PARAMETRIC STUDIES ON THE LIQUID FEED DMFC

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The effects of the operating conditions, i.e. cell temperature, oxygen gas or air pressure, methanol liquid flow rate and methanol concentration, on the performance of a small scale (9 cm^2 area) Liquid Feed Direct Methanol Fuel Cell (LFDMFC) have been studied. The cell's best performance is achieved when operated at a temperature of 90°C, near ambient pressure, flow rate of 2.09 ml/min equivalent to a velocity of approximately 0.1 cm s^{-1} of an aqueous solution of 2 molar methanol. Short term durability tests have shown the good stability of the cell performance over a period of around 30 hrs. The maximum cell power recorded was 0.98 W with oxygen gas and 0.88 W with air at the same pressure.

Key words: fuel cell, direct methanol, polymer electrolyte, electrochemical, electrocatalysis.

INTRODUCTION

Hydrogen-oxygen fuel cells based on the solid polymer electrolyte are presently being used for vehicular applications. Since hydrogen is difficult both to store and transport, the most recent attention has been given to the DMFC.

In the LFDMFC, methanol in an aqueous solution is directly oxidised to carbon dioxide and water on a catalytically active anode, made from a Nafion/Teflon bonded Pt-Ru catalysts dispersed onto carbon. At the cathode oxygen is reduced using a similar electrode to the anode but with only platinum catalyst. The existence of the electrochemical losses at both electrodes in such fuel cell lead to a reduction in overall performance from the theoretical thermodynamic maximum [1-4]. Research has thus focused on efforts to minimise these losses. A liquid feed DMFC with power output of 0.2 W/cm^2 at an operational temperature of 95°C and 4 bar oxygen pressure has been reported by Ravikumar and Shukla[5]. They claimed that this performance was due to improvements of both catalyst and cell engineering. Catalyst loading used were 5 mg/cm^2 on either electrode. They also pointed out that the optimised methanol concentration that could be used without significant methanol cross-over, from the anode to the cathode, is 2 molar. This was determined by an in situ measurement of both electrodes performances in the DMFC at various methanol concentration and operation temperature.

The most recent work on the LFDMFC has been carried out by Shukla et al[6]. They reported results of a two cell stack (50 cm^2) with a power output of approximately 2.2W at 65°C and 2.4W at 90°C, using oxygen at atmospheric pressure.

In this paper, we report the results of parametric studies, i.e. cell temperature, oxygen gas or air pressure, methanol liquid flow rate and methanol concentration, on the performance of a small scale Liquid Feed Direct Methanol Fuel Cell (LFDMFC).

EXPERIMENTAL

Catalyst preparation and MEA fabrication: Catalysts for both electrodes were prepared at our laboratory according to the procedure fully outlined elsewhere [5]. Each of the electrodes consists of a backing layer, a gas diffusion layer, and a reaction layer. A teflonised carbon cloth (E-TEK, type A) of 0.35mm thickness is employed as the backing layer in both electrodes. To prepare the gas diffusion layer, the required quantity of ISP was added to a pre-teflonised Ketjen Black carbon to make the paste required. The resultant paste was spread onto the carbon cloth and dried in an air oven at 85^{o}C for five minutes. To prepare the reaction layer, the required quantity of Pt-Ru/C (anode) or Pt/C (cathode) was mixed with 10 wt% teflonised carbon. The required quantity of Nafion solution (Aldrich) was added to the mixture with continuous stirring. The paste thus resulted is spread onto the gas diffusion layer of the electrode and dried in an air oven at 85°C for five minutes. The catalyst content on the anode was maintained at 2 mg/cm^2 while that on the cathode was 1 mg/cm^2. A thin layer of Nafion solution was spread onto the surface of each electrode. The MEA was obtained by hot pressing the anode and cathode on either side of the pre-treated Nafion 117 proton exchange membrane at 100 kg/cm^2 and 125^{o}C for 3 minutes. The thickness of the MEA is approximately 0.8 mm depending on the diffusion layer thickness.

