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A Nafion®-based co-planar electrode amperometric sensor for methanol determination in the gas phase†

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Abstract. A co-planar electrode device, fabricated with all electrodes (working, counter and reference) on the same face of a Nafion® polymer electrolyte membrane, is proposed for the amperometric detection of gaseous methanol using Pt as the working electrode. Clear voltammetry is obtained for methanol oxidation from its vapours in equilibrium with methanol aqueous solutions, both in the absence and presence of oxygen in the gas stream. Using an appropriate pulse sequence to keep the indicator electrode active, methanol vapours in the 1–13 Torr partial pressure range (in equilibrium with methanol aqueous solutions in the 1–10% w/w concentration range) could be determined, in a constant potential, amperometric mode. The methanol detector could be operated both in a nitrogen stream and (in what is essential for practical applications) in an air atmosphere too, with estimated detection limits of 1·2 and 1·4 Torr respectively.

Keywords. Electrochemical sensors; methanol; polymer electrolytes; Nafion®.

1. Introduction

The determination of dissolved methanol in a wide concentration range is essential for a variety of cases ranging from plant, foodstuff and drug trace analysis to monitor industrial process streams and fuel cell feeds. The determination of methanol vapours in equilibrium with methanol solutions provides an alternative way to monitor methanol in many of the above applications.

Examples of methanol vapour sensors include mainly conductivity sensors, based either on polypyrrole-based devices with detection limits in the 0·1–10 Torr range[1,2] or on semiconducting oxides with detection limits down to 0·1 Torr,[3] but also chemically modified quartz microbalance sensors with detection limits lower than 0·1 Torr.[4] Although galvanic ethanol sensors used for breath alcohol levels testing have long been available (e.g. the 'breathalyzer'-see for example ref. 5), alcohol electrochemistry on Nafion®-based electrode assemblies has mainly focused on fuel cell research aspects (even when methanol concentrations down to 0·3 Torr were used see for example ref. 6). Very few all-solid Nafion®-based alcohol vapour amperometric sensors have appeared in the literature and as an example a fuel-cell type ethanol sensor[7] and a Nafion®-covered microelectrode methanol sensor[8] can be mentioned here.

Commercially available amperometric gas sensors usually involve a metallised gas-permeable porous material in contact with an internal electrolyte (see for example, the early refs 9, 10). This type of design has been found to lead to slow response times due to gas diffusion through the porous medium (which is also flooded to a certain extent with the liquid electrolyte) and to limited lifetime, due to occasional drying out of the liquid electrolyte film present on the internal side of the membrane. The use of a solid ionic conductor as an electrode substrate allows the active electrode material to be directly exposed to the gas sample, improving the response time and sensitivity of the device.[11–13] All-solid electrochemical gas sensors, where the solid ionic conductor e.g. Nafion®,[14,15] antimonic acid[16,17] or Zr phosphates and phosphonates[18,19] is sandwiched between the working and counter electrodes, have already been tested.

An alternative design for all-solid amperometric gas sensors has been proposed by Hodgson *et al*[20] for SO_2 determination and Wallgren *et al*[21,22] for O_2

†Dedicated to the memory of the late Professor S K Rangarajan

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determination. In that design all the electrodes are deposited or attached on the same face of the ionic conductor in the form of continuous metal layers, separated by an uncovered strip of the electrolyte, and in direct contact with the gas sample. It has been suggested, that due to the non-porous nature of the electrodes and the arrangement of that design, the gas is reacting not only at the large solid electrolyte membrane/metal interface, after diffusing through the polymer membrane, but also (under high mass tranfer rates) at the line formed between the working electrode metal layer, the solid electrolyte and the gas sample. Potential advantages of this co-planar electrode design include faster response times and higher sensitivities per useful electrode area due to the additional contribution to the signal by the electrode perimeter. The mass-transport rates of the gas to the sensing electrode are higher at those locations since no significant membrane or liquid film barrier are expected at that locus of the electrode reaction. Furthermore, smaller quantities of precious metal catalyst could be used for the working electrode as the reaction is preferentially occurring at the edge of the deposit and hence a thin line of catalyst should suffice. Finally, the labour-intensive stacking steps required for the fabrication of sandwich-type designs could be avoided. The use of Nafion® as the ionic substrate in the new sensor design is a convenient first choice for a material since there is an extensive literature regarding oxygen reduction at the Pt/Nafion® interface (see refs 23–26, to mention a few).

