THE APPLICATION OF DOW CHEMICAL'S PERFLUORINATED MEMBRANES IN PROTON-EXCHANGE MEMBRANE FUEL CELLS

G.A. Eisman
The Dow Chemical Company
Freeport, Texas 77541

Dow Chemical's research activities in fuel cells revolve around the development of perfluorosulfonic acid membranes useful as the proton transport medium and separator. The following work will outline some of the performance characteristics which are typical for such membranes.

INTRODUCTION

The use of fuel cells as a power source has been successful for manned space applications on short-lived missions as is evident from the Gemini, Apollo and Orbiter missions. In the latter two programs, the alkaline technology has been the system of choice; whereas the Gemini program experimented with the proton-exchange membrane technology (PEM). Although the alkaline technology has enjoyed a certain degree of popularity among the various fuel cell concepts for space applications, there are no clear-cut favorites for one fuel cell technology over others when the duty cycle becomes long as it would in extensive long-lived missions.

Until recently, the PEM fuel cell technology has been a laboratory curiosity except for a few brief missions during the Gemini program. Although attractive for many reasons, including long life (Ref. 1) and reduced failure rates as a result of pressure upsets (when compared to free electrolyte systems), the lower power and efficiency characteristics have kept the technology shelved. Recently, Dow Chemical developed a new perfluorosulfonic acid proton transporting ionomer which can be applied in fuel cells (Ref. 2-3). The results of tests with the Dow membrane as reported in the literature (Ref. 4-7), have demonstrated that the materials have a significantly reduced internal resistance. For fuel cells, this reduced resistance translates directly to performance and efficiency since a membrane with this characteristic results in significantly enhanced proton transport rates with a lower emf driving force.

The performance of a proton-exchange ionomer in a fuel cell is related to many factors, some of which include membrane ionic activity, hydration level, visco-elastic properties, as well as electrode characteristics, cell design, and mode of operation. This paper will be concerned with the properties of the Dow materials which are related to performance characteristics of a PEM fuel cell system.

EXPERIMENTAL

The Dow experimental membrane utilized in this study is characterized by having an ion-exchange capacity of 1.13 and being .013 cm in thickness. All cell tests were carried out in a single cell 50 cm^2 active area PEM fuel cell designed and built by the Hamilton-Standard Corp. for Dow Chemical. The cell is a modified version of the hardware delivered to Los Alamos National Laboratory under a transportation contract with Hamilton-Standard (NASA Contract #P.O. No.9-X53-D6272-1).

The current interrupt experiments were carried out using a home-made fast response switching device coupled to a Nicolet storage oscilloscope.

The membrane and electrode assemblies were fabricated using proprietary techniques. The electrode loadings were 2 mg/cm^2/side.

RESULTS AND DISCUSSION

Membrane Properties

The new perfluorosulfonic acid membranes recently introduced by Dow Chemical, as referenced above, exhibit significantly lower IR losses resulting in membranes which can be operated at ultra-high current (power) levels. This behavior is presented in Figure 1 along with the state-of-the-art performance characteristics for a commercially available fuel cell membrane manufactured by DuPont under the tradename Nafion ®. As can be seen from the data, the Dow materials can generate substantially higher current densities than systems utilizing the DuPont material. The voltage losses which appear to be great at 3500 amps/ft^2 (3771 amps/cm^2) are actually a result of using high resistant cell plates and hardware. It is approximated that the loss due to the cell hardware is close to 200 mv.

Although the membrane is capable of higher current levels, the attractive characteristic and one which will be critical for long space flights is the higher voltage at the lower current densities, i.e., 100 - 500 amp/ft^2. This enhanced voltage is a direct result of the reduced internal resistance of the membrane which is attributed mainly to the high sulfonic acid ionic content responsible for proton transport. The advantages of such a higher voltage are many, but the most important is an increase in the total electrochemical efficiency.

The Dow membrane is based on chemistry which leads to a reduced mass in the side-chain which is bonded to the long CF$_2$ backbone. Presented in Figure 2 is the chemistry for the synthesis of the monomer and the copolymerization step with the tetrafluoroethylene; while in Figure 3, the resultant structure is depicted. Also presented in Figure 3 for comparative purposes is the structure of DuPont's Nafion.

The membrane properties pertinent for fuel cell operation are tabulated in Table 1 for the Dow fuel cell membranes. Such characteristics as ionic conductivity, water permeability, gas permeation, and properties related to mechanical strength are listed. The data presented in the table covers a range rather than single data points because, at this time, Dow has prepared numerous membranes of different ion exchange capacity which all have been successfully tested in fuel cell operation.

