

Fuel crossover in direct formic acid fuel cells

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Abstract

This work studies formic acid crossover in a direct formic acid fuel cell under different operating conditions. Comparison with methanol crossover in a direct methanol fuel cell is included. The effects of cell conditioning, temperature, fuel concentration, and Nafion[®] thickness on the rate of formic acid crossover are examined. The effects of temperature, concentration, and membrane thickness are qualitatively similar to those with methanol, but overall crossover rates are much lower. Under the same operating conditions, it is found that formic acid has a crossover flux rate that is approximately one-sixth that of methanol. Measurement of the CO₂ membrane permeation flux is performed to determine its contribution to a bias that it might cause in the quantification of crossover.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) using formic acid as a fuel are receiving increasing attention. Direct formic acid fuel cells (DFAFCs) operate remarkably more efficiently than direct methanol fuel cells (DMFCs) due to the higher open-cell potential of formic acid oxidation, the faster electro-oxidation kinetics for formic acid, and a lower rate of fuel crossover [1]. As a result, DFAFCs are predicted to be among the first commercial small fuel cells to appear on the market [2].

For any PEMFC, the fuel fed to the negative electrode (anode) can permeate the membrane to the positive electrode (cathode). This phenomenon reduces fuel utilization, results in a detrimental mixed current, competes for and potentially poisons the cathode catalyst and thereby decreases the efficiency of the oxygen reduction reaction, and hinders contact of the surface of Nafion[®] with oxidant gas by the formation of liquid films [3–5]. It is widely accepted that methanol permeation, or crossover, is one of the most significant problems with DMFCs, and therefore,

many studies have been performed to investigate and quantify this behaviour. Because the interest in DFAFCs is relatively new, only a few studies on formic acid crossover have been reported to date. Rhee et al. [6] found that in a permeation cell, the rate of formic acid crossover through a Nafion[®] membrane was approximately two-orders of magnitude smaller than that of methanol. Wang et al. [7] studied the crossover current of formic acid in half-cell configurations and observed a formic acid crossover current that was approximately 5 or 10 times less than that of methanol. While these studies showed that formic acid is less likely to permeate a Nafion[®] membrane, by virtue of the cell design, it was not possible to make measurements of crossover under the influence of factors present in the actual fuel cell environment. For example, crossover data from a permeation cell does not include the contribution of electro-osmotic drag which is a factor in crossover in a real fuel cell environment, particularly at high current densities. Half-cell measurements of crossover currents are inaccurate as it can be expected that the applied voltage can increase the crossover flux of formate ions [8].

The purpose of this paper is to present the measurement of the rate of formic acid crossover in a real fuel cell environment for which the operating variables are systematically changed. In this study, we investigate the influence of membrane pretreatment,

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membrane thickness, fuel concentration, and cell temperature on the crossover rate of formic acid. The rate of methanol crossover is measured for the purposes of comparison.

In the presentation of data, crossover is reported as a current, with units of mA cm⁻². Crossover is calculated using the formula:

$$j_{\text{crossover}} = M_{\text{fuel}} N_{\text{elec}} F \quad (1)$$

where M_{fuel} is the molar flux of fuel crossover (based on a CO₂ detector signal), N_{elec} the number of electrons per molecule of fuel that are transferred in the fuel cell's preferred electrochemical reaction, and F is the Faraday number. For formic acid and methanol, the values of N_{elec} are 2 and 6, respectively. This may seem to bias the comparison between methanol and formic acid, but it in fact simply reflects the advantage that DFAFCs have over DMFCs with respect to Faradaic efficiency. As defined, crossover current is interchangeably referred to as equivalent crossover current or crossover rate.

