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Methanol crossover effect on the cathode potential of a direct PEM fuel cell

V. A. PAGANIN, E. SITTA, T. IWASITA and W. VIELSTICH
Instituto de Química de São Carlos, Universidade de São Paulo, C.P.780, CEP 13560-970, São Carlos, SP, Brazil
*(*author for correspondence, e-mail: vielstic@terra.com.br)*

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Abstract

The potential of the oxygen cathode in a direct methanol fuel cell is strongly influenced by the crossover of methanol through the poly-electrolyte membrane. In the presence of methanol, oxygen is reduced at the cathode already at open circuit and the equivalent amount of methanol is oxidized. This results in the formation of a mixed potential, up to 200 mV negative to the original oxygen potential. In this work, the anode and cathode potentials of a DMFC are monitored *in situ*, using a *dynamic hydrogen electrode* (DHE). For the first time, the effect of crossover on the cathode potential as function of time is presented. Methanol and ethanol as fuels are compared. Changing from methanol to hydrogen, the influence of methanol crossover on the cathode potential can also be followed as function of current density. It is already known that, in addition to the consumption of fuel and oxygen with the formation of a mixed potential, a purely chemical reaction takes place at the platinum surface. A quantitative determination of the respective CO_2 formation is presented here.

1. Introduction

Several investigations have focused on the direct methanol fuel cell, and have shown that the performance of the cell is strongly affected by methanol crossover from the anode to the cathode compartment [1–4]. This phenomenon is accompanied by a reduction in cell voltage, which depends on experimental parameters such as fuel concentration, applied current density, stoichiometric factor and temperature [3, 4]. At the cathode methanol is oxidized to CO_2 and the amount of CO_2 formed was determined at the outflow of both, anode and cathode [5]. In 1996 Lucsak et al. [6] suggested that at the cathode outlet, CO_2 originates not only from the methanol oxidation at the cathode, but also from the crossover of CO_2 produced at the anode. During the following years, a detailed investigation of the CO_2 crossover was performed [2–4]. Müller et al. [3] have shown, that increasing the current density, increases CO_2 crossover due to the higher CO_2 formation at the anode. At the same time, with increasing current density a decay of methanol crossover occurs, due to the concentration drop at the interface. The results of Müller et al. [3] are shown in Figure 1.

In studies of methanol crossover only the reduction of the DMFC voltage has been measured [2–4]. However, due to the large overpotential on both cathode and anode a detailed study of the problem requires the knowledge of the individual electrode potential, as done in the present work. For this purpose a reference electrode in form of a dynamic hydrogen electrode (DHE) [7] was placed on the cathode side of the membrane electrode assembly (see Figure 2) [8]. This reference electrode allowed measurement of the potential shift at the oxygen cathode (a mixed potential [9]), due to a simultaneous electrochemical methanol oxidation and oxygen reduction. With the help of the DHE as a reference, the development of the mixed potential was followed as function of time and current density.

The loss of fuel and oxygen occurs not only due to the electrochemical processes giving rise to a mixed potential as described above; also a purely chemical reaction consumes methanol and oxygen [10]. This reaction additionally increases the amount of CO_2 formed at the cathode. In the present work, we present the results of a quantitative determination of CO_2, formed through the heterogeneous chemical reaction.

2. Experimental

Electrodes having a geometric area of 4.6 cm^2 and a noble metal content of 1 mg Pt/cm^2, were prepared using 20 wt% Pt/C (E-TEK) and 20 wt%Pt + 10 wt%Ru/C (Johnson Matthey) as catalysts for the cathode and anode respectively. A diffusion layer was

