

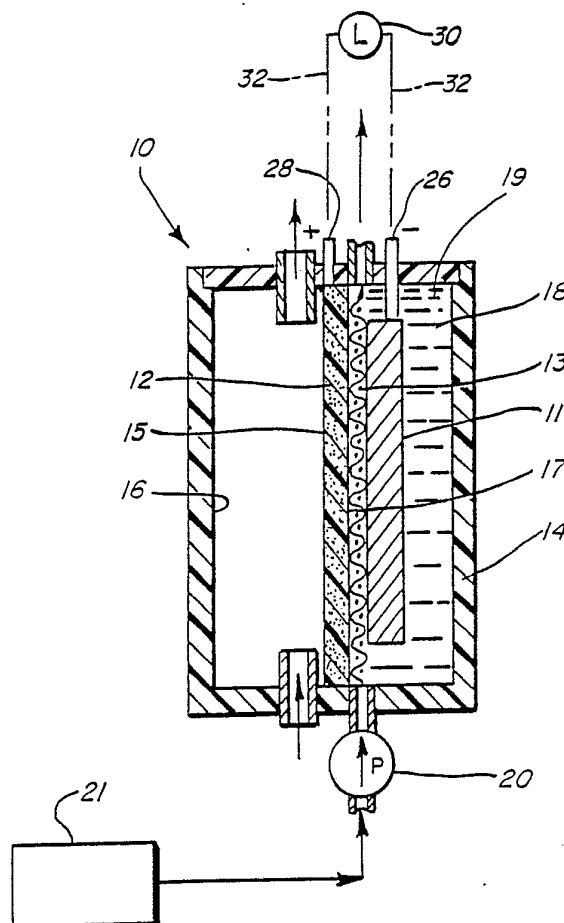


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁴ : C25B 9/00, 11/03, 11/12 C25B 13/00, H01M 4/86, 4/90 H01M 4/96	A1	(11) International Publication Number: WO 88/ 06643 (43) International Publication Date: 7 September 1988 (07.09.88)		
<table border="0" style="width: 100%;"> <tr> <td style="vertical-align: top; width: 50%;"> (21) International Application Number: PCT/US88/00622 (22) International Filing Date: 2 March 1988 (02.03.88) (31) Priority Application Number: 020,777 (32) Priority Date: 2 March 1987 (02.03.87) (33) Priority Country: US (60) Parent Application or Grant (63) Related by Continuation US 020,777 (CIP) Filed on 2 March 1987 (02.03.87) (71) Applicant (for all designated States except US): GOULD INC. [US/US]; 10 Gould Center, Rolling Meadows, IL 60008 (US). </td> <td style="vertical-align: top; width: 50%;"> (72) Inventors; and (75) Inventors/Applicants (for US only) : GORDON, Arnold, Z. [US/US]; 23714 Woodway Road, Beachwood, OH 44122 (US). YEAGER, Ernest, B. [US/US]; 2 Bratenahl Place, Apartment 5F, Cleveland, OH 44108 (US). TRYK, Donald, S. [US/US]; 2206 Delaware Road, Cleveland Heights, OH 44118 (US). HOS-SAIN, M., Sohrab [US/US]; 13590 Cedar Road, University Heights, OH 44118 (US). (74) Agent: ZELLER, James, P.; Marshall, O'Toole, Gerstein, Murray & Bicknell, Suite 2100, Two First National Plaza, Chicago, IL 60603 (US). (81) Designated States: DE (European patent), FR (European patent), GB (European patent), JP, US. Published <i>With international search report.</i> </td> </tr> </table>			(21) International Application Number: PCT/US88/00622 (22) International Filing Date: 2 March 1988 (02.03.88) (31) Priority Application Number: 020,777 (32) Priority Date: 2 March 1987 (02.03.87) (33) Priority Country: US (60) Parent Application or Grant (63) Related by Continuation US 020,777 (CIP) Filed on 2 March 1987 (02.03.87) (71) Applicant (for all designated States except US): GOULD INC. [US/US]; 10 Gould Center, Rolling Meadows, IL 60008 (US).	(72) Inventors; and (75) Inventors/Applicants (for US only) : GORDON, Arnold, Z. [US/US]; 23714 Woodway Road, Beachwood, OH 44122 (US). YEAGER, Ernest, B. [US/US]; 2 Bratenahl Place, Apartment 5F, Cleveland, OH 44108 (US). TRYK, Donald, S. [US/US]; 2206 Delaware Road, Cleveland Heights, OH 44118 (US). HOS-SAIN, M., Sohrab [US/US]; 13590 Cedar Road, University Heights, OH 44118 (US). (74) Agent: ZELLER, James, P.; Marshall, O'Toole, Gerstein, Murray & Bicknell, Suite 2100, Two First National Plaza, Chicago, IL 60603 (US). (81) Designated States: DE (European patent), FR (European patent), GB (European patent), JP, US. Published <i>With international search report.</i>
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(54) Title: IONOMER MEMBRANES IN PRESSURE TOLERANT GAS DIFFUSION ELECTRODES**(57) Abstract**

Gas diffusion electrodes (12) and gas generating or consuming electrochemical cells (10) utilizing the same. The electrode (12) comprises an electronically conductive and electrochemically active porous body defining respective gas and electrolyte contacting surfaces (15, 17), with an ionomeric ionically conductive membrane disposed over the electrolyte contacting surface (17). The membrane comprises a hydrophilic anion exchange resin which is substantially impermeable to gas flow.



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IONOMER MEMBRANES IN PRESSURE
TOLERANT GAS DIFFUSION ELECTRODES

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BACKGROUND OF THE INVENTION

Field of the Invention

10 This invention relates generally to gas
diffusion electrodes and, more particularly, this
invention relates to gas diffusion electrodes adapted
for use in electrochemical cells utilizing an aqueous
alkaline electrolyte and consuming or generating a gas
15 via the electrochemical process occurring within the gas
diffusion electrode.

Description of Related Art

20 The use of gas diffusion electrodes in fuel
cells and metal-air batteries is well known. Gas
diffusion electrodes have also been used in the
electrolysis, either oxidation or reduction, of gaseous
reactants. It is also possible to generate gases in
such electrodes. In general, gas diffusion electrodes
25 take the form of solid porous (gas and liquid permeable)
bodies formed at least in part of an electronically
conductive, electrochemically active material, and may
include a catalyst. Such electrodes generally define an
electrolyte contacting surface and a gas contacting
30 surface. Electrochemical oxidation and reduction occur
at the points in the electrode where the gas to be
oxidized or reduced contacts both the electrolyte and
the active material of the electrode. In the case of
gas generation, electrolyte contacts the active material
35 and gas is generated at this interface.

