The impact of mass transport and methanol crossover on the direct methanol fuel cell

K. Scott [a,*], W.M. Taama [a], P. Argyropoulos [a], K. Sundmacher [b]

[a] *Chemical and Process Engineering Department, University of Newcastle upon Tyne, Newcastle Upon Tyne, NE1 7RU, UK*
[b] *Max-Planck-Institut fur Dynamik Komplexer Technischer Systeme, D-39120 Magdeburg, Germany*

Abstract

The performance of a liquid feed direct methanol fuel cell based on a Nafion® solid polymer electrolyte membrane is reported. The cell utilises a porous Pt–Ru-carbon supported catalyst anode. The effect of cell temperature, air cathode pressure, methanol fuel flow rate and methanol concentration on the power performance of a small-scale (9 cm² area) cell is described. Data reported is analysed in terms of semi-empirical models for the effect of methanol crossover by diffusion on cathode potential and thus cell voltage. Mass transfer characteristics of the anode reaction are interpreted in terms of the influence of carbon dioxide gas evolution and methanol diffusion in the carbon cloth diffusion layer. Preliminary evaluation of reaction orders and anode polarisation agree with a previous suggested mechanism for methanol oxidation involving a rate limiting step of surface reaction between adsorbed CO and OH species. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Direct methanol fuel cell; Mass transport; Methanol crossover

1. Introduction

The direct methanol fuel cell (DMFC), based on a solid polymer electrolyte (SPE) in the form of a proton conducting membrane, has the attraction of no liquid acidic or alkaline electrolyte and uses methanol, either as vapour or liquid. The structure of the DMFC is a composite of two porous electrocatalytic electrodes on either side of a solid polymer electrolyte (SPE) membrane. The direct methanol fuel cell (DMFC) is a promising power source for a range of applications including transportation and portable power sources. The thermodynamic reversible potential (298 K) for the overall cell reaction in the DMFC is 1.214 V, which is comparable to 1.23 V for the hydrogen fuel. A current advantage of the hydrogen cell is that hydrogen oxidation at the anode is very fast and consequently the performance of the hydrogen cell is better than that of methanol cell. For methanol the oxidation kinetics are inherently slower as a result of intermediates formed during methanol oxidation [1]. Oxidation of intermediates to carbon dioxide requires the adsorption of oxygen containing species (e.g., OH, H_2O). Adsorption of these species does not occur substantially until potentials well above the reversible potential of the anode [2]. In fuel cells, platinum alone is not a sufficiently active methanol oxidation electrocatalyst and the promotion of methanol oxidation has been actively studied. Currently significant results have been achieved with the use of binary catalysts, notably Pt–Ru. With these catalysts the second metal forms a surface oxide in the potential range for methanol oxidation [3].

Recent developments in electrode fabrication techniques and better cell designs have brought dramatic improvements in cell performance in small-scale DMFCs operating on vaporised fuel. 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 [4]. To date an essential condition for the high performance of a DMFC is the use of low concentrations of methanol. At concentrations higher than approximately 2 mol dm⁻³, the cell voltage declines significantly due to permeation of methanol through the SPE (Nafion®) membrane, i.e., methanol crossover [4]. This permeation results in a mixed

potential at the cathode with a significant loss in oxygen reduction performance and also poor fuel utilisation. Thus, an important area to improve the DMFC performance is in polymer membrane electrolytes. Much of the research on SPE fuel cells systems has used Nafion®, from DuPont, although other materials have been used, e.g., polybenzimidazole [5] and perfluorinated sulphonimides [6], as polymer electrolyte membranes to reduce methanol crossover. Limitations in the vapour fed DMFC are the energy used to vaporise the aqueous based fuel and the requirement to separate the unused fuel from the anode exhaust gas containing substantial quantities of carbon dioxide. These factors, together with potential problems in cell thermal management and water management, have focused attention on liquid feed DMFCs, where in principle the carbon dioxide can be simply disengaged from the liquid fuel using standard gas liquid separators.

A number of authors have reported performance data for liquid feed DMFCs, e.g., Ravikumar and Shukla [7], Surampudi et al. [8], Valdez et al. [9], Narayana et al. [10], Surampudi et al. [8] reported the performance of a DMFC with solid polymer electrolyte (Nafion®) using a supported Pt/Ru catalyst anode of unknown manufacture. The influence of temperature and methanol concentration was briefly reported. The performance of a small stack of 5 cells (25 cm^2 cross-section) at temperatures of less than 60°C has been reported [9]. The catalyst loading was 4 mg cm^{-2} of an in house produced Pt/Ru catalyst supported on carbon. Both pieces of research confirmed that higher temperatures produced higher cell power. Power densities between approximately 150 to 300 mW cm^{-2} have been reported for liquid feed DMFC using different fabrication procedures (mainly undisclosed) [10]. In addition a membrane material (unidentified) with a significantly reduced crossover of methanol in comparison to Nafion® is reported. 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 [7]. 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 mol dm^{-3}. Overall the existence of electrochemical losses at both electrodes in the DMFC lead to a significant reduction in overall performance, from the theoretical thermodynamic maximum [11,12] and thus a focus of research is to minimise these losses.

Several researchers have reported limiting current densities for methanol oxidation [7,13]: Kaurenan and Skou [13] attributed this limiting current behaviour to saturation coverage of absorbed OH on the platinum surface. Observed limiting current on platinum supported catalysts occur at potentials of approximately 0.65 V (vs. RHE) where the fractional coverage of OH is 0.5, as predicted by a Langmuir isotherm. Measurements of methanol oxidation using linear sweep voltammetry, at 5 mV s^{-1}, on platinum

rotating discs by Chu and Gilman [14] show a definite hydrodynamic influence. Peak methanol oxidation currents (measured in 0.5.M H_2SO_4 and 1.0 M methanol) at approximately 0.75 V (vs. RHE) decrease with increasing rotation rate.

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; limiting current densities are obtained, at 0.5 to 1.0 M methanol concentrations, which are approximately proportional to the methanol concentration. And at potentials between approximately 0.2 to 0.4 V (vs. DHE) (current density 50 to 250 mA cm^{-2}) the methanol reaction order apparently changes from a positive to a negative value, as the methanol concentration increases from 1.0 M to 2.0 M. Similar behaviour is seen in the data of Kaurenan and Skou [13].

Noticeably the limiting current densities observed by Ravikumar and Shukla [7] are very much lower, at equivalent methanol concentrations, than those of Kaurenan and Skou [13]. The electrode structures used were significantly different. Kaurenan and Skou 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}, Ravikumar and Shukla 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. It is believed that this carbon cloth offers a significant resistance to methanol diffusion to the catalyst layers and that, at least in the work of Ravikumar and Shukla, limiting current densities are associated with a diffusion limitation of methanol. This mass transfer limitation would appear to occur before any possible limiting current effects associated with OH coverage.

The purpose of this research was to investigate the influence of mass transport and methanol crossover on the DMFC made with Pt–Ru carbon supported catalysts, bonded with Nafion®. Cell performance data is presented over a range of methanol concentrations, and flowrates, and cell temperatures. Models for the open circuit potential in the presence of methanol crossover and for cell voltage, current density response are developed.