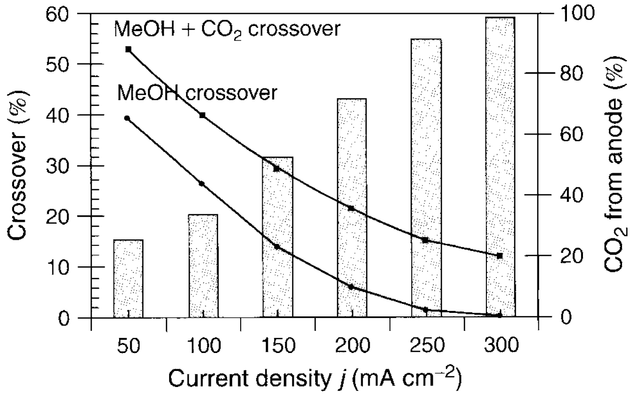

Fig. 1. Dependence of methanol and carbon dioxide crossover rate (left axis) on current density as measured using gas chromatography. The bars show the percentage of CO_2 coming from the anode (crossover) (right axis) [Taken from ref. 2 with permission].

first formed on a carbon cloth (PWB-3, Stackpole) by applying Vulcan carbon XC-72 (E-TEK) suspended in PTFE (Teflon® TE 306A, DuPont) and sintering at 330 °C. Then the catalyst layer (Pt/C or PtRu/C) suspended in a Nafion® solution (DuPont, ~5.5 wt%), was applied onto the diffusion layer. The electrode was then heated for 1 h at 80 °C [11].

The membrane-electrode-assembly (MEA) was prepared by hot-pressing the catalysts on both sides of a pre-treated Nafion 117 membrane (H^+, Du Pont) at 125 °C and 5 MPa, during 2 min. The MEA was placed between graphite plates in which channels were machined for the circulation of the reagents (oxygen at the cathode and alcohol solutions at the anode).

The reference electrode was constructed by pressing two platinized palladium–gold grids in the form of discs (6 mm diameter) each on one side of the membrane (Figure 2). Hydrogen was produced on one of these grids by connecting them to a DC source outside the cell. This electrode, so-called DHE [7], keeps a constant potential of ca. −2 to −5 mV vs RHE, at some μA of current.

The solutions were prepared with MilliQ water from Millipore® and p.a. methanol (J. T. Backer,). The methanol/oxygen PEMFC experiments were carried out at 70 °C by applying constant currents. Hydrogen, Oxygen and alcohol solutions were fed at room temperature (28 ± 2 °C) and atmospheric pressure. In all experiments, the flow of gases was 80 ml min^{-1}. The flow rate of methanol solution was either 1 ml min^{-1} or 0.5 ml min^{-1}, as indicated in the figure caption.

Electrochemical data were obtained using a potentiostat Solartron 1285 and the software Corrware or power supply Dawer 3005.

3. Results and discussion

On the Pt surface of a DMFC cathode, methanol crossover gives rise to several processes as follows.

(i) On separate places at the electrode surface, oxidation of methanol and reduction of oxygen occur simultaneously

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (1)$$

$$O_2 + 4H^+ + 4e^- \rightarrow H_2O \quad (2)$$

These reactions give rise to a mixed potential at the cathode.

(ii) A heterogeneous chemical reaction between methanol and oxygen occurs [9],

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O \quad (3)$$

(iii) Also, methanol adsorption can cause blocking of the surface due to the formation of adsorbed organic residues and carbon monoxide, producing an additional shift of potential [12]:

