Short communication

A potentiometric method of monitoring methanol crossover through polymer electrolyte membranes of direct methanol fuel cells

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Abstract

Methanol crossover from the anode to the cathode through the polymer electrolyte membrane (PEM) has been one of the detrimental factors affecting the performance of direct methanol fuel cells (DMFCs). Extensive research work has been in progress for developing CH_3OH crossover tolerant electrolyte membranes. The need for assessing CH_3OH crossover by an easier and faster method than the conventional CO_2 analysis method has become significant. For this, a potentiometric method has been developed and tested using the Nafion membrane. By recording the potential (E) of a PtRu/C electrode in 0.2 M H_2SO_4 supporting electrolyte during CH_3OH crossover, 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 CH_3OH on either side of the polymer electrolyte membrane, CH_3OH crossover rate has been calculated. This method is expected to be useful in studying polymer electrolyte membranes and also in industry as a quality control technique. The method can also be used to sense methanol concentration.

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1. Introduction

Research and development activities on direct methanol fuel cells (DMFCs) have gained importance in recent years because of their potential applications as stationary and portable power sources [1–3]. Methanol crossover is one of the problems that impedes the commercial development of DMFCs [4,5]. This involves transport of CH_3OH through the polymer electrolyte membrane (PEM) from the anode half-cell to the cathode half-cell. The CH_3OH crossover occurs by diffusion as a result of the concentration gradient and also due to electro-osmotic drag. The anode experiences a decreased coulombic efficiency due to the loss of fuel. Additionally, the crossed CH_3OH undergoes oxidation on the cathode at which oxygen reduction alone is intended to occur. As a result, the cathode experiences a mixed potential, thereby resulting in a decreased potential of the cathode reaction. Due to these effects, there is a decrease in the overall cell voltage and in the performance of the fuel cell.

Nafion film is the most widely studied PEM for application in DMFCs. However, the CH_3OH crossover rate through the Nafion is rather high [6]. There have been several studies reported on development of alternate membranes, which are more resistant to methanol crossover, and also less expensive than the Nafion film [6–8]. Attempts to modify the Nafion membrane have also been reported [9]. It is inferred from these reports that the CH_3OH crossover is monitored by measuring the CO_2 concentration in the gaseous products of the cathode. The most commonly used method of CO_2 measurement is by using an optical IR CO_2 sensor [10]. Measurement by precipitation as $BaCO_3$ has also been reported [10,11]. In these methods, it is assumed that the CH_3OH crossed to the cathode is completely oxidized to CO_2, which is unlikely. Furthermore, the crossover of CO_2 from the anode half-cell into the cathode half-cell is ignored [10]. Thus, the measurement of CH_3OH crossover by monitoring CO_2 at the cathode is likely to be inaccurate. Design and operation of a methanol sensor based on the amperometric methods has been reported by Narayanan et al. [12]. All these methods, however, rely on full fuel cell protocols. For faster screening of the electrolyte membranes, it is essential to investigate alternate methods of monitoring CH_3OH crossover.

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In the present study, a new potentiometric method is developed and tested. By monitoring the potential of a PtRu/C electrode, the rate of CH_3OH crossover is calculated. This technique is expected to be useful to assess the resistance of polymer electrolyte membranes for CH_3OH crossover.

2. Experimental

PtRu/C electrodes were prepared using PtRu alloy powder (Alfa Aesar) on a hydrophilic carbon paper. The PtRu catalyst powder (20%) was mixed with 10% Nafion resin (5% solution in a mixture of alcohols and water, Aldrich) and 70% distilled water followed by sonication for about 10 min. A carbon paper (Toray) of 0.17 mm thickness was sectioned to 10 mm × 10 mm size, and the catalyst mix was brushed on it followed by drying in stream of air at ambient temperature. Brushing and drying were repeated thrice to get a catalyst loading of 8 mg cm^{-2}. The coated carbon paper was air-dried for about 24 h. Electrical connection was obtained by a copper wire attached through a conducting silver paint (Alfa Aesar) at the edge of the electrode. The silver paint and copper wire were masked by means of silicone sealant and air-dried for about 24 h before using the electrodes.