In this paper, we present results aiming to expand the use of the co-planar electrode Nafion®-based sensor in the amperometric detection of gaseous methanol, using Pt as the working electrode. The high mass transfer rates occurring at this device are expected to have an additional advantage in the case of amperometric methanol detection in oxygen containing gas streams. Oxygen is known to interfere with methanol electrochemistry on Pt in acid since the onset potential of its reduction coincides with the onset potential for methanol oxidation.[27] Although methanol oxidation is known to be always under kinetic control and thus not affected by an increase in mass transfer rates, the mixed control region of oxygen reduction is expected to shift to more negative potentials in that case and the methanol oxidation currents do not need background correction in oxygen-containing samples.

The specific objectives of this paper have been (i) the electrochemical characterization of the Pt/Nafion® all-solid device by means of Pt surface electrochemistry, (ii) the voltammetric study of methanol oxidation from methanol vapours in equilibrium with aqueous methanolic solutions in the absence and presence of oxygen and (iii) the amperometric determination of methanol vapours in equilibrium with aqueous solutions of methanol in the 1–10% w/w (0·3–3 M) concentration range (corresponding to a methanol vapour pressure range of ca. 1–13 Torr),[28,29] both in the presence and absence of oxygen.

2. Experimental details

2.1 *Planar sensor fabrication*

Nafion® membranes (Nafion® 117 protonic form, 180 μm thick, Aldrich) were washed thoroughly with distilled water before stored in distilled water. A piece of membrane, of typical dimensions of 40 × 40 mm, was cut when required and dried using lint-free tissue paper prior to use. The metal layers of the working and counter electrodes (WE and CE) were vacuum-deposited onto the polymer substrates using varying numbers of deposition cycles with a PS3 E500C Series 3 Polaron sputter-coater. A coating step of 1*s* gave a ca. 1·5 nm thick platinum layer and the final Pt layer thickness of the sensors was 360 nm. A 0·5 mm thick stainless steel sheet with machined openings was used as a mask during vacuum metal deposition of the electrode layers. A piece of the membrane with the mask was attached tightly to a 40 mm square stainless steel slide before being placed in the sputtering chamber. Electrical contacts between commercial insulated wires and the metal deposits were made either with the help of Ag-loaded epoxy resin (RS) with Araldite epoxy resin (RS) providing mechanical strength to the contact or with crocodile clips in contact with small pieces of aluminium foil pressed onto the electrode surfaces. In the last case the aluminium foil was acting as a current collector. For three-electrode experiments (majority of experiments) a strip of screen-printed Ag/AgCl electrode was placed between the working and counter electrode layers and pressed onto the membrane at ca 1 mm distance from the working electrode with a crocodile clip. A top-view drawing of the device used for three-electrode experiments is given in figure 1. The lengths of the working electrode (WE) and the counter electrode (CE) parallel to each other are 5 mm and 30 mm respectively and these were separated by a Nafion® path 5 mm wide.

2.2 *Electrochemical equipment*

For three-electrode experiments two different potentiostats were used. For preliminary cyclic voltammetry and oxygen concentration step experiments, a Radiometer Voltamaster 21® potentiostat, interfaced to a 486 PC by a Duo 18 A/D converter, was used. The majority of experiments were performed with an Autolab PGSTAT30 potentiostat controlled by GPES software version 4.5 for Windows 95.

