

Electropolymerized porphyrin films as methanol barriers in direct methanol fuel cells

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Abstract

Methanol crossover from the anode side to the cathode site across the membrane in direct methanol fuel cells causes loss of fuel and catalyst poisoning. Many reports deal with the modification of the commonly used Nafion® membrane or the development of new polymer membranes exhibiting reduced methanol permeability. The present study reports on the use of tetra(*ortho*-amino-phenyl)porphyrin ((*o*-NH₂)TPP) as the methanol barrier when electropolymerized on a direct methanol fuel cell cathode. Using the electrochemical quartz crystal microbalance and atomic force microscopy techniques, the (poly(*o*-NH₂)TPP) films which efficiently reduced methanol permeability were shown to be non-porous, 0.55 μm thick and characterized by a high density (0.94 g/cm³) and high porphyrin site concentration (1.4 M). For a glassy carbon electrode electrodeposited with Pt (Pt/GC), the oxygen reduction current density in 1 M H₂SO₄ at +0.1 V decreases from 0.42 to 0.23 mA/cm² in the presence of 0.5 M methanol while a similar electrode coated with the electropolymerized porphyrin shows almost no decrease after methanol addition (0.58 and 0.56 mA/cm², respectively). For Pt/C electrodes with a surface morphology coarser than that of Pt/GC, the surface was first coated with electropolymerized aniline-2-sulfonic acid (PAS) and then with the electropolymerized porphyrin. The ratio of oxygen reduction currents after and before adding 0.25 M methanol was approximately 90% in this case. Experiments in a two-electrode configuration showed that it is possible to operate a DMFC with low current output without using an electrolytic membrane separating the anode from the cathode, provided that the cathode is coated with a bilayer of PAS/poly(*o*-NH₂)TPP.

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1. Introduction

Recently, much attention has been devoted to low-temperature solid polymer electrolyte fuel cells (PEFCs) fed directly by liquid methanol. However, at present, two major problems must be overcome before the direct methanol fuel cell (DMFC) can validly be proposed for practical application. One problem is the slow oxidation kinetics on the anode catalyst. The second is methanol diffusion from the anode to the cathode side across the polymer electrolyte membrane, the so-called “methanol crossover”. This causes loss of fuel, reduced cathode potential (due to catalyst poisoning) and excess thermal load in the cell, which are encountered in low-power

DMFCs, although to a lesser extent. In order to overcome this problem, two major attempts have been made. One is to enhance the oxidative reaction kinetics on the anode, although the efficiency of catalysts currently available is not yet satisfactory. The second attempt is to use a membrane possessing high proton conductivity along with low methanol permeability. Poly(perfluoro-sulfonic acid) (Nafion®) membranes are commonly used as solid electrolytes in DMFCs, owing to their high ionic conductivity and good chemical and thermal resistance [1,2]. However, it has been found that over 40% of the methanol can be wasted in DMFCs across such membranes [3]. The DMFC technology would benefit greatly, both in terms of energy efficiency and output voltage, from a drastic reduction of the methanol crossover. Attempts to develop new polymer membranes exhibiting reduced methanol permeability have

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been reported [4–8], including basic polymers doped with inorganic acids [9]. Recently, a Pd-impregnated nanocomposite Nafion[®] membrane showed a lower permeability for methanol [10] and alternative fuels (such as formic acid) with reduced crossover rates through Nafion[®], have also been considered [11]. The concept presented in the present report is different and deals with thin films which are electropolymerized directly on the cathodes of DMFCs and which significantly reduce the amount of methanol reaching these cathodes.

In the past, we have investigated the electrochemical process for the formation of polymeric films (electropolymerization) of non-metallated and metallated films of amino (*ortho*, *meta* and *para*), dimethylamino-, hydroxo-, and pyrrole-phenyl substituted porphyrins [12]. The films are stable, adherent and electroactive over a broad potential range. Moreover, these films, when coated on an oxygen cathode, do not hinder the oxygen reduction process since they permit permeability of oxygen as well as conduction of charge (protons and electrons). We have also shown that some of the electropolymerized metalloporphyrin films, especially those containing Co(II)/Co(III) ions can be used as efficient catalysts for oxygen reduction [12–14]. Catalytic and analytical applications of electropolymerized metalloporphyrins have been reviewed by Bedioui et al. [15]. In the present study, we exploit the non-metallated porphyrin films as barriers for methanol diffusion to DMFC cathodes and as an example, we describe the barrier properties of polymeric films of tetra(*ortho*aminophenyl)porphyrin (poly(*o*-NH₂)TPP).

2. Experimental

Electrochemistry was conducted with an EG&G273 potentiostat and a conventional three-electrode cell with Ag|AgCl|KCl(satd.) as the reference electrode. A Seiko EG&G (model QCA 917) electrochemical quartz microbalance (EQCM) and Pt-coated quartz crystals with a surface area of 0.2 cm² and normal resonant frequency of ~9 MHz were used.

