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A solid polymer electrolyte-based ethanol gas sensor

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Platinum-based membrane-electrode assemblies have been prepared to make electrochemical measurements of breath alcohol levels. Measurements are made by using a solid polymer electrolyte ethanol–air fuel cell. A diffusion membrane is placed in the feed compartment to limit the cell response by ethanol diffusion. The cell is found suitable for the realization of gaseous ethanol sensors. Reproducible cell responses are obtained over several hundreds of cycles. The cell current is proportional to the ethanol concentration in the feed compartment and to the thickness of the diffusion membrane. The transient response of the cell is simulated using Fickian phenomenological equations. Calculated results are in good agreement with experimental data.

1. Introduction

Measurements of alcohol blood levels are becoming prevalent in order to enforce drinking and driving laws. While analysis of blood samples is generally required for conviction in a law court, routine analysis requires the use of portable and easy to operate devices which can be used directly in police cars. The measurement of alcohol concentration in the breath is a valid method because the alcohol concentration in alveolar air is proportional to the alcohol concentration in blood. The ratio which is 2100 to 1 is well established.

At present, in France, ethanol concentration in the blood is limited to 0.5 g dm^{-3}. Methods used for analysing breath samples are based on the colour change of an indicator chemical reacting with ethanol. These methods suffer from a lack of accuracy and the gas analyser cannot be used more than once. This results in an elevated price and the chemicals must be disposed of after use. There is a need for more convenient devices.

Among the electrochemical techniques which can be used for measuring alcohol levels in breath samples, the ethanol-air fuel cell based on SPE® (Solid Polymer Electrolyte, registered trademark of Hamilton Standard, Windsor Locks, USA) technology has not been investigated so far. The SPE® cell consists of two noble metal electrodes deposited on either side of a proton conducting membrane, usually Nafion® (Nafion is the registered trademark of E.I. du Pont de Nemours, Wilmington, DE, USA, for its perfluorosulfonic acid materials). Noble metal based electrodes have to be used because of the high acidity of the membrane. The SPE® concept can be used in many applications. Papers related to hydrogen–oxygen fuel cells [1–4], pure water electrolysis [5–8], and ozone generation [9, 10] provide a large body of information about this technique. A review of SPE® applications is given in [11].

In this paper, the possibility of using a platinum-based SPE® composite for the development of an ethanol gas sensor is investigated. To remain as close as possible to the conditions of the air expelled by breathing, the cell is fed with an ethanol–water–air mixture by using standardized alcoholic solutions. A diffusion membrane is placed in the feed compartment to limit the cell response by ethanol diffusion. The diffusion membrane is a hydrophobic PTFE film to avoid water condensation.

2. Experimental details

2.1. *Materials*

Nafion® 117 (equivalent weight 1100 and dry thickness 0.178 mm) perfluorosulfonic membranes (du Pont de Nemours) were used as the solid polymer electrolyte. $[Pt(NH_3)_4]\,Cl_2 \cdot H_2O$ (Johnson Matthey) was used to prepare the plating solutions. The reducing agent was sodium borohydride (Merck). Pure water (resistivity of 18 MΩ cm at 20 °C) was used for the preparation of the plating and alcoholic solutions. PTFE films (Gore-Tex® from Core Co. of thickness 60 μm, porosity 78% and with an average pore diameter 0.2 μm) were used as diffusion membranes. Standardized alcohol solutions were prepared from 99.9% ethanol (Prolabo).

2.2. *Preparation of the composite*

The platinum composite was prepared as detailed elsewhere [12]. Briefly, the Nafion® membrane initially in the H$^+$ form was soaked for 15 min in a 10^{-2} M aqueous solution of platinum tetramine. The