2.3 *Cell and gas mixtures*

Experiments were carried out in a 500 ml glass cell, equipped with a wall-jacket and a gas inlet and outlet. The temperature of the cell was controlled by circulating water in the jacket from a thermostatic bath (25°C). The composition of the atmosphere in the cell was maintained by gas feeds (of either laboratory compressed air with 21% oxygen or pure nitrogen supplied by Air Products Ltd, 99·998%) that were first passed through two Dreschler-type flasks at a ca 100 ml min^{-1} flow rate. To achieve 100% relative humidity, the distilled water was used in both flasks (humidity was confirmed with a TESTO6400 RS hygrometer). For methanol vapour determination experiments the down-stream Dreschler-flask contained 1, 2, 3, 4, 6 and 8·5% w/w methanol too (corresponding to 0·3, 0·6, 0·9, 1·2, 1·8 and 2·6 M methanolic solutions respectively). In this way the methanol vapour partial pressure in equilibrium with its aqueous solution is varied accordingly staking up values of 1·2, 2·7, 4·4, 6·1, 8·9 and 11·7 Torr respectively, as estimated from saturated methanol vapour pressure x-y-T data.[28,29]

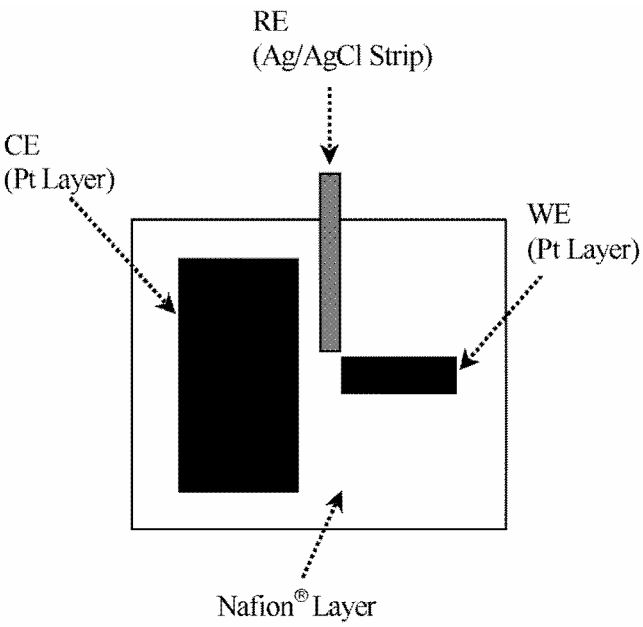

Figure 1. Schematic representation (top-view) of the Pt (vs Ag/AgCl)/Nafion®/Pt planar electrode device.

3. Results and discussion

3.1 *Surface electrochemistry of Pt working electrode layer in contact with hydrated Nafion®*

Figure 2 presents a fast potential sweep voltammogram (50 mV/s) recorded at a Pt (vs Ag/AgCl)/Nafion®/Pt-device in a water-saturated nitrogen atmosphere. The general features of hydrogen adsorption/desorption and oxide formation/stripping, that are characteristic of platinum surface electrochemistry can be seen. Compared to typical voltammograms recorded in sulfuric acid, the peaks for hydrogen adsorption/desorption are not clear but this is a common finding of the enormous Pt/Nafion® literature. For example, Mitsushima *et al*[30] who studied oxygen reduction at Pt microelectrodes in various polymer electrolytes, reported similar features that they attributed to partial polymer blocking of the hydrogen adsorption sites.

From the cathodic charge corresponding to H-adsorption between +0·2 V and –0·2 V vs Ag/AgCl (which is calculated from figure 2 to be 160 μC) and the charge reported to correspond to a monolayer of H-adsorption on 1 cm^2 of Pt 210 $\mu C/cm^2$,[31] it follows that the effective electrode area is 0·761 cm^2. The fact that this value is similar to the nominal WE

