

# The degree and effect of methanol crossover in the direct methanol fuel cell

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## Abstract

A simple model is presented to describe the permeation of methanol from the anode to the cathode in direct methanol fuel cell (DMFC). Measured permeation rates of water and methanol through Nafion® 117 under varied pressure differentials across the membrane are used to determine key parameters in the model. This model is able to explain the effect of oxygen pressure at the cathode and methanol concentration at the anode on the measured cell voltage–current response of the DMFC. © 1998 Elsevier Science S.A.

*Keywords:* Methanol; Fuel cell; Solid polymer

## 1. Introduction

Faced with the challenge of a rapid expansion in global transportation and its subsequent impact on the environment, fuel cells are expected to fill an important role in the replacement of the internal combustion engine. The direct methanol fuel cell (DMFC) has several advantages which suit its application to ground transportation, including high efficiency, very low emissions, a potentially renewable fuel source and fast and convenient refuelling. The direct methanol fuel cell based upon solid polymer electrolyte (SPE) has the additional advantage of no liquid acidic or alkaline electrolyte.

Recent developments in electrode fabrication techniques and better cell designs have brought dramatic improvements in cell performance in small-scale DMFCs. Typically, power densities higher than  $0.18 \text{ W cm}^{-2}$  are achievable, and power densities higher than  $0.3 \text{ W cm}^{-2}$  have been reported [1,2]. A major problem as yet unresolved with the direct methanol fuel cell is that of methanol crossover from the anode to the cathode due to the high diffusivity of methanol in the typical perfluorosulphonate membranes used. This crossover causes depolarisation losses at the cathode and conversion losses in lost fuel. The ideal solution to the problem is to use membranes which are much less permeable to methanol transport than

to hydrated protons. Such polymer electrolytes however have not yet been produced. Operation of the anode with almost complete methanol fuel utilisation will cause significant polarisation losses at the anode and hence at the moment practical solutions will rely on physical or chemical separation of the methanol from the exhaust cathode stream.

This paper is concerned with identifying and analysing the effect of methanol crossover on the DMFC performance. As with all fuel cells the DMFC exhibits a pseudo-linear cell voltage–current relationship at intermediate values of cell current density. A considerable increase in cell performance could be obtained by reducing the steepness of the slope in the pseudo-linear region of the typical I–V curve of a DMFC. This slope, while suggestive of an IR drop, cannot be accounted for by the membrane resistance alone; the membrane should be fully hydrated in a DMFC due to the large proportion of water present in the fuel feed. Therefore, its area resistance (calculated from its resistivity as measured with ac impedance) would have a value of around  $0.1 \Omega \text{ cm}^2$ , as is typically measured using the current interruption method. Likewise, a large contribution to internal resistance due to electrode manufacture can be ruled out, as similarly made (in this laboratory)  $\text{H}_2/\text{O}_2$  cells have exhibited a much reduced slope.

An essential condition for the successful operation of a DMFC is the use of a pressurised oxygen or air supply to the cathode. Such cells are typically run with oxygen at 1

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to 5 bar above atmospheric pressure. Another important factor is the concentration of methanol in the water–methanol mixture fed to the anode. At concentrations higher than around 2 M, the cell voltage declines significantly due to poisoning of the cathode electrocatalyst by methanol that has permeated through the Nafion® membrane.

We have measured permeation rates of water and methanol using a membrane–electrode assembly (MEA) and membrane alone, installed in a small-scale (2 cm<sup>2</sup> exposed area) cell assembly under typical DMFC operating conditions. A model was used to account for the effects of gradients in concentration and pressure, and the electro-osmotic drag of permeant molecules. Methanol crossover can explain the steep pseudo-linear slope in the I–V plots, as well as the anomalously large effect of oxygen overpressure on cell performance.