The Nafion 117 membrane (Du Pont) of 0.18 mm thickness was treated in hydrogen peroxide, distilled water and dilute H_2SO_4, successively, and stored in dilute H_2SO_4. The membrane of area 12.5 cm^2 was clamped between two glass cells by means of an O-ring joint. Each of the glass cells of about 150 ml capacity had a provision to introduce the PtRu/C electrode, a Pt foil electrode and a Ag/AgCl, KCl (sat.) reference electrode. The potential values are given against this reference electrode. An experiment was started by taking 120 ml of 0.2 M H_2SO_4 solution into each of the cells. The electrolyte was stirred by means of Teflon coated magnetic paddles during the experiment. The potential of the PtRu/C electrode was monitored for about an hour to ensure a stable value. The required volume of CH_3OH was added to one of the cells (cell A) and an equal volume of distilled water to the other cell (cell B) to maintain equal hydrostatic pressure, and also equal concentration of the supporting electrolyte on both sides of the polymer electrolyte membrane. The potential of the PtRu/C electrode in cell B was recorded for a few hours using a Solartron potentiostat/galvanostat model SI 1287. The experiments were carried out at 20 ± 1 °C.

3. Results and discussion

A schematic variation of CH_3OH concentrations in cell A and cell B during crossover is shown in Fig. 1. The concentration (C_A) in cell A decreases and the concentration (C_B) in cell B increases with time till the process of crossover reaches an equilibrium state. At this stage, the concentration of CH_3OH is equal on either side of the polymer electrolyte membrane. Since the volumes of the supporting electrolyte
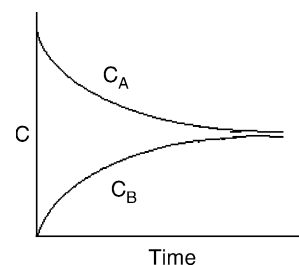

Fig. 1. Schematic time dependent variation of concentrations (C) of CH_3OH in the electrolyte of cell A (concentration: C_A) in which CH_3OH is taken, and in the electrolyte of cell B (concentration: C_B) into which CH_3OH crosses through a polymer electrolyte membrane.

in both cells are equal, the equilibrium concentration is equal to half of the concentration of CH_3OH initially taken in the cell A. The rate (mol cm^{-2} s^{-1}) of CH_3OH crossover is given as:

$$-\frac{dn}{dt} = \left(\frac{v}{1000P}\right)\left(\frac{dC_B}{dt}\right) \tag{1}$$

where n is the number of moles of CH_3OH crossing an area of P (cm^2) at time t (s), v (ml) is the volume of the electrolyte in cell B, and C_B is expressed in mol l^{-1}.

It is known that PtRu/C is the best catalyst known for CH_3OH oxidation [13]. In the absence of CH_3OH, that is, before the crossover starts taking place, the PtRu/C electrode in cell B experiences a mixed potential. The value of the potential is close to 0.50 V in 0.2 M H_2SO_4. After CH_3OH reaches cell B, the electrode senses the CH_3OH and its potential tends to shift. The mechanism of electro-oxidation of CH_3OH is complex in nature because the reaction involves a transfer of six electrons resulting in mixed potential. Formation of several reaction intermediates producing CO_2 as the final product is reported [14]. Nevertheless, it is recognized that a dissociative adsorption of CH_3OH on the electrode surface is considered to be the important step in the mechanism [14]. Accordingly, the following equilibrium is assumed to be established at the PtRu/C electrode.

$$PtRu + CH_3OH = PtRu(CH_2OH) + H^+ + e^- \tag{2}$$
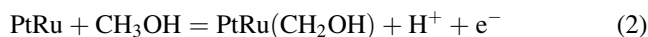
The potential (E') of reaction (2) is related to concentrations (Nernst equation) as:

$$E' = E^0 - \left(\frac{RT}{F}\right)\ln\left(\frac{C_B}{\theta_{ad}C_{H^+}}\right) \tag{3}$$

where E^0 is the standard electrode potential and θ_{ad} the surface coverage by the adsorbed species. From Eq. (3), we get,

$$C_B = \theta_{ad}C_{H^+}\exp\left(F\frac{E^0 - E'}{RT}\right) \tag{4}$$

By differentiation of Eq. (4),

$$\frac{dC_B}{dt} = -k'\exp\left(F\frac{E^0 - E'}{RT}\right)\left(\frac{dE'}{dt}\right) \tag{5}$$

In the above differentiation, it is assumed that the concentration terms, namely, θ_{ad} and C_{H^+} are invariant with time. An empirical constant k' (mol V^{-1} l^{-1}) is included in Eq. (5) to balance the equation with respect to the dimensions. From Eqs. (1) and (5), we get,

$$\frac{dn}{dt} = \left(\frac{k'v}{1000P}\right)\exp\left(F\frac{E^0 - E'}{RT}\right)\left(\frac{dE'}{dt}\right) \tag{6}$$

