Methanol permeability in perfluorosulfonate proton exchange membranes at elevated temperatures

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A simple electrochemical method for the measurement of the permeability of methanol in proton exchange membranes equilibrated with a supporting liquid electrolyte at elevated temperatures is proposed. Carbon supported platinum working electrodes are placed to both sides of the membrane sample and serve as concentration sensors. Methanol is added to one or both sides of the membrane and the permeability is calculated from the time responses of anodic peak currents on the two working electrodes. Experimental results are given for Nafion® 117 perfluorosulfonate membrane in 2.0 M H_2SO_4 at 60 and 70 °C.

List of symbols

A	geometric area (cm^2)
c	concentration ($mol\,cm^{-3}$)
D	diffusivity ($cm^2\,s^{-1}$)
E	potential vs RHE (V)
ΔE	activation energy ($kJ\,mol^{-1}$)
H	Henry law constant ($atm\,mol^{-1}\,cm^3$)
j	current (mA)
K	rate constant ($cm^3\,s^{-1}$)
K^*	partition coefficient
l	thickness (cm)
N	molecular flux ($mol\,cm^{-2}\,s^{-1}$)
p	pressure (atm)
t	time, (s)
T	temperature (°C)
V	volume (cm^3)
ε	volume fraction
τ	time constant (s)

Superscripts and subscripts

d	diffusion
e	evaporation
i	index, 1: glass cell; 2: sample holder
max	maximum
Me	methanol
ref	reference
w	water
t	total
0	initial double layer charging
1	anodic peak

1. Introduction

There has been renewed interest in the direct oxidation methanol fuel cell (DMFC) concept during the last few years. This has mainly been due to the improvements of the methanol oxidation catalyst performance based on improved fundamental understanding of the basic reaction phenomena on platinum based alloys [1–3]. Furthermore, the use of perfluorosulfonate proton exchange membranes, e.g. Nafion® 117 by DuPont, has made it possible to increase the reaction temperature to 80–110 °C which has lead to considerable improvements as compared to earlier work in sulfuric acid at 60 °C [4–6]. However, perfluorosulfonate membranes are known to be quite permeable to methanol [7, 8] leading to methanol crossover to the oxygen cathode in the DMFC. This crossover causes losses in terms of lost fuel and

cathode depolarization due to a mixed oxygen reduction/methanol oxidation potential at the cathode [9–12]. Despite these setbacks the perfluorosulfonate membranes have been successfully applied to DMFC single cells [5, 6].

Methanol can be supplied to the DMFC anode as a dilute solution in water either in liquid or vapour phase [5, 6]. The liquid feed concept would be highly preferred from an engineering point of view due to a more compact design and simplified thermal and water management in the DMFC stack [5].

Verbrugge [7] has used a radioactive tracer method to measure the methanol diffusivity in Nafion® equilibrated with sulfuric acid at room temperature. The method appears very accurate and may be used for further analysis, but special equipment and radio isotopes are needed to carry out such experiments. Furthermore, Kato *et al.* [13] has reported on permeabilities of different alcohols in Nafion®. However, as they used trimethyl ammonium $(CH_3)_3NH^+$ as the counter ion and the other membrane surface

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was facing a vacuum in their experiments, their work has little relevance to DMFC application. Thus, the permeability of methanol in perfluorosulfonate membranes at practical DMFC operation temperatures is still not well known, leading to some uncertainty of the extent of the crossover flux and its importance to the overall cell energy balance and efficiency [8, 9]. Furthermore, simple methods based on generally available equipment to measure the permeability would be of considerable value in comparing different pretreatment methods for perfluorosulfonate membranes or alternative electrolyte membranes [14] with the presently used materials.

In this paper we present a simple electrochemical method to measure methanol permeability in proton exchange membranes. The method is applied to measure methanol permeability in Nafion® 117 in the temperature range 60–70 °C. The problems associated with the present setup are discussed and an improved setup proposed.

2. Experimental details

The membrane sample was placed into a PTFE sample holder on top of a thermostated Pyrex glass cell with a 2.0 M sulfuric acid supporting electrolyte, see Fig. 1. The liquid volumes were 20 ml in the sample holder and 125 ml in the glass cell. One platinum working electrode serving as a methanol concentration sensor was placed in the sample holder and another in the glass cell. A mercury/mercurous sulfate (MMS) reference electrode and a platinized platinum foil counter electrode were placed in the glass cell. Both volumes of the supporting electrolyte were agitated by magnetic stirrers and purged

continuously with nitrogen. The potentials of the working electrodes were controlled by means of a potentiostat, and a switching relay with a timer was used to switch between the two working electrodes.

Methanol was added to one or both sides of the membrane and the time response of the working electrodes were recorded in a 30 min switch on/switch off sequence. During the switch on sequence the working electrode was continuously cycled at $25\,\mathrm{mV\,s^{-1}}$ between predetermined potential limits in the double layer region of the platinum surface [3, 15] and the peak current in the anodic scan of the voltammogram was taken as a measure of methanol concentration. The potential limits were selected to avoid any contribution of hydrogen desorption or oxygen adsorption to the anodic peak current and in a way that the methanol oxidation peak lay well within the scanning region over the whole concentration range of interest, see Table 1. The scanning rate was selected as a compromise between minimum double layer charging current at zero methanol concentration and maximum number of cycles during the switch on sequence. Finally, the peak currents over the 30 min switching sequence were averaged for further analysis.