2. Experimental equipment

The DMFC, shown schematically in Fig. 1, had a cross-sectional area of 9 cm^2. The cell was fitted with one membrane electrode assembly (MEA) sandwiched between two graphite blocks each of which had flow beds, in the form of parallel channels, for methanol or oxygen/air flow. The cell was held together with two plastic insulation sheets and two stainless steel or aluminium backing plates
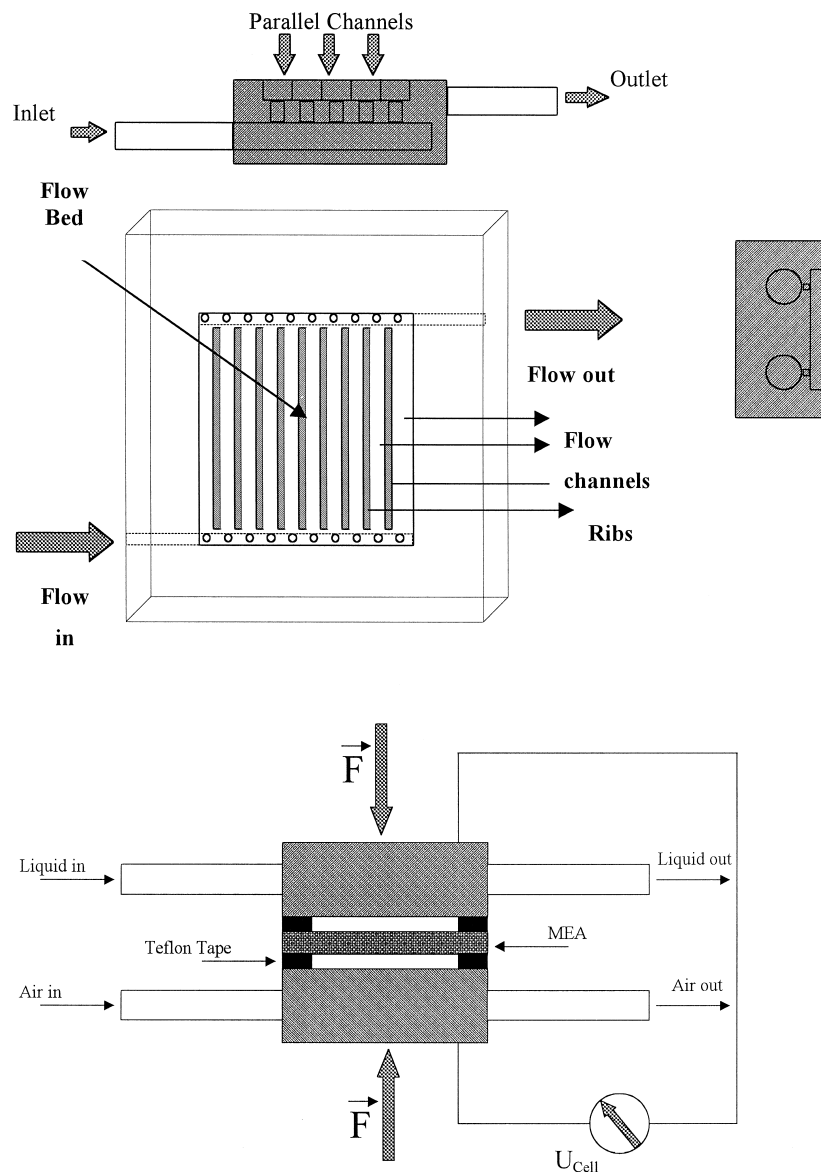
Fig. 1. Experimental cell design.

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 in order 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 cell was 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 kept the cell at a constant temperature. Air was supplied from cylinders, at ambient temperature, and the pressure regulated by pressure regulating valves. All connections between the cells and equipment were with PTFE tubing, fittings and 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 (ketjenblack 600) 10 wt.% teflonised carbon. The catalysed layer, consisting of 35 wt.% Pt–15 wt.%Ru (2 mg cm^{-2} metal loading) dispersed on carbon (ketjen) and bound with 10 wt.% Nafion®, from a solution of 5 wt.% Nafion® dissolved in a mixture of water and lower aliphatic alcohol's (Aldrich), was spread on this diffusion backing layer.

Catalyst used was Johnson Matthey Technology Centre developmental material. 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
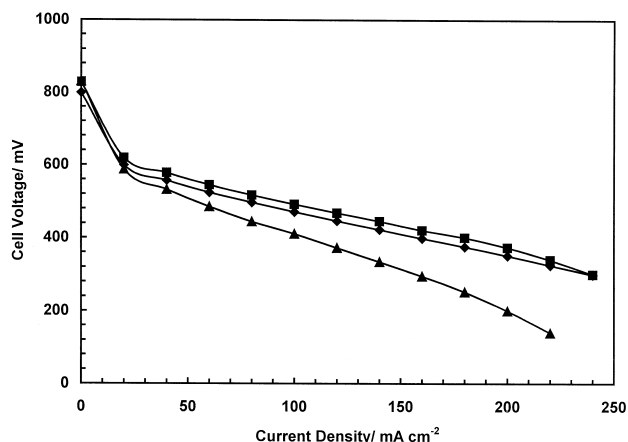
Fig. 2. The effect of conditioning, at 100 mA cm^{-2} on the DMFC cell voltage performance (0.83 cm^3 min^{-1}, Cell temperature 363 K, 2 mol dm^{-3} methanol solution). ▲: 1st set, ◆: 72 h, ■: 120 h operation.

membrane for 1 h in 5 vol.% H$_2$O$_2$ and 1 h in 1 mol dm^{-3} H$_2$SO$_4$ 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 vs. 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 potential. Several MEAs were tested in this research to ascertain reproducibility of the data. In all the data reported it is apparent that the values of open circuit potential are significantly lower than the theoretical thermodynamic maximum; broadly in the region of 600 mV to 750 mV. Typically operating at an applied current density of approximately 20 mA cm^{-2} results in a further loss of 200 mV. Further reduction in cell potential with increased current density is then a result of polarisation of electrodes and cell resistance, which is influenced by variation in cell operating parameters. We have reported elsewhere [15] that good cell performance depends on appropriate conditioning of the electrode assembly without current withdrawal. Thus, the data reported here were obtained after allowing 48 h to condition a new MEA in the test cell at 75°C and atmospheric pressure with continuous feed of 2 mol dm^{-3} methanol solution. In addition cell performance is also improved by maintaining the cell with an applied load for several hours (see Fig. 2). This pre-treatment also indicates that a relatively stable performance is achieved under continuous operation.

3. Results

There are several variables which will affect the cell voltage, current density response of the DMFC-temperature of fuel, methanol concentration, oxygen partial pressure and fuel and oxidant flows. This is in addition to the effect of the proton exchange membrane, catalyst preparation and overall electrode structure. In the small cells used

here there is little impact on performance associated with oxidant flows as these were significantly above stoichiometric requirements. At low cathode gas flow-rates flooding of the cathode structure may occur, restricting access of oxygen to the cathode and thus causing mass transport limitations. This factor will be more important for larger scale operation, which is the focus of ongoing research.

