

## ADVANCES IN SOLID POLYMER ELECTROLYTE FUEL CELL TECHNOLOGY WITH LOW PLATINUM LOADING ELECTRODES

S. SRINIVASAN, E. A. TICIANELLI, C. R. DEROUIN and A. REDONDO

*Los Alamos National Laboratory, M.S. D429, Los Alamos, NM 87545 (U.S.A.)*

### Summary

The Gemini Space program demonstrated the first major application of fuel cell systems. Solid polymer electrolyte fuel cells were used as auxiliary power sources in the spacecraft. There has been considerable progress in this technology since then, particularly with the substitution of Nafion for the polystyrene sulfonate membrane as the electrolyte. Until recently the performance was good only with high platinum loading ( $4 \text{ mg cm}^{-2}$ ) electrodes. This paper presents methods to advance the technology by: (i) use of low platinum loading ( $0.35 \text{ mg cm}^{-2}$ ) electrodes; (ii) optimization of anode/membrane/cathode interfaces by hot-pressing; (iii) pressurization of reactant gases: most important when air is used as cathodic reactant; and (iv) adequate humidification of reactant gases to overcome the water management problem. The high performance of the fuel cell with the low loading of platinum appears to be due to the extension of the three dimensional reaction zone by introduction of a proton conductor, Nafion. This was confirmed by cyclic voltammetry.

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### Introduction

#### *The solid polymer electrolyte fuel cell — the first demonstration of application of fuel cell systems*

Historically, the first major application of fuel cells systems was in the Gemini space flights, and for this purpose the solid polymer electrolyte fuel cell system of the General Electric Company was chosen [1]. The main advantages of fuel cell systems for space applications are the high power and energy densities with respect to weight and volume, high efficiency, few moving parts, minimum noise and vibration, and reliability. The General Electric solid polymer electrolyte fuel cell system, rated at a power level of 1 kW, was used as an auxiliary power source in the space vehicles, and the pure water, the product of the fuel cell reaction, was used for drinking purposes by the astronauts.

Though the fuel cells performed quite well for space missions of 1 - 2 weeks duration, there were some problems with this technology, *e.g.*, the

power densities attained were still not high enough ( $<50 \text{ mW cm}^{-2}$ ); the polystyrene sulfonate ion exchange membrane was not stable under the electrochemical environments in the cell; and the platinum loading was quite high. It is for these reasons that the alkaline fuel cell system was chosen for the later Apollo program and the space shuttle flights.

*Progress in solid polymer electrolyte fuel cell technology since its utilization in Gemini space flights*

The General Electric Company pursued the development of solid polymer electrolyte fuel cells after their use in the Gemini space flights. The major breakthrough was the identification of the perfluorinated sulfonic acid polymer, Nafion, produced by DuPont, as the electrolyte. The main advantages of Nafion over polystyrene sulfonic acid membranes are: (i) the higher acidity because of the presence of the fluorocarbon rather than hydrocarbon groups (the fluorine atom is electron withdrawing); and (ii) the higher stability of the C—F compared with the C—H bond under the electrochemical environments [2]. However, progress in this technology was slow due to the "drying out" of the membrane during operation of the systems.

The General Electric Company made more progress with the solid polymer electrolyte technology for water electrolysis than for fuel cells [3]. The main reason for this is that the membrane can be maintained wet during electrolytic hydrogen production. Excess water is fed to the anode compartment where oxygen is produced, and a considerable number of water molecules are carried along with the protons to the cathode where hydrogen evolution occurs. Using high surface area unsupported platinum ( $2 - 4 \text{ mg cm}^{-2}$ ) for the cathode and a ternary mixed oxide (Ru, 50%; Ir, 25%; Ta, 25%, total  $4 \text{ mg cm}^{-2}$ ) for the anode catalyst, the cell performance was  $1.00 \text{ A cm}^{-2}$  at  $1.85 \text{ V}$  at  $80^\circ \text{C}$ . Water electrolyzers with a power input of  $50 \text{ kW}$  were designed, built, and demonstrated.

The major problem encountered with the General Electric fuel cell was maintaining the membrane wet under operating conditions. Proper humidification of the reactant gases is necessary. The water management in this cell is controlled by: (i) transport of water molecules from anode to cathode; (ii) production of pure water at the cathode; (iii) water loss by evaporation from the membrane. The General Electric Company solved the water management problem by: (i) internal humidification of the reactant gases in a separate chamber; and (ii) differential pressurization, *i.e.*, using a higher pressure on the cathode side ( $10 \text{ atm}$  with air) than on the anode side ( $2 \text{ atm}$  with hydrogen). The noble metal loading in the General Electric/Hamilton Standards-United Technology Corporation (GE/HS-UTC)\* fuel cell is still high ( $4 \text{ mg cm}^{-2}$  Pt on anode as well as on cathode), because unsupported platinum particles are used as electrocatalyst. The unsupported platinum particles are mixed with Teflon particles and hot pressed on to the

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\*The General Electric Company solid polymer electrolyte technology was purchased by Hamilton Standards-United Technology Corporation.

membrane. A wet-proofed carbon paper is attached to the catalyst layer. The conductive, wet-proofed carbon fiber paper prevents flooding of the catalyst layer-gas interface and serves to transport electrons from the current collector plate to the cathode. The support side for the anode is an unattached, wet-proofed carbon fiber paper. The carbon fiber paper prevents the membrane from creeping into the current collector grooves and transfers electrons from the catalyst layer to the current collector. Good performances were obtained in this cell with hydrogen/oxygen as reactants at 105 °C with a pressure of 2 atm on the anode side and 10 atm on the cathode side. Thus a cell potential of 0.825 V at 300 mA cm<sup>-2</sup> was obtained. These cells could generate current densities of 1 A cm<sup>-2</sup> at a cell potential of 0.5 V. The slope of the cell potential *versus* current density plot in the linear region was 0.3 ohm cm<sup>2</sup>.