Fuel Cell Test Results

The hardware used during the membrane performance tests is a modified version of the cell presented in Figure 4. The hardware utilizes carbon/Kynar plates with a 50 cm^2 active area. There is a heat exchanger on each side of the reactor compartment and an internal humidification compartment.

Presented in Figure 5 is a polarization curve of the membrane previously described. As can be seen from the figure, the membrane is capable of operating at high efficiencies at low current densities or lower efficiencies at high current densities. The resistance in the ohmic region is .220 ohm-cm^2 (2.37X10^{-4} ohm-ft^2). This data contains the resistance of the package and therefore is not an IR free number. It should also be pointed out that the polarization data at each point was recorded only after the system appeared to reach equilibrium at the given current density. Figure 6 is a plot of the same data as Figure 5 but expanded in the region of 0 to 500 amps/ft^2.

Although steady-state performance can be achieved at any current density demonstrated in the polarization data of Figure 5, the voltage of the cell vs. time at a single current density (200 amps/ft^2) for a relatively short period of operation is presented in Figure 7. These data include predetermined shut-down periods on a daily basis. As can be seen from the plot, the voltage over the time element investigated was invariant.

Current interrupting was carried out in order to determine the electronic resistance effects of the hardware and remaining ionic resistance and over-voltage of the membrane and electrode package. The tests were carried out at 100 amps/ft^2 (and less) due to a limitation in the interrupting switching device. A typical result of the tests is depicted in Figure 8 for the current membrane under study. As can be seen from the data presented in the figure, the IR free component is approximately 15 mv at this current density and was measured at approximately 50 microseconds after the current break. This translates to an internal resistance of 3 milliohms at 100 amps/ft^2 (5 total amps) or .15 ohms-cm^2. When the IR free voltage (.933) at 100 amps/ft^2 is subtracted from the open circuit potential (1.05 V) the resulting voltage due to the membrane, membrane/electrode, and electrode overvoltages, amounts to approximately 117 millivolts. In order to determine the package ohmic contribution, the cell resistance is subtracted from the slope data. Such a calculation yields .07 ohm-cm^2 (.222 - .15 ohm-cm^2). A list of IR free values vs. at current densities between 25 and 100 amps/ft^2 are presented in Table 2.

In order to determine the response times for the membrane and electrode assembly in the Dow hardware utilizing a Dow perfluorosulfonic membrane, a series of tests was carried out not unlike the above whereby the current was "interrupted" numerous times. In these tests, the cell was allowed to reach equilibrium at the desired current density prior to the interruption. The cell voltage was monitored as a function of time and recorded (Figure 9) during each interruption. As can be seen from the data, the time required to shut the electronic component of the cell off was on the order of 50 microseconds. Such a rapid shut-down rate should be construed to be an advantage from an operating (safety) point of view.

In addition to proceeding from a power producing mode to open circuit, the response times were also monitored for when the system is at open circuit and then dropped across a resistance to generate the 100 amps/ft^2. The results of these tests are essentially identical to those when the current path was opened, both in behavior as well as response time.

For a power device to be practical the cell response time must be fast and efficient and without the generation of transients. In both of the above response time tests, the time required to reach various percentages of full power are presented in Table 3. In all cases, it is seen that the time to reach full "on" power was short, but in all cases 90% of full power was achieved within 80 milliseconds.

Finally, since the fuel cell was turned off and on several times throughout the test, it is important to demonstrate the reliability and resiliency of the PEM system by presenting polarization data after such system upsets. The series of polarization curves generated throughout the week-long run was carried out in order to determine if changes were occurring to the membrane/electrode assembly. Presented in Figure 10 is a series of current-voltage sweeps (IR included) taken at the times labeled on each curve. After the numerous on-off cycles, as determined from the polarization behavior, no apparent degradation was taking place.