## 2. Experimental

MEAs studied in this work were made in the following manner (Fig. 1): 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<sup>-2</sup> metal loading) dispersed on carbon (ketjen) and bound with 10 wt.% Nafion®, was spread on this diffusion backing layer. The cathode was constructed similarly, using a diffusion layer bound with 15 wt.% PTFE, and 1 mg cm<sup>-2</sup> Pt black (Aldrich) with 10 wt.% Nafion® as the catalyst layer. The purpose of the uncatalysed layers was primarily to provide a flat surface for the catalyst. The electrodes were placed either side of a Nafion® 117 membrane (Aldrich), which had been previously boiled for 1 h in 5 vol% H<sub>2</sub>O<sub>2</sub> and 1 h in 1 M H<sub>2</sub>SO<sub>4</sub> 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<sup>-2</sup> for 3 min at 135°C. The

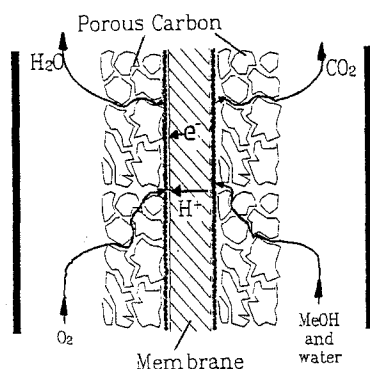


Fig. 1. Schematic diagram of the membrane–electrode assembly.

resulting MEA was installed in the cell after pressing, and hydrated with water circulated over the anode at 96°C for several hours.

Permeate was collected from the cathode outlet in a liquid nitrogen cold trap, typically over periods of 30 to 90 min, and weighed. In the case of the methanol–water mixture, the concentration of methanol in the collected sample was determined by GC (Cambridge AI GC95). Helium was used as the carrier gas to avoid the problem of carrier gas condensation in the cold trap.

The cell itself was not heated, but the fuel feed was preheated in a heater–vaporiser unit under temperature control (Eurotherm 808), and the temperature on the external surface of the graphite flow beds was recorded.

## 3. Performance of the DMFC

The effect of oxygen pressure at the cathode of the cell is shown in Fig. 2. An increase in O<sub>2</sub> pressure increases the potential at open circuit, and the values of potential at all current densities. It also slightly decreases the slope of the voltage–current pseudo-linear region (50–250 mA cm<sup>-2</sup>). At higher current densities increased oxygen pressure also reduces the impact of mass transport limitations.

The theoretical increase in potential for the oxygen reduction reaction at the cathode upon pressurisation of the oxygen supply can be calculated from [3]

$$\Delta E = b \ln \left( \frac{P_2}{P_1} \right) \quad (1)$$

where  $b$  is the Tafel slope (60 mV decade<sup>-1</sup> at 25°C). This equation assumes that electrochemical reaction order is one.

Under the fuel cell operating conditions ( $T = 80^\circ\text{C}$ ), the expected increase in cell voltage when operating at 1 bar overpressure would be around 42 mV. In practice it is found to be approximately 120 mV (Fig. 2). Clearly, kinetics alone cannot explain the effect of the pressure differential. An interesting feature of Fig. 2 is that for a cell operating with oxygen at atmospheric pressure, in the low current density region, the usual sharp drop in potential (around 150 mV) from open circuit is not seen, due to the significantly lower open circuit value. This behaviour can be accounted for by the platinum cathode becoming poisoned with methanol. It thus appears that pressurising the oxygen reduces the crossover of methanol, leading to higher cell voltages.

If methanol crossover is a cause of a reduction in cell voltage it would be expected that a higher concentration of methanol in the feed to the anode would decrease the cell voltage as a result of potentially higher rates of transport through the membrane. This would assume that the higher concentration of methanol does not produce a greater

