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Performance of a direct methanol fuel cell*

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The performance of a direct methanol fuel cell based on a Nafion® solid polymer electrolyte membrane (SPE) is reported. The fuel cell utilizes a vaporized aqueous methanol fuel at a porous Pt–Ru–carbon catalyst anode. The effect of oxygen pressure, methanol/water vapour temperature and methanol concentration on the cell voltage and power output is described. A problem with the operation of the fuel cell with Nafion® proton conducting membranes is that of methanol crossover from the anode to the cathode through the polymer membrane. This causes a mixed potential at the cathode, can result in cathode flooding and represents a loss in fuel efficiency. To evaluate cell performance mathematical models are developed to predict the cell voltage, current density response of the fuel cell.

Keywords: *fuel cell*, *methanol*, *solid polymer electrolyte*, *model*, *platinum catalyst*

1. Introduction

The direct methanol fuel cell (DMFC) uses methanol, in the form of vapour or liquid, as fuel and is based on a solid polymer electrolyte. It operates at relatively low temperatures (<100 °C). The structure of the DMFC is a composite of two porous electrocatalytically active 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 DMFC has several advantages which suit its application to transportation, including high efficiency, very low emissions, a potentially renewable fuel source and fast and convenient refuelling. It uses methanol, in the form of vapour or liquid, to generate electrical energy. The direct methanol fuel cell based upon solid polymer electrolyte (SPE) has the additional advantage of no liquid acidic or alkaline electrolyte. The thermodynamic reversible cell potential for the overall cell reaction is 1.214 V, which compares to 1.23 V for the hydrogen fuel cell and, consequently, has generated the interest in the DMFC as an alternative power source.

The 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 the methanol cell. For methanol, six electrons must be exchanged for complete oxidation and consequently the oxidation kinetics are inherently slower. The slower kinetics are a result of intermediates formed during methanol oxidation [1]. Oxidation of the intermediates to carbon dioxide requires the adsorption of an oxygen containing species (e.g., OH, H_2O). Adsorption of these species does not occur substantially until potentials well above open circuit values [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].

Much of the research on SPE fuel cells systems has used Nafion®, or similar, membranes. To date an essential condition for the successful operation of a DMFC is the use of a pressurized oxygen or air supply to the cathode. Another important factor is the concentration of methanol in the water-methanol mixture fed to the anode. At concentrations higher than around 2 molar, the cell voltage declines significantly due to poisoning of the cathode electrocatalyst by methanol that has permeated through the SPE (Nafion®) membrane, i.e. methanol crossover [4]. Thus an important area to improve the DMFC performance is in polymer membrane electrolytes. Recent work has reported the use of polybenzimidazole [5] and perfluorinated sulphonimides [6] as polymer electrolyte membranes as a means of reducing the impact of methanol crossover.

Recent developments in electrode fabrication techniques and better cell designs have brought dra-

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matic improvements in cell performance in small-scale DMFCs. 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 [7]. These power densities are, however, substantially lower than those obtained with hydrogen fuel cells, 0.6 – 0.7 W cm^{-2}, while the platinum anode catalyst loading can be substantially lower (0.1 mg Pt cm^{-2}). The research reported here is for single cell performance of the DMFC using Nafion® 117 membranes and the modelling of the cell to predict the cell voltage–current density characteristics.

2. Experimental details

Tests on the DMFC were performed with a cell, shown schematically in Fig. 1, with a cross-sectional area of 5 cm^2. The cell was fitted with one membrane electrode assembly (MEA) sandwiched between two graphite blocks with parallel channel flow paths cut out for methanol and oxygen/air flow. The cell was held together between two aluminium backing plates using a set of retaining bolts positioned around the periphery of the cell. 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 to heat and vaporize the methanol. Oxygen was supplied from cylinders at ambient temperature, bubbled through water for humidification, and the pressure regulated at inlet 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 carbon cloth support (E-Tek, type A) upon which was spread a thin layer of uncatalysed (ketjenblack 600) carbon, bound with 10 wt % Nafion® from a solution of 5 wt % Nafion® dissolved in a mixture of water and lower aliphatic alcohols (Aldrich). The catalysed layer, consisting of 50 wt % Pt–Ru (2 mg cm^{-2} metal loading) dispersed on carbon (ketjen) and bound with 10 wt % Nafion®, was spread on this diffusion backing layer. Details of catalyst preparation are described elsewhere [8]. In brief the catalysts are using oxidation of colloidal Pt/Ru dispersions. This chemistry is based on soluble sulphito complexes of the form $Na_6Pt(SO_3)_4$ and $Na_4Ru(SO_3)_3$ and gives rise to 2 nm Pt–O particles adsorbed on the carbon. On chemical or electrochemical reduction, 2 nm particles of Pt, Ru or Pt–Ru are formed. The cathode was constructed using a similar method as for the anode, using a diffusion layer bound with 15 wt % PTFE, and 1 mg cm^{-2} Pt black (Aldrich) with 10 wt % Nafion® as the catalyst layer. The electrodes were placed either side of a pretreated Nafion® 117 membrane (Aldrich). This pretreatment 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. The resulting MEA was installed in the cell after pressing, and hydrated with water circulated over the anode at 96 °C for several hours.