Fig. 3, shows cell polarisation data, at 363 K, for methanol concentrations in the range 0.125 mol dm^{-3} to 2.0 mol dm^{-3}. The methanol concentration affects the open circuit voltage and the cell voltage characteristics generally. Limiting current characteristics are apparent at the low methanol concentrations, less than 0.5 mol dm^{-3}. The open circuit voltage is higher at lower methanol concentrations. In the regions of current density when mass transport limitations are absent cell voltages are higher with lower methanol concentrations. This overall behaviour is a result of the combined effects of methanol mass transport to the anode, anode polarisation characteristics and methanol crossover to the cathode.

3.1. Open circuit voltage characteristics

In theory the DMFC open circuit cell voltage $U_{cell,O}$ can be determined, from the Nernst equation, if the polymer electrolyte membrane prevents any mixing of anode reactants and cathode reactants:

$$U_{cell,O} = U_{cell,O}^{\theta} + \frac{RT}{6F} \ln \left\{ \left(\frac{a_{CH_3OH,a} a_{H_2O,a}}{a_{H_2O,c}^2} \right) \left(\frac{P_{CO_2,a}}{1.0} \right)^{-1} \right.$$
$$\left. \times \left(\frac{P_{O_2,c}}{p^{\theta}} \right)^{3/2} \right\} \tag{1}$$

where a_i refers to activity of species i (carbon dioxide: CO$_2$, methanol: CH$_3$OH, water: H$_2$O and oxygen: O$_2$). Thus, Eq. (1) predicts increasing cell voltages for increasing liquid phase methanol activity in the anode compartment.
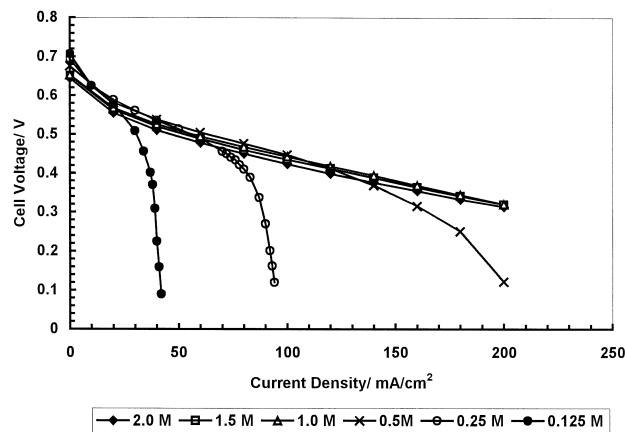

Fig. 3. The effect of methanol concentration on DMFC cell voltage characteristics (363 K, 2.0 bar Air, 1.36 cm^3 min^{-1}). Values of methanol concentration on figure.

Fig. 4 shows the typical variation in open circuit potential with methanol concentration, air pressure and temperature. In contrast to the theoretical behaviour the open circuit voltage decreases as the methanol concentration
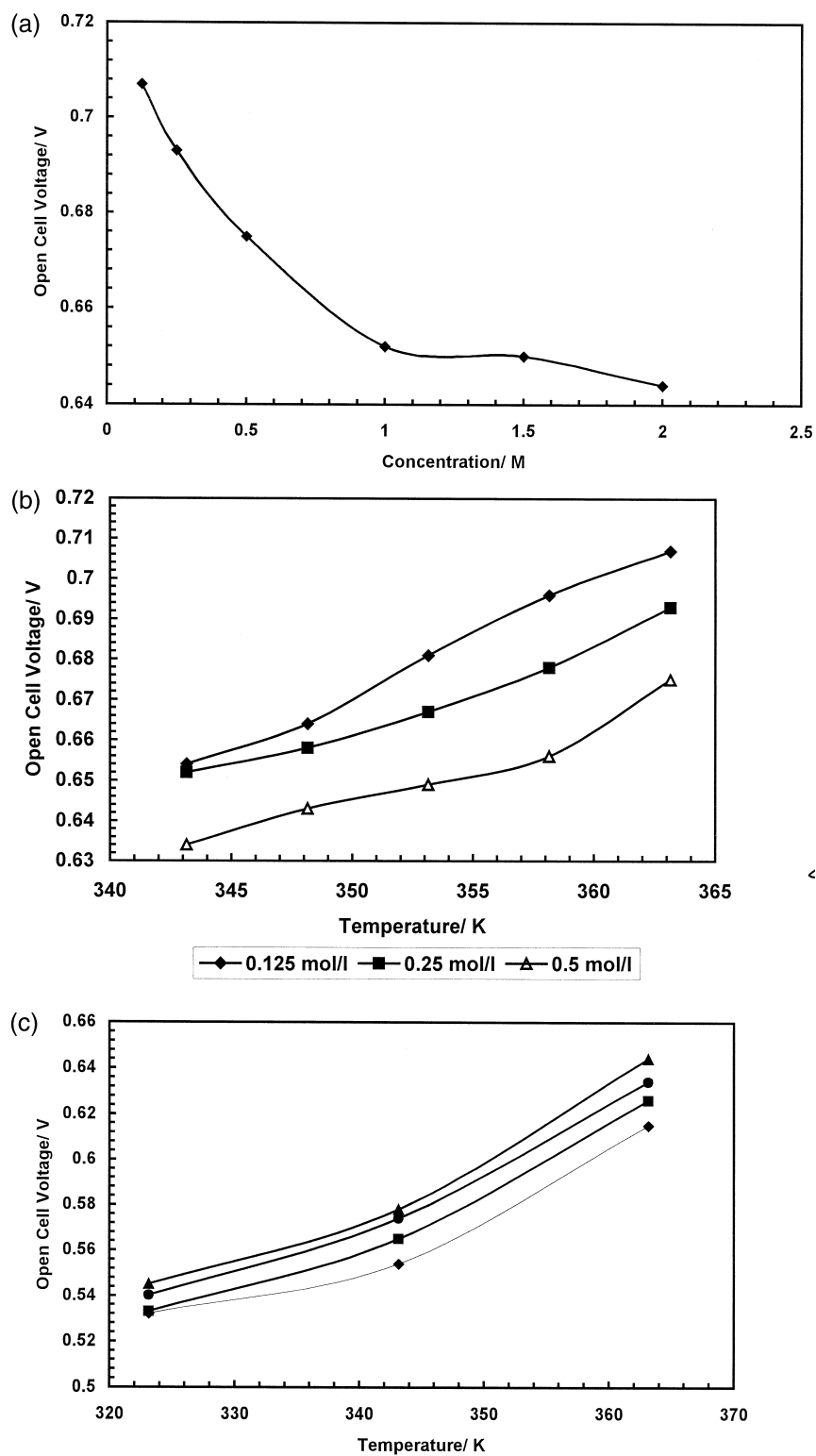

