

Short communication

Estimating the methanol crossover rate of PEM and the efficiency of DMFC via a current transient analysis

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Received 16 April 2006; received in revised form 28 May 2006; accepted 6 June 2006

Available online 1 August 2006

Abstract

This work describes a relatively easy transient method for estimating the methanol crossover rate of proton exchange membrane (PEM) and the efficiency of direct methanol fuel cell (DMFC). The method uses a DMFC that includes an anode and cathode chamber; a PEM arranged between the anode and the cathode, and a small motor fan connected to the DMFC. An aqueous solution of methanol is fed into the anode chamber while the motor fan is operated in a loading state, allowing the methanol to crossover to the cathode. The methanol crossover rate of PEM and the efficiency of DMFC are obtained by the current transient analysis.

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Keywords: DMFC; PEM; Crossover; Fuel cell; Methanol

1. Introduction

Fuel cells are highly efficient devices with very low emissions. These cells represent a potentially renewable fuel source and enable fast and convenient refueling. Direct methanol fuel cells are preferred over other fuel cell configurations as they have many advantages. For example, since the methanol fuel is fed directly into the fuel cell, a chemical pre-processing stage is unnecessary. Therefore, direct methanol fuel cells are typically simple to construct and are appropriate for various applications that require portable power supplies. In these fuel cells, the crossover of a reactant from one electrode to another is undesirable. Reactant crossover generally reduces reactant utilization efficiency and degrades the performance of the fuel cell. In solid polymer electrolyte direct methanol fuel cells, the ion exchange membrane may be permeable to methanol, which therefore contacts the membrane before it participates in the oxidation reaction and can crossover to the cathode side. Diffusion of the methanol fuel from the anode to the cathode reduces the efficiency of fuel utilization and degrades the performance of the fuel cell. Accordingly, a so-called “chemical short” occurs because methanol electro-oxidation proceeds at the same time as

oxygen electro-reduction at the cathode. Essentially, as methanol crosses over, it can be oxidized at the cathode. This reaction is normally incomplete, and usually results in the production of CO. The CO produced, in turn, poisons the existing catalysts, which generally comprise platinum black. Hikita et al. determined the methanol crossover rates by continuously measuring the concentration of CH₃OH, CO and CO₂ in the exhaust gas of the cathode [1]. Verdrugge, using a radioactive tracer method, measured the methanol diffusivity of Nafion® equilibrated with sulfuric acid at room temperature [2]. Kauranen and Skou developed an approach for the measurement of the permeability of methanol in proton exchange membranes equilibrated with a supporting liquid electrolyte at elevated temperatures. The time responses of anodic peak currents on two working electrodes yield estimates of the permeability of a Nafion® 117 perfluorosulfate membrane to ethanol [3]. Narayanan et al. measured the methanol crossover rates by estimating the carbon dioxide content of the cathode exit stream. Crossover rates were reported as an equivalent current density of methanol oxidation [4]. Ramya and Dhathathreyan directly measured methanol flux rates across Nafion® membranes by an electrochemical method using a flooded electrolyte cell with two compartments separated by a membrane, with various concentrations of methanol [5]. Tricoli et al. studied the proton conductivities and methanol crossover rate in two commercially available, partially fluorinated membranes. The methanol crossover rate was monitored by mea-

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asuring the steady state current at the cathode when methanol was introduced into the anode [6]. Methanol crossover from the anode to the cathode through the Nafion[®] PEM detrimentally influences the performance of direct methanol fuel cells. The need to evaluate methanol crossover by an easier and faster method than conventional CO₂ analysis method has become significant. A potentiometric method has been reported by Prakash and co-workers [7], it has been shown that the slope (dE/dt), of E versus t (time) curve, is proportional to the crossover rate. From the time required to reach the equilibrium concentration of CH₃OH on either side of the polymer electrolyte membrane, CH₃OH crossover rate has been calculated. In this work, the methanol crossover rate of PEM and the efficiency of DMFC were estimated by measuring the transient voltage and the current at the DMFC when methanol was introduced into the anode.