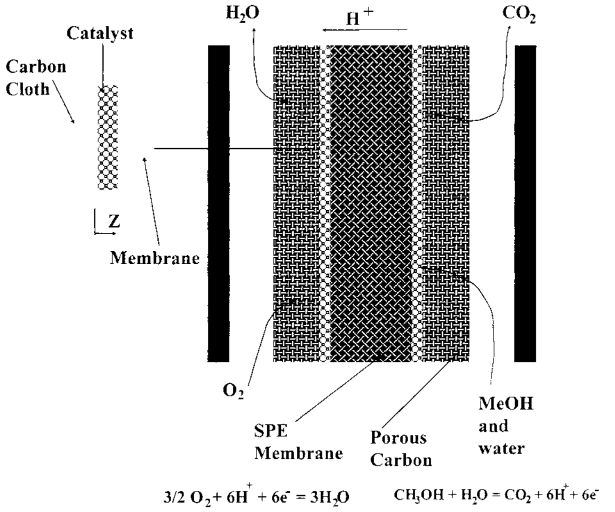

Fig. 1. Schematic diagram of the model direct methanol fuel cell.

3. Cell performance

In the operation of the DMFC there are several variables which will affect the cell voltage, current density response-temperature of fuel, methanol concentration, oxygen partial pressure and fuel and oxidant flows. This is in addition to the effect of the type of proton exchange membrane, membrane thickness, catalyst preparation and overall electrode structure. In the small cells used here there is little impact on performance associated with fuel and oxidant flows except at low flow rates where flooding of the cathode structure may occur or when carbon dioxide removal from the anode is hindered.

The effect of oxygen pressure on the cell voltage–current density response of the cell is shown in Fig. 2. At pressures above a nominal atmospheric operation there is a significant improvement in performance. This improvement, as shown in Fig. 3, amounts to over 120 mV increase in cell potential at a given

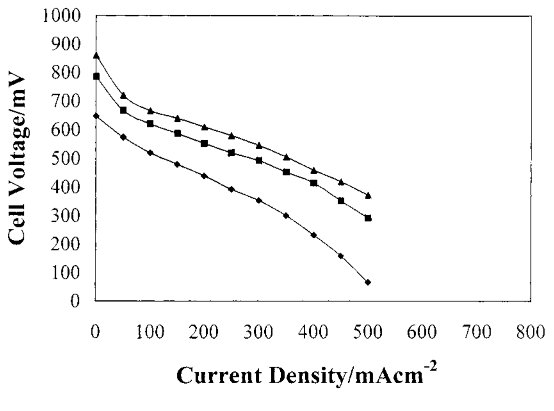

Fig. 2. The effect of oxygen pressure on the voltage, current density response of the DMFC. 80 °C, 1.0 kmol m^{-3} methanol. Oxygen pressure: (◆) 0 barg; (■) 1 barg; (▲) 2 barg.

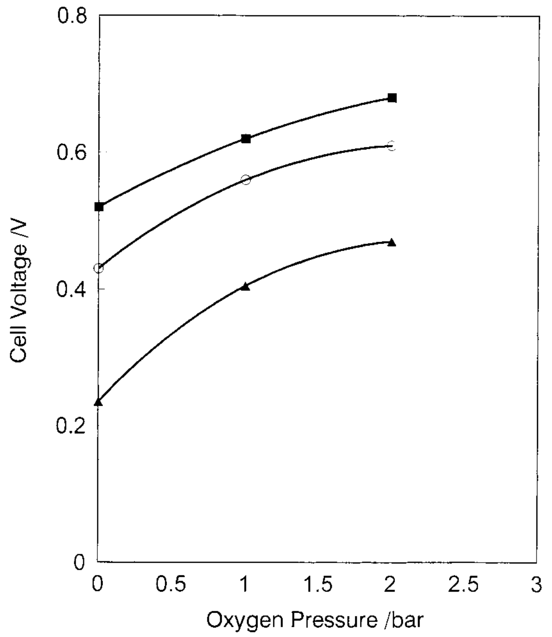

Fig. 3. The variation of DMFC cell voltage with oxygen pressure, 80 °C, 1.0 kmol m^{-3} methanol. Current density: (■) 100, (○) 200 and (▲) 400 mA cm^{-2}.