Scanning force microscopy (SFM) was performed on an LS-Solver (NT-MDT, Zelenograd, Russia) scanning probe microscope, using OTESP probes (Olympus, Tokyo, Japan) in intermittent contact mode. The surface morphology was measured in the center of the film. The film thickness was determined by measuring over the sharp step formed at the abrupt film edge. The height was then calculated to be the difference of the most probable height taken from separate histograms of the upper and lower levels. Since the surfaces had significant roughness, the uncertainty in this value was taken to be the mean of the rms roughness of the upper and lower levels.

Oxygen reduction was studied on Pt-coated glassy carbon electrodes (Pt/GC) or carbon paper electrodes coated with platinized carbon (Pt/C). Glassy carbon electrodes cast in Teflon (Metrohm, $A = 0.07 \text{ cm}^2$) were first polished with a water emulsion of 0.3 μm alumina and then coated with Pt as an oxygen reduction catalyst by applying a current density of 5 mA/cm² for 10 min from a 10⁻² M H₂PtCl₆ + 1 M H₂SO₄ solution at room temperature. The Pt/C electrodes were supplied by E-TEK and consisted of TGFH-120 Toray carbon paper and a coating of 10% Pt/C, 0.5 mg/cm² Pt loading. Masking paint was used in this case in order to expose only 1 cm² to the electrolytic solution.

Electropolymerization of (*o*-NH₂)TPP was achieved from a 1 mM solution of (*o*-NH₂)TPP in 1 M H₂SO₄ by cyclic voltammetry in the range 0 to +1.2 V or by chronoamperometry at a potential of +1.2 V.

Coating of the electrodes with polyaniline sulfonic acid (PAS) was carried out by applying a constant potential of +1 V for 10 min in a solution containing 1 M H₂SO₄ and 5 × 10⁻² M of monomeric aniline-2-sulfonic acid (AS).

Coating the electrodes with Nafion[®] was achieved by dipping the electrodes in a 5% Nafion[®] solution for 1/2 h and drying in air.

The anode in the two-electrode configuration was an EFCG electrode supplied by E-TEK and consisted of: TGPH-120 Toray carbon paper, 10% Pt/Ru/C (1:1 a/o), 0.5 mg/cm² Pt/Ru. Part of the anode (PtRu/C) and cathode (E-TEK, Pt/C) were brushed with masking paint so that only 1 cm² was exposed to the electrolytic solution (1 M H₂SO₄, 60 °C). Oxygen reduction at the cathode and methanol oxidation at the anode were driven by a potentiostat and took place in an ordinary electrochemical cell with only the electrolyte solution separating the two electrodes.

3. Results

Using the EQCM apparatus, (*o*-NH₂)TPP was electropolymerized on a Pt-coated quartz crystal by cycling the potential in the range 0 to +1.2 V. An oxidation wave with $E_{1/2}$ of ~0.75 V followed by a steep current density increase at ~+1 V are observed in the cyclic voltammogram shown in Fig. 1(a). This behavior is typical of aminophenyl porphyrins undergoing electropolymerization in acidic aqueous solutions [12]. Fig. 1(b) depicts the frequency changes during the potential scan. It can be seen that the main frequency decrease (mass increase) is observed when scanning the potential in the range 0.8–1.2 V, which is consistent with the two anodic processes observed in the cyclic voltammogram (Fig. 1(a)). A mass increase is observed not only when scanning positively but also when reversing the potential direction, probably indicating that the

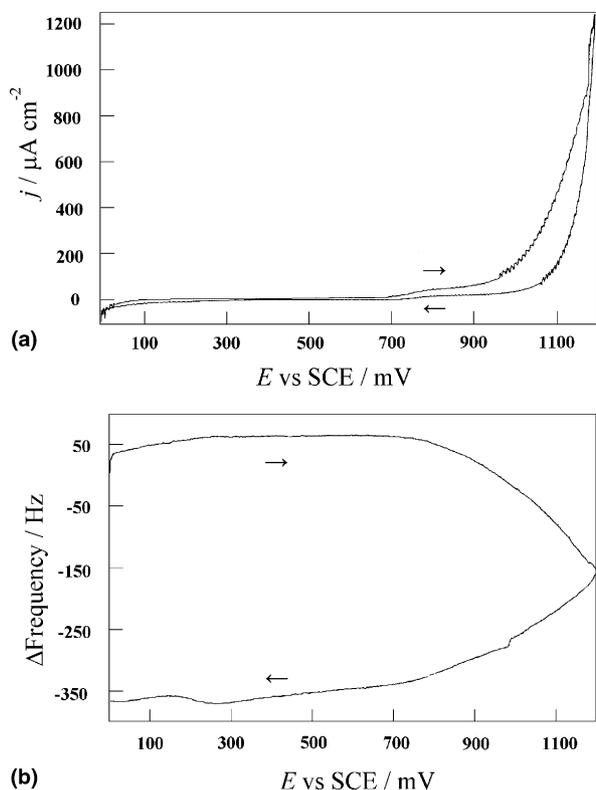


Fig. 1. (a) Cyclic voltammogram (2 mV/s) for 1 mM (*o*-NH₂)TPP in 1 M H₂SO₄ at a Pt-coated quartz crystal. (b) Frequency dependence on potential.