Rather low methanol concentrations were used to ensure linear concentration current response, and to minimize the ohmic losses as well as convective methanol transport in electroosmotic water flow [16, 17] through the membrane. For the same reasons, relatively small working electrodes of 4.0 mm in diameter were used. 40 wt % Pt on carbon (XC-72R by E-TEK Inc.) was used as the catalyst material on the working electrodes. PTFE bonded and carbon cloth supported electrodes were fabricated according to [18].

The vertical setup was problematic because some air became trapped below the membrane sample when the sample holder was placed on the top of the glass cell. Very extensive stirring was needed in the glass cell to remove this trapped air and further to prevent the accumulation of CO_2 or H_2 produced at the working and counter electrodes, respectively, under the sample holder during the experiment. The extensive stirring, in turn, caused dissolution of oxygen from the surrounding air to the supporting electrolyte which was clearly seen as asymmetry between the anodic and cathodic scans at zero methanol concentration. Continuous nitrogen bubbling was needed to suppress the oxygen dissolution to acceptable limits.

Nafion® 117 membrane was boiled in dilute H_2O_2, distilled water and 1.0 M sulfuric acid before the experiments [17], and equilibrated for a minimum of
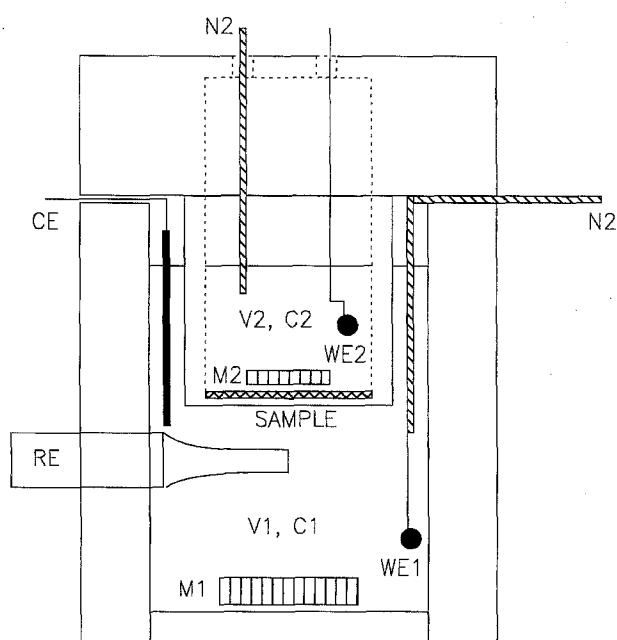

Fig. 1. Experimental setup: (CE) counter electrode, (RE) reference electrode, (WE) working electrode, (M) stirring magnet, (N2) nitrogen inlet, (C) concentration, and (V) volume.

Table 1. Scanning limits for the voltammograms

T /°C	E_{low} /V vs RHE	E_{high} /V vs RHE
60	0.30	0.80
70	0.25	0.75

5 h with distilled water or 2.0 M sulfuric acid for each measurement temperature. The sample diameter was 30 mm.

3. Theoretical analysis of the time response

At low methanol concentration, the balance between methanol concentration and vapour pressure may be assumed to follow Henry's law:

$$p_{Me} = H_{Me} c_{Me} \qquad (1)$$

and therefore the loss of methanol due to evaporation and the nitrogen bubbling is taken to be proportional to the concentration:

$$V_i \frac{dc_i}{dt} = -K_{ei} c_i \qquad (2)$$

where V_i is the liquid volume, c_i is methanol concentration and K_{ei} is an evaporation rate constant in reservoir i (i = 1 for the glass cell and i = 2 for the sample holder). If the diffusion between the reservoirs is discarded, the time response of Equation 2 is

$$c_i(t) = c_{i0} \exp(-t/\tau_{ei}) \qquad (3)$$

where t is the time, c_{i0} initial methanol concentration, and the time constant τ_{ei} is given by

$$\tau_{ei} = \frac{V_i}{K_{ei}} \qquad (4)$$

If both reservoirs are assumed well stirred, the diffusion rate from reservoir 1 to reservoir 2 is

$$N_d = \frac{D_{Me} A_m}{l_m} (c_1 - c_2) \qquad (5)$$

where D_{Me} is the effective (superficial) methanol diffusivity in the membrane, A_m is the cross-sectional membrane area and l_m the thickness of the membrane. According to [7, 16, 17], the effective diffusivity may be calculated from

$$D_{Me} = \left(\frac{\varepsilon_w K_{Me}^*}{\tau_w} \right) D_{Me}^W \qquad (6)$$

where ε_w is the volume fraction of water in a hydrated membrane, K_{Me}^* is a partition coefficient for methanol concentration in bulk water and membrane pore water, τ_w is the tortuosity of the water pores and D_{Me}^W methanol diffusivity in bulk water.