CONCLUSIONS

The results of tests utilizing a new experimental membrane useful in proton-exchange membrane fuel cells were presented. The high voltage at low current densities can lead to higher systems efficiencies while, at the same time, not sacrificing other critical properties pertinent to membrane fuel cell operation. A series of tests to determine response times indicated that "on-off" cycles are on the order of 80 milliseconds to reach 90% of full power. The IR free voltage at 100 amps/ft^2 was determined and the results indicating a membrane/electrode package resistance to be .15 ohm-cm^2 at 100 amps/ft^2.
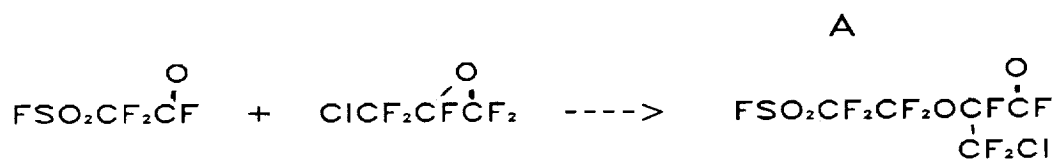
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6. Vanderborgh, N. E.; Spirio, C. A.; Huff, J. R.; "Advanced Fuel Cell Systems for Transportation Applications," Proceedings of the International Seminar on Fuel Cell Technology and Applications, The Netherlands, 26 October, 1987, pp 253-262.

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FIGURE 1
VOLTAGE-CURRENT POLARIZATION DATA

VOLTAGE

DOW

NAFION-117
80 PSI-O2/40 PSI-H2
....

CURRENT DENSITY (ASF)
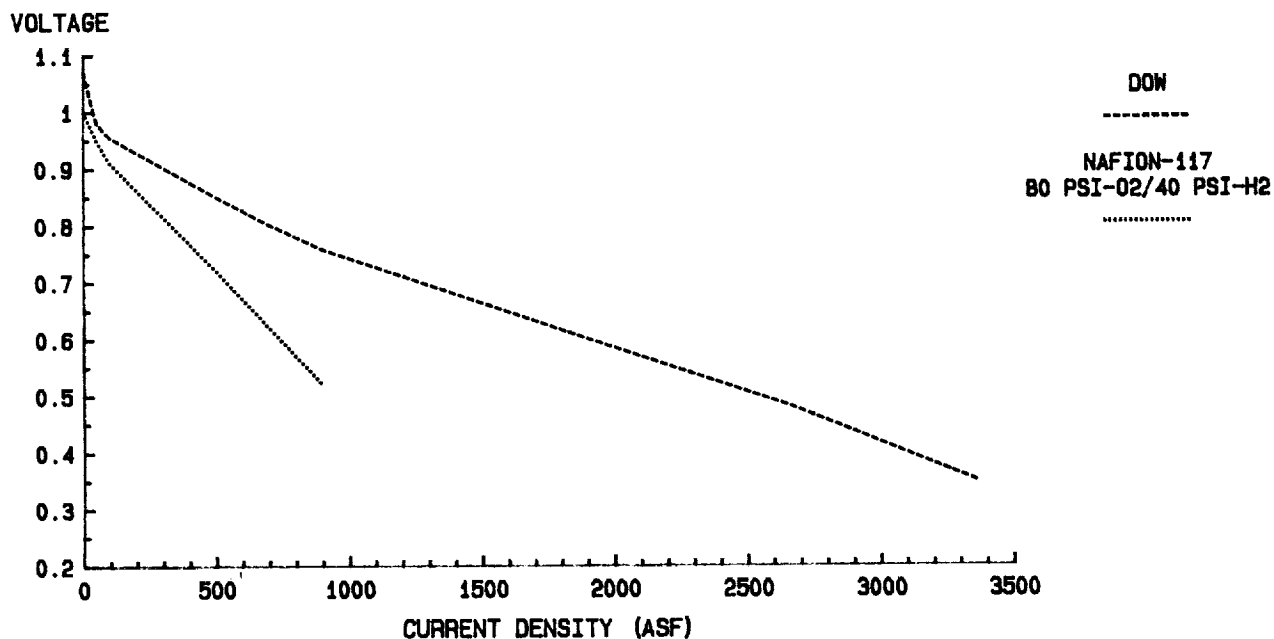
H2/O2 40/60 PSIG 80 C
2 MG/CM2/SIDE Pt

FIGURE 2

CHEMISTRY OF THE DOW CHEMICAL COMPANY

A

FSO_2CF_2CF + $ClCF_2CFCF_2$ ----> $FSO_2CF_2CF_2OCFCF$
                                                    CF_2Cl

B

A + Na_2CO_3 -----> $FSO_2CF_2CF_2OCF=CF_2$

B + $CF_2=CF_2$ ----> POLYMER

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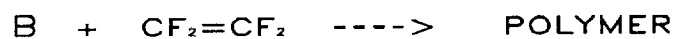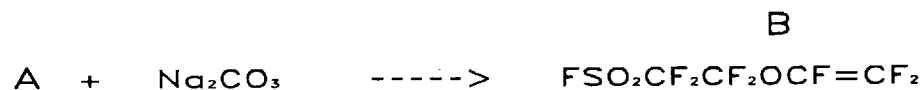
FIGURE 3
POLYMER STRUCTURES