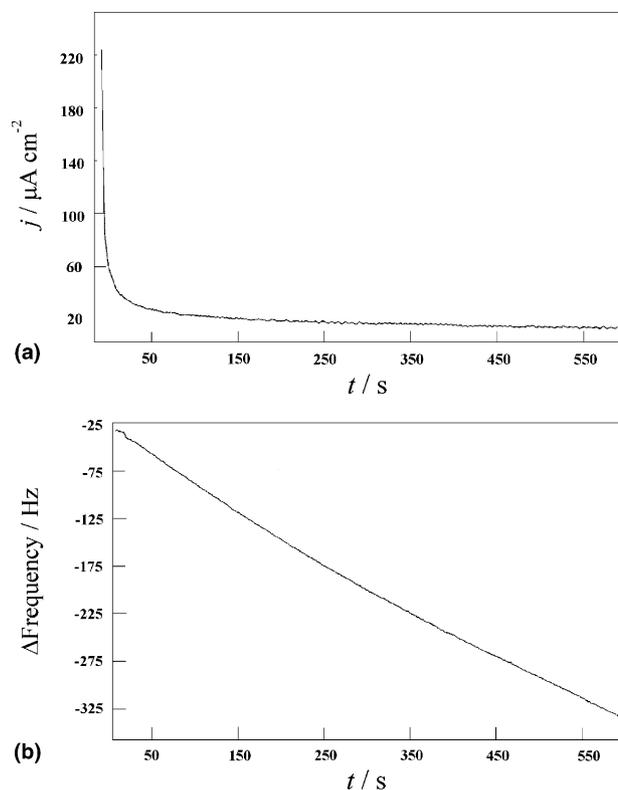


Fig. 2. (a) Chronoamperometry at +1.2 V for the same type of electrode and for the same solution as in Fig. 1. (b) Frequency dependence on potential.

electropolymerization process is slow and persists during the negative scan in this potential range. Electropolymerization of (*o*-NH₂)TPP can also proceed by applying a constant positive potential and Figs. 2(a) and (b) show the current and frequency behavior of a Pt-coated quartz crystal during chronoamperometry at +1.2 V. It can be seen from these figures that the current initially decreases steeply without mass accumulation and this can be attributed to double layer charging. This is followed by a lower current decrease and mass accumulation increase due to the electropolymerization process.

A thin polymeric film on a Pt-coated quartz crystal was obtained by chronoamperometry at +1.2 V for 10 min and characterized by AFM. Mass accumulation according to frequency decrease during the electropolymerization process was 4.4 μg/cm² and the AFM image showed a porous structure as depicted in Fig. 3(a). In contrast, Fig. 3(b) shows an AFM image of a thicker film obtained by cyclic voltammetry (0 to +1.2 V, 10 cycles), in which mass accumulation during the electropolymerization process was 51.7 μg/cm². It can be seen from these images that while pores with an average diameter of ~1000 nm were observed in the thinner film, this porous structure could not be detected in the thicker film. Moreover, good overlapping was observed along the boundaries separating the thick polymer layers. The

thickness was evaluated by cross-sectional height measurements between polymer-coated and uncoated regions of the thick film (Fig. 4(a)) to be 0.55 ± 0.1 μm (Fig. 4(b)). The average density was therefore calculated to be 0.94 g/cm³ for this film and the concentration of the porphyrin sites is therefore 1.4 M, compared to 0.85 M for poly[Co(II)(*o*-NH₂)TPP] films on SnO₂-coated glass electrodes and evaluated using surface profilometry thickness measurements [16]. Attempts to produce thicker films by cyclic voltammetry (>10 cycles) or chronoamperometry (*t* > 10 min) were unsuccessful: the topography was almost identical and the thickness did not exceed the above value.

Electropolymerization of (*o*-NH₂)TPP was carried out by cyclic voltammetry on a Pt/GC electrode using the same conditions as mentioned above for the EQCM experiments and the effect of methanol on oxygen reduction at this electrode was compared to that of a polymer-uncoated Pt/GC electrode. Fig. 5 shows chronoamperometric curves obtained for oxygen reduction at room temperature at a potential of +0.2 V in a solution of 1 M H₂SO₄ + 1 M methanol supplied continuously with air for the polymer-coated and uncoated Pt/GC electrodes (curves (A) and (B), respectively). It can be seen from the figure that when the electrode is coated with the methanol barrier film, the steady oxygen reduction current density at +0.2 V and in the presence of