Fuel cell assembly: A liquid feed DMFC was assembled employing the MEA. Both electrodes were contacted on their rear with gas/liquid flow field plates machined from impregnated high density graphite blocks in which channels were formed. The channels machined to achieve minimum mass polarisation in the cell. The ribs between the channels make the electrical contact to the back of the electrodes and conduct the current to the external circuit. Electrical heaters supplied by Watson Marlow were placed behind each of the graphite blocks in order to heat the cell to the desired operational temperature. The graphite blocks were also provided with electrical connectors for electrical contacts and small holes to accommodate thermocouples.

RESULTS AND DISCUSSIONS

After allowing 48 hrs to condition a new MEA in the test fuel cell at 75^{o}C and atmospheric pressure with continuous feed of 2M methanol, the galvanostatic polarisation data were obtained at various operating conditions. Several MEAs were tested to ascertain reproducibility of the data.

Effect of Methanol Flow Rate: The performance characteristics of the cell were obtained at various methanol flow rate. These flow rates are low and are equivalent to linear velocities in the flow channels of 0.04 to 0.1 cm s^{-1} and Reynolds numbers of 0.8 to 2.0. Higher liquid flow rates were avoided because the cell heating system has a limiting capability in maintaining the cell at the required temperature, i.e. 90^{o}C. The data collected during the air and oxygen operations (2 bar pressure, 90^{o}C and 2M methanol) are presented in Figures 1a-1c. Figure 1a shows the results obtained for the air operation, during which the lower flow rate (0.84 ml min^{-1}) was giving a better cell performance up to current densities of 240 mA/cm^2. There is a clear indication of cell starvation of methanol at higher current densities where current starts to fall due to a

mass transport limitation. Similar behaviour is seen in Figure 1b for the oxygen operation. As the flow rate increases (2.09 ml min^{-1}) a better cell performance was obtained at higher current densities. In general, there is not a large effect of flow rate on the cell performance. Table 1 summarises the cell performances at 50, 100, 200 and 300 mA/cm^2 for both air and oxygen operations. The difference between air and oxygen operation, in terms of cell voltage at a particular current density, is approximately 50 mV. This difference in voltage falls at higher current densities, e.g. at 300 mA/cm^2 it is 30 mV.

Table 1

Current Density mA/cm^2	**50**	**100**	**200**	**300**
Air Operation Cell Voltage/ mV	**560**	**503**	**410**	**329**
Oxygen Operation Cell Voltage/ mV	**615**	**555**	**462**	**360**

Figure 1c shows the cell output power for air and oxygen operations. The maximum difference between the two is about 10.2% at 300 mA/cm^2. For the lower current densities (up to 100 mA/cm^2) this difference is smaller. The maximum power density is approaching a value of approximately 110 mW/cm^2. This means that a practical DMFC system could be designed to operate with air rather than oxygen.

Effect of Methanol concentration: Results are presented in Figure 2. for 2.0 bar air operation, 90^oC cell temperature and 0.84 ml/min flow rate. At values of high current density the significance of a low concentration of methanol becomes apparent as a trend towards the current approaching a mass transport limit. At lower current densities, in the range of 100 to 200 mA/cm^2 there is an optimum concentration of approximately 1.5 M. At low current densities the cell performance is better at the lowest concentration of methanol used.

Effect of Cell temperature: Figure 3 presents the data obtained at 65^oC and 90^oC cell temperature for both air and oxygen operation. Other conditions are 1.34 ml/min flow rate for 2 molar methanol solution and 2 bar cathode side pressure. Higher temperature clearly improves the cell power performance.

Effect of air/oxygen cathodic pressure: Results are presented in figures 4a-4b for oxygen and air operations respectively. Figure 4a shows that there is only a small difference in cell performance when it operates near ambient pressure (0.05 bar oxygen) and higher oxygen gas pressure (2 bar). This is a great advantage for practical liquid feed DMFC stack were it can be operated under atmospheric pressure with high efficiency, i.e. power output. Figure 4b presents a comparison between near atmospheric pressure and 2.0 bar air pressure operations. The data follow similar a trend to that with oxygen and this means there are real possibilities of a LFDMFC operation at atmospheric air pressure. Tables 4a and 4b summarise the performance of the cell for both operations at different current densities.