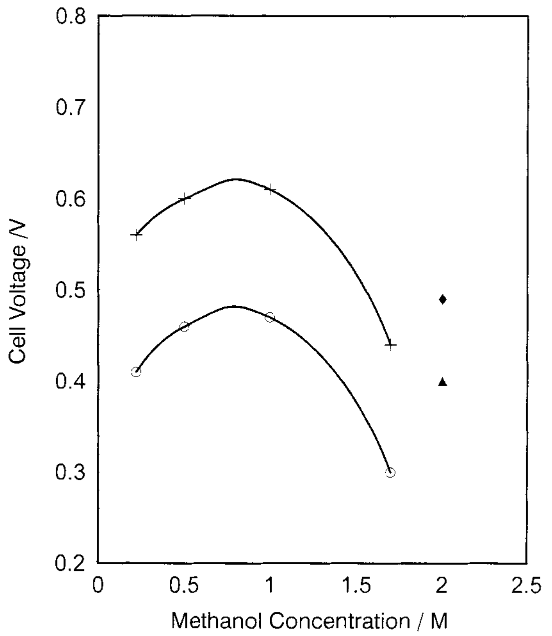

Fig. 5. The variation of DMFC cell voltage with methanol concentration. 80 °C, 1.0 barg oxygen. Current density: (+) 200 and (○) 400 mA cm^{-2}. Pressure 2 barg oxygen (◆) 200 and (▲) 400 mA cm^{-2}.

current density at pressures of 1–2 bars. This improvement cannot be explained by the effect of oxygen pressure on the cathode potential and is believed to be due to a reduced effect of methanol crossover on catalyst 'poisoning' at the higher pressure.

Figures 4 and 5 show the effect of methanol concentration on the cell performance. At the higher concentration of 1.7 kmol m^{-3} there is a significantly poorer performance (i.e., lower cell voltage) than at the lower concentration of 0.22 kmol m^{-3}. At a given current density the cell voltage goes through a maximum value (Fig. 5) at an approximate concentration of 1.0 kmol m^{-3}. As shown in Fig. 5 the cell voltage can be increased at the higher methanol concentrations by increasing the oxygen pressure at the cathode. This behaviour has important implications on eventual larger size cell operation. Clearly high concentrations, much above 2.0 kmol m^{-3} of methanol cannot be used in operation, even if higher oxygen pressures were to be used. The use of aqueous solutions of methanol has an indirect beneficial effect on cell operation; maintaining a humidified atmosphere in the cell which helps maintain the required hydration of the membrane. The wide range of methanol concentrations (down to approximately 0.2 kmol m^{-3}) which give satisfactory performance means that, on scale-up to cells with greater fuel residence times, the depletion of methanol will not be too critical. However, the accumulation of carbon dioxide from the methanol oxidation may influence the degree of conversion which can be achieved while retaining good cell performance. Research using CFD modelling and experimental trials is currently assessing the effect of carbon dioxide production on the flow of fuel in the anode flow channels and in the carbon cloth backing layers of the membrane electrode assemblies. A major practical implication of the use of aqueous methanol and the lower limit of the concentration is that of recovery of methanol from the exhaust anode vapour. This will require an additional source of energy and additional equipment in the final fuel cell system. Furthermore there will be greater changes in the fuel and oxidant temperatures in larger cells and the use, and control, of a thermal management system will be more critical.

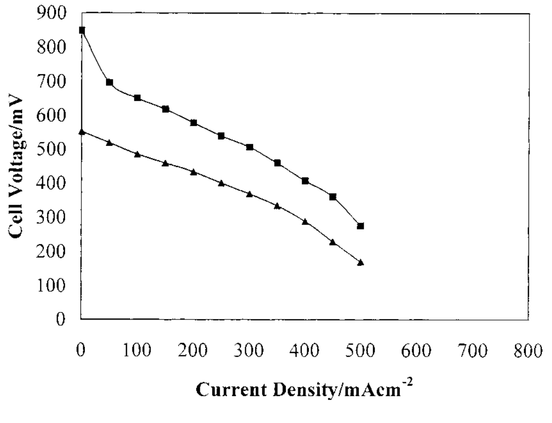

Fig. 4. The effect of methanol concentration on the voltage, current density response of the DMFC. 100 °C, 1.0 barg oxygen. Concentration: (■) 1.7 and (▲) 0.22 M methanol.

The power densities achieved by the DMFC are shown in Fig. 6 as a function of current density. Power densities reach maximum values approaching 0.2 W cm^{-2}, at current densities of approximately 400 mA cm^{-2}. Power densities are lowest at the highest methanol concentration used and are highest with the greater oxygen pressure of 2 bar. Power densities of 0.3 W cm^{-2} have been reported in similar work on the DMFC using oxygen at 5 bar pressure

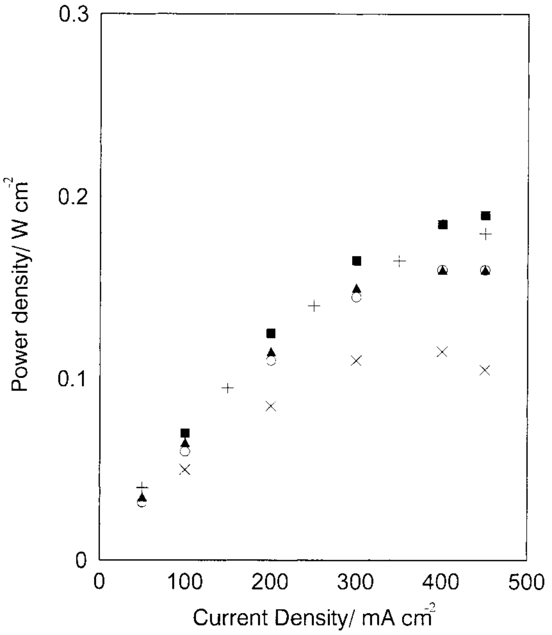

Fig. 6. Variation of DMFC power density with current density. Key: (▲) 0.22 kmol m^{-3}, 100 °C, 1.0 bar oxygen; (○) 1.0 kmol m^{-3}, 80 °C, 1.0 bar oxygen; (■) 1.0 kmol m^{-3}, 80 °C, 2.0 bar oxygen; (×) 1.7 kmol m^{-3}, 100 °C, 1.0 bar oxygen; (+) 0.5 kmol m^{-3}, 110 °C, 2.0 bar oxygen.

