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An Electrochemical Investigation of Methanol Crossover in DMFCs

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Abstract: Methanol crossover and its effect on the open-circuit voltage (OCV) in DMFCs were studied using cyclic voltammetry and chronoamperometry under stationary condition and at ambient temperature. An H-shape cell was constructed and a simulative DMFC test was carried out to investigate methanol crossover through Nafion 117 from anode to cathode. The results revealed that the amount of methanol in the cathode side is dependent upon the time of penetration. As the concentration of methanol increased, the hydrogen adsorption-desorption on the surface of electrode was suppressed and a shoulder peak appeared during the forward sweep for methanol oxidation. The simulative DMFC test also showed that the methanol crossover caused a sudden decline in the OCV.

Key words: Methanol crossover, Methanol oxidation, Cyclic voltammetry, Chronoamperometry

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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]. Methanol is an attractive fuel because its energy density is much higher than that of hydrogen, and it is an inexpensive liquid that is easy to handle, store and transport[2]. DMFCs provide the most versatile options for clean and efficient power production[3]. It can be a useful power source over a wide spectrum of energy requirements, from national defense to civil use and many other fields. As a fuel cell, DMFCs are the most promising candidates for portable power applications.

A thermodynamic reversible potential for a methanol oxygen fuel cell is 1. 18 V at 25 . This value is comparable to that for a hydrogen oxygen fuel cell, which is 1. 23 V[4]. However, in practice, DMFCs have a much lower open circuit voltage (OCV). One of the major reasons is that methanol can cross through the proton exchange membrane (PEM), such as Nafion, to reach the cathode side via physical diffusion (by a concentration gradient) and electroosmotic drag (by protons). Such crossover not only results in a waste of fuel, but also causes an internal chemical short to the fuel cells and lowers the cell performance. Most of the methanol crossing over will be electrochemically oxidized at the cathode. Such an oxidation reaction lowers the cathode potential and also consumes some cathode reactant[5-7].

The two most commonly used methods of deter-

mining methanol crossover to date are monitoring the CO_2 flux from the cathode effluent gas and electrochemical techniques. The former is mainly using an optical IR CO_2[8] sensor or gas chromatography[9]. Measurement by precipitation as $BaCO_3$ has also been reported[10]. The method of CO_2 measurement is convenient for studying effects on methanol crossover of DMFC operating conditions, particularly cell current density. In this method, it is assumed that the CH_3OH crossed to cathode is completely oxidized to CO_2, which is unlikely in practical operation. Furthermore, the crossover of CO_2 from the anode to the cathode is ignored. Thus, the measurement of CH_3OH crossover by monitoring CO_2 at the cathode is likely to be inaccurate and requires lengthy and careful calibration when used.

Electrochemical techniques are also widely used to study methanol crossover. A voltammetric method has been developed in Los Alamos National Laboratories[7]. During the measurement, nitrogen was introduced into the cathode side and a positive voltage was applied using a power supply. The reaction occurring at the cathode is the oxidation of methanol that crosses through the membrane. When the applied voltage is high enough to quickly oxidize all the methanol diffusing to the cathode side, a limiting current is achieved. This limiting current approximately represents the rate of methanol crossover at an open circuit. By recording the potential (E) of a PtRu/C electrode using potentiometric method during CH_3OH crossover, it was found that the slope (dE/dt) of E versus t (time) curve is proportional to methanol crossover rate[11]. From the time required to reach the equilibrium concentration of CH_3OH on both sides of the PEM, the methanol crossover rate can be calculated. A new and convenient approach was established to estimate methanol permeability through such simple electrochemical techniques as cyclic voltammetry and chronoamperometry[12]. Experiments were carried out in a two-compartment cell with the membrane separating the compartments. From the slope of permeability curve at various intervals, the methanol permeability has been calculated. The abovementioned methods

are more convenient and faster than conventional CO_2 analysis method, but can only provide information on methanol crossover at an open circuit, which is different from conventional CO_2 analysis method.

In addition, differential electrochemical mass spectrometry (DEMS) was first developed and introduced by Wolter and Heitbaum in early 1980's[12]. A methanol sensor based on the amperometric method and direct measuring the methanol concentration method was also used to study methanol crossover[13].

In this work, the methanol crossover through Nafion 117 was investigated using cyclic voltammetry and chronoamperometry. An H-shape cell was constructed and a simulative DMFC test was carried out to investigate methanol crossover on OCV at ambient temperature.