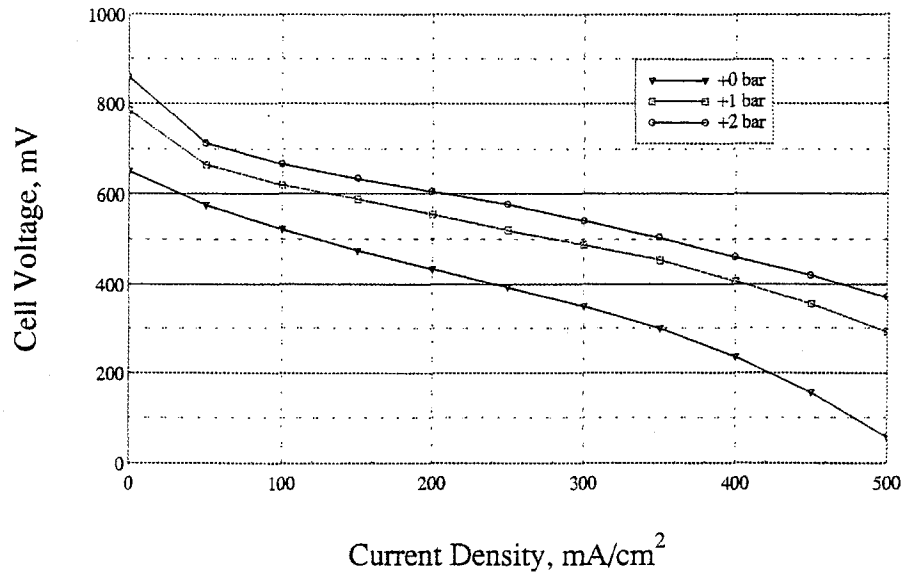


Fig. 2. The effect of oxygen cathode side pressure on the performance of the direct methanol fuel cell. 80°C, 1.0 M methanol.

increase in voltage due to the enhancement of anode potential. Effect of methanol concentration (using concentrations instead of activities) can be predicted from

$$\Delta E = b \ln \left( \frac{c_2}{c_1} \right)$$

Increasing the concentration of methanol in the fuel feed above 1.0 M, to 1.7 M, causes a considerable drop in cell voltage, as can be seen in Figs. 2 and 3. This is despite the fact that cell operation with 1.7 M methanol is at 100°C, where the higher temperature is generally expected to increase cell voltage. This can only be as a result of

increased methanol crossover poisoning the cathode. It is interesting that a relatively low methanol concentration, of 0.22 M, gives a relatively good performance, comparable with that for a 1.0 M concentration at the same oxygen over pressure (1 bar). This will help the future operation of the DMFC when the consumption of the methanol fuel increases during stack operation.

#### 4. Model of methanol permeation

We develop here a relatively simple model of methanol transport through the cation-exchange membranes in

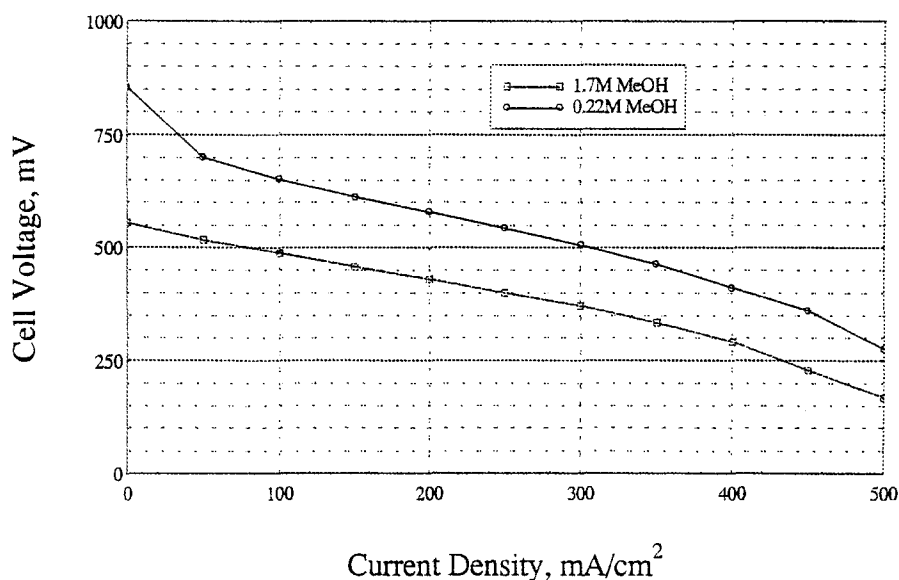


Fig. 3. The effect of methanol concentration on the cell performance. 100°C, 1 bar oxygen pressure.

DMFC membrane electrode assemblies and its effect on cathode overpotential. The model is used as a basis of interpreting the effect of key variables, e.g., oxygen pressure and methanol concentration on cell voltage characteristics of the DMFC.