[7]. Using air at 5 bar, a power density of 0.21 W cm^{-2} at 800 mA cm^{-2} has been obtained. These power densities are very high by comparison with conventional DMFCs; and the stability of these MEAs was such that, in one run at 400 mA cm^{-2}, (0.14 W cm^{-2}), no deterioration in performance was observed over 18 days operation. Power densities reported by other researchers [9], at higher temperatures have values of 0.38 W cm^{-2} at 130 °C, using 5 bar pressure oxygen and 0.25 W cm^{-2} with 3 bar pressure air, at 110 °C. A difference of 30–50 °C in the operating temperature makes a significant difference in the cell performance. For example at a constant cell voltage of 0.5 V, a reduction in current density from 450 to 170 mA cm^{-2} is seen when the temperature is decreased from 130 to 80 °C, using Nafion® 112 membrane. Nafion® 112 has approximately half the resistance of Nafion® 117 when used in a DMFC [17]. When these two factors of temperature and membrane material are allowed for, the recent reported performance of the DMFC are very comparable. For example, 0.35 at 97 °C [7] cf. 0.385 at 130 °C [9] both using 5 bar oxygen. In cells operating at these higher temperatures of 130 °C, there are potential problems in dehydration of the SPE membrane. In addition the use of high pressure oxygen is not a realistic option for practical DMFCs considered for transport, which are likely to use air at modest pressure supplied by blowers rather than compressors.

4. Mathematical model of the DMFC

The reactions which occur in the DMFC are as follows:

$$\text{anode:}\quad CH_3OH + H_2O = CO_2 + 6\,H^+ + 6\,e^- \qquad (1)$$

$$\text{cathode:}\quad 3/2\,O_2 + 6\,H^+ + 6\,e^- = 3\,H_2O \qquad (2)$$

A model which is used to evaluate the cell performance should allow for the variation in the concentrations of the above reaction species in the cell, and the associated mass transport processes. The model should also allow for variations in electrode potential in the porous electrode structures and allow for the transport of species across the SPE membrane. The cell performance model in this paper is used to calculate the overall cell voltage, which can be written as

$$V_{\text{cell}} = E_{\text{cell}} - \eta_{\text{an}} - \eta_{\text{cat}} - \eta_{\text{xover}} - \eta_{\text{ohmic}} \qquad (3)$$

where E_{cell} is the difference between the half-cell potentials of the anode and cathode, at the reference current density i_0, corrected for the thermodynamic effects of temperature and pressure. The anode and cathode overpotentials η_{an} and η_{cat} are described by Tafel kinetics at the electrodes, and a one-dimensional potential and concentration distribution is calculated within the thickness of the catalyst layers. Ohmic overpotential, η_{ohmic}, is calculated for the resistance of the membrane, and the effect of methanol crossover (i.e., the crossover overpotential, η_{xover}) is calculated from the flux of methanol through the membrane.

The model structure of the DMFC, shown in Fig. 1, consists of a flow channel cut into a graphite flow-bed, through which the reactant flows. Adjacent to the channel is the diffusion region of the electrode, comprised of a highly-porous carbon cloth backing layer and a thin layer of uncatalysed Nafion-bound carbon black. The model for diffusion through the carbon fibre cloth is not developed here and it is assumed that the effect of diffusion through the highly porous structure is small under realistic operating conditions [10].

Next to the porous carbon diffusion region is the layer of porous electrocatalyst, followed by the Nafion® membrane. The porous electrode has a thickness 1, with the oxygen/electrode interface at $z = 0$ and the electrode/membrane interface at $z = 1$. A similar structure exists on the other side of the membrane. The model for the DMFC accounts for changes in potential in these regions and allows for the transfer of methanol from the anode to the cathode and its effect on the performance of the cathode. The major assumptions adopted in the model are as follows:

(i) The cell temperature is assumed to be constant and uniform.
(ii) The concentration of reactant is taken as the weighted average of the inlet and outlet concentrations.
(iii) The pressure is uniform within each cell compartment.
(iv) Due to the thinness of the diffusion region of the electrodes, transport in this region is not considered.

(v) Due to the high electronic conductivity of the carbon substrate and graphite flow-beds, no voltage drop is considered to occur through the thickness of the electrode, or along the flow channels.

(vi) The membrane is considered to be fully hydrated.

(vii) Electrode kinetics can be described by the Tafel equation.

$$i(z) = i_0 c(z)/c_0 \ \exp\{\eta(z)/\beta\} \tag{4}$$

where i_0 is the exchange current density at the reference potential, c_0 is the reactant concentration at the oxygen/electrode interface, and β is a constant related to the Tafel slope.