Table 4a

Current Density mA/cm^2	**50**	**100**	**200**	**300**
0.05bar Oxygen, Cell Voltage/ mV	**570**	**515**	**430**	**340**
2bar Oxygen, Cell Voltage/ mV	**600**	**546**	**462**	**302**

Table 4b

Current Density mA/cm^2	**50**	**100**	**200**	**300**
0.05bar Air, Cell Voltage/ mV	**525**	**462**	**379**	**298**
2bar Air, Cell Voltage/ mV	**547**	**495**	**402**	**307**

CONCLUSIONS

Measurements have shown that the optimised operation conditions for a 9 cm^2 cell are as follows; 90^{o}C cell temperature, ambient air or oxygen pressure, up to 2.09 ml/min flow rate of 2M methanol concentration. Overall over the range of flow rates considered there is not considerable effect of liquid flow rate on the cell performance, the difference is less than 5 %.

Short term durability tests have been conducted and have shown that the cell performance is stable over a fairly long period of time, around 30 hours. The power output of the cell was 110 mW/cm^2.

REFERENCES

K. B. Prater, J. Power Sources, 51, 129 (1994).

J. M. Leger and C. Lamy, Ber. Busenges. Phys. Chem., 94, 1021 (1990).

M. Hogarth, P. Christensen A. Hamnett and A. K. Shukla, J. Power Sources, 55, 87 (1995).

M. Hogarth, P. Christensen A. Hamnett and A. K. Shukla, J. Power Sources, in print (1997).

M. K. Ravikumar and A. K. Shukla, J. of the Electrochemical Soc. 143, 2601 (1996).

A.K. Shukla, personal communication, 1997

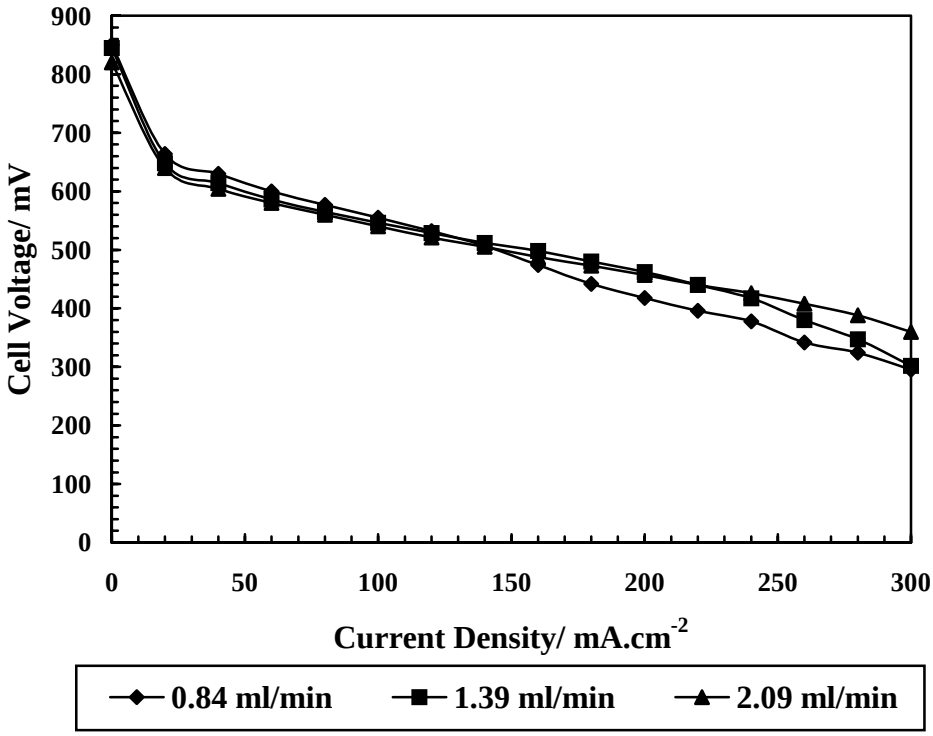

Figure (1a) : Effect of methanol flowrate on cell performance for air operation

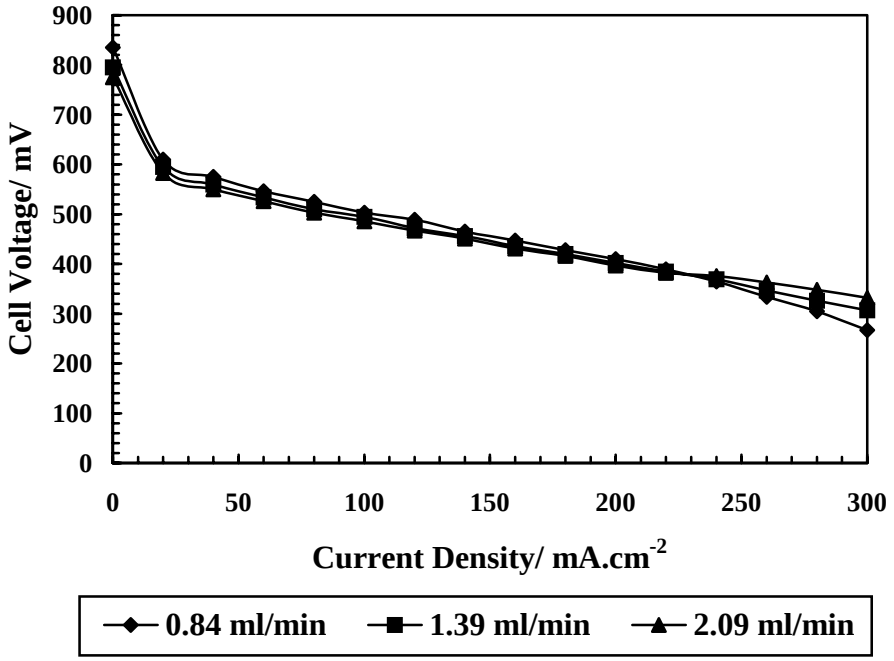

Figure (1b) : Effect of methanol flowrate on cell performance for oxygen operation