The performance of the GE/HS-UTC cell was not satisfactory with air as the cathode reactant. In spite of the high pressure, the cells reached a limiting current density at only about 300 mA cm<sup>-2</sup> and 105 °C.

Ballard Technologies Corporation in Canada has made significant advances in solid polymer electrolyte fuel cell technology. The detailed design and assembly of single and multicells have not been published; however, it appears to be quite similar to the GE/HS-UTC fuel cell. Electrodes with a high platinum loading and Teflon are attached to the membrane. The major improvement in performance appears to be due to the utilization of a Dow membrane instead of Nafion as the electrolyte layer. The Dow membrane has about 1/2 to 3/4 the equivalent weight of Nafion; hence, its conductivity and water retention capability are considerably better than Nafion. It has been reported that at about 3 atm pressure and an operating temperature of 80 °C, cell potentials of 0.68 V and 0.55 V are attained at current densities of 2 A cm<sup>-2</sup> with H<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/air, respectively, as reactants. The slopes of the cell potential *versus* current density plots in the linear region are only 0.1 and 0.2 ohm cm<sup>2</sup>, respectively. The thickness of the Dow membranes used in these fuel cells is 75 - 100 μm, whereas the thickness of the Nafion membrane in the GE/HS-UTC fuel cells is 175 - 200 μm. The higher conductivity of the Dow membranes and the smaller thickness account for the lower slope of the linear region in the Ballard fuel cell, as compared with that in the GE/HS-UTC fuel cells (0.3 - 0.4 ohm cm<sup>2</sup>).

Siemens in Germany is also using the GE/HS-UTC technology to develop fuel cell systems for submarine power applications. Siemens has, like Ballard Technologies Corporation, reported high-power densities with H<sub>2</sub> and O<sub>2</sub> as reactants under pressure.

One of the critical problem areas in the solid polymer electrolyte fuel cell technology is water management. Ergenics Power Systems, Inc. (EPSI), is using a novel approach to solve this problem. In this fuel cell, the cell construction permits internal transport of water for humidification of the gases and, hence, of the membrane. Currently, efforts have focussed on atmospheric pressure operation. Single and multicell stacks have been built and tested with this design. The cells are operated at 50 - 60 °C and with

H<sub>2</sub>/air as reactants; at 200 mA cm<sup>-2</sup>, the cell potential is about 0.65 V. The slopes of the linear region in the cell potential-current density plots are 0.42 and 0.80 ohm cm<sup>2</sup> with H<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/air, respectively, as reactants. EPSI is developing a 200 W fuel cell system coupled with hydrogen and oxygen storage systems sufficient for 8 - 12 h. This fuel cell system will be used for power requirements by astronauts during their space flights.

The Dow Chemical Company is developing membranes for utilization in fuel cells and chlor-alkali cells. Membrane and electrode assemblies are being prepared and tested by this organization in GE/HS-UTC fuel cell test stations.

### *Needed advances in technology and scope of present paper*

Recently [4], it was demonstrated that by incorporation of a proton conductor, Nafion, into the fuel cell electrode structures containing carbon supported platinum electrocatalyst, the same level of performance of the half cell reactions (hydrogen oxidation and oxygen reduction) in fuel cells can be achieved as in the GE/HS-UTC fuel cell, but with only one tenth of the noble metal loading (*i.e.*, 0.35 mg cm<sup>-2</sup> versus 4.0 mg cm<sup>-2</sup>). Nafion, rather than platinum, will become the most expensive material in the solid polymer electrolyte fuel cell once the technology is developed for utilizing the low noble metal loading in fuel cell electrodes. Thus, either alternatives for Nafion need to be found (the Dow membrane appears very promising but its price is unknown), or power densities of about 1 W cm<sup>-2</sup> need to be achieved to reduce the effective cost of the membrane. According to the work at GE/HS-UTC, the water management problem was overcome with differential pressurization. Such a solution has complexities in developing a multicell stack, and an alternative approach is needed.

The present work demonstrates improvements in performance of solid polymer electrolyte fuel cells with respect to efficiency, power density, and lifetime by:

- (i) utilization of low platinum loading electrodes impregnated with a proton conductor (Nafion);
- (ii) optimization of anode/membrane/cathode interface by hot pressing the electrode onto the solid polymer electrolyte under pressure and at a temperature close to that of the membrane glass transition temperature;
- (iii) pressurization of reactant gases, which is essential when air is used as the cathodic reactant;
- (iv) adequate humidification of the gases to overcome the water management problem.

## **Experimental**

### *Design and assembly of single cells*

Three types of single cells were used in the present work. For most of the experiments, a single cell made with carbon (Union Carbide nuclear

grade graphite) end plates was used. The graphite end plates contain gas feed inlets and outlets, ribbed channels for gas flow behind the electrodes, and holes for cartridge heaters and a thermocouple. After positioning the membrane and electrode assembly between the graphite end plates, the latter were clamped between stainless steel plates that were insulated from the cell body with PTFE sheets. The active cell area (geometric) in this cell is  $5 \text{ cm}^2$ . For the control cell, the GE/HS-UTC membrane and electrode assembly was used. In the test cells, as-received and Nafion-impregnated Prototech electrodes were hot pressed to Nafion membranes at  $120 \text{ }^\circ\text{C}$  and 50 - 60 atm pressure for 30 s. In one experiment, the Nafion-impregnated Prototech electrodes were hot pressed onto a Dow membrane. The reactant gases were externally humidified in this cell.