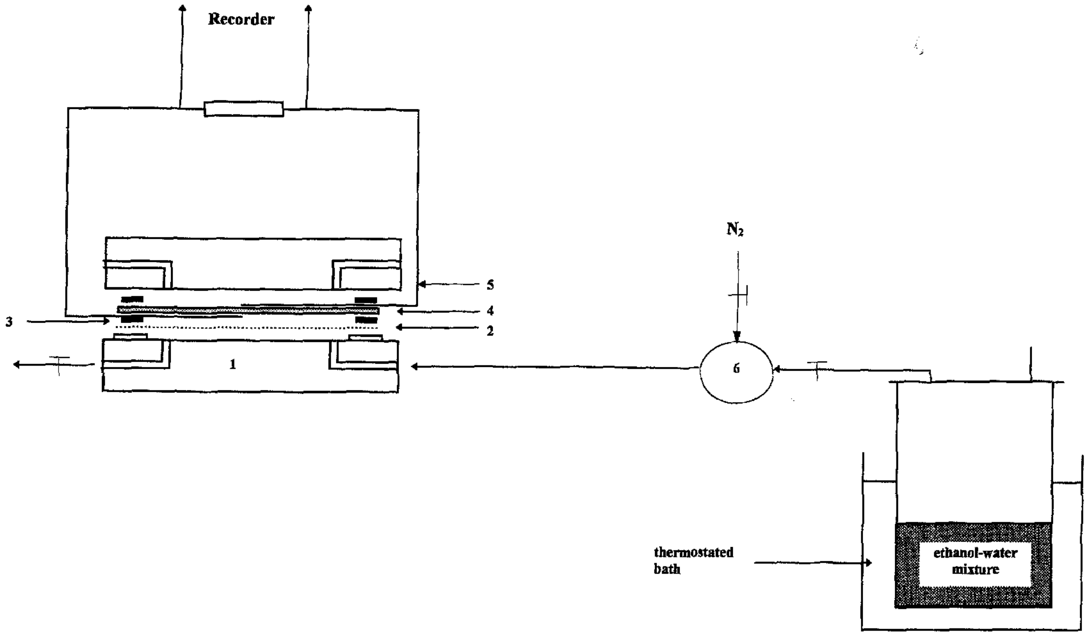

Fig. 1. Schematic diagram of the cell used for the electrochemical measurements. (1) Polysulfone® frame; (2) Gore-Tex® diffusion membrane; (3) Teflon® gasket; (4) SPE® composite; (5) platinum wire; (6) volumetric pump.

membrane was then washed thoroughly with water and immersed for 2 h in a 3 g dm^{-3} NaBH$_4$ reducing solution. The same operation was repeated twice to increase the amount of platinum deposited. Membrane-electrode composites with typical loadings of 1.5 mg Pt cm^{-2} were obtained. The composites were then equilibrated in a 1 M sulfuric acid solution to remove the remaining impurities resulting from the preparation process, washed thoroughly with pure water, and mounted in the test cell.

2.3. *Test cell*

Measurements were made in the cell pictured in Fig. 1. The diffusion membrane was mounted in the feed compartment against the SPE® composite. Platinum wire was used as current collector. Breath samples were simulated by passing air through standardized alcoholic solutions placed in a thermostated bath. The bath temperature was set to 34 °C, in order (i) to remain close to the human body temperature, and (ii) to monitor the partial pressure of ethanol above the standardized solutions. Samples (1.0 cm^3) of the gaseous mixture above the solution were injected into the feed compartment (0.6 cm^3) of the test cell, at the back of the diffusion membrane, by using a volumetric pump. The time variation of the cell current was then recorded. At the end of the test, the cell was short circuited until the signal returned to the base line and the feed compartment was cleaned with a flow of nitrogen.

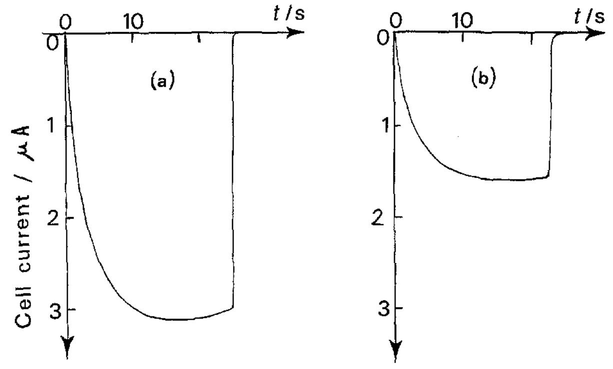

Fig. 2. Effect of ethanol concentration on the cell response (data were collected with one diffusion membrane).Ethanol concentration: (a) 1 g dm^{-3}; (b) 0.5 g dm^{-3}.