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Electrochemical cells utilizing such electrodes generally comprise the gas diffusion electrode, a spaced counter electrode, a liquid electrolyte (which is generally aqueous) which contacts both the counter electrode and the gas diffusion electrode, and a gas which contacts the gas diffusion electrode either (1) for reduction or oxidation of the gas or (2) produced via electrolytic generation. Circuit connections are disposed between the counter and gas diffusion electrodes. Additionally, the counter electrode may also be a gas diffusion electrode. A well known example of such a design is the H_2/O_2 fuel cell.

Electrochemical batteries, for example, the metal-air type, commonly utilize either an aqueous alkaline or neutral (e.g., saline) electrolyte, while fuel cells may commonly utilize either acidic electrolytes or alkaline electrolytes. Other types of electrolytes are also used, depending upon the specific gas which is consumed or generated.

The use in electrochemical batteries of an oxygen-containing gas such as air which is reduced at the gas diffusion electrode is well known. However, the gas need not be oxygen-containing nor need it be reduced at the gas diffusion electrode. For example, hydrogen gas is oxidized in some fuel cells. The present invention is generally applicable to all such types of gas diffusion electrodes and cells.

The electronically conductive material in a gas diffusion electrode typically may be carbon. Additionally, a wide variety of catalysts such as platinum or transition metal organometallic catalysts (such as porphyrins) are available.

In various applications, it is desirable that either or both the liquid electrolyte and the gaseous electrode reactant be flowed through the body of the cell over the electrode surfaces. Flowing electrolyte

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and/or flowed gaseous reactant are of course accompanied by a pressure drop across the cell, especially on the electrolyte side. This can lead to excess pressures either on the gas-side or the electrolyte-side of the electrode. Furthermore, it may be desirable in certain circumstances to operate at an elevated gas pressure with respect to the electrolyte pressure. One example of such a situation would be one in which the performance is increased by pressurizing the gaseous reactant. In battery and fuel cell applications, it is desirable to obtain as high a cell voltage as possible at any given current density. One means of accomplishing this is to utilize a relatively high gas pressure or flow rate.

15 The use of a porous (e.g. typically 30-60% porosity) gas diffusion electrode, however, poses difficult flow management problems. When gas pressure exceeds liquid electrolyte pressure by a sufficient amount, "blow-through" of gas through the electrode into the liquid electrolyte results. In conventional gas diffusion electrodes, this so-called "blow-through pressure" is usually much lower than is desirable for tolerance of substantial differential pressures between the gas and liquid sides of the cell.

25 For example, while it may be desirable to operate a cell at a gas vs. liquid differential pressure of up to 10 psi or more, typical air cathodes exhibit a gas blow-through pressure of less than about 0.25 psi. If the differential pressure exceeds the blow-through pressure, pumping of gas into the liquid electrolyte may result. (Typical blow-through pressures range from 0-1 psi, and are determined primarily by interfacial tension and pore size distribution.)

35 Conversely, if the liquid electrolyte pressure is higher than the gas pressure and the differential pressure exceeds the liquid bleed-through pressure,

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liquid may be pumped into the gas side of the cell, which may result in liquid in the gas manifold, with consequent pumping problems and a decrease in cell performance and useful cell life due to flooding of the active layer of the electrode.

In gas-generating cells it is customary for the gas to be generated on the front face (electrolyte-side) of the electrode. The gas is thus generated as bubbles in the electrolyte, which can lead to removal of electrolyte from the cell and increased ohmic losses. Generation of gas in a gas diffusion electrode is more desirable because the gas can exit the cell directly through the back of the electrode. Operation in this mode would require a certain amount of pressure tolerance. Even higher pressure tolerance would be required if the gas is generated in a pressurized state.

If the differential pressure between the gas and liquid sides of an electrochemical cell using a porous gas diffusion electrode is to be maintained at a low level, impractical pressure management problems result, especially in view of the fact that pressure levels vary from point to point on each side of the electrode.

The problems described are not readily amendable to correction by the use of a gas barrier material between the gas and electrolyte sides of the electrode, since such barriers tend to block the flow of electrolytic ions through the electrode and also strongly contribute to voltage losses or do not allow operation at a sufficiently high current density for the desired application. It is desirable to maintain the potential across the electrode at as positive a level as possible while maintaining as high a current density as possible. For example, it may be desired to operate a cell at a current density of up to as high as 500 mA/cm², typically at 100 mA/cm², while minimizing the

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voltage loss across the electrode. A voltage loss of less than 0.05 volts is preferred with voltage losses of up to 0.25 volts being generally acceptable.

One approach to solving these problems is disclosed in Juda and Ilan U.S. Patent No. 4,614,575 (September 30, 1986), which involves the use of nonionic polymeric hydrogel as a layer applied by painting onto the electrolyte side of the gas diffusion electrode. The maximum pressure tolerance disclosed by the Juda, et al. patent is less than or equal to 40 inches of water (1.44 psi or 10.0 kPa), which is significantly less than that possible with the present invention.

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SUMMARY OF THE INVENTION

5 It is an object of the present invention to overcome one or more of the problems described above.

According to the present invention, an ionomeric, ionically conductive, substantially gas impermeable membrane is disposed over substantially the entire electrolyte contacting surface of a gas diffusion
10 electrode adapted for use in a gas generating or consuming electrochemical cell utilizing an aqueous alkaline liquid electrolyte. The membrane comprises a hydrophilic anion exchange resin, and is applied directly on the electrolyte contacting surface in a
15 preformed state.

The invention also comprehends an electrochemical cell comprising the coated gas diffusion electrode spaced from a counter electrode and in contact with an aqueous alkaline liquid electrolyte. A gas to
20 be oxidized, reduced or generated is in contact with the gas side of the electrode, and circuit connections are disposed between the counter and gas diffusion electrodes.

The electrode and cell of the invention are
25 capable of operating at very high gas vs. electrolyte differential pressures at high current densities without significant voltage loss.

Other objects and advantages of the invention will be apparent to those skilled in the art from a
30 review of the following detailed description taken in conjunction with the drawings and the appended claims.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a transverse sectional view of one embodiment of an electrochemical cell in which the invention may be utilized;

Fig. 2 is a schematic sectional view of a typical gas diffusion electrode with which the invention may be utilized;

Fig. 3 is a sectional view of an electrode holder useful in testing gas diffusion electrodes;

Fig. 4 is a schematic exploded perspective view of an electrode assembly adapted for use with the electrode holder of Fig. 3;

Fig. 5 is a schematic transverse sectional view of a gas diffusion electrode useful in the embodiments of Figs. 3 and 4;

Fig. 6 is a series of polarization curves exhibited by an electrode made according to the invention;

Fig. 7 is a series of polarization curves exhibited by another embodiment of an electrode made according to the invention;

Fig. 8 is a plot of potential vs. time for oxygen reduction carried out with the electrode of Fig. 7; and

Fig. 9 is a series of polarization curves for another embodiment of the invention at varying temperatures at a differential pressure of 1 psi (6.9 kPa).