A new cell with an active electrode area of  $10 \text{ cm}^2$  and internal humidification was designed and fabricated. In the new cell, separate humidification chambers for the anodic and cathodic reactants are adjacent to the respective electrodes. In each of these chambers a Nafion membrane/porous titanium sheet composite separates the water and gas flow compartments. The water that permeates through the Nafion membrane humidifies the reactant gases. The area for humidification of the gases is four times the electrode area.

The third cell assembly is the one designed and constructed by GE/HS-UTC. The active area of the electrodes in this cell is  $50 \text{ cm}^2$ . This cell also incorporates a humidification chamber split into two separate compartments for the humidification of the reactant gases. Platinum particles were deposited within the membrane to serve as a catalyst for the combination of hydrogen and oxygen gases in case cross-mixing occurred. The GE/HS-UTC test station is well equipped for the supply and removal of reactant gases, water for humidification of gases, temperature and pressure control, and electrochemical measurements (cell potential *versus* current density and life testing). Safety features for turning off the system when there is a cell failure or other emergency are also incorporated in the test station.

### *Optimization of humidification of reactant gases*

The preliminary experiments, carried out in the  $5 \text{ cm}^2$  cell with external humidification, proved to be valuable in optimizing the humidification conditions for the reactant gases. The water management in the solid polymer electrolyte is complex because protons that are formed by the oxidation reaction tend to carry 4 - 6 molecules of water per proton from the anode to the cathode. The situation is made even more complex with the Nafion-impregnated electrodes because the micropores in the active layer tend to dry out. This increases the cell resistance. Another problem is that water formed at the oxygen electrode can cause flooding. Further complication arises when operating the cells at close to  $100 \text{ }^\circ\text{C}$  — the desired operating temperatures to obtain better electrocatalysis and minimize carbon monoxide poisoning effects. Under these conditions, the vaporization losses become significant.

The water management problem, however, is not as serious as it was originally thought for the following reasons:

(i) the concentration gradient that is set up in the membrane and electrode assembly, due to water drag by protons and production of water at the cathode, is sufficiently high to transport water at fast enough rates back from cathode to anode;

(ii) vaporization losses can be minimized by operating the cells at higher pressures and temperatures and by adequate humidification;

(iii) it is necessary to humidify the gases at temperatures of about 5 - 10 °C above the cell temperature to prevent the drying out problem, particularly within the pores of the Nafion-impregnated electrodes.

In the 10 cm<sup>2</sup> and 50 cm<sup>2</sup> cells with internal humidification, the humidification chambers are probably at a slightly higher temperature, but because the water diffuses through the Nafion membrane in a vapor or drop-let form, the efficiency of humidification is high.

#### *Measurements of cell potential as a function of current density at different temperatures and pressures*

Cell potential-current density measurements were made periodically by interrupting the constant current density operation to obtain lifetime performance data. For this purpose the measurements in the 5 and 10 cm<sup>2</sup> cells were made using the PAR Model 173 Potentiostat/Galvanostat. For higher current density measurements, a power supply with a higher current output was used. More recently, a Hewlett Packard programmable power supply 6033A and an IBM micro-computer were interfaced with the electrochemical cell to obtain the cell potential *versus* current density data.

Measurements were made as a function of temperature and pressure. The initial studies were carried out at 25 and 50 °C at atmospheric pressure. The more recent experiments were carried out at 50 and 75 °C and at pressures of 1 - 5 atm above atmospheric pressure. The high frequency resistance measurements were made in the cells to obtain ohmic overpotentials. However, this measurement does not yield the ohmic overpotential within the porous electrode structure due to its behavior like a transmission line. An a.c. impedance spectroscopic method will have to be used to obtain this resistance.

The GE test station is well equipped for obtaining cell potential-current density data in the 50 cm<sup>2</sup> cell. This test station can also be adapted when using the 10 cm<sup>2</sup> cell with internal humidification. A set of experiments was carried out with 50 cm<sup>2</sup> Nafion-impregnated Prototech electrodes hot pressed on to Nafion membranes. In all cases, measurements were made with hydrogen/oxygen and hydrogen/air as reactants.

#### *Lifetime studies*

A few experiments were carried out to determine the long term performance of the electrodes. For this purpose, the cells were maintained at a constant current density (100 - 200 mA cm<sup>-2</sup>) and the potentials followed as

a function of time. There were periodic interruptions for either making cell potential *versus* current density measurements or cyclic voltammetric studies.

*Cyclic voltammetry on electrodes to ascertain electrochemically active surface area*

This technique proved to be quite valuable to ascertain the electrochemically active surface area of the electrodes. For this purpose, the PAR 173 Potentiostat/PAR 175 Programmer was used. Cyclic voltammograms were generally recorded at  $100 \text{ mV s}^{-1}$ . Argon gas was passed through the test electrode compartment and hydrogen through the counter electrode compartment. Due to the negligible overpotential, the counter electrode also served satisfactorily as the reference electrode.