2 Experimental

Pretreated Nafion membranes (117) were stored in ultra-pure water before used. The previous thermal history of the membranes was found to affect the ability of the membrane to take up water. Hence, membranes for all the studies were subjected to the same treatment and a fresh membrane was used for each study.

Electrochemical measurements were carried out in an H-shape cell with the membrane separating the two compartments as anode and cathode sides. Cyclic voltammetry and chronoamperometry were used to study the methanol permeability of the membrane in a conventional three-electrode cell. A carbon supported platinum on a glassy carbon (Pt/C/GC) and a smooth platinum electrode were used as the working and counter electrodes. The base electrolyte was 0.5 mol· L^{-1} H_2SO_4. Saturated calomel electrode (SCE) was used as a reference electrode throughout the experiments. The initial voltage and sweep rate were -0.241V (vs SCE) and 50 mV· s^{-1}, respectively, throughout the CV tests. Permeability was studied by introducing required volume of 1 mol· L^{-1} CH_3OH in 0.5 mol· L^{-1} H_2SO_4 to anode side of the cell and an equal volume of 0.5 mol· L^{-1} H_2SO_4 to cathode side. By analyzing the solution of the cathode side in-

situ, methanol permeability was obtained. In chrono-amperometric measurements, a potential of 0.85 V against SCE reference electrode was applied and the steady-state currents were determined. A simulative DMFC test was carried out using the H-shape cell to study methanol crossover on OCV. The carbon supported RuPt and carbon supported Pt were, respectively, used as the anode and cathode catalysts. Adding required volume of 1 mol· L^{-1} CH$_3$OH in 0.5 mol· L^{-1} H$_2$SO$_4$ to anode side of the cell and an equal volume of 0.5 mol· L^{-1} H$_2$SO$_4$ to cathode side. Air was supplied to the cathode side by a compressor at ambient pressure. Cyclic voltammetry was used to analyze the solution in the cathode side ex-situ after the cell operated for different periods of time. A series of standard methanol solutions were also obtained using cyclic voltammetry in a home-made half cell for a comparison. All the electrochemical experiments were performed using AUTOLAB PGSTAT30 electrochemical workstation and at ambient temperature.

3 Results and Discussion

Figure 1a shows typical CV curves for standard methanol solutions in 0.5 mol· L^{-1} H$_2$SO$_4$. The regions of hydrogen adsorption-desorption (I) and methanol oxidation (II) are enlarged for more detailed information. The current densities and potentials of Peak A are given in Fig 1b. In general, the peak current density (I_p) and peak potential (E_p) for methanol oxidation (Peak A) during the forward sweep were found to rise with an increase in methanol concentration as evident in Fig 1b. This could be attributed to the increased coverage with methanol as the concentration increases, which might decrease the amount of adsorbed oxygen containing species (OH$_{ads}$) on the surface of the electrode. The amount of increased OH$_{ads}$ formation at a more positive potential results in a faster rate of methanol oxidation and accordingly increases the current density of peak "A"[14]. On the other hand, as the concentration increases, the peak related to methanol oxidation showed a shoulder at a lower potential (indicated as

