton-exchange membrane fuel cells ("PEMFC's) are beginning to make their appearance in prototype vehicles such as the Daimler-Chrysler Ne-Car series. PEMFC's will also soon be used as part of a distributed power generation strategy, designed to run on steam-reformed natural gas. PEMFC's for portable power and uninterruptible power supplies are also being developed. However, for the commercialization of PEMFC's to proceed beyond the demonstration stage and into the mass marketplace, the costs of the principal components of the fuel cell stack must be reduced substantially from current levels.

In order to reduce final product costs, one must either reduce the material costs of the component parts or reduce the cost of manufacturing or, preferably, both. The most expensive component part of a PEMFC, according to a recent Arthur D. Little study, will be the bipolar separator plate. See, Appendix 1. The bipolar plate is estimated to cost roughly four to five times as much as the rest of the components of the fuel cell (i.e., membrane, electrodes and catalyst) combined. In dollar terms, according to the study, the bipolar plates would cost about $194/kW and the rest of the fuel cell stack would cost about $40/kW. In the second phase of this project, the inventor designed and fabricated a much simplified bipolar separator plate for use with his fuel cell.

The bipolar plate is the backbone of the fuel cell stack. The bipolar plate performs several critical functions in the operation of the PEMFC: (1) it prevents cross-mixing of the fuel (usually hydrogen or a reformed hydrogen-rich gas) with the oxidant gas (usually air); (2) it provides a low-resistance pathway for the electricity generated by the electrochemical reaction in a bipolar electronic configuration; and (3) it allows the fuel and oxidant gases to be readily distributed to the appropriate fuel cell electrode (either fuel or oxidant) via the cell manifolds and flow-fields of the plate. In addition, for larger fuel cell stacks, a means should be provided in the bipolar plate structure to cool the stack while in operation. Traditionally, the bipolar plate has been made from a block of graphite, into which flow-field channels have been machined. One of the principal reasons for the choice of this material for the plate is that graphite is very non-corrosive in the electrochemical environment of the fuel cell. Unfortunately, because of the machining costs, bipolar plates fabricated in this manner are extremely expensive on a per kilowatt basis.

The search for less expensive materials and less costly fabrication methods has resulted in a number of novel PEMFC bipolar plate designs, which are described in the literature. Titanium "platelets" with stamped flow-fields have been suggested by H Power[1]. H Power has also devised a unique system of alternating plastic or ceramic platelets, sandwiched between conductive microscreen platelets[2]. Titanium plates with a foamed metal flow-field are being developed by Lynntech[3]. Dr. Mahlon Wilson has fabricated bipolar plates using a combination of stainless steel (for the plate itself) and stainless steel wire mesh (for the flow-fields and cooling channels)[4].

With regard to graphite-based plates, Dr. Leonard Marianowski, et. al., of the Institute of Gas Technology has made bipolar plates that are molded from a mixture of graphite powders, carbon cloth and a resinous binder[5]. The IGT plates have several unique features: the "ridge and channel" flow-field configuration can be impressed into the plates during the molding process; the plate includes gas flow "conduits" into the electrode area, thereby eliminating the need for a separate gasket; product water, produced on the oxidant side of the electrochemical reaction, can be used to internally humidify the proton-exchange membrane with an appropriate pressure differential; and cooling channels are also molded into the plate. The IGT plates could, more properly, be called bipolar "plate and gasket assemblies" because a separate gasket is not needed in this design. Oak Ridge National Laboratories is also pursuing development of a molded carbon fiber and phenolic resin bipolar separator plate.[6]

Ballard Power Systems has patented a bipolar plate laminate, comprised of two thin graphite sheets with a metal insert[7]. Flow-fields are stamped, or otherwise impressed into the soft graphite sheet, thereby eliminating the costs associated with machining. The metal plate is shielded by the graphite from the oxidizing environment of the fuel cell. The metal plate performs a gas separation function, and may possibly also be used to cool the individual cells in the fuel cell stack.

All of these PEMFC bipolar plates offer advantages over machined plates, especially with respect to mass-production capability and the potential for lower costs. Depending on the application intended for the fuel cell stack, one variety of bipolar plate may be preferable to another. For example, for stationary applications where the size and weight of the fuel cell stack **are not** significant engineering issues, the IGT molded bipolar plate would appear to offer a very good combination of low cost/mass-production capability. Because of the cooling channels located between the faces of each plate, only about 8 cells can be stacked per lineal inch of the fuel cell stack. However, IGT indicates that its molded bipolar plates can be produced for about US$10 per kilowatt[8], which is a remarkable achievement given the assumed cost of PEMFC bipolar plates in the Arthur D. Little study. IGT is in the process of making its plates commercially available.

For portable and vehicular applications where size and weight **are** important engineering issues to be addressed, the Ballard Power Systems laminated bipolar plate appears to provide a very good alternative. The Ballard laminated bipolar plate allows for increased "cell stacking density" because the graphite and metal sheet construction permits extremely thin bipolar plates to be fabricated. The laminated plates should also prove to be very light-weight given this structure. A separate gasket will be required with the plates. Unlike IGT, however, Ballard may or may not keep its plates proprietary, since it has not yet announced whether it will make them commercially available to other fuel cell manufacturers.

II.
Plate and Gasket Assembly Design

An investigation was begun in order to determine whether an extremely thin, light-weight and inexpensive unitized bipolar "plate and gasket assembly" (a "PGA") could be fabricated from commercially available precursor materials for PEMFC's. Because of its corrosion-resistant and electronic characteristics, graphite was chosen as the substrate material for the plate portion of the PGA. The graphite product used in the PGA's was a thin graphite sheet sold by Alfa Aesar of Ward Hill, Massachusetts as its product number 10832. The as-received graphite sheet is 10 mils (0.25 mm) thick. The material is extremely flexible. It can be cut to size using stamping equipment and internal manifolds can be stamped into the plate during the same processing step. The number of internal manifolds incorporated into the graphite substrate depends on whether the fuel cell stack will use pressurized air (or oxygen) as the oxidant. There will normally be two fuel internal manifolds: fuel/in and fuel/out. If pressurized oxidant is used there may be one or two additional manifolds: oxidant/in and oxidant/out. See, Appendix 6. On the other hand, if a blower and plenum design is used, with the PEMFC stack being operated in a convection mode, one or both of the internal oxidant manifolds may be eliminated.

While the softness and flexibility of the graphite substrate makes stamping extremely easy, it does create a further complication in the PGA design. The PEMFC bipolar plate must be somewhat rigid in order to provide internal support for the membrane and electrode assemblies ("MEA's") of the fuel cell stack. Ballard has dealt with this particular problem by incorporating a metal sheet into the laminated graphite plate. The metal sheet provides an "endoskeleton" for the otherwise flexible graphite[9].

A second approach, and the one taken here, is to employ an "exoskeleton" structure for the graphite substrate. An PGA exoskeleton can be formed by using a rigid gasket material, such as polycarbonate or polypropylene, which is then bonded to both sides of the flexible graphite substrate. A four manifold rigid gasket is shown in Appendix 7. In order to permit the flow of the reactant gases (e.g., hydrogen and air) from the manifolds into the electrodes of the MEA, "port channels" are scored or stamped into the interior legs of the gasket. The oxidant port channels may be top to bottom in one gasket, as in Figure 3, and the fuel port channels may then be left to right in the second gasket on the opposite side of the graphite substrate.

In order to provide a gas-tight seal with the membrane portion of the MEA, a compressible gasket material is applied to the surface of the rigid gasket, making the gasket a "rigid/compressible gasket". When the PGA's and the MEA's are compressed between endplates in the stack, the rigid/compressible gasket both seals the individual cells and allows distribution of the reactant gases through the port channels to the appropriate fuel cell electrode, either fuel or oxidant. In this particular design the electrode seating area is about 25cm^2, although much larger PGA's are possible with longer exoskeletal rigid/compressible gaskets. A conceptual design of longer rigid/compressible gaskets with cooling fins and a non-conductive screen separator is shown in Appendix 8.

The next problem presented by PEMFC bipolar plate design is the flow-fields. Flow-fields are located in the "electrode seating area" of the PGA. See, Appendix 6. The flow-fields serve the crucial functions of (1) allowing the reactant gases to reach and to enter the fuel cell electrodes and (2) allowing removal of depleted reactant gases and product water, which is formed by the electrochemical reaction between the fuel and the oxidant. At least one of the flow-fields in the PGA design is carbon cloth. See, Appendix 6. Carbon cloth is the selected material because it is gas permeable, electronically conductive and non-corrosive. Carbon cloth further allows the reactant gases to reach all areas of the fuel cell electrodes through the weave of the cloth. It also provides a compressible electronic contact juncture between the fuel cell electrodes and the graphite substrate of the PGA. The second flow-field may be carbon cloth, an imprinted pattern in the graphite substrate or, in some cases, unimprinted graphite. The carbon cloth flow-field(s) is then tacked to the graphite substrate. Compressible gasket material is applied at the edges or corners of the carbon cloth and one of the MEA's is fitted into the electrode seating area, resulting in an "MEA/PGA assembly". A PEMFC stack is comprised of multiple MEA/PGA assemblies stacked between endplates. See, Appendix 9.

As multiple MEA/PGA assemblies are stacked, a final design problem is presented. The fuel cell stack generates waste heat. Excessive heat can dry out the membrane and adversely effect fuel cell performance. Consequently, some provision must be made for the removal of waste heat from the stack. In the conceptual design, the graphite substrate is extended beyond the edges of the rigid/compressible gasket to form a cooling fin. Adjacent fins are separated by an electronically insulating material, such as anodized aluminum screen, to prevent short circuits. The fins of each individual cell can then be either air or liquid cooled. An additional cooling method would use process gas and evaporative cooling. By removing the oxidant/out manifold (see Appendix 8), the depleted air and product water are vented to the cooling fin area. This architecture would allow cooling of each individual cell in the stack by means of thermal transfer along the plane of the graphite substrate, process gas cooling and also evaporative cooling using the product water from the cell.