(viii) The overpotential caused by methanol crossover is directly proportional to the concentration of methanol at the cathode.

The appropriate expressions for these potential contributions in Equation 3 are

$$E_{\text{cell}} = E^0_{\text{cell}} + \Delta T\left(\frac{\partial E}{\partial T}\right) - \Delta N\frac{RT}{nF}\ln\left(\frac{P_2}{P_1}\right) \tag{5}$$

$$\eta_{\text{ohmic}} = \frac{It_{\text{m}}}{\sigma_{\text{m}}} \tag{6}$$

$$\eta_{\text{xover}} = \chi j_{\text{MeOH}} \tag{7}$$

The porous electrocatalyst layer model predicts the current distribution within the electrode caused by a mixture of poor mass transport (diffusion) and low protonic conductivity. Each electrode region is described by the same model structure with different parameters used in the appropriate solution. Protonic resistivity within the electrode is given by ρ, the effective catalyst surface area per unit volume is γ and D denotes the effective reactant diffusivity within the porous electrode.

The distribution in overpotential is given by

$$\frac{\mathrm{d}^2\eta(z)}{\mathrm{d}z^2} = \rho\gamma i(z) \tag{8}$$

The rate at which the flux of reactant (gradient of concentration) changes in the electrode is related directly to the local current density, and is written as

$$\frac{\mathrm{d}^2c(z)}{\mathrm{d}z^2} = \frac{\gamma}{DnF}i(z) \tag{9}$$

where F is the faradaic constant and n is the number of electrons involved in the reaction.

The boundary values relevant to this problem are

$$\begin{aligned} c(0) = c_0 \quad &\text{and} \quad \left.\frac{\mathrm{d}c}{\mathrm{d}z}\right|_l = 0 \\ \left.\frac{\mathrm{d}\eta}{\mathrm{d}z}\right|_{\mathrm{O}} = 0 \quad &\text{and} \quad \eta(l) = E \end{aligned} \tag{10}$$

The solution of these equations can be simplified by adopting reduced variables as follows: $\bar{z} = z/l$, $\overline{C} = c/c_0$, $\bar{\eta} = \eta/E$ and $\bar{i} = i/i_0$ so that

$$\frac{\mathrm{d}^2\bar{\eta}}{\mathrm{d}\bar{z}^2} = \left(\frac{l^2}{E}\rho\gamma i_0\right)\bar{c}\ \exp\left\{\frac{E}{\beta}\bar{\eta}\right\} \tag{11}$$

$$\frac{\mathrm{d}^2\overline{C}}{\mathrm{d}\bar{z}^2} = \left(\frac{l^2}{c_0}\frac{\gamma i_0}{DnF}\right)\bar{c}\ \exp\left\{\frac{E}{\beta}\bar{\eta}\right\} \tag{12}$$

Permeation of methanol (methanol flux) through a Nafion® membrane, of thickness t_{m} will take place under the driving forces of concentration and pressure gradients, and electroosmosis

$$\begin{aligned} j_{\text{MeOH}} = &-\frac{D_{\text{m,MeOH}}}{t_{\text{m}}}\Delta c_{\text{m,MeOH}} \\ &-\frac{c_{\text{cat,MeOH}}K}{t_{\text{m}}}\Delta P + \frac{\gamma_{\text{MeOH}}}{n_{\text{an}}F}I \end{aligned} \tag{13}$$

$$\gamma_{\text{MeOH}} \cong x^0_{\text{MeOH}}\lambda_{\text{H}_2\text{O}}$$

Assuming that the permeate is entrained in the carrier gas flow at a rate proportional to c_2, the concentration of methanol at the permeate membrane interface, we can write

$$j = kc_2 \tag{14}$$

We have measured permeation rates for water, methanol and a water–methanol mixture through Nafion® 117 and calculated the values of k and K from the data [4].

Assuming that the methanol-covered fraction of the surface area has a lower free energy for oxygen reduction, in which case the overpotential produced by methanol crossover is proportional to the flux,

$$\eta_{\text{xover}} = \chi j_{\text{MeOH}} \tag{15}$$

where χ is an empirical constant to be determined.

This model predicts that the overpotential due to methanol crossover will have a current-independent term, affected by the pressure differential, and a current-dependent term (producing an *iR*-like drop) due to electroosmosis of methanol. By measuring the effect of pressure differential on flux and on overpotential (correcting for kinetic effects) we have determined a value for χ, and then estimated λ_{MeOH}.

In the case of the methanol consuming anode an additional term should, in principle, be considered in the material balance equation describing the effect of methanol crossover by an electroosmotic drag. It is assumed that the extent of this methanol drag is not large in comparison to the associated transfer of water.

The equations describing the concentration and potential distribution within the electrode are solved numerically using the finite difference method and Newman's BAND algorithm for the resulting simultaneous nonlinear equations (using modified NL3BAND.C software [11,12]). There are several parameters and data which have to be estimated to solve the above model. Details of these are given in Appendix 1.