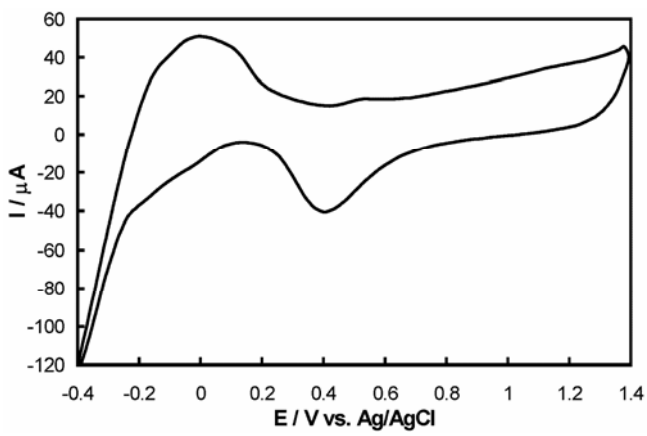

Figure 2. Voltammogram recorded at 50 mV/s in a water-saturated nitrogen stream at Pt (vs Ag/AgCl)/Nafion®/Pt planar device.

area of 0·625 cm^2 indicates that the sputtered Pt layer on Nafion® is smooth (as confirmed also by SEM and STM measurements which is not shown here) and that, despite the current distribution inhomogeneity of the co-planar electrode arrangement, most of this film is electroactive in the current range studied.

3.2 *Methanol oxidation and determination from nitrogen-containing streams*

Figure 3 presents cyclic voltammograms recorded at 5 mV/s in 6% and 4% w/w methanol/water–saturated nitrogen streams passing over the Pt/Nafion® detector, together with the background voltammogram of a pure water-saturated nitrogen stream. It can be seen that the positive-going scan shows the overall methanol oxidation picture of dissolved methanol oxidation.[32] A bell-shaped peak was recorded at ca. +0·6 V vs Ag/AgCl corresponding to methanol oxidation on a Pt surface partially covered with PtO surface oxides and a voltammetric wave at more positive potentials, corresponding to methanol oxidation on a surface completely covered with oxides. During the reverse negative-going potential sweep, methanol oxidation only starts to occur when the oxide begins to strip-off at potentials more negative than +0·5 V, giving rise to an oxidation peak at ca. +0·3 V. Another feature of the voltammogram is the increased oxidation currents when compared to similar dissolved methanol sensors; this was also reported by Nakajima and Kita.[6] They used metal electrodes bonded to solid polymer electrolyte membranes to study methanol vapor oxidation at various partial pressures from 0·3 to 6 Torr and found oxidation currents of 10^3 times larger than the equivalent dissolved methanol sensor.

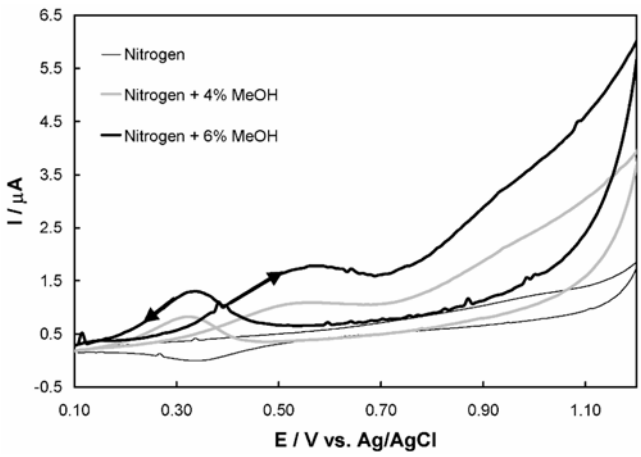

Figure 3. Voltammograms recorded at 5 mV s^{-1} in a pure water–saturated nitrogen stream and in 4% and 6% w/w methanol/water solution-saturated nitrogen streams, at a three-electrode Pt (vs Ag/AgCl)/Nafion®/Pt planar device.