2. Experimental

2.1. Membrane–electrode assembly and single-cell fabrication

Catalyst inks were prepared by sonication of water, small-chain aliphatic alcohols, ionomer solution, and catalyst powder (Johnson Matthey HiSPEC 6000 PtRu for anode, Johnson Matthey HiSPEC 1000 Pt black for cathode). To prepare the electrodes, the inks were sprayed on to carbon paper (Toray, 20% PTFE wet-proofed) that was previously treated with a thin layer of PTFE, carbon black, and glycerol. The catalyst loading for both the anode and the cathode was 3 mg cm⁻². The fabricated electrodes were dried at 80 °C for at least 1 h and subsequently hot-pressed to either side of a piece of pre-conditioned Nafion[®] 112, 115, or 117. The resulting membrane–electrode assemblies (MEAs) had active electrode areas of 10.89 cm². The MEAs were housed in a single-cell assembly. All tests were performed with 5 ml min⁻¹ of fuel and 250 sccm of humidified oxygen at 1 atm. fed to the anode and the cathode, respectively. Unless stated otherwise, the cell temperature was maintained at 30 °C.

2.2. Fuel crossover measuring system

The experimental set-up used to measure fuel crossover in a real fuel cell operating environment was similar to those employed to measure methanol crossover by previous investigators [4,5,9–12]. The cathode exhaust, which could include both reacted and unreacted permeated fuel, was fed to a catalytic afterburner containing palladium pellets and maintained at 400 °C. It was verified that this afterburner converted all entering fuel to CO₂. The resulting CO₂ was measured using a gas chromatograph (DONAM Instruments, Inc., DS6200) equipped with a flame ionization detector. Nitrogen was fed to the injection line of the gas chromatograph as a sweep gas at 100 sccm. The CO₂ concentration was then correlated to the rate of fuel crossover. This method is based on the assumption that per-

meated formic acid and methanol are completely oxidized to CO₂ gas. The primary drawback with this assumption is that it counts any detected CO₂ as permeated, catalytically oxidized fuel. Any CO₂ formed at the anode that permeates the membrane will exaggerate the measurement of the rate of fuel crossover. This systematic error and attempts to quantify it are addressed further in subsequent sections.

2.3. CO₂ crossover measuring system

To improve the accuracy of the fuel crossover measurement, the rate of CO₂ permeation by diffusion through Nafion[®] was measured in an independent experiment. In this experiment, a CO₂-saturated stream of water was fed to the anode of a fuel cell fabricated with an MEA that did not contain a catalyst layer. Additionally, different flow rates of CO₂ gas were fed to the anode, each corresponding stoichiometrically to the amount of CO₂ produced by formic acid electro-oxidation for a range of current densities. The cathode was fed a sweep gas, which together with the permeated CO₂, was exhausted and detected by a CO₂ analyzer (VAISALA, M170 measurement indicator and DMP74B dewpoint probe). The CO₂ permeation rate for a range of CO₂ feed rates, which simulated different current densities, was recorded.

3. Results and Discussion

3.1. Effect of membrane conditioning

It is common practice to condition a new PEMFC to hydrate the membrane, activate the catalyst layer, and effect pore alignment prior to standard operation. Ha et al. [13] have shown that DFAFC performance is enhanced if the cell is first operated under a load with methanol as the fuel [13]. These authors did not, however, determine the reason for the enhancement, but suggested that such methanol conditioning changes the anode layer and possibly has an effect on pore alignment. Membrane swelling caused by contact with the methanol may also occur. In light of the potential effect that methanol conditioning has on the membrane, we have investigated its influence on formic acid crossover.

Methanol conditioning consisted of performing two slow cell polarizations at 80 °C using methanol and hydrated oxygen. Fig. 1 shows the cell polarization of a DFAFC carried out before and after methanol conditioning for a range of formic acid concentrations. Comparison of Fig. 1(a and b) shows two trends. First, the performance of the cell is enhanced by the conditioning for all concentrations of formic acid. The maximum power density is increased from 75 to 97 mW cm⁻². Second, in Fig. 1(a), there is relatively little difference between the polarization in 10, 13, or 15 M formic acid. After the methanol conditioning, however, the three polarization curves are much more resolved, with polarization becoming more severe as the concentration is increased. This suggests that the membrane is more susceptible to permeation.