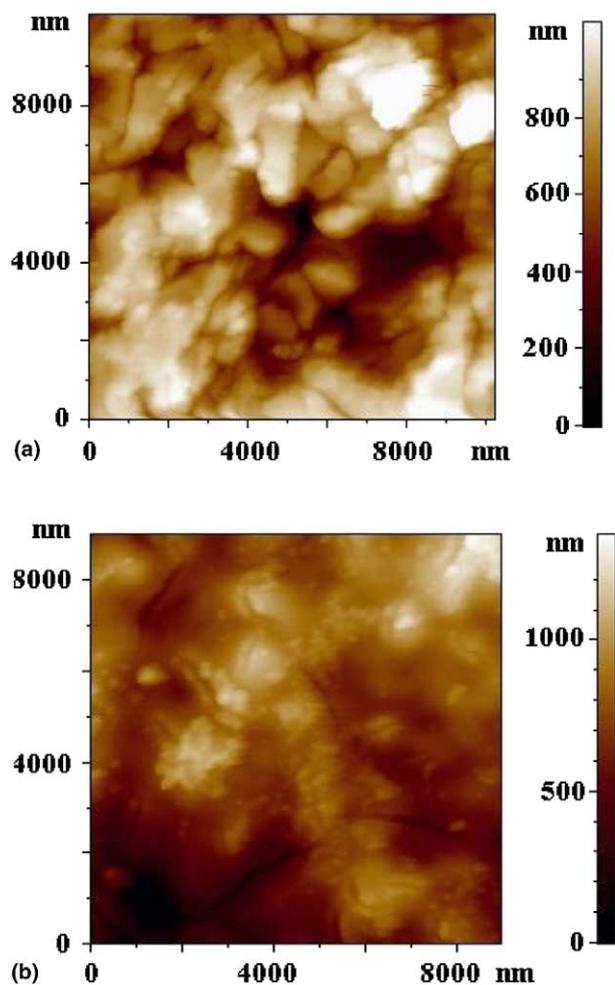


Fig. 3. AFM topographic images taken for poly(*o*-NH₂)TPP films on a Pt-coated quartz crystal. (a) Film produced by chronoamperometry for 10 min at +1.2 V in a solution of 1 M H₂SO₄ containing 1 mM (*o*-NH₂)TPP. (b) Film produced by cyclic voltammetry (0 to +1.2 V, 1 mV/s, 10 cycles).

1 M methanol is $-105 \mu\text{A}/\text{cm}^2$. However, in the absence of this film, the steady oxygen reduction current density is only $-0.3 \mu\text{A}/\text{cm}^2$. This means that the methanol barrier film causes less methanol to reach the electrode and thus less catalytic platinum catalytic sites are poisoned by methanol and are therefore available for oxygen reduction.

Fig. 6(a) shows oxygen reduction polarization curves (at a scan rate of 5 mV/s) obtained in 1 M H₂SO₄ solution at 60 °C supplied continuously with air (100 cc/min) for the polymer-coated Pt/GC electrode in the absence (curve A) and presence of 0.5 M methanol (curve B). Fig. 6(b) shows oxygen reduction polarization curves (5 mV/s) obtained in the same solution and conditions as in Fig. 6(a) for the bare Pt/GC electrode in the absence (curve A) and presence of 0.5 M methanol (curve B).

Table 1 summarizes the currents obtained at the two potentials for the bare and polymer-coated Pt/GC electrodes.

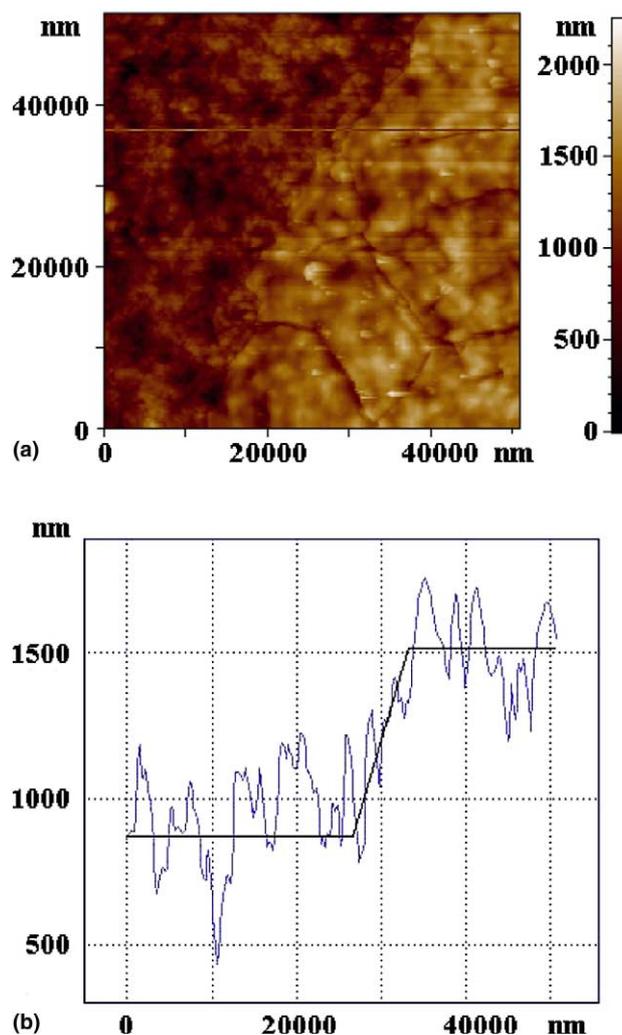


Fig. 4. (a) AFM topographic image taken of a poly(*o*-NH₂)TPP film on a Pt-coated quartz crystal. The film was produced by cyclic voltammetry in the range 0 to +1.2 V (10 cycles, 1 mV/s) in a solution of 1 M H₂SO₄ containing 1 mM (*o*-NH₂)TPP. (b) AFM cross-section diagram of the above film (along the line in figure (a) crossing the Pt and Pt/polymer regions).