## Results and discussion

### *Analysis of cell potential-current density relations*

The cell potential-current density data were analyzed using an equation of the form:

$$E = E_o - b \log i - R_i i \quad (1)$$

The assumption made in this equation is that mass transport limitations are negligible, which is generally the case until the current densities are close to the limiting current density. In eqn. (1),  $E_o$  is a constant, and if it is assumed that the hydrogen oxidation reaction is considerably faster than the oxygen reduction reaction:

$$E_o = E_r + 2.303 \frac{RT}{\alpha F} \log i_o \quad (2)$$

where  $E_r$  is the reversible potential for the cell, and  $i_o$  and  $\alpha$  are the exchange current density and transfer coefficient for the oxygen reduction reaction. In eqn. (1),  $b$  is the Tafel slope for the oxygen reduction reaction and  $R_i$  is the slope of the linear region in the  $E$  *versus*  $i$  plot, the predominant contribution being ohmic overpotential, with smaller ones due to activation and mass transport control. The parameters,  $E_o$ ,  $b$  and  $R_i$  were evaluated by non-linear least squares fits to the experimental points. Typical cell potential *versus* current density plots for:

- (i) the control cell with GE/HS-UTC membrane and electrode assembly;
- (ii) the test cell with the as-received Prototech electrode hot-pressed onto a Nafion membrane;
- (iii) the Nafion-impregnated electrode hot-pressed on to a Nafion membrane,

are presented in Fig. 1. The solid lines that represent the computer generated plots show excellent agreement with the experimental points. The results obtained in the cell with the  $50 \text{ cm}^2$  electrodes and  $\text{H}_2/\text{O}_2$  and  $\text{H}_2/\text{air}$  as reactants at  $50^\circ \text{C}$  are plotted in a linear manner ( $E$  *versus*  $i$ ) in Fig. 2

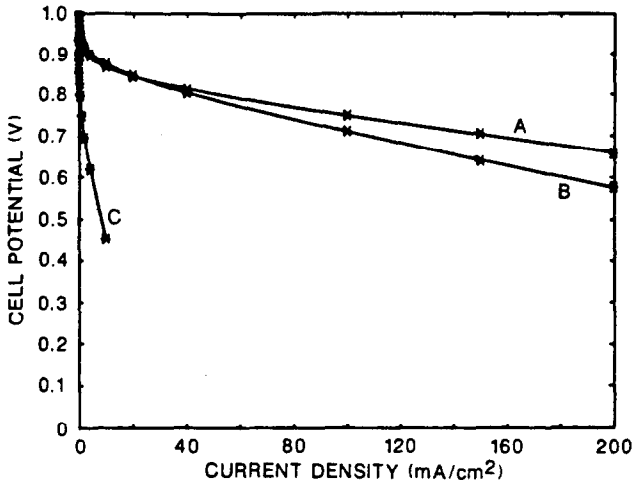


Fig. 1. Cell potential/current density plots for  $H_2/O_2$  fuel cells at  $50^\circ C$  and 1 atm pressure (electrodes  $5\text{ cm}^2$ ): A and C, Nafion-impregnated and as-received Prototech electrodes ( $0 - 35\text{ mg cm}^{-2}$  Pt) hot-pressed to Nafion membranes; B, GE/HS-UTC membrane and electrode ( $4\text{ mg cm}^{-2}$  Pt). Solid lines, computer generated plots;  $\star$ , experimental points.

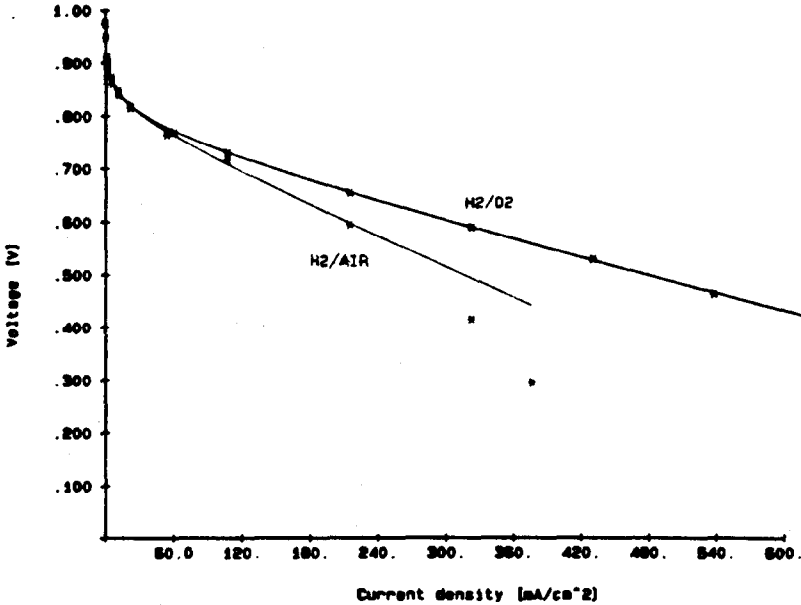


Fig. 2. Cell potential/current density plots for  $H_2/O_2$  and  $H_2/air$  fuel cells at  $50^\circ C$  and 1 atm pressure (electrodes  $50\text{ cm}^2$ ). Nafion-impregnated Prototech electrodes ( $0.35\text{ mg cm}^{-2}$  Pt) hot-pressed to Nafion membrane. Solid lines, computer generated plots;  $\star$ , experimental points.



