

Estimation of the membrane methanol diffusion coefficient from open circuit voltage measurements in a direct methanol fuel cell

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Abstract

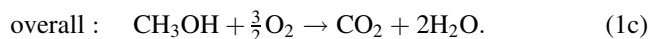
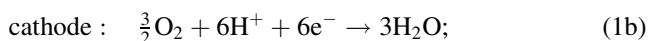
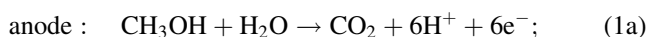
Direct methanol fuel cells (DMFCs) are attractive for several applications, however, at present, methanol crossover from the anode to the cathode appears to be a major limitation. For this reason, as one of the alternatives, membrane technology tries to obtain new methanol-impermeable polymer electrolytes. In this sense, it would be interesting to develop easy methods to check the new materials in relation to the methanol transport. In this work, a simple model is presented which permits to estimate easily the methanol diffusion coefficient of the membrane of a DMFC from open circuit voltage (OCV) measurements. The model has been checked in a DMFC using Nafion membranes as electrolyte. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Direct methanol fuel cell (DMFC); Methanol crossover; Cation exchange membrane; Open circuit voltage

1. Introduction

A fuel cell is an electrochemical engine which can convert the free energy change of a chemical reaction directly into electrical energy, analogously to the combustion process which occurs in a heat engine, but in a fuel cell this can take place at much lower temperatures and reduced polluting emissions. For this reason, the fuel cells are expected to fill an important role in the replacement of the internal combustion engines. Among the variety of types of fuel cells under development, the direct methanol fuel cells (DMFCs) using polymer electrolyte membranes are promising candidates for the application of portable power sources, electric vehicle and transport applications, because they do not require any fuel processing equipment, which simplifies the design and operation conditions and because they can be operated at low temperatures of 60–130 °C.

In a DMFC, methanol is oxidised to carbon dioxide at the anode and oxygen is reduced to water at the cathode according to the following reaction scheme:



A polymer electrolyte membrane separates the anode and the cathode compartments. The protons produced in the anode reaction (1a), are transported via migration to the cathode catalyst layer where they are consumed for oxygen reduction (1b). The electrons move to a current collector adjacent to the anode catalyst layer and are transported to the cathode layer through the external circuit.

One of the major chemical problems is the transport of methanol from the anode to the cathode through the membrane, usually known as methanol crossover, due to the high diffusivity of methanol in the typical perfluorosulphonate membranes used [1,2]. This crossover causes depolarisation losses at the cathode and conversion losses in lost fuel [3]. For this reason, one of the alternatives to try to solve this problem is the membrane technology trying to obtain new methanol-impermeable polymer electrolytes [4–6]. In this sense, it would be interesting to have simple methods to check the new materials from the point of view of the methanol transfer.

In this paper, a simple model is presented to try to estimate easily the impact of the methanol crossover on the open circuit voltage (OCV) of a methanol fuel cell by studying the influence of the cathode pressure. From this model, the diffusion coefficient of the membrane can be estimated from the OCV measurements. The model has been checked in a DMFC using Nafion membranes as electrolyte.

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2. Theory

The overall cell voltage for a DMFC can be written as

$$V_{\text{cell}} = E_{\text{cell}} - \eta_{\text{an}} - \eta_{\text{cat}} - \eta_{\text{ohmic}} - \eta_{\text{xover}} \quad (2)$$

where E_{cell} is the difference between the half-cell potentials of the anode and cathode. At the reference, current density i_0 , η_{an} and η_{cat} are the anode and cathode overpotentials, respectively, η_{ohmic} the overpotential due to the ohmic drop in the system and η_{xover} is the overpotential due to de methanol crossover through the membrane. Eq. (2) does not take into account the mass transport limitation at the electrocatalyst surfaces, which would produce an additional mass transport overpotential due to limitations in diffusion rate through the porous electrode structures.

