Use of electropolymerized films of