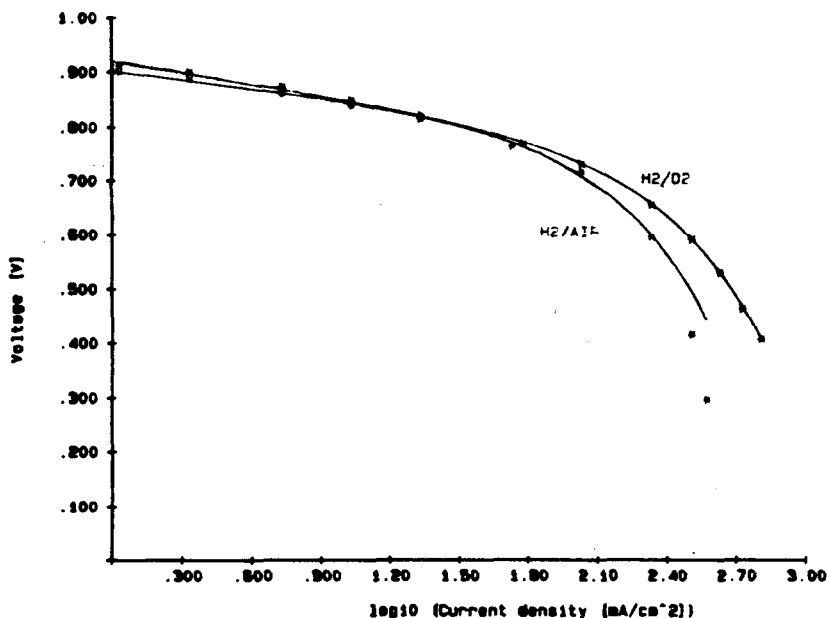


Fig. 3. Cell potential/log current density plots for H<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/air fuel cells at 50 °C and 1 atm pressure (electrodes 50 cm<sup>2</sup>). Nafion-impregnated Prototech electrodes hot-pressed to Nafion membrane. Solid lines, computer generated plots; ★, experimental points.

and in a semilogarithmic manner ( $E$  versus  $\log i$ ) in Fig. 3. These figures also confirm the excellent agreement between the computer generated plots and experimental points.

The electrode kinetic parameters for the control cell with the GE/HS-UTC membrane and electrode assembly, and for the test cells with the Prototech electrodes (as-received and Nafion-impregnated) hot pressed on to Nafion or Dow membrane, are summarized in Table 1. Also shown in this Table are the high frequency resistance and the current density at a cell potential of 0.7 V. The following conclusions can be drawn from the results in Table 1:

(i) the control cell with the GE/HS-UTC membrane and electrode assembly and the test cells with the Nafion-impregnated electrodes exhibit similar electrode kinetic parameters.

(ii) the differential resistance ( $R_i$ ) of the cell is at least 50% higher for the hydrogen/air fuel cells as compared with hydrogen/oxygen fuel cells. This is not the case in phosphoric acid fuel cells (typical results also given in Table 1). The reason for this anomalous behavior with solid polymer electrolyte fuel cells is probably due to a greater degree of mass transport and ohmic limitations with air instead of oxygen as the cathodic reactant.

(iii) The differential resistance in the test cell with as-received Prototech electrodes is at least an order of magnitude higher than in the test cells with Nafion-impregnated Prototech electrodes. The high frequency resistance is

TABLE 1

Electrode kinetic parameters for fuel cells obtained by method of least squares fit of cell potential-current density measurements using eqn.  $E = E_o - b \log i - R_i i$

Cell #, type	Temperature (°C)	$E_o$ (V)	$b$ (V)	$R_i$ (ohm cm <sup>2</sup> )	$R_{HF}$ (ohm cm <sup>2</sup> )	Current density at 0.7 V (mA cm <sup>-2</sup> )
PEM 3 <sup>a</sup> , H <sub>2</sub> /air	50	0.924	0.068	1.808	0.88	60
PEM 3, H <sub>2</sub> /O <sub>2</sub>	50	0.950	0.055	1.214	0.88	120
PEM 3, H <sub>2</sub> /air	25	0.928	0.049	3.342	—	55
PEM 3, H <sub>2</sub> /O <sub>2</sub>	25	0.957	0.055	1.906	—	80
PEM 5 <sup>b</sup> , H <sub>2</sub> /air	50	0.721	0.099	26.250	1.05	1
PEM 5, H <sub>2</sub> /O <sub>2</sub>	50	0.760	0.091	21.600	1.05	2
PEM 5, H <sub>2</sub> /air	25	0.757	0.098	31.510	—	1
PEM 5, H <sub>2</sub> /O <sub>2</sub>	25	0.7	0.092	21.960	—	2
PEM 6 <sup>c</sup> , H <sub>2</sub> /air	50	0.878	0.052	1.438	0.73	70
PEM 6, H <sub>2</sub> /O <sub>2</sub>	50	0.934	0.049	0.851	0.73	150
PEM 6, H <sub>2</sub> /air	25	0.878	0.040	1.976	—	50
PEM 6, H <sub>2</sub> /O <sub>2</sub>	25	0.932	0.066	0.866	—	120
PEM D/120 <sup>d</sup> , H <sub>2</sub> /air	25	0.849	0.065	1.469	0.65	40
PEM D/120, H <sub>2</sub> /O <sub>2</sub>	25	0.885	0.062	0.877	0.65	80
PEM D/120, H <sub>2</sub> /air	50	0.888	0.058	1.402	0.43	50
PEM D/120, H <sub>2</sub> /O <sub>2</sub>	50	0.914	0.069	0.580	0.43	120
PEM D/120, H <sub>2</sub> /air	75	0.854	0.057	1.281	—	40
PEM D/120, H <sub>2</sub> /O <sub>2</sub>	75	0.890	0.065	0.715	—	100
PA <sup>e</sup> , H <sub>2</sub> /air	150	0.893	0.103	0.656	0.46	40
PA, H <sub>2</sub> /O <sub>2</sub>	150	0.962	0.105	0.624	0.46	100

<sup>a</sup>PEM 3: GE/HS-UTC membrane and electrode assembly.

<sup>b</sup>PEM 5: Prototech electrode/Nafion membrane.

<sup>c</sup>PEM 6: Nafion impregnated Prototech electrode/Nafion membrane.

<sup>d</sup>PEM D/120: Nafion impregnated Prototech electrode/Dow membrane.

<sup>e</sup>PA: Phosphoric acid fuel cell.

nearly the same in all cells. These results correlate well with the considerably higher electrochemically active surface areas in the electrodes where there is either a higher noble metal loading or an extension of the three dimensional reaction zone.

(iv) The high frequency resistances are considerably less than the differential resistances of the cell in all cases except one. This behavior can be interpreted on the basis that the high frequency resistance does not include the resistance within the electrodes due to mass transport and ohmic limitations.