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DETAILED DESCRIPTION OF THE INVENTION

Fig. 1 illustrates a typical embodiment of an electrochemical battery utilizing a gas diffusion electrode. This particular cell is an aqueous alkaline lithium-air cell. It is to be understood that the present invention is not limited to use in electrochemical batteries, nor to cells in which gas is consumed. Rather, the invention finds wide applicability in cells in which gas is either consumed or produced, via either reduction or oxidation, in which any of various electrolytes are used, etc.

The cell of Fig. 1 is described in detail in U.S. Patent No. 4,528,249 (July 9, 1985) the disclosure of which is incorporated by reference.

In Fig. 1, an electrochemical cell, generally designated 10, includes an anode 11, a gas consuming cathode 12, and a metal screen 13 interposed between the anode 11 and cathode 12 within an outer housing 14. In the embodiment of Fig. 1, the screen 13 is in electrical contact with the cathode 12, and is in mechanical (but not electrical) contact with the anode 11.

In the exemplary embodiment, the anode 11 comprises a lithium anode, which may comprise elemental lithium metal or lithium alloyed with alloying material such as small amounts of aluminum.

The screen 13 is not in electrical contact with the anode 11, due to the presence of an insulting, porous lithium hydroxide (LiOH) film which is formed on the anode surface by contact thereof with humid air, and is well known in the art. It is to be noted, however, that this particular feature is peculiar to the aqueous lithium-air cell. In other types of metal-air batteries and fuel cells, either an electrically insulating porous separator layer or a simple electrolyte gas would be used. It should also be noted that the screen 13 is

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necessary to help restrain the gas diffusion electrode 12 against the gas pressure.

The cathode 12 is in this case an air cathode through which atmospheric air flows. Those skilled in the art, however, will recognize that such a cathode may operate with any oxygen-containing gas.

One surface 15 of the cathode 12 is exposed to ambient atmosphere (or a source of another oxygen-containing gas) in a chamber 16 of the housing 14, and the opposite surface 17 of the cathode 12 is contacted by the liquid electrolyte 18 which is flowed through a second chamber 19 in the housing 14 as by a suitable pump 20. In the illustrated embodiment, the electrolyte is provided from a reservoir 21 for suitable delivery when needed.

In Fig. 1, the anode 11 and cathode 12 each terminate in a respective terminal 26 or 28, and are connected to a load 30 through suitable circuit connections 32.

Typically, the cathode 12 comprises a structure formed of a suitable porous hydrophobic material, such as polytetrafluoroethylene (PTFE), mixed with carbon black, both pure and catalyst-containing. A preferred form of the cathode 12 is described below in connection with Fig. 2.

The screen 13 illustratively may comprise a woven metal wire screen formed of suitable non-corroding metal, which in the case of alkaline electrolyte may be nickel or silver plated nickel. If desired, the screen 13 may serve as a current collector if connected to the terminal 28.

In the embodiment of Fig. 1, liquid electrolyte, in this case an aqueous alkaline electrolyte such as aqueous lithium hydroxide, is flowed through the chamber 19 by means of the pump 20. As such, there is a pressure drop across the chamber 19 in the direction of flow.

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Further, air is flowed through the chamber 16 by means not shown, and there is a small pressure drop across the chamber 16 in the direction of flow by virtue thereof. However, those skilled in the art will
5 recognize that the pressure drop across the gas chamber 16 is small in comparison to that in the electrolyte chamber 19.

As set forth above, Fig. 1 is intended to be exemplary only, as the invention is applicable to any of
10 a variety of types of gas diffusion electrodes and electrochemical cells.

Fig. 2 is a schematic depiction of the structure of a preferred embodiment of the cathode 12. As shown in Fig. 2, the electrode 12 is formed
15 essentially of a two or three component laminate defining the gas contacting surface 15 and the opposed electrolyte contacting surface 17. An electronically conductive porous gas carrier layer 40 defines the gas contacting surface 15 and typically is a mixture of a
20 hydrophobic material such as porous PTFE (e.g. Teflon brand PTFE) with a carbon black such as Shawinigan black (Chevron Chemical Co., Olefins and Derivatives Div., Houston, TX). A so-called "active layer" 42 comprises a layer 44 which comprises a mixture of carbon black, or
25 catalyst supported on carbon black, and PTFE. An optional layer 46 of catalyst is disposed on the layer 44 at an interface 50. As shown in the schematic of Fig. 2, layers 44 and 46 appear to be discrete layers, but in practice may define a single layer or two layers,
30 since the catalyst is generally adsorbed onto the surface of the material of layer 44. In some cases, the materials of the three layers 40, 44 and 46 may be intermixed in a single layer.

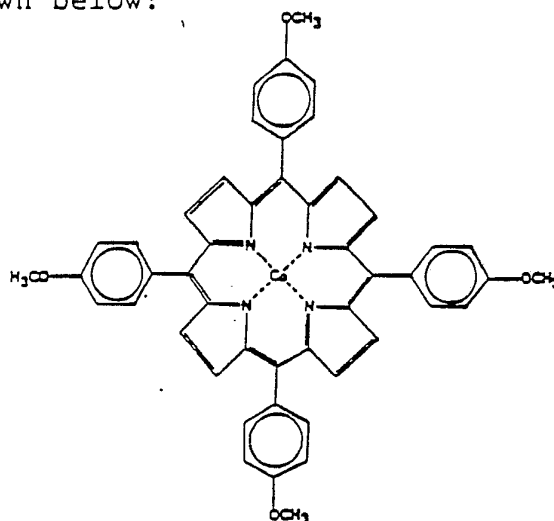
The entire structure of the electrode 12 of
35 Fig. 2 is porous, generally exhibiting a porosity of 30-60%.

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A typical catalyst forming the layer 44 is heat-treated cobalt tetramethoxyphenyl porphyrin (CoTMPP) on a carbon black such as Vulcan XC-72 (Cabot Corp., Billerica, MA). The heat treatment is typically
5 done at 400-1000°C in inert gas. The structure of CoTMPP is shown below:

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The material is a currently preferred catalytic material. Other catalysts include platinum,
20 MnO₂ and transition metal macrocycles other than CoTMPP.

The function of the layer 40 is to allow ready transmission of gas to the active layer 44. Its hydrophobicity also acts to repel liquid electrolyte which exists in the active layer 44 in order to avoid
25 leakage of the liquid electrolyte into the gas side of the cell. It also provides electronic conductivity.