III.

Experimental Two-cell Unit Test

In order to test the viability of this extremely simplified and inherently inexpensive PGA design, a two-cell PEMFC unit was constructed. The MEA's were purchased from BCS Technology of Bryan, Texas. Each MEA had an active electrode area of 22cm^2. The membrane was Nafion 115. The membrane had the same exterior dimensions as the PGA, i.e., 3 1/4 inches by 3 1/4 inches. Manifold slots were cut in the membrane to correspond to the manifold slots in the PGA. The endplates were gold-plated copper and polycarbonate insulators. Rigid/compressible gaskets were affixed to both endplates. At the oxidant endplate, a piece of carbon cloth was affixed to that plate. No carbon cloth was employed at the fuel side endplate.

The PGA employed in this particular test was the simplest version of the various PGA embodiments discussed above. This PGA had carbon cloth on the oxidant side and smooth graphite on the fuel side.

The oxidant was pressurized air. The air was able to enter and exit the oxidant-side fuel cell electrode via the manifolds and port channels and through the weave of the carbon cloth flow-field. Depleted air and product water from the electrochemical reaction were ejected from the oxidant side by means of a slow air bleed on the oxidant side. The fuel, which in this test was neat hydrogen, was able to enter the fuel-side electrode because the interface between the smooth graphite and the rough carbon cloth of the fuel cell electrode does not form a gas seal. A four slot PGA was utilized and a cooling fin was not included because the heat from the electrochemical reaction could be beneficially employed to heat the two-cell unit. Neither the hydrogen nor the air were externally humidified. The membrane was kept sufficiently moist by the product water from the reaction alone.

The anode and cathode of the fuel cell were attached to resistors of known value and the voltage across each resistor was recorded by computer. Current values were computed using Ohm's law and V/I curves were then plotted. Since the purpose of the test was to confirm the performance of the PGA, no attempt was made to optimize the performance of the two-cell PEMFC. The results, as shown in Appendix 10, are well within the range of anticipated cell performance given the moderate operating conditions of this test, i.e., hydrogen and air at 30psig and internal cell temperature at less than 50°C and given the MEA employed in the test. Consequently, PGA's are a potential candidate to replace machined graphite bipolar plates in mass-produced PEMFC's.

IV.
Costs and Commercialization

It is generally accepted in the industry that for PEMFC's to achieve significant market penetration the cost for the fuel cell stack should not exceed about US$50 per kilowatt. PGA's have an inherently low cost structure. The principal material costs are flexible graphite sheet (about US$4.50 per square meter) and carbon cloth (about US$25.00 per square meter). The gasket costs are nominal. A PGA having an electrode seating area of 100 cm^2 requires about 200 cm^2 of flexible graphite and about 200 cm^2 of carbon cloth (for two carbon cloth flow-fields per PGA). About fifty PGA's can be fabricated per square meter of flexible graphite and carbon cloth. Assuming the other Arthur D. Little cost estimates are accurate, the commercial breakpoint of US$50 per kilowatt may well be achievable with PGA's.[10]

In addition to a low cost structure, PGA's also are light-weight and permit an increase in cell stacking density to about 20 cells per lineal inch, or about 2.5 inches for fifty cells. These benefits will principally be of importance for portable and vehicular applications.

In short, while obstacles to commercialization still remain[11], PGA's represent a cost-effective bipolar separator plate option available to PEMFC manufacturers, which should enable reduction of overall fuel cell stack costs to the target commercialization price level for the mass market of US$50 per kilowatt.

Funding for this project[12] was provided by the United States Department of Energy, Office of Industrial Technologies, under Grant No. DE-FG01-97EE15679, whose support is gratefully acknowledged.

Footnotes

1. Spear, U.S.Pat.No. 5,858,567 (January 12, 1999).
2. Spear, U.S.Pat.No. 5,863,671 (January 26, 1999).
3. Meeting Abstracts, Batteries and Fuel Cells for Portable Applications and Electric Vehicles, 1997 Joint International Meeting of the Electrochemical Society and the International Society of Electrochemistry, p.194 (Paris, France).
4. Wilson, U.S.Pat.No. 5,798,187 (August 25, 1998).
5. Koncar and Marianowski, U.S.Pat.No. 5,942,347 (August 24, 1999).
6. See, Oak Ridge National Laboratories website: www.ornl.gov
7. Washington et al., U.S.Pat.No. 5,300,370 (April 5, 1994); Wilkinson et al., U.S.Pat.No. 5,527,363 (June 18, 1996).
8. Fuel Cell Directory, available from Fuel Cells 2000, a not-for-profit organization, 1625 K Street, NW, Suite 790, Washington, D.C. 20006. Website: www.fuelcells.org.
9. See footnote 7.
10. One recent study even suggests that PEMFC stacks can, in mass production, be fabricated for $18 to $28/kW. See, Lomax, et al., Directed Technologies, Inc., Arlington, Virginia, "Detailed Manufacturing Cost Estimates for Polymer Electrolyte Membrane (PEM) Fuel Cells for Light Duty Vehicles", prepared for Ford Motor Company under Prime Contract No. DE-AC02-94CE50389 with the United States Department of Energy, Office of Transportation Technologies (August 1998). The primary cost savings identified by Lomax are in membrane production and bipolar separator plate design and fabrication.
11. Even with reductions in fuel cell stack costs, PEMFC commercialization issues still remain with respect to hydrogen production and storage. A compact steam-reformer, operating on a natural gas feedstock can supply a mixed gas stream consisting of hydrogen and carbon dioxide. For on-site applications, the mixed gas stream can be injected directly into the fuel cell and the tail gas vented. For vehicular applications, the same steam-reformer could be employed during off-peak use to supply hydrogen for storage in hydride tanks onboard a fuel cell-powered vehicle. Recent advances in hydrogen separation and storage technology, using silica-coated hydride materials, permit the hydrogen in the mixed steam-reformer gas stream to be simultaneously separated and adsorbed. See, Heung et al., U.S.Pat.No. 5,965,482 (October 12, 1999). Eventually, hydrogen may be generated directly from biomass using biochemical enzymatic hydrogen production technology. See, Woodward, U.S.Pat.No. 5,942,424 (August 24, 1999).
12. Patent applications are pending with respect to the PGA's described in this article.

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Improving Reservoir Conformance Using Gelled Polymer Systems

Final Report
September 25, 1992 to July 31, 1996

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October 1997

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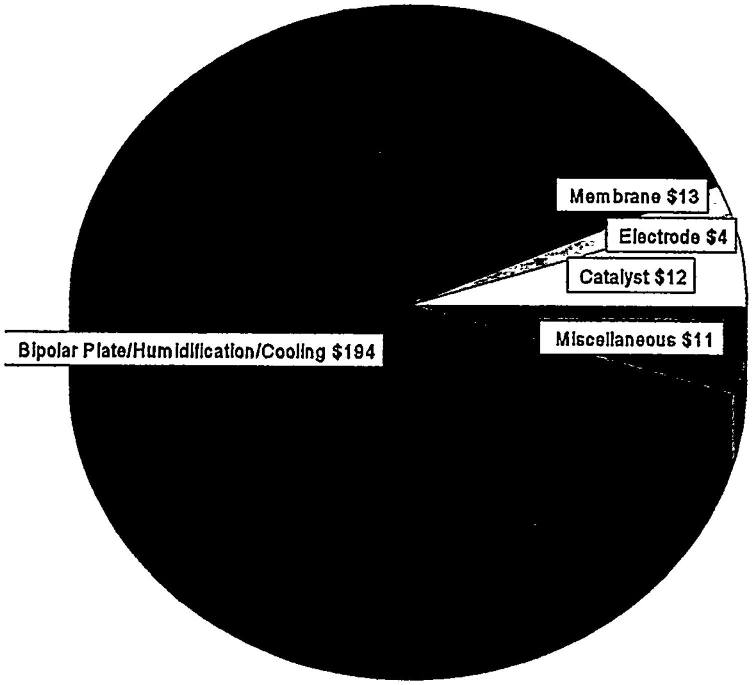

Figure 1. Estimate of PEMFC Stack Component Costs ($/kW)
Department of Energy:
A.D. Little

US005716664A

United States Patent [19]

Marchetti

[11] **Patent Number: 5,716,664**

[45] **Date of Patent: Feb. 10, 1998**

[54] **METHOD OF MAKING A HYDROPHILIC, GRAPHITE ELECTRODE MEMBRANE ASSEMBLY**

[76] Inventor: **George A. Marchetti**, 5726 S. Grand Ave., Western Springs, Ill. 60558

[21] Appl. No.: **667,521**

[22] Filed: **Jun. 19, 1996**

Related U.S. Application Data

[63] Continuation of Ser. No. 586,626, Dec. 22, 1995.