If consumption of methanol by the electrochemical reaction as well as convective transport of methanol in the membrane are assumed small, the coupled differential equations for the time responses of the methanol concentrations in reservoirs 1 and 2 are as follows:

$$V_1 \frac{dc_1}{dt} = -K_{e1} c_1 - \frac{D_{Me} A_m}{l_m} (c_1 - c_2) \qquad (7)$$

$$V_2 \frac{dc_2}{dt} = -K_{e2} c_2 - \frac{D_{Me} A_m}{l_m} (c_2 - c_1) \qquad (8)$$

If $c_1 \gg c_2$ or $c_2 \gg c_1$, Equations 7 and 8 may be approximated by

$$V_i \frac{dc_i}{dt_i} = -\left(K_i + \frac{D_{Me} A_m}{l_m} \right) c_i \qquad (9)$$

at the beginning of the experiment. The time response of Equation 9 is

$$c_i(t) = c_{i0} \exp(-t/\tau_{ti}) \qquad (10)$$

in which the time constant τ_{ti} is

$$\frac{1}{\tau_{ti}} = \frac{1}{\tau_{ei}} + \frac{1}{\tau_{di}} \qquad (11)$$

in which τ_{di} is the time constant due to diffusion and given by

$$\tau_{di} = \frac{V_i l_m}{D_{Me} A_m} \qquad (12)$$

The methanol oxidation reaction taking place on the working electrodes is

$$CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^- \qquad (13)$$

Further details of the multistep reaction are supplied in [1–3]. At low methanol concentration a linear peak current concentration response is assumed:

$$j_i = j_{i0} + j_{i1} \frac{c_i}{c_{ref}} \qquad (14)$$

in which j_{i0} is the double layer charging current measured at zero methanol concentration, and j_{i1} is the peak current measured at the reference concentration of $c_{ref} = 40$ mM. Both j_{i0} and j_{i1} are taken as constants.

Combination of Equation 14 with Equation 3 or Equation 10 gives a time response:

$$j_i(t) = j_{i0} + j_{i1} \frac{c_{i0}}{c_{ref}} \exp(-t/\tau_i) \qquad (15)$$

Here τ_i is τ_{ei} or τ_{ti} depending on the experimental conditions.

Fitting Equation 15 to the experimental data may be used to estimate j_{i1} and τ_{ei} or τ_{ti}. j_{i0} is estimated by fitting

$$j_i = j_{i0} = \text{constant} \qquad (16)$$

to the data measured at zero methanol concentration.

Exact values for D_{Me}, τ_{e1} and τ_{e2} (or K_{e1} and K_{e2}) are found by numerical simulation of Equations 7 and 8 by the following boundary conditions:

$$\begin{cases} c_1(t=0) = c_{10} \\ c_2(t=0) = c_{20} \end{cases} \qquad (17)$$

$$\begin{cases} \left. \dfrac{dc_1}{dt} \right|_{t=t_{max}} = 0 \\ \left. \dfrac{dc_2}{dt} \right|_{t=t_{max}} = 0 \end{cases} \qquad (18)$$

in which $t_{max} = 30$ h, combined with a least squares optimization algorithm for the model parameters. The numerical simulation was performed by Newman's band algorithm [20].

4. Results

4.1. Signal response

The electrode responses as functions of methanol concentration were calibrated by adding the same

methanol concentration to both sides of the membrane sample. The cyclic voltammograms at the end of the first 30 min sequences are shown as functions of the concentration in Fig. 2(a) and (b). The current peaks corresponding to methanol oxidation are clearly visible and observed below the higher potential limit. The peak height can as a first approximation be taken as a linear function of the methanol concentration.

A clear decay of the peak current was observed during the 30 min switch on sequence on both electrodes, see Fig. 3(a) and (b). However, the peaks currents were almost recovered during the switch off sequence. The changes within a switch on sequence were attributed to the consumption of the organic intermediate adsorbed onto the electrode surface during the switch off sequence (fast initial decay) and possibly some surface poisoning (slow decay at the end of the sequence). The changes between the sequences were attributed to methanol diffusion through the membrane, evaporative losses and possible electrode poisoning. The rate of electrochemical conversion of methanol on the working electrodes was very low. Finally, the peak

currents over the switch on sequences were averaged, and the averages were taken as functions of the methanol concentration, see Fig. 3(a) and (b).

The signal level on the two electrodes was different due to differences in the stirring conditions, ohmic resistances and possibly intrinsic electrode activities.

The electrodes were cycled for one 30 min sequence each in the pure supporting electrolyte before each experiment to ensure reproducible electrode surfaces. The voltammograms and j_{i0} as fitted in Equation 16 were well reproduced by the end of the period in these experiments indicating efficient removal of the dissolved oxygen and no permanent poisoning of the electrodes. Therefore, it is also believed that the current decay between the successive 30 min sequences is mainly due to evaporative losses.

