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

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Summary

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 [1], and reduced failure rates as a result of pressure upsets (when compared with 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 [2, 3]. The results of tests with the Dow membrane, as reported in the literature [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 e.m.f. 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.
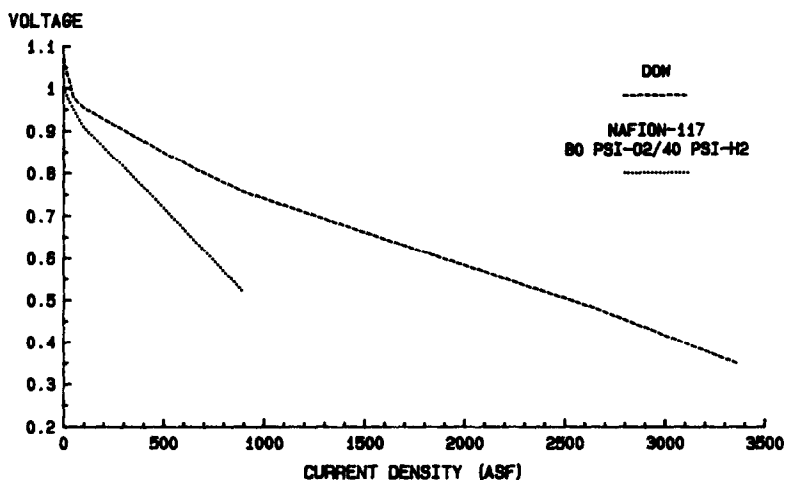
Experimental

The Dow experimental membrane utilized in this study is characterized by having an ion-exchange capacity of 1.13 and being 0.013 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 Fig. 1, along with the state-of-the-art

Fig. 1. Voltage—current polarization data.

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 A ft^{-2} (3771 A cm^{-2}) are actually a result of using high resistance 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 A 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. The chemistry for the synthesis of the monomer and the copolymerization step with the tetrafluoroethylene is presented in Fig. 2, while in Fig. 3, the
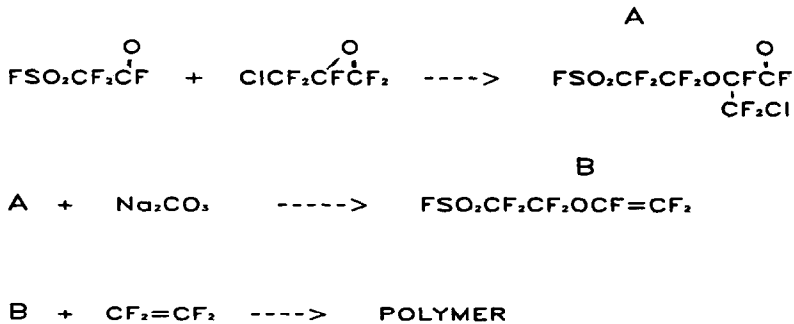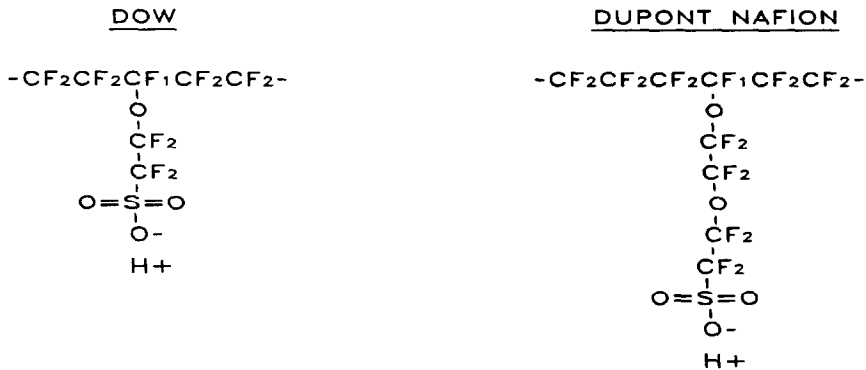

Fig. 2. Chemistry of the Dow Chemical Company.

Fig. 3. Polymer structures.

TABLE 1

Membrane properties

Ionic conductivity (Ω cm)$^{-1}$	0.1 - 0.2
Tensile strength (psi)	2500 - 4000
Water uptake (%)	38 - 60
Water permeability (cm^3 (cm^2 s)$^{-1}$)	4.5×10^{-2}
Gas permeation (cm^3 cm(cm^2 cmHg s)$^{-1}$)	
Hydrogen	5×10^{-9}
Oxygen	2.5×10^{-9}

resultant structure is depicted. Also presented in Fig. 3 for comparative purposes is the structure of DuPont's Nafion.