(v) The Tafel slope for the cell with the as-received Prototech electrodes is nearly twice that in the other cells. This is because of the combined effects of activation and ohmic overpotential in the former and only activation overpotential in the latter.

*Significant effects of pressure on performance of fuel cells with hydrogen/air as compared with hydrogen/oxygen as reactants*

Operation at pressures of at least 3 atm above atmospheric is essential to attain high power densities in solid polymer electrolyte fuel cells for at least three reasons.

(i) At higher pressures and temperatures, and with adequate humidification, water loss from the membrane by evaporation or carry-over with the reactant gases is reduced.

(ii) Higher pressures are required for operating the cells at close to 100 °C, which is favored from an electrode kinetic point of view, and it also increases the tolerance of the anode to carbon monoxide (which may be at a level of 0.1 to 0.3% in the anode fuel stream).

(iii) Higher pressures improve the electrode kinetic performance of the cells.

Two types of pressure effects are observed. A slight increase of pressure (0.1 atm) above 1 atm has a stronger effect on the performance of hydrogen/air than on hydrogen/oxygen fuel cells (Fig. 4). Thereafter, the increase of performance with pressure is nearly the same in both cases.

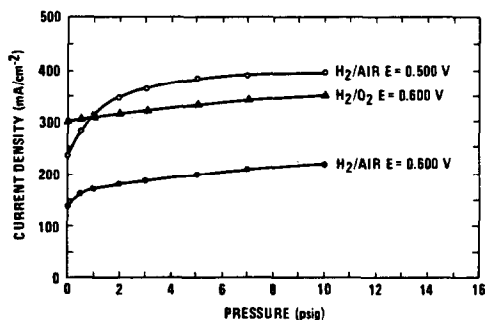


Fig. 4. Current density at constant cell potential/pressure plots at 50 °C for H<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/air fuel cells (electrodes 50 cm<sup>2</sup>), Nafion-impregnated Prototech electrodes (0.35 mg cm<sup>-2</sup> Pt) hot-pressed to Dow membrane.

The pressure and temperature effects in the cell with the 50 cm<sup>2</sup> electrode on the electrode kinetic parameters are presented in Tables 2 and 3. Figures 5 and 6 exhibit the effect of pressure on the cell potential *versus* current density plots at 80 °C with hydrogen/oxygen and hydrogen/air as reactants. The increase in cell potential ( $\Delta E$ ) with pressure at a constant current density due to enhanced electrode kinetics should follow the equation:

$$\Delta E = b \log P_2/P_1 \quad (3)$$

where  $P_2$  is the higher pressure and  $P_1$  the lower one. One can observe from Figs. 5 and 6, as well as from Tables 2 and 3 (the value of  $E_o$ ), that pressure effects are higher than expected (except for the case when the pressure is increased from 40 to 60 psig with air). The thermodynamic effect of pressure on the reversible potential is small. The higher potentials observed

TABLE 2

Electrode kinetic parameters for fuel cells obtained by method of least squares fit of cell potential-current density measurements using eqn.  $E = E_o - b \log i - R_i i$   
 Cell with 50 cm<sup>2</sup> electrodes, H<sub>2</sub>/O<sub>2</sub> reactants.

Temperature (°C)	Pressure above atmospheric (psig)	$E_o$ (V)	$b$ (V)	$R_i$ (ohm cm <sup>2</sup> )	Current density at 0.7 V (mA cm <sup>-2</sup> )
50	0	0.920	0.066	0.509	120
50	20	0.944	0.067	0.470	180
50	40	0.956	0.060	0.484	210
50	60	0.971	0.061	0.465	250
70	20	0.956	0.063	0.382	240
70	40	0.972	0.066	0.387	300
70	60	0.980	0.057	0.376	340
80	20	0.954	0.066	0.350	240
80	40	0.972	0.063	0.332	310
80	60	0.981	0.059	0.333	360

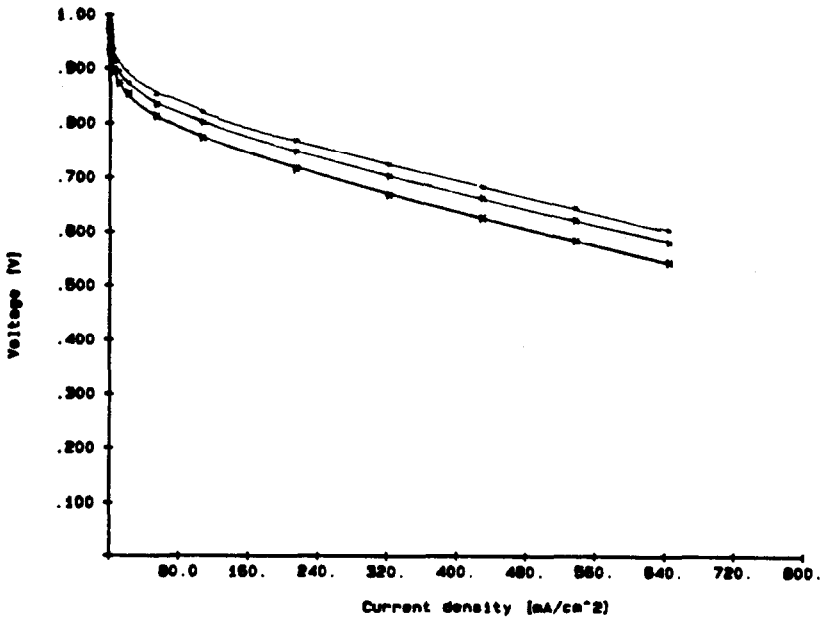


Fig. 5. Cell potential/current density plots for H<sub>2</sub>/O<sub>2</sub> fuel cell at 80 °C and pressures of 20, 40 and 60 psig (electrodes 50 cm<sup>2</sup>). Nafion-impregnated Prototech electrodes (0.35 mg cm<sup>-2</sup>) hot-pressed to Nafion membrane. Solid lines, computer generated plots; \*, experimental points.