The peak currents $j_{i1} c_{i0}/c_{ref}$ were initially calibrated to the methanol concentration in the range $c_{i0} = 0$–60 mM on the two working electrodes at $60\,°C$ by fitting Equation 15 to the first 5 h data of the experiments with the same methanol concentration on both sides of the membrane. A reasonable linearity was achieved in the results shown in Fig. 4.
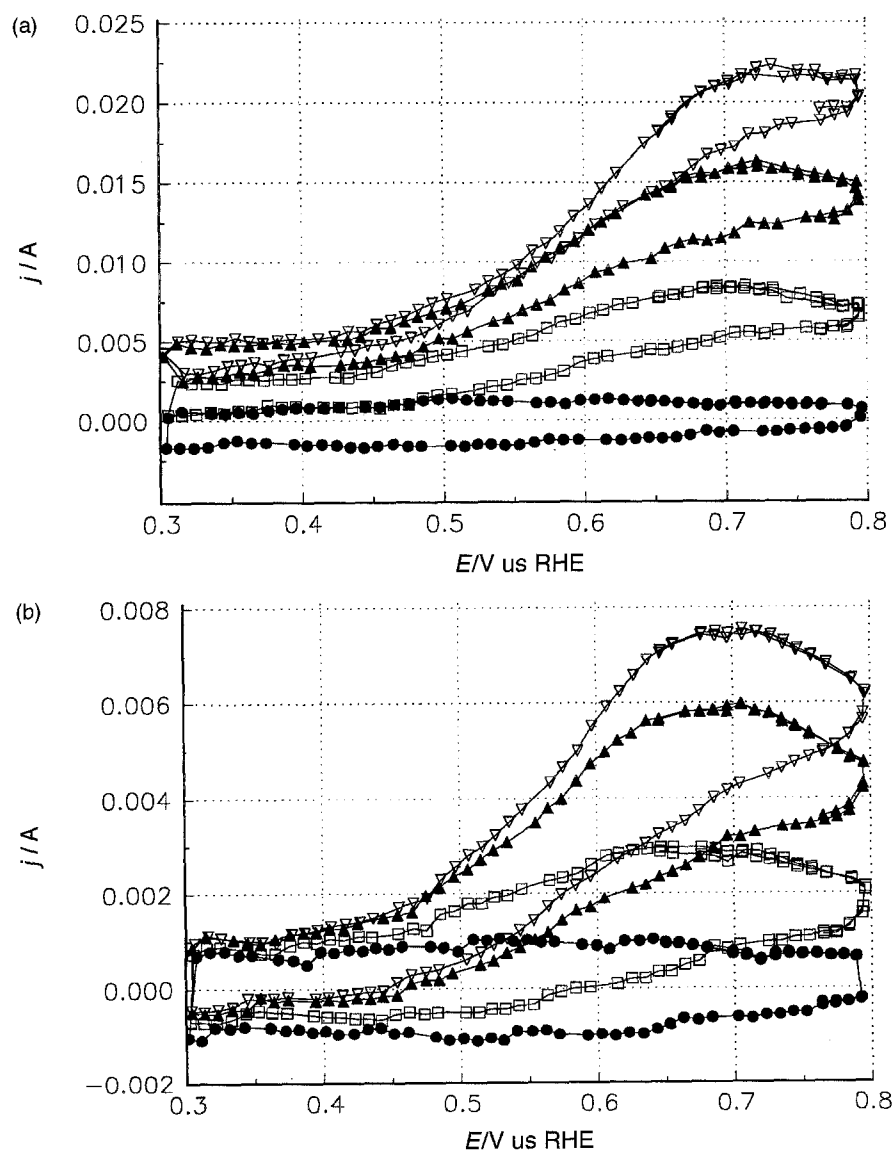

