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THE PROTON EXCHANGE MEMBRANE FUEL CELL - A STRONG CANDIDATE AS A POWER SOURCE FOR ELECTRIC VEHICLES

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ABSTRACT

Electric vehicles will play a significant role in solving energy and environmental problems. The new clean air laws in California mandate the sale of zero emission vehicles by 1998, (2% of total vehicle sales increasing to 10% by the year 2005). The only vehicle power systems that can meet the zero emission requirement are battery or fuel cell power systems with on-board hydrogen. Initial sales requirements will be met by battery powered vehicles for use in an urban setting (range of less than 150 miles/day). Long range general purpose vehicles will require fuel cells. Of all fuel cell types, the proton exchange membrane fuel cell (PEMFC) system is presently the strongest candidate. The PEMFC uses platinum as a catalyst and at present electrode loading levels will require substantially more per vehicle than is presently used in catalytic converters. This paper highlights the progress made in air breathing, low platinum loading PEMFCs at the Center for Electrochemical Systems and Hydrogen Research (CESHR). The effects of platinum loading, and operating pressure are described and an analysis of air compression energy and its net affect on fuel cell performance is presented.

INTRODUCTION

The energy crisis in 1973 stimulated the development of batteries and fuel cells as power sources for electric vehicles. The R&D expenditure since 1973 for developing advanced batteries for electric vehicles has exceed that of fuel cells by at least a factor of ten. Recent fuel cell developments indicate that the PEMFC may be a the first fuel cell to be commercialized for vehicle use. Even though the attainable power and energy densities in PEMFCs may be sufficient to serve as a sole power source for electric vehicles, a hybrid propulsion system (i.e. a PEMFC with advanced batteries) appears more attractive due to lower capital cost[1].

The General Electric Company invented PEMFCs (originally referred to as solid polymer electrolyte fuel cells). Historically, this fuel cell was the first to find an application (auxiliary power source in NASA's Gemini space vehicles, 1960s). Due to the low performance and stability of the proton conducting membrane at that time (polystyrene sulfonic acid), the PEMFC was displaced by alkaline fuel cells for the subsequent space missions (Apollo, Space Shuttle). General Electric continued to made advances in the 1970s by replacing polystyrene sulfonic acid membranes with DuPont's Nafion membranes. High levels of performance were attained[2].

The organizations which were responsible for making major strides in the 1980s, are Ballard Power Systems, Inc. (BPSI) and Ergenics Power Systems, Inc. (EPSI). BPSI demonstrated high power density electrodes and built 5 kW prototype units for military applications. Recently they have been engaged in designing and constructing an array of 5 kW modules (120 kW gross power) for a transit bus propulsion system. EPSI incorporated novel humidification and water removal systems in 200 W and 1 kW systems and utilized hydrides for supplying hydrogen to the electrochemical cell stack.

The BPSI and EPSI PEMFCs contain high platinum loadings (about 4 mg/cm^2) in each electrode (8 mg/cm^2 of membrane area). A novel method was developed at Los Alamos National Laboratory (LANL) to utilize low platinum loading electrodes in PEMFCs and attain performances close to those in PEMFCs with high platinum loading electrodes. The attainment of high energy efficiencies and high power densities in fuel cells with low platinum loading electrodes, first at LANL and then at CESHR was made possible using the following procedures: (i) impregnation of a proton conductor into the electrode structure to enhance the three-dimensional reaction zone just as when using a liquid electrolyte; (ii) hot-pressing of the proton conductor-impregnated electrodes to the proton conducting membranes at a temperature close to that of the glass transition temperature; (iii) optimize humidification of reactant gases; (iv) operation at elevated temperatures and pressures; (v) localization of platinum near the front surfaces of the electrodes by using thinner active layers and depositing a very thin layer of platinum on the front surface; and (vi) use of membrane with higher conductivities and water retention characteristics.

CESHR AIR BREATHING FUEL CELL DATA

The CESHR fuel cell experimental data and analysis is presented in the following text and Figures 1 through 7. All data was taken using single test cells with 5 cm^2 electrodes. The electrode membrane assemblies were fabricated using porous gas diffusion electrodes and proton conducting polymer membranes (Dow Chemical, 125 μm thickness). The fabrication method and a schematic of the test cell is provided in reference[3]. The fuel cell gases were humidified and temperature regulated. The performance evaluation was conducted using a computer controlled power supply (HP 6033A) and a data acquisition unit (HP 3421A) interconnected through a GPIB bus.