2. Results and discussion

Figure 2 shows typical cell responses obtained for two different ethanol concentrations. A twofold decrease in ethanol concentration results in a twofold decrease in the cell response. The steady state current is obtained in about 20 s, thus permitting rapid analysis. Once the cell is short-circuited, the signal returns to the base line within a few seconds, enabling successive tests. No response was obtained by injecting water–air mixtures. The value of the resistor used to record the transient current did not significantly change the cell response, suggesting that electrode processes are rate limiting. Individual electrode potentials were not measured.

To check the reproducibility of the signals, several hundred tests were performed. Figure 3 shows the cell response obtained for four inputs of the gaseous mixture at different time. The cell response was found reproducible within ±2%. A lack of reproducibility was however observed over a period of one week, independently of the number of tests performed. This change in the cell response was attributed to the dehydration of the Nafion® membrane. Poisoning of the platinum electrode by the products resulting from ethanol oxidation may also explain the changes in the cell response. These problems were solved by immersing the composites in 1 M sulfuric solutions.

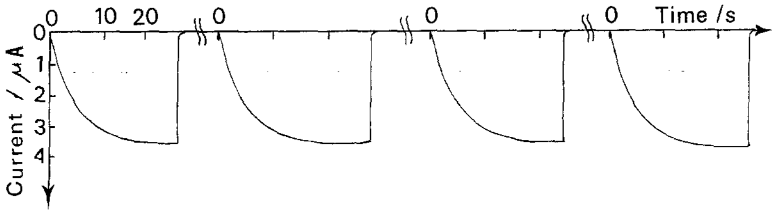

Fig. 3. Cell response to four inputs of an ethanol-air mixture; (a) 1st input; (b) 10th input; (c) 100th input; (d) 500th input. Ethanol concentration = 1 g dm^{-3}.

The proportionality seen in Fig. 2 between cell current and ethanol concentration is observed in the concentration range 0–2 wt %. This linear relation suggests that the cell current is limited by ethanol diffusion across the diffusion membrane. But such relationship can also be attributed to a first order rate in ethanol [13, 14]. To check whether diffusion of ethanol is rate limiting, the cell response was measured by stacking from 1 to 9 diffusion membranes. Results obtained are shown in Fig. 4. Transient cell responses obtained by using from 1 to 9 diffusion membranes are shown in Fig. 4(a). Form Fig 4(b) it appears that the linear relationship between the cell current and the thickness of the diffusion membrane appears only when at least four diffusion membranes are used. With less than four diffusion membranes, the cell response is limited by electrode kinetics. This case is less favourable since any modification of the electrode surface (e.g., air contamination) will result in significant changes in the cell response. This is especially true when platinum is used as electrocatalyst because of its high sensitivity to poisoning.