The requisite consumption or generation of gas takes place in the active layer 44 where gas and liquid meet in the presence of the active material and optional
30 catalyst, as is well known in the art.

Fig. 3 illustrates an electrode holder useful in measuring characteristics of gas consuming or generating electrodes. The electrode holder, generally designated 60, comprises a solid body 62 of a
35 nonconductive material defining a gas inlet passage 64 communication with a cell gas chamber 66 which in turn

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communicates with a gas outlet passage 68. (A typical material of construction for the body 62 is 3M's Kel-F brand chloro fluorocarbon polymer.) An annular electrode seat 70 is defined in the body 62 in order to position an electrode assembly (not shown in Fig. 3) which includes a gas diffusion electrode, generally designated 72, adjacent the cell chamber 66. A conductive (e.g. platinum) wire 74 contacts the seat 70 and extends therefrom through the outlet passage 68. A threaded plug 76 of the same material as the body 62 retains an electrode assembly 80 (shown in Fig. 4) in place in the body 62.

Fig. 4 illustrates the electrode assembly, generally designated 80, which includes the gas diffusion electrode 72 of Fig. 3. The electrode 72 is shown in schematic form in Fig. 4 and formed as cylindrical disk defining gas and electrolyte contacting surfaces 82 and 84 respectively. These surfaces are analogous to surface 15 and 17 of Fig. 1. An annular conductive metal (e.g. platinum) ring 86 is disposed on the gas surface 82 between the gas surface 82 and an annular rubber gasket 88. A similar rubber gasket 90 is disposed on the electrolyte side of the electrode 72 between the electrolyte contacting surface 84 and an annular ring 92 of the same material as the body 62.

When the assembly 80 is in place in the seat 70 of the electrode holder 60, the ring 86 is in electrical contact with the wire 74 and acts as a current collector.

The electrode 72 as shown in Figs. 3 and 4 is schematic and these figures do not illustrate certain components such as the hydrophobic backing layer and associated screens. Fig. 5 illustrates an exploded sectional schematic view of a typical embodiment of the diffusion electrode 72. A silver plated nickel screen 100 is adjacent to and in contact with an electronically

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conductive hydrophobic backing layer 102, typically of Telfon brand PTFE plus carbon black, which defines the surface 82. An active layer 104, which may include a catalyst on carbon black, is adjacent to the layer 102 and defines the surface 84. A membrane 106 is applied to the surface 84 and is in contact with a steel reinforcement screen 108. The membrane 106 is described in detail below.

When constructed, the screen 100 is not in physical or electrical contact with the ring 86 and thus merely acts as a physical restraint. The gas inlet passage 64 and gas outlet passage 68 are connected with gas flow regulating means (not shown) which regulate the flow of gas through the passages 64 and 68 and the cell chamber 66, and thus the gas pressure in the chamber 66.

Those skilled in the art will recognize that the screens 100 and 108 may be imbedded in the layers 102 or 106, respectively, and that the layers 102 and 104 may form a single homogeneous layer if desired.

When the electrode 72 is in place in the assembly 80 in the electrode holder 60, a central circular segment of each of the electrode sources, respectively. The electrode holder body 62 is positioned in a test cell such that the electrode surface 84 is exposed to a flowing or non-flowing (e.g. stirred) electrolyte. The remainder of the cell and associated temperature control means, etc. are omitted for clarity.

For operation at elevated gas/electrolyte differential pressures, the steel screen 108 acts as a reinforcement to prevent physical rupture of the electrode 72. Flow-through of gas from the cell chamber 66 through the electrode 72 into the electrolyte side of the cell is prevented by the membrane 106 as described below.

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The membrane 106 is a preformed membrane which is applied directly to the active layer surface 84 of the electrode preferably without adhesives or other intervening layers. The membrane is of an ionomeric anionic exchange resin which is substantially impermeable to the gross passage of gas. The material is an anion exchange resin and thus conducts hydroxide (OH) ions as well as water. It is also possible for bulk electrolyte to slowly diffuse through the membrane. The electrode 72 may thus be effectively wetted through the membrane 106, while the membrane 106 is virtually impermeable to gas flow.

The membrane 106 is ionomeric, and is quite hydrophilic and readily contains and transfers ionic charge, thus allowing for minimal excess voltage loss relative to conventional gas diffusion electrodes.

Although relative performance varies, any of a wide variety of anion exchange membranes are suitable. Several are available from the RAI Research Corporation and from Sybron Chemical, Inc. Both are distributed by The Electrosynthesis Company, Inc. of East Amherst, New York, under the trademarks RAIPORE® and IONIC, respectively. For example, RAIPORE R-1035 anion exchange membrane is a quaternized vinylbenzylamine grafted polytetrafluoroethylene film available in 1 mil (0.025 mm) thickness. RAIPORE R-4035 anion exchange membrane is a quaternized vinylbenzylamine graft on a 2 mil (0.051 mm) preformed fluorinated polymer film. RAIPORE R-5035 (L or H) anion exchange membrane is a quaternized vinylbenzylamine grafted polyethylene exchange membrane available in 8 mil thickness. This material is available in low or high electrolytic resistances. IONAC MA 3475 anion exchange membrane comprises a quaternized tetraalkyl ammonium polymer and is 16 mils (0.41 mm) thick.

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A currently preferred anion exchange membrane is the caustic-resistant membrane (AR 108-401) from Ionics, Inc. of Watertown, Massachusetts. This material also comprises a quaternized (tetraalkyl) ammonium polymer and is approximately 1.0 mm (about 40 mils) thick.

In general, useful membrane materials are characterized as being hydrophilic anionic exchange resins and these are understood by the art to contain cationic functional groups.

In practice, the membrane may be applied to the electrode active layer surface by mere application of pressure.

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EXAMPLES

The following specific examples are intended to illustrate the practice of the invention but are not to be considered limiting in any way.

The following generalized experimental procedure was followed in each example.

Cobalt tetramethoxyphenyl porphyrin (CoTMPP) was adsorbed on Vulcan XC-72 carbon (Cabot) by agitating a suspension of the latter in a solution of 10^{-4} M CoTMPP in acetone for at least 24 hours. The amount of the adsorbed macrocycle was calculated spectrophotometrically by determining its loss from the filtered solution. The solid catalyst/carbon was air-dried and then heat-treated to 450°C in a horizontal tube furnace under continuous flow of purified argon.

Porous gas-fed electrodes were fabricated as follows: dilute (~2 mg/mL) Teflon T30 B aqueous suspension (Du Pont) was slowly added to an aqueous suspension of the catalyst/carbon while the latter was ultrasonically agitated. The mixed suspension was then filtered with a 1µm pore size polycarbonate filter membrane. The paste was shaped into a 1.75 cm diameter disk in a stainless steel die using hand pressure. This disk was then applied to another disk, ~0.5 mm thick, of Teflon-carbon black hydrophobic porous sheet material (Eltech Systems Corp., Fairport Harbor, OH) which contained a silver-plated Ni mesh. This dual layer disk was pressed at 380 kg cm⁻² at room temperature and then heat-treated at 290°C for 2 hours in flowing helium.