Fig. 4. The effect of operating parameters on the DMFC open circuit voltage. (a) The effect of methanol concentration (363 K, 2.0 bar Air, 1.36 cm^3 min^{-1}). (b) The effect of temperature (1.36 cm^3 min^{-1}. 2.0 mol dm^{-3} methanol solution). Values of concentration on figure. (c) The effect of temperature (1.36 cm^3 min^{-1}. 2.0 bar air) Values of concentration on figure. (d) The effect of cathode pressure on open circuit voltage (1.36 cm^3 min^{-1}. 2.0 mol dm^{-3} methanol) values of temperature on figure.
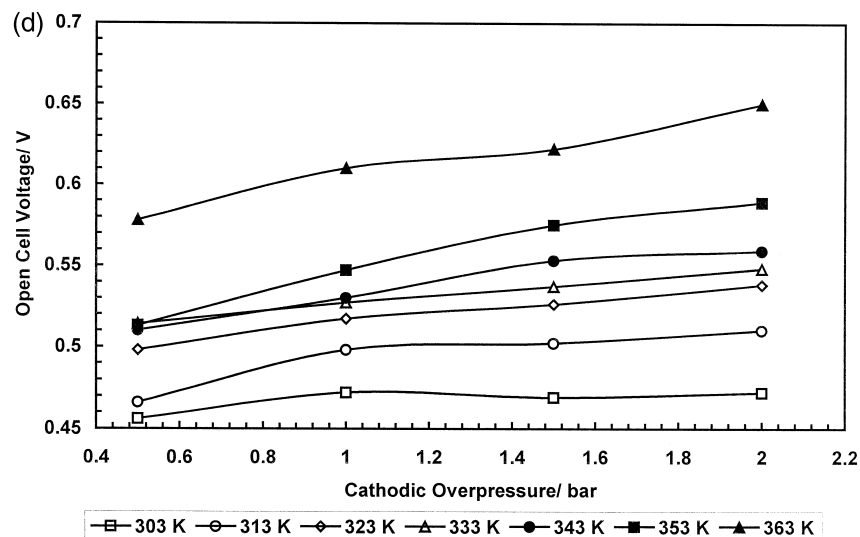
Fig. 4 (continued).

increases (Fig. 4a), in an approximate logarithmic manner, which is due to the fact that the PEM is permeable to protons and water, and also methanol. Consequently, there is a crossover flux of methanol from the anode to the cathode which is a major reason why the observed cell voltages are in the range of 0.6 to 0.7 V, whereas Eq. (1) predicts a value of $U_{cell,O} = 1.2$ V at 90°C. Higher methanol concentrations will increase the rate of methanol diffusion across the membrane and thus, under steady state conditions, higher concentrations of methanol are present at the cathode. We will report elsewhere the methanol diffusion characteristics of Nafion® membranes [16]. Higher methanol concentrations at the cathode will increase the cathode polarisation due to the mixed potential caused by methanol oxidation. However, as we have discussed, and has been reported by others, the oxidation of methanol, on platinum, is not a first order reaction but exhibits a reaction order which decreases, from 1.0 to negative values, with an increase in methanol concentration. Over a significant range of methanol concentrations the reaction order is approximately 0.5 [17,18]. Thus, the influence of methanol crossover on the cathode mixed potential will be complex. To allow for the effect of methanol concentration the following semi-empirical equation for the open circuit voltage is proposed

$$
U_{cell,O} = U_{cell,O}^{\theta}(1 - \beta) + \frac{RT}{F}\ln\left\{ k_{21}^{*}(T)\left(a_{CH_3OH,a}\right)^{1-1/\beta}\right.
$$
$$
\left. \times \left(\frac{P_{CO_2,a}}{p^{\theta}}\right)^{-1}\left(\frac{P_{O_2,c}}{p^{\theta}}\right)^{3/2}\right\} \qquad (2)
$$

This expression gives a good fit to experimental data. The parameter values which were determined from a least-squares fit of the experimental data, are $\beta = 0.56$ and $k_{21}^{*}(90°C) = 2.4 \times 10^3$. This β-value is quite close to charge transfer factors which are typical for electrochemical reactions.

The variation in open circuit potential with temperature, for three methanol concentrations (Fig. 4b), exhibit an approximate linear variation. This corresponds to the prediction of Eq. (2), when the temperature dependency of k_{21}^{*} follows the Arrhenius relation:

$$
k_{21}^{*}(T) = k_{21}^{*}(T_{ref})\exp\left\{ -\frac{E_{a,2} - E_{a,1}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right\} \qquad (3)
$$

The activation energy was found to be $(E_{a,2} - E_{a,1}) = 48.5$ kJ/mol. This may be qualitatively considered to be the difference between the activation energies for oxygen reduction (index 2) and methanol oxidation (index 1).

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, may be impeded slightly by a high cathode air pressure Fig. 4d shows the variation in open circuit potential with cathode air pressure, which is in qualitative agreement with predicted behaviour. At the higher temperature there is an approximate 60 mV increase in potential with an increase in pressure from 0.5 to 2.0 bar.

It is worth noting that diffusion of methanol across the membrane is likely to be the dominant process of methanol crossover at low current densities, less than 200 mA cm^{-2}. This is because, as observed in the data of Ren and Gottesfeld [19], for water transfer across Nafion®, water transport is predominantly by a diffusion driven process at these values of current density. In addition measurement of methanol crossover in operating cells, to be reported [20], shows that the concentration in the cathode exhaust is almost independent of current density. Thus, the model equation for the effect of methanol crossover on open circuit voltage may, as a first approximation, be used to
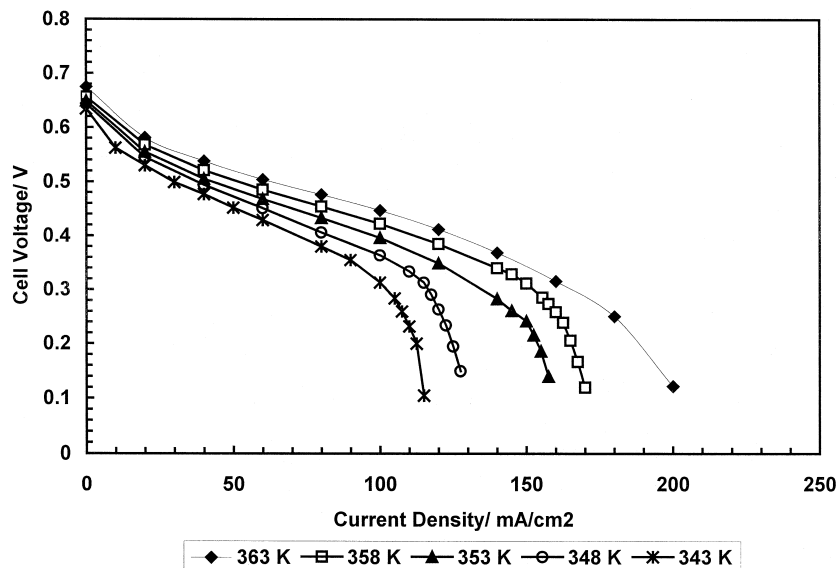
Fig. 5. The effect of cell temperature on the cell voltage characteristics. (2.0 bar Air, 1.36 cm^3 min^{-1}, 0.5 mol dm^{-3} methanol).

quantify the methanol crossover effect for active cell operation.