Fig. 2 presents the rates of formic acid crossover when using 6 M formic acid, measured before and after methanol condi-

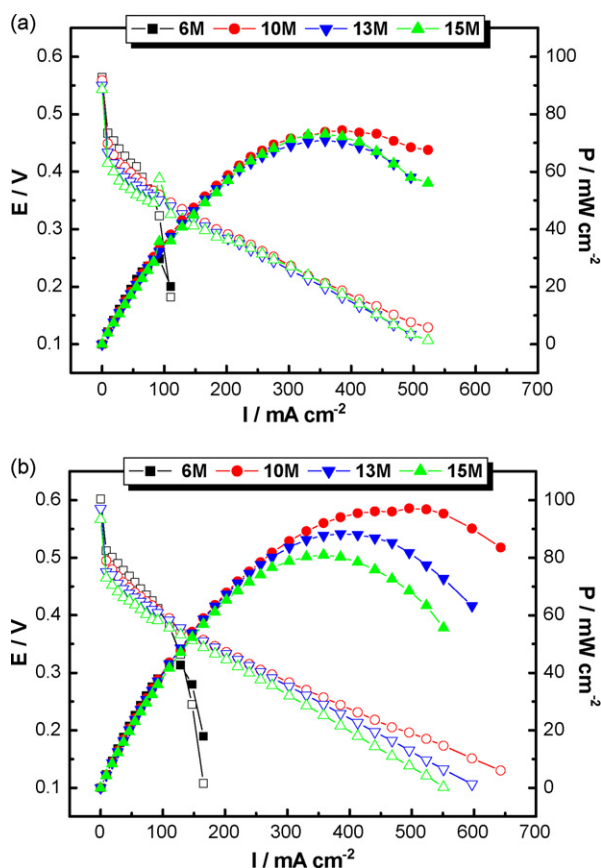


Fig. 1. Cell polarization (a) before and (b) after methanol conditioning using different concentrations of formic acid. The membrane is Nafion[®] 115 and cell temperature is maintained at 30 °C.

tioning of the cell. At the open-circuit voltage (OCV), methanol conditioning increases the rate of crossover by more than 4-fold. In order to avoid such influences on membrane properties by methanol, all subsequent experiments in this work were carried out without methanol conditioning.

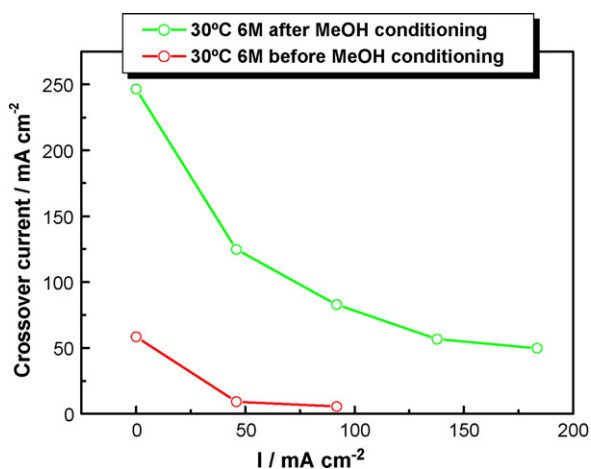


Fig. 2. Rate of formic acid crossover before (square symbols) and after (round symbols) methanol conditioning. Data obtained with a 6 M formic acid solution. The membrane is Nafion[®] 115 and cell temperature is maintained at 30 °C.