It can be seen from Figs. 6(a) and (b) and from Table 1 that while only 55% of the current for oxygen reduction at +0.1 V remains after the addition of methanol for the electrode which is not coated with a methanol barrier film, 96% of the current remains under the same conditions for the electrode coated with the methanol barrier film. The fact that almost no methanol crosses the barrier film can also be concluded from the very low oxidation current density observed after the addition of methanol at +0.5 V (originating from methanol oxidation) for the electrode coated with the barrier film, compared to the very high current density observed for the non-coated electrode (0.01 and 19.7 mA/cm², respectively).

The reactivity of the commercial Pt/C electrode towards the cathodic reduction of oxygen in a 1 M H₂SO₄

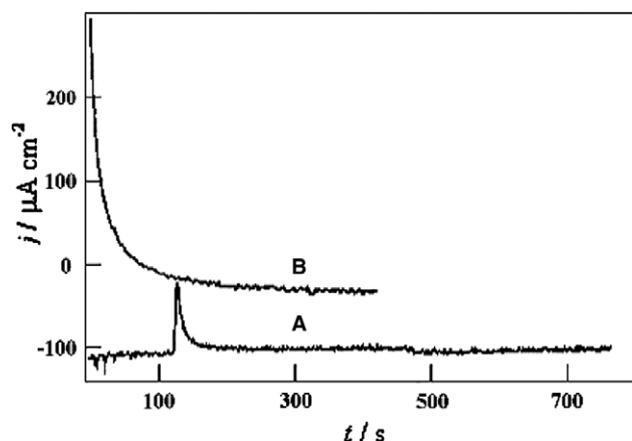
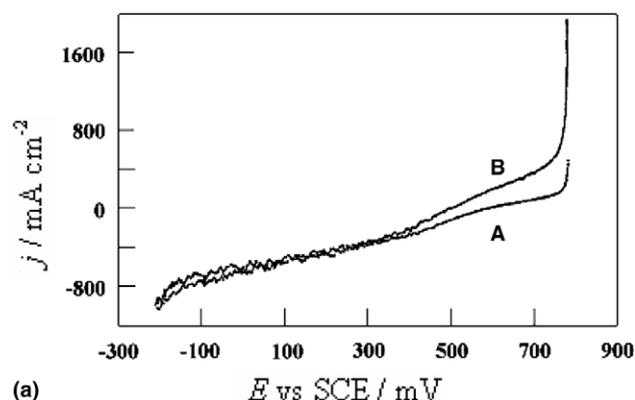
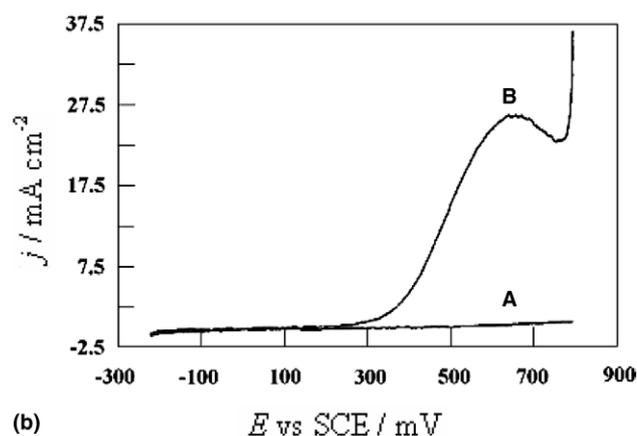


Fig. 5. Chronoamperometric curves for oxygen reduction at +0.2 V in a solution of 1 M H₂SO₄ + 1 M methanol constantly supplied with air (100 cc/min) for Pt/GC coated with poly(*o*-NH₂)TPP (A) and for uncoated Pt/GC (B) according to details given in Fig. 4.



(a)



(b)

Fig. 6. Oxygen reduction polarization curves (5 mV/s) obtained in a solution of 1 M H₂SO₄ at 60 °C continuously supplied with air (100 cc/min) for the poly(*o*-NH₂)TPP/Pt/GC (a) and Pt/GC electrode (b) in the absence (A) and presence of 0.5 M methanol (B).

solution at 60 °C and continuously bubbled with air is low. This can be deduced by the polarization curve A (obtained at a scan rate of 1 mV/s) in Fig. 7. This has been demonstrated for other Pt/C electrodes for which substantial oxygen reduction currents were observed at

Table 1
Oxygen reduction current densities obtained from polarization curves (Fig. 6(a) and (b)) in 1 M H₂SO₄ at 60 °C for the bare and polymer-coated Pt/GC electrodes

Electrode	Current density ^a at +0.1 V (mA/cm ²)	Current density ^a at +0.5 V (mA/cm ²)
Polymer-coated electrode, absence of methanol	-0.58	-0.14
Polymer-coated electrode, presence of 0.5 M methanol	-0.56	+0.01
Bare electrode, absence of methanol	-0.42	-0.31
Bare electrode, presence of 0.5 M methanol	-0.23	+19.7

^a Negative and positive currents are for cathodic and anodic currents, respectively.