Fig. 2. Cyclic voltammograms on electrode 1 in the glass cell (a) and electrode 2 in the sample holder (b) as functions of methanol concentration recorded at $25\,mV\,s^{-1}$ at $60\,°C$. Concentrations: (●) 0, (□) 20, (▲) 40 and (▽) 60 mM.
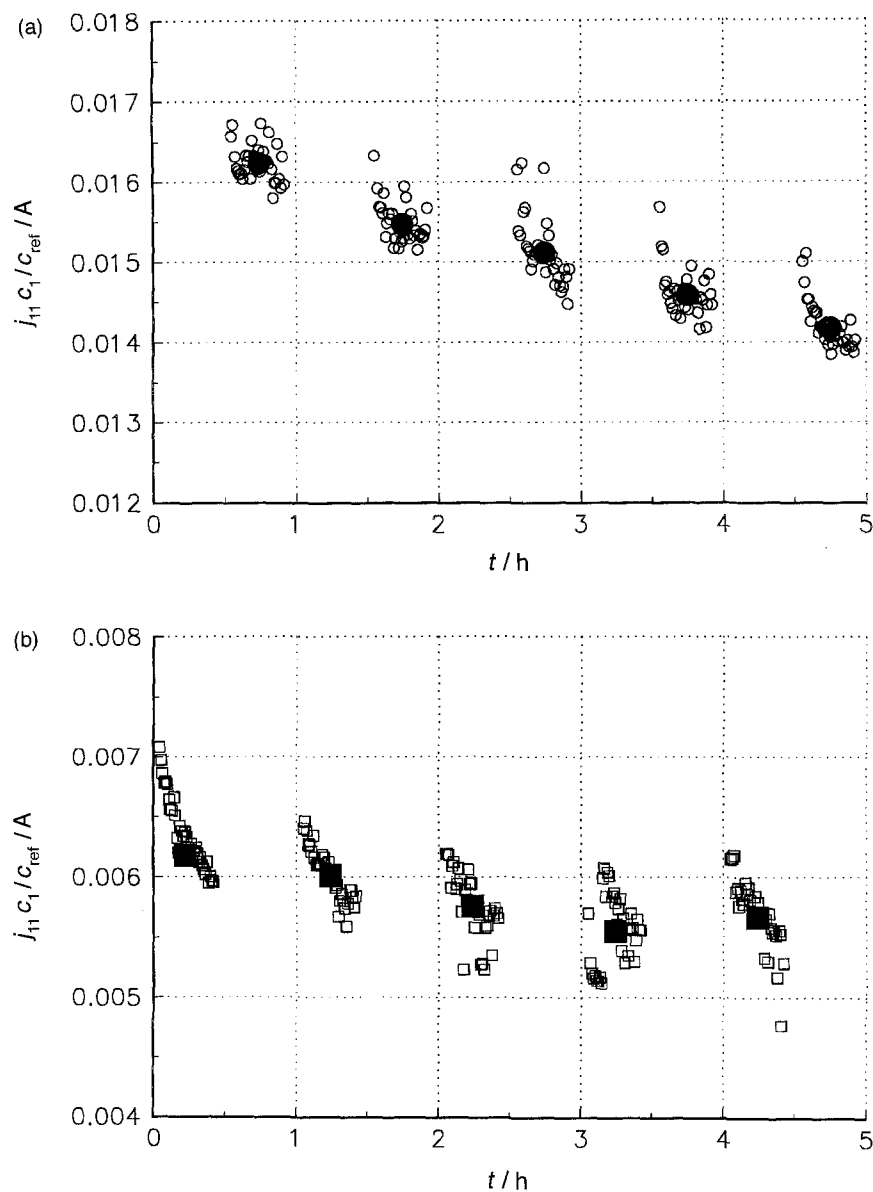
Fig. 3. Anodic peak currents and their averages on electrode 1 in the glass cell (a) and electrode 2 in the sample holder (b) over several 30 min switch on sequences. Key: (a), (O) peak current; (●) average current; (b), (□) peak current; (■) average current.
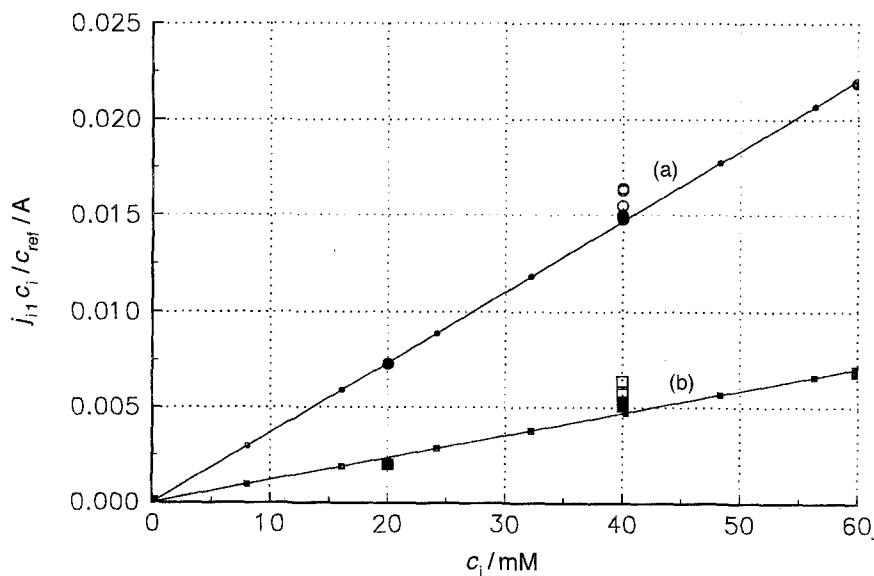

Fig. 4. Averaged peak currents $j_{i1}c_i/c_{ref}$ as functions of methanol concentration on electrodes 1 and 2 at 60 °C (●, ■). The scattering of the least squares optimized values from experiments 1–4 in Table 3 shown as reference (O, □). Key: (●) $j1$; (■) $j2$. Curves: (a) $j = 3.671 \times 10^{-4}c$; (b) $j = 1.175 \times 10^{-4}c$.

Table 2. Initial values for the model parameters

Exp.	T /°C	c_{10} /mM	c_{20} /mM	j_{10} /mA	j_{20} /mA	j_{11} /mA	j_{21} /mA	$10^6 D_{Me}$ /cm² s⁻¹	τ_{e1} /h	τ_{e2} /h
1	60	40	0	1.3	1.0	16.2	4.7	4.0	36	38
2	60	40	0	1.3	1.0	16.1	4.7	4.0	36	38
3	60	0	40	1.3	1.0	14.7	5.7	4.0	36	38
4	60	40	40	1.3	1.0	14.9	5.1	4.0	36	38
5	70	40	0	1.3	1.1	21.3	6.9	4.2	19	24
6	70	0	40	1.3	1.1	22.7	6.1	4.2	19	24
7	70	40	40	1.3	1.1	24.1	7.7	4.2	19	24

4.2. Reproducibility of the experiments and parameter estimation

The double layer charging currents j_{i0} were completely reproducible on both electrodes.