3.2. Cell polarisation characteristics

Fig. 5 shows the cell polarisation behaviour for a 0.5 mol dm^{-3} methanol solution at temperatures between 343 and 363 K. Cell voltages and limiting currents are both higher at higher temperatures. The effect of temperature on limiting current behaviour is particularly significant, showing an approximate 100% increase in value for the 20 K increase in temperature.

The limiting current densities for methanol oxidation increase with methanol concentration as shown in Fig. 6, over the range of temperatures considered. Deviation from proportionality are possibly due to several factors which include the influence of gas evolution at the anode, bubble size, and methanol flow rate and conversion. At higher methanol concentrations, the rate of carbon dioxide evolution increases, which may both increase mass transport rate by an increase in turbulence and decrease mass transport rate by physically limiting the methanol solution flow to the anode layer, i.e., reducing the liquid fraction in the carbon cloth and porous diffusion layers.
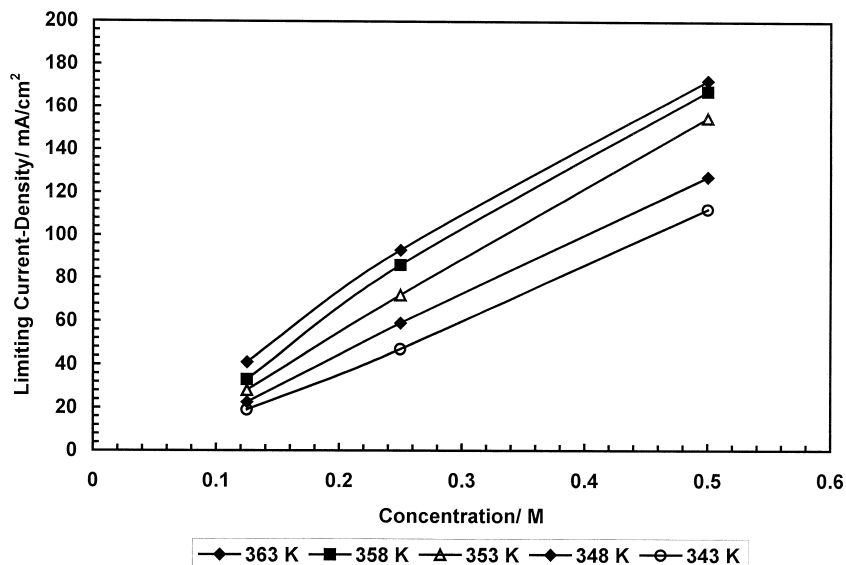

Fig. 6. Variation in limiting current densities with methanol feed concentration (1.36 cm^3 min^{-1}. 2.0 mol dm^{-3}).

The influence of methanol conversion in this data can be demonstrated by considering values of Damkoehler numbers, Da, for the system defined as

$$Da = \frac{\frac{jA_{cell}}{6F}}{QC_o} \qquad (4)$$

where j is the current density, A_{cell} is the cross-sectional area of the cell, Q is the volumetric flow rate and C_o the methanol inlet feed concentration. Da is the ratio of methanol reaction rate and methanol supply rate to the cell, and is equivalent to conversion of methanol in the cell. Values of Da obtained at limiting current conditions at the lower methanol concentrations are less than 0.25 although they are not independent of the solution concentration (See Fig. 7). At the higher values of Da, the ''average'' concentration of methanol in the cell will be less than the inlet concentration. This ''average'' concentration will depend upon the flow behaviour in the cell and the volumetric flow rate of carbon dioxide gas. If for example, as an approximation, the ''average'' is the arithmetic mean of inlet and exit concentrations, then, with a Damkoehler number of 0.25, the mean methanol concentrations for 0.125 and 0.5 mol dm^{-3} methanol concentrations will be approximately 0.11 and 0.438 mol dm^{-3}, respectively. That is, as expected, average values of j_{lim} should be proportional to inlet concentration. This would tend to suggest that factors other than methanol conversion influence the variation of Da, or j_{lim}, with concentration.

A second factor may be the anode side hydrodynamics. Typical Damkoehler numbers used in this work (methanol solution flow rates 0.68 to 2.7 cm^3 min^{-1}) are less than 0.1 when mass transport limitations are not experienced. Thus, methanol conversions in the cell are small. The effect of methanol solution flow rate on cell polarisation behaviour is not significant over the range of flow rates considered. Values of Reynolds number based on the hydraulic mean diameter of the rectangular channels are at a maximum of 22 over the range of flows considered. At such low Reynolds number, the flow would be laminar in the channel for single-phase flow and the Sherwood number, Sh, would be constant.

$$Sh = \frac{k_e d}{D_{meoh}} = 3.66 \qquad (5)$$

where k_e = mass transfer coefficient, D_{meoh} is the diffusion coefficient methanol in water.

From this mass transfer relationship, with $D = 2.8 \times 10^{-9}$ m s^{-1}, the mass transfer coefficient is approximately

$$k_e = \frac{2.8 \times 10^{-9}}{2 \times 10^{-3}} = 3.66 = 5.2 \times 10^{-6} \text{ m s}^{-1} \qquad (6)$$

This predicted value of mass transfer coefficient compares with experimental values of 5.3 to 5.6×10^{-6} m s^{-1}, at 363 K, thus suggesting, on first analysis, that at low methanol concentrations, the limiting current characteristics of the DMFC may be controlled by hydrodynamics in the channel. However, it should be remembered that the hydrodynamic regime in the flow channel is a two-phase flow of methanol solution and carbon dioxide bubbles and thus mass transfer coefficients are likely to be greater than those predicted by a simple single-phase laminar flow model.

Mass transfer at gas evolving electrodes has been measured for ferrocyanide oxidation in the case of simultaneous oxygen evolution by Fouad and Sedahmed [21]. By allowing for differences in diffusion coefficient of ferrocyanide ion and methanol this data gives mass transfer coefficients in the range of approximately 2.7×10^{-5} to
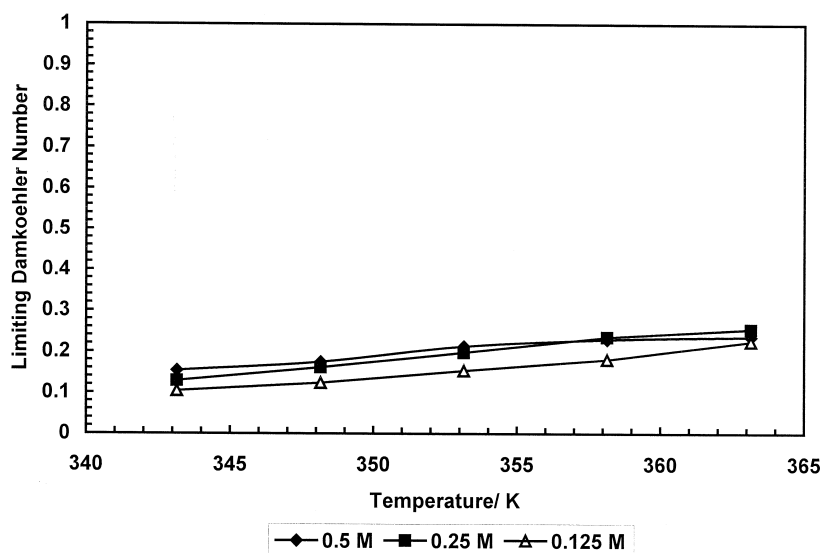

Fig. 7. Variation of Damkoehler number at limiting current conditions with temperature (1.36 cm^3 min^{-1}. 2.0 bar air).