Although the voltammetric peak at +0·6 V did depend on methanol concentration, this variation showed poor linearity and furthermore its height was not stable with time. It is well-known that the oxidation rate of methanol on a clean platinum anode is initially large but decays quickly due to partial oxidation products, which build up on the surface and effectively poison the electrode. Pletcher *et al*[32] in their experiments used cycling or pulsing of the electrode through the potential range where platinum oxide is formed to activate the platinum surface. Fedkiw *et al*[33] introduced a pulsed potential measurement of methanol oxidation, which on average increased the currents by nearly two orders of magnitude above the steady-state current at the same potential. To avoid current deterioration during the continuous monitoring at constant potential, a potential sequence consisting of +1·6 V for 10s (cleaning pulse)/0 V for 120 s (equilibration pulse)/+0·6 V for 180 s (measurement pulse) was applied to the electrodes. During the cleaning pulse all adsorbed organic intermediates and products are expected to be oxidized and removed from the surface while the onset of oxygen evolution should offer mechanical cleaning too. The equilibration pulse at 0 V is necessary for the stripping-reduction of Pt oxides formed during the cleaning pulse and for methanol adsorption on a clean Pt surface. Finally, the measurement pulse was chosen in the potential range of the first oxidation peak which is generally more reproducible and shows a stronger variation with concentration. The resulting current-time transients seen in figure 4 were reproducible on periodic application of the sequence for at least 8 h. A variation of the steady state current from the background value is observed for methanol concentrations in the 2–8·5% w/w range. The Inset to figure 4 shows that for gaseous methanol oxidation at the Pt/Nafion® interface in nitrogen, a near-linear correlation exists between the oxidation current at +0·6 V (collected 120 s after the application of the pulse) and methanol concentration. The detection limit estimated by repeating 5 measurements at the 2% w/w level was 1% w/w (corresponding to 1·2 Torr of methanol vapour pressure).

3.3 *Methanol oxidation and determination from air-containing streams*

Before probing any possible interference of oxygen with methanol determination, we carried out preliminary experiments in air streams in the absence of methanol. Figure 5(a) shows slow potential sweep (5 mV s^{-1}) cyclic voltammograms in water saturated air and nitrogen streams in the potential range that methanol oxidation is studied. It is seen that at potentials more negative than ca. +0·4 V vs Ag/AgCl a clear rise of the cathodic current is observed. Figure 5(b), presenting similar voltammograms, shows that, when the negative potential limit is extended to –0·35 V, then a well-defined S-shaped voltammogram is observed, typical for oxygen reduction at Pt in an acidic environment (see ref. 34). It is seen that, unlike Au where the oxygen reduction current in the planar sensor arrangement is never under mass transfer control,[21,22] in the case of a Pt WE, where oxygen reduction kinetics are faster, a limiting current is observed, revealing the existence of a thin mass transfer barrier (either a liquid hymen at the WE/Nafion®/gas line interface or the Nafion® membrane underneath the WE deposit).

The limiting current recorded was proven to depend linearly on oxygen concentration in the stream within the 4–21% v/v range (results not shown). However, the oxygen reduction voltammetric wave at this Nafion®-based device is shifted to more negative potentials when compared to the similar one in an acidic aqueous environment[34]). This can be attributed to a hindrance of oxygen reduction kinetics at the organic moieties of the Pt/Nafion® interface and/or to high mass-transfer rates (due to the additional contribution of gas phase diffusion to the perimeter of the electrode layer) which in turn shift the mixed control region of the wave to higher overpotentials. Whatever the origin of this shift, it is expected to be beneficial for the simultaneous study of methanol oxidation that starts to occur at potentials more positive than ca +0·30 V vs Ag/AgCl.

Figure 6 presents voltammograms in water-saturated air and air + methanol streams and reveals a clear signal for methanol oxidation above the background current in air samples containing methanol vapours. The background reduction current (observed at potentials less positive than +0·50 V) is now higher than that for nitrogen streams (see figure 3), due to oxygen reduction. This current only affects the methanol oxidation picture during the reverse, negative-going potential scan, suppressing