The peak currents j_{i1} were sensitive to stirring and nitrogen bubbling and were not completely reproducible from one experiment to another. However, it is assumed that the stirring and bubbling conditions are reasonably stable and a linear current concentration response is maintained within an individual experiment. Therefore, Equation 15 was always fitted to the first 5 h data of the electrode or electrodes in contact with initial methanol concentration to get an approximate value for j_{i1}. The fit of Fig. 4 was used to estimate j_{i1} on the electrode with zero initial methanol concentration. j_{11} and j_{21} were then taken as variable model parameters in addition to D_{Me}, τ_{e1} and τ_{e2} into the least squares optimization. The scattering of the optimized j_{i1} in different experiments at 60 °C is also shown in Fig. 4.

The scattering of and need for the least squares optimization of the j_{i1} values decreases the reliability and accuracy of the method in the present setup. However, as the measured time responses of the concentration curves were close to the theoretical ones and the model parameters were reproduced reasonably well under the assumption of constant j_{11} and j_{21} within an experiment, it is believed that the method is reliable within given confidence limits.

Initial values for τ_{ei} were estimated by fitting of Equation 15 to the data of the experiment with 40 mM methanol on both sides of the membrane. As τ_1 turned out to be smaller than τ_2, it was concluded that

$$\begin{cases} \tau_{e1} < \tau_1 \\ \tau_{e2} > \tau_2 \end{cases} \tag{19}$$

The differences between τ_i and τ_{ei} is due to methanol diffusion from the sample holder (volume 2) to the glass cell (volume 1).

Initial values for D_{Me} were estimated by fitting of Equation 15 to the first 5 h data of the experiment with 40 mM initial concentration in the sample holder (c_{20} = 40 mM) and no methanol in the glass cell (c_{10} = 0 mM). D_{Me} was then calculated from Equations 10 and 11 using data from [16, 17] for l_m.

The initial values for the model parameters in different experiments at 60 and 70 °C are given in Table 2.

No stable signal was reached during the 30 min switch on sequence at 50 °C. This is believed to be due to combined effects of excessive oxygen dissolution and slow removal of the surface intermediates adsorbed on the working electrode surface during the switch off sequence. No reliable results could be reached at 80 °C either due to excessive evaporation of both methanol and water from the cell.

4.3. Optimized model parameters at 60 and 70 °C

The least squares optimized model parameters in the different experiments at 60 and 70 °C are given in Table 3 and the optimized theoretical curves with experimental data at 60 °C in Figs 5–7. In case of 40 mM initial methanol concentration in the glass cell (c_{10} = 40 mM) and no methanol in the sample holder (c_{20} = 0 mM), a clear minimum is found in the least squares optimization algorithm, see Experiments 1, 2 and 5 in Table 3 and Fig. 5. This type of experiment gives the most reliable values for the model parameters.

For 40 mM in the sample holder (c_{20} = 40 mM) and

Table 3. Least squares optimized model parameters

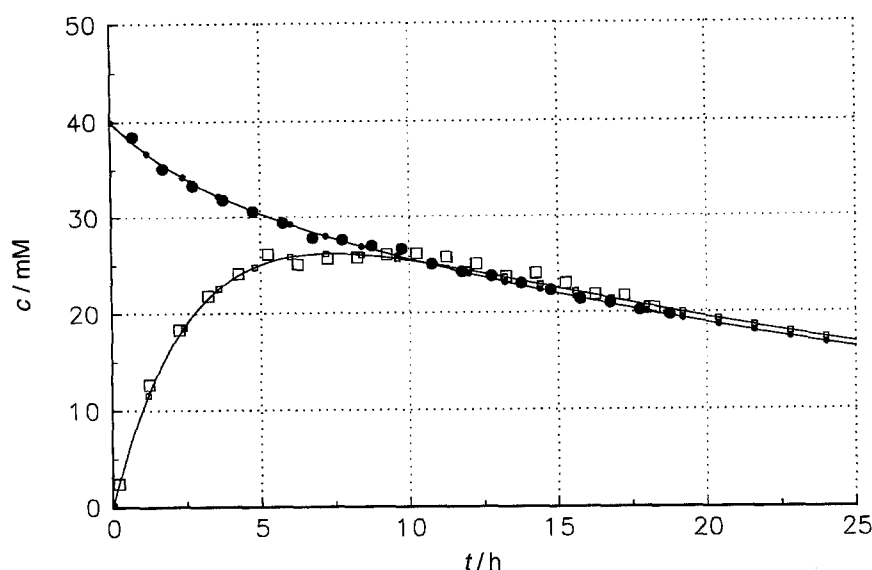| Exp.	T /°C	c_{10} /mM	c_{20} /mM	j_{10} /mA	j_{20} /mA	j_{11} /mA	j_{21} /mA	$10^6 D_{Me}$ /cm² s⁻¹	τ_{e1} /h	τ_{e2} /h
1	60	40	0	1.3	1.0	16.4	6.6	4.9	33	42
2	60	40	0	1.3	1.0	16.3	5.5	5.2	34	39
3a	60	0	40	1.3	1.0	14.8	5.8	4.6	31	55
3b				1.3	1.0	15.5	5.7	4.8	20	50
4	60	40	40	1.3	1.0	14.8	5.1	4.9	35	46
5	70	40	0	1.3	1.1	21.5	7.9	5.5	21	30
6a	70	0	40	1.3	1.1	21.3	6.3	5.5	18	35
6b				1.3	1.1	23.5	6.2	5.6	12	70
7	70	40	40	1.3	1.1	23.6	7.8	5.4	20	31