Permeation of water and/or methanol through a Nafion<sup>®</sup> membrane will take place under the driving forces of concentration ( $\Delta c$ ) and pressure gradients, and electro-osmosis. If we assume Fickian diffusion and a linear concentration gradient through the thickness of the membrane,  $l$ , (i.e., the effective diffusivity,  $D$ , is independent of concentration), then we can write the diffusive component as

$$-\frac{D\Delta c}{l} \tag{2}$$

This flux is counteracted by the pressure differential ( $\Delta P$ ) across the membrane acting on the permeate at the membrane–permeate interface. This effect can be expressed as

$$-\frac{c_2 K}{l} \Delta P \tag{3}$$

where  $K$  is a constant related to the effective hydraulic permeability and  $c_2$  is the concentration of methanol at the cathode side of the membrane.

Therefore, the total flux of permeate through the membrane is given by

$$j = -\frac{D}{l} \Delta c - \frac{c_2 K}{l} \Delta P \tag{4}$$

A third term describing electro-osmotic flux can also be added as described later (Section 4.2).

Assuming that the permeate is entrained in the carrier gas flow at a rate proportional to  $c_2$ , then the flux is proportional to the concentration  $c_2$  and we can write

$$j = kc_2 \tag{5}$$

The constant  $k$  is essentially a mass transfer coefficient for the cathode backing layer and flow channel.

Substituting Eq. (4) for  $c_2$  and rearranging, we obtain

$$j = \frac{1}{a + b\Delta P} \tag{6}$$

where

$$a = \frac{l}{Dc_1} + \frac{1}{kc_1} \tag{7}$$

and

$$b = \frac{K}{kc_1 D} \tag{8}$$

with the  $c_1$  the feed side methanol concentration.

Eq. (6) can now be used to analyse permeation rate data and determine appropriate parameters.

#### 4.1. Permeation data analysis

Figs. 4–6 show permeation rates for water, methanol and a water–methanol mixture through Nafion<sup>®</sup> 117 as a function of helium pressure on the permeate side of the membrane. In all cases the permeation rate decreases as the helium pressure increases. Best fit curves of the form of Eq. (6) were found using Easyplot<sup>®</sup> graph plotting

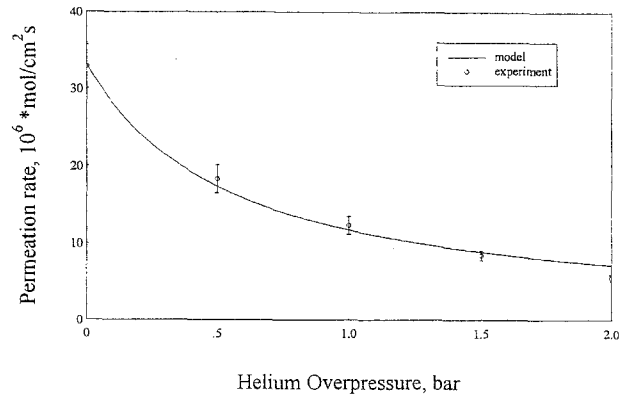


Fig. 4. Permeation rate of water through Nafion<sup>®</sup> 117.96°C.

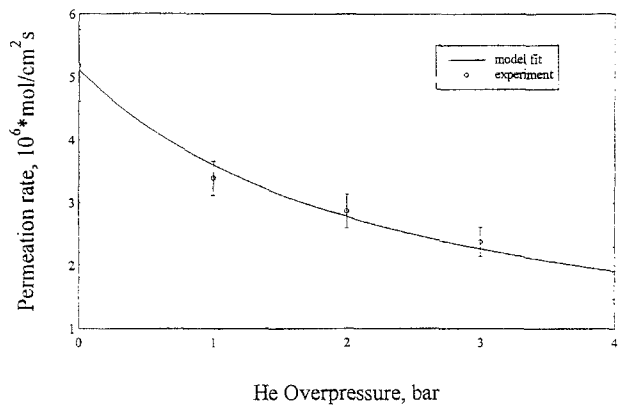


Fig. 5. Permeation rate of methanol through Nafion<sup>®</sup> 117.70°C.