5. Results and discussion

The experimental data have shown that there is a significant effect of increasing the oxygen pressure on cell performance which cannot be predicted from thermodynamic or kinetic behaviour. This is due to

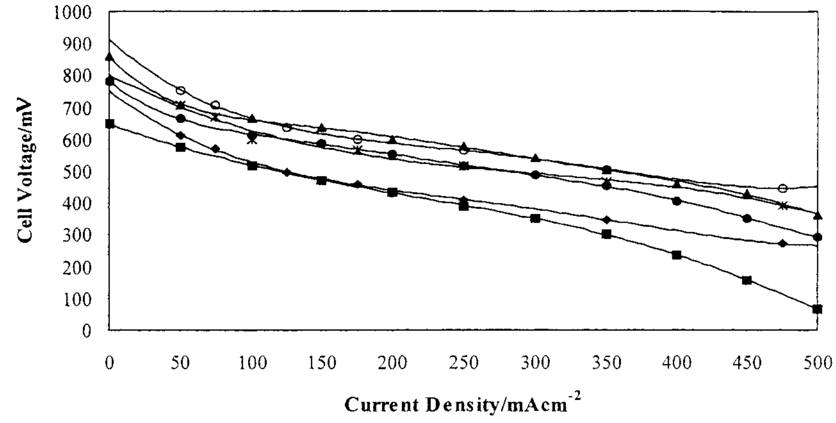

Fig. 7. The model prediction of the performance of the DMFC. 80 °C, 1.0 kmol m^{-3} methanol. Key: (◆) 0, (*) 1, and (○) 2 barg oxygen. Experiment: (■) 0, (●) 1 and (▲) 2 barg oxygen.

the significant effect of methanol crossover on the cathode performance and thus the mathematical model was developed to account for this phenomenon on the cell performance. The predictions of the model and the experimental cell performance are compared in Fig. 7. The agreement between the model and the experimental data is good over a significant range of practical operating current densities, up to approximately 350–400 mA cm^{-2}. The poorer agreement at low current densities is partly due to the assumption of Tafel kinetics and the relatively simple model for the effect of poisoning of the cathode due to methanol. At current densities above 300 mA cm^{-2}, the experimental data depart significantly from the predictions of the model. This disagreement between model and experiment can be explained by a mass transport effect in the electrodes at the catalyst surface. The effect is more pronounced the lower the oxygen pressure which suggests that oxygen mass transport limitation is significant at high current densities. Models are currently under development [10] which will allow for the mass transport effects evidenced at high current densities. This is based on a mass transport limitation at the electrocatalyst surfaces which produces a mass transport overpotential, η_{MT}, due to limitations in gas diffusion rate through the porous electrode structures. This mass transport effect is defined in terms of a local equivalent mass transport coefficient, k_{l}, as

$$\eta_{\mathrm{MT}} = -\beta \ln(1 - i/nFC_0k_{\mathrm{l}}) \qquad (16)$$

This approach is more empirical than the model discussed in this paper due to the difficulties in determining the mass transport effects at the catalyst surface. Good agreement between the model and experiment, as shown in Fig. 9, have been obtained with this approach. Further details are to be reported elsewhere [10].

There are now significant developments being made in the production of SPE membranes which have much lower permeation rates for methanol than Nafion. In addition research is also active in the production of more methanol tolerant cathodes and thus it is interesting to compare the behaviour of the DMFC with and without the influence of methanol crossover at the cathode. This would indicate the ideal fuel cell characteristics if methanol crossover could be eliminated. Figure 8 compares the DMFC performance with and without the effect of methanol crossover as predicted by the model. Clearly, when the factor of methanol crossover is removed there is a significant change in the cell characteristics, cell

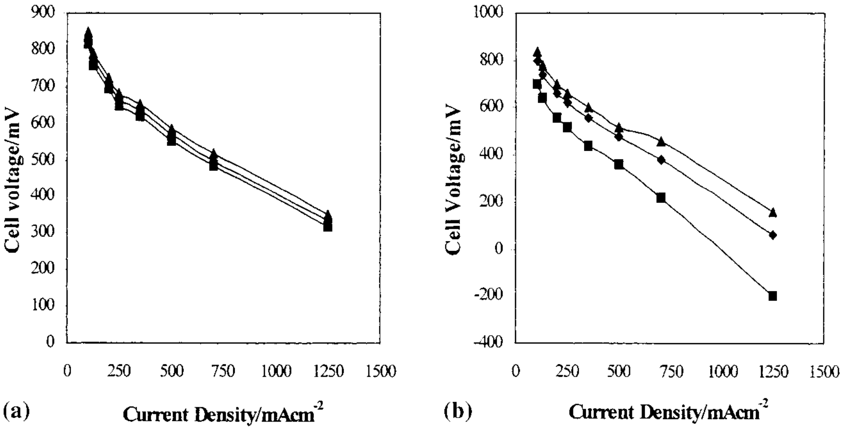

Fig. 8. The predicted variation of cell voltage with current density for the DMFC. 85 °C, 0.75 kmol m^{-3}. Key: (■) 0, (◆) 1 and (▲) 2 barg oxygen. (a) Without methanol crossover; (b) with methanol crossover.