[51] **Int. Cl.**^{6} **H01M 4/88**

[52] **U.S. Cl.** **427/115**; 429/42

[58] **Field of Search** 429/30, 33, 40, 429/42, 44; 427/115; 502/101; 263/448

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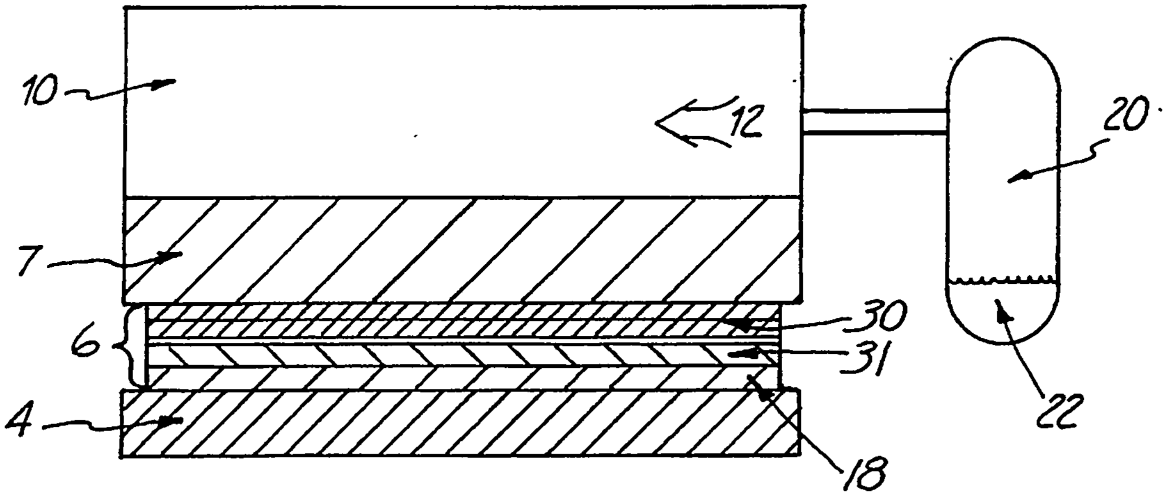
Attorney, Agent, or Firm—Janal M. Kalis

[57] **ABSTRACT**

The present invention includes a gas-permeable, hydrophilic, graphite fuel cell electrode for use in conjunction with an ionomer membrane. The fuel cell electrode includes a roughened, interstitial graphite surface enclosing micropores, upon which is deposited a catalyst for contacting an ionomer membrane. The graphite electrode has a thickness of about 40 microns.

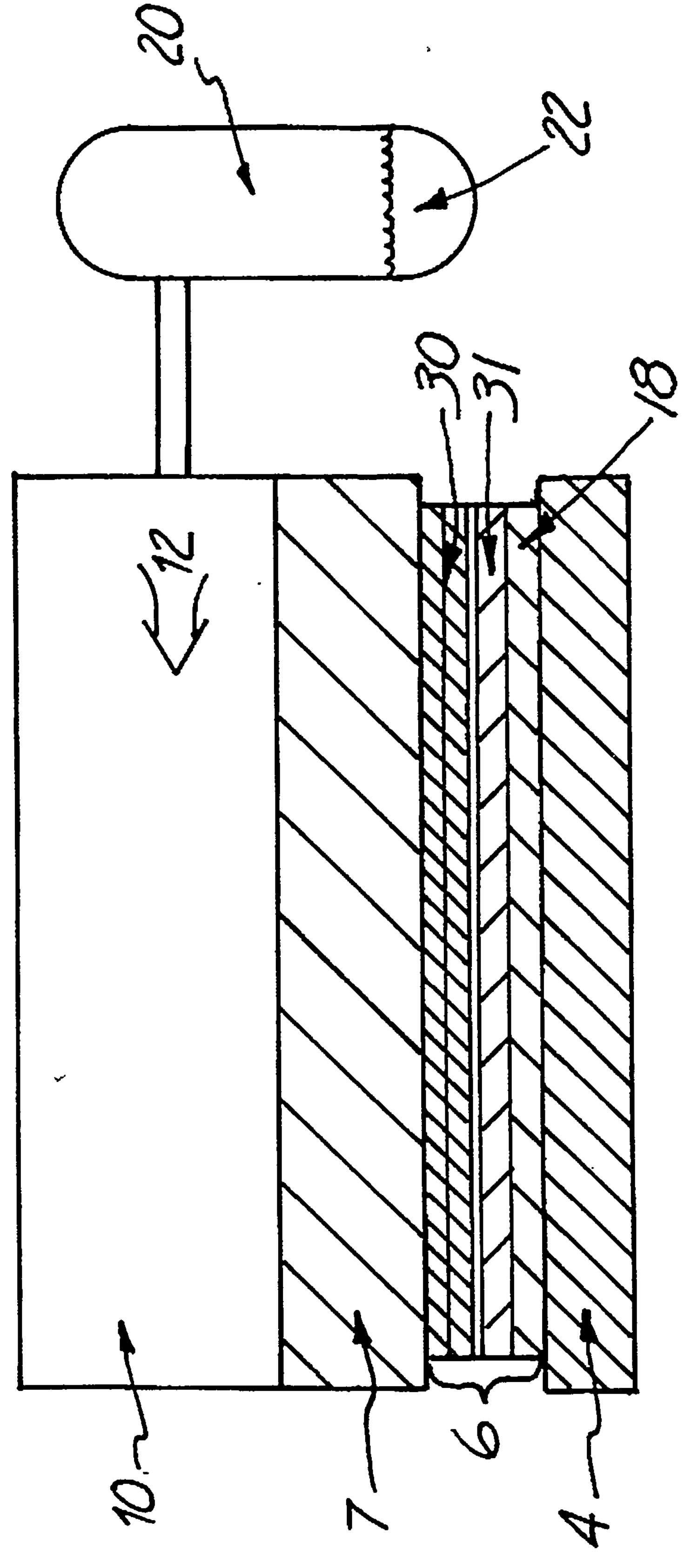
6 Claims, 2 Drawing Sheets



ACRONYMS AND ABBREVIATIONS

ACHRE	Advisory Committee on Human Radiation Experiments
AF	activity fraction
AMAD	Activity median aerodynamic diameter
CEDR	Comprehensive Epidemiological Data Resource
CR	concentration ratios
DNA	deoxyribonucleic acid
DRMIA	Dosimetry Registry of the Mayak Industrial Association
EPA	Environmental Protection Agency
EPR	electron paramagnetic resonance
FISH	fluorescence in situ hybridization
GPA	glycophorin-A
HEHF	Hanford Environmental Health Foundation
ICD-9	International Classification of Diseases-9th Revision clinical Modification
ICRP	International Commission on Radiological Protection
LANL	Los Alamos National Laboratory
NHRTR	National Human Radiobiology Tissue Repository

Figure 2



NIST	National Institute of Standard and Technology
OSTI	Office of Scientific and Technical Information
PHA	phytohemagglutinin
PNNL	Pacific Northwest National Laboratory
RBC	red blood cells
RES	reticuloendothelial system
RNA	ribonucleic acid
USTUR	United States Transuranium and Uranium Registries
UW	University of Washington
WSU	Washington State University
WWW	World Wide Web

uncommon. In order for ionomer membrane fuel cells to achieve commercial viability, the amount of costly, precious metal catalyst per unit area must be substantially reduced from those levels.

A second approach to extending the three-phase boundary of an ionomer membrane fuel cell has been to use a laser to create tiny cavities in the membrane itself. These cavities serve to make the membrane a three-dimensional surface and thereby increase its overall surface area. High platinum loadings appear to be required in this design as well, in order to take advantage of the increased surface area and to extend the three-phase boundary into the cavities.

A third approach has been to extend the three-boundary into the body of a pre-catalyzed, hydrophobic electrode by using liquid Nafion®. The liquid Nafion® flows into the body of the electrode, thereby extending the three-phase boundary. The electrode itself contains very small quantities of platinum catalyst. The low catalyst loading is possible because the electrode serves as an electronically conductive support for the catalyst. Unfortunately, because the electrode is hydrophobic, its performance suffers because of electronic resistance within the electrode and humidification difficulties.

Thus, state-of-the-art fuel cell electrodes, when used in conjunction with an ionomer membrane, have three principal deficiencies. First, the electrodes rely upon a pressure contact between carbon particles in a Teflon® binder for electrical conductivity. Even with a graphite cloth backing, there is significant electronic resistance within the electrode because of this type of binding reliance. Second, maintaining humidification of the membrane is difficult and requires an elaborate subsystem. Third, the most successful fuel cell designs to date, using an ionomer membrane, have required high levels of platinum catalyst loadings for effective operation.

SUMMARY OF THE INVENTION

The present invention includes a gas-permeable, hydrophilic, graphite fuel cell electrode for use in conjunction with an ionomer membrane. The fuel cell electrode includes a first graphite portion, terminating in a first surface for contacting fuel or oxidant. The electrode also includes a second graphite portion enclosing micropores, adjacent and integral to the first portion. The second portion terminates in a second pre-roughened surface, opposing the first surface, for contacting fuel or oxidant. The fuel cell electrode also includes a catalyst that is deposited onto the second pre-roughened surface to form a catalyzed graphite surface.

The present invention also includes a fuel cell assembly. The assembly includes a fuel side current collector, a fuel side electrode, an ionomer membrane contacting the fuel side electrode, an oxidant side electrode, and an oxidant side current collector. The oxidant side electrode is substantially identical to the fuel side electrode and opposes the fuel side electrode, also contacting the ionomer membrane.

The present invention further includes a method for making a hydrophilic fuel cell electrode with an interstitial surface and an ionomer membrane conformed to adhere to the interstitial surface. The method reforms the ionomer membrane from a flat material into a three-dimensional material, thereby extending the three-phase boundary. The method includes hot-pressing a pre-roughened graphite main body to an ionomer membrane surface under pressure. The membrane is forced into shallow channels of the pre-roughened interstitial graphite surface, adhering to the surface and is molded into the surface.

The present invention further includes a method for making a hydrophilic, graphite fuel cell electrode. The method includes providing a graphite main body. The graphite main body is free of particles of Teflon® and carbon. The graphite has a density about one-half that of pure graphite. The graphite is roughened and thinned to a thickness of about 40 microns. The graphite main body has a first substantially smooth surface and an opposing second roughened surface enclosing micropores and mesopores.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention may be better understood from the following detailed description when read with reference to the drawings in which:

FIG. 1 shows a schematic cross-sectional view of the electrodes of the present invention installed in a hydrogen fuel cell; and

FIG. 2 shows a schematic cross-sectional view of the layers of the electrode of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The fuel cell electrode of the present invention includes a main body that is made entirely of graphite. The graphite has a density of about one-half that of pure graphite. The main body of the fuel cell electrode includes a first substantially smooth surface and an opposing roughened surface that encloses micropores and mesopores. The roughened surface of the graphite main body is roughened with an abrasive material, such as sandpaper, to increase its surface area. A catalyst is deposited upon the roughened surface to form a catalyzed graphite surface.