In order to evaluate the absolute value of methanol cross-over rate at a potential E' of reaction (2) from Eq. (6), it is essential to have the value of the constant k'. It may be possible to obtain the value of k' from a standardization technique. Alternately, the rate of crossover can be estimated from an independent measurement of the electrode potential, as discussed later. However, for a relative estimation of the rates of CH$_3$OH crossover through polymer electrolyte membranes, it is worth noting that (dn/dt) is proportional to (dE'/dt). Assuming that the measured potential (E) of the PtRu electrode, which is a mixed potential, experiences a shift due to reaction (2) alone, the (dE'/dt) in Eq. (6) can be approximated to (dE/dt). Thus, at a given potential, we may write,

$$\frac{dn}{dt} = k\frac{dE}{dt} \tag{7}$$

where the constant $k = [k' v \exp(F(E' - E^0)/(RT))]/(1000P)$.

The potential of a PtRu/C electrode was measured in 0.2 M H$_2$SO$_4$ containing CH$_3$OH of different concentrations. The steady values of potential exhibit Nernstian response on the concentration of as shown in Fig. 2. The slope of the plot is 0.062 V, which is close to 0.059 V that is expected from Eq. (3) for reaction (2). Thus, it is most likely that reaction (2) is the potential determining step.

The variation of potential of a PtRu/C electrode was recorded during CH$_3$OH crossover, and the experiments were repeated with several concentrations of CH$_3$OH and the supporting electrolyte. It was found that the results do not depend on the concentration of H$_2$SO$_4$ up to a concentration of 5 M tested. On the other hand, the concentration of methanol showed a strong influence on the data. E versus t curve is shown in Fig. 3, typically for 0.2 M H$_2$SO$_4$ support-

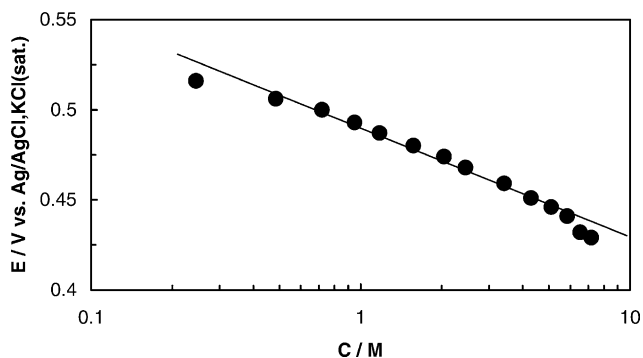Fig. 2. Potential (E) of PtRu/C electrode in 0.2 M H$_2$SO$_4$ as a function of concentration (C) of CH$_3$OH on logarithmic scale.
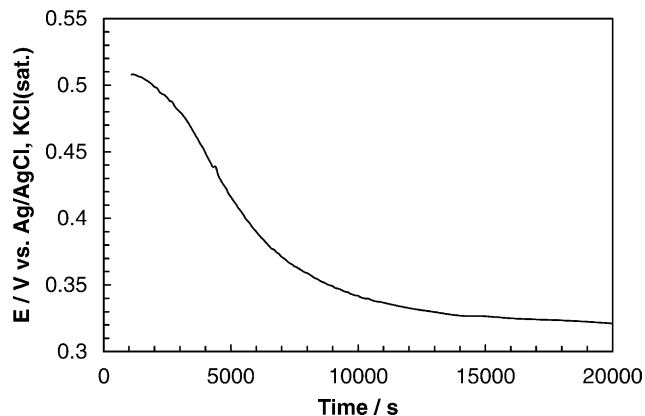

Fig. 3. Variation of potential (E) of PTRu/C electrode in cell B during CH$_3$OH crossover.

ing electrolyte containing 2 M CH$_3$OH. Before the addition of methanol to 0.2 M H$_2$SO$_4$ in cell A, the potential of the electrode was found to be nearly constant for a few hours. After the addition of methanol at a concentration of 2 M, there was a time lag before the potential started shifting, due to slow stirring of the electrolyte. After commencement of methanol crossing the membrane from cell A to cell B, the potential of the PtRu/C electrode in cell B shifted rapidly in the beginning followed by a slow shift (Fig. 3). At the end of the experiment, E was nearly constant due to reaching of equilibrium concentrations of methanol in cell A and cell B.

The data of Fig. 3 were used to calculate (dE/dt) at various times in the region of the potential shift. The variation of (dE/dt) is shown in Fig. 4 as a function of time. Initially, the value of (dE/dt) is high at about 35 μV s^{-1}, and it decreases with time reaching a value of 5 μV s^{-1} after about 2 h. Because (dE/dt) is proportional to the rate of CH$_3$OH cross-over, the initial high rate of diffusion is reflected in the high values of (dE/dt). As the concentration of CH$_3$OH increases in cell B, the diffusion becomes slower, and therefore, the values of (dE/dt) decrease (Fig. 4).

