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Limiting current behaviour of the direct methanol fuel cell

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Abstract

Limiting current density data for a liquid feed direct methanol fuel cell based on a Nafion® solid polymer electrolyte membrane are reported. The cell uses a membrane electrode assembly composed of porous Pt–Ru–carbon supported catalyst anode, Pt–carbon supported cathode covered by carbon cloth backing layers. The effect of cell temperature, air cathode pressure, methanol fuel flow rate, temperature and methanol concentration on the limiting current behaviour are described. Limiting current data are interpreted in terms of hydrodynamics and diffusion limiting effects in the porous catalyst structure and carbon cloth backing layers. In practical fuel cells the temperature of the feed and the cell are different due to heat transfer requirements and this factor is shown to influence performance. It is also demonstrated that cell operation is possible with a methanol solution vaporised into an inert gas stream.

Keywords: Direct methanol fuel cell; Solid polymer electrolyte; Mass transfer

1. Introduction

The liquid feed direct methanol fuel cell (DMFC), based on a solid polymer electrolyte (SPE), is seen as a potential power source in static and transport applications, due to its inherent simplicity of operation, e.g. conversion of a dilute aqueous based fuel into a gaseous product. Currently significant power performance has been achieved with the use of catalysts based on Pt–Ru, e.g. [1–11]. Typically, power densities higher than 0.18 W cm^{-2} are achievable, and power densities higher than 0.3 W cm^{-2} have been reported [3]. For high performance of a DMFC relatively low concentrations of methanol are required. At concentrations higher than approximately 2 M, the cell voltage declines significantly due to permeation of methanol through the membrane, i.e. methanol crossover. This permeation results in a mixed potential at the cathode with a significant loss in oxygen reduction performance and also poor fuel utilisation. At lower methanol concentrations power density performance is lower, but this is generally observed at the higher current densities where limiting current characteristics start to become evident.

The mechanism of methanol oxidation can be represented as follows [12]:

$$CH_3OH \rightarrow CO_{ads} + 4H^+ + 4e^- \quad (1)$$

$$H_2O \rightarrow OH_{ads} + H^+ + e^- \quad (2)$$

$$CO_{ads} + 2OH_{ads} \rightarrow CO_2 + H_2O \quad (3)$$

It is generally thought that the rate controlling step is surface reaction between CO_{ads} and OH_{ads}. It has been proposed that methanol and hydroxyl groups are adsorbed on different parts of the surface on carbon supported platinum. However despite significant research on methanol oxidation, the mechanism is not fully known and the adsorption of the various reactive

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intermediates may involve a combination of single site and dual site processes [13].

Limiting current densities for methanol oxidation at SPE based electrodes have been reported [7,12]: Kauranen and Skou [12] attributed this limiting current behaviour to saturation coverage of absorbed OH on the platinum surface. Ravikumar and Shukla [7] have reported data for the DMFC using platinum–ruthenium catalysts for methanol oxidation. If such limiting current behaviour did not occur then in principle lower methanol concentrations could be used which would improve the system engineering requirements.

The DMFC is a complex system based on a porous electrocatalytic electrode. Its operation as a liquid feed system is further complicated by the feature of evolution of carbon dioxide gas from the surface of the membrane electrode assembly. In this respect the DMFC has similarities with other gas-evolving electrodes as has been observed in visualisation of gas evolution [14].

The purpose of this research was to investigate the limiting current density characteristics of the DMFC and explore the influence of cell temperature and methanol solution feed temperature, oxygen gas or air pressure, methanol liquid flow rate and methanol concentration on the cell behaviour.

2. Experimental equipment

Tests on the DMFC were performed with a cell with a cross-sectional area of 9 cm^2 (Fig. 1). The cell was fitted with one membrane electrode assembly (MEA) sandwiched between two graphite blocks which had a flow bed, in the form of parallel channels, cut out for methanol and oxygen/air flow. The cell was held together with two plastic insulation sheets and two stainless steel or aluminium backing plates using a set of retaining bolts positioned around the periphery of the cell. Electrical heaters, supplied by Watson Marlow, were placed behind each of the graphite blocks to heat the cell to the desired operating temperature. The graphite blocks were also provided with electrical contacts and small holes to accommodate thermocouples. The fuel cells were used in a simple flow rig, which consisted of a Watson Marlow peristaltic pump to supply aqueous methanol solution, from a reservoir, to a Eurotherm temperature controller which was keeping the cell at a constant temperature. Air was supplied from cylinders, at ambient temperature, and the pressure regulated by pressure regulating valves.

MEAs studied in this work were made in the following manner: the anode consisted of a Teflonised (20%) carbon cloth support (E-Tek, type 'A'), of 0.3 mm thickness, upon which was spread a thin (diffusion layer) layer of uncatalysed (Ketjen black 600) 10 wt.% Teflonised carbon. The catalysed layer, unless otherwise specified consisted of 35 wt.% Pt–15 wt.% Ru (2 mg cm^{-2} metal loading) dispersed on carbon (Ketjen) and bound with bound with 10 wt.% Nafion® from a solution of 5 wt.% Nafion® dissolved in a mixture of water and lower aliphatic alcohols (Aldrich), was spread on this diffusion backing layer. A thin layer of Nafion® solution was spread onto the surface of each electrode. Electrode preparation are described in detail elsewhere [4]. The cathode was constructed using a similar method as for the anode, using a thin diffusion layer bound with 10 wt.% PTFE, and 1 mg cm^{-2} Pt black with 10 wt.% Nafion® in the catalyst layer. The electrodes were placed either side of a pre-treated Nafion® 117 membrane. This pre-treatment involved boiling the membrane for 1 h in 5 vol.% H_2O_2 and 1 h in 1 M H_2SO_4 before washing in boiling Millipore water (>18 mΩ) for 2 h with regular changes of water. The assembly was hot-pressed at 100 kg cm^{-2} for 3 min at 135°C.

Cell voltage versus current density response was measured galvanostatically, by incrementally increasing the current from open circuit and measuring the cell potential and then reducing the current incrementally again measuring the cell voltage. The data reported here were obtained with one MEA, unless otherwise stated. The MEA was conditioned before use in two stages: for 48 h in the test cell, in 2.0 M methanol solution at 75°C, and then by maintaining the cell with an applied load of 100 mA cm^{-2} for several hours. This pre-treatment resulted in stable performance under continuous operation.

3. Methanol mass transport

Ravikumar and Shukla [7] have reported data for the DMFC using platinum–ruthenium catalysts for methanol oxidation. The electrode structure comprises a Nafion® membrane onto which are pressed Nafion® bonded carbon supported catalysts. Although there is limited data, two features are noticeable:

1. At potentials between approximately 0.2 and 0.4 V (vs. DHE) (current density 50–250 $mAcm^{-2}$) the methanol reaction order apparently changes from a positive to a negative value, as the methanol concentration increases from 1.0 to 2.0 M.
2. Limiting current densities are obtained, at 0.5–2.0 M methanol concentrations, which are approximately proportional to the methanol concentration.