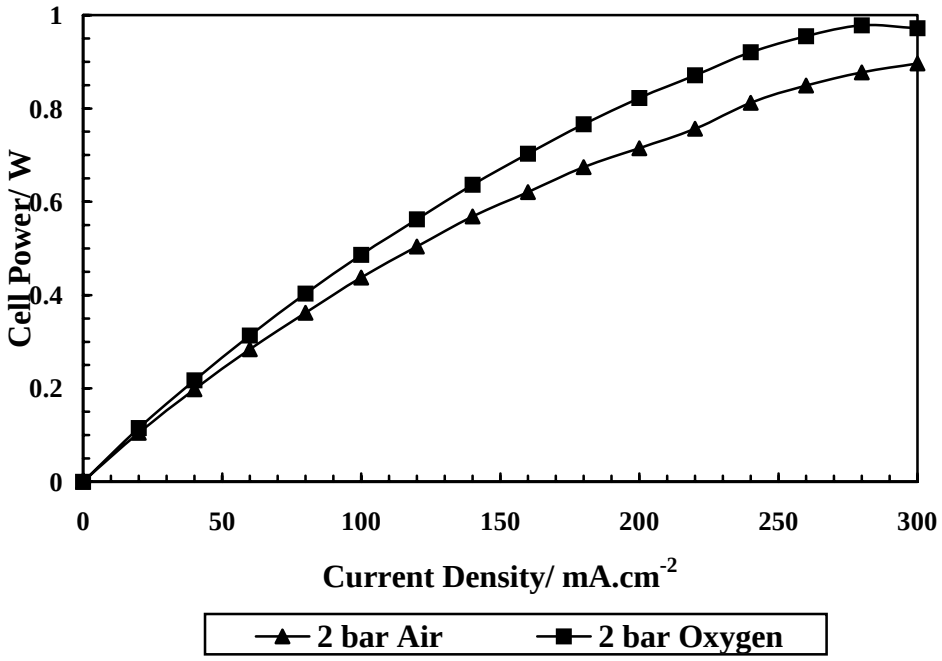

Figure (1c) : Cell power output

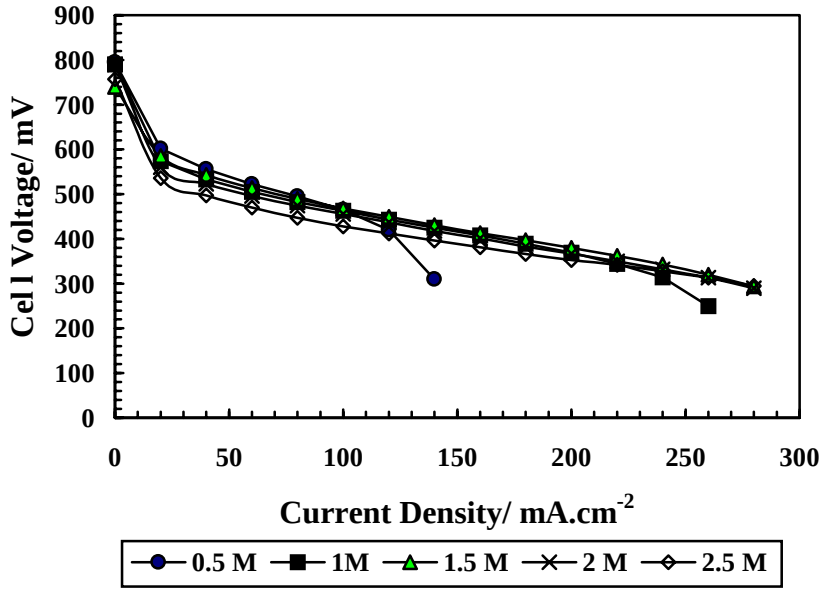

Figure (2): Effect of methanol concentration on