The gas-fed electrode was placed in a Teflon-Kel-F electrode holder as shown in Fig. 3. The gas (O₂ or air) pressure was applied to the back-side (hydrophobic layer) of the electrode and was monitored at the outlet. A needle valve at the outlet was used to regulate the gas pressure.

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The O₂ reduction measurements for the gas-fed electrodes were done galvanostatically in a concentrated alkaline electrolyte (0.5 M LiOH in 2:1 v/v 50% NaOH and 45% KOH) at 80-83°C with a research potentiostat (Stonehart Associates, Model BC1200). This potentiostat is equipped with positive feedback IR drop compensation and correction circuits. The IR drop correction adjustment is made while monitoring the potential on an oscilloscope, with the current repetitively interrupted for 0.1 ms every 1.1 ms. This procedure corrects for any IR drop that is external to the electrode itself. Nickel foil was used as the counter electrode and a Hg/HgO, OH⁻ reference electrode was used. The polarization curves were recorded under steady-state conditions.

Fig. 6 depicts a polarization curve for oxygen reduction at one atmosphere pressure (i.e. substantially zero pressure differential between gas and electrolyte sides of the electrode) with a one mm thick layer of Ionics, Inc. anion exchange membrane applied to the electrolyte side of the electrode with a stainless steel screen applied over the membrane. The curves depict operation using both air and pure oxygen with the electrodes in a fully broken-in state at a temperature of 80-83°C.

Fig. 6 demonstrates that a current density of 100 mA/cm², a potential of approximately -0.116 V was obtained using oxygen. The is good performance, the potential being approximately 45 mV more negative than that obtained for an electrode without the membrane.

Fig. 7 illustrates the results of oxygen reduction tests using air or oxygen (Run 1 and 2) and oxygen after the electrode had been fully broken-in for 18 hours at a current density of 100 mA/cm² (Run 3), all at a differential gas to electrolyte pressure of 1 psi. This represent a twofold increase in overpressure

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compared to the upper practical limit of prior art.
This test was carried out at a temperature of 80-83°C.

Comparison of the polarization curves of Figs. 6 and 7 indicates that at least equivalent performance is obtained according to the invention at elevated differential pressures as is obtainable at zero differential pressure.

Fig. 8 depicts the variation of potential with time for oxygen reduction carried out with the electrode of Figs. 6 and 7 at a gas/electrolyte differential pressure of 1 psi at a constant current density of 100 mA/cm² at 80-83°C.

As can be seen, potential continuously improved (i.e. became less negative) over time. Thus, at a constant current density a steady improvement in voltage was observed. This is probably due in part to improved wetting of the electrode during use, but is not believed to be exclusively due to this factor.

The polarization curves of Fig. 9 depict the temperature effect on oxygen reduction polarization curves for the electrode of Figs. 6 through 8 operated at 1 psi gas/electrolyte differential pressure.

As seen in Fig. 9, at current densities above about 1 mA/cm², better results (in terms of higher potential) are exhibited at higher temperatures for any given current density. This phenomenon is reversed below about 1 mA/cm², probably due to mixed potential control effects.

The test of Fig. 9 was carried out with pure oxygen as the feed gas on electrodes that had been partially broken in (2 hours only).

Another advantage of the invention is the fact that the polymer membrane stabilizes catalysts absorbed in the electrode by preventing or inhibiting dissolving of the catalysts in the electrolyte, thus preventing degradation of performance over time due to catalyst

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dissolution. In fuel cells, electrolyte tends to redistribute itself within the body of the cell. A further advantage is that this is prevented according to the invention. Furthermore, in some cases not only is potential loss minimized but voltage can actually be improved.

Operation at high current densities (e.g. up to about 1 A/cm²) or more is possible according to the invention.

Examination of the polarization curves presented above shows that according to the invention, very great increases in current (i.e. in current density) are available with only minor increases in the potential driving force over a wide range of current densities.

The foregoing detailed description is given for clearness of understanding only, and no unnecessary limitations are to be inferred therefrom, as modifications within the scope of the invention will be obvious to those skilled in the art.

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CLAIMS

We claim:

5 1. A gas diffusion electrode adapted for use
in a gas generating or consuming electrochemical cell
utilizing an aqueous alkaline liquid electrolyte, said
electrode comprising an electronically conductive and
electrochemically active porous body defining respective
10 gas and electrolyte contacting surfaces, and an
ionomeric ionically conductive membrane disposed over
substantially the entire said electrolyte contacting
surface, said membrane comprising a hydrophilic anion
exchange resin and being substantially impermeable to
15 gas flow.

2. The electrode of claim 1 wherein said
membrane is formed prior to application to said
electrolyte contacting surface and is disposed directly
20 on said electrolyte contacting surface.

3. The electrode of claim 1 wherein said
resin comprises a polymer backbone grafted with
quaternized vinyl benzene amine.
25

4. The electrode of claim 3 wherein said
polymer backbone comprises a fluorinated polymer.

5. The electrode of claim 4 wherein said
30 polymer backbone comprises polytetrafluoroethylene.

6. The electrode of claim 1 wherein said
resin comprises a quaternized ammonium polymer.

35 7. The electrode of claim 6 wherein said
resin comprises a tetraalkylammonium polymer.

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8. The electrode of claim 1 wherein said porous body comprises a laminate of a porous hydrophobic layer defining said gas contacting surface, and a porous active layer defining said electrolyte contacting surface, said active layer comprising an electrochemically active material.

9. The electrode of claim 8 wherein said electrochemically active material comprises carbon.

10. The electrode of claim 8 wherein a catalyst is adsorbed on said active material.

11. The electrode of claim 10 wherein said catalyst is cobalt tetramethoxyphenyl porphyrin.

12. An electrochemical cell, comprising:
(a) a gas diffusion electrode comprising an electronically conductive and electrochemically active porous body defining respective gas and electrolyte contacting surfaces, and an ionomeric ionically conductive membrane disposed over substantially the entire said electrolyte contacting surface, said membrane comprising a hydrophilic anion exchange resin and being substantially impermeable to gas flow;
(b) a counter electrode spaced from said gas diffusion electrode;
(c) an aqueous alkaline liquid electrolyte in contact with said counter electrode and with said membrane on said electrolyte contacting surface of said gas diffusion electrode;
(d) either a gas to be consumed via oxidation or reduction or gas formed via electrolytic generation in contact with said gas contacting surface of said gas diffusion electrode; and,

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(e) circuit connections between said gas diffusion electrode and said counter electrode.