TABLE 3

Electrode kinetic parameters for fuel cells obtained by method of least squares fit of cell potential-current density measurements using eqn.  $E = E_o - b \log i - R_i i$   
 Cell with 50 cm<sup>2</sup> electrodes, H<sub>2</sub>/air reactants.

Temperature (°C)	Pressure above atmospheric (psig)	$E_o$ (V)	$b$ (V)	$R_i$ (ohm cm <sup>2</sup> )	Current density at 0.7 V (mA cm <sup>-2</sup> )
50	0	0.902	0.047	0.898	60
50	20	0.929	0.046	0.930	120
50	40	0.945	0.043	1.012	140
50	60	0.959	0.061	1.035	150
70	20	0.929	0.053	0.919	120
70	40	0.940	0.045	0.884	150
70	60	0.948	0.040	0.944	160
80	20	0.920	0.046	0.666	120
80	40	0.940	0.053	0.577	160
80	60	0.949	0.041	0.756	190

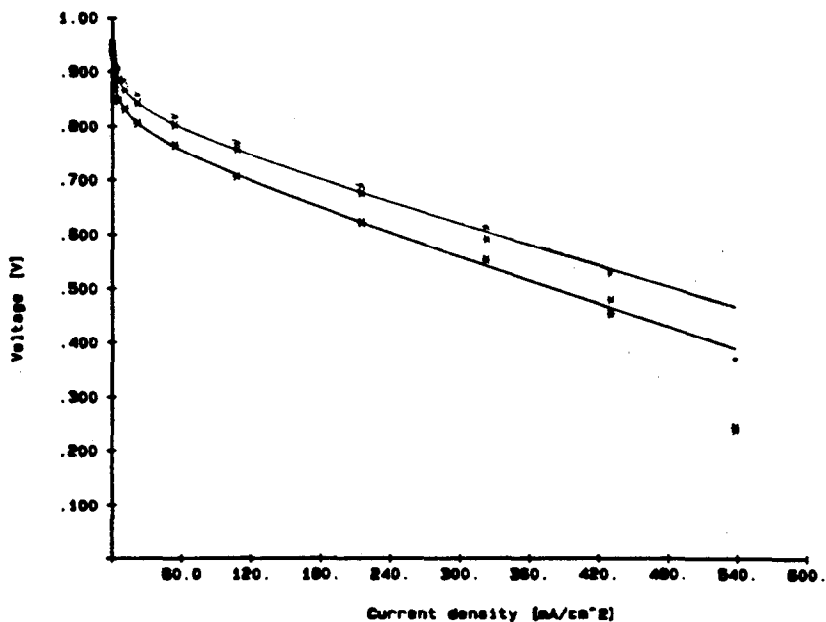


Fig. 6. Cell potential/current density plots for H<sub>2</sub>/air fuel cell at 80 °C and pressures of 20, 40 and 60 psig (electrodes 50 cm<sup>2</sup>). Nafion-impregnated electrodes (0.35 mg Pt cm<sup>-2</sup>) hot-pressed to Nafion membrane. Solid lines, computer generated plots; ★, experimental points.

(when compared with eqn. (3)) can be explained by assuming that higher pressure favors water management, particularly humidification in the fuel cell (*i.e.*, within the electrode and the membrane). A theoretical analysis of the pressure effect is in progress and will be the subject of a future communication.

#### *Stable long term performance*

Several cells were subjected to life testing, mostly with hydrogen/air as reactants. Cells were operated under constant load (100, 150 mA cm<sup>-2</sup>). The cell that was tested for the longest period was the one with the Nafion-impregnated electrode, hot-pressed on to a Dow membrane (Fig. 7). The life testing was interrupted periodically to record cell potential *versus* current density data or cyclic voltammograms. Life testing on the cell with the 50 cm<sup>2</sup> electrode was also carried out at the three temperatures and three pressures with oxygen as the cathodic reactant; it was possible to maintain stable cell potentials at a constant current density of 500 mA cm<sup>-2</sup>. With air as the cathodic reactant, the maximum current density at which the cell potential remained constant for at least an 8 h period was 200 mA cm<sup>-2</sup>. The present work demonstrates that with proper external humidification of the reactant gases (*i.e.*, at a temperature of 5 - 10 °C above the cell temperature), there was hardly any performance variation with time.

#### *Cyclic voltammetry on electrodes to ascertain electrochemically active surface area*

One of the main problems with the use of this technique with supported electrocatalysts is that the carbon features (double layer charging, redox behavior of surface active groups on carbon, for example, quinone/hydroquinone) mask the hydrogen adsorption/desorption characteristics. Also, if the anodic limit is extended beyond 1 V/RHE, oxidation of carbon occurs. In spite of these problems, the technique proved to be useful to ascertain the electrochemically active surface of the electrodes. As seen in Fig. 8, the coulombic charge over the entire potential scan is approximately the same for the GE/HS-UTC and the Nafion-impregnated Prototech electrodes, but an order of magnitude less for the as-received Prototech electrodes. This increase in electrochemically active surface area correlates well with the observed cell potential-current density plot (Fig. 1) and also with the values of differential resistances of the cells in the linear regions of these plots. The results clearly demonstrate the extension of the three dimensional reaction zone by incorporation of a proton conductor into the electrode containing a low noble metal loading.