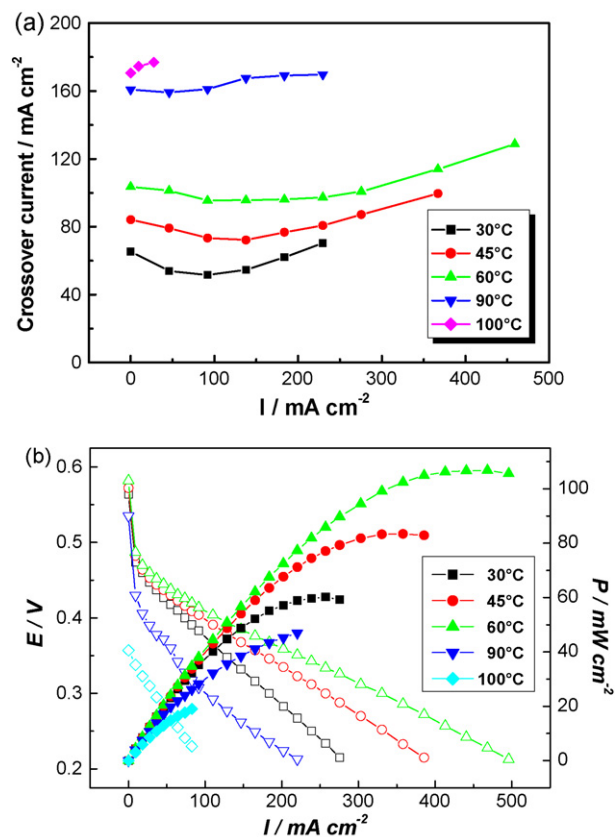


Fig. 3. Effect of cell temperature on (a) formic acid crossover and (b) cell performance. A 13 M solution of formic acid is fed to the anode, and oxidant humidified at 90–95% relative humidity to the cathode.

3.2. Effect of cell configuration and operating conditions

Crossover and polarization data for a DFAFC operated at different temperature are given in Fig. 3. The result in Fig. 3(a) clearly show that formic acid crossover increases with cell operating temperature. This behaviour, which was expected, agrees qualitatively with the half-cell results of Wang et al. [7] and is similar to the case of methanol [7,12]. The cell potential fluctuates at 100 °C and is possibly due to interactions associated with the vaporization of formic acid and water.

The data in Fig. 3(b) show an increase in cell performance with temperature, until 60 °C, despite an increase in formic acid crossover. As the temperature is raised from 60 to 90 °C, the performance dramatically decreases. The measured formic acid crossover increases by nearly 60% with this temperature change, and is certainly a contributing factor to the degradation in performance.

The most interesting feature of Fig. 3(a) is the increase in measured crossover at higher current densities. This is contrary to what is expected from theory and what has been reported for methanol crossover in a real fuel cell environment by previous researchers [4,5,12], who found a monotonic decrease in crossover with increasing current density. As the current density increases, so does fuel consumption in the anode catalyst layer. It is therefore expected that the fuel concentration at the interface between the anode catalyst layer and the membrane is

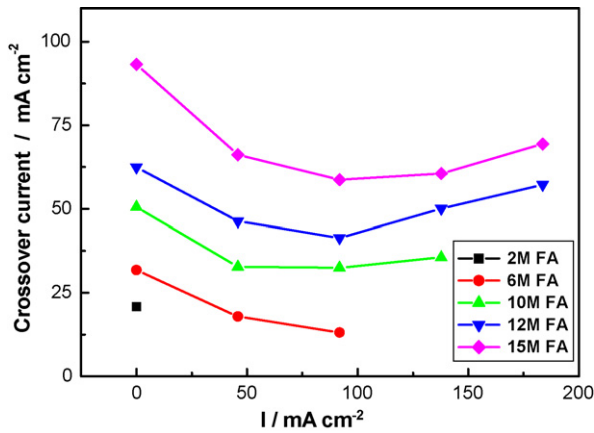


Fig. 4. Effect of formic acid concentration on crossover. Cell maintained at 30 °C.

reduced and the chemical potential for permeation is decreased. An apparent increase in crossover at higher current densities is observed in nearly all crossover measurements and is probably due to a systematic error in the detection method employed. The systematic error, its consequences, and attempts to quantify and eliminate it will be discussed in detail in a later section.

The measured formic acid crossover increases with fuel concentration, as shown in Fig. 4. This is expected as higher fuel concentrations will result in higher concentration gradients at the membrane. Consequently, this concentration effect is the reason why DMFCs are generally limited to the use of less than 2 M methanol [14]. As in the crossover data for temperature variation presented in Fig. 3, the measured crossover apparently increases at current densities above about 100 mA cm⁻².