The fuel cell data is presented in the form of polarization and performance curves. The polarization curves show the single cell voltage and electrode current density. The performance curves present the electrode power density (voltage x current density) and the chemical to electrical efficiency based on the higher heating value of hydrogen.

Electrode Platinum Loading

In Figure 1 polarization data is present that compares high and low platinum loading electrodes on air and oxygen. Oxygen is not practical for fuel cell use on an electric vehicle (due to storage) but is given for comparison. The platinum loading presented are 10.0 and 0.45 mg/cm^2 of electrode area. This translates to 20.0 and 0.9 mg/cm^2 of membrane material and is considered as being very high and low values.

The polarization curve is typically characterized by three regions, an initial region followed by a linear region, and finally a mass transfer limited region. The initial region shows an initial steep drop in the cell potential due to slow cathode kinetics. With sufficient voltage drop (0.1 to 0.15 volts) the kinetics are high and are no longer limiting. The linear region is characterized by a linear voltage drop primarily due to ionic resistance in the electrolyte. As the current density further increases, the polarization curve enters the mass transfer limited region. Cell potential drops off rapidly primarily due to the inability of oxygen to reach reaction sites fast enough. This inability may be caused by a combination of an oxygen gradient through the electrode, nitrogen blanketing and or process water blockage.

Figure 1 shows that oxygen and higher platinum loading increases the cell voltage at a given current density. Consider the two oxygen curves, the high platinum loading curve is offset approximately

60 mV higher than the low loading curve, neither curve shows mass transfer limitations (data was not taken to the reach this region). The air curves at the beginning of the linear region have an offset of approximately 60 mV but the spread increases to > 100 mV as the potential drops due to mass transfer limitations. This may be explained by the high platinum loading having more reaction sites available, thus mass transfer limitations occur at a high current density. Severe mass transport problems with air are encountered at current densities greater than 1.0 A/cm². Within the linear region the difference between air and oxygen for the same platinum loading is approximately 60 mV.

Figure 2 presents the Figure 1 data in a performance curve form. The ordinate is electrode power density in W/cm² and is an indication of how compact the fuel cell could be constructed. A higher electrode power density means less surface electrode area will be needed to achieve a given power level. The abscissa is electrode efficiency based on the higher heating of hydrogen. Higher efficiency translates to greater fuel economy thus a smaller on-board hydrogen storage system and or a longer vehicle range. It should be noted that lower efficiency translates also to greater heat generation within the fuel cell.

The curves indicate that there is a trade off between power density and efficiency. A higher power density is achieved at a lower efficiency, a peak is reached where the power density and efficiency declines. At no time would it be advantageous to operate the fuel cell beyond the peak power density.

The figure shows that oxygen and higher platinum loading increases the fuel cell power density and efficiency. The high platinum loading air case increases the peak power density by approximately 33% (0.3 to 0.4 W/cm²). However this is accomplished at great cost to platinum utilization, 48.8 g of platinum/kW compared to 2.9 g/kW for the low platinum loading case (factor of 17). Considering a hybrid vehicle (fuel cell battery combination) may require 25 kW of fuel cell power this translates to 1220g and 72.5 g respectively. The average conventional vehicle contains 3 g of platinum.

Using an example design power density of 0.25 W/cm² the higher platinum loading increases efficiency from 43.5% to 49% thus resulting in a high fuel economy. Cyclic voltametric was used to determine the elctrochemically active surface area of the 0.45 mg Pt/cm² electrode and it was found to be about 15% to 20% leaving significant opportunity for further increases in performance[4].

Operating Pressure

In Figure 3 polarization curves are presented for operating pressures of 1 and 5 atmospheres utilizing low platinum loading electrodes. Pressurization significantly increases the performance when operating on air or oxygen. Consider the oxygen curves, the voltage increase with pressure at 400 mA/cm² is approximately .09 volts increasing in difference to 0.13 volts at 1800 mA/cm². This phenomena is particularly pronounced in the air curves where the voltage spread occurs rapidly. The 5 atmosphere air case achieves 0.6 volts at 1000 ma/cm² while the 1 Atm curve can only produce 475 mA/cm², greater than a factor of 2 decline in current density. It would seem logical that to achieve high performance from a fuel cell, the gases should always be compressed. For oxygen breathing fuel cells this is not a problem as the oxygen will be generally available in a compressed state. However, for an air breathing electric vehicle fuel cell the pressurization will require energy. The following section analyzes this energy requirement and its effect on fuel cell performance.