The membrane properties pertinent for fuel cell operation are given 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 cover a range rather than single data points because, at this time, Dow has prepared numerous membranes of different ion exchange capacity which have all 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 Fig. 4. The hardware utilizes carbon/Kynar plates with a 50 cm^2 active area. There is a heat exchanger on each
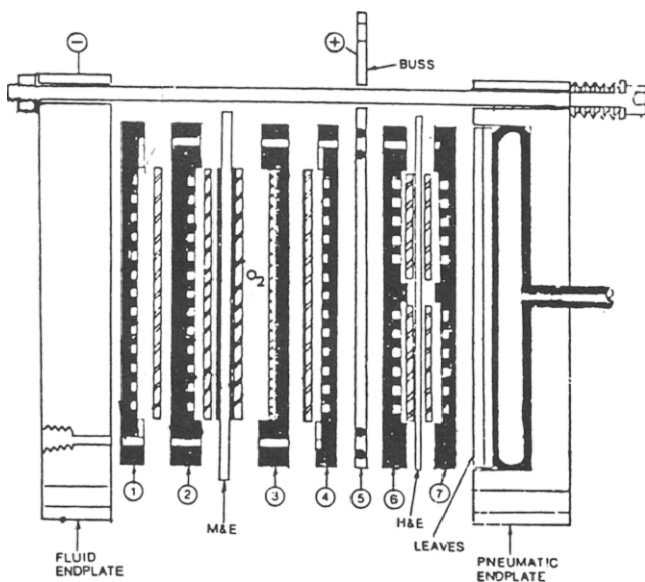

Fig. 4. Cell hardware.

side of the reactor compartment and an internal humidification compartment.

A polarization curve of the membrane previously described is shown in Fig. 5. 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 0.220 Ω cm^2 (2.37×10^{-4} Ω ft^2). These data contain the resistance of the package, and therefore are not *IR* free numbers. It should also be pointed out that the polarization data at each point were recorded only after the system appeared to reach equilibrium at the given current density. Figure 6 is a plot of the same data as Fig. 5 but expanded in the 0 - 500 A ft^{-2} region.
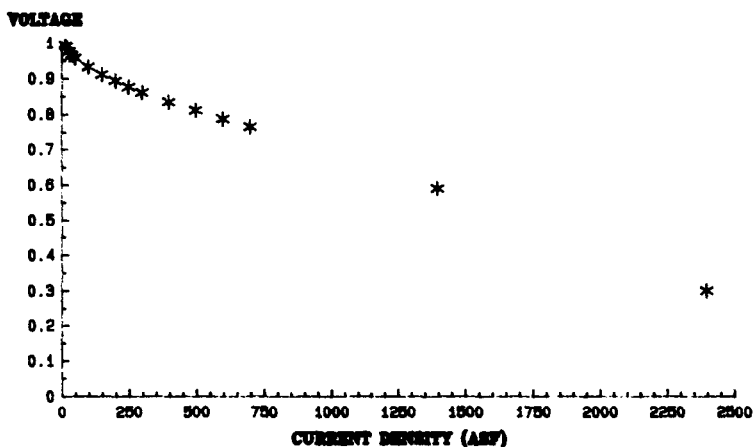
40/60 PSIG H2/O2
1.1 STOICH H2: 2 STOICH O2
2mg Pt/CM^2/SIDE

Fig. 5. Voltage–current polarization data. Hydrogen/oxygen 80 °C.
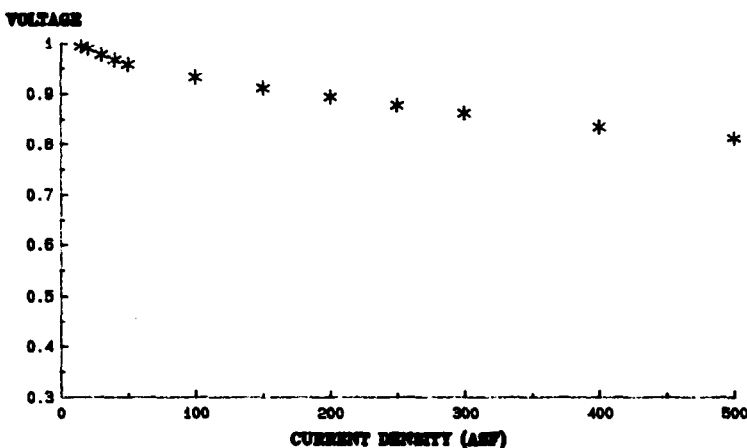
40/60 PSIG H2/O2 80 C
1.1 STOICH H2: 2 STOICH O2
2mg Pt/CM^2/SIDE

Fig. 6. Voltage–current polarization data. 0 - 500 A ft^{-2}.