The data of Fig. 3 may also be treated in a different way. Because the rate of diffusion of CH$_3$OH depends on the concentration of CH$_3$OH initially taken in the cell A, the time needed to reach a certain value of shift in potential (ΔE) is also considered to be useful. In Fig. 5, time as a function of (ΔE) is shown. As the concentration of CH$_3$OH decreases, there is an increase in the time needed for attaining a certain magnitude of ΔE.

The above results suggest that the measurement of the electrode potential is useful in assessing the CH$_3$OH crossover across polymer electrolyte membranes. This is an easy and convenient way for assessing the crossover resistance of the membranes, relatively, by a comparison of (dE/dt) versus t curves (Fig. 4), or t versus ΔE curves (Fig. 5). Furthermore, an approximate CH$_3$OH crossover rate is estimated by noting the time required to reach the plateau potential (Fig. 3) corresponding to the equilibrium concentration. Since the initial concentration of CH$_3$OH taken in cell A for the data of Fig. 2 is 2 M, an equilibrium concentration of
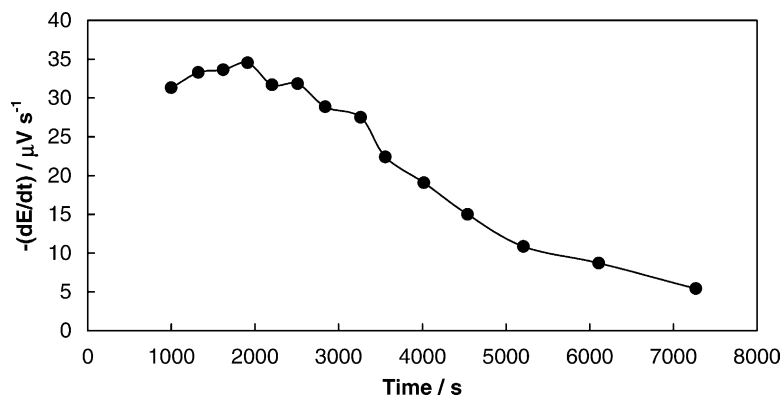
Fig. 4. Variation of (dE/dt) during CH_3OH crossover.
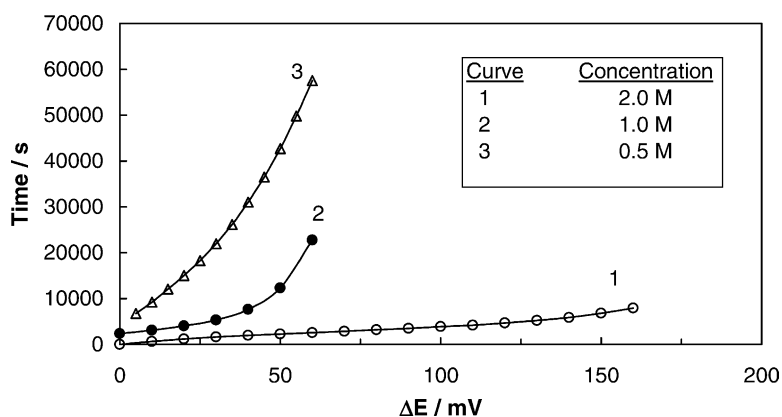
Fig. 5. Methanol crossover time as a function of shift in potential (ΔE), for different initial concentrations of CH_3OH taken in cell A.

1 M and the corresponding time of 330 min are used, and an average crossover rate is calculated using Eq. (1). A value of about 36 $\mu mol\ cm^{-2}\ min^{-1}$ is obtained. Similarly, the crossover rates of 10 $\mu mol\ cm^{-2}\ min^{-1}$ and 3 $\mu mol\ cm^{-2}\ min^{-1}$ are obtained for the initial concentrations of 1 M and 0.5 M, respectively. These values are in close agreement with the data reported in the literature [6], wherein a value of 6.7 $\mu mol\ cm^{-2}\ min^{-1}$ is reported for the Nafion 117 membrane when the initial concentration of CH_3OH is 0.1 M in a supporting electrolyte of 0.5 M H_2SO_4.

The values of crossover rates given above are approximate due to an error in identification of the actual time of reaching the equilibrium concentrations of methanol on either side of the PEM. Nevertheless, the parameter (dE/dt) is useful as a quality control tool to assess the crossover resistance of PEMs in research laboratories and also in industry. The method also has the potential to be used for methanol sensing.

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