Energy of Air Compression

By compressing the air going into a fuel cell stack the partial pressure of the oxygen is increased and the stack performance is improved. However the energy for compression must be supplied by the fuel cell system, and the net fuel cell performance is therefore less than the stack performance. The air compression process can be adiabatic or isothermal and part of the compression energy may be recovered by an expander such as a turbine. To simplify the following analysis, it is assumed the compression to be performed by an ideal adiabatic compressor with no energy recovery upon expansion. All values are calculated on a per cm² basis for the electrode (specific values).

The specific power needed to operate the compressor (w_C/cm² of electrode area) is proportional to the reaction rate, (the amount of air needed, $\dot{m}_{air}$, g/hr) and the pressure ratio (P_2/P_1). The stoichiometric mass fuel ratio of oxygen to hydrogen is 8 to 1. Air contains 23.18% oxygen by mass, 21.99 % by volume. . Therefore the stoichiometric mass fuel ratio of air to hydrogen is 34.5 to 1. However due to nitrogen blanking of the electrode the fuel cell will probably be operated between 1.5 and 3.0 stoichiometric mixtures of air.

The specific amount of air mass needed for the electrode (g/hr/cm²) is dependent on the current density (i, amps/cm²). The mass needed can be determined by Faradays' Law - 96487 coulombs per gram equivalent of consumed hydrogen. Faradays' Law translates to 26.8 amp hrs/g of H_2, or 26.8 amp hrs/34.5 g of air assuming a 1 stoichiometric mass fuel ratio. Inverting this value results in 1.287 g of Air/hr/i per stoichiometric mass fuel ratio. The specific rate of air use as a ratio of current density is as follows:

(1)
$$\frac{\dot{m}_{air}}{i} = \frac{1.287}{3600} \times \text{\# of Stoich. Mixtures} \qquad \frac{\text{g/second}}{\text{amp/cm}^2}$$

The specific energy to adiabatically compress Air is as follows:

(2)
$$E_{1-2} = C_p T_1 \left[\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} - 1 \right] \qquad \frac{J}{g}$$

Where		
	E_{1-2}	Energy of Adiabatic Compression
	C_p	Specific Heat (Air 1.004 J/(g K))
	T_1	Inlet Air Temperature
	P_1	Inlet Air Pressure
	P_2	Fuel Cell Air Pressure
	k	Specific Heat Ratio (Air 1.4)

Multiplying the specific rate of air use, $\frac{\dot{m}_{air}}{i}$ and the specific energy of compression results in specific power of compression for the electrode (w_C/i):

(3)
$$\frac{w_C}{i} = \frac{1.287}{3600} \times \text{\# of Stoich. Mixtures} \times C_p T_1 \left[\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} - 1 \right] \qquad \frac{W}{\text{amp/cm}^2}$$

The electric power to operate the compressor (w_C) comes from the fuel cell. Thus the gross specific fuel cell power (w_{FC}) is the summation of the specific electric load power (w_{FCL}) and specific compressor power (w_C)

(4)
$$w_{FC} = w_{FCL} + w_C = V_{cell} \times i \qquad W$$

Consider that the compressor is in series with the electrical load as in Figure 4. Both the electrical load and compressor received the same specific current (i) with the respective voltage drops for the compressor (v_C) and the electrical load (v_L) being in proportion to the specific powers w_{FCL} and w_C:

$$(5) \qquad w_{FC} = w_{FCL} + w_C = i \times (v_L + v_C) \qquad W$$

The specific work of compression is simply the product of the specific amps and the voltage drop due to the compressor:

$$(6) \qquad w_C = i \times v_C \qquad W$$

Rearranging and applying the specific energy of compression equation results in the following:

$$(7) \qquad v_C = \frac{w_C}{i} = \frac{1.287}{3600} \times \text{\# of Stoich. Mixtures} \times C_p\, T_1 \left[\frac{P_2}{P_1}^{\frac{k-1}{k}} - 1 \right] \qquad V$$

It is important to note that the effective compressor voltage v_C is a function of the number of stoichiometric mixtures, the initial air temperature T_1 and the pressure ratio P_2/P_1 only. Thus the effect of air compression can be simply presented on a polarization diagram as a reduction in voltage. The reduced voltage curve then may be used to determine the impact air compression has on power density and efficiency. Note that the analysis considered the compressor in series with the electrical load for ease of explanation, the effective result in equation #7 also applies to a parallel placement of the compressor.