$$CH_3OH + Pt \rightarrow CO_{ad} + 6H^+ + 6e^- \quad (4)$$

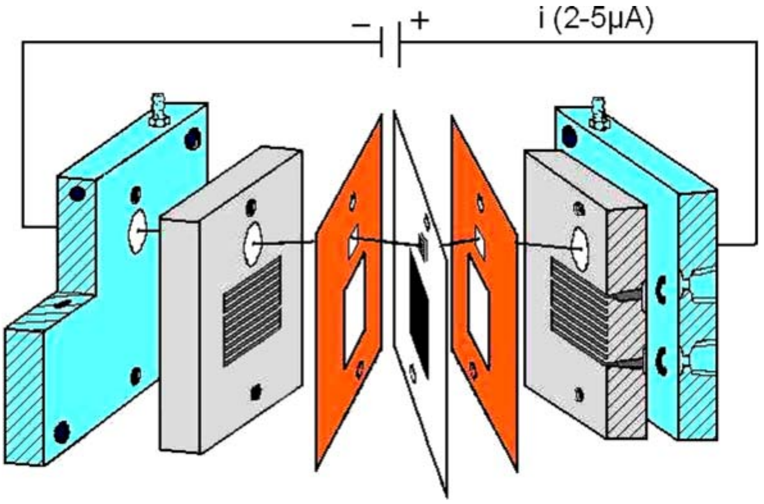

Fig. 2. Representation of the single PEM cell montage, showing the DHE and the connection to the external DC source.

3.1. *Equilibration of a mixed potential at the oxygen cathode of a PEM methanol fuel cell*

The open circuit potential of the gas-diffusion Pt/C cathode fed with humidified O_2 was measured as a function of time using the dynamic hydrogen reference electrode (DHE), described in the Experimental section. The experiment was started introducing pure water in the anode compartment and changing then to a methanol/water mixture. The results are given in Figure 3 for two different methanol concentrations. At the beginning, the open circuit potential of the oxygen cathode, at around 1.0 V vs DHE, is observed. This potential, corresponds to the undisturbed cathode, as the anode chamber is fed only with water. At a time indicated by the arrows in the figure (after about 750 s), the liquid at the anodic chamber was changed from pure water to either 0.4 M or 2 M CH_3OH solution, with a flow rate of 1 ml min^{-1} and 0.5 ml min^{-1}, respectively. After about 100 s, pronounced changes in the cathode potential are observed due to the methanol crossover. The delay in the response is mainly produced by the time needed for the new liquid to reach the cell. For the 2 M methanol solution, an initial steep fall in potential is observed. This is caused by the reduction of the oxygen adsorbate on the surface (see part 3.2 below). Then the potential of the freshly reduced surface increases towards more positive values (in direction to the thermodynamic oxygen potential). But, after reaching a maximum above 1.0 V, it decreases markedly, approaching a steady value, which depends on methanol concentration. Simultaneous methanol oxidation and oxygen reduction occur and the equilibrium situation is reflected in a stationary mixed potential at around 0.8 V, i.e. 0.2 V below the o.c. potential of the undisturbed cathode. For the 0.4 M CH_3OH solution the changes in potential are almost the same, but the initial negative transient is missing, probably due to a lower rate of the reducing processes at the surface for the lower methanol concentration. The use of air instead of oxygen gave a similar result.

The considerations above are supported by the fact that this dynamic behavior is also produced by ethanol crossover as shown in Figure 4, where the curve for the 2 M CH_3OH experiment is also plotted for comparison. As observed, ethanol, produces a more severe loss in potential at the cathode.

3.2. *Equilibration of methanol potentials at platinum electrodes without the influence of oxygen*

It is interesting to compare the effects described above with the response of an oxide covered Pt electrode in methanol solution in the *absence of oxygen*. For this experiment a three electrode electrochemical cell with smooth platinum as working electrode was used. The cell was filled with a 0.4 M CH_3OH/0.1 M H_2SO_4 solution. In order to start with a defined oxygen coverage of the surface, the electrode was first kept at a potential of 1.4 V RHE for 100 s. Then the circuit was opened and the potential–time response was recorded (Figure 5, curve (a)). The steep drop in potential confirms that methanol is able to rapidly reduce the