In the absence of applied current, the overpotential due to the ohmic drop and the anode and cathode overpotentials does not exist, and Eq. (2) is reduced to the OCV:

$$(V_{\text{cell}})_{I=0} = \text{OCV} = E_{\text{cell}} - \eta_{\text{xover}}. \quad (3)$$

Let suppose that the cell temperature is constant and uniform in the DMFC. The corresponding corrections by the thermodynamic effect of increasing pressure from a value P_1 to a value P_2 for the E_{cell} will be [7]

$$E_{\text{cell}} = E_{\text{cell}}^0 - \Delta N \frac{RT}{nF} \ln \left(\frac{P_2}{P_1} \right) \quad (4)$$

where ΔN is the change of the mole number, n the number of electrons involved in the reaction, and E_{cell}^0 is the cell voltage at pressure P_1 and temperature T .

At the atmospheric pressure, the influence of the temperature on the value of E_{cell} is given by [7]

$$E_{\text{cell}}^0 = (E_{\text{cell}}^0)^0 + \Delta T \left(\frac{\partial E}{\partial T} \right)_P \quad (5)$$

where $(E_{\text{cell}}^0)^0 = 1.213$ V is the standard potential for reaction (1c).

considered, the flux of the methanol through the membrane will take place under the driving forces of concentration and pressure gradients. If we assume Fickian diffusion and a linear concentration gradient through the membrane of thickness δ_{mem} , the methanol flux can be expressed as

$$J_{\text{MeOH}} = -\frac{D_{\text{mem}}}{\delta_{\text{mem}}} (C_2 - C_1) - C_2 \frac{K_{\text{mem}}}{\delta_{\text{mem}}} (P_2 - P_1) \quad (7)$$

where D_{mem} is the effective methanol diffusivity of the membrane, K_{mem} the constant related to the effective hydraulic permeability, C_1 (P_1) and C_2 (P_2) are the concentration (pressure) in the anode and cathode sides of the membrane, respectively.

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

$$J_{\text{MeOH}} = kC_2 \quad (8)$$

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

Eq. (7) expresses the flux of methanol as a function of the pressure difference and the concentration of methanol on both sides of the membrane. Really, in an operating DMFC, the methanol concentration in the anode side of the membrane is, in general, different than the methanol feed concentration (C^*) due to the methanol diffusion process in the anode structure electrode. Thus, C_1 will be unknown in general and it would be better to express J_{MeOH} as a function of C^* .

The flux of methanol across the electrode structure is given by

$$J_{\text{MeOH}} = \frac{D_{\text{el}}}{\delta_{\text{el}}} (C^* - C_1) \quad (9)$$

where δ_{el} and D_{el} are the thickness and the diffusion coefficients of the anode electrode.

Taking into account that, when the steady-state is reached, the flux of methanol through the electrode structure and the one through the membrane are the same, from Eqs. (7) to (9), the methanol flux can be expressed as

$$J_{\text{MeOH}} = \frac{(D_{\text{mem}}/\delta_{\text{mem}})C^*}{1 + (D_{\text{mem}}\delta_{\text{el}}/D_{\text{el}}\delta_{\text{mem}}) + (D_{\text{mem}}/\delta_{\text{mem}}k) + (K_{\text{mem}}/k\delta_{\text{mem}})\Delta P} \quad (10)$$

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 [8], then

$$\eta_{\text{xover}} = \chi(J_{\text{MeOH}}) \quad (6)$$

where χ is an empirical constant to be determined and J_{MeOH} is the methanol flux through the membrane. In the DMFC

which expresses the methanol transfer through the membrane as a function of the difference of pressure between the cathode and the anode, the methanol feed concentration and the parameters characterising the methanol transport through the membrane.