Each of two graphite electrodes is hot-pressed to an ionomer membrane at each of the roughened surfaces to form a bonded electrode/membrane assembly comprising the two electrodes and the ionomer membrane sandwiched between the two electrodes.

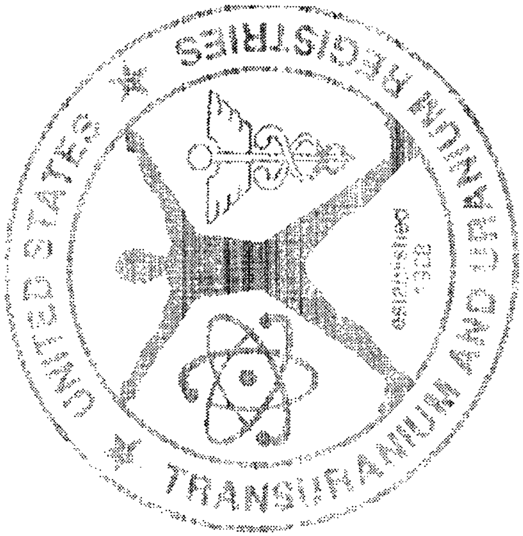
Once assembled, the bonded assembly is placed in a folded sheet of plastic and is pressed in a rotary press three or four times. The non-catalyzed portions of each of the graphite electrodes are stripped off by this pressing step, leaving only a thin layer of catalyzed graphite on either side of the ionomer membrane. Each of these thin layers serve as one of either the fuel or oxidant electrode, respectively.

Following this stripping process step, the graphite main bodies of the electrodes are approximately 40 microns thick. Micropores and mesopores enclosed in the roughened surface of each electrode permit the reactant gases and humidification to reach the catalyst layer and the ionomer layer.

Neither Teflon® nor carbon particles form any part of the fuel cell electrodes in the assembly of the present invention. In one embodiment, the graphite in the main body of each electrode is obtained from a graphite precursion material, manufactured by Johnson and Matthey, Product No. 10832. The graphite precursion material, as received, has a density which is one-half that of pure graphite and is 0.254 mm thick. The as-received material is neither gas-permeable nor appreciably hydrophilic.

In one embodiment, the graphite precursion material is roughened on one side using 320 grit, emery cloth sandpaper made by the 3M Company of Minneapolis, Minn. The graphite is hand-sanded in one direction 10 times. The graphite is then rotated 90° and sanded 5 times in the rotated direction. Waste from the sanding is removed from the graphite with a damp tissue. The purpose of the sanding is

Administrative



if any, visible holes remain, to form an electrode with a first side and a second side. The smooth surface of the electrode is then stripped off with tape. The electrode is pressed one final time with a Teflon® surface on an internal side of the electrode and sandpaper on an external side. It is contemplated that the electrode may be mass-produced by using high-speed, rotary presses with rollers that have been preroughened to simulate the effect of the sandpaper grit.

The processed graphite electrode is approximately 75 microns thick and is very flexible. The electrode resembles a piece of paper with respect to its thickness and flexibility. The electrode includes the smooth surface that is relatively smooth and permits gas flow through micropores created by the processing. The electrode also includes the roughened surface with micropores and mesopores in the graphite.

The electrode permits excellent gas flow from the roughened surface of the electrode to the smooth surface via the micropores and mesopores in the processed material. It has been found that since sintered hydrophobic Teflon® is not used to create the gas channels, humidified hydrogen gas readily supplies all of the moisture necessary to maintain hydration of the membrane, even at elevated internal fuel cell temperatures. Additionally, the internal electronic resistance of the graphite electrode of this process embodiment is extremely low, being approximately 0.2 ohms from the smooth surface of the electrode to the current collection points on the roughened surface of the electrode.

The present invention is a radical departure from prior attempts to create a fuel cell electrode which is compatible with an ionomer membrane. Instead of a hydrophobic electrode, the present invention includes a hydrophilic electrode, which allows continuous humidification of the membrane. Instead of trapping water within the membrane, as current state-of-the-art electrodes do, the hydrophilic fuel cell electrode allows humidification to be continually resupplied with the fuel and/or oxidant. The membrane is thereby continuously hydrated, and the intractable water management problem heretofore associated with ionomer membrane fuel cells is eliminated.

In addition, since the electrode is comprised entirely of graphite, the electrical conductivity of the electrode is very good. Furthermore, since the catalyst is deposited onto a roughened surface of the electrode, which forms a high-surface area, structural and electronic support, the amount of catalyst loading can be significantly reduced when compared to the high catalyst loading fuel cells discussed above.

The high catalyst loading fuel cells use unsupported platinum black to catalyze the reaction and to conduct the electric current generated. By using the graphite electrode of the present invention for catalyst support and for electronic conductivity, the catalyst loading can be reduced since the electrode, not the platinum, is chiefly relied upon for electrical conductivity.

The improved hydrophilic fuel cell electrodes according to the present invention are shown in a fuel cell 2 illustrated in FIG. 1. The fuel cell 2 is centered around an electrolyte matrix 4 which is an ionomer membrane. The, ionomer membrane 4 in the preferred embodiment is a solid polymer electrolyte manufactured by DuPont under the brand name Nafion® with a thickness of 0.175 mm. The membrane 4 is located between a pair of electrodes, anode 6 and cathode 8.

The Nafion® membrane is preferably cleaned by conventional methods prior to installation and use. In one embodiment, the membrane is cleaned with an aqueous solution of hydrogen peroxide, about 5 percent by weight, to remove organic impurities. The membrane is then soaked in a solution of 0.5 molar sulfuric acid to remove metal impurities and is rinsed in distilled water to remove remaining sulfuric acid. This method of cleaning is described in the J. Electro Analytical Chem. 251 No. 2, Sep. 23, 1988 at page 275.

A gas-permeable current collector is connected to anode 6 by a pressure contact. The current collector must be composed of a material which does not structurally deteriorate or lose electrical conductivity in the fuel cell environment. Materials such as stainless steel, titanium, nickel or graphite can be used. The current collector 7 is preferably a gas-permeable frit made of sintered material. A second gas-permeable, current collector 9 is connected to cathode 8. The fuel cell 2 is activated when current collectors 7 and 9 are connected to an electrical load 11 completing an electrical circuit. Electrical load 11 may be any electrical device, such as a light bulb or motor.

The anode 6 is placed between the ionomer membrane 4 and the gas or fuel manifold 10 which contains fuel 12. In this embodiment, the fuel 12 is hydrogen gas, at a pressure of one atmosphere. The interface between fuel manifold 10 and anode 6 allows the flow of fuel 12 to the anode 6. The cathode 8 is placed between the electrolyte matrix 4 and the oxidant manifold 14 through which oxidant 16 flows at a pressure of about 4 atmospheres. The interface between the oxidant manifold 14 and the cathode 8 allows the flow of oxidant 16 to cathode 8. In this embodiment, the oxidant 16 is compressed, breathable air. Surface 18 of anode 6 in contact with electrolyte membrane 4 contains a catalyst material. This material is typically a metal and, in the preferred embodiment, the catalyst is platinum. Similarly, surface 20 of the cathode 8 contacts electrolyte matrix 4 and also contains a platinum catalyst layer according to the preferred embodiment. The hydrogen gas may be humidified by passing it through a water chamber 21 before it enters the hydrogen manifold. Water in the water chamber can be heated with a high resistance electrical coil 22.

Hydrogen gas 12 from manifold 10 diffuses through anode 6 towards electrolyte membrane 4. As the hydrogen gas 12 is adsorbed by the catalyst 18, the bonds between the hydrogen molecules are broken by the oxidation reaction, producing hydrogen ions and free electrons. The hydrogen ions then diffuse through the electrolyte membrane 4 to interface 20 located proximate to cathode 8. The electrons preferentially flow from anode 6 to current collector 7 since electrolyte membrane 4 is an electronic insulator. The electrons thus flow towards cathode 8 by means of current collector 9, creating a current and generating a voltage to drive electric load 11. This voltage is equivalent to the potential difference between anode 6 and cathode 8. In the preferred embodiment, this potential difference is approximately 1 volt at open circuit. Voltage will vary with the current drawn through the load. Of course, this voltage may be increased to any desired voltage by putting multiple fuel cells in series. High-voltage fuel cell batteries can be fabricated in this manner using the invention as a principal component. The electrons move through current collector 9 and diffuse through cathode 8 where upon, arrival, they are recombined with the oxidant and the hydrogen ions. Simultaneously, oxidant 16 diffuses through cathode 8 and is adsorbed by the catalyst 20 to react with the hydrogen ions and arriving electrons in a reduction reaction to form water.