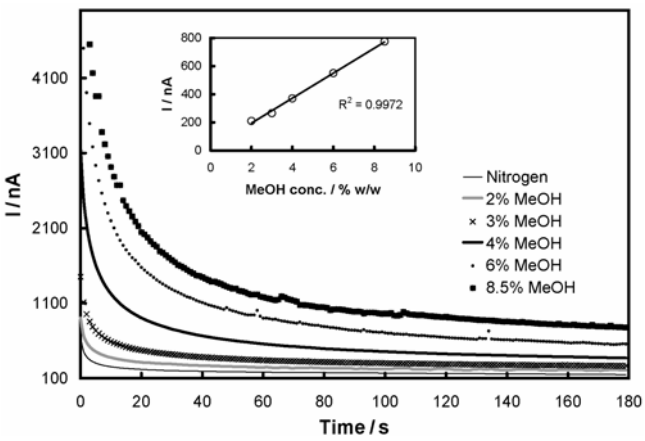

Figure 4. Current-time transients at Pt (vs Ag/AgCl)/Nafion®/Pt planar device at the measurement potential of +0·6 V (within the pulse sequence used) in water–saturated nitrogen and nitrogen + methanol vapour streams. Inset: Variation of the currents collected at 120 s vs methanol concentration in the gas equilibration solutions.

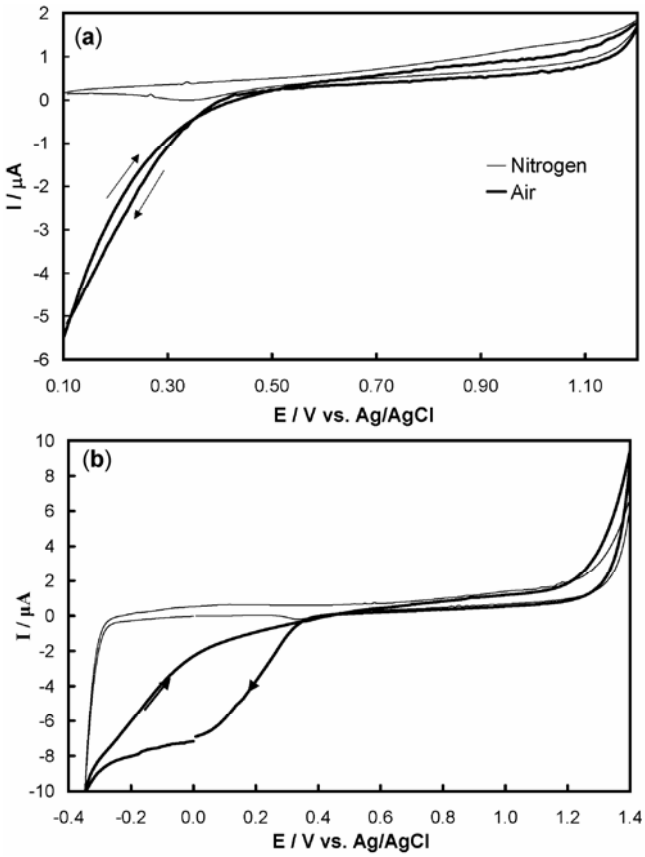

Figure 5. Voltammograms recorded at a three-electrode Pt (vs Ag/AgCl)/Nafion®/Pt planar device, at 5 mV s^{-1} sweep rate, in water–saturated air and nitrogen streams (**a**) in a limited potential window and (**b**) in an extended potential range.

the peak usually observed on an oxidefree Pt surface (see figure 3). The interference of oxygen reduction background currents means that recorded voltammograms need to be background-corrected (inset of figure 6) if the reverse peak is to be identified. However, from an electroanalytical point of view it is important that the methanol oxidation current at potentials above ca. +0·50 V is hardly influenced by oxygen reduction. Apart from the dependence of oxygen reduction on increased mass transfer rates discussed above, the separation of the two signals