Supposing that the anode pressure is kept constant at P_1 , and the pressure of the cathode is changed to a value P_2 , from Eqs. (3), (6), (8) and (10), we have

$$\text{OCV} = E_{\text{cell}}^0 - \Delta N \frac{RT}{n_{\text{cat}}F} \ln \left(\frac{P_2}{P_1} \right) - \chi \left[\frac{(D_{\text{mem}}/\delta_{\text{mem}})C^*}{1 + (D_{\text{mem}}\delta_{\text{el}}/D_{\text{el}}\delta_{\text{mem}}) + (D_{\text{mem}}/\delta_{\text{mem}}k) + (K_{\text{mem}}/k\delta_{\text{mem}})(P_2 - P_1)} \right] \quad (11)$$

where ΔN is the change in the number of moles in the cathode reaction and n_{cat} is the number of electrons involved in the cathode reaction.

From Eq. (11), the OCV of the DMFC can be expressed as

$$\text{OCV} = E_{\text{cell}}^0 - D^0 \ln \left(\frac{P_2}{P_1} \right) - \frac{\gamma}{M + G(P_2 - P_1)} \quad (12)$$

where

$$\gamma = \chi \frac{D_{\text{mem}}}{\delta_{\text{mem}}} C^* \quad (13)$$

$$D^0 = \Delta N \frac{RT}{n_{\text{cat}} F} \quad (14)$$

$$M = \frac{D_{\text{mem}} \delta_{\text{el}}}{D_{\text{el}} \delta_{\text{mem}}} + \frac{D_{\text{mem}}}{\delta_{\text{mem}} k} + 1 \quad (15)$$

$$G = \frac{K_{\text{mem}}}{k \delta_{\text{mem}}} \quad (16)$$

Eq. (11) expresses the behaviour of the OCV as a function of the current, the anode feed methanol concentration, and the pressure difference between both sides of the membrane, as well as the geometric parameters of the membrane and the electrodes and the properties of methanol transfer.

If it is considered that due to the methanol oxidation in the cathode the concentration of methanol in the cathode catalyst is very small [9], when any current is applied and there is no electroosmotic contribution to the methanol crossover, we can use the approximation $C_1 - C_2 \sim C_1$ in the methanol diffusion process across the membrane, and

$$M \sim 1 + \left(\frac{D_{\text{mem}} \delta_{\text{el}}}{D_{\text{el}} \delta_{\text{mem}}} \right) \quad (17)$$

3. Experimental

Electrodes for the membrane electrode assemblies (MEAs) studied in this work were commercial E-TEK electrodes. The anode electrode was an ELAT/VHL/DS/VS Doubled sided Version 2-ELAT electrode (Pt–Ru)Ox Power (1:1 a/o) with 5.0 mg/cm² (Pt–Ru)Ox loading. The cathode electrode was an EFCG Electrode on TGPH-120 toray Carbon paper, with 2.0 mg/cm² Pt Black loading. The electrodes were placed either side of a Nafion[®] 115(or 117) membrane (Aldrich), which was previously boiled for 1 h in distilled water. A thin layer of uncatalysed carbon paper was placed either sided of the MEA.

The concentration of methanol in the water–methanol mixture fed to the anode was 5 mol/l and air was used in the cathode side. Methanol solution with pure water was pumped into the anode channel of the cell through the vaporiser controlled at the same temperature as the cell with a flow rate of 56 ml/h and air at 0.350N l/min (l/min under normal conditions) was used as cathode fuel. The temperature of the cell was in all the studied cases 120 °C.

Table 1

Operation conditions of the cell and geometric parameters of the membrane electrode assembly

Cell temperature (K)	393
Methanol concentration (mol/m ³)	5 × 10 ³
Methanol flow rate (ml/h)	56
Air flow rate(l/min)	0.350N
Anode pressure (atm)	1
Anode electrode thickness (m)	3.23 × 10 ^{−4}
Cathode electrode thickness (m)	3.30 × 10 ^{−4}
Membrane thickness (Nafion 115)	1.35 × 10 ^{−4} m
Membrane thickness (m) (Nafion 117)	2.06 × 10 ^{−4}
Membrane active area (m ²)	2.5 × 10 ^{−3}

The active area of the MEA was 25 cm². In Table 1, a summary of the operation conditions and of the known parameters of the system are shown.