2. Mathematical

Before the mathematical analysis, the following terms must be defined.

M_T : total amount of methanol charged (mol); M_O : amount of methanol electro-oxidized (mol); M_C : amount of crossover methanol (mol); E_f : efficiency of DMFC (%); R_C : crossover rate (mol cm⁻² s⁻¹); t : time required for electro-oxidation current to fall from I to zero (s); A : active area of electro-oxidation (cm²); I : current (A); n : number of electrons exchanged; F : Faraday's constant (96480 A s mol⁻¹).

The mathematical expression of the characteristics of a direct methanol fuel cell may be simplified by the equation,

$$(M_T - M_O) - M_T(1 - E_f) - R_C t A = 0 \quad (1)$$

where,

$$E_f(\%) = \frac{M_O}{M_T - M_C} \times 100 \quad (2)$$

$$M_O = \frac{1}{nF} \int I dt \quad (3)$$

In two experiments under identical operating conditions but different charging volumes of methanol solution, Eq. (1) becomes the following simultaneous equations:

$$\begin{aligned} (M_{T1} - M_{O1}) - M_{T1}(1 - E_f) - R_C t_1 A_1 &= 0; \\ (M_{T2} - M_{O2}) - M_{T2}(1 - E_f) - R_C t_2 A_2 &= 0 \end{aligned} \quad (4)$$

Rearranging, we get:

$$M_{T1} E_f - t_1 A_1 R_C = M_{O1}; \quad M_{T2} E_f - t_2 A_2 R_C = M_{O2} \quad (5)$$

The above simultaneous equations can be transformed into matrix form $Ax = b$ where,

$$A = \begin{bmatrix} M_{T1} & -t_1 A_1 \\ M_{T2} & -t_2 A_2 \end{bmatrix}, \quad x = \begin{bmatrix} E_f \\ R_C \end{bmatrix} \quad \text{and} \quad b = \begin{bmatrix} M_{O1} \\ M_{O2} \end{bmatrix}$$

The simultaneous equations can be easily solved by the inverse matrix:

$$x = A^{-1}b \quad (6)$$

The methanol crossover rate of PEM (R_C), and the efficiency of DMFC (E_f), can be easily computed from Eq. (6) using Microsoft Excel[®].

3. Experimental

The methanol crossover rate and the efficiency of direct methanol fuel cell were measured using the experimental system shown in Fig. 1. The method uses a DMFC that includes an anode chamber for the electrochemical oxidation of the methanol, a cathode chamber for the electrochemical reduction of oxygen; a Nafion[®] proton conducting membrane arranged between the anode and the cathode, and a small dc motor fan connected to the DMFC. An aqueous solution of the methanol is fed to the anode chamber while the dc motor fan is operated in a loading state, enabling the methanol to crossover to the cathode, where it is oxidized. The transient voltage and current are measured using a digital-meter and the methanol crossover rate and the efficiency of direct methanol fuel cell (DMFC) are determined from the transient analysis of voltage and current. The membrane electrode assembly (MEA) in this work was made in the following manner [8].

1. The anode comprises a carbon cloth support (0.17 mm × 10 cm × 10 cm) upon which was spread a thin layer of uncatalyzed carbon, bound with 10 wt.% Nafion[®] from a solution of 5 wt.% Nafion[®] dissolved in a mixture of water and lower aliphatic alcohol. The catalyzed layer, consisting of 30 wt.% Pt–Ru (2 mg cm⁻² metal loading) dispersed on carbon and bound with 10 wt.% Nafion[®], was spread on the diffusion backing layer.
2. The cathode was constructed similarly, using a diffusion layer bound with 10 wt.% PTFE and 1 mg cm⁻² Pt black with 10 wt.% Nafion[®] as a catalyst.
3. The electrodes were placed either side of a Nafion[®] 117 membrane (0.18 mm thickness, area 10 cm²), which had already been boiled for 1 h in 5 vol.% H₂O₂ and 1 M H₂SO₄, before washing in pure water for 2 h.
4. The assembly was hot-pressed at 100 kg cm⁻² for 5 min at 135 °C. The resulting MEA was installed in the cell following pressing, and hydrated with water over the anode at 85 °C for several hours.