Electrodes 6 and 8 are similar. Anode 6, which is connected to current collector 7 according to the invention, is shown in FIG. 2. This figure is not drawn to scale in order to clearly illustrate surface 18, which is the catalyst interface to electrolyte membrane 4. The anode 6 is in direct physical

DOE/NV-325

NTSWAC (Rev. 2)
May 1999

Nevada Test Site Waste Acceptance Criteria

Prepared by the

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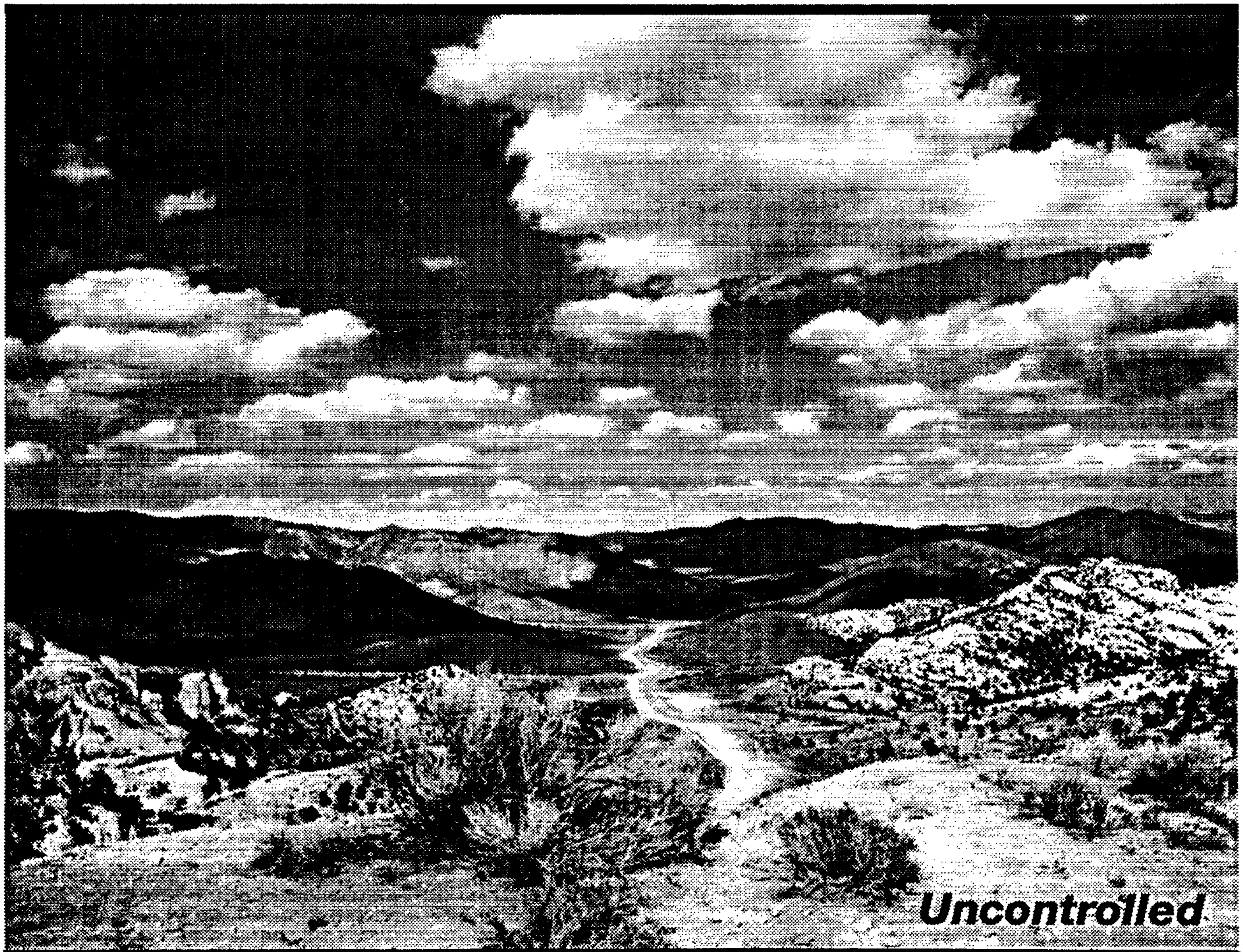
Nevada Operations Office
Waste Management Division



Uncontrolled

bonding the graphite main body to an ionomer membrane so that the toughened catalyzed graphite surface is in contact with the membrane to form an electrode; and

stripping graphite from the graphite main body so that the remaining graphite main body is about 40 microns thick.

2. The method of claim 1 wherein the catalyst is platinum.

3. The method of claim 1 wherein the graphite is stripped from the graphite main body by treatment in a rotary press.

4. A method for reducing catalyst requirement in a fuel cell electrode by conforming a flat surface of an ionomer membrane component of the electrode to an interstitial surface of a graphite main body of the electrode, thereby increasing surface area of the membrane comprising:

providing a graphite main body wherein the graphite has a density about one-half that of pure graphite and wherein the graphite main body has a smooth surface and a roughened interstitial surface;

applying a catalyst to the roughened interstitial surface to form a catalyzed graphite surface;

hot-pressing and molding the ionomer membrane onto the roughened interstitial surface of the graphite;

bonding the graphite main body to the ionomer membrane so that the toughened catalyzed graphite surface is in contact with the membrane to form an electrode; and

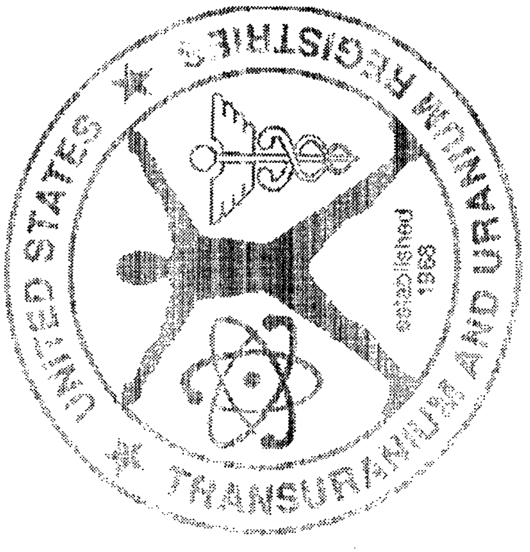
stripping away the majority of the graphite of the graphite main body so that the remaining graphite main body is about 40 microns thick.

5. The method of claim 4 wherein the catalyst is platinum.

6. The method of claim 4 wherein the graphite is stripped by treatment in a rotary press.

* * * * *

Appendix H
Distribution List



RF SPUTTER DEPOSTION OF PT CATALYST ON GRAPHITIC FUEL CELL ELECTRODES

Pt catalyst was deposited on graphitic electrodes under different conditions and for different lengths. The process was similar under all circumstances. A graphitic electrode was placed on a platform inside a high vacuum chamber with base pressures of 2 X 10^{-6} torr. A small amount of Ar was flowed through the chamber, enough to bring the system pressure up to 40 mtorr. An RF discharge was then initiated and the material (usually pure Pt) was deposited onto the substrate from a 2 in. target. RF power at the target was kept at 50W.

The thickness of the film was determined by the amount of time the material was sputtered. The rate of film deposition was determined by producing Pt film standards on glass slides under identical conditions. The film thickness was found using a diamond stylus Sloan profilometer. Rates were determined for two different substrate – target distances, 2 in. and 4 in. Deposition rates under these conditions were 7 Angstroms/min. and 1.75 Angstroms/min., respectively. This ensured a relatively slow deposition rate, encouraging a rough microstructure and consequently high surface area.

ROOM TEMPERATURE Pt DEPOSITIONS

Pt was deposited onto graphitic substrates maintained at room temperature (23°C). Ar pressure was 40 mtorr and the RF power was 50W. The substrate was 2 inches from the target, giving a deposition rate of 7 Angstroms/min. Deposition times for these samples ranged from 30 min. to 300 min. Resulting in film thicknesses ranging from 210 Angstroms to 2100 Angstroms.

The two figures show powers and voltages of operating fuel cells with different Pt catalyst loadings. Pt loadings in excess of 500 Angstroms gave power values of around 3.5 Watts (0.6 V and 0.6 amps through a 1 ohm load). Higher Pt loadings did not increase the performance significantly.

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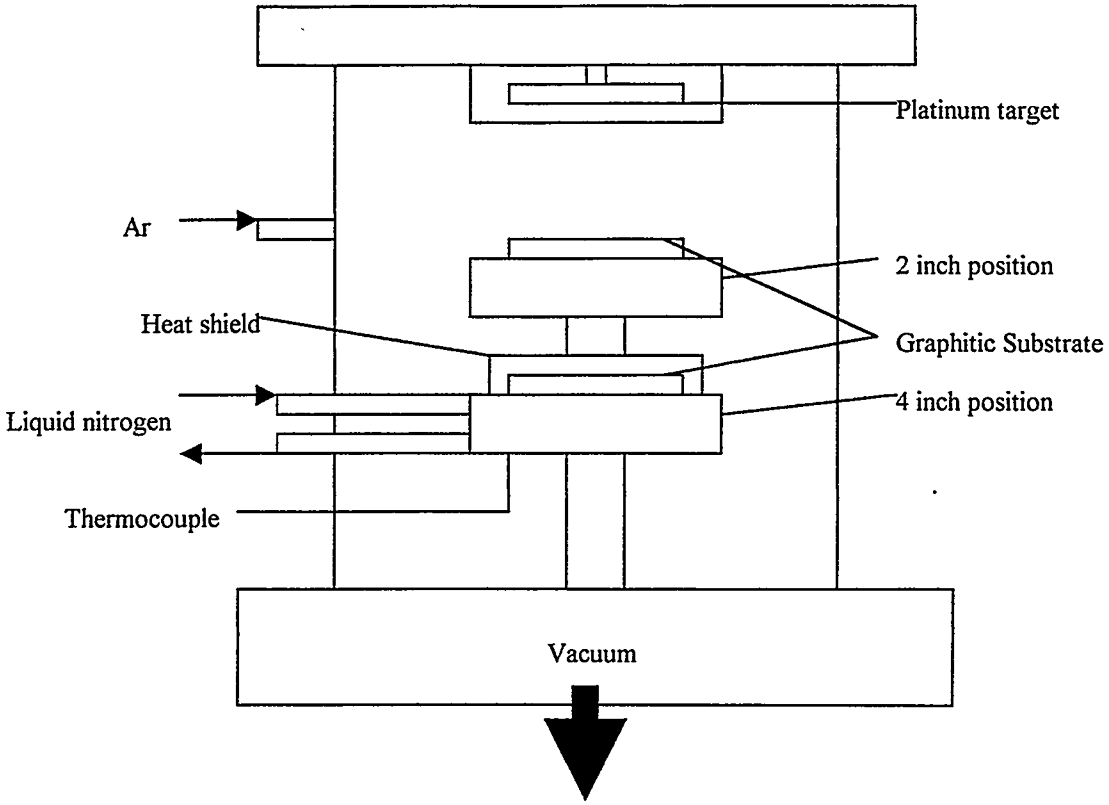
ROOM TEMPERATURE Pt/Cu ALLOYS

Pt/Cu alloys were deposited onto graphitic substrates by using an RF target made of alternating strips of Pt and Cu. Ar pressure was 40 mtorr and RF power was 50W. Substrate-target distances were 2 inches resulting in 7 Angstroms/min. deposition rates. The resulting film stoichiometry and uniformity were verified with Auger and ESCA analysis.