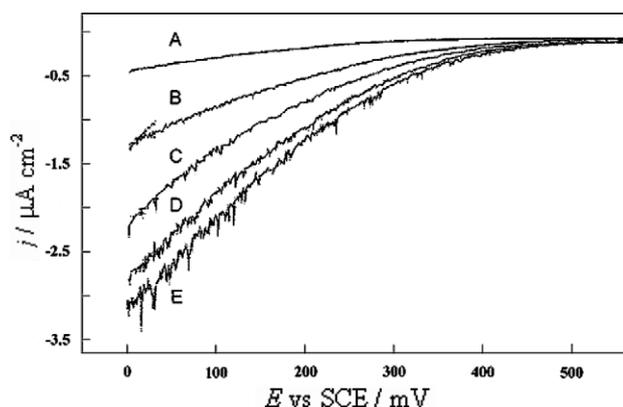


Fig. 7. Oxygen reduction polarization curves (1 mV/s) obtained in a solution of 1 M H₂SO₄ at 60 °C continuously supplied with air (100 cc/min) for an as-received commercial Pt/C electrode (A) and after “electrochemical digging” at +1.1 V for 0.3 (B), 1 (C), 2 (D) and 3 h (E).

potentials more negative than $\sim +0.5$ V vs. SHE [17]. However, we found that after applying a potential of +1.1 V in the same solution and at the same temperature as indicated above, the polarization curves obtained for oxygen reduction show higher current densities. This is shown in Fig. 7 for different times of treatment at +1.1 V (curves B–E are for 1/2, 1, 2 and 3 h of treatment, respectively). After a 3 h treatment, the oxygen reduction current density at +0.15 V increased from 0.18 to 1.6 mA/cm², i.e., an 8.9 fold increase. This effect is attributed to result from the evolution of oxygen due to electrochemical oxidation of water at +1.1 V. The gas evolved in narrow pores contained in the electrode structure probably causes the increase of the catalytic effective area, a process that we call: “electrochemical digging”. Increase of the catalyst effective area was also deduced from cyclic voltammetric experiments conducted in the negative potential range in 1 M H₂SO₄ at 60 °C. A reduction peak at -0.3 V attributed to the H⁺/

H₂ couple was observed and the peak current increased by a factor of 2 when increasing the “digging” time from 1 to 3 h. This is in reasonable correlation with the current density increase observed from the corresponding oxygen reduction polarization curves (ratio of 1.7 at +0.2 V; Fig. 7, curves C and E).

Attempts to coat Pt/C electrodes with an efficient poly(*o*-NH₂)TPP methanol barrier coating were unsuccessful, probably due to the coarser surface morphology of these electrodes compared to that of the Pt/GC electrodes. It was therefore necessary to coat the surface that has undergone “electrochemical digging” with a thicker polymeric film which smoothes the surface morphology. The polymer which we found to be suitable for this purpose is PAS which was coated on the surface by electropolymerization of the monomer aniline-2-sulfonic acid (AS). The polymerization of sulfonated-substituted anilines has been reported [18,19] and sulfonated polyaniline has been reported to have better processing ability (solubility) and higher thermal stability than doped polyaniline and a pH-independent conductivity from 0 to 14 [20,21]. Similarly to the electropolymerization of aniline, this can be achieved in acidic aqueous solutions by applying a constant positive potential or by cycling the potential in the positive range. Chronoamperometry at +1 V showed rapid PAS accumulation on the electrode surface as observed using the EQCM technique (Fig. 8): the current density showed a steep initial decrease followed by a more moderate decrease (Fig. 8(a)) while significant mass accumulation was observed only during the last stage (Fig. 8(b)). As also indicated in the case of the electropolymerization of (*o*-NH₂)TPP (Fig. 2), the initial current decrease is probably due to double layer charging.

Fig. 9 shows the oxygen reduction polarization curves obtained for a Pt/C electrode after the “electrochemical digging” procedure and after coating with PAS by chronoamperometry (curves A and B, respectively). From Fig. 9, it can be deduced that the polymeric coating does not perturb oxygen diffusion to the catalytic layer. Moreover, this coating even increases the electrode reactivity towards oxygen reduction, probably due to the introduction of proton conductive sulfonic acid groups into the catalytic layer, as also reported for the incorporation of Nafion[®] ionomer in fuel cell electrodes [22,23]. The surface coverage of PAS at this stage, as estimated by the EQCM technique, was 2.3×10^{-8} mol/cm². Continuation of the coating process, however, caused a decrease of the oxygen reduction current (not shown in the figure), probably due to decrease of oxygen permeability onto thicker polymeric films. A poly(*o*-NH₂)TPP methanol barrier film was coated by electropolymerization at constant potential on top of the PAS layer and the current densities obtained at +0.05 V before and after addition of 0.25 M methanol in solution