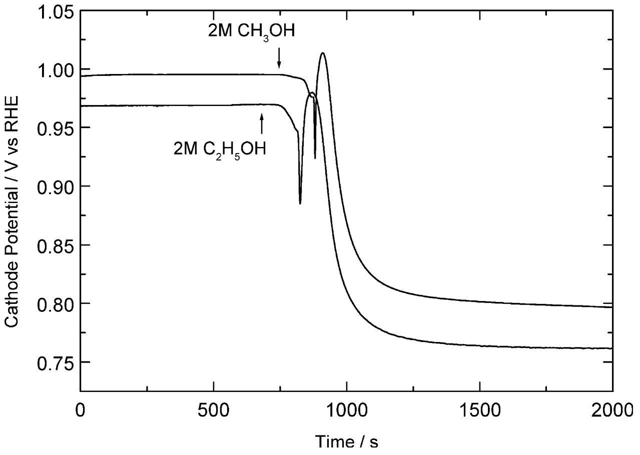

Fig. 4. Equilibration of the open circuit potential as in this figure but comparing the dynamic behavior resulting from a 2 M methanol solution with the effect of a 2 M ethanol solution.

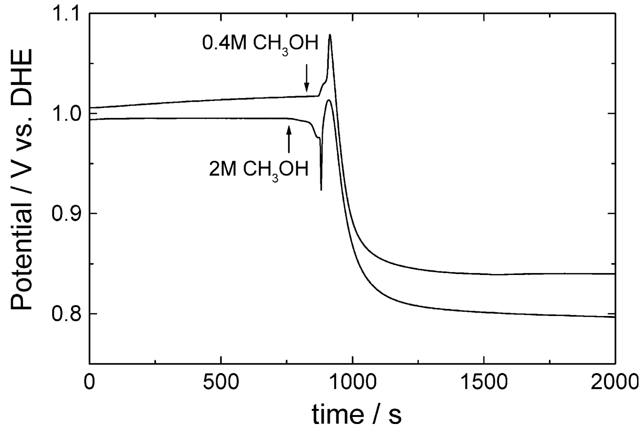

Fig. 3. Open circuit potential for an oxygen Pt/C cathode (4.6 cm^2) in a PEMFC (Nafion 117) at room temperature. Anode compartment, initially fed with pure water at 0.5 ml min^{-1}, then changed to 0.4 M and 2 M CH_3OH at the time indicated by the arrows. Cathode gas: humidified O_2 at 30 °C.

oxidized Pt surface. The potential changes are sharper for the more concentrated methanol solution, i.e., the rate of oxide reduction increases with methanol concentration (curve (b)). At the freshly reduced Pt surface, a rather low potential is initially established, which passes through a minimum between 0.2 and 0.3 V vs RHE and then approaches a steady value at 0.45–0.50 V. These values are much lower than the mixed potential observed in the presence of O_2. We just observe here, the open circuit potential of the smooth platinum electrode in the presence of the methanol. The result of a blank experiment is also shown (curve (c)). In this case, after polarizing the working electrode for 100 s at 1.4 V in the absence of methanol (0.1 M H_2SO_4) the current was interrupted and the open circuit potential was monitored. A very slow decay of potential is observed, giving values above 1 V after 10 min.

3.3. *Mixed potential during current load*

In Figure 6, the cell voltage and the electrode potentials for the PEM methanol fuel cell are shown (full symbols). For comparison, the same cell was operated using hydrogen at the anode and the cathode potential for this case is also plotted in Figure 6 (open symbols). The lower potential of the cathode in the methanol FC as compared to the H_2/O_2 FC, is due to the methanol crossover. This potential shift diminishes with increasing current, i.e., with higher methanol consumption at the anode surface. The cathode performance of the methanol cell approaches the behavior observed at the H_2/O_2 FC. As pointed out in the introduction and shown in Figure 1, a lowering of methanol crossover is produced with increasing current density. This decrease in crossover proves that the main mechanism is methanol diffusion along the concentration gradient. The drift of methanol by water and solvating protons, often invoked as the reason for crossover, seems to be of lesser importance.