Figure 5 presents the results of equation # 7. The effect of stoichiometric mixtures is to linearly increase the effective compressor voltage while the pressure ratio effect is a power function. Utilizing the analysis, the air curves of Figure 3 are presented in Figure 6. The 1 atmosphere case is unaffected while the 5 atmosphere curve is simply reduced by 0.125 V to represent the result of adiabatically compressing 2 stoichiometric mixtures. The figures shows that the 1 atmosphere condition actually out performs the 5 atmosphere condition up to 0.62 V/425 mA where the two curves cross.

Figure 7 presents the Figure 6 data as performance curves. The curves show that when compressor energy is not considered, pressurization significantly increases both power density and efficiency e.g., 1 atmosphere, 0.31 W/cm² and 35 % efficiency, 5 atmosphere, 0.64 W/cm² and 36 % efficiency. The fuel cell stack efficiency gain with pressure is most pronounced by considering a design power density of say 0.25 W/cm². At this condition the 1 atmosphere case has an efficiency of 43.5% while the 5 atmosphere case has an efficiency of 51.5%. This translates to an approximate fuel saving of 20%.

However when adiabatic compressor energy for 2 stoichiometric mixtures is considered, the peak power is reduced from 0.64 W/cm² and 36% efficiency to 0.49 W/cm² and 28% efficiency, a loss in power density and efficiency. The efficiency drop may be most significant as it translates to a larger on-board hydrogen storage system. For the example design power density of 0.25 W/cm² the efficiency drops to 42%, a lower efficiency than the 1 atmosphere case.

Air compression improves platinum utilization, Comparing the 1 and 5 atmosphere cases, the platinum utilization increases from 2.9 g of platinum/kW to 1.8 g/kW (factor of 1.6 reduction). Considering a hybrid vehicle (fuel cell battery combination) may require 25 kW of fuel cell power, this translates to 72.5 g and 45 g respectively. The average conventional vehicle contains 3 g of platinum and thus these values are still an order of magnitude greater. However future research will probably remove this barrier by incremental improvements in platinum utilization or its outright replacement as a catalyst.

CONCLUSIONS

Mandates for zero emission vehicle are stimulating the development of fuel cells as a power systems for electric vehicles. The PEMFC is a favored technology due to its use of a solid electrolyte, cold start capability, high power density, and efficiency characteristics. This paper presented performance data on the effects of electrode platinum loading and operating pressure.

The use of platinum as a catalyst is a major obstacle to the wide spread use of PEMFCs for transportation. Present low loading electrodes would use an order of magnitude more platinum per vehicle than is presently used in catalytic converters. Future research will probably remove this barrier by incremental improvements in platinum utilization or its outright replacement as a catalyst. Air compression increases the fuel cell power density and thus the platinum utilization is improved. However the energy for compression must be supplied by the fuel cell system, and the net fuel cell performance is therefore less than the stack performance. Through analysis it was found that the theoretical effect of air compression can be simply related to a constant reduction in stack voltage. The reduced voltage curve then may be used to determine the impact air compression has on power density and efficiency.

The trade off between power density, efficiency and platinum utilization is complex and will depend on the vehicle mission requirements. The optimum combination will also depend on the cost of hydrogen and its associated on-board storage system, and finally the availability of platinum and its cost. The future development of alloy electrocatalysts and the optimization of electrode structure will in all probability enhance the performances. From a systems point of view a variable speed *smart* air compressor may be necessary to balance the conflicting goals of power density and efficiency.