Fig. 5. Measured and least squares optimized time response of the methanol concentration with the initial methanol concentration in the glass cell ($c_{10} = 40$ mM, $c_{20} = 0$ mM) in Experiment 1 at 60 °C. Key: (●) $c1$; (□) $c2$.

no methanol in the glass cell ($c_{10} = 0$ mM), the convergence of the least squares algorithm is not as good as in the case of the previous type of experiment which is due to the quite fast current decay on electrode 2 in the sample holder and small maximum current on electrode 1 in the glass cell, see Fig. 6. This is because the liquid volume in the sample holder is much smaller than in the glass cell. Two different least squares minima are found: one with low j_{11} and high τ_{e1} (experiments 3a and 6a in Table 3) and another with high j_{11} and low τ_{ei} (experiments 3b and 6b in Table 3) showing that the signal level on electrode 1 is not high enough for accurate distinction between the two. In the former case, the other model parameters are closer to those determined from the other experiments. However, as the time constant τ_{e2} associated with methanol diffusion through the membrane, see Equation 12, is low (approximately 3 h) in comparison with τ_{e2}, the selection between the two minima only has a small effect on the value of D_{Me}.

For 40 mM methanol on both sides of the membrane, the values of τ_{ei} from the other experiments are well reproduced at 60 °C, see Fig. 7. However, the least squares minimum corresponding to the opti-

mum value of D_{Me} is very flat which makes the determination of the diffusivity less reliable than in the first type of experiment.

Comparison of Tables 2 and 3 shows that the optimized values of j_{11} are close to the initial values from fitting of Equation 15. However, use of Fig. 4 only for j_{11} estimation leads to poor accuracy. Fitting of Equation 15 to the first 5 h data of $c_{10} = 0$ mM and $c_{20} = 40$ mM experiments gives too high values for τ_{t2} leading to too low values for D_{Me}. Fitting of Equation 15 to the $c_{10} = 40$ mM and $c_{20} = 40$ mM type of the experiment gives a good estimate for τ_{e1} but somewhat too low a value for τ_{e2}.

The average values of the least squares optimized D_{Me} from Table 3 and a value recalculated from [7] using Equation 12 are shown in the Arrhenius plot:

$$\ln(D_{Me}) = \ln(D_{Me}^0) - \frac{\Delta E}{RT} \qquad (20)$$

of Fig. 8. The fit gives an activation energy of 11.6 kJ mol^{-1}. However, as discontinuities have been observed in the temperature range 40–60 °C in Arrhenius plots for oxygen diffusivity and proton conductivity in Nafion® [21], a wider set of
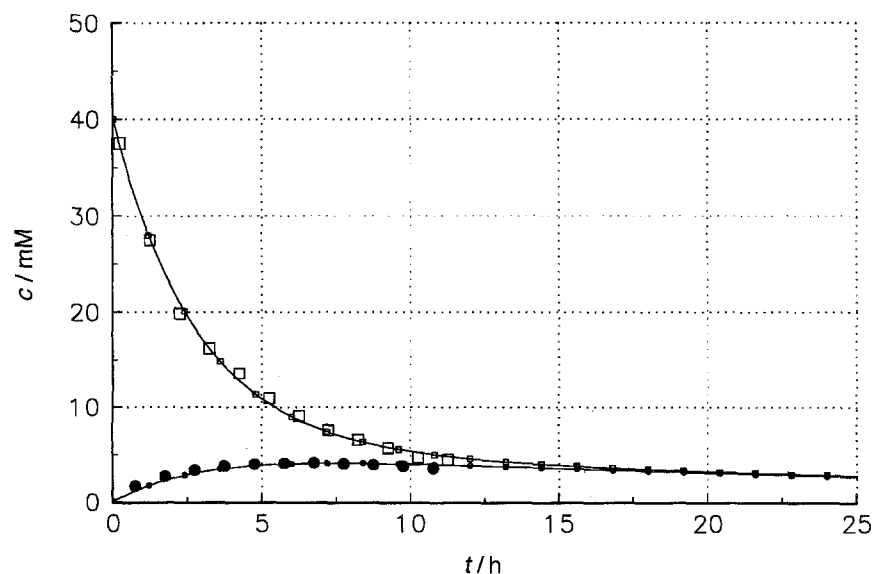