The measured limiting currents and effective mass transfer coefficients, k_{eff}, determined from

$$k_{\text{eff}} = \frac{j}{nFC_{\text{MeOH}}} \tag{6}$$

are given in Table 1, as calculated from the published data (Kauranen and Skou [12,15] and Ravikumar and Shukla [7]).

Noticeably the limiting current densities observed by Ravikumar and Shukla (Table 1) are very much lower, at equivalent methanol concentrations, than those of Kauranen. In two sets of the data [7,15], the mass transfer coefficient is approximately constant whereas in a third set [12] this is not the case; mass transfer coefficient decreases with an increase in methanol concentration. The electrode structures used were significantly different:

1. Kauranen and Skou [12] used a 50 μm thick anode layer (40 wt.% Pt on Vulcan XL-72R) with a Pt loading of 1.0 mg Pt cm^{-2} and no carbon cloth, or paper, diffusion layer.
2. Ravikumar and Shukla [7] used a catalyst layer made from Pt–Ru supported onto Ketjen black with a loading of 5 mg cm^{-2} of catalyst, which was covered with a carbon cloth 'diffusion layer', 0.3 mm thick.
3. Kauranen and Skou [15] also used a Pt–Ru supported catalyst covered by a carbon cloth diffusion layer.

The DMFC is a complex porous electrode system due to the thin three dimensional structure of the electrocatalyst region, the porous diffusion layers and the generation of carbon dioxide gas. The limiting

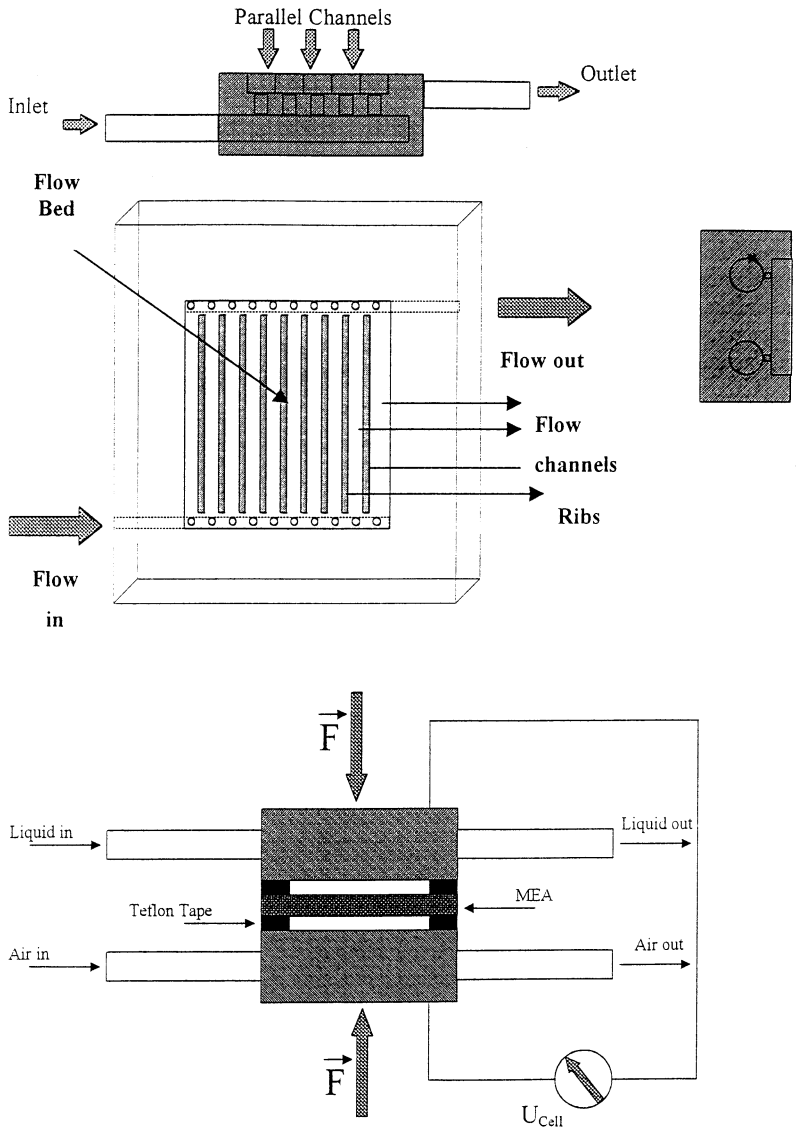

Fig. 1. Schematic of experimental equipment.

Table 1
Limiting current densities and effective mass transfer coefficients for methanol oxidation [7,12,15]

Methanol concentration (mM)	Limiting current density (mA cm^{-2})			k_L (ms^{-1})		
	Kauranen [12] (80°C)	Ravikumar [7]	Kauranen [15] (80°C)	Kauranen [12]	Ravikumar [7]	Kauranen [15]
20			20			1.7×10^{-5}
30	75			4.0×10^{-5}		
50			50			1.7×10^{-5}
100	150		90	2.5×10^{-5}		1.5×10^{-5}
200			190			1.6×10^{-5}
300	290			1.6×10^{-5}		
500		110 (70°C)			3.7×10^{-6}	
		180 (95°C)			6.0×10^{-6}	
1000		220 (70°C)			3.7×10^{-6}	
		360 (95°C)			6.0×10^{-6}	
1500		360 (70°C)			4.0×10^{-6}	

current behaviour of the DMFC is due to mass transport limitations of methanol supply to the catalyst caused by:

1. Hydrodynamic mass transfer at the surface of the cloth on the MEA.
2. Diffusion mass transfer in the carbon cloth and anode diffusion layer.
3. Diffusion mass transfer in the catalyst layer and at the catalyst surface.

The combined effect of the three above mentioned mass transfer effects can be simply expressed as follows:

$$\frac{1}{k_{\text{eff}}}=\frac{1}{k_{\ell}}+\frac{1}{k_{\text{cl}}}+\frac{\ell}{\xi k^*} \tag{7}$$

where k_{ℓ} is the hydrodynamic mass transport coefficient, k_{cl} is the carbon cloth mass transport coefficient and ξk^* is the effective electrochemical methanol oxidation rate constant in the catalyst layer, where ξ is an effectiveness factor for the catalyst.

Eq. (7) enables the overall mass transfer behaviour of the DMFC to be analysed in terms of three separate, but interactive components. The porous electrocatalyst layer is considered as a thin pseudo two dimensional structure where, due to the potential distribution, activity is at a region next to the membrane surface.