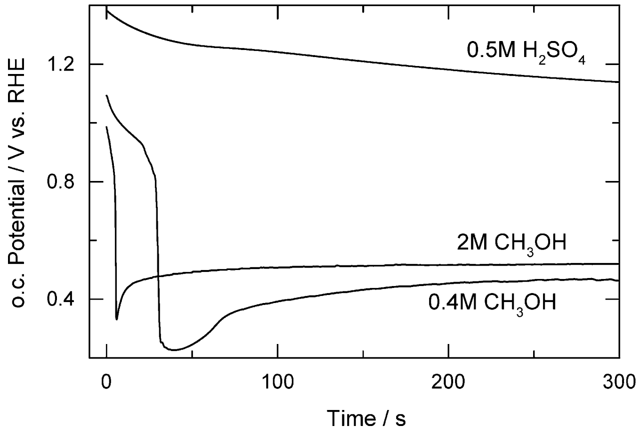

Fig. 5. Effect of methanol in solution on the open circuit potential of a smooth platinum electrode after polarization at 1.4 V for 100 (oxide layer formation), in (a) 0.4 M CH_3OH/ 0.1 M H_2SO_4, (b) 2 M CH_3OH/ 0.1 M H_2SO_4 solution; (c) blank experiment in 0.1 M H_2SO_4.

The effect on the cathode potential is demonstrated here for the first time. It is clear, that measurements of the cell voltage (also plotted in Figure 6) do not allow an effective evaluation of this effect.

3.4. *Heterogeneous chemical reaction of methanol and oxygen at the cathode*

Experiments using the cell shown in Figure 7 were undertaken in order to check whether carbon dioxide can be formed from CH_3OH and O_2 via a chemical reaction as indicated in Equation (3). Both working and counter electrodes were Pt/C gas-diffusion electrodes. As a reference, a hydrogen electrode in the supporting electrolyte solution was used. The back of the working electrode faces a small (2 cm^3) chamber from which a given gas can be supplied to the working electrode. The

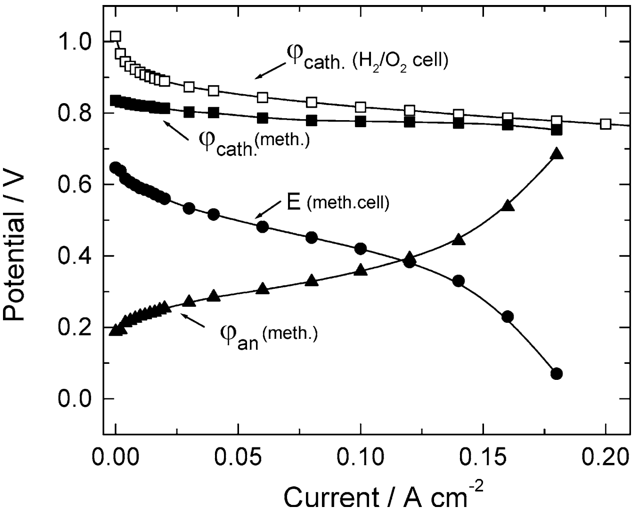

Fig. 6. Cell voltage, E_{cell}, and electrode potentials, φ, (vs DHE) as function of current density. Open symbols for cathode potential of a hydrogen/oxygen FC, closed symbols for methanol/oxygen FC. Flow of dry O_2 (1bar) at the cathode, flow of 0.4 M CH_3OH solution at a rate of 0.5 ml min^{-1}.

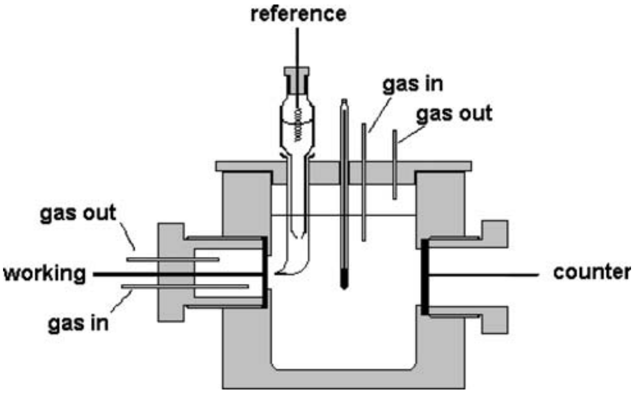

Fig. 7. Electrochemical cell for determination of CO_2, formed out of a purely chemical reaction at the surface of a 20% Pt/C gas-diffusion electrode (0.4 mgPt cm^{-2}).