4. Results and discussion

The influence of the cathode pressure on the OCV of a DMFC using Nafion membranes has been studied. Figs. 1 and 2 show, for membranes Nafion 115 and 117, respectively, the OCV values obtained at different cathode pressures in the 1–5 atm interval. The anode pressure was always the atmosphere pressure. As can be observed, in all the studied pressure interval, the increase of the cathode pressure increases the OCV of the cell, in agreement with the results obtained by other authors [10,11]. However, a significant change of the increase slope is observed at a pressure around 2 atm, in such a way that the increase slope becomes lower at pressures higher than 2 atm.

In order to check the model presented in Section 2, the values of the OCV obtained as a function of the cathode pressure can be fitted to Eq. (12) by using a three-parameter (γ , M and G) non-linear regression method for the two used membranes. To this purpose, several scientific statistic packages exist to analyse experimental data. The theoretical foundation of these tools can be found in [12,13]. We have used in this work a minimization χ^2 method which permits to estimate the better values of the adjustable parameters γ , M and G and their statistical errors. In Eq. (12), E_{cell}^0 and D^0 can be estimated from Eqs. (5) and (14), respectively. However, it is necessary to take into account the phase diagrams of water [14] to explain the slope change observed in the experimental data. At the cell temperature (120 °C) the water existing in the cathode compartment will be gaseous water at pressures below 2 atm and liquid water from 2 atm. This implies, from reaction (1b), that the value of ΔN will be −1.5 and +1.5 for the liquid and gaseous cases, respectively, and thus, the value of D^0 will be +0.00846 V (−0.00846 V) for the gaseous (liquid) case, and it is not possible to fit the experimental OCV values to Eq. (12) in all the studied pressure interval. For this reason, the values of the OCV obtained in the 1–2 atm and in the 2–4 atm intervals, where