The effect of membrane thickness on formic acid crossover, is presented in Fig. 5. As expected and as is the case for methanol, membrane thickness and crossover are inversely related. Above 100 mA cm⁻², Nafion[®] 117 shows more crossover, but this occurs at the same range where the measured crossover begins to increase with current density. This increase with current density is suspected to be a systematic error, and thus the data at lower current densities are most reliable.

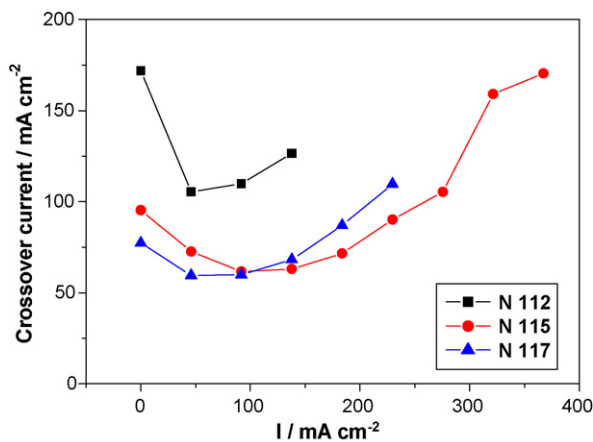


Fig. 5. Effect of Nafion[®] membrane thickness on formic acid crossover. Cell operated at 30 °C.

3.3. Comparison of formic acid and methanol crossover

To provide a direct comparison between the crossover rates of DFAFCs and DMFCs, methanol was employed as fuel and crossover rates were measured under similar operating conditions as those employed for the DFAFCs. The crossover rate of methanol as a function of loading and fuel concentration is shown in Fig. 6(a). As expected, the rate of fuel crossover increases with concentration. As in other data presented, an increase in crossover occurs at higher current densities. The polarization curves for methanol at different concentrations are given Fig. 6(b). The resulting power densities are much less than those for formic acid. For example, the maximum power density produced is only 33 mW cm⁻², while at the same voltage formic acid yielded nearly three times the power density. It should be noted that the cell used to obtain the DFAFC and DMFC data was manufactured using materials and fabrication methods optimized for a DMFC, not a DFAFC.

The relatively sluggish electro-oxidation kinetics of methanol together with its greater rate of crossover limits the concentrations used to no higher than 10 M. A graphical comparison of the rates of crossover for methanol and formic acid is given in Fig. 7. For 6 and 10 M feed solutions, at the OCV, the rate of methanol crossover is approximately twice that of formic acid, see Fig. 7(a). As more load is applied, the measured difference

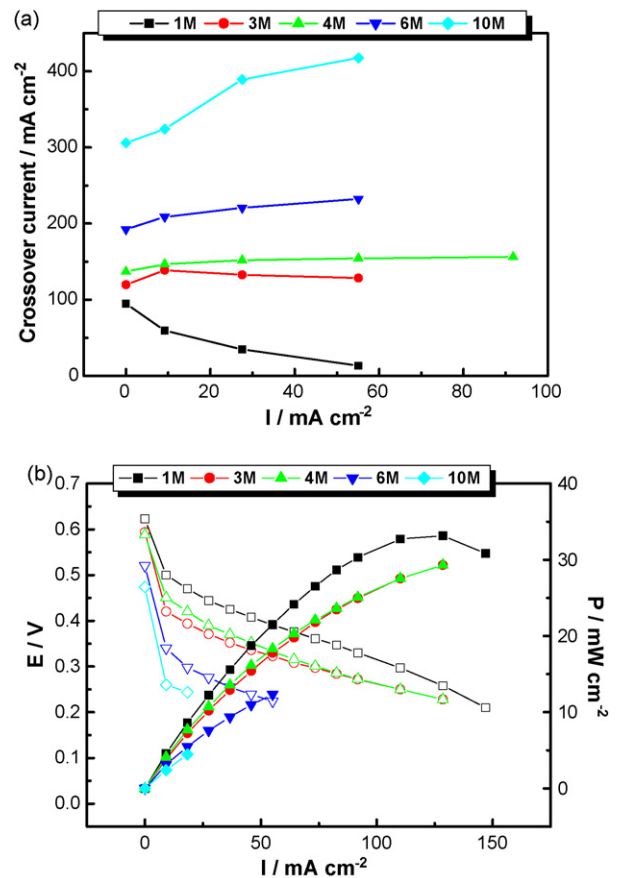


Fig. 6. Effect of methanol concentration on (a) crossover and (b) cell performance. Cell operated at 30 °C.