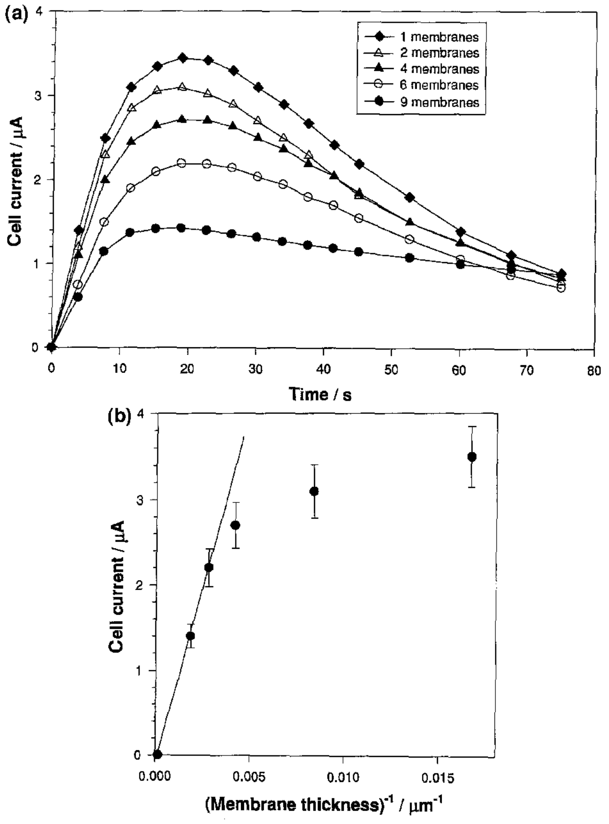

Fig. 4. (a) Cell current against time obtained by stacking up to nine diffusion membranes: (●) 9, (○) 6, (▲) 4, (△) 2 and (◆) 1 membrane. (b) Peak current against the thickness of diffusion membrane.

With nine diffusion membranes, a linear relationship is also observed between cell current and ethanol in the concentration range 0–2 wt %. But in this case, the linear dependence is due to ethanol transport across the diffusion membrane.

3. Analysis of the cell response

The transient response of the cell has been simulated to confirm that ethanol diffusion across the Gore–Tex® membrane is rate controlling.

3.1. *Description of the model*

The test cell is represented in cross-section across the thickness (Fig. 5). The transient response of the cell is simulated assuming a limitation by transport of gaseous ethanol in the diffusion membrane as suggested by the experimental results. Gas transport across the diffusion membrane follows Fick's second law:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (1)$$

The time variation of the ethanol concentration in the feed compartment is obtained by summing the instantaneous ethanol fluxes at $x = 0$:

$$C(t) = C_o - \frac{S}{V}D\int_0^t \frac{\partial C}{\partial x}|_{t,x=o}\mathrm{d}t \qquad (2)$$

where S is the surface of the diffusion membrane contacting the feed compartment and V is the volume of the feed compartment.

The Instantaneous current of the cell is given by

$$i(t) = -nFD\frac{\partial C}{\partial x}|_{x=L} \qquad (3)$$

3.2. *Electrode processes*

Several papers have appeared in the literature over the past decades concerning the electrooxidation of methanol [15–20] and ethanol [13, 21] on platinum. Following the work of Rightmire *et al.* [13], electrooxidation of ethanol at platinum in acidic medium is assumed to be a four electron process leading to the formation of acetic acid:

$$C_2H_5OH + H_2O \longrightarrow CH_3COOH + 4H^+ + 4e^-$$

The counter reaction at the positive electrode is not considered in this work but is assumed to be the

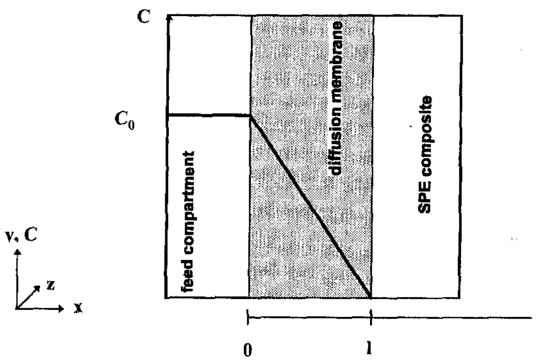

Fig. 5. Cross-section through the test cell.

reduction of oxygen leading to the formation of water:

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

Results obtained with hydrogen–oxygen SPE® fuel cells have shown that the platinum–air electrode can deliver several tens of mA cm^{-2} with relatively low overvoltages [7] whereas ethanol oxidation is significantly slower [15]. It is therefore assumed that oxygen reduction is not rate limiting.

3.3. *Boundary conditions and numerical details*

Ethanol concentration in the gas phase at equilibrium with a given standard solution is taken from [22]. The strong nonideal behaviour of diluted aqueous ethanol solutions is taken into account. At 34 °C, ethanol concentration in the gas phase at equilibrium with a 1 g dm^{-3} aqueous solution is 0.43 mg dm^{-3} of gas.