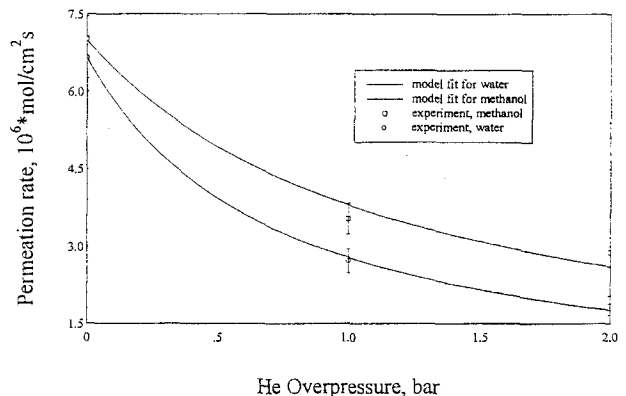


Fig. 6. Permeation rate of methanol and water through Nafion<sup>®</sup> 117 from a 50% by volume mixture. 81°C.

software. Using the values of  $a$  and  $b$  thus obtained allows the calculation of  $k$  and  $K$ .

The values of  $c_1$  can be calculated from the values for the maximum number of water or methanol molecules absorbed by the membrane per sulphonate group (21 for water, 24 for methanol), equivalent weight of the polymer (1100) and dry density ( $2.0 \text{ g cm}^{-3}$ ), and the amount by which the polymer swells (40% in volume). The diffusion coefficient of water in Nafion<sup>®</sup> at 30°C is given by Zawodzinski and Springer [4] as  $7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . Using the temperature dependence given by Springer et al. [5], we can calculate the diffusion coefficient as

$$D_{\text{m,H}_2\text{O}} = 7.3 \times 10^{-6} \times \exp\left\{2436\left(\frac{1}{303} - \frac{1}{273 + T}\right)\right\} \quad (9)$$

For methanol, we can use the same temperature dependence as for water, with the reference value given by Kato et al. [6] for methanol in Nafion<sup>®</sup> 125, multiplied by the volume fraction of solvent in swollen Nafion<sup>®</sup>, to obtain an effective diffusion coefficient,

$$D_{\text{m,MeOH}} = 3.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ at } 50^\circ\text{C}$$

Thus, we can calculate the values of  $k$  and  $K$  as shown in Table 1. These values follow the expected trend, increasing with temperature for a given species (water or methanol).

#### 4.2. Effect of electro-osmosis

It is logical to assume that in a working DMFC, the electro-osmotic flux of water, caused by protons dragging solvating water molecules through the membrane, will be accompanied by an electro-osmotic flux of methanol [7,8]. We can include an electro-osmotic term in Eq. (4) to give an expression for the total flux as,

$$j = -\frac{D}{l}\Delta c - \frac{c_2 K}{l}\Delta P + \frac{\lambda}{nF}I \quad (10)$$

where  $\lambda = \lambda_{\text{MeOH}}$  is the number of moles of methanol per proton transferred by electro-osmosis and  $I$  is the cell current.

Combined Eqs. (5) and (6) and rearranging, we obtain,

$$j = \left(\frac{Dc_1}{l} + \frac{\lambda}{nF}I\right) / \left(1 + \frac{D}{kl} + \frac{K}{kl}\Delta P\right) \quad (11)$$

Eq. (11) is a relatively simple equation which describes the methanol flux through the membrane. To utilise this in predicting cell performance, we need to know what effect the methanol flux has on the cathode performance. A first approximation would be to assume a methanol coverage,  $\theta$ , proportional to the methanol concentration:

$$\theta \propto c_{2,\text{MeOH}} \quad (12)$$

We can then imagine that the methanol-covered fraction of the surface area has a lower free energy for oxygen reduction, so that the effective free energy is,

$$\Delta G_{\text{eff}} = (1 - \theta)\Delta G_{\text{free}} + \theta\Delta G_{\text{poisoned}} \quad (13)$$

Now because the free energy for oxygen reduction has been reduced by the presence of methanol and that this is proportional to the concentration of methanol, then if the methanol concentration is proportional to the rate of supply of methanol, the overpotential produced by methanol crossover is proportional to the flux:

$$\eta_{\text{xover}} = \chi j_{\text{MeOH}} \quad (14)$$

where  $\chi$  is an empirical constant to be determined and  $j_{\text{MeOH}}$  is the flux of methanol that can be calculated from Eq. (11).

This model predicts, then, 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 electro-osmosis of methanol.