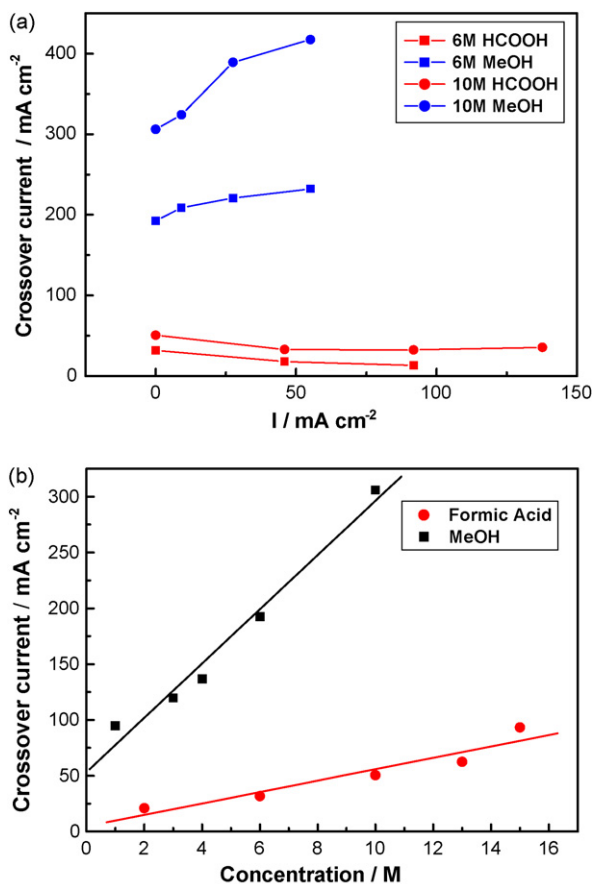


Fig. 7. Comparison of crossover flux for methanol and formic acid: (a) at 6 M and 10 M and under a load (b) at OCV.

becomes more pronounced, though permeated CO₂ might be affecting the accuracy of the measurements. The crossover of both methanol and formic acid measured at the OCV for varying concentrations is demonstrated in Fig. 7(b). An approximately linear dependence is observed for both fuels, with the slope for methanol being approximately six times that for formic acid. The data in Fig. 7(b) are of particular significance, because when operating at OCV, the systematic error that was encountered at higher current densities, likely a consequence of permeated CO₂, is minimized.

The measured rates of methanol crossover are similar to those reported by Jiang and Chu [19], and by Dohle et al. [5], however different operating conditions and cell fabrication materials and methods make a direct comparison impossible.

3.4. Determination of systematic error

In the crossover fluxes presented above, a fairly consistent feature was observed. However, at current densities above approximately 100 mA cm⁻², the measured rate of fuel crossover increased. This is opposite to theoretical expectation. Electro-oxidative fuel conversion in the catalyst layer increases directly with current density, reducing the amount of fuel that is available to permeate the membrane as current density increases. This expectation has been validated by the measure-

ments of methanol crossover made by previous researchers [4,5,9–12]. The increase in measured crossover is therefore deemed a systematic error present in our experimental set-up. Local temperature effects induced at higher current densities but not captured by the bulk temperature measurement might be one cause of the increased crossover at higher power densities. The most likely cause of the anomalous trend, however, is anodic CO₂ crossover, which would be detected by the gas chromatograph and counted as permeated fuel, thus exaggerating the measured rate of fuel crossover. Membrane permeation of anodic CO₂ is possible by two well-known mechanisms namely, diffusion and electro-osmotic drag. Increasing current density is known to increase the contribution of both of these mechanisms. The following experiments were conducted to quantify and identify the phenomena responsible for this error.