5 13. The cell of claim 12 wherein said gas is an oxygen containing gas.

14. The cell of claim 13 wherein said gas is air.

10 15. The cell of claim 12 wherein at least one of said liquid electrolyte and said gas are flowed through said cell.

15 16. The cell of claim 12 wherein said membrane is formed prior to application to said electrolyte contacting surface and is disposed directly on said electrolyte contacting surface.

20 17. The cell of claim 12 wherein said resin comprises a polymer backbone grafted with quaternized vinyl benzene amine.

25 18. The cell of claim 17 wherein said polymer backbone comprises a fluorinated polymer.

19. The cell of claim 18 wherein said polymer backbone comprises polytetrafluoroethylene.

30 20. The cell of claim 12 wherein said resin comprises a quaternized ammonium polymer.

21. The cell of claim 20 wherein said resin comprises a tetraalkylammonium polymer.

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22. The cell of claim 12 wherein said porous body comprises a laminate of a porous hydrophobic layer defining said gas contacting surface, and a porous active layer defining said electrolyte contacting surface, said active layer comprising an electrochemically active material.

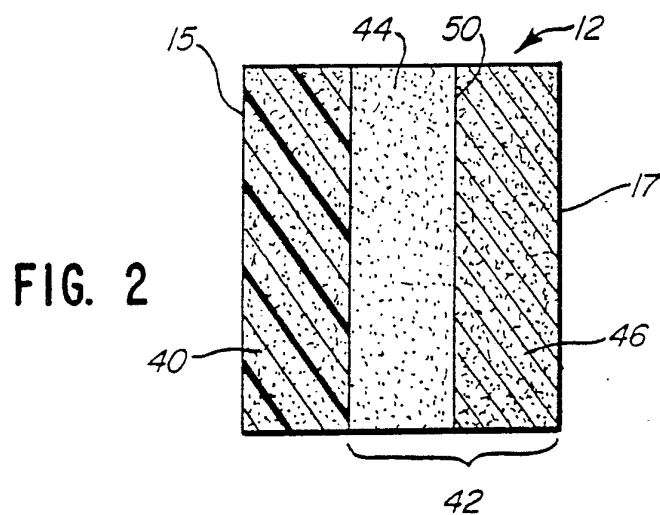
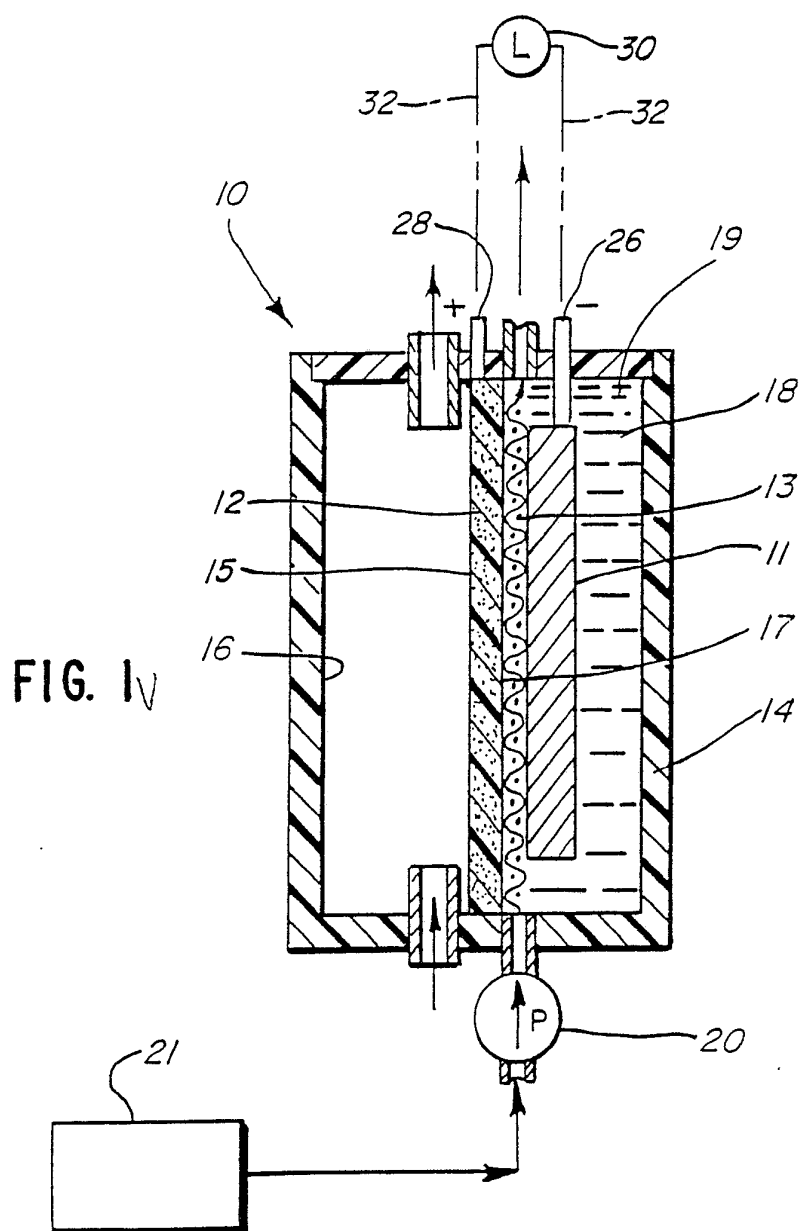
23. The cell of claim 22 wherein said electrochemically active material comprises carbon.