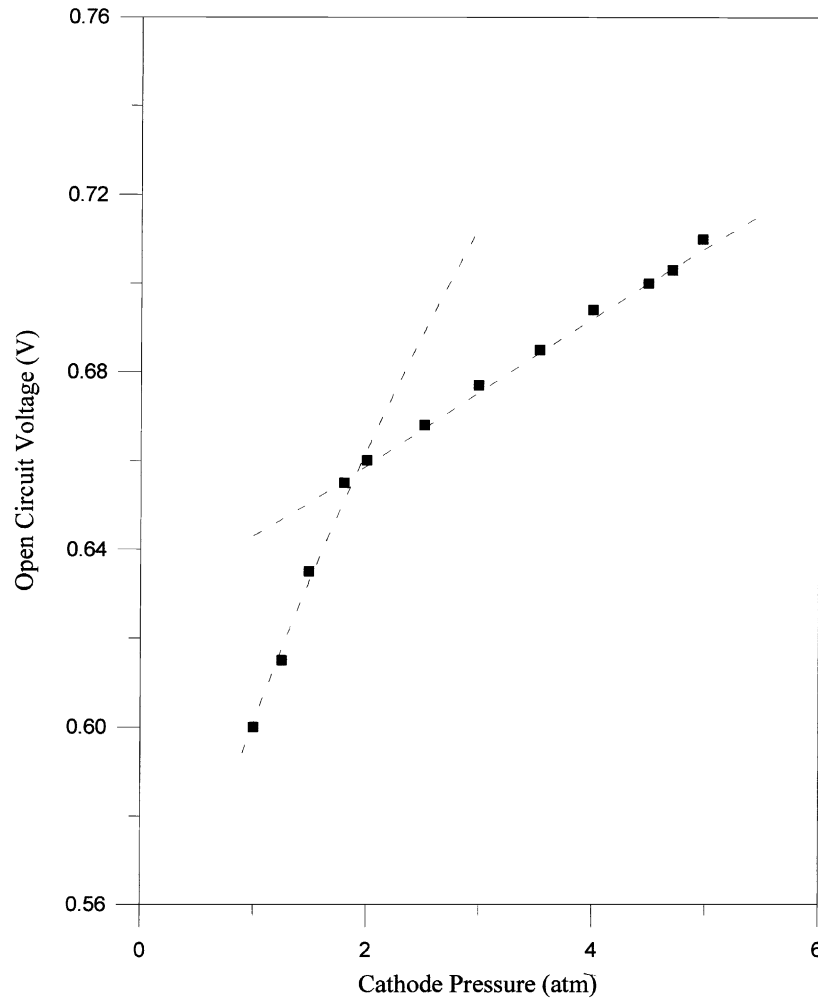


Fig. 1. OCV versus cathode pressure for Nafion 115 membrane. The dotted lines correspond to Eq. (12).

the value of D^0 is a constant, have been separately fitted to Eq. (12) by using a non-linear regression method. The values of the adjustable parameters in the two pressure intervals are shown in Table 2. The theoretical lines are shown in Figs. 1 and 2 for membranes Nafion 115 and 117, respectively, together with the experimental points in the two pressure intervals. As can be observed, the fits can be considered satisfactory in the corresponding indicated pressure intervals.

For the two membranes, as can be observed in Table 2, the values of parameters M and γ obtained in the two pressure intervals are, within the experimental errors, similar. Only a significant difference was observed in parameter G , which is one higher order of magnitude in the (1–2) atm pressure interval, where the water in the cathode is in vapour phase. It may be due to the fact that transfer coefficient depends on the nature gas or liquid of the water in the cathode.

If we suppose, the diffusion of methanol in the catalyst layer is given by [15,16]

$$D_{el} = 2.8 \times 10^{-5} \exp \left[2436 \left(\frac{1}{353} - \frac{1}{T} \right) \right] \quad (18)$$

at 120 °C, the value estimated for the diffusion coefficient of the cathode electrode is $5.7 \times 10^{-5} \text{ cm}^2/\text{s}$. If the thicknesses of the anode electrode and the membrane are known, using these values and the value obtained for parameter M , it is possible to estimate the methanol diffusion coefficient of the membrane from Eq. (17). The obtained values are shown in Table 2 for Nafion 115 and 117. These values are in agreement with the data found in the literature for the diffusion coefficient of this kind of membranes [1,2,8] and, as can be expected, it is lower for the membrane of higher thickness. From Eq. (13) it is also possible to estimate the value of χ . The obtained values are also shown in Table 2. As can be observed, the values are in agreement with the results obtained in the literature for similar systems [8].

In order to study, the influence of the cell operating on the diffusion coefficient of a Nafion 115 membrane sample, the OCV values were measured at different cathode pressures after a time of operating of the cell in three times. The results are shown in Fig. 3. As can be observed, the OCV values decrease when the time of operation increases, which indicates a loss of the fuel cell performance. Moreover, the