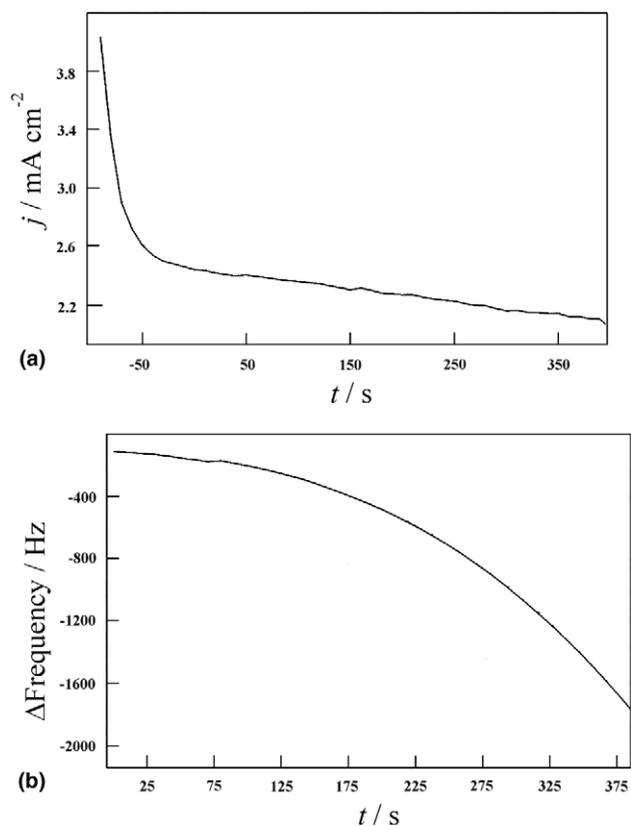


Fig. 8. PAS coating on a Pt-coated quartz crystal by chronoamperometry at +1 V in a solution of AS (5×10^{-2} M) and H₂SO₄ (1 M). Dependence of current (a) and frequency (b) on time.

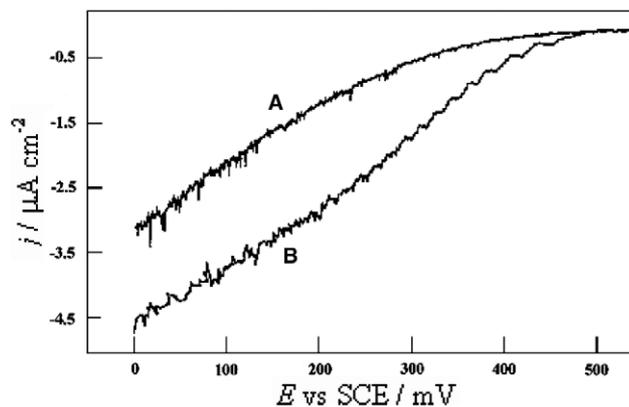


Fig. 9. Oxygen reduction polarization curves (1 mV/s) obtained in a solution of 1 M H₂SO₄ at 60 °C continuously supplied with air (100 cc/min) for a Pt/C electrode after “electrochemical digging” at +1.1 V for 3 h (A) and after coating with PAS by chronoamperometry at +1 V for 10 min in a solution containing 1 M H₂SO₄ and 5×10^{-2} M AS (B).

are summarized in Table 2 for increasing times of the electropolymerization.

From Table 2, it can be deduced that increasing the electropolymerization time from 2 to 5 h increases the oxygen reduction current obtained in the absence of methanol. Moreover, a smaller decrease of the current is

observed after addition of methanol which indicates that less methanol crosses the coating when increasing the electropolymerization time from 2 to 5 h. A further increase from 5 to 9 h causes a decrease of the current in the absence of methanol with only a small contribution to the ratio of currents after and before the methanol addition (current ratio increases from 89.7% to 90.5%).

The performance of the electrode towards oxygen reduction in the presence of methanol after “electrochemical digging” and coating with PAS/poly(*o*-NH₂)TPP was compared to that of a similar electrode which had been treated by “electrochemical digging” but which had not been coated with PAS/poly(*o*-NH₂)TPP. Instead, this electrode was coated with adsorbed Nafion[®] (irreproducible oxygen reduction polarization curves were obtained when dosing the surface with known volumes of a Nafion[®] solution). Fig. 10 shows the oxygen reduction polarization curves obtained in 1 M H₂SO₄ + 0.5 M methanol at 60 °C (air flow rate: 100 cc/min) for the Nafion[®]-treated electrode (curve A), compared to the electrode coated with PAS/poly(*o*-NH₂)TPP (curve B). It can be clearly seen from this figure that methanol poisons the Nafion[®]-coated electrode much more than the electrode with the PAS/poly(*o*-NH₂)TPP coating. This can be deduced by the high anodic current densities observed at high positive potentials for the Nafion[®]-coated electrode (+2 mA/cm² at +0.5 V compared to −0.03 mA/cm² at the same potential for the other electrode) as well by the higher cathodic current densities for oxygen reduction obtained for the electrode with the PAS/poly(*o*-NH₂)TPP coating (−3.7 mA/cm² at +0.05 V, compared to −1.4 mA/cm² at the same potential for the Nafion[®]-coated electrode).