DOW

$$-CF_2CF_2CF_1CF_2CF_2-$$
$$O$$
$$CF_2$$
$$CF_2$$
$$O=S=O$$
$$O-$$
$$H+$$

DUPONT NAFION

$$-CF_2CF_2CF_2CF_1CF_2CF_2-$$
$$O$$
$$CF_2$$
$$CF_2$$
$$O$$
$$CF_2$$
$$CF_2$$
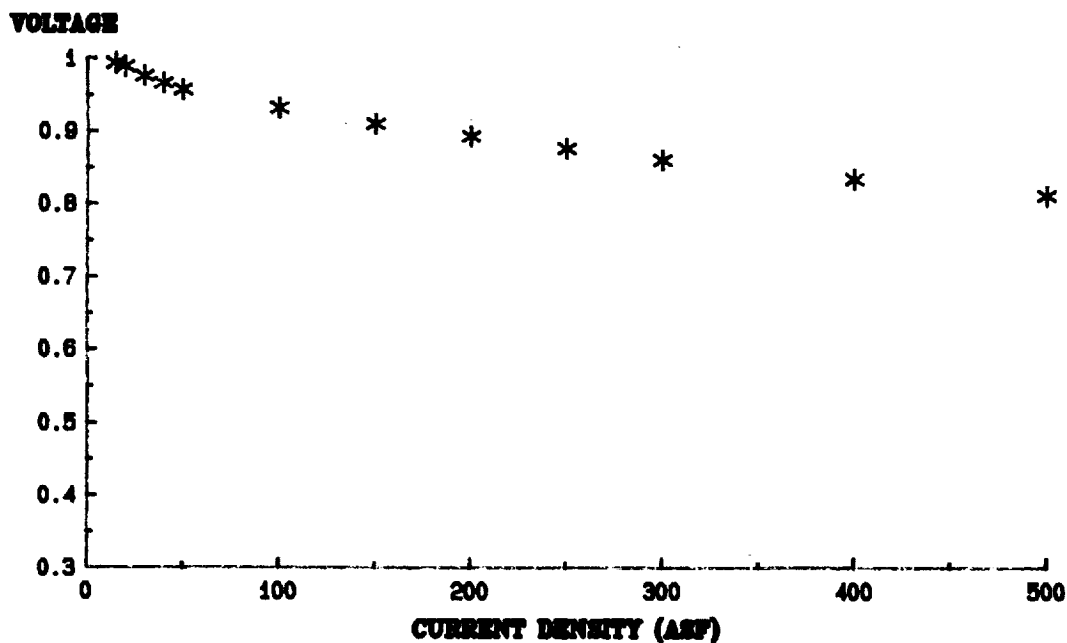$$O=S=O$$
$$O-$$
$$H+$$
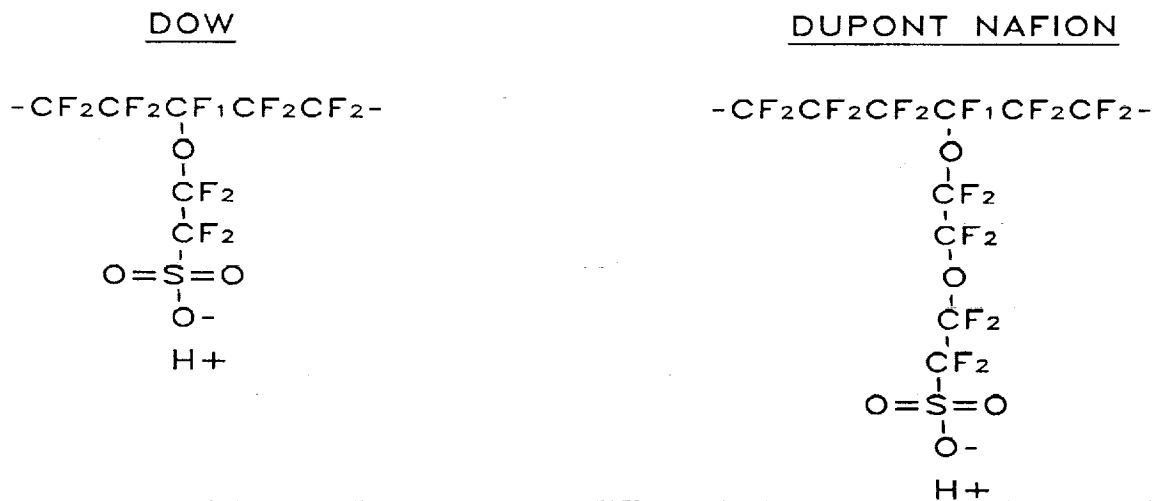
FIGURE 4
CELL HARDWARE
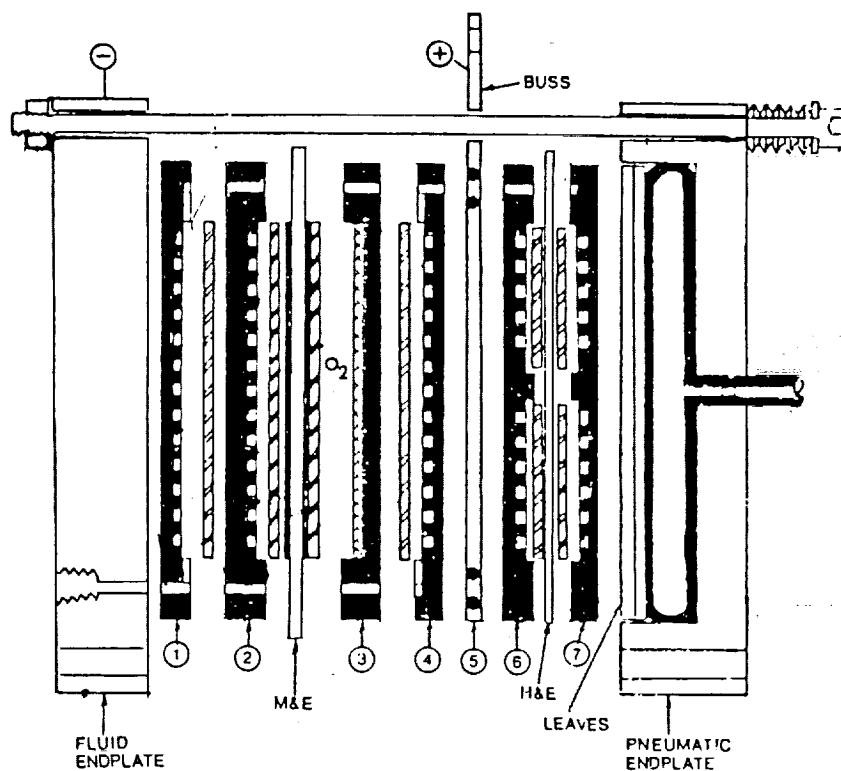
FIGURE 5