3.4×10^{-5} m s^{-1} for current densities of to 100 to 200 mA cm^{-2}. The values of mass transport coefficients are clearly greater than experimentally measured. Thus, factors other than anode side flow conditions would appear to limit mass transport in the DMFC.

In the case of the DMFC gas is evolved from the surface of a carbon cloth positioned well away from the active electrode region. Thus, overall estimates of mass transfer effects in the DMFC are very approximate. Even allowing for this uncertainty it is believed that there will be a significant resistance to mass transport in the carbon cloth MEA backing layer, where methanol diffusion would have to proceed in a relatively convection free environment.

Diffusion mass transfer in the cloth depends upon the liquid void fraction and the cloth pore structure and can be represented by

$$j = nFk_c^0 e_c^m \Delta C_{cl} \tag{7}$$

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 frequently $m = 1.5$, and $k_c^0 = (D_{meoh})/(\ell_{cl})$, where ℓ_{cl} is the cloth thickness.

The cloth thickness is around 280 microns and with a diffusion coefficient of $2.8 \ 10^{-9}$ m^2 s^{-1} a mass transfer coefficient for the cloth is

$$k_c^0 = \frac{2.8 \times 10^{-9}}{280 \times 10^{-6}} = 10^{-5} \, \mathrm{m\,s^{-1}}. \tag{8}$$

The volume fraction of methanol solution in the carbon cloth during operation is difficult to measure although can

in principle be modelled using capillary pressure theory, which is outside the scope of this study although is a subject of current DMFC modelling [22]. However, in the range of liquid volume fraction of 0.6 to 0.8, limiting current densities are between approximately 1400 to 2150 A m^{-2}, for a 0.5 mol dm^{-3} methanol solution. These limiting current densities are in the range of experimental values. Thus, not surprisingly, mass transport limitations occur with relatively low concentrations of methanol researched in DMFC operation. In view of the fact that the product carbon dioxide gas must also escape from the electrode through the cloth and thus inhibit the mass transport of methanol, limiting currents are likely to be significantly lower than estimated above.

These estimations would indicate the major mass transfer effect in the DMFC is diffusion in the carbon cloth or in the porous carbon diffusion layers. Methanol diffusion in the catalyst layers would in itself not be a rate limiting factor.

3.3. Preliminary methanol oxidation model analysis

An exact interpretation of methanol oxidation kinetics from cell polarisation data, in the absence of single electrode potential data, is extremely difficult. However, a preliminary insight into the mechanism can be obtained, by examining the variation in cell current density with methanol concentration and temperature at fixed values of cell potential. Fig. 8 shows the variation in cell current density with methanol concentration at fixed values of cell voltage. On the basis that the predominant cause of voltage reduction with increase in current density is due to anodic
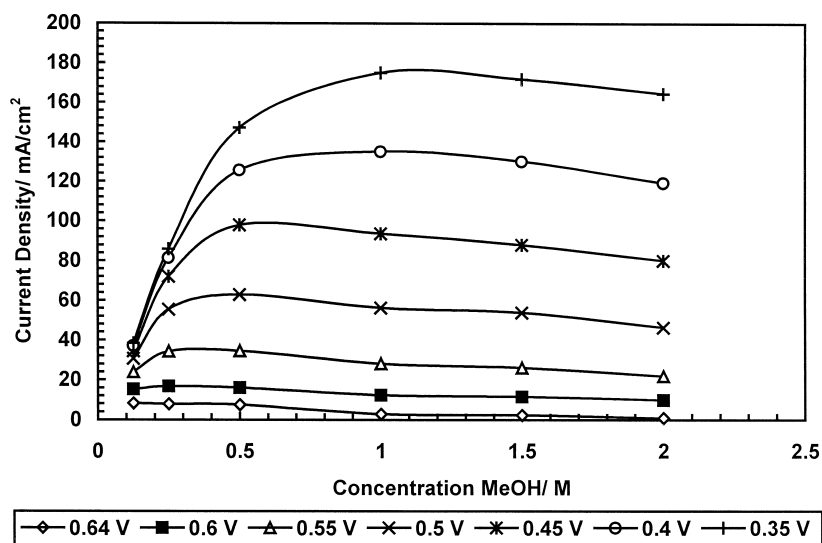

Fig. 8. Variation of current density with methanol concentration. (363 K, 2.0 bar air, 1.36 cm^3 min^{-1}). Values of cell voltage shown on figure.
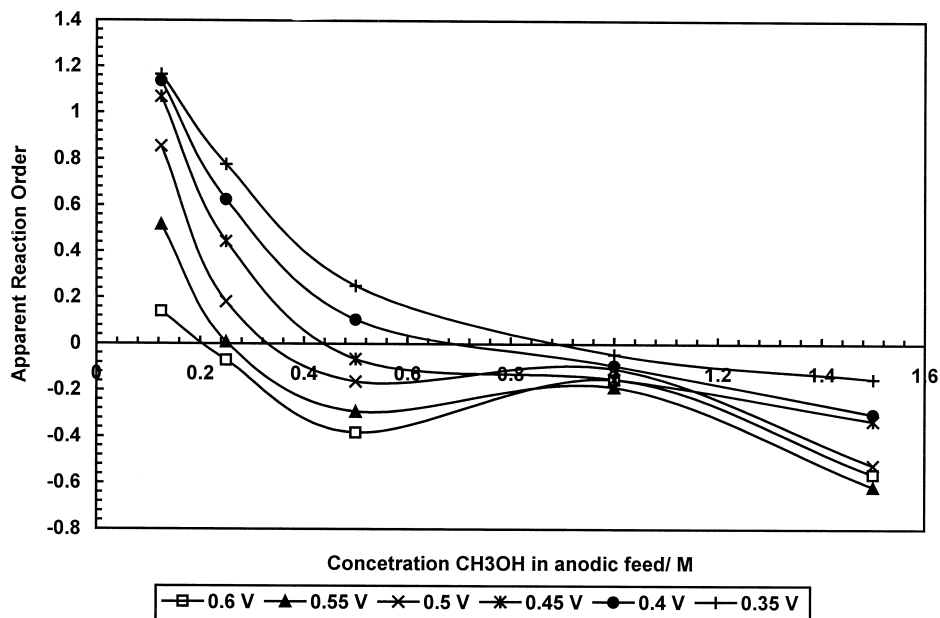
Fig. 9. Apparent reaction order for methanol oxidation as a function of methanol concentration. (363 K, 2.0 bar air, 1.36 cm^3 min^{-1}). Values of cell voltage shown on figure.