24. The cell of claim 22 wherein a catalyst is adsorbed on said active material.

25. The cell of claim 24 wherein said catalyst is cobalt tetramethoxyphenyl porphyrin.

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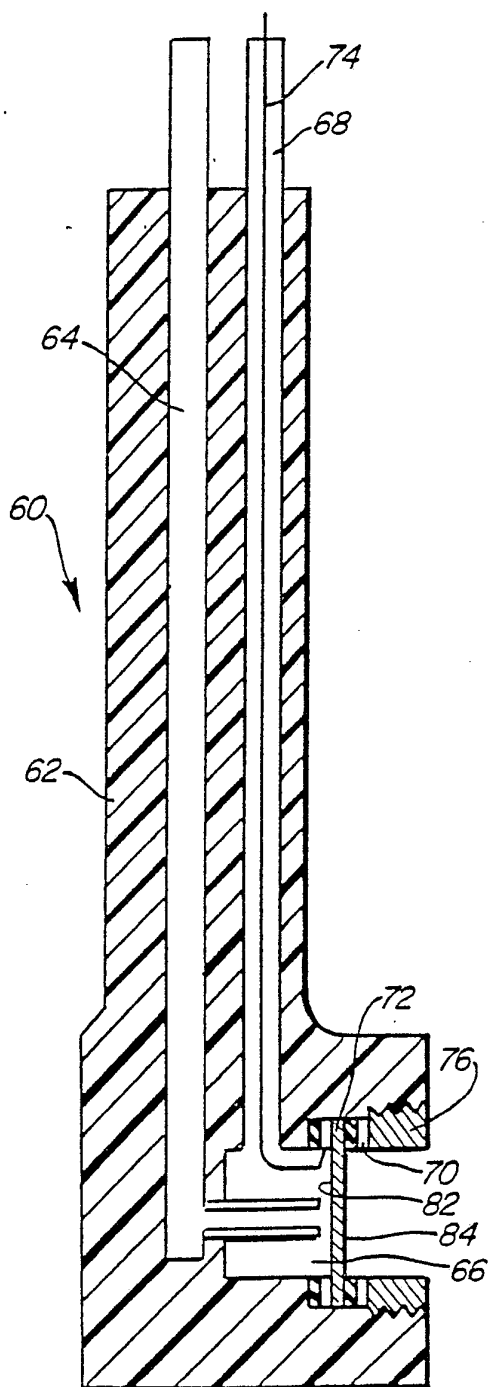


FIG. 3

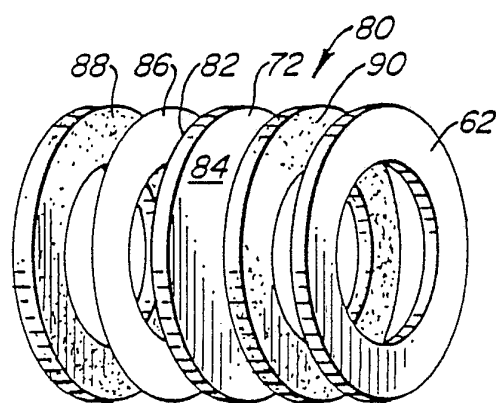
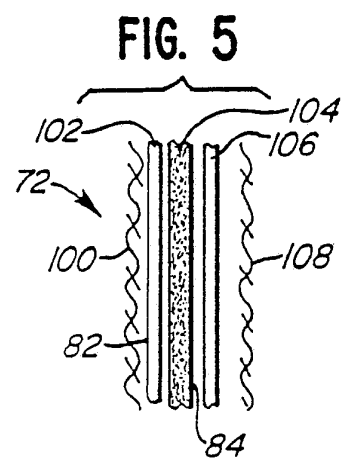