The value of k_{ℓ} in Eq. (7) depends on the hydrodynamics in the channel as well as on gas bubble liberation at the surface. Diffusion mass transfer in the cloth depends upon the liquid void fraction and the cloth pore structure and can be represented by

$$j=nFk_{\text{cl}}^{\circ}e_{\text{c}}^{m}\Delta C_{\text{cl}} \tag{8}$$

where ΔC_{cl} is the concentration change over the cloth thickness, e_{c} is the liquid voidage, m is an empirical parameter which allows for cloth tortuosity and porosity and is frequently = 1.5, and $k_{\text{cl}}^{\circ}=(D_{\text{MeOH}})/(\ell_{\text{cl}})$, where ℓ_{cl} is the cloth thickness.

At conditions when mass transport is not limiting performance, diffusion and electro-osmotic transfer influence methanol transport across the membrane associated with the generation of protons. At limiting current conditions the mass transfer of methanol to the anode due to diffusion and electro-osmotic transfer across the membrane is not a factor.

3.1. Mass transport at gas-evolving electrodes

In the case of the DMFC gas liberation is from the surface of a carbon cloth positioned away from the active electrode region. This gas evolution is, as observed in flow visualisation studies [14], not uniformly distributed and has similarities to gas evolution observed at planar electrodes. Mass transfer at gas-evolving electrodes has been measured for oxygen evolution [16] and chlorine evolution [17] at vertical electrodes. That data for oxygen evolution can be correlated, allowing for differences in gas evolution rates for oxygen evolution and carbon dioxide evolution with current density, as a function of current density, j_{O_2}, by the expression:

$$k_{\text{av}}=4.4\times10^{-6}(j_{\text{O}_2}/3)^{0.32} \tag{9}$$

where k_{av} is the average mass transfer coefficient.

The data for chlorine evolution is presented graphically [16] as the variation in diffusion layer thickness with current density. This data can be correlated, allowing for differences in gas evolution rates for oxygen evolution and carbon dioxide evolution, with current density as:

$$k_{\text{av}}=558D_{\text{MeOH}}(j_{\text{Cl}_2}/3)^{0.5} \tag{10}$$

where D_{MeOH} is the diffusion coefficient for methanol.

Alternative measurements on mass transfer enhancement due to gas bubbles at flat vertical electrodes have been obtained by a number of research groups. For example data from Ref. [18] can be correlated by

$$k_{av} = 0.97 \times 10^{-6} j^{0.25} \quad (11)$$

Fig. 2 shows the typical effect of gas evolution, i.e. current density, on mass transfer coefficient as predicted by the above correlations. The correlation for gas-evolving electrodes gives mass transfer coefficients in the range of $0.4–1.8 \times 10^{-5}$ ms^{-1}, for current densities in the range 100–2000 A m^{-2}. For gas-sparged electrodes, mass transfer coefficients are much lower, in the range of $0.3–0.6 \times 10^{-6}$ m s^{-1}. The experimental determined mass transfer coefficients (Table 1) are in the range of those predicted by correlations (Fig. 2).

It is anticipated that the overall mass transfer behaviour of the liquid feed DMFC is influenced by the gas liberation at the surface of the diffusion layer and is similar to that of a gas-evolving electrode. Thus, the effect of an increase in gas evolution rate, i.e. current density, should be to increase the mass transfer coefficient. This behaviour is not discernible in published data [7,12,15] on limiting currents for methanol oxidation, because the carbon cloth can offer a significant resistance to methanol diffusion to the catalyst layers, which will increase as the volume of gas in the diffusion layer increases, i.e. current density increases.

Overall the effect of increased current density on the mass transfer characteristics of carbon cloth based anodes in the DMFC is a combined effect of; enhancement due to increased gas evolution at the cloth surface and suppression due to decreased liquid volume in the cloth.

4. Results and discussion

Fig. 3 shows the effect of cell temperature on cell polarisation behaviour for the DMFC operating with 0.25 M methanol at a feed solution flow rate of 2.0 cm^3 min^{-1}. Cell voltage is lower at lower temperatures as a result of the expected effect on methanol oxidation kinetics. Up to a temperature of 100°C there is an increase in the limiting current of operation. Above 100°C there were problems in operation as limiting current density was approached; oscillation in voltage were observed. The oscillations are associated with operation near, or at, the boiling point of the methanol solutions, with relatively large quantities of carbon dioxide gas generation which cause considerable vaporisation of methanol at the anode. At lower current density the expected benefit of higher temperatures, i.e. higher cell voltage is seen.

The variation in effective mass transfer coefficient with temperature, for a methanol concentration of 0.25 M, is shown in Fig. 4. Values of k_{eff} increase from approximately 3.6×10^{-6} to 7.2×10^{-6} ms^{-1} with temperatures of 70–95°C. This approximate doubling in mass transfer coefficient with temperature increase is partly due to increase in methanol diffusion coefficient with temperature. From work by Kauranen and Skou [19], the variation in diffusion coefficient is given by

$$D_{MeOH} = 4.9 \times 10^{-10} e^{\left(2436\left(\frac{1}{333}-\frac{1}{T}\right)\right)} \text{ m}^2\text{s}^{-1} \quad (12)$$

In the range 70–95°C the value of diffusion coefficient increase only by approximately 55%, from 6.08×10^{-10} to 9.83×10^{-10} m s^{-1}. An additional effect created by the higher temperatures may be enhanced

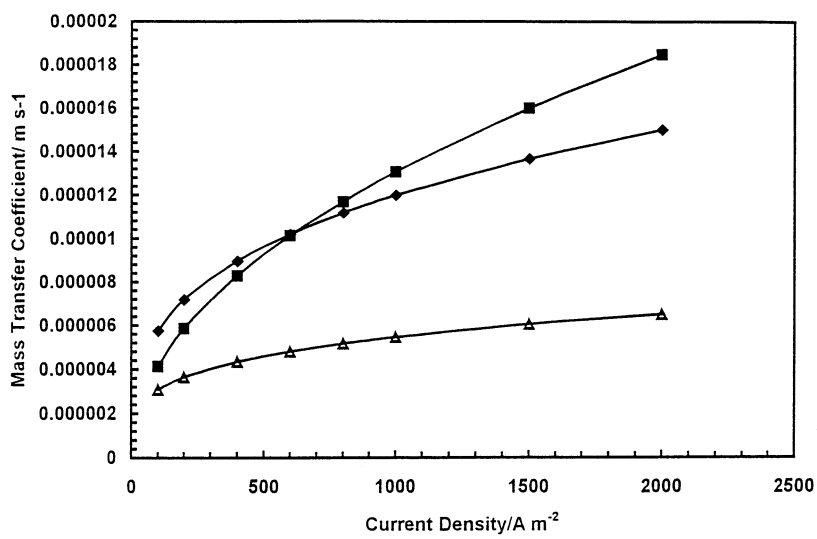

Fig. 2. The effect of current density on predicted mass transfer coefficients for methanol oxidation at gas-evolving and gas-sparged electrodes. (△) Eq. (11), (■) Eq. (10), (◆) Eq. (9).