Although steady-state performance can be achieved at any current density demonstrated in the polarization data of Fig. 5, the voltage of the cell *versus* time at a single current density (200 A ft^{-2}) for a relatively short period of operation is presented in Fig. 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 interruption was carried out in order to determine the electronic resistance effects of the hardware and remaining ionic resistance
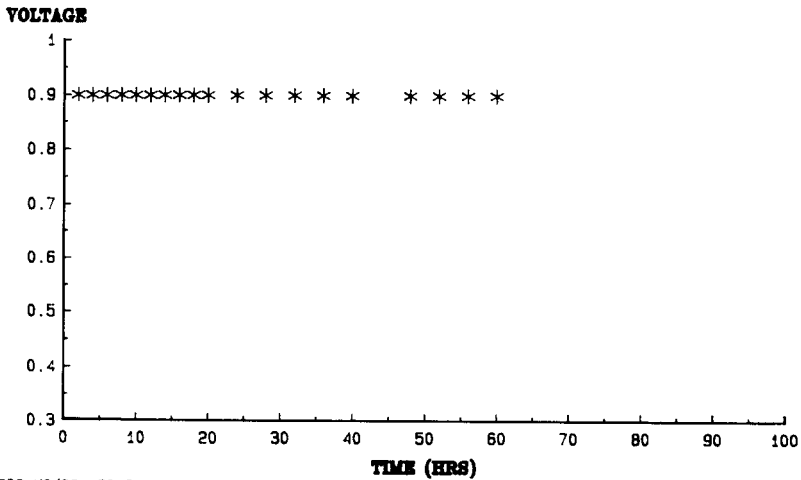
40/60 PSIG H2/O2   80 C
1.1 STOICH H2: 2 STOICH O2
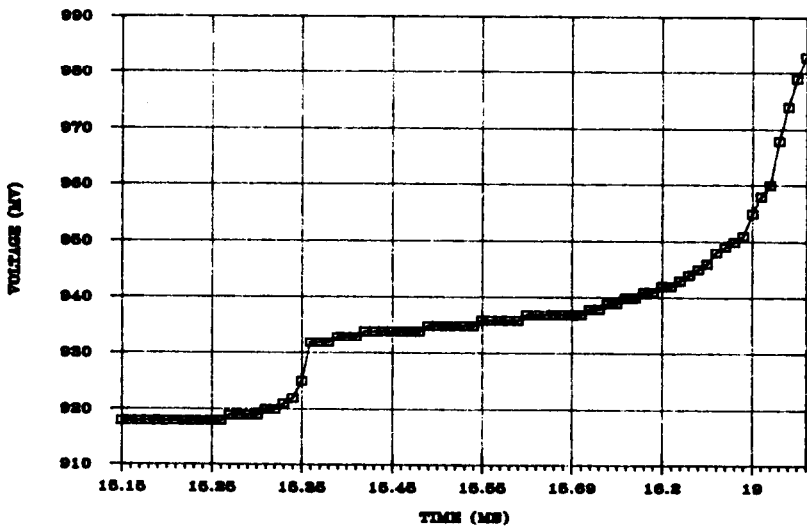2mg Pt/CM^2/SIDE

Fig. 7. Voltage *vs.* time (h) (200 A ft^{-2}).

Fig. 8. Response time 100 A ft^{-2} - OCV.

and over-voltage of the membrane and electrode package. The tests were carried out at 100 A ft^{-2} (and less) due to a limitation in the interrupting switching device. A typical result of the tests is depicted in Fig. 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 μs after the current break. This translates to an internal resistance of 3 mΩ at 100 A ft^{-2} (5 total A) or 0.15 Ω cm^2. When the *IR* free voltage (0.933) at 100 A 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 mV. In order to determine the package ohmic contribution, the cell resistance is subtracted from the slope data. Such a calculation yields 0.07 Ω cm^2 (0.222 − 0.15 Ω cm^2). A list of *IR* free values *versus* current densities between 25 and 100 A ft^{-2} is 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 those above, whereby the current was "interrupted" numerous times. In these tests, the cell was