By measuring the effect of pressure differential on flux and on overpotential (correcting for kinetic effects), it should be possible to find a value for  $\chi$ , from which it should then be possible to estimate  $\lambda_{\text{MeOH}}$ .

Table 1  
Permeation parameters for Nafion<sup>®</sup> 117

		$T$ (°C)	$D_{\text{m}}$ ( $\text{cm}^2 \text{ s}^{-1}$ )	$c_1$ ( $\mu\text{mol cm}^{-3}$ )	$l$ (cm)
Pure water through Nafion <sup>®</sup>		96	$3.07 \times 10^{-5}$	$2.73 \times 10^4$	0.0206
Water–methanol mix through MEA	58 mol% H <sub>2</sub> O	81	$2.32 \times 10^{-5}$	$1.58 \times 10^4$	0.0206
	42 mol% CH <sub>4</sub> O	81	$1.68 \times 10^{-5}$	$1.27 \times 10^4$	0.0206
Pure methanol through Nafion <sup>®</sup>		70	$1.35 \times 10^{-5}$	$3.03 \times 10^4$	0.0206
$a$ ( $\text{cm}^2 \text{ s}^{-1} \mu\text{mol}^{-1}$ )	$b$ ( $\text{cm}^2 \text{ s}^{-1} \text{ atm}^{-1} \mu\text{mol}^{-1}$ )	$k$ ( $\text{cm s}^{-1}$ )	$K$ ( $\text{cm}^2 \text{ s}^{-1} \text{ atm}^{-1}$ )		
0.0302	0.0551	$6.5 \times 10^{-3}$	$3.0 \times 10^{-4}$		
0.1505	0.2089	$6.7 \times 10^{-4}$	$5.1 \times 10^{-5}$		
0.1430	0.1203	$1.70 \times 10^{-3}$	$4.35 \times 10^{-5}$		
0.1950	0.0826	$2.28 \times 10^{-4}$	$7.71 \times 10^{-6}$		

### 4.3. Calculating the values of $\chi$ and $\lambda_{\text{MeOH}}$

We first need to estimate values of  $k$  and  $K$  at the temperature of interest. For methanol, we have two values of  $k$  and  $K$  (N.B.  $k$  depends on flow rate to some unknown degree) which we assume in the first instance will be exponentially dependant on the temperature, such that,

$$k = k_0 \exp\left(-\frac{B}{T}\right)$$

and similarly for  $K$ . From the values (calculated in the paper), we can estimate

$$k = 2.74 \times 10^{24} \exp\left(-\frac{22187.5}{T}\right)$$

$$K = 1.17 \times 10^{19} \exp\left(-\frac{19098}{T}\right)$$

Values of temperature are in Kelvin. These estimates of should be reasonable for temperatures not too far from the measured values at 70 and 80°C.

We use the data for  $V$  versus  $I$  at three different oxygen over-pressures to obtain the parameters. First, the potential values must be corrected to subtract the effect of pressure on the kinetics of the cathode reaction. The value of this effect is given by  $b \ln(P_2/P_1)$ , where  $b$  is the Tafel slope.

Next, we can take the linear portions of the polarisation curves, and assume that the overpotential, after subtracting the effects of methanol crossover, can be described as a linear function of the current. Then we consider that the major cause of loss in the cell potential after the initial fall due to activation polarisation is due to a cell resistance. Thus, the cell voltage can be written,

$$E = p - qI - \chi j_{\text{MeOH}} \quad (15)$$

where the last term is the overpotentials due to methanol crossover (Eq. (14)).

By plotting  $E$  against  $I$ , we can obtain intercepts and gradients. In fact, by writing the potential as  $E = E_{\text{int}} + E_{\text{grad}} I$ , and comparing with the previous equation, we have

$$E_{\text{int}} = p - \chi X_1$$

$$E_{\text{grad}} = -q - \lambda X_2$$

where  $X_1$  and  $X_2$  are given, respectively by

$$X_1 = \frac{Dc_1}{l\left(1 + \frac{D}{kl} + \frac{K}{kl}\Delta P\right)}$$

and

$$X_2 = \frac{1}{nF\left(1 + \frac{D}{kl} + \frac{K}{kl}\Delta P\right)} \quad (16)$$

as results from Eq. (11).