cell performance for air operation

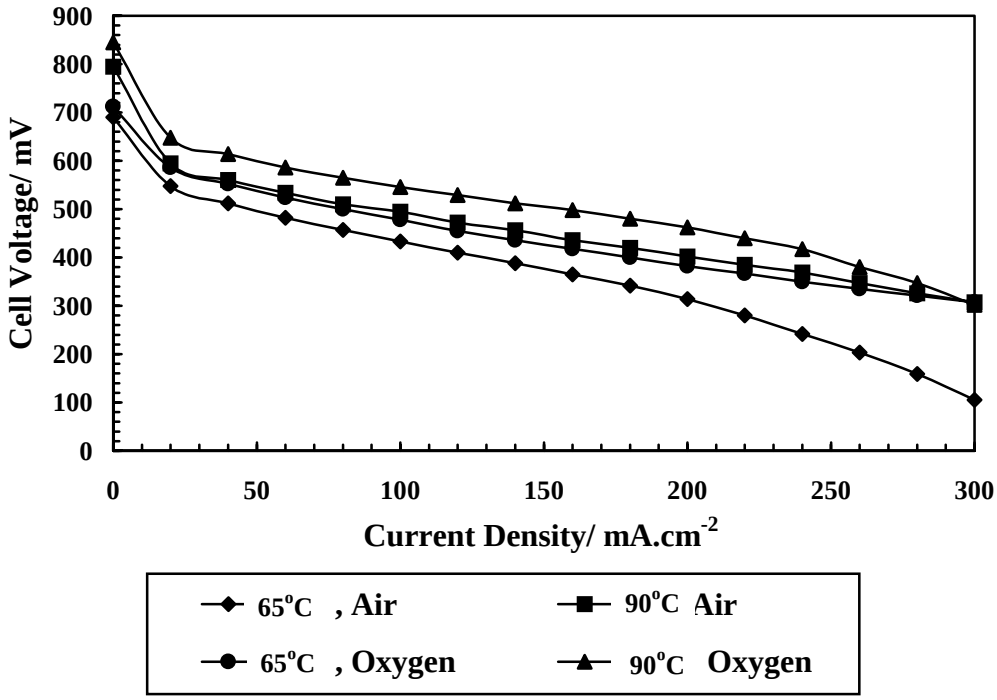

Figure (3) : Effect of cell temperature on cell performance for air and oxygen operation