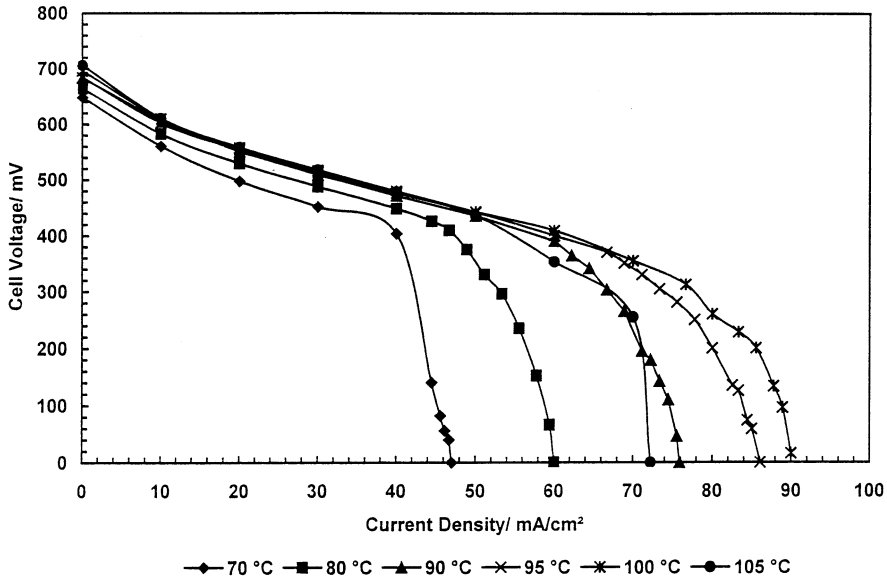

Fig. 3. The effect of cell temperature (70–110°C) on DMFC polarisation behaviour (0.25 M methanol, feed solution flow rate of 2.0 $cm^3\ min^{-1}$, air pressure 1.5 barg, air flow rate 800 $cm^3\ min^{-1}$).

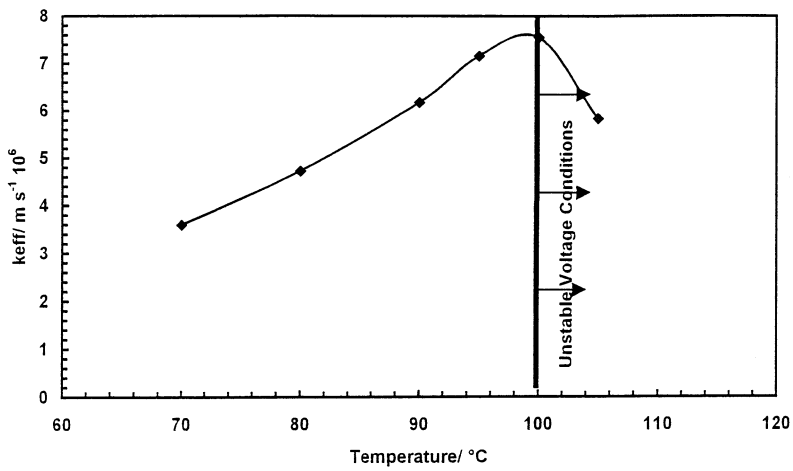

Fig. 4. Variation of effective mass transport coefficient with temperature (70–110°C) (0.25 M methanol, feed solution flow rate of 2.0 $cm^3\ min^{-1}$, air pressure 1.5 barg, air flow rate 800 $cm^3\ min^{-1}$).

mass transport due to bubble liberation at the surface of the MEA. At higher temperatures a higher bubble velocity in the diffusion layers can lead to an increase in liquid voidage which in turn increases the effective mass transfer in the carbon cloth. It is not known whether a higher rate of CO_2 generation (higher current density) increases the gas velocity in the cloth or increases the gas voidage in the cloth. In addition higher temperatures will increase the methanol and water transfer through the Nafion® membrane which will influence the mass transport rate of methanol at the anode.

The typical effect of methanol concentration on the limiting current density of the DMFC is shown in Fig. 5 for a temperature of 90°C. There is a general increase in limiting current with increase in concentration whilst at low current densities higher methanol concentrations cause a reduction in voltage at fixed current densities. The open circuit voltage is also higher at lower methanol concentrations. This latter effect is predominantly a result of methanol crossover causing a mixed potential at the cathode, which is higher with higher concentrations of methanol.

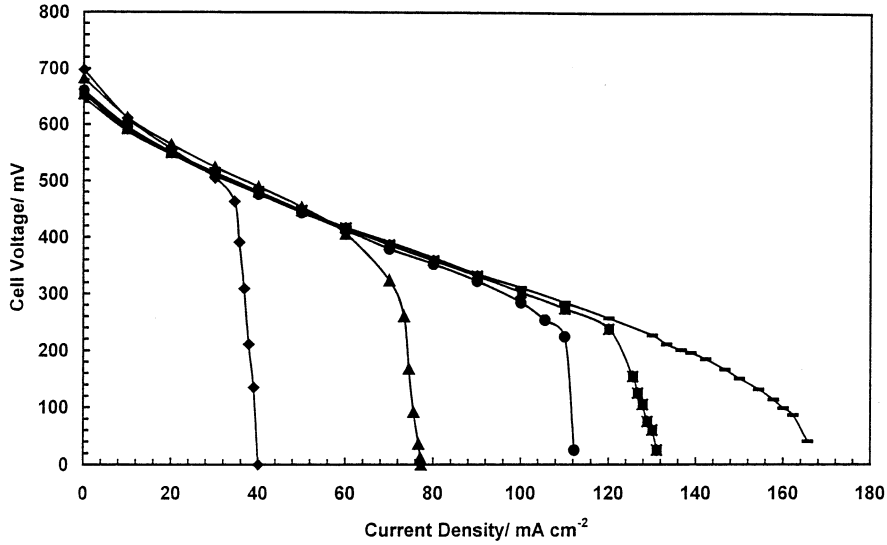

Fig. 5. The effect of methanol concentration (0.125–0.625M) on cell polarisation behaviour (363 K, feed solution flow rate of 2.0 $cm^3\ min^{-1}$, air pressure 1.5 barg, air flow rate 800 $cm^3\ min^{-1}$). Concentration values: (◆) 0.125, (▲) 0.25, (●) 0.375, (■) 0.5, and (–) 0.625 M.