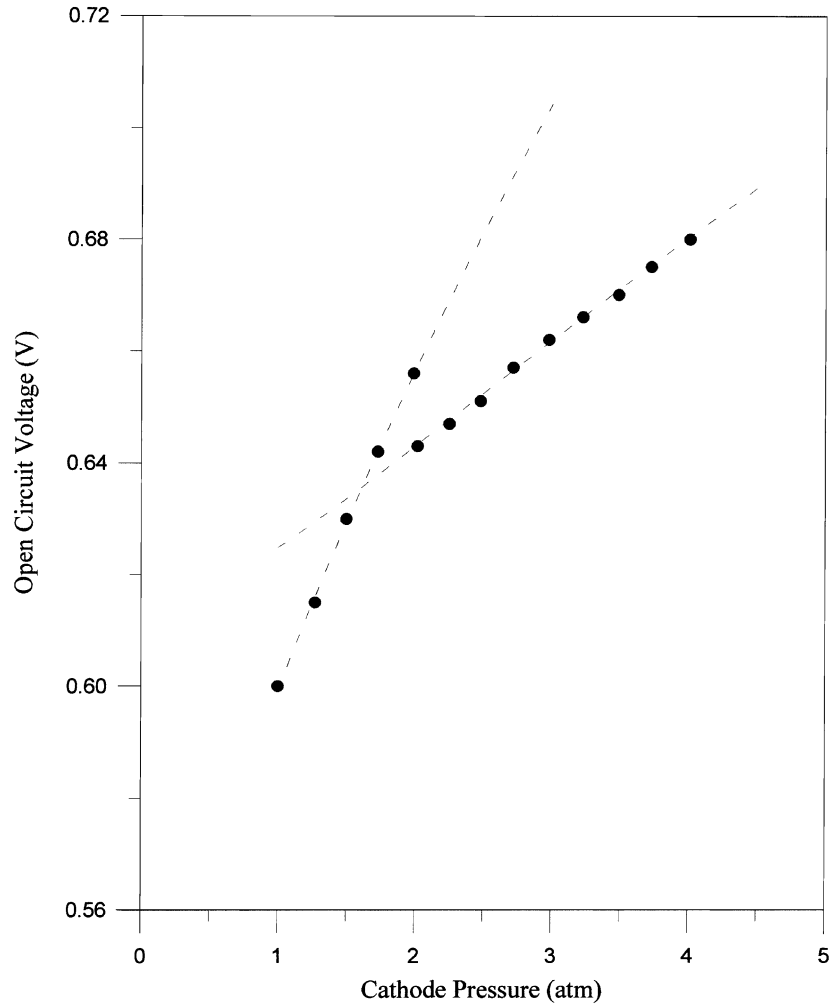


Fig. 2. OCV versus cathode pressure for Nafion 117 membrane. The dotted lines correspond to Eq. (12).

influence of the time of operation seems lower at higher cathode pressure.

By following the same procedure previously described, the value of the different adjustable parameters were estimated from Eq. (12) in the 2–5 atm pressure interval, as well as the values of D_{mem} and χ from Eqs. (13) and (17), in order to analyse the cause of the decrease. They are shown in Table 3. In Fig. 3, the theoretical lines are shown together

with the experimental points. As can be observed, the agreement can be considered satisfactory.

The obtained results show that an increase of the methanol diffusion coefficient of the membrane, as well as a decrease on parameter G occurs after a time of using of the DMFC. This may be due to the time of operating of the cell cause a damage in the membrane, which becomes less impermeable to the methanol transfer.

Table 2

Values of the different adjustable parameters for membranes Nafion 115 and 117 in the two pressure intervals

Parameter	Nafion 115		Nafion 117	
	$P_2 < 2$ atm	$P_2 > 2$ atm	$P_2 < 2$ atm	$P_2 > 2$ atm
γ (V)	1.26 (± 0.24)	1.20 (± 0.06)	1.01 (± 0.04)	1.00 (± 0.02)
M	1.77 (± 0.30)	1.79 (± 0.08)	1.43 (± 0.06)	1.45 (± 0.03)
G (atm^{-1})	0.15 (± 0.03)	0.060 (± 0.003)	0.109 (± 0.005)	0.052 (± 0.001)
D_{mem} (10^{-9} m ² /s)	1.83	1.88	1.56	1.63
χ (V m ² /mol)	18	17	27	25
K_{mem}/k (10^{-5} m/atm)	2.1	0.8	2.2	1.1