ACKNOWLEDGMENTS

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FIGURE 1: POLARIZATION CURVE - AIR AND OXYGEN AT HIGH AND LOW ELECTRODE PLATINUM LOADING

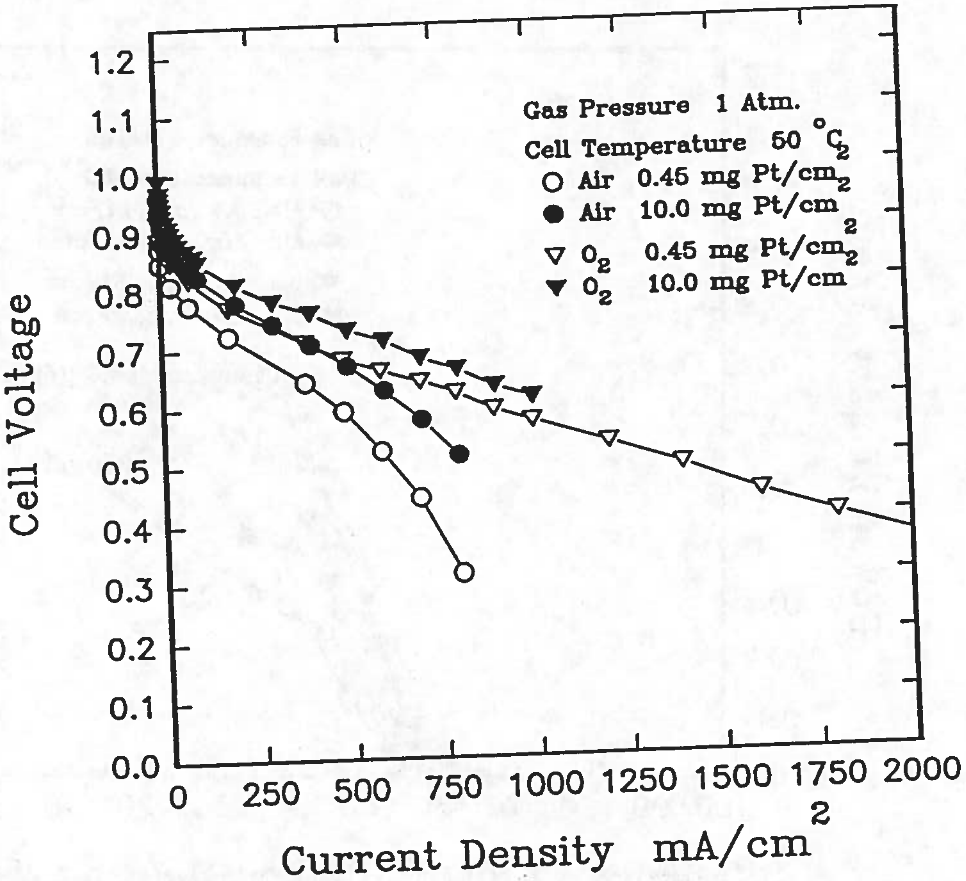