LIQUID NITROGEN TEMPERATURE Pt DEPOSITIONS

Pure platinum was deposited from a 2 inch Pt target onto graphitic substrates placed 4 inches below the target. Deposition rates were found to be about 1.25 A/min. The temperature of the substrates were cooled with liquid nitrogen. The substrate temperature was maintained at –180° C. A screen heat shield was placed above the substrate to protect the substrate from heat caused by the sputtering process. Also, it served to decrease the energy of the impinging Pt particles, inducing colloidal formation. The resulting Pt film was intended to be a stack of Pt colloidal spheres. Surface area of the platinum would then be extremely high.



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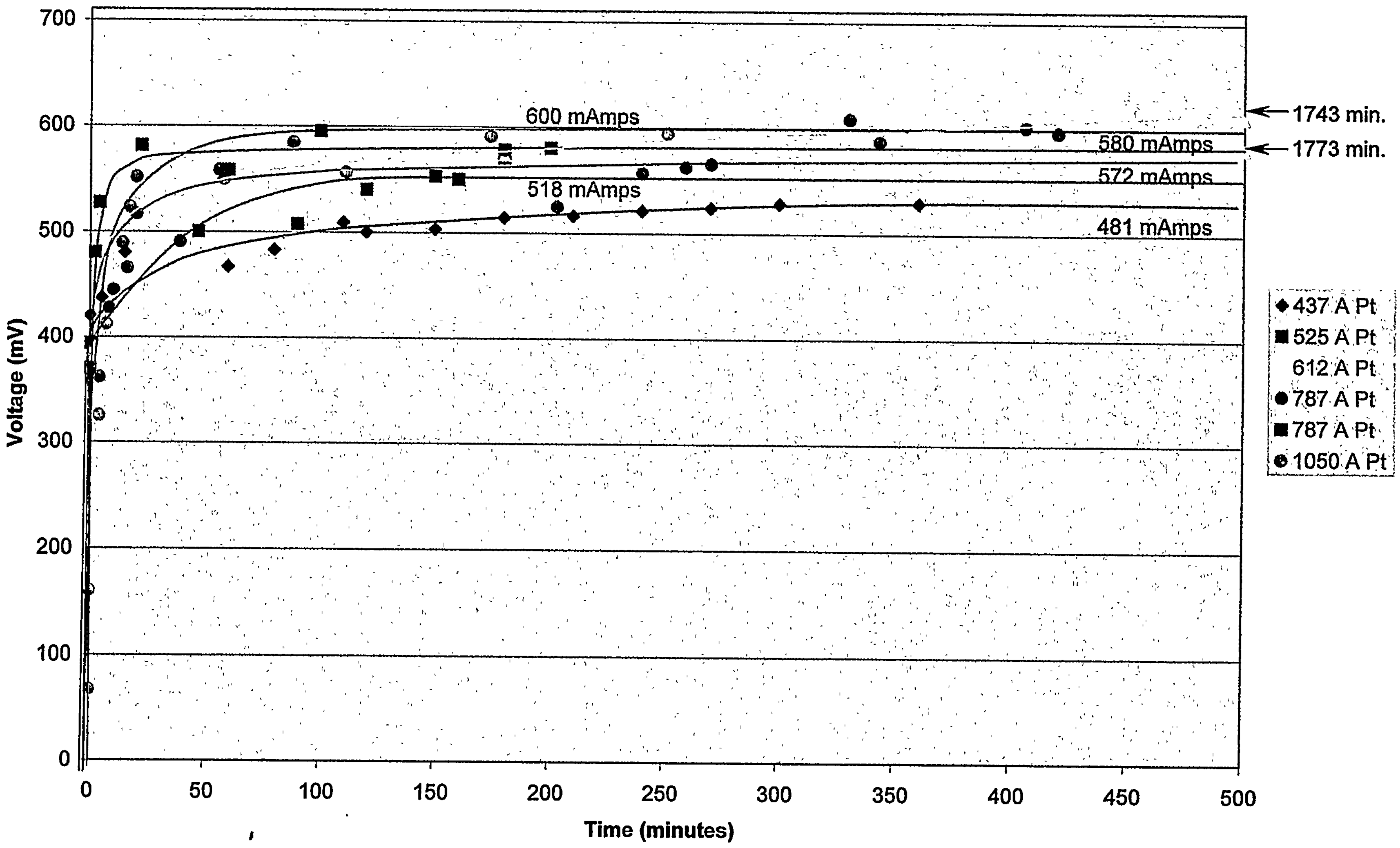
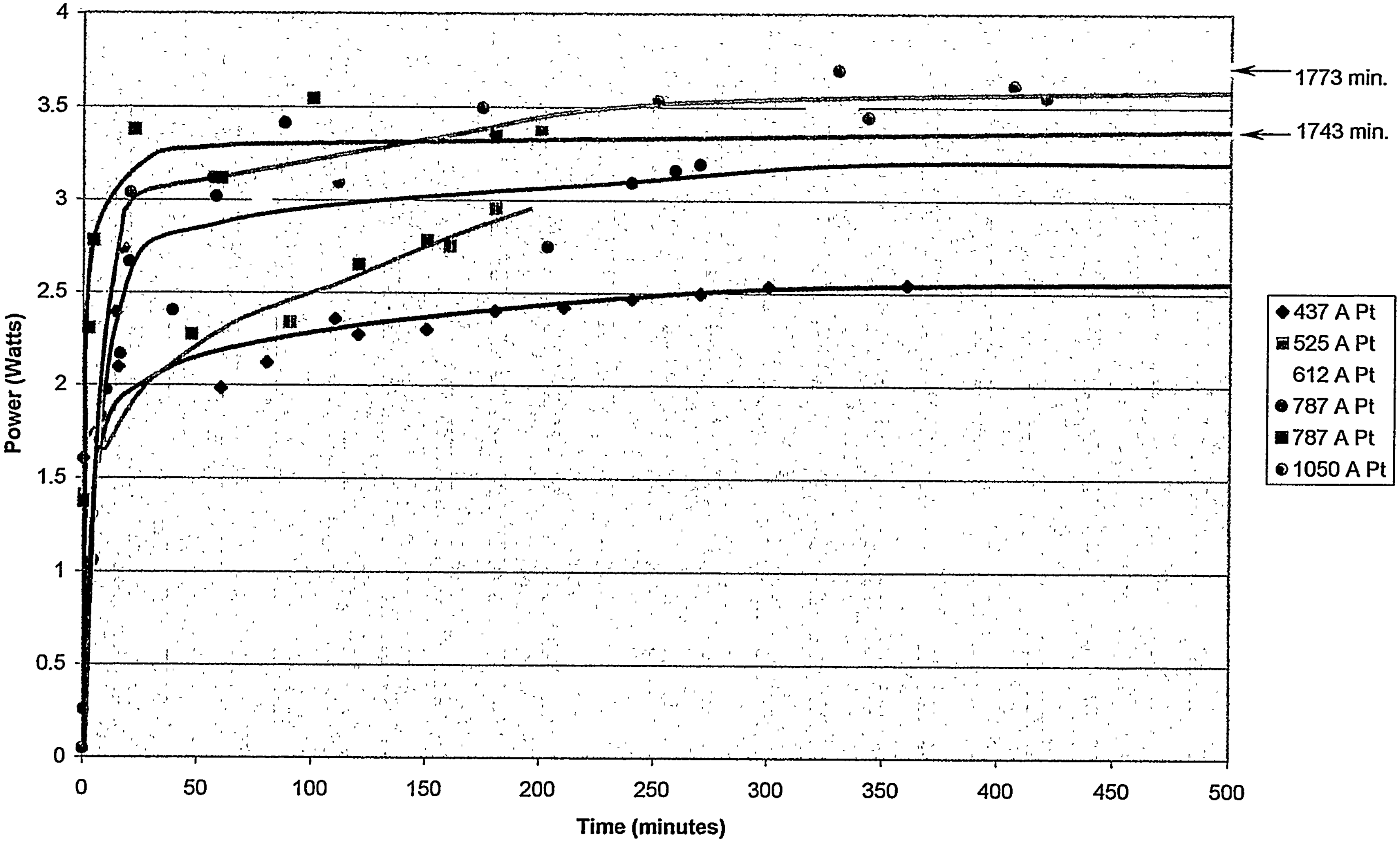
Voltage at Different Catalyst Loadings