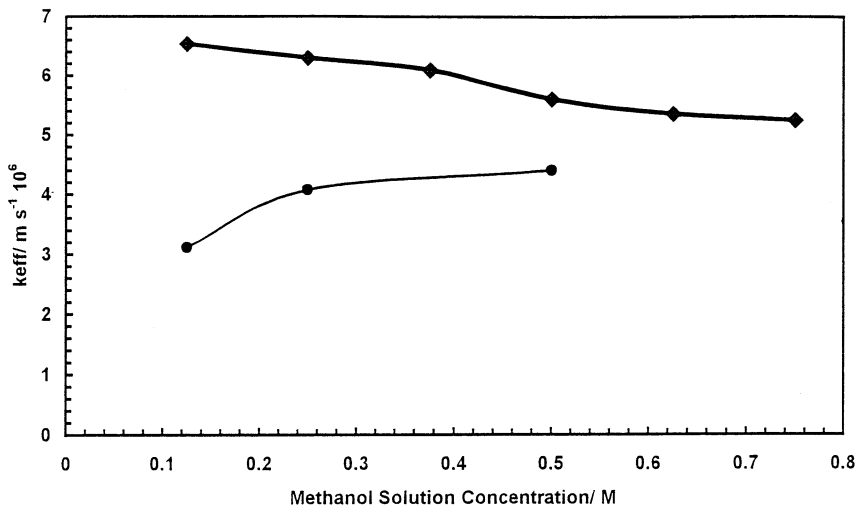

Fig. 6. The effect of methanol concentration on mass transport coefficient. (◆) 90°C, feed solution flow rate of 2.0 $cm^3\ min^{-1}$, air pressure 1.5 barg, air. (○) 70°C, feed solution flow rate of 1.3 $cm^3\ min^{-1}$, air pressure 2.0 barg.

The variation of effective mass transfer coefficient with methanol concentration is shown in Fig. 6 for two different temperatures (70 and 90°C) and methanol solution flow rates (2.0 and 1.3 $cm^3\ min^{-1}$). At lower temperatures of operation where limiting current densities and mass transfer coefficients are low there is an increase in mass transfer coefficient with methanol concentration. At the higher temperature, i.e. 90°C, there is an decrease in mass transfer coefficient with concentration. This complex variation in mass transport coefficient with methanol concentration is due to several interactive effects.

The methanol concentration influences mass transport in several ways; at low methanol concentrations limiting currents are lower and therefore lower gas evolution rates result. Lower gas evolution rates will reduce any hydrodynamic influence on the mass transport rate at the carbon cloth, or locally at the surface of the anode catalyst. The gas evolution rate will influence the voidage of the liquid in the carbon cloth, which will

in turn affects the methanol diffusion rate. Lower methanol concentrations also reduce methanol transfer by diffusion and electro-osmosis, through the membrane, due to a lower current density of operation, which will also reduce the methanol transfer rate to the anode. The local temperature and pressure at the anode will also influence mass transport rates. Higher temperatures increase the local vaporisation rate of methanol into carbon dioxide gas formed at the anode, which will reduce the effective liquid phase concentration. A further complication arises in that the DMFC can also operate in the vapour phase with methanol supplied by in an inert gas, e.g. carbon dioxide. The methanol mass transfer in the gas will benefit from higher diffusion rate than experienced in liquid, whilst being inhibited by the flow of gas away from the anode.

Overall the complex phenomena in the DMFC require detailed physicochemical analysis, which is beyond the scope of this paper but is a subject of ongoing research [20].

4.1. Effect of methanol solution flow rate

The influence of anode side channel hydrodynamics, on limiting current density behaviour, was initially investigated by varying the methanol solution flow rate in the range 2–12 $cm^3 min^{-1}$ (Re 16–96) at a temperature of 90°C (Fig. 7). With flow rates of between 2 and 4 $cm^3\ min^{-1}$ there is no significant influence on behaviour while at higher flow rates a gradual decrease in limiting current is seen as flow rate increases (Fig. 7). Flow rate influences the limiting currents, and also polarisation characteristics in general, in two ways; through differences in conversion of methanol, i.e. methanol concentration in the cell, and through changes in temperature at the anode (and to a lesser extent at the cathode). To allow for the influence of methanol conversion in the cell, it is useful to investigate the mass transfer effect as a function of the Damkoehler number, defined as:

$$\mathrm{Da} = \frac{\frac{jA_{\mathrm{cell}}}{6F}}{QC_{\mathrm{o}}} \tag{13}$$

where Da is the Damkoehler number, A_{cell} is the cross sectional area of the cell, Q is the volumetric flow rate and C_{o} the methanol feed concentration.

Da is the ratio of methanol reaction rate and methanol supply rate to the cell. The average methanol concentration in the cell is therefore approximately $C = C_{\mathrm{o}}(1 - 0.5\mathrm{Da})$. Fig. 8, plots effective mass transfer coefficients as a function of Damkoehler number, for a temperature of 90°C and methanol solution flow rate of 2 $cm^3\ min^{-1}$. Mass transfer coefficients are estimated from the average concentration allowing for consumption of methanol by oxidation. The range of flow rates extends down to values of 0.2 $cm^3\ min^{-1}$ at which the Damkoehler number approaches 0.5. At the high Damkoehler numbers (0.2–0.5) effective mass transfer coefficient increases with decreasing Da number, indicating a beneficial effect of increase in flow rate. At such low flow rates the large volumes of carbon dioxide gas generated in the cell, can have a major effect on cell behaviour, as observed in flow visualisation studies. At lower values of Da, the mass transfer coefficient apparently decreases with increase flow rate. This effect is due to a second major effect of flow rate, which influences the actual temperatures at the catalyst layers. Higher flow

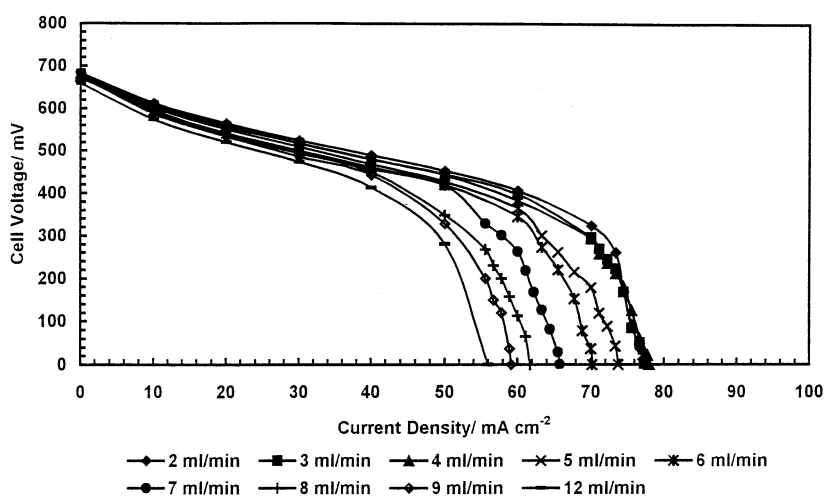

Fig. 7. The effect of methanol solution flow rate (2–12 $cm^3\ min^{-1}$) on polarisation characteristics and limiting currents (0.25 M, 90°C, air pressure 1.5 barg, air flow rate 800 $cm^3\ min^{-1}$).