Fig. 11 shows the voltammograms obtained in 1 M H₂SO₄ at 60 °C for a two-electrode configuration in which the Pt/C cathode has been treated as described above (“electrochemical digging” and then coating with PAS/poly(*o*-NH₂)TPP) and a commercial PtRu/C electrode was used as the anode. Oxygen, continuously supplied as air, is reduced at the cathode and methanol is oxidized at the anode (0.25 and 0.5 M for curves A and B, respectively) and currents are obtained in the absence of a conventional membrane, which separates the reactants. The currents increase when air is replaced by oxygen (curve C). The current at +0.06 V increases by a factor of 2.3 instead of ~5 when replacing air by

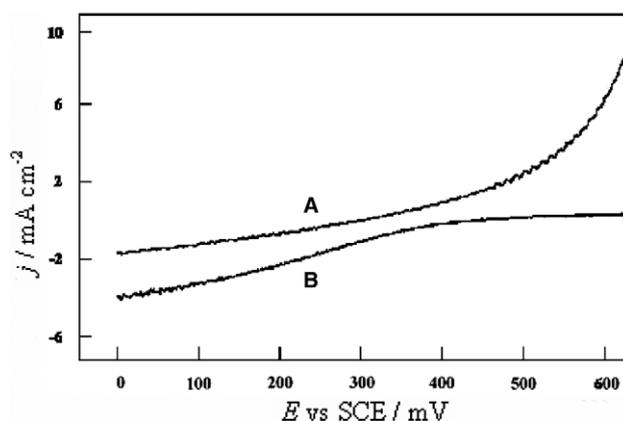


Fig. 10. Oxygen reduction polarization curves (1 mV/s) obtained in a solution of 1 M H₂SO₄ at 60 °C continuously supplied with air (100 cc/min) for a Pt/C electrode after “electrochemical digging” and coated with Nafion[®] by dipping in a 5% Nafion[®] solution for 1/2 h. (A) compared to a similar electrode coated with PAS and poly(*o*-NH₂)TPP (B).

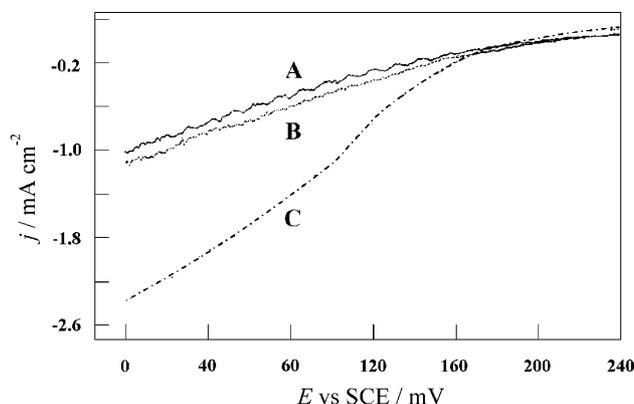


Fig. 11. Current–potential curves (1 mV/s) for a two-electrode configuration with poly(*o*-NH₂)TPP/PAS/Pt/C as the cathode and 10%Pt–Ru/C as the anode in a solution of 1 M H₂SO₄ at 60 °C continuously supplied with air (100 cc/min) in the presence of 1% (A) and 2% methanol (B) and under the same conditions as (B) but with oxygen (100 cc/min, C).

oxygen, indicating oxygen mass transfer limitation. This figure demonstrates the concept we developed: it is possible to operate a DMFC without using a high cost electrolytic membrane separating the cathode from anode if the cathode is coated with a thin film which efficiently prevents (or reduces) permeation of methanol

Table 2

Oxygen reduction current densities obtained in the absence and presence of 0.25 M methanol in 1 M H₂SO₄ at 60 °C after increasing (*o*-NH₂)TPP electropolymerization time by chronoamperometry at +1.2 V

Electro-polymerization time (h)	Current density at +0.05 V without methanol (mA/cm ²)	Current density at +0.05 V with 1% methanol (mA/cm ²)	Ratio of current densities after and before adding methanol (%)
2	3.95	3.29	83
5	4.38	3.93	89.7
9	3.46	3.13	90.5

through the catalytic layer of the cathode. Assuming that higher oxygen fluxes do not impose extreme limitations on oxygen transport through the barrier film, the low power output obtained in this stage is anticipated to increase by proper use of a gas diffusion cathode. Moreover, more efficient and selective methanol oxidation catalysts with lower Pt content at the cathodes will also improve the performance of the cell, since oxygen reaching the anode is reduced at this electrode and therefore reduces the overall current.

4. Conclusions

Using electrochemical, EQCM and AFM techniques, it has been shown that thin films (0.55 μm thick) of (*o*-NH₂)TPP electropolymerized on smooth electrodes show reduced methanol permeability and allow efficient cathodic reduction of oxygen in methanol-containing solutions. Permeation of methanol to the surface of electrodes with coarser morphology, such as those used in fuel cell technology can be significantly suppressed by first coating the electrode with electropolymerized aniline-2-sulfonic acid and then with poly(*o*-NH₂)TPP. Preliminary two-electrode configuration experiments demonstrate operation of a single chamber fuel cell. The lack of a membrane would help to miniaturize fuel cells since it is much more difficult to seal miniature ion-exchange membranes. Such a device relies on only partial oxidation of the fuel when mixed with oxygen and on sufficient selectivity of the cathode and anode catalysts, as reported for a high temperature solid oxide fuel cell [24]. Such selectivity exists in biofuel cells operating on glucose, which is not separated from ambient oxygen [25]. Continued advances in the development of thin polymeric methanol barrier films, significant reduction in the Pt catalyst content and development of selective catalysts are essential for the realization of an efficient and low cost single chamber DMFC.

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