#### **Conclusions**

The emphasis of the work presented in this paper was to attain a high level of performance in solid polymer electrolyte fuel cells with electrodes

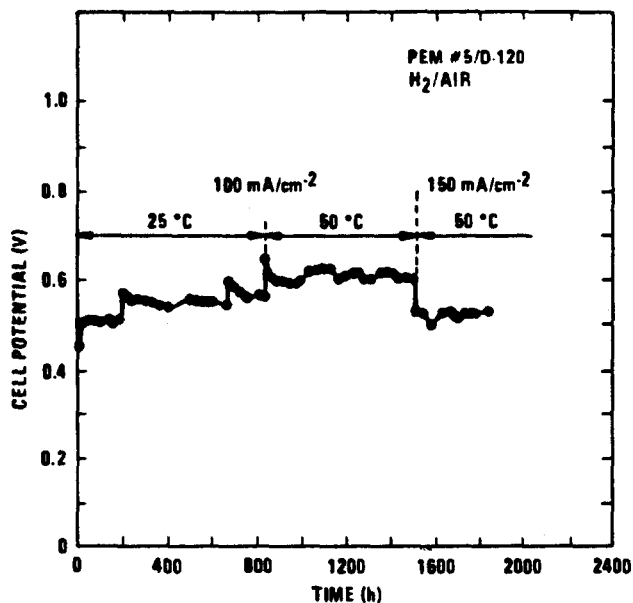


Fig. 7. Life testing of  $H_2$ /air fuel cell (electrodes  $5\text{ cm}^2$ ). Nafion-impregnated Prototech electrodes hot-pressed to Dow membrane.

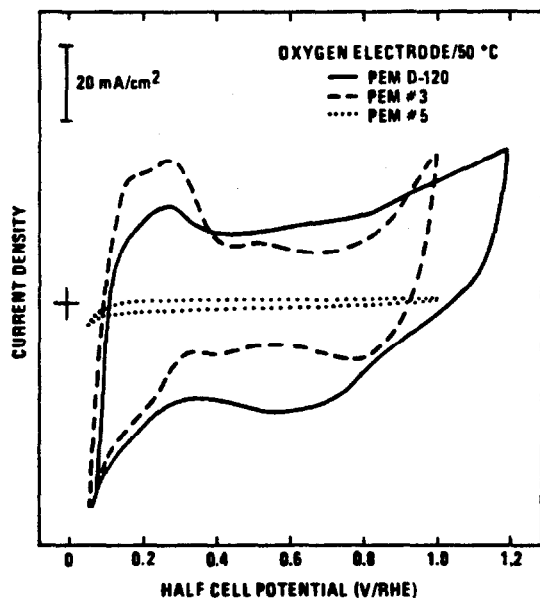


Fig. 8. Cyclic voltammograms on oxygen electrodes in fuel cells (electrodes  $5\text{ cm}^2$ ). PEM D-120-cell with Nafion-impregnated Prototech electrodes ( $0.35\text{ mg cm}^{-2}\text{ Pt}$ ) hot-pressed to Dow membrane; PEM #3-cell with GE/HS-UTC membrane and electrode assembly ( $4\text{ mg cm}^{-2}\text{ Pt}$ ); and PEM #5-cell with as-received Prototech electrodes ( $0.35\text{ mg cm}^{-2}\text{ Pt}$ ) hot-pressed to Nafion membrane.

containing a low platinum loading ( $0.35 \text{ mg cm}^{-2}$  as compared with state-of-the-art  $4 \text{ mg cm}^{-2}$ ). The following conclusions can be drawn from the results obtained.

(i) By impregnation of the Prototech electrodes ( $0.35 \text{ mg cm}^{-2}$  Pt) with a proton conductor, there appears to be an extension of the three dimensional reaction zone in the porous electrode structure and a considerable improvement in the fuel cell performance. The fuel cell performance obtained is practically the same as with the state-of-the-art membrane and electrode assembly ( $4 \text{ mg cm}^{-2}$  of Pt). Confirmation of the extension of the three dimensional reaction zone is demonstrated (a) by the analysis of the experimental results using eqn. (1) — the slope of the cell potential-current density curve in the linear region in the cell with the as-received Prototech electrode is an order of magnitude higher than in the cell with the Nafion-impregnated Prototech electrode; and (b) by ascertaining the electrochemically active surface areas using the cyclic voltammetric technique.

(ii) Analysis of the cell potential/current density curves using eqn. (1) shows that the Tafel slope for the oxygen reduction reaction in the cells with the state-of-the-art membrane and electrode assembly, and with the Nafion-impregnated electrodes, is approximately  $0.060 \text{ V/decade}$ . In the cell with the  $50 \text{ cm}^2$  electrode, the Tafel slope with hydrogen/air as reactants is  $0.045 \text{ V/decade}$ . This Tafel slope appears to be independent of temperature and pressure. The Tafel slope in the cell with the as-received Prototech electrode is about  $0.095 \text{ V/decade}$ , and this may be interpreted as being due to the combined effects of activation and ohmic control.

(iii) It is essential to hot press the electrodes onto the membrane at a temperature of  $120 \text{ }^\circ\text{C}$  (glass transition temperature for Nafion) and under pressure ( $50 \text{ atm}$ ) to minimize activation and ohmic overpotential.

(iv) There is a significant pressure effect in the low range ( $0 - 2 \text{ psig}$ ) on the performance of the cells, with hydrogen/air as reactants. Above this pressure, both hydrogen/air and hydrogen/oxygen fuel cells show a linear increase in current density at a constant cell potential, with pressure.

(v) Optimal humidification of the reactant gases ( $5 - 10 \text{ }^\circ\text{C}$  above the cell temperature) is necessary to obtain stable long term performances.

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