polarisation, apparent reaction orders for methanol, N_{app} can be determined from this data as

$$N_{app} = \left(\frac{\partial \ln i}{\partial \ln C_{MeOH}} \right)_{T, U_{cell}} \tag{10}$$

Fig. 9, shows the variation of apparent reaction order with methanol concentration. At low methanol concentrations the reaction order is 1.0 at low potentials, reflecting

the mass transport control of the oxidation. At methanol concentrations, above 1.0 mol dm^{-3}, reaction order is negative indicating a hindrance of methanol oxidation kinetics by adsorbed methanol reaction intermediates. Overall methanol oxidation reaction orders vary from approximately 1.0 towards -0.5 over the range of methanol concentrations considered. Clearly this analysis is very approximate and the data in Fig. 9 are influenced by other
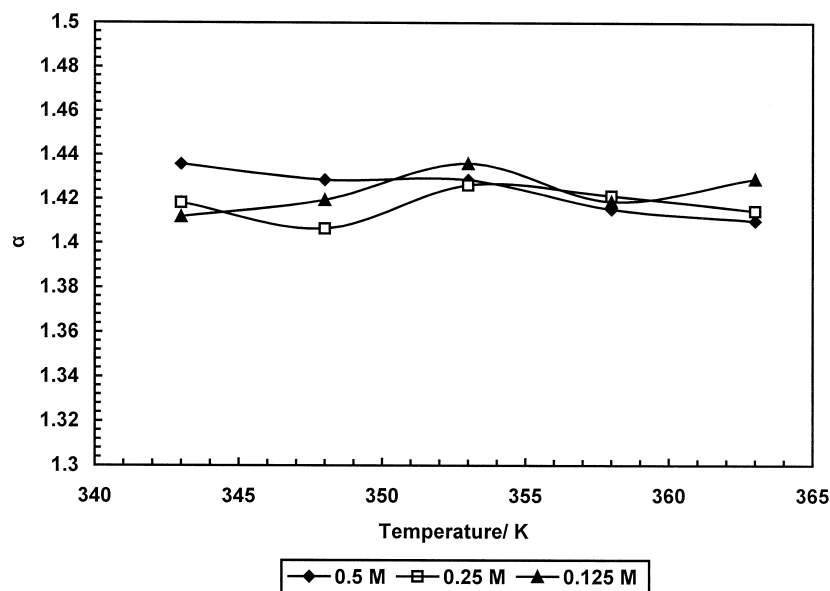

Fig. 10. Values of apparent transfer coefficients for methanol oxidation (2.0 bar air, 1.36 cm^3 min^{-1}).

phenomena in the DMFC, notably methanol cross-over to the cathode. However, the variation in reaction order agrees with that seen in the data of Bagotsky and Vasilyev [17] and more recently observed by Kauranen and Skou [13] and Ravikumar and Shukla [7]. These authors have not explained this behaviour from a mechanistic point of view. This subject is to be reported in a subsequent publication [18] in which methanol oxidation is analysed on the basis of Temkin and Langmuir kinetics for adsorbed intermediates.

The cell voltage vs. current density cell characteristics are derived from the combined effects of polarisation at both electrodes, mass transport and cell internal resistance. It is possible to estimate apparent transfer coefficients for methanol oxidation from cell polarisation data assuming that the predominant loss in voltage is due to anodic polarisation and cathode polarisation and that IR losses are predominantly due to the membrane (IR_{mem}) which can be estimated from published conductivity values of Nafion$^{®}$.

In the absence of mass transport limitations the combined anode (η_a) and cathode (η_c) activation overpotentials are:

$$\eta_c + \eta_a = (U_{cell,o} - U_{cell}) - IR_{mem} \qquad (11)$$

Fig. 10, shows the variation in transfer coefficients, $\alpha_a + \alpha_c$, with temperature and concentration, obtained from the cell polarisation data in the high potential (low current density) region. The near constant value of approximately 1.42 hints that, a two electron transfer may be involved in the rate determining step for methanol oxidation, assuming, as experimentally observed, the transfer coefficient for oxygen reduction is approximately 0.5. This data agrees with that observed experimentally by Bagotsky and Vasilyev [17] and the mechanism for the oxidation involving a rate determining step of reaction of adsorbed OH with adsorbed CO. This analysis is approximate as the presence of methanol at the oxygen reduction cathode has, as observed by Chu and Gilman [14], an effect on the apparent transfer coefficient.
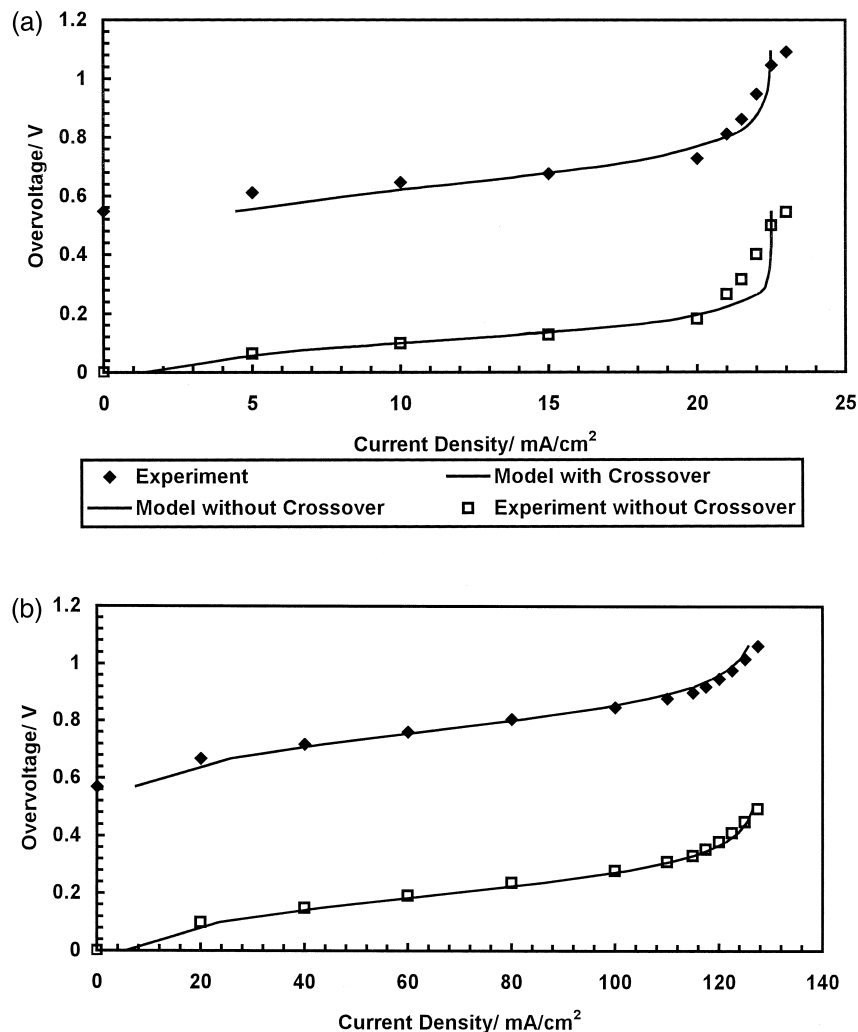

Fig. 11. Variation of overall polarisation ($\eta_a + \eta_c$) with current density as predicted by the DMFC empirical model. (348 K, 2.0 bar air, 1.36 cm^3 min^{-1}). (a) 0. 125 mol dm^{-3} methanol. (b) 0.5 mol dm^{-3} methanol.