3.4.1. Effect of temperature

As shown in Section 3.2, increasing cell temperature exerts a considerable influence on the rate of fuel permeation. Coincidentally, as the current density is increased, the rate of waste heat generation at the MEA increases at a rate greater than that given by a linear dependence. Thus, it is possible that as the current density is increased, the local temperature of the membrane is increased and becomes considerably higher than that of the controlled, bulk temperature measured in the graphite flow-field block, relatively far from the MEA. To test this assumption, measurements of temperature near the MEA were made while the cell was cycled through a very slow upward and downward polarization scan. Over the course of the 1 h test, the temperatures of the anode and cathode increased 7 and 4 °C above the bulk temperature of 30 °C, respectively. As shown in Fig. 3, such temperature increases are not sufficient to cause a significant increase in crossover. Thus, elevated membrane temperature is not the cause of the increase in measured crossover at higher current densities.

3.4.2. Effect of CO₂ diffusion

The rate of CO₂ production by fuel electro-oxidation increases in proportion with the current density and, because it is produced in the anode catalyst layer, it has immediate diffusion access to the adjacent membrane. Thus, the driving force for cross-membrane diffusion of CO₂ is increased at higher current densities.

Although many early researchers attempting to quantify methanol crossover by measuring the CO₂ at the outlet of the cathode neglected to consider the effect of CO₂ permeation [16,17], there has since been a consensus that anodic CO₂ crossover can constitute a significant portion of the CO₂ signal [18,19]. In fact, some researchers have shown that with increasing current densities, it is possible that the majority (up to 95%) of the signal can be attributed to permeated CO₂ [5,15,20]. Note that, in most cases, these measurements of CO₂ permeation include the combined effects of both molecular diffusion and electro-osmotic drag.

Determination of the CO₂ crossover rate by diffusion would allow justification of the anomalous trend in the measurements

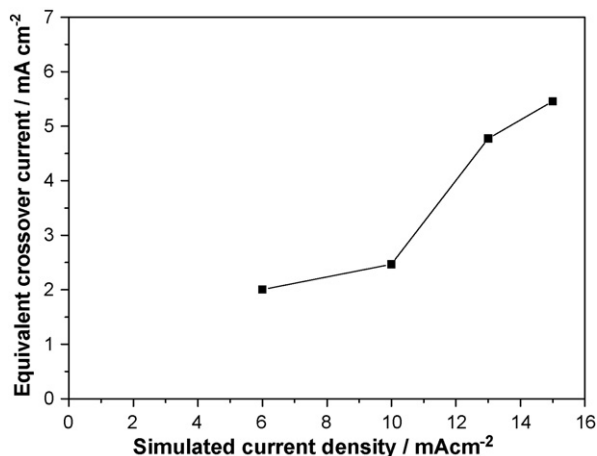


Fig. 8. Rate of anodic CO₂ permeation by diffusion. Equivalent crossover current calculated on a formic acid basis ($N_{\text{elec}} = 2$). A two-phase mixture of CO₂ gas, at a flow rate corresponding stoichiometrically to the amount of CO₂ gas produced at a specific current density (simulated current density), and CO₂-saturated water was fed to the anode flow-field of a cell. The cell was manufactured according to the procedure in Section 2, but with no catalyst layer. Cell maintained at 60 °C.

reported above. To this end, the experiment described in Section 2.3 was performed to isolate and quantify the rate of CO₂ diffusion through the membrane. The rate of CO₂ diffusion crossover for a range of CO₂ production rates at 60 °C is shown in Fig. 8. The equivalent CO₂ crossover current was calculated on a formic acid basis ($N_{\text{elec}} = 2$). Though the range of simulated current density is not broad, a nearly linear profile is attained. Extrapolation of the trend to CO₂ production rates corresponding to a current density of 100 mA cm⁻² predicts a CO₂ crossover rate of approximately 35 mA cm⁻², i.e., of the same order of magnitude as the total measured formic acid crossover at the same temperature (~ 100 mA cm⁻²). For methanol, extrapolation to a current density of 100 mA cm⁻² predicts a CO₂ crossover rate of approximately 100 mA cm⁻², also of the same order of magnitude of the methanol crossover measurement.