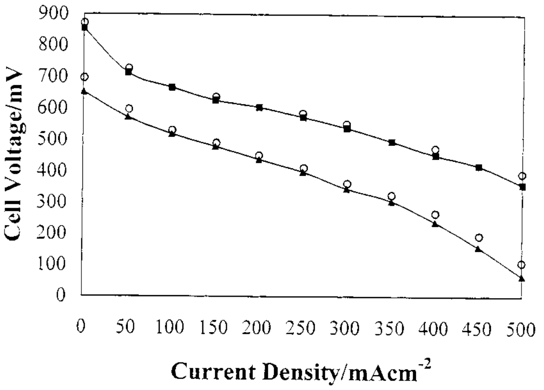

Fig. 9. The effect of mass transport on the model prediction of the DMFC performance. 80 °C, 1.0 M methanol. Experimental: (▲) 0 and (■) 2 barg oxygen. Model prediction: (○).

voltages are significantly improved and are much less sensitive to the effect of oxygen pressure. Predicted power densities are correspondingly higher, for example at 500 mA cm^{-2} the predicted value is approximately 0.28 W cm^{-2} compared to an experimental value of approximately 0.18 W cm^{-2} with 2 bar oxygen at the cathode. This indicates the potential improvements which can be realized with current anode catalysts and MEA fabrication procedures.

6. Conclusions

The research is based on new effective, high performance, catalyst formulations for the anode in DMFCs. This, together with the production of new electrode membrane assemblies, has enabled the production of high performance polymer electrolyte DMFCs based on supported Pt–Ru catalyst and commercial perfluorosulphonic acid membrane (Nafion®). The results of this work have shown that acceptable performance of the polymer electrolyte DMFC can be achieved at modest temperatures of 80 °C using vaporized aqueous methanol feeds. Power densities approaching 0.2 W cm^{-2} are achieved with the current DMFC. Higher temperatures of operation increase the values of power density and cell potential, at fixed current densities. The power performance can also be improved by operating at higher oxygen pressures at the cathode. However, both these factors have implications in the operation of practical cell stacks. In particular for transportation, low pressure air is the only real practical choice. The performance of the DMFC achieved in this research is comparable to, or better than, that achieved by other research groups around the world. With improved anode catalysts and lowered methanol crossover rates even greater improvements in power density are expected, making the DMFC a serious competitor to on-board methanol reformer and reformate fuel cell systems.

We have successfully modelled the DMFC and are able to predict the cell power performance over a wide range of operating conditions. The mathematical model of the MEA is based on the variation of reactant concentrations and overpotentials in the catalyst layers. The model also incorporates the influence of methanol crossover from anode to cathode based on a combination of diffusion, electroosmotic drag, and pressure. Improvements in the model are currently being researched to improve the predictions of the DMFC at high current densities.

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Appendix 1

The following details the equations used to estimate the parameters in the mathematical model of the DMFC.

(a) *Temperature effect on cell voltage*
From thermodynamics, we have

$$\left(\frac{\partial E}{\partial T}\right)_P = \frac{\Delta S}{nF} \tag{17}$$

where E is the electric potential. Assuming ΔS is constant over the temperature range considered, then the change in cell voltage can be written as $\Delta T \Delta S/nF$.

For the methanol oxidation reaction,

$$CH_3OH + 3/2\,O_2 \longrightarrow CO_2 + 2\,H_2O \tag{18}$$

$$\left(\frac{\partial E}{\partial T}\right)_{\text{liq}} = -0.140\,\text{mV K}^{-1}$$

$$\left(\frac{\partial E}{\partial T}\right)_{\text{gas}} = +1.043\,\text{mV K}^{-1}$$

(b) *Pressure effect on cell voltage*
From thermodynamics, we have

$$\left(\frac{\partial E}{\partial P}\right)_T = -\frac{\Delta V}{nF} \tag{19}$$

which, on integration, gives

$$\Delta E = -\Delta N \frac{RT}{nF} \ln\left(\frac{P_2}{P_1}\right) \tag{20}$$

For the oxygen reduction reaction,

$$2H^+ + 1/2\,O_2 \longrightarrow H_2O \tag{21}$$

we obtain ΔN for the liquid and gaseous cases as -0.5 and $+0.5$, respectively. At 80 °C, increasing the pressure to 2 atm will increase the voltage by 10.5 mV.