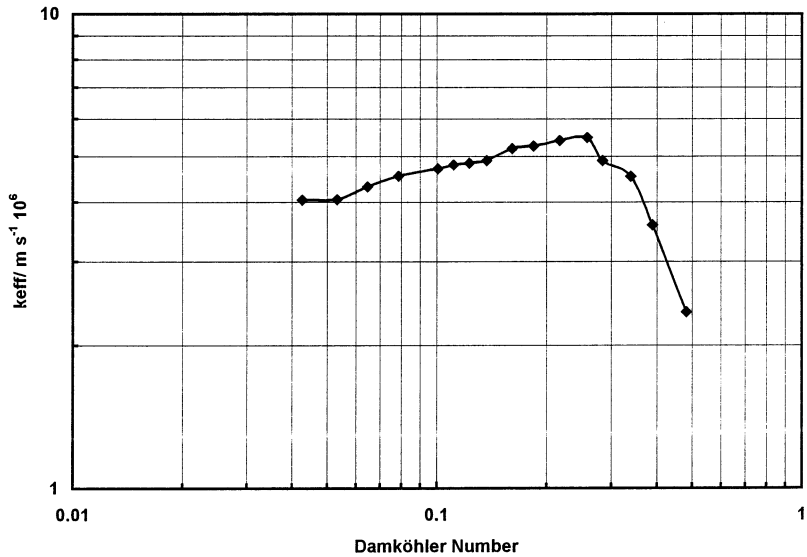

Fig. 8. The influence of Damkoehler number on effective mass transfer coefficients for methanol oxidation (2 cm^3 min^{-1}, 0.25 M, 90°C, air pressure 1.5 barg, air flow rate 800 cm^3 min^{-1}).

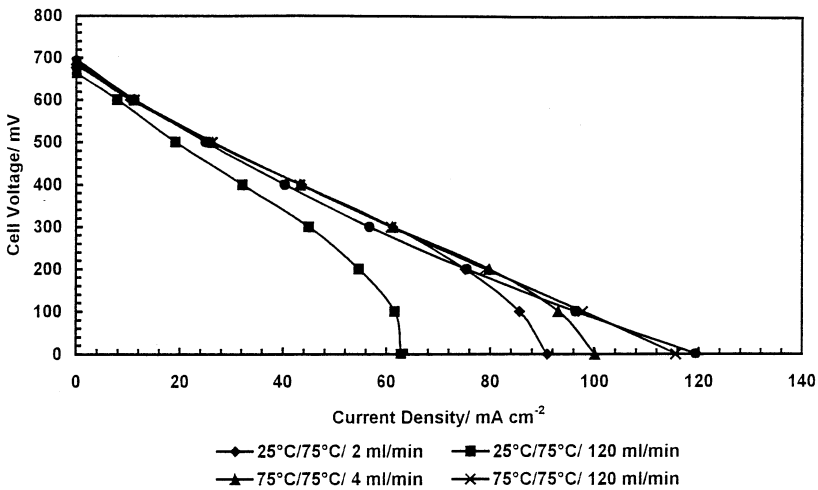

Fig. 9. The effect of feed temperature and cell temperature on the performance of the DMFC * (0.5 M, oxygen pressure 1.5 barg). * Values in legend given as feed temperature/cell temperature/anode side flow rate.

rates of relatively cold feed increases the heat removal from the catalyst layer causing a decrease in performance as observed in the cell polarisation data of Fig. 7. This is illustrated further in Fig. 9 where data are presented with feed and cell held at different temperature combinations and methanol flowrates. At high flow rates a cold feed (25°C) and higher cell temperature (75°C) produce the poorer cell performance. With feed and cell at the same temperature there is a reduced effect of flow rate as limiting current is approached.

A comparison of the effect of cell and flow temperature combinations on the variation in current density at zero-cell potential with Damkoehler number is given in Fig. 10 for a methanol solution concentration of 0.5 M. The effect of a cold feed (relative to the cell temperature) is to reduce cell performance. The issue of cell and feed temperature requirements are important considerations in fuel cell development, especially for larger scale units, where temperature control and thermal management are important. In practical operation the fuel cell and fluid temperatures will be different. Fluids entering the cell will act as medium for heat removal

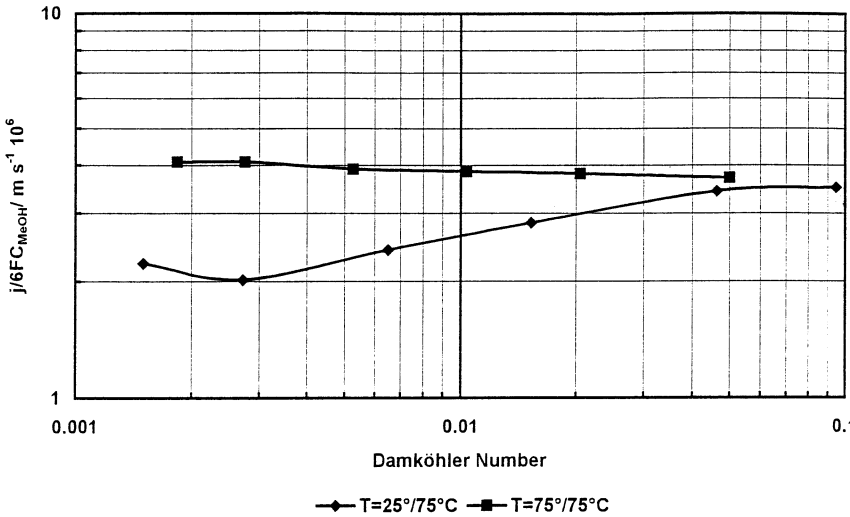

Fig. 10. The variation in cell current density with Damkoehler number at different feed and cell temperatures (0.5 M, oxygen pressure 1.5 barg). Values in legend given as feed temperature/cell temperature and current density scale is expressed as $j/(6FC_o)$.