In the above experiment, the CO₂ was fed to the cell via the anode flow-field, and thus in order to permeate to cathode side and be detected, it must diffuse from the bulk solution in the flow-field, through both gas-diffusion layers, both micro-porous layers, and the membrane. Certainly, a considerable amount of the CO₂ fed to the anode is unable to diffuse out of the bulk, and is exhausted from the anode flow-field. This is in contrast to a realistic fuel cell environment, where the CO₂ is produced entirely in the anode catalyst layer, and can readily diffuse directly across the membrane. Also, other researchers [5,15] have shown that CO₂ crossover increases appreciably when fuel concentration increases. In the experiment conducted here, only water is used. Thus, it can be concluded that the measurements of CO₂ permeation by diffusion are much lower than those that are expected in a real fuel cell environment. Therefore, CO₂ permeation by diffusion can be expected to contribute considerably to the fuel crossover signal for the crossover measurements presented above, and can explain the observed increase in crossover at higher current densities.

3.4.3. Electro-osmotic drag of CO₂

In addition to molecular diffusion, a final mechanism for anodic CO₂ crossover is electro-osmotic drag. This phenomenon is known to be an appreciable factor in anodic species crossover [16,17,19,21]. Because it is a convective mode of transport, as current densities are increased the effect of electro-osmotic drag will also increase. Drake et al. [18] recently isolated the effect of electro-osmotic drag on CO₂ at ambient conditions. Over the small range of current density that they analyzed, it was estimated that the electro-osmotic drag of CO₂ through Nafion® 117 can be calculated according to the equation:

$$F_{\text{conv}} = \alpha_{\text{CO}_2} i_{\text{cell}} \quad (2)$$

where F_{conv} is the CO₂ crossover current caused solely by electro-osmotic drag; α_{CO_2} the drag coefficient for CO₂ convection; i_{cell} is the current density of the fuel cell. With the use of methanol and formic acid, α_{CO_2} is 1.03 and 0.34, respectively. According to this estimate, for a DMFC and a DFAFC each operating at 100 mA cm⁻², the electro-osmotic drag would contribute 103 and 34 mA cm⁻², the respectively, of equivalent crossover current to a measurement. These values should be considered with caution, however. Different operating conditions, MEA materials, and fabrication procedures will certainly have an affect on the contribution of the electro-osmotic drag of CO₂ [12]. For example, in some of the measurements of formic acid crossover reported in this work, 34 mA cm⁻² of equivalent crossover is more than the entire signal. Nevertheless, electro-osmotic drag might be expected as a main contributing factor to the increase in the measured crossover at higher current densities observed in most of the crossover measurements performed in this work.

4. Conclusions

Crossover of formic acid in a real DFAFC operating environment under various operating conditions has been measured for the first time. A comparison of formic acid and methanol crossover under similar conditions has also been undertaken. Formic acid crossover is found to increase with both temperature and concentration, and generally decreases with membrane thickness. Methanol conditioning of the formic acid cell prior to operation with formic acid enhances formic acid crossover considerably. Most substantially, methanol crossover is six times greater than formic acid crossover under the same operating conditions.

From crossover flux measurements at current densities over approximately 100 mA cm⁻², an anomalous trend of increasing fuel crossover is detected. Supplementary experiments show that this trend is attributable to the sensitivity of the method used for crossover measurement to cross-membrane CO₂ permeation. Such permeation is known to be caused by a combination of diffusion and electro-osmotic drag, and is shown to occur at rates that are sufficient to explain the anomalous results. Consequently, the measurements made at lower current densities, where CO₂ permeation is not significant, are considered to be the most accurate.

Acknowledgement

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