FIGURE 2: PERFORMANCE CURVE - AIR AND OXYGEN AT HIGH AND LOW ELECTRODE PLATINUM LOADING

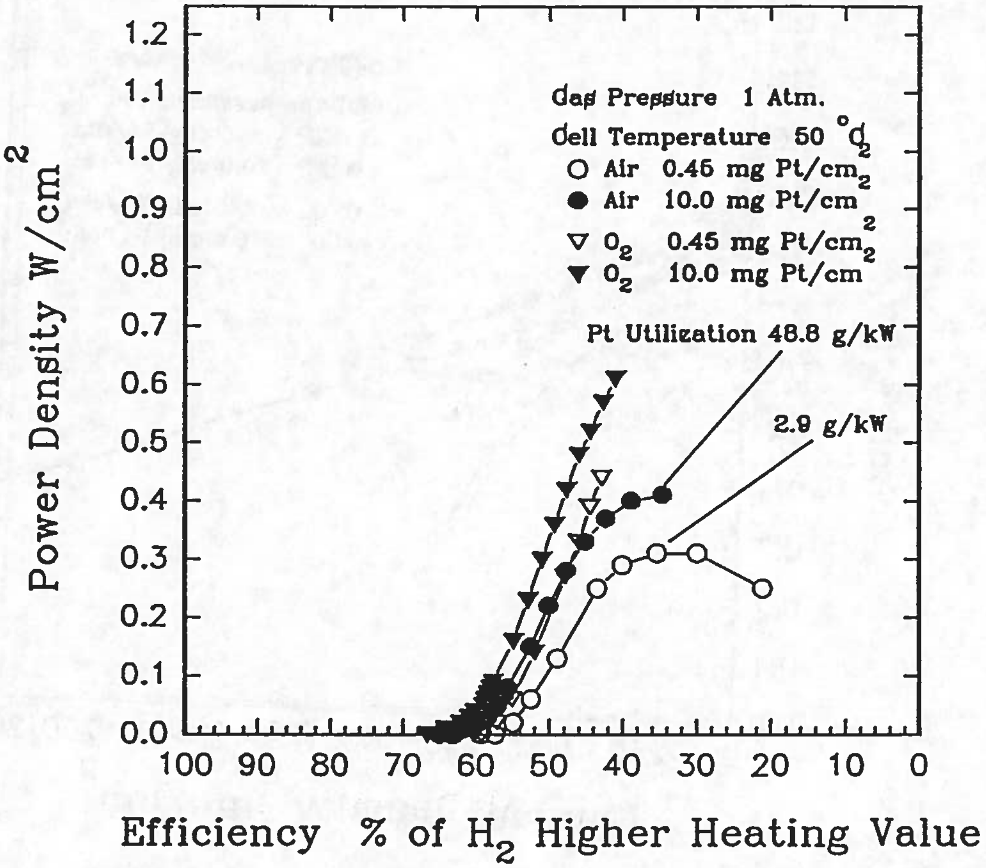

FIGURE 3: POLARIZATION CURVE - AIR AND OXYGEN AT 1 AND 5 ATMOSPHERES PRESSURE

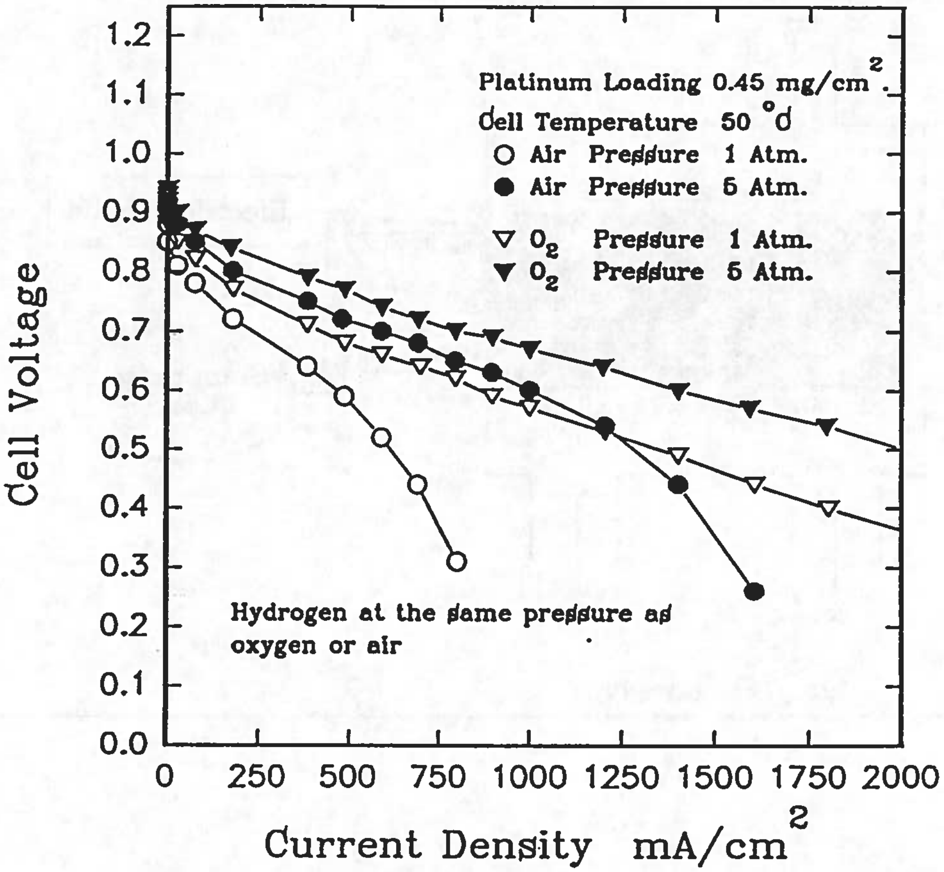