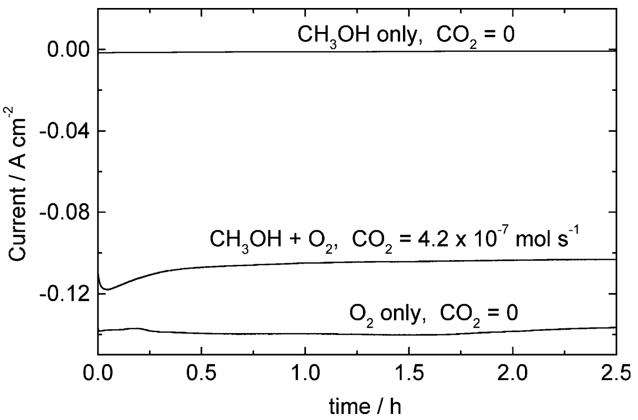

Fig. 8. Current vs time curves at 0.3 V vs RHE, measured in the cell of Figure 7. Using (a) 2 M CH_3OH + 0.5 M H_2SO_4, N_2 supplied to the gas chamber, (b) the same solution, but O_2 supplied to the gas chamber, (c) with 0.5 M H_2SO_4 (without methanol) oxygen supplied to the gas chamber; rates of CO_2 formation during the 2.5 h experiments in mol s^{-1} as indicated.

gas leaving the chamber flows through a 0.5 M $Ba(OH)_2$ + 0.1 M $BaCl_2$ solution, where CO_2, if formed, can be detected by precipitation of barium carbonate.

In the following experiment the cell was filled with 2 M CH_3OH + 0.5 M H_2SO_4 solution and the potential of the working electrode was kept at +0.3 V RHE while N_2 was supplied to the gas chamber. As shown by the curve (a) in Figure 8, the current measured during 2.5 h was close to zero and no CO_2 formation was observed. This result is as expected since at 0.3 V no methanol electrooxidation occurs. In a second run the same solution was used and O_2 was supplied to the gas chamber. A cathodic current due to oxygen reduction at 0.3 V was observed (curve (b) in Figure 8). In this case CO_2 was formed and the analysis of the solution indicated a rate of 4.2×10^{-7} mol s^{-1}. Thus, a purely chemical reaction between CH_3OH and O_2 is responsible for the CO_2 formation, since curve (a) shows that methanol cannot be electro-oxidized at the applied potential. The gas consumption via the chemical reaction lowers the amount of O_2 available for the electroreduction to H_2O. The corresponding loss in current can be established by comparing with the current for oxygen reduction measured in the absence of methanol (curve c in Figure 8). Here the current density is ca. 30 mA cm^{-2} higher than in curve (b), and in this case no CO_2 is produced.

4. Conclusions

Using an *in situ* DHE reference, the effect of crossover on the cathode potential can be separated from the overall reduction in cell voltage. The cathode potential under load depends on methanol concentration via the establishment of a mixed potential and the consumption of oxygen in a heterogeneous chemical reaction.

It is shown that the main effect of the methanol transport through the membrane is determined by diffusion along the concentration gradient; the transfer of methanol via the drift of water and solvated protons is of minor importance.

The negative shift of the cathode potential, up to 200 mV, and the consumption of methanol and oxygen via the electrochemical and chemical reaction occur under open circuit conditions. Crossover of ethanol as fuel shows even a stronger negative effect on the cathode potential.

The purely chemical reaction of methanol and oxygen to CO_2 at the platinum surface of the cathode, as quantitatively measured at 0.3 V, lowers the rate of oxygen reduction by more than 20%.

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