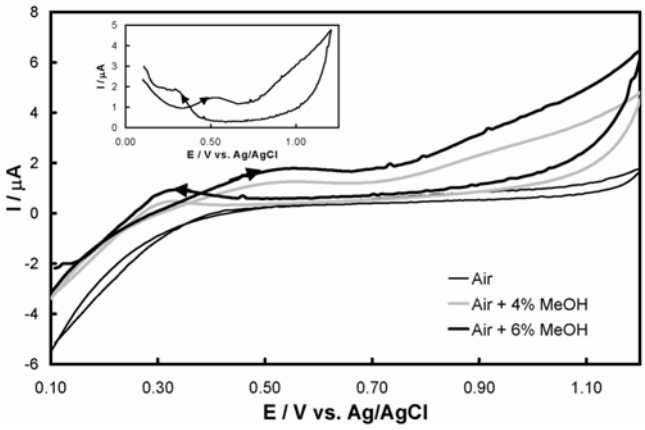

Figure 6. Voltammograms recorded at 5 mV s^{-1} in a pure water–saturated air stream and in 4% and 6% w/w methanol/water solution–saturated air streams, at a three-electrode Pt (vs Ag/AgCl)/Nafion®/Pt planar device. Inset: Background (air)-corrected voltammogram for methanol oxidation from a 6% w/w methanol/water solution- saturated air stream.

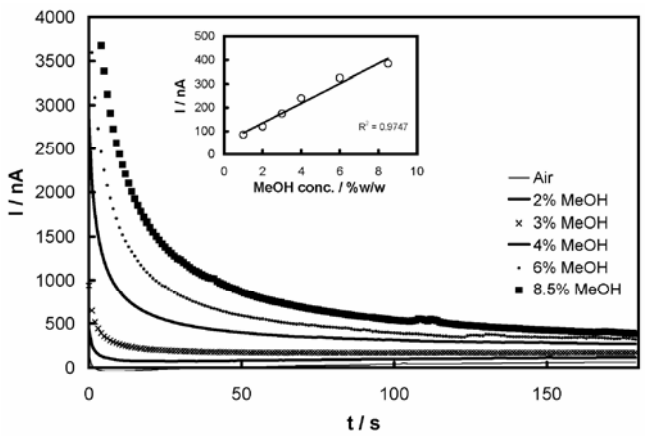

Figure 7. Current-time transients at Pt (vs Ag/AgCl)/Nafion®/Pt planar device at the measurement potential of +0·6 V (within the pulse sequence used) in water–saturated air and methanol + air vapour streams. Inset: Variation of the currents collected at 120 s vs methanol concentration in the gas equilibration solution.

can also be interpreted by the poisonous effect of methanol on oxygen reduction. A shift of the oxygen reduction voltammetric wave of more than 0·15 V has been reported at rotating Pt disc electrodes in acidic electrolytes, even for very dilute solutions of methanol.[27]

Again, a series of amperometric experiments was performed at a constant potential of +0·60 V in water-saturated streams of varying methanol vapour content (figure 7), following the same pulsing sequence described above for nitrogen streams. A variation of the steady state current from the background value was observed again for methanol solution concentrations in the 1–8·5% w/w range. The inset to figure 7 shows that for gaseous methanol oxidation at the Pt/Nafion® interface in air, a near-linear correlation exists between the oxidation current at +0·6 V (collected 120 s after the application of the pulse) and methanol concentration. The detection limit estimated by repeating 5 measurements at the 2% w/w level was 1·2% w/w (corresponding to 1·4 Torr of methanol vapour pressure).

4. Conclusions

(i) Co-planar electrode devices, that can be prepared by a single-step procedure on a Nafion® electrolyte layer, exhibit clear electrochemistry and are thus candidates for all-solid electrochemical sensors. (ii) Pt (vs Ag/AgCl)/Nafion®/Pt co-planar electrode devices responded to methanol vapour concentration changes both under voltammetric and amperometric conditions. (iii) Using an appropriate pulse sequence, methanol vapours in the 1–13 Torr partial pressure range (in equilibrium with methanol aqueous solutions in the 1–10% w/w concentration range) could be determined using the Pt (vs Ag/AgCl)/Nafion®/Pt devices, in a constant potential, amperometric mode. (iv) The methanol detector could be operated both in a nitrogen stream and (in what is essential for practical applications) in an air atmosphere too, with estimated detection limits of 1·2 and 1·4 Torr respectively. Although these limits are rather high, the simple detector proposed here could find applications in crude monitoring of methanol levels (e.g. in methanol fuel cell systems).

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