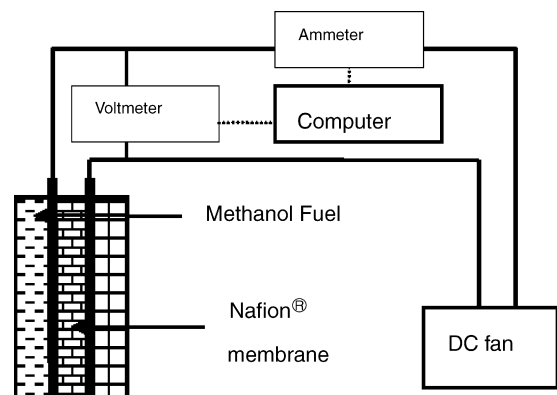


Fig. 1. Block diagram of the experimental set-up.

The fuel chamber (0.5 cm thick with an area of 10 cm²) was filled with 1, 2 and 3 cm³ 10 vol.% aqueous methanol solution, for the first, second and third measurements, respectively. All tests were performed at an ambient temperature of 25 °C and at atmospheric pressure. The voltage and current of the DMFC were monitored for approximately 12 h to ensure a stable approach to zero current.

4. Results and discussion

The open-circuit cell voltages of the DMFC are in the range 0.6–0.7 V, which is much lower than the thermodynamically expected value of approximately 1.23 V. This effect is known to be caused by formation of mixed potentials due to undesired side reactions at both electrodes. The overall cell voltage comprises the open-circuit cell voltage, the overpotentials at anode and cathode and the ohmic loss in the PEM, and is given by

$$E_{\text{cell}} = E_{\text{cell}}^0 - \eta_a + \eta_c - \left(\frac{d^M}{K^M} \right) i_{\text{cell}}$$

where E_{cell} is the overall cell voltage; E_{cell}^0 the standard electrode potential; η_a the overpotential at anode; η_c the overpotential at cathode; d^M the membrane thickness; K^M the membrane conductivity, and i_{cell} is the current density.

Figs. 2 and 3 plot the transient voltage and current of the DMFC, with each measurement performed at a different charging volume (1, 2 and 3 cm³) with a particular fuel solution. The fuel solution is 10 vol.% methanol in water. The cell voltage response after a step change of the methanol feed concentration was performed in the dynamic experiments, reducing the methanol concentration from 10 to 0 vol.%. The observed increase in cell voltage after a sudden decrease in the methanol feed concentration is notable. Fig. 2 demonstrates that the cell voltage (after a certain delay) first rises before falling. The voltage increases as the concentration overpotential (η_a) at the anode decreases because of amounts of proton increasing. However, the quantity of methanol crossing over to the cathode over time, results in a mixed potential, thereby lowering the overall cell voltage, although fairly small.

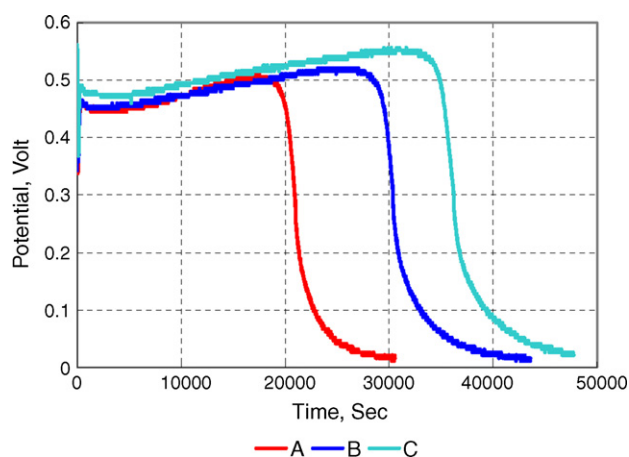


Fig. 2. Voltage transients monitored during electro-oxidation using 10 vol.% methanol solution: (A) 1 cm³, (B) 2 cm³, and (C) 3 cm³.