VOLTAGE – CURRENT POLARIZATION DATA
HYDROGEN OXYGEN 80 C
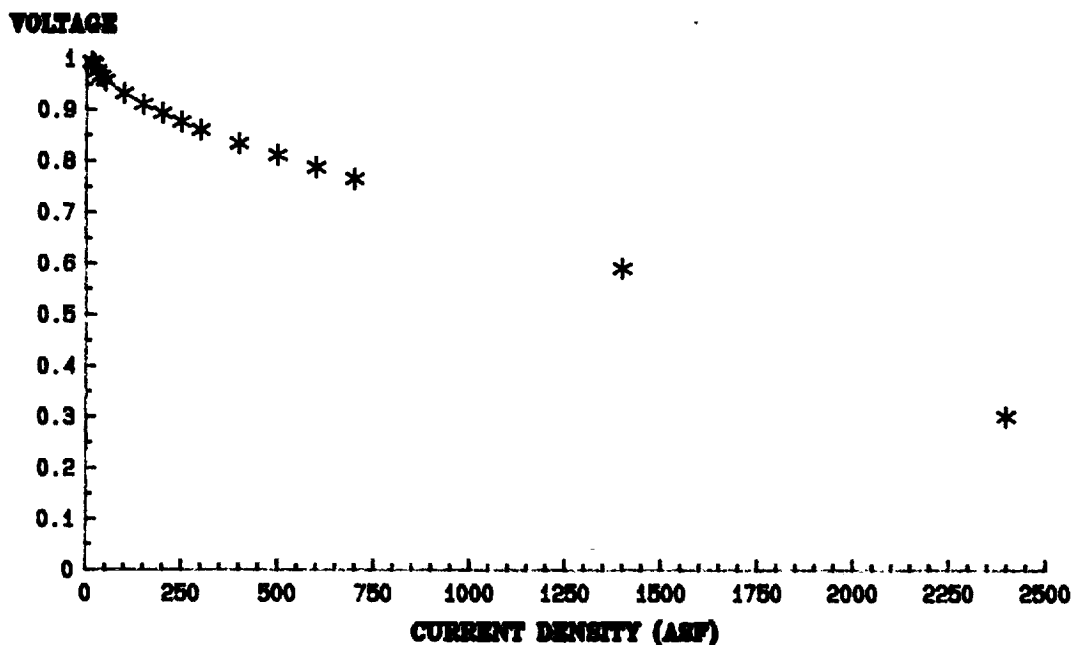
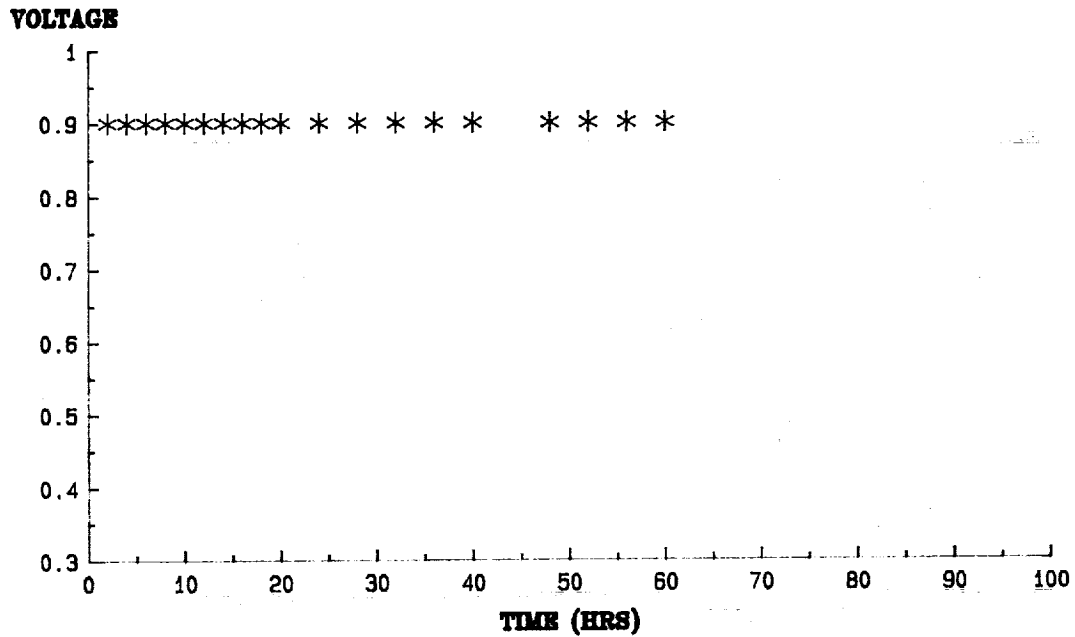40/60 PSIG H2/O2
1.1 STOICH H2: 2 STOICH O2
2mg Pt/CM^2/SIDE