TABLE 2

IR free voltage *vs.* current density

Current density (A ft^{-2})	IR free-cell voltage (mV)
25	3
50	6
75	11
100	15
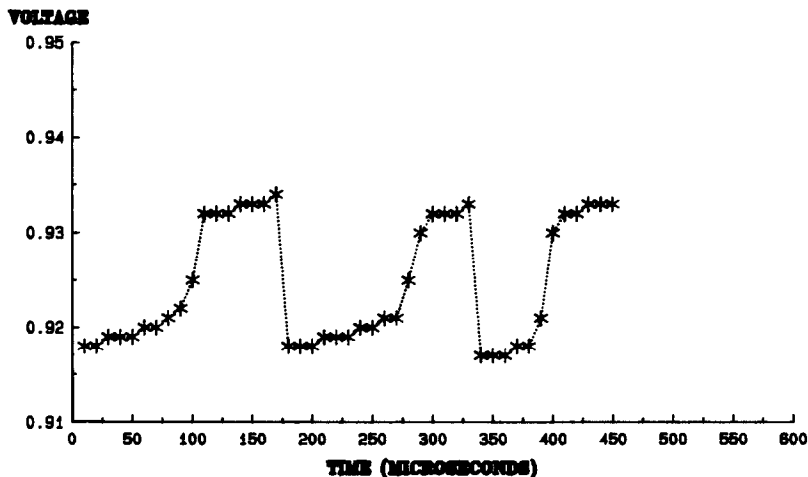
40/60 PSIG H2/O2 80 C
1.1 STOICH H2 2 STOICH O2
2mg Pt/CM^2/SIDE

Fig. 9. Current interruption (100 A ft^{-2} - OCV).

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 (Fig. 9) during each interruption. As can be seen from the data, the time required to shut off the electronic component of the cell was of the order of 50 μs. 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 is then dropped across a resistance to generate the 100 A

TABLE 3

Response time *vs.* percent. full power. Open circuit - 100 A ft^{-2}

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 A ft^{-2} 0.915 V.
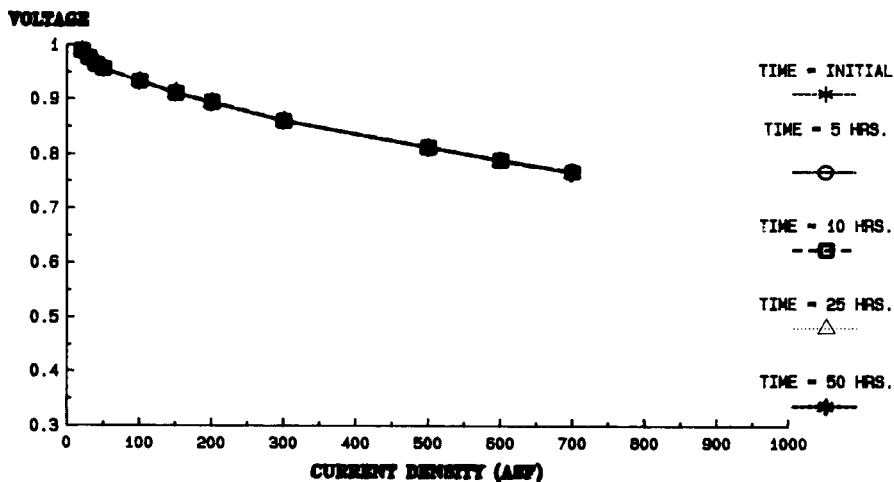
Fig. 10. Voltage *vs.* current density. Polarization data *vs.* run time.

ft^{-2}. The results of these tests are essentially identical to those when the current path was opened, both in behavior and in 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 ms.

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 in the membrane/electrode assembly. A series of current–voltage sweeps (*IR* included), taken at the times labeled on each curve, is shown in Fig. 10. No apparent degradation occurred following the numerous on–off cycles, as determined from the polarization behavior.

Conclusions

The results of tests utilizing a new experimental membrane useful in proton-exchange membrane fuel cells are presented. The high voltage at low current densities can lead to higher system 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 of the order of 80 ms to reach 90% of full power. The *IR* free voltage at $100\ A\ ft^{-2}$ was determined and the results indicated a membrane/electrode package resistance of $0.15\ \Omega\ cm^2$ at $100\ A\ ft^{-2}$.

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