In the calculations, the ethanol concentration in the feed compartment varies with time while the concentration on the other side of the diffusion membrane is set equal to zero. No special assumption was made concerning the equilibrium in the feed compartment–diffusion membrane interface because of the relatively high porosity of the diffusion membrane. Dilution of the feed mixture by the remaining nitrogen in the feed compartment is taken into account by considering the input and feed compartment volumes.

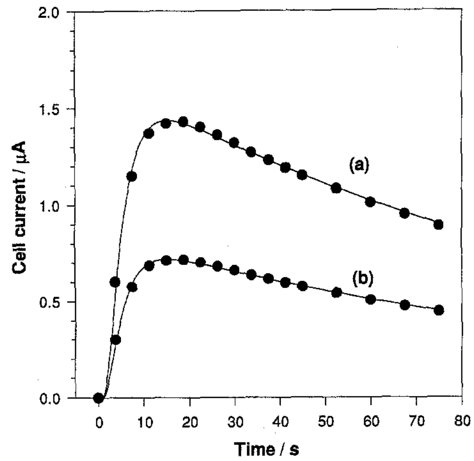

Fig. 6. Analysis of the transient response of the cell. Comparison of experimental (●) and calculated (—) data. Data were collected with nine diffusion membranes. Ethanol concentration: (a) 1.0 g dm^{-3}; (b) 0.5 g dm^{-3}.

The solutions $i(t)$ to the model were obtained numerically. Numerical analysis was used because ethanol concentration in the feed compartment varied with time. The derivatives of first and second order were approximated using the finite difference method:

First order derivative

$$\frac{\partial C}{\partial x}\Big|_t = \frac{C(x+1,t) - C(x,t)}{\Delta x} \tag{4}$$

second order derivative

$$\frac{\partial^2 C}{\partial x^2}\Big|_t = \frac{C(x+1,t) + C(x-1,t) - 2C(x,t)}{(\Delta x)^2} \tag{5}$$

The grid was refined until stable values were obtained.

3.4. *Comparison of experimental and calculated results*

Figure 6 shows the measured and calculated transient response of the cell fed with two different ethanol concentrations. The experimental set of data is taken from Fig. 4(a), with nine diffusion membranes. Adjustment between the measured and calculated sets of data was obtained with a diffusion coefficient of $1.2 \times 10^{-4}\,cm^2\,s^{-1}$. For comparison, the diffusion coefficient of methanol in Gore-Tex® membranes is reported to be about $4 \times 10^{-3}\,cm^2\,s^{-1}$ at 298 K [23].

The fit between measured and calculated data is satisfactory. At the foot of the curve, a sharp rise is observed experimentally. The calculated curves show an inflexion point because it is assumed, in the initial conditions, that ethanol concentration is equal to zero at each point across the membrane thickness. A time lag is therefore required before the first molecules of ethanol reach the platinum electrode. Experimentally, between two consecutive experiments, it may be assumed that a certain amount of ethanol remains in the diffusion membrane and the initial conditions are slightly different.

After a maximum value reached in about 20 s, the current begins to decrease. The model accounts for this observation which is due to the time decrease of the ethanol concentration in the feed compartment.

4. Conclusions

Platinum-based SPE® composites have been found suitable for the realization of ethanol gas sensors. Ethanol oxidation is rate-controlling, with a first order rate in ethanol. By using a diffusion membrane of adequate thickness, it is however possible to limit the cell response by ethanol diffusion. Reproducible cell responses are obtained and the peak current is proportional to the ethanol concentration in the standardized solutions.

The major problems encountered in testing the captor were (i) the progressive dehydration of the Nafion® membrane, and (ii) the slow but steady poisoning of the cell, probably by the products of ethanol oxidation. This results in a change of the base line and an increase in the time required for the cell voltage to return to zero. These problems were solved by immersing the composites in a sulfuric acid solution.

By using real breath samples, the rate of poisoning was found greater but the general characteristics of the captor remained unchanged. More stable results are expected by using platinum-ruthenium electrodes because ruthenium is less prone to poisoning.

Acknowledgements:

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