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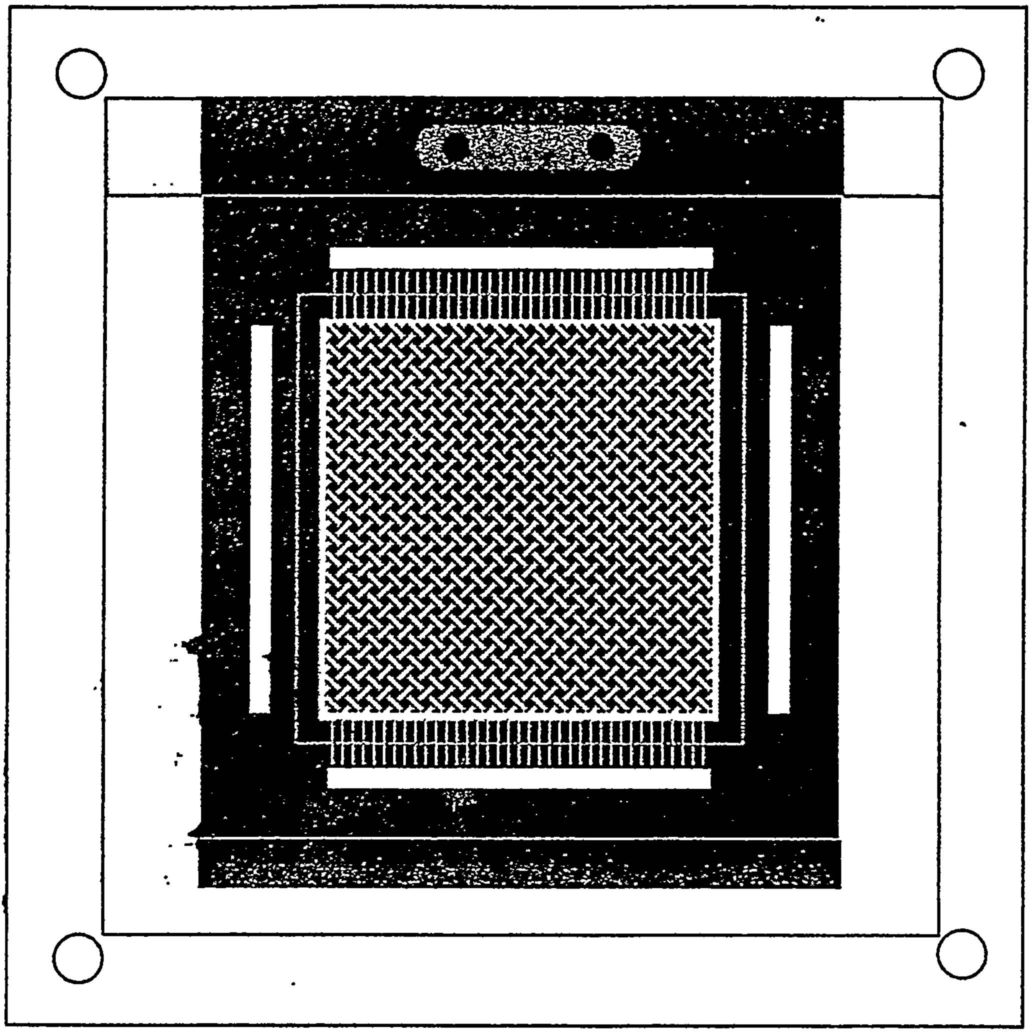

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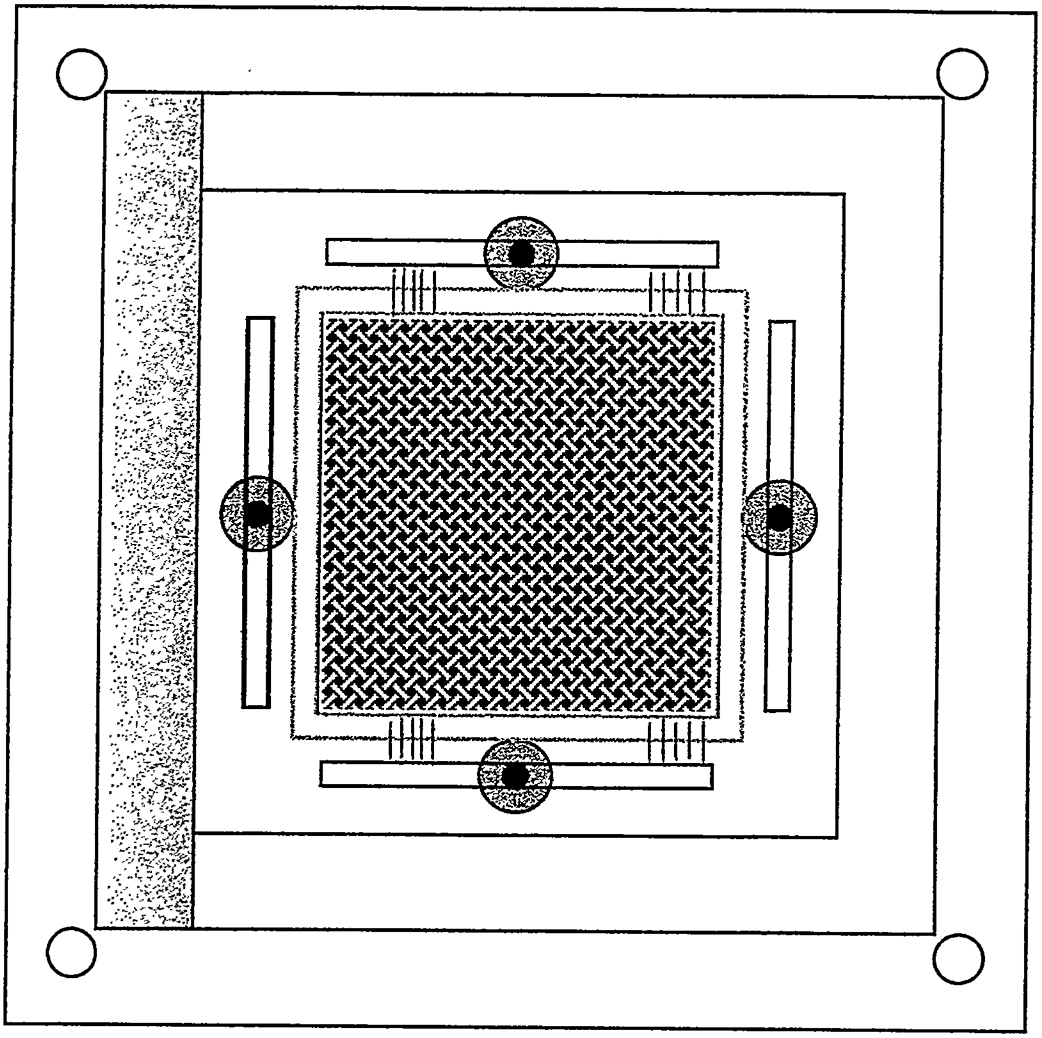

Figure 3

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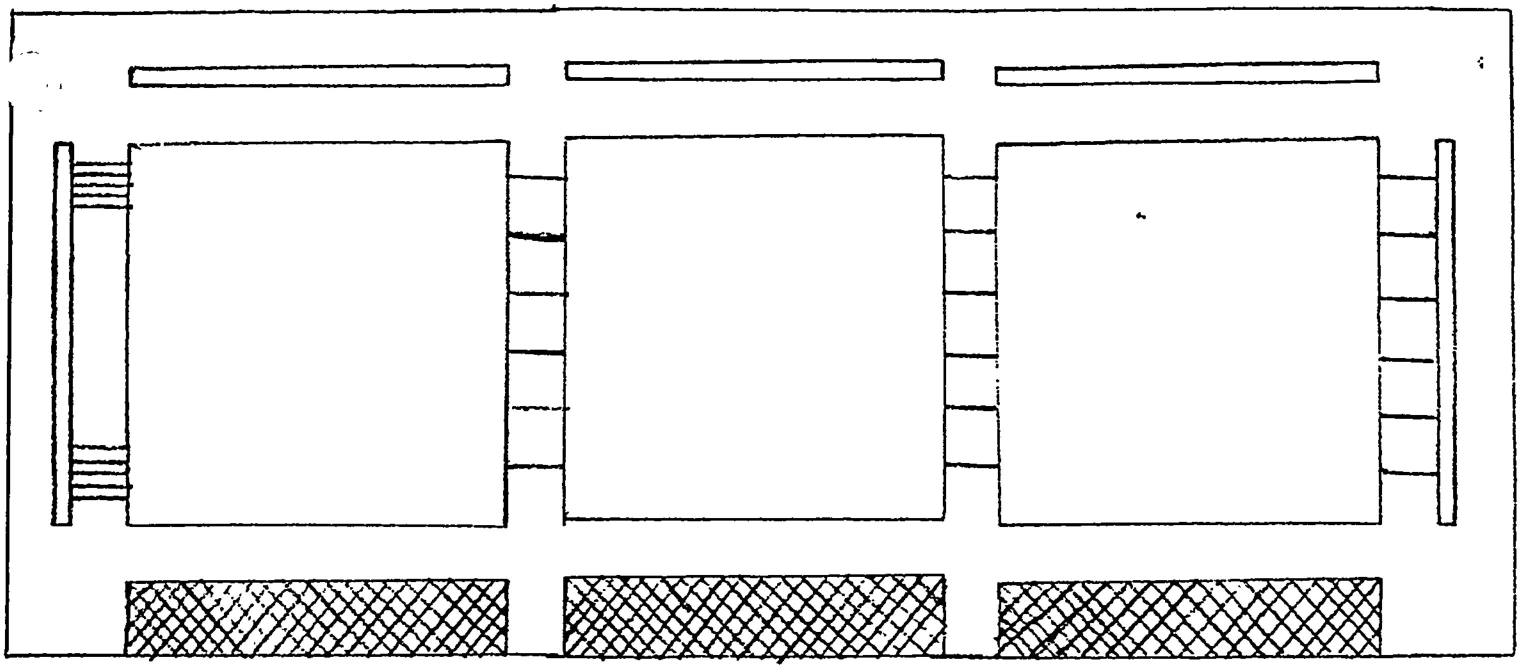
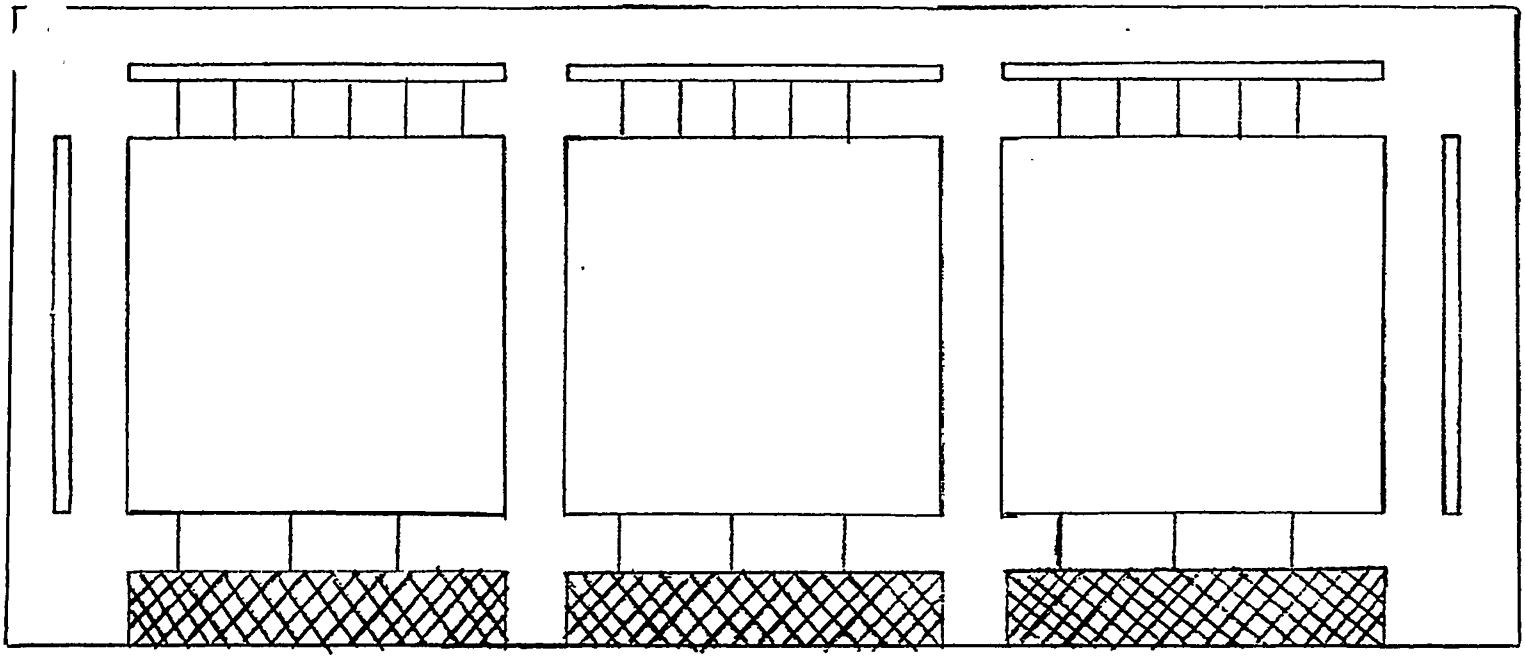