FIG. 4

FIG. 6

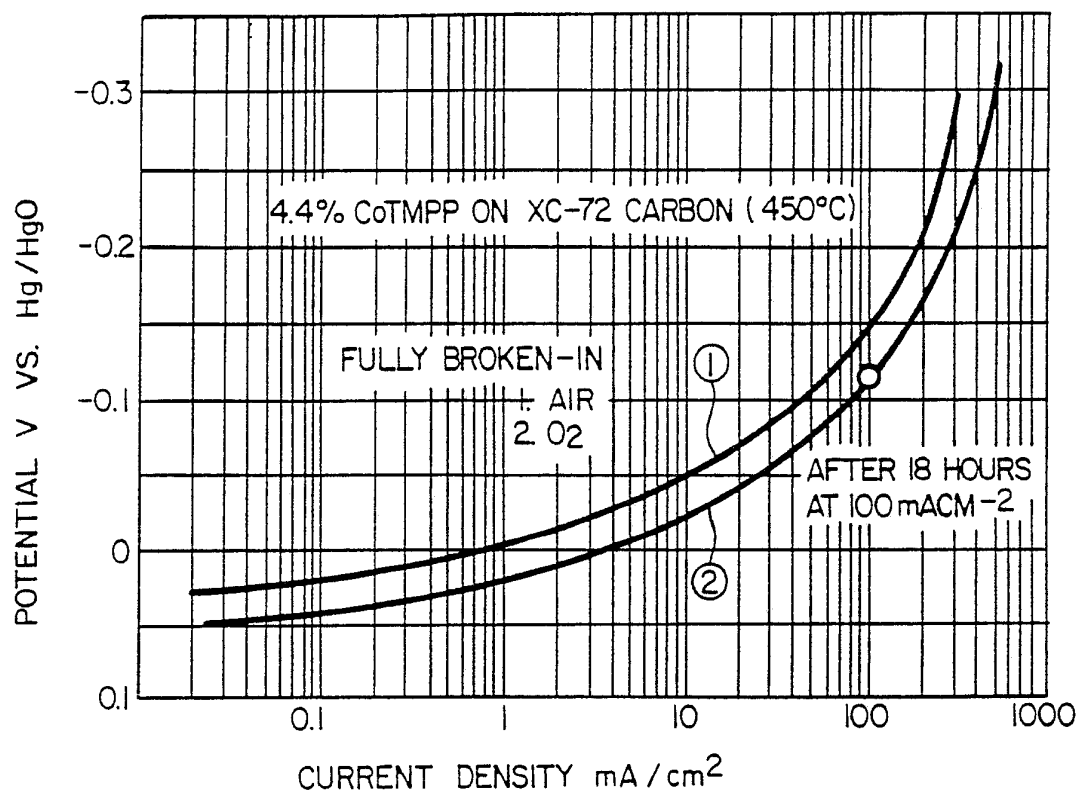


FIG. 7

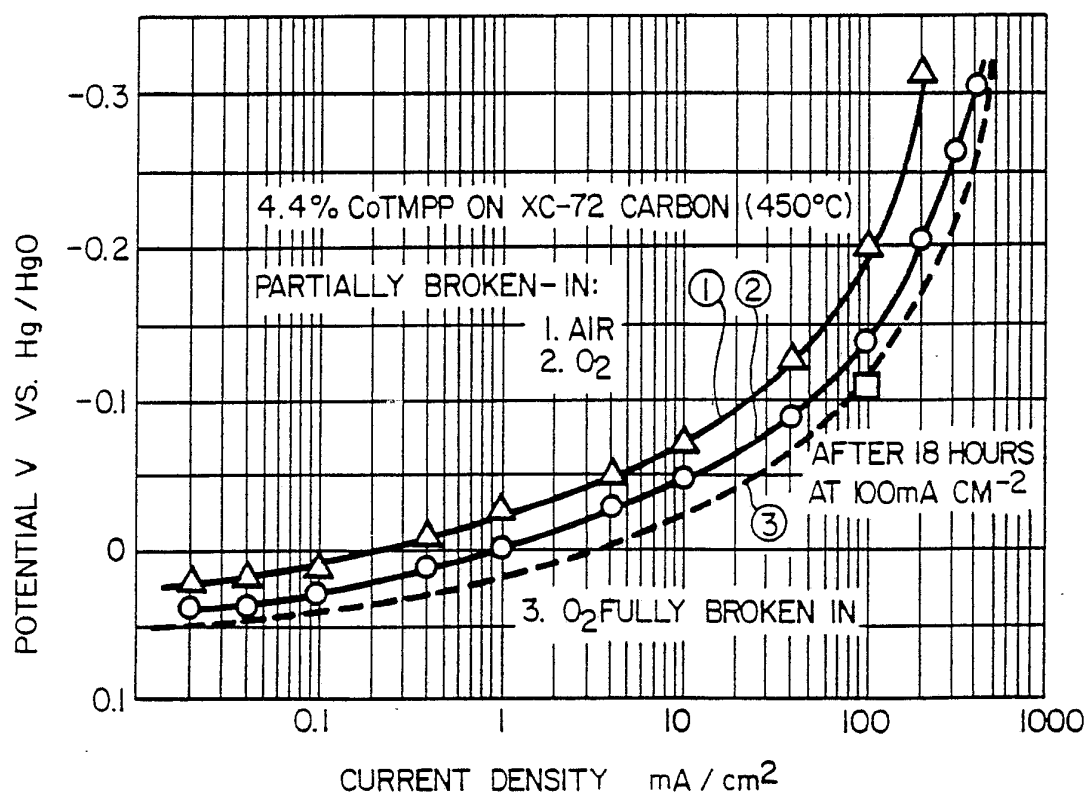


FIG. 8

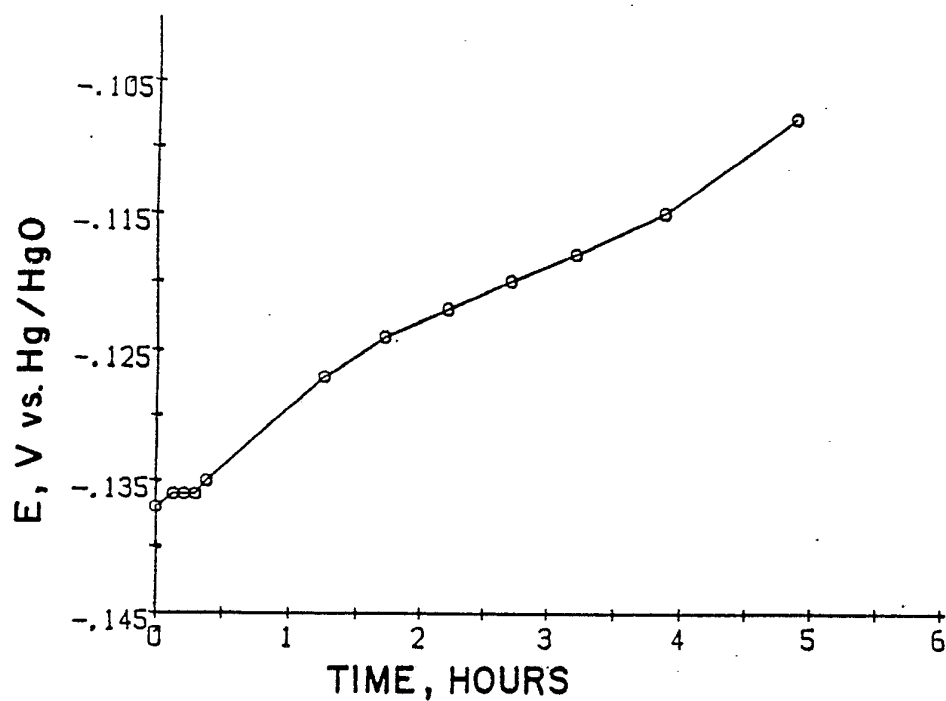
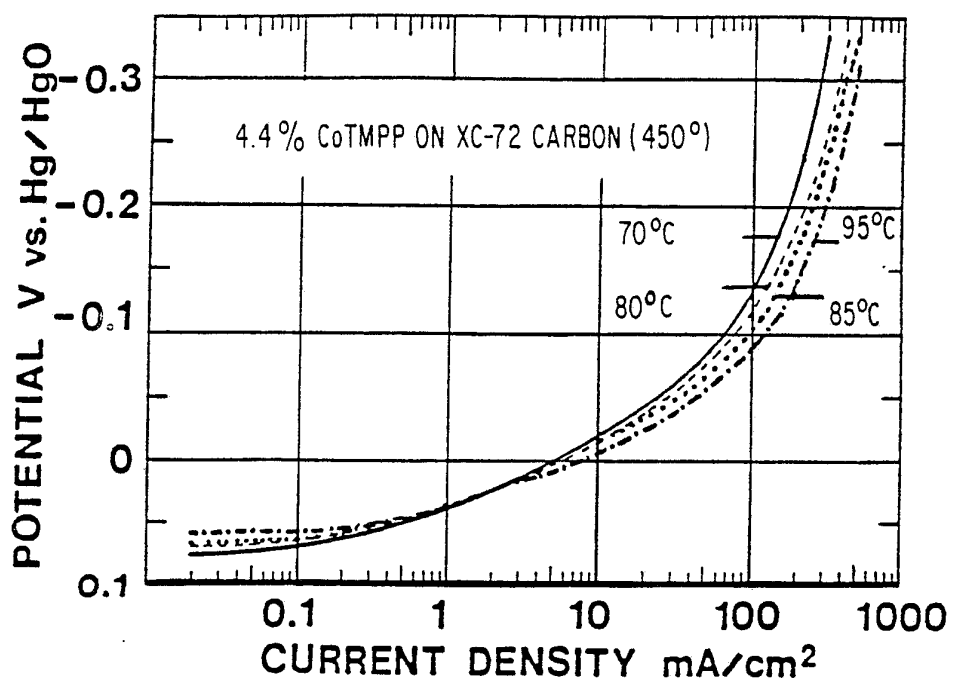


FIG. 9



INTERNATIONAL SEARCH REPORT

International Application No. PCT/US88/00622

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC(4): C25B9/00, 11/03, 11/12, 13/00 HO1M 4/86, 4/90, 4/96		
USC1: 204/252, 282, 283, 294, 296		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	204/252, 282, 283, 294, 296 429/41-43	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
<u>X</u>	U.S. A, 4,090,931 (MOTANI)	1-2 and 6-7
Y	23 May 1978 See entire document.	3-5
Y	U.S. A, 4,615,954 (SOLOMON)	8-25
	07 October 1986 See entire document.	
A, E	U.S. A, 4,732,660 (FLOWMAN)	
	22 March 1988 See entire document.	
* Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
02 May 1988		08 JUN 1988
International Searching Authority		Signature of Authorized Officer
ISA/US		Kathryn Gorgos