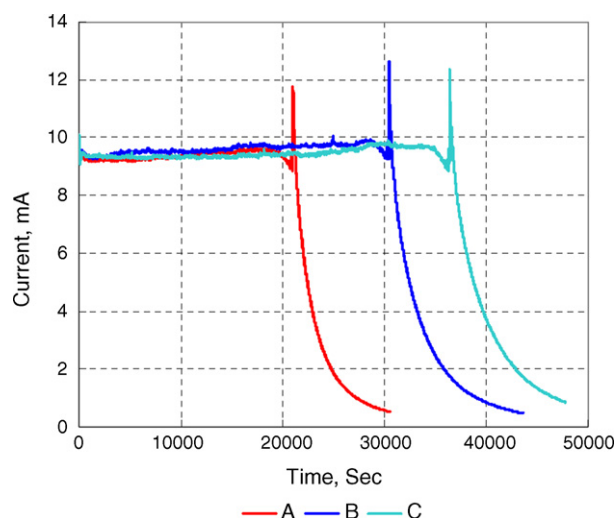


Fig. 3. Current transients monitored during electro-oxidation using 10 vol.% methanol solution: (A) 1 cm³, (B) 2 cm³, and (C) 3 cm³.

The current transient returns to the same shape and magnitude, controlled by the reduction of oxygen in the air-breath cathode. The current peak in Fig. 3 is associated with the stopping of a dc motor fan when methanol is emptied in the fuel solution. The data in Table 1 were used to calculate the crossover rate (R_C) and the efficiency (E_f) at various fuel charging volumes in the three tests. R_C is low at about 34.67 mol cm⁻² h⁻¹ after the second test, and increases with running time to 45.2 mol cm⁻² h⁻¹ after the third test. The efficiency (E_f) is low, at around 24.3% after the second test, and increases with the running time to 26.4% after the third test. The results may reveal the effect of the swelling of PEM on the methanol crossover and the efficiency of DMFC.

Table 1
Parameters and measurements

	Test 1	Test 2	Test 3
Known parameters			
Methanol concentration (vol.%)	10	10	10
Active area, A (cm ²)	1.5	3	4.5
Methanol charged (cm ³)	1	2	3
Methanol charged, M_T (mmol)	2.5	5.1	7.6
Measured parameters			
Electro-oxidized, M_O (mmol)	0.4	0.6	0.7
Time of crossover, t (h)	8.5	12.1	13.3
Analysis results			
Methanol crossover, M_C (mmol)			
Tests 1–2	0.031	0.045	0.049
Tests 1–3	0.038	0.055	0.060
Crossover rate, R_C (mol cm ⁻² h ⁻¹)			
Tests 1–2	3.467E–5	3.467E–5	3.467E–5
Tests 1–3	4.52E–5	4.52E–5	4.52E–5
Efficiency, E_f (%)			
Tests 1–2	24.3	24.3	24.3
Tests 1–3	26.4	26.4	26.4

5. Conclusions

A relatively simple transient method, which does not require fitting analyses, was presented. The proposed method simply yields, in situ, an estimate of the methanol crossover rate of PEM and the efficiency of DMFC; it can be considered to be a useful tool for use in DMFC R&D.

Acknowledgement

The authors are grateful to the National Science Council, Republic of China for their valuable support in the completion of this work (contract no. 94-2212-E-150-031).

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