Fuel Side



Oxidant Side

Figure 4

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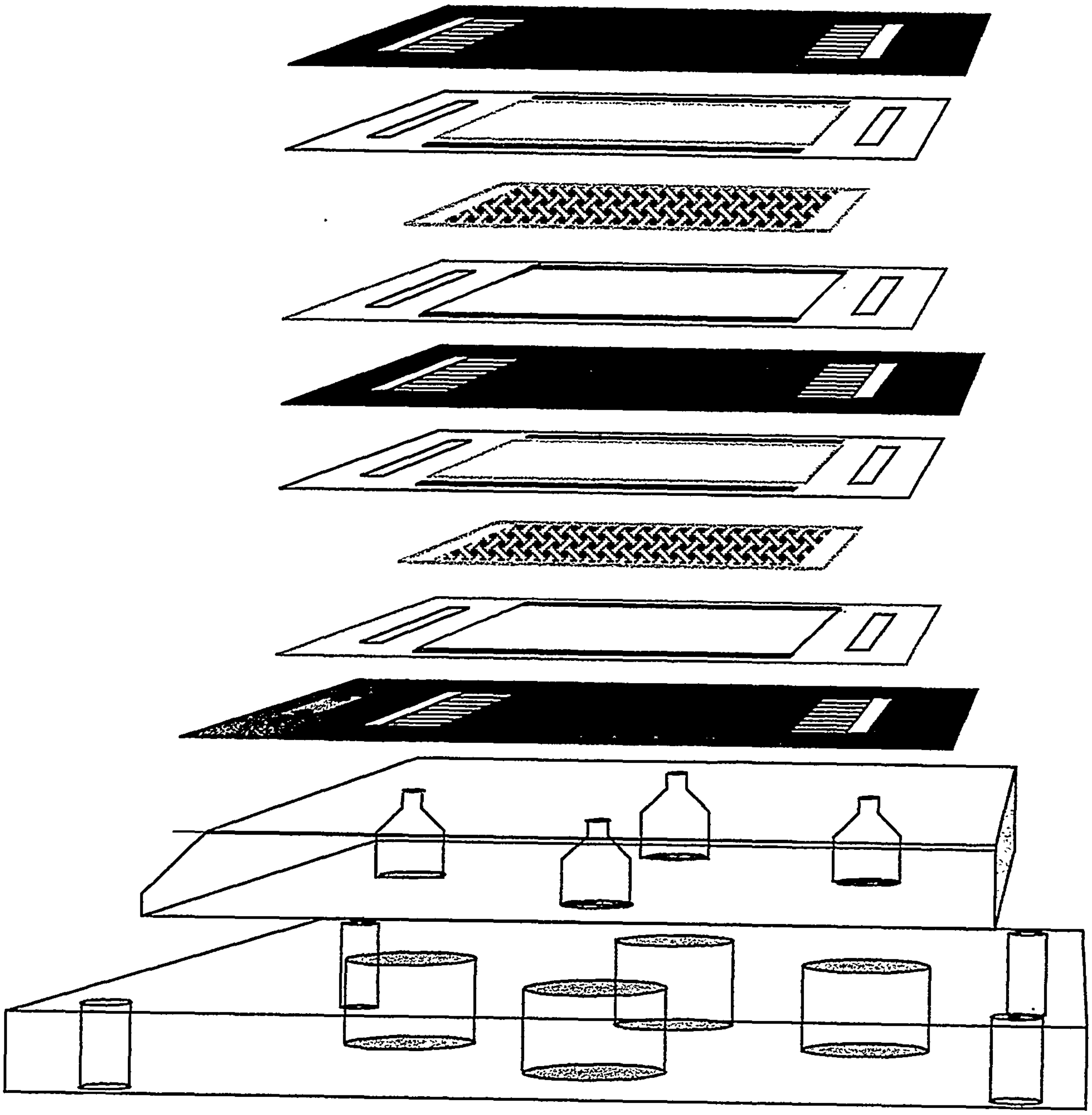

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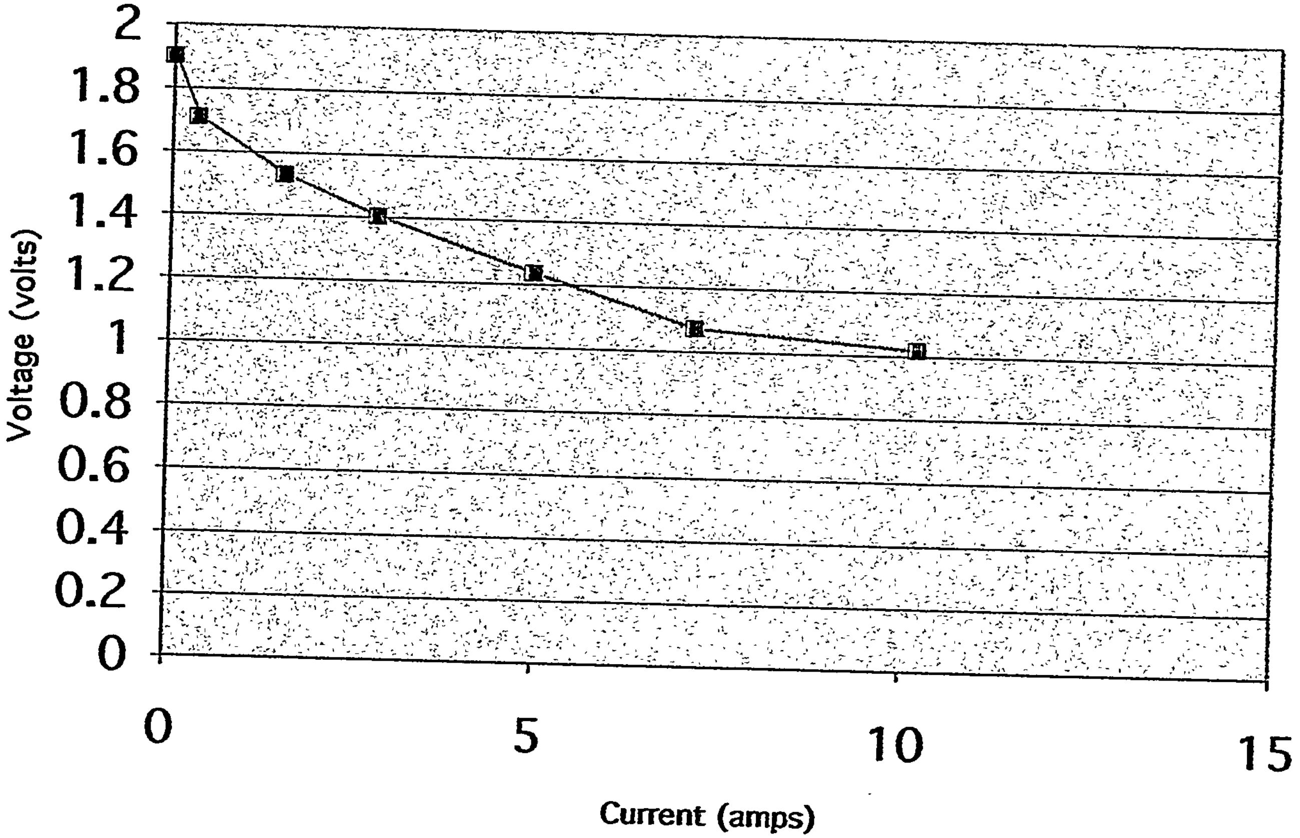
CANADA

V/I Curve for Fuel Cell with 2 MEAs and GM Bipolar Plate



Operating Conditions:
30psig H2 / 30psig Air
Internal Temperature:
43 C
External Humidification:
none
Double MEA:
22 cm2 Electrode Area Each

Data Values

Resistor (ohms)	Potential (Volts)	Current (amps)
open	1.902	0
5	1.71	0.34
1	1.53	1.53
0.5	1.4	2.81
0.25	1.24	4.94
0.15	1.07	7.15
0.1	1.02	10.18