Fig. 6. Measured and least squares optimized time response of the methanol concentration with the initial methanol concentration in the sample holder ($c_{10} = 0$ mM, $c_{20} = 40$ mM) in Experiment 3a at 60 °C. Key: (●) $c1$; (□) $c2$.
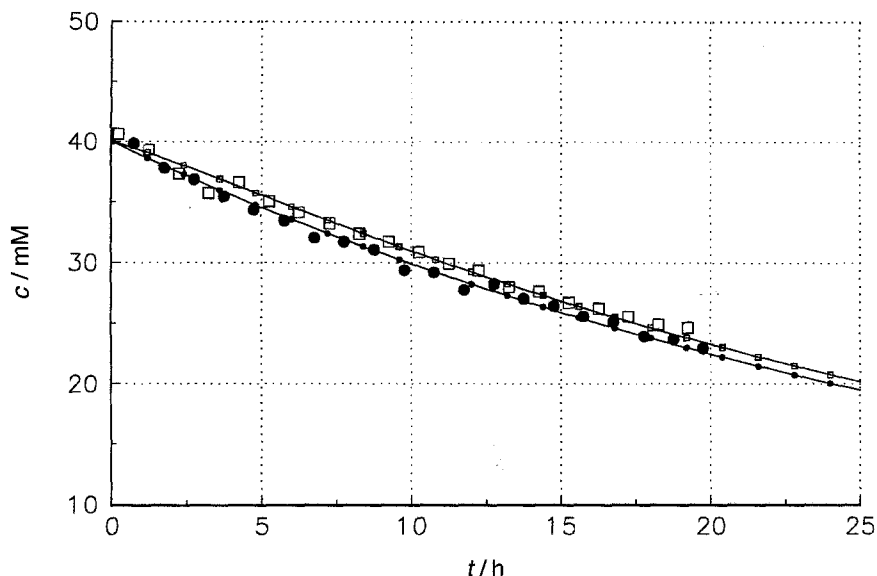
Fig. 7. Measured and least squares optimized time response of the methanol concentration with the initial methanol concentration on both sides of the membrane ($c_{10} = 40$ mM, $c_{20} = 40$ mM) in Experiment 4 at 60 °C. Key: (●) $c1$; (□) $c2$.

experiments should be made for more accurate determination of the activation energy.

Methanol diffusivity in water D_{Me}^{w} could not be calculated from D_{Me} for the temperature dependencies of the partition coefficient K_{Me} and the tortuosity of the water pores τ_w are unknown.

5. Conclusions

Methanol permeability in perfluorosulfonate (or other) proton exchange membranes equilibrated with sulfuric acid (or other supporting electrolyte) can be measured at realistic DMFC operating conditions using the simple electrochemical method presented in this paper. The curve fitting procedure used for the initial value estimation can be used for quick semiquantitative comparison of different membranes and pretreatments. However, numerical simulation is needed for more exact determination of the parameters of the theoretical model used for the permeability assessment.

The accuracy of the measurements performed in the present setup and analysed by the exact simulation method has been ±5% at 60 and 70 °C. At lower and higher temperatures, slow removal of surface intermediates and excessive evaporation from the cell, respectively, limit the use of the present setup. It is believed that the measurement accuracy could be further improved and the temperature range extended if a horizontal setup with equal liquid volumes on both sides of the membrane sample and more reproducible stirring and purging conditions were used.

The superficial diffusivity (or permeability) of methanol, see Equations 6 in Nafion® 117 is $(4.9\pm 0.2) \times 10^{-6}$ cm^2 s^{-1} at 60 °C, and the activation energy is about 12 kJ mol^{-1}.
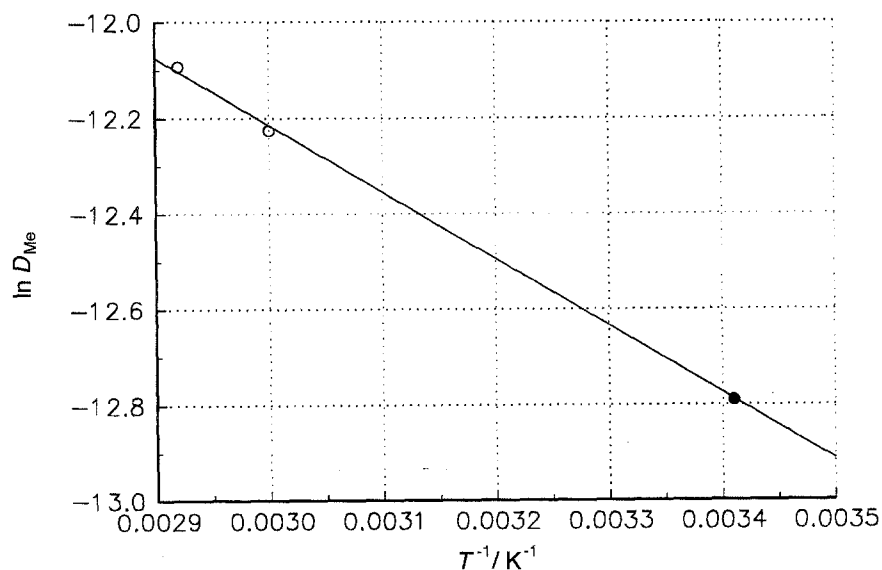
Acknowledgements

Fig. 8. Arrhenius plot for the superficial methanol diffusivity in Nafion® 117. Key: (○) this study; (●) [7]. Curve equation: $\ln D_{Me} = -8.02 - 1398/T$.

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