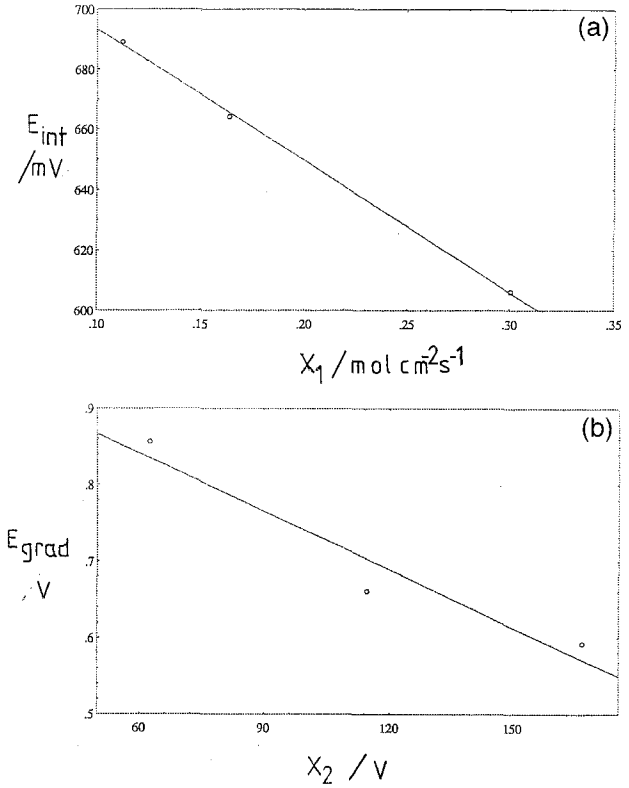


Fig. 7. Correlation of voltage current response data to determine the parameters  $\chi$  (a) and  $\lambda$  (b).

Therefore, by plotting the intercepts and gradients against the values  $X_1$  and  $X_2$  (shown in Fig. 7a,b), we can obtain values of  $\chi$  and  $\lambda_{\text{MeOH}}$ , respectively.

The values thus obtained are,

$$\chi = 3.43 \times 10^5 \text{ V (mol cm}^{-2} \text{ s}^{-1})^{-1}$$

$$\lambda = 0.164 \text{ MeOH/H}^+$$

From the results of the correlation of methanol permeation data and the calculation of the appropriate parameters the simple model which describes the impact of methanol permeation on cell voltage–current response gives quite good agreement with the experimental data, in the current density range of 50 to 300 mA cm<sup>-2</sup>, as shown in Fig. 8. The agreement is not accurate at low and high values of current densities, which is caused by the assumption of linearity between  $E$  and  $I$  in the model.

The final equation which enables cell voltage to be determined will be of the form

$$E = E_{\text{cell}} - \eta_{\text{an}} - \eta_{\text{cat}} - \eta_{\text{cover}} - \eta_{\text{ohmic}} \quad (17)$$

where  $E_{\text{cell}}$  is the difference between the half-cell potentials of the anode and cathode, at the reference current density  $i_0$ , corrected by the thermodynamic effect of temperature according to:

$$E_{\text{cell}} = E_{\text{cell}}^0 + \Delta T \frac{\partial E}{\partial T} - \Delta N \frac{RT}{nF} \ln\left(\frac{P_2}{P_1}\right) \quad (18)$$