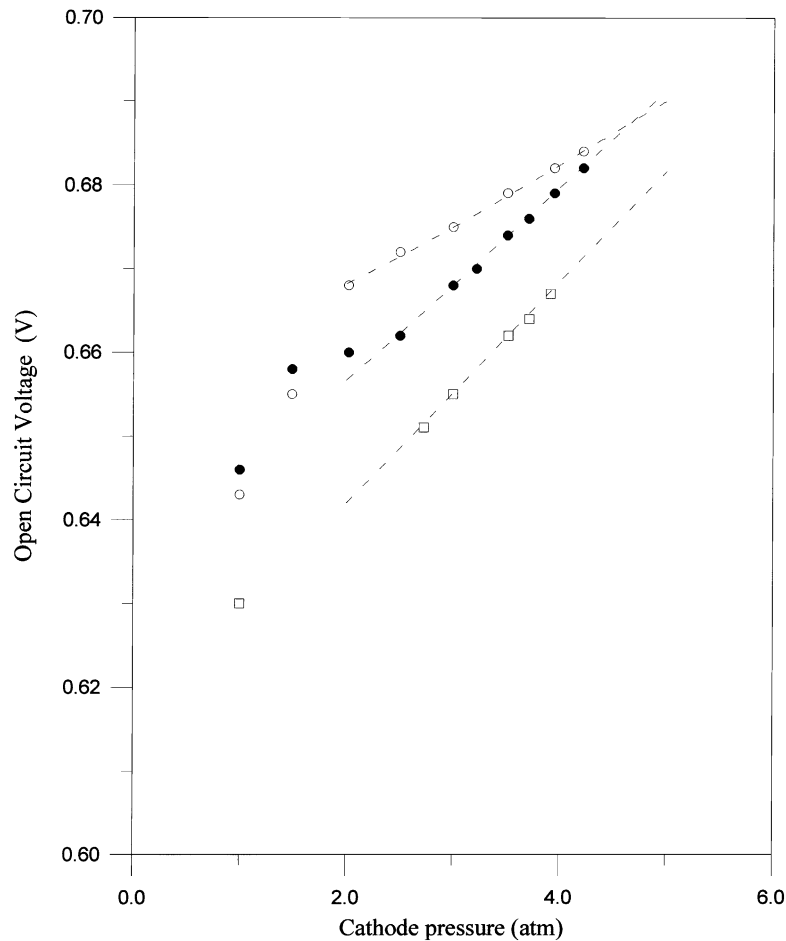


Fig. 3. OCV as a function of the cathode pressure for Nafion 115 membrane at different DMFC operation times. The dotted lines correspond to Eq. (12); (○) first measurement; (●) second measurement; (□) third measurement.

Table 3

Values of the different adjustable parameters for membrane Nafion 115, in the (2–5) atm pressure interval

Parameter	Nafion 115		
	First measurement	Second measurement	Third measurement
γ (V)	1.22 (± 0.02)	1.23 (± 0.04)	1.21 (± 0.02)
M	1.79 (± 0.03)	1.85 (± 0.06)	1.85 (± 0.03)
G (atm^{-1})	0.047 (± 0.002)	0.044 (± 0.002)	0.031 (± 0.008)
D_{mem} (10^{-9} m ² /s)	1.85	1.99	1.99
χ (V m ² s/mol)	18	17	16
K_{mem}/k (10^{-5} m/atm)	0.63	0.59	0.42

5. Conclusions

The OCVs of a DMFC have been obtained at different cathode pressures. The obtained results show that the increase of the cathode pressure increases the OCV values of the direct fuel cell.

A theoretical model has been developed which incorporates the influence of the methanol crossover based on a combination of diffusion and permeation to explain the

observed behaviour of the OCV versus the cathode pressure. The agreement between the theoretical predictions and the experimental results can be considered satisfactory. From this model the methanol diffusion coefficient of the used membrane can be estimated on an easy way.

The diffusion coefficient for Nafion membranes has been estimated on the order of magnitude of 10^{-5} cm²/s, in agreement with the results obtained by other authors for this kind of membranes.

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