Peak C), methanol dissociation and adsorption on the electrode surface also suppressed the adsorption-desorption of hydrogen and decreased their peak current densities.
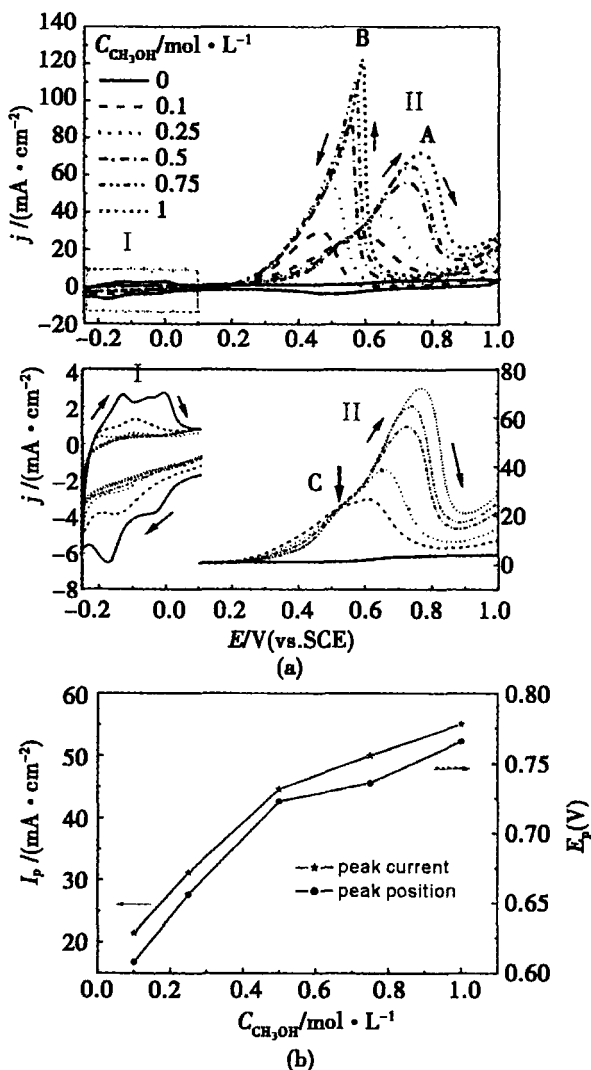

Fig 1 Cyclic voltammograms for standard methanol solutions in 0.5 mol· L^{-1} H$_2$SO$_4$ solution with the enlarged hydrogen regions(a) and the detailed information for Peak A (b)

scan rate: 50 mV· s^{-1}

Cyclic voltammograms obtained from the cathode side of H-shape cell after different periods of time at a room temperature and under a stationary condition are provided in Fig 2. The cathode initially contained 0.5 mol· L^{-1} H$_2$SO$_4$ solution, while the anode contained 0.5 mol· L^{-1} H$_2$SO$_4$ and 1 mol· L^{-1} CH$_3$OH

solutions. After each time interval, the solution of the cathode side was analyzed in-situ using cyclic voltammetry. It can be seen that the peak current density for methanol oxidation (Peak A) during the forward sweep increased with time of penetration increasing, indicating the increased amount of methanol crossed from the anode side to the cathode side. Compared the CV curves in Fig 2 with the standard CV curves in Fig 1a, the shapes of methanol oxidation peaks (A and A) and shoulder peaks (C and C), as well as the hydrogen adsorption-desorption behaviors remained unchanged, while the shape of Peak B ' observed during the reverse scan was more well-defined than that of Peak B.

The chronoamperomograms obtained at the anode and cathode sides of H-cell after different permeation time are presented in Fig 3. The steady-state current densities were then evaluated and plotted against the permeation time in Fig 3c. It is evident that the steady-state current density for methanol oxidation increased with permeation time in the cathode side but decreased in the anode side. After 48 hours, the current densities for methanol oxidation were found not to be equal showing no equilibrium of methanol in both sides. The oxidation current density for the cathode side is only 4. 26 mA· cm^{-2} while that for the anode side is 7. 02 mA· cm^{-2}. The results were significantly different from that reported by Ramya[15] due to different pretreated membranes and different experimental systems. It should be pointed that there was no agitation in the present work.

Using the H-shape cell, a simulative DMFC test was carried out to study the effect of methanol crossover on OCV. The OCV as a function of operating time is shown in Fig 4. It was observed that the OCV gradually increased at the beginning, then declined rapidly from 0. 42V to 0. 11V (indicated by an arrow), and finally stabilized at about 0. 1V after one and half an hour. The decrease in OCV might be caused by the crossover of methanol from the anode to cathode. To verify this point, the solution in the cathode side was analyzed ex-situ using cyclic voltammetry after the simulative DMFC cell was operated at