(c) *Conductivity of Nafion®*
The conductivity of Nafion® is given by the following relation [13]. As a reference point, we use a.c. measurements performed in our laboratory which give the conductivity as $0.073 \pm 0.008\,\text{S cm}^{-1}$, with a similar value for recast Nafion® films, at 25 °C. This gives,

$$\sigma_m = 0.073 \exp\left[1268\left(\frac{1}{298} - \frac{1}{T}\right)\right] \tag{22}$$

(d) *Diffusion coefficients of water and methanol in Nafion® 117*
The variation of diffusivity with temperature can generally be described by

$$D_i = D_{i,\text{ref}} \exp\left[\frac{\Delta E}{R}\left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right] \tag{23}$$

For the diffusion of water through Nafion® 1155 E.W., Yeo and Eisenberg [14] calculated a value for $\Delta E/R$ of 2416 K. Springer *et al.* [15] found a value of 2436 K. We use the latter value, as it pertains to measurements on Nafion® 117. For a reference value, the PGSE measurements of Zawodzinski and Springer [16] are $D_{m,\text{water}} = 7.3 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}$ at 80 °C, so that

$$D_{m,\text{water}} = 7.3 \times 10^{-6} \exp\left[2436\left(\frac{1}{353} - \frac{1}{T}\right)\right] \tag{24}$$

For methanol in Nafion®, we use the same activation energy as for water, since there is a paucity of results in this area. For a reference point, we refer to the work of Kauranen and Skou [17] who measured a (superficial) diffusivity, $D_{m,\text{MeOH}} = 4.9 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}$ at 60 °C, giving

$$D_{m,\text{MeOH}} = 4.9 \times 10^{-6} \exp\left[2436\left(\frac{1}{333} - \frac{1}{T}\right)\right] \tag{25}$$

(e) *Diffusion coefficients in the catalyst layers*
The diffusion of methanol in the catalyst layer is assumed to have a similar temperature dependence as in Nafion® and using a reference value for methanol in water at 80 °C given by Kauranen [17], we obtain

$$D_{r,\text{MeOH}} = 2.8 \times 10^{-5} \exp\left[2436\left(\frac{1}{353} - \frac{1}{T}\right)\right] \tag{26}$$

When multiplied by the porosity–tortuosity factor, ε, we obtain the effective diffusion coefficient.

The value of λ_{MeOH} is assumed to be given simply by

$$\lambda_{\text{MeOH}} = x^0_{\text{MeOH}} \lambda_{H_2O} \tag{27}$$

where λ_{H_2O} is [14] 2.0–2.9 H_2O/H^+ [16] in fully hydrated Nafion® 117. We use the average value of 2.5.

(f) *Dependence of* i_0 *on temperature*
Parthasarathy *et al.* [18] give the temperature dependence of the electrode kinetics of oxygen reduction as

$$i_{0,\text{cat}} = i^{\text{ref}}_{0,\text{cat}} \exp\left[8804\left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right] \tag{28}$$

For methanol oxidation at the anode, Troughton [8] measured the activation energy for a Pt–Ru supported catalyst as $70\,\text{kJ mol}^{-1}$, giving

$$i_{0,\text{an}} = i^{\text{ref}}_{0,\text{an}} \exp\left[8420\left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right] \tag{29}$$

The Tafel slope for the oxidation reaction is estimated from Troughton's work as 46 mV/factor of e at 80 °C.

Appendix 2: Values of parameters

The following values of parameters were used in the model:

$$\varepsilon = 0.3$$
$$b_{\text{cat}} = \frac{RT}{F}\,V/\text{factor of } e$$
$$b_{\text{an}} = 46 \times \frac{T}{353}\ \text{mV/factor of } e$$
$$l_{\text{an}} = 1.5 \times 10^{-3}\,\text{cm}$$
$$l_{\text{ca}} = 5 \times 10^{-3}\,\text{cm}$$
$$n_{\text{an}} = 6$$
$$n_{\text{cat}} = 4$$
$$F = 96\,458\,\text{C mol}^{-1}$$
$$(\gamma i_0)_{\text{cat}} = 7.14\,\text{A cm}^{-3} \text{ at } 298\,\text{K}$$
$$E_{0,\text{cat}} = 0.355\,\text{V}$$
$$(\gamma i_0)_{\text{an}} = 6.25\,\text{A cm}^{-3} \text{ at } 333\,\text{K}$$
$$E_{0,\text{an}} = 0.265\,\text{V}$$
$$P_{\text{an}} = 1\,\text{atm}$$
$$P_{\text{cat}} = 2\,\text{atm}$$
$$v_{m,\text{an}} = 0.17$$
$$v_{m,\text{cat}} = 0.05$$
$$\lambda_{H_2O} = 2.5\,H_2O/H^+$$
$$K = 6186 \exp\left(-\frac{7100}{T}\right)\,\text{cm}^2\,\text{s}^{-1}\,\text{atm}^{-1}$$

$$k = 5.926 \times 10^{-8}\ \exp\left(-\frac{9756}{T}\right)\ \mathrm{cm\ s^{-1}}$$

$$t_{\mathrm{m}} = 0.0206\,\mathrm{cm}$$

$$c_{0,\mathrm{MeOH}} = 1 \times 10^{-3}\,\mathrm{mol\ cm^{-3}}$$

$$\chi = 1.51\,\mathrm{V\ mol^{-1}\ cm^{2}\ s}$$

$$R = 8.314\,\mathrm{J\ mol^{-1}\ K^{-1}}$$

$$\lambda_{\mathrm{MeOH}} = 2.48 \times 10^{-2}\ \mathrm{MeOH/H^{+}}$$

$$x_{\mathrm{MeOH}} = 0.0184$$