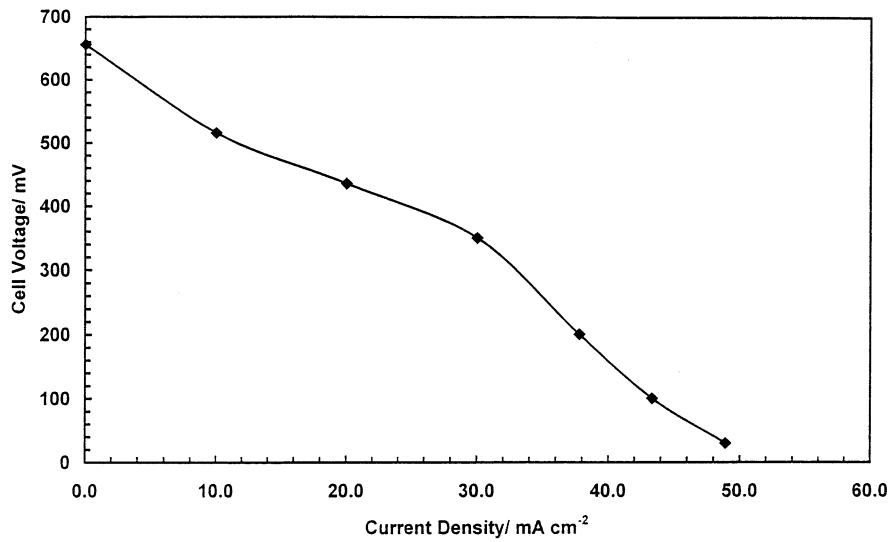

Fig. 11. Performance of the DMFC operated with methanol solution vaporised into an inert gas stream (80°C cell temperature, solution concentration 0.25 M, N_2 flow rate 1600 $cm^3\ min^{-1}$, 1.5 barg O_2, 800 $cm^3\ min^{-1}$).

and thus temperature control of the cells. The influence of this factor on larger cell performance is currently the subject of a detailed cell stack model [21].

A significant feature of the effect of using low flow rates is that high conversions of methanol are feasible. The Damkoehler number is a direct measure of methanol conversion in the liquid and values of 0.5 and greater have been achieved at low methanol flow rates of 0.2 $cm^3\ min^{-1}$ with 0.25 M concentration. The volume of CO_2 released is large under these conditions, as observed in flow visualisation studies [14] and equates to volumetric gas fractions up to 0.8–0.9, in the total two-phase fluid volume exiting the cell. An advantage of high conversions is the reduced amount of methanol in the exhaust CO_2 gas stream which has to be recovered during practical cell operation.

It is conceivable that in operation, the cell will change from a liquid feed operation to a vapour feed operation at some position in the flow channel. The source of methanol is that vaporised from the liquid into the inert carbon dioxide gas. We have operated the DMFC, with feed consisting of methanol vaporised into an inert gas, nitrogen, stream. Fig. 11 shows the typical performance, for a temperature of 80°C with a

0.25 M methanol solution, where a modest cell operation is apparent with, what are, low effective vapour phase concentrations. The mol fraction of methanol as estimated from vapour liquid equilibrium calculations [21] is approximately 0.006 for the 0.25 M methanol liquid concentration. Overall issues such as internal vaporisation and gas volume fractions are important when considering the overall performance of large scale DMFC stack systems.

4.2. Catalyst loading and oxidant pressure

In attempts to maximise the current output from the DMFC, at low methanol liquid feed concentrations, we examined the influence of catalyst loading. Fig. 12 shows data for three catalyst loading (0.5, 2.0 and 4.0 mg cm^{-2}) at a temperature of 90°C. With a 0.25 M methanol solution, doubling the Pt/Ru catalyst loading has a small effect on cell performance; both increasing