OCV for 10 hours. The CV curve from the standard solution of 1 mol· L^{-1} CH$_3$OH (Fig 1a), the CV curve obtained from the cathode side of H-cell under stationary for 10h (Fig 2a) are compared with the CV curve from the cathode side of H-cell operated at OCV for 10h in Fig 5. It is obvious that the peak of methanol oxidation appeared, suggesting the presence of methanol crossed from the anode to the cathode. However, as compared with those observed from the standard methanol solution, the position, shape and magnitude of Peak A and B were significantly different. Nevertheless, for the same permeation time (10 h) in 1 mol· L^{-1} CH$_3$OH, methanol crossed through Nafion 117 from anode to cathode under stationary condition was more severe than that operated at OCV condition.
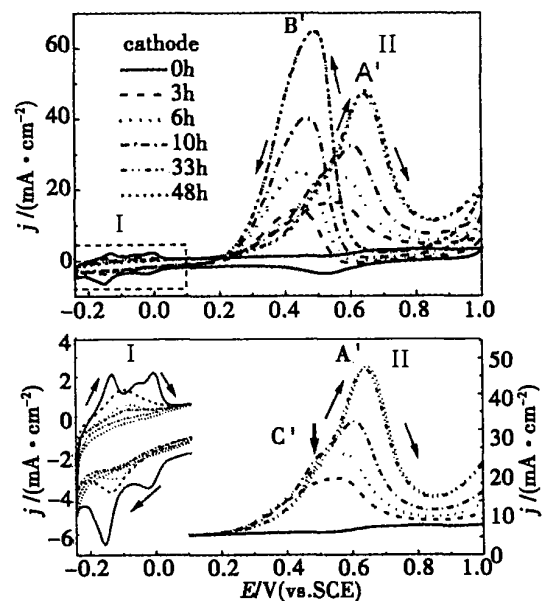

Fig 2 Cyclic voltammograms obtained at the cathode side of H-cell after different time intervals with the enlarged hydrogen regions

4   Conclusions

Methanol crossover through Nafion membranes (117) was investigated directly by cyclic voltammetry and chronoamperometry. The amount of methanol in the cathode side was dependent on the time of penetration. The peak current density and potential for methanol oxidation during the forward sweep in-
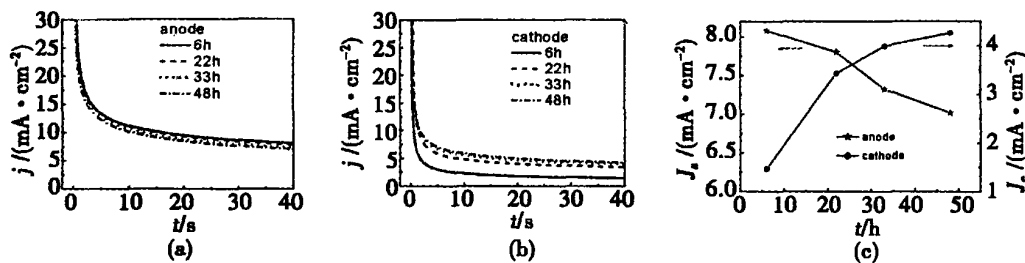
Fig 3　Chronoamperomograms obtained at the anode side (a) and cathode side (b) of H-cell after different time intervals variation of the steady-state current densities with permeation time (c)
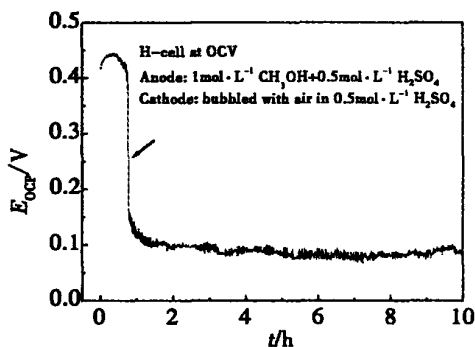

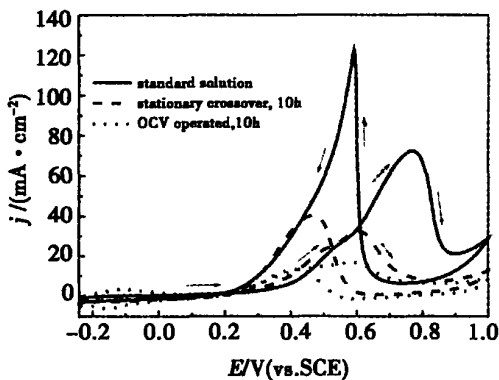Fig 4　Variation of OCV with operating time during a simulative DMFC test

Fig 5　A comparison of voltammograms obtained at the cathode side of H-cell under stationary condition for 10 h and after the cell was operated at OCV for 10 h

creased, while the desorption and adsorption of hydrogen on the electrode surface were suppressed with an increase in methanol concentration. During the simulative DMFC test, it was found that the OCV rose gradually at the beginning then declined rapidly from 0.42 V to 0.11 V, and finally stabilized at about 0.1 V after one and half an hour.

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DMFC

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