FIGURE 4: FUEL CELL SCHEMATIC

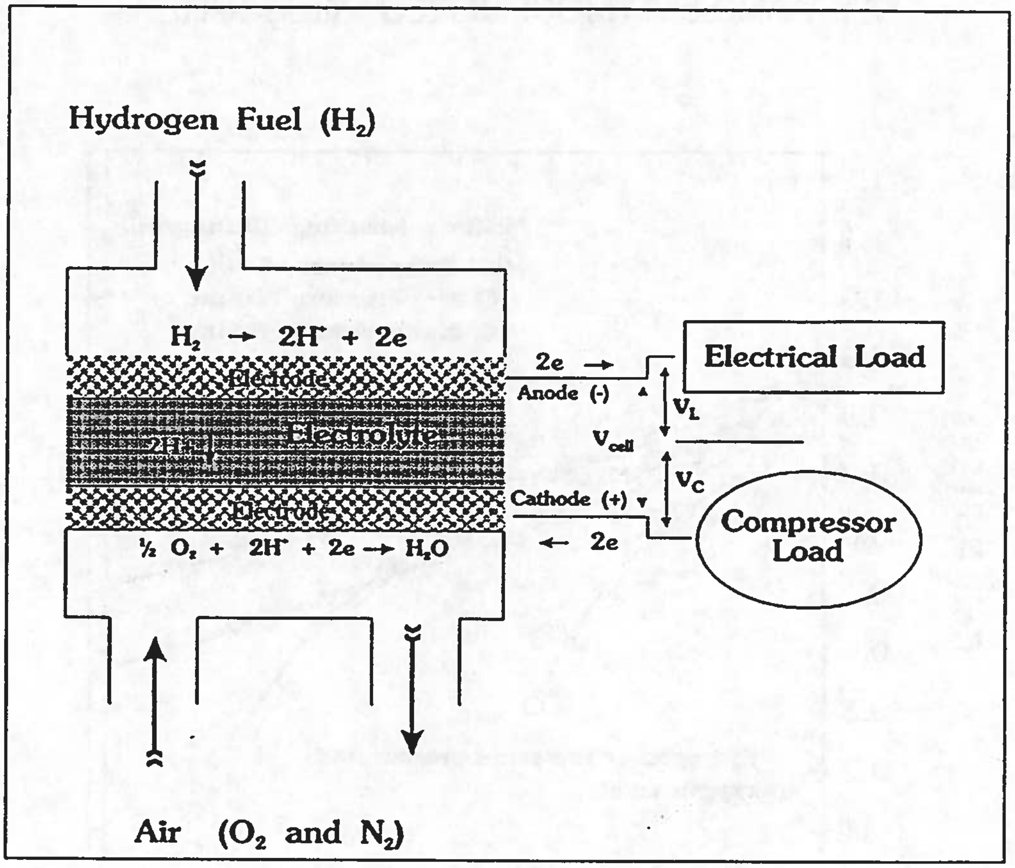

FIGURE 5: EFFECTIVE VOLTAGE LOSS DUE TO ADIABATIC AIR COMPRESSION

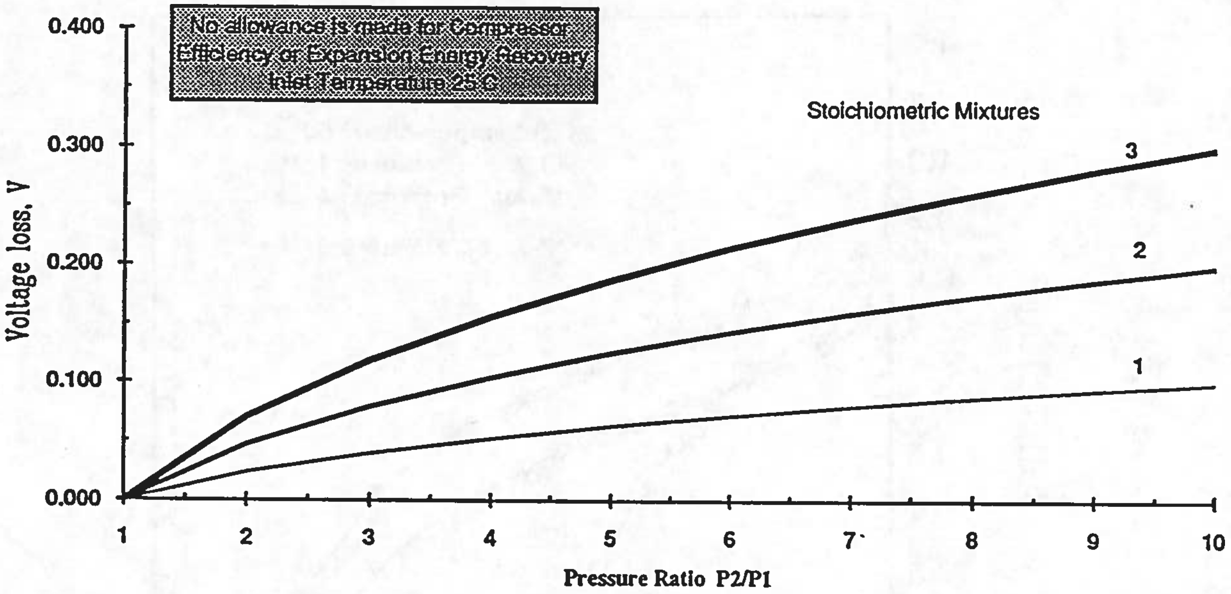