FIGURE 6
VOLTAGE–CURRENT POLARIZATION DATA
0 --> 500 ASF

40/60 PSIG H2/O2 80 C
1.1 STOICH H2: 2 STOICH O2
2mg Pt/CM^2/SIDE

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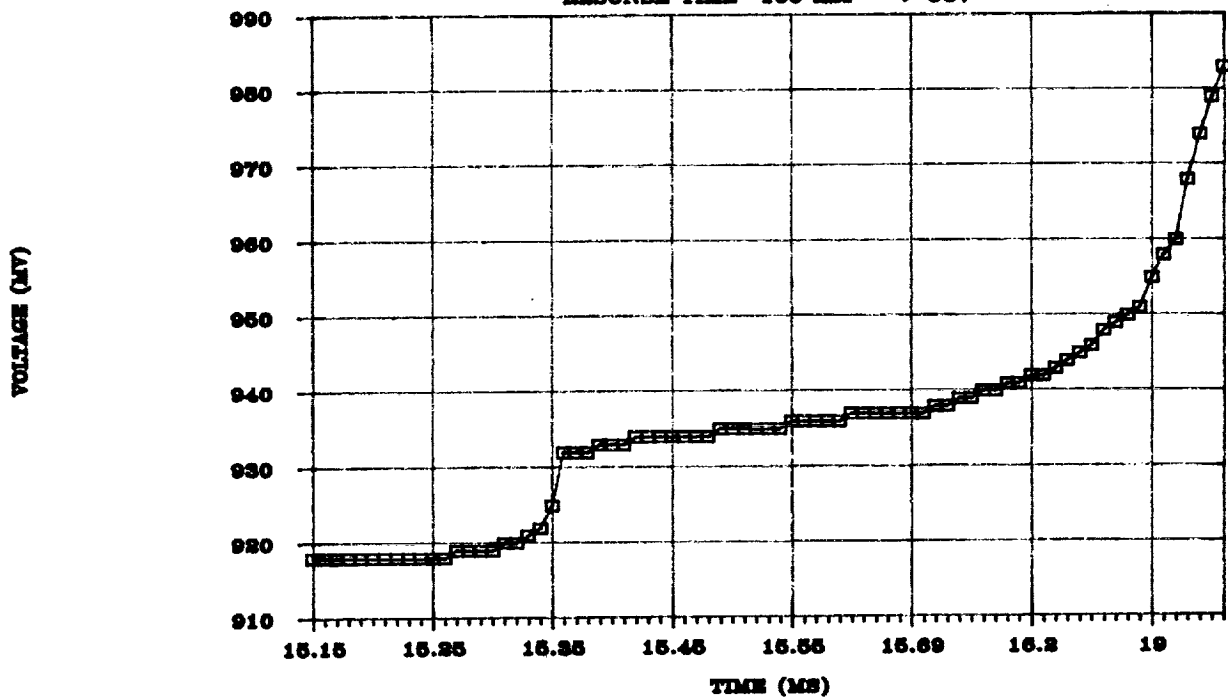## FIGURE 7
VOLTAGE VS. TIME (HRS)
200 ASF

VOLTAGE

40/60 PSIG H2/O2 80 C
1.1 STOICH H2: 2 STOICH O2
2mg Pt/CM^2/SIDE

FIGURE 8

RESONSE TIME   100 ASF ---> OCV

VOLTAGE (MV)

TIME (MS)

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FIGURE 9
CURRENT INTERRUPTION
100 ASF --> OCV
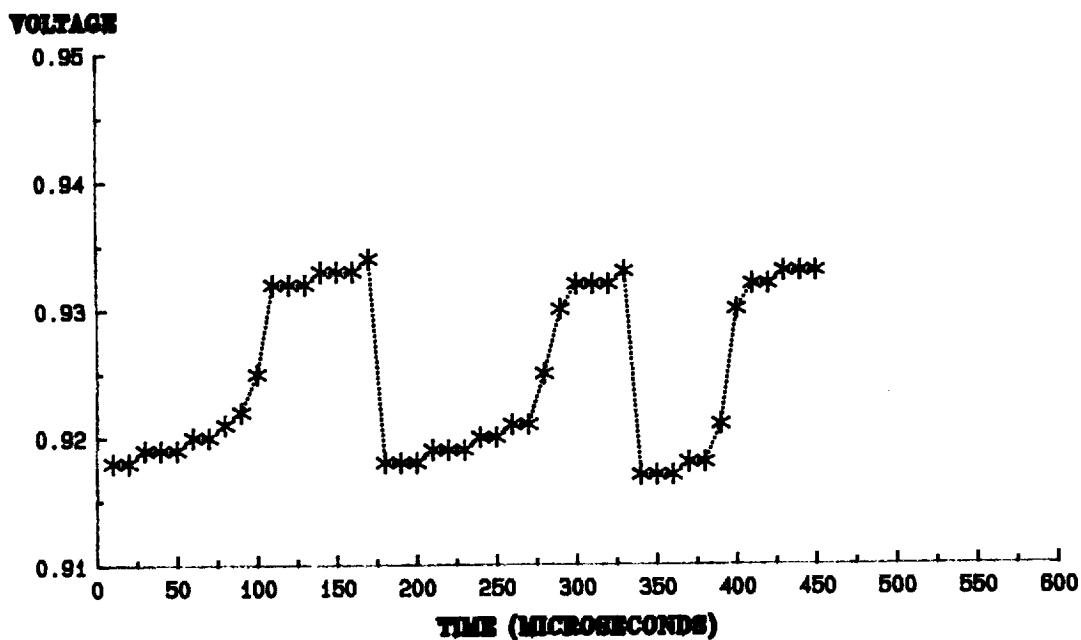
40/60 PSIG H2/O2 80 C
1.1 STOICH H2 2 STOICH O2
2mg Pt/CM^2/SIDE

FIGURE 10
VOLTAGE VS. CURRENT DENSITY
POLARIZATION DATA VS. RUN TIME

TIME = INITIAL
---*---

TIME = 5 HRS.