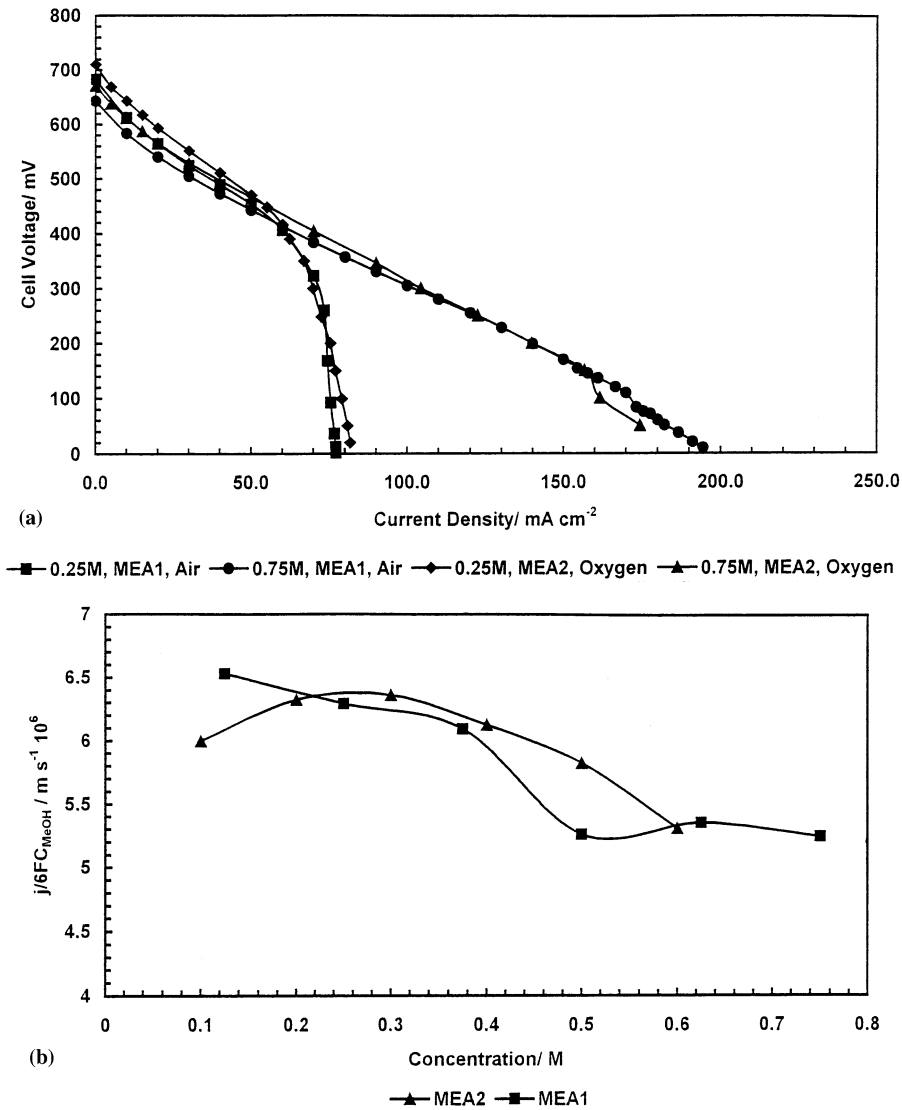

Fig. 12. The effect of catalyst loading on cell performance (90°C, 2.0 cm^3 min^{-1}). MEA1: 4 mg cm^{-2} catalyst, MEA2: 2 mg cm^{-2} catalyst, MEA3: 0.5 mg cm^{-2} catalyst. (a) Cell voltage response with of MEA1 and MEA2 (air/oxygen flow rate flow rate 800 cm^3 min^{-1}, 1.5 barg air/oxygen). (b) Variation in cell current at zero-cell voltage with methanol feed concentration. Current density scale is expressed as $j/(6FC_o)$ (air/oxygen flow rate flow rate 800 cm^3 min^{-1}, 1.5 barg air/oxygen). (▲) MEA2: 2 mg cm^{-2} catalyst, (■) MEA1: 4 mg cm^{-2} catalyst. (c) Cell voltage response with 2.0 M methanol solution for MEA2 and MEA3 (air flow rate flow rate 800 cm^3 min^{-1}, 1.5 barg air). (◆) MEA2: 2 mg cm^{-2} catalyst, (△) MEA3: 0.5 mg cm^{-2} catalyst.

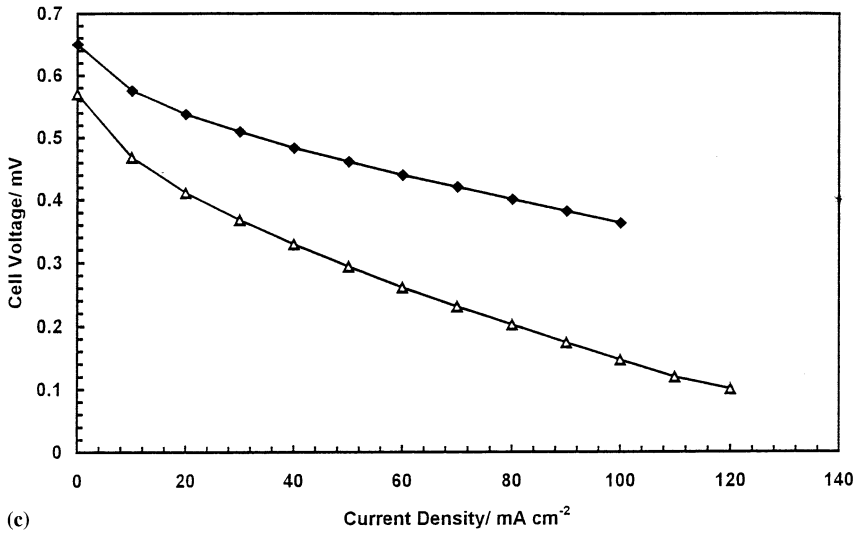

Fig. 12. (*Continued*)

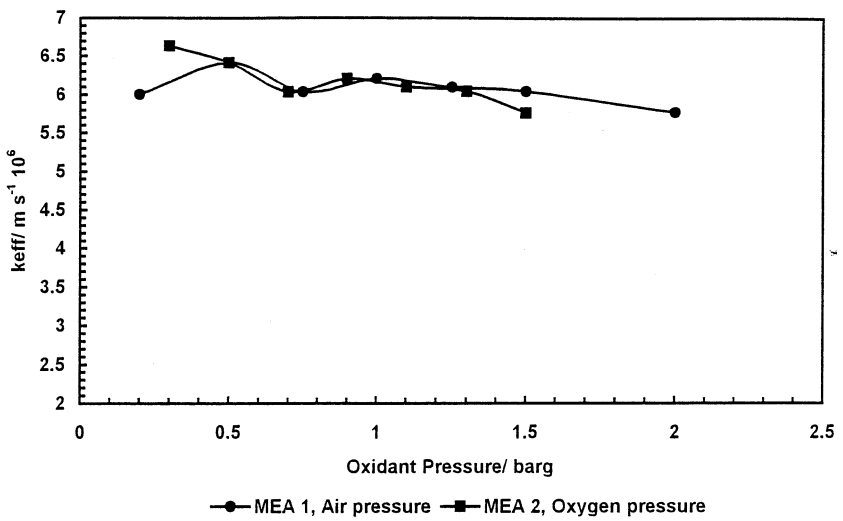

Fig. 13. The effect of cathode air pressure on DMFC mass transfer coefficient (90°C, 2.0 cm^3 min^{-1} flow rate, 0.25 M methanol solution). (●) MEA1: 4 mg cm^{-2} catalyst, (■) MEA2: 2 mg cm^{-2} catalyst.

cell voltage, at a fixed current density, and increasing limiting current density. This is a further indication that the limiting current densities are associated with a mass transport process of methanol supply to the catalyst as opposed to surface adsorption behaviour. From a comparison of the variation of cell current density at zero-cell potential with methanol concentration, as shown in Fig. 12(b), the performance of MEAs with different catalyst loading is similar. However, cell polarisation data with a much lower catalyst concentration (0.5 mg cm^{-2}), with 2 M methanol (Fig. 12(c)) demonstrates a much-reduced performance. Thus certainly with the current catalyst compositions used there is an optimum loading for maximum cell performance.

It is generally anticipated that a reduction in the oxygen (or air) pressure in the cathode of a DMFC will reduce cell performance due to a reduction in cathode potential, which may be accentuated by the effect of methanol crossover from the cathode. The crossover of methanol, although predominantly due to diffusion and electro-osmosis, can be reduced slightly by a high cathode air pressure. However the effect of air pressure on limiting current behaviour is small, as shown in Fig. 13, for two catalyst loading in the MEA, at a tempera-

ture of 90°C and solution concentration of 0.25 M. There is only a small decrease in mass transfer coefficient as cathode pressure increases which is due to a higher cathode pressure restricting, to some extent, methanol transfer through the catalyst layer and membrane.

5. Conclusions

The limiting current density characteristics of a liquid feed direct methanol fuel cell, based on a Nafion® solid polymer electrolyte membrane with a porous Pt–Ru–carbon supported catalyst anode. are influenced significantly by the temperature of cell operation and, to a lesser extent, the concentration of methanol solution. The mass transport limitation arises from the diffusion of methanol in the carbon cloth covering the MEA and from the hydrodynamic influence of gas bubbles in the flow channel. The thermal condition of the feed, in relation to the cell temperature, is shown to influence performance in that with a feed cooler than the cell higher flow rates of methanol solution decrease performance. It is possible that, at higher temperatures of operation, internal vaporisation of methanol into the carbon dioxide gas stream changes the operating behaviour of the fuel cell. It has been shown that cell operation is possible with a methanol solution vaporised into an inert gas stream.

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