FIGURE 6: POLARIZATION CURVE - AIR AT 1 AND 5 ATMOSPHERES PRESSURE AND EFFECT OF ADIABATIC COMPRESSION

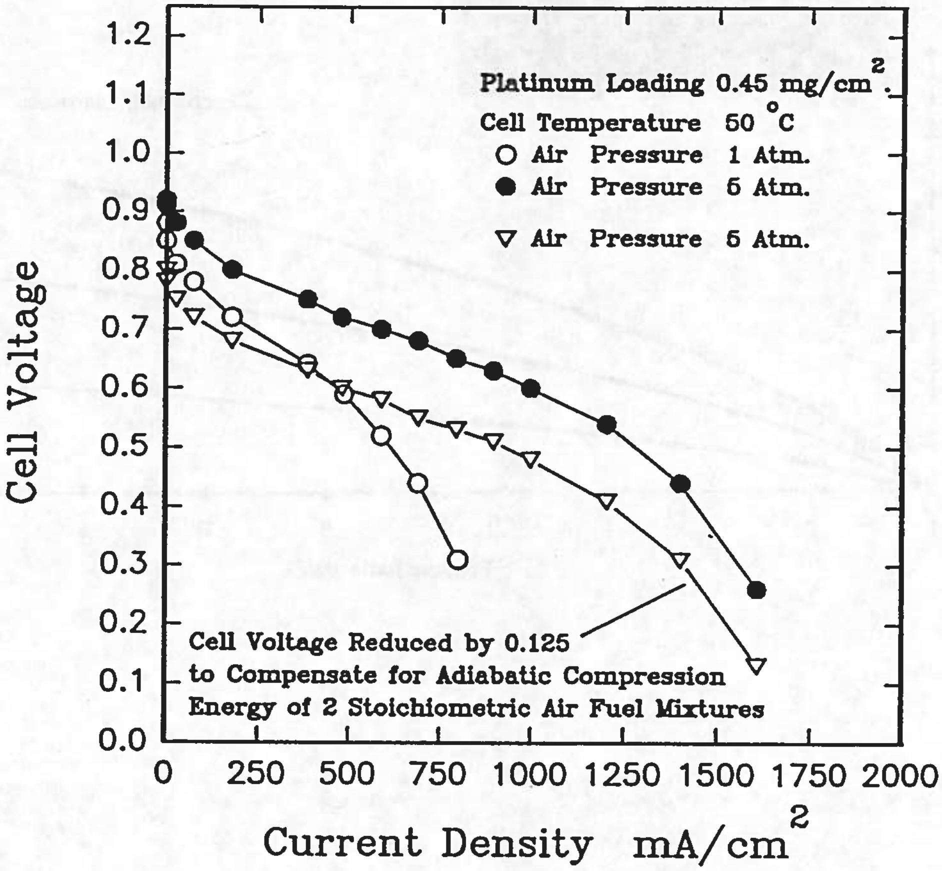

FIGURE 7: PERFORMANCE CURVE - AIR AT 1 AND 5 ATMOSPHERES PRESSURE AND EFFECT OF ADIABATIC COMPRESSION