---O---

TIME = 10 HRS.
---🗖-

TIME = 25 HRS.
......△......

TIME = 50 HRS.
---*---

40/60 PSIG H2/O2 80 C
1.1 STOICH H2 2 STOICH O2
2mg Pt/CM^2/SIDE

123
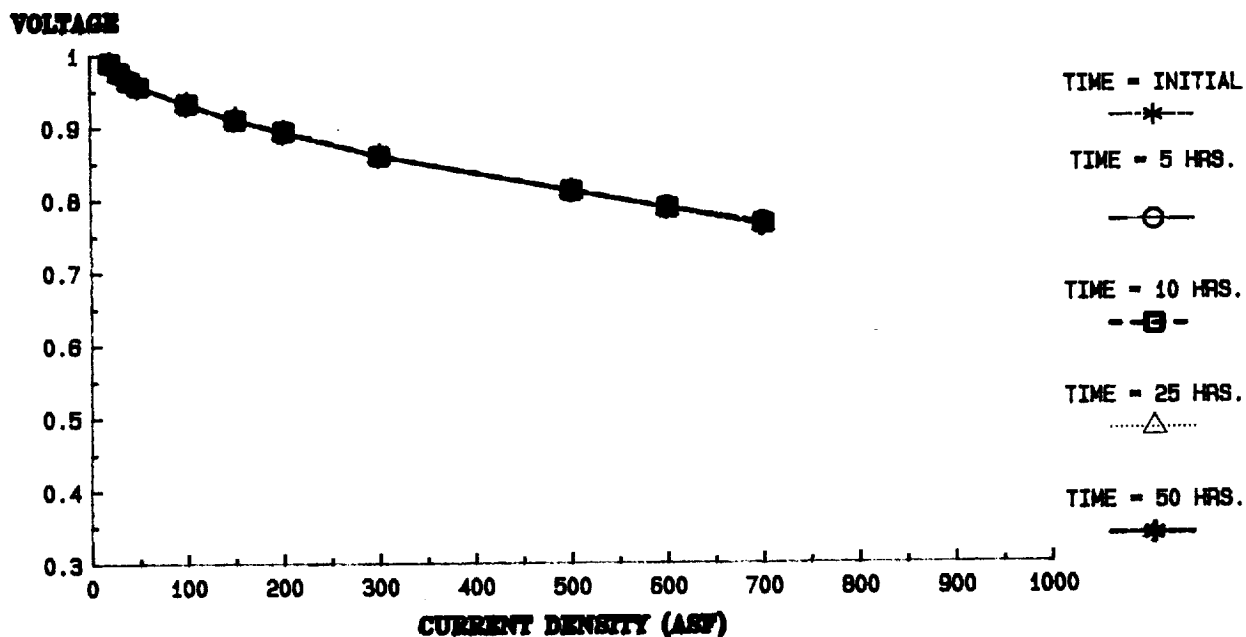
TABLE 1
MEMBRANE PROPERTIES

IONIC CONDUCTIVITY	.1 – .2 (OHM–CM)^–1
TENSILE STRENGTH	2500 – 4000 PSI
WATER UPTAKE	38 – 60%
WATER PERMEABILITY	4.5 x E–2 CC/(CM2*SEC)
GAS PERMEATION	
HYDROGEN	5 X E–9 CC–CM/(CM^2*CM Hg*SEC)
OXYGEN	2.5 X E–9

TABLE 2
IR FREE VOLTAGE VS. CURRENT DENSITY

CURRENT DENSITY (ASF)	IR FREE – CELL VOLTAGE(MV)
25	3
50	6
75	11
100	15

TABLE 3

RESPONSE TIME VS. PERCENT FULL POWER
OPEN CIRCUIT --> 100 ASF

% FULL POWER	TIME (MS)
10	2
20	5
30	8
40	12
50	16
60	21
70	28
80	41
90	51
97	81

OPEN CIRCUIT VOLTAGE   1.023 V
VOLTAGE AT 100 ASF   .915 V