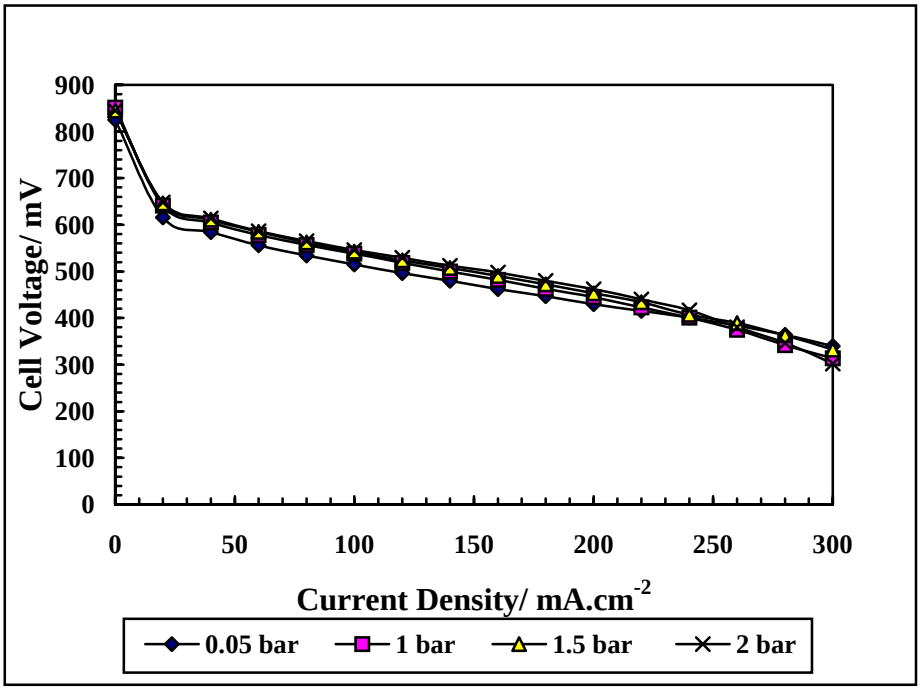

Figure (4a) : Effect of cell temperature on cell performance for oxygen operation

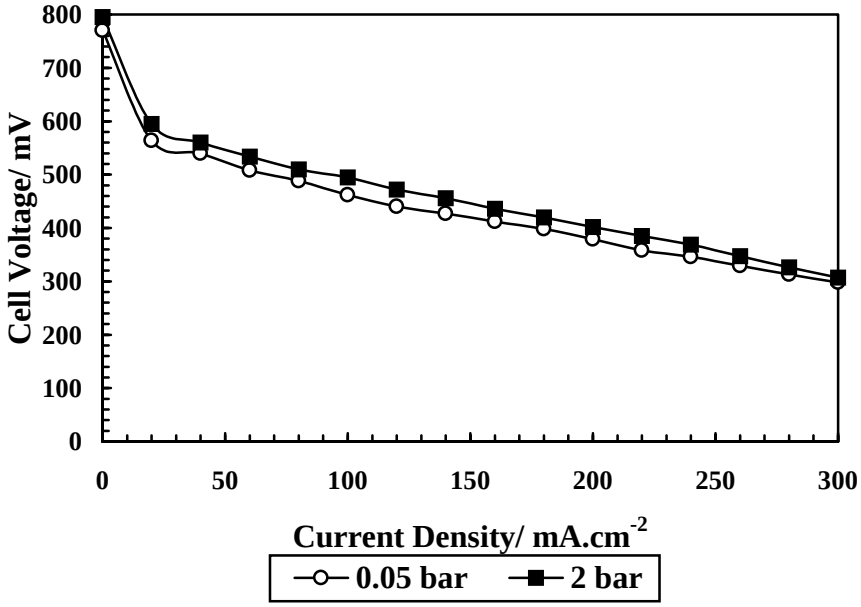

Figure (4b) : Effect of cell temperature on cell performance for air operation