3.4. Overall correlation of data

Open circuit voltage as predicted from Eq. (2), combined with anode and cathode polarisation, as expressed by Tafel equations, i.e., $j = j_o e^{\frac{aF\eta}{RT}}$ and mass transport overpotential for oxygen reduction and methanol oxidation $\{(\eta_c + \eta_a)_{conc}\}$ can be used to produce an empirical model which predicts the variation of cell voltage;

$$\eta_c + \eta_a = (U_{cell,o} - U_{cell}) - IR_{mem} - (\eta_c + \eta_a)_{conc} \quad (12)$$

Fig. 11, shows the variation in overpotential with current density as predicted by the model. The model is in reasonable agreement with experimental data for the two methanol concentrations considered. Data is shown as the overvoltage from experimental open circuit values and as the overvoltage from the thermodynamic standard cell potential.

4. Conclusions

This research has shown that the performance of the LFDMFC is affected by several parameters, notably cell temperature, methanol concentration and cathode oxygen supply and pressure. Highest power densities are achieved at higher temperatures and cathode oxygen pressures. The selection of methanol concentration, for maximum power density, depends upon the current density and in principle will be optimised for specific applications. Overall, methanol flow rates, over the range considered, did not effect cell performance. Similarly the influence of methanol concentration is not crucial within the range of 1 to 2.0 mol dm^{-3}. A more critical issue is the methanol conversion in the cell and thus the amount of carbon dioxide produced.

Short-term durability tests have been conducted and have shown that cell performance is stable over a fairly long period of time, around 30 h. The cell responds well to intermittent use as applied in this research. However, there is a need to fully evaluate the DMFC over prolonged periods (months to years) of dynamic operation.

At the moment the performance of the DMFC, for the MEA used in this work, with a liquid feed is not as good as that with a vapour fed cell; maximum power densities are some 50% lower. This poorer performance is due to several factors including the restricted operating temperature range used in the liquid feed system ($< 100°C$), a high degree of methanol crossover and to factors associated with the use of liquid fuel in electrodes originally designed for gas or vapour feed cells.

The performance of the DMFC, at higher current densities, has been shown to be limited by a mass transport process, which mainly occurs, by diffusion in the carbon cloth. A semi-empirical model gives good prediction of the effect of operating parameters on open circuit voltage. An approximate mechanistic analysis of cell potential behaviour has generated values of transfer coefficients and reaction orders for methanol oxidation which agree with previous published information. From the models of open circuit voltage, mass transport and methanol oxidation kinetics a reasonably accurate model of cell voltage behaviour has been produced.

5. Notation

A_{cell}	cross-sectional area of cell
a_i	Activity of species i
C_o	Inlet methanol feed concentration
d	Width of channel
D_{meoh}	Diffusivity of methanol
e_c	Voidage of carbon cloth
$E_{a,j}$	Activation energy for Arrhenius Eq. (3)
F	Faraday's constant
I	Cell current
j	Current density
k_{21}^*	Constant defined in Eq. (2)
k_c^o	Mass transfer coefficient of cloth
k_e	Mass transfer coefficient
l_{cl}	Thickness of cloth
m	Constant defined in Eq. (7)
n	Number of electrons in methanol oxidation
N_{app}	Apparent reaction order
p^θ	Total pressure
P_i	Partial pressure of species i
Q	Volumetric flow rate
R	Gas constant
R_{mem}	Resistance of membrane
T	Temperature
$U_{cell,O}$	Theoretical Open cell voltage
Da	Damkohler number
Sh	Sherwood number
β	Parameter defined in Eq. (2)
ΔC_{cl}	Concentration change over carbon cloth
η	Overpotential

Subscripts

a	anode
c	cathode
conc	concentration
a	anode

Sundmacher by a research fellowship during his stay at Newcastle University.

References

[1] J.M. Leger, C. Lamy, Berichte der Bunsen-Gesellschaft fur Physikalische Chemie 94 (9) (1990) 1021–1025.

[2] D.S. Cameron, G.A. Hards, B. Harrison, R.J. Potter, Platinum Metals Review 31 (4) (1987) 173–181.

[3] G.L. Troughton, A. Hamnett, Bull. Electrochem. 7 (1991) 488.

[4] K. Scott, W.M. Taama, J. Cruickshank, J. Power Sources 65 (1997) 159.

[5] J.S. Wainwright, J.T. Weng, R.F. Savinell, M. Litt, J. Electrochem. Soc. 142 (1995) L121.

[6] Direct methanol Fuel Cell Review Meeting, Dept. of Energy and Advanced Research Projects Agency, Baltimore, April 26–27, 1994, Executive Summary.

[7] M.K. Ravikumar, A.K. Shukla, J. Electrochem. Soc. 143 (1996) 2601.

[8] S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. LaConti, J. Kosek, G.K. SuryaPakash, G.A. Olah, J. Power Sources 47 (1994) 377.

[9] T.I. Valdez, S.R. Narayanan, H. Frank, W. Chun, Proceedings of the 12th Annual Battery Conference on Applications and Advances, 1997, p. 239.

[10] S.R. Narayana, G. Halpert, W. Chum, B. Jeffries-Nakamura, T.I. Valdez, H. Frank, S. Surampudi, Proceedings of the Power Sources Conference, Cherry Hill, NJ, USA, 1996.

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

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

[13] P.S. Kaurenan, E. Skou, J. Electroanal. Chem. 408 (1996) 189.

[14] D. Chu, S. Gilman, J. Electrochem. Soc. 141 (1994) 1770.

[15] K. Scott, W.M. Taama, P. Argyropoulos, Accepted for publication, J. App. Electrochem.

[16] K. Scott, S. Kramer, K. Sundmacher, W.M. Taama, P. Argyropoulos, for submission to J. Membrane Science.

[17] Bagotski, Vasilyev, Electrochimica Acta 1323 (1967) 12.

[18] K. Scott, for submission to J. Electroanalytical Chemistry.

[19] X. Ren, W. Henderson, S. Gottesfeld, J. Electrochem. Soc. 144 (9) (1997) L267.

[20] R. Reeve, P.A. Christensen, K. Scott, to be submitted to J. App. Electrochem.

[21] M.G. Fouad, G.H. Sedahmed, Electrochimica Acta 17 (1972) 665.

[22] K. Sundmacher, K. Scott. Chem. Eng. Sci., in press.