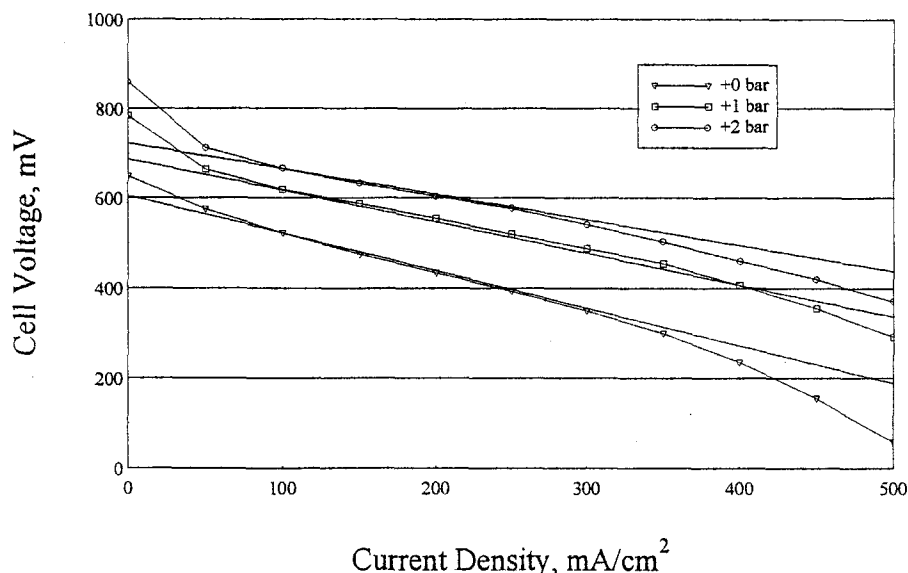


Fig. 8. Comparison of experimental and model performance of the DMFC.

The ohmic overpotential is calculated from the resistance of the membrane, i.e.,

$$\eta_{\text{ohmic}} = Il / \sigma_m \quad (19)$$

where  $\sigma_m$  = membrane conductivity.

Eq. (17) above can be written as

$$E = p^1 - b^1 \ln I - q^1 I - \chi j_{\text{MeOH}} \quad (20)$$

where  $p^1$ ,  $b^1$  and  $q^1$  are constants,  $b^1$  is essentially the sum of slopes of the polarisation curves for anode and cathode.

In principle an improved fit to the data used to determine the values  $\chi$  and  $X$  can be obtained using Eq. (20) rather than Eq. (15). However the overpotentials in the catalysts layers vary with position and  $I$  [9], which in effect means  $b^1$  is not constant. Thus this approach could itself be applied only approximately and does not result in significant improved estimates of  $\chi$  and  $\lambda$ . This is clearly to be expected as the analysis of data has been designed to determine the values of the parameters  $\chi$  and  $\lambda$  which are used to describe the effect of methanol crossover on cathode overpotential.

The model of methanol permeation through the membrane is currently being applied in more sophisticated models of operating DMFCs [9].

## 5. Conclusions

From the measurements of methanol permeation rates through Nafion® cation exchange membranes a simple model of the DMFC has been developed which enables the prediction of the cell voltage characteristics. The model can be extended to incorporate more accurate electrode

kinetics, for example Butler–Volmer and the impact of diffusion mass transport and distributions of potential and concentrations in both the anode and the cathode. To be more generally applied to other systems with perhaps different membranes the appropriate permeation rates would need to be measured. An obvious improvement in the model will come about when the effect of methanol on the cathodic reduction of oxygen is more thoroughly explored. However it is hoped that this work will help to increase interest in the effect of methanol crossover in DMFCs, and that further work will lead to more refined models.

$b$	Tafel slope ( $\text{V decade}^{-1}$ )
$j$	permeation rate ( $\mu\text{mol cm}^{-2} \text{s}^{-1}$ )
$D_{m,i}$	effective diffusion coefficient of $i$ in the membrane ( $\text{cm}^2 \text{s}^{-1}$ )
$c$	concentration ( $\mu\text{mol cm}^{-3}$ )
$c_1$	concentration at feed–membrane interface ( $\mu\text{mol cm}^{-3}$ )
$c_2$	concentration at permeate–membrane interface ( $\mu\text{mol cm}^{-3}$ )
$\Delta c$	$c_2 - c_1$ ( $\mu\text{mol cm}^{-3}$ )
$E$	potential (V)
$F$	Faraday constant ( $9.6488 \times 10^{-2} \text{ C } \mu\text{mol}^{-1}$ )
$l$	membrane thickness (cm)
$P$	pressure (bar)
$k$	rate of permeate removal ( $\text{cm s}^{-1}$ )
$K$	constant related to effective hydraulic permeability ( $\text{cm}^2 \text{s}^{-1} \text{atm}^{-1}$ )
$T$	temperature (K)
$\theta$	methanol coverage
$\eta$	overpotential (V)
$\chi$	constant used to define methanol crossover overpotential
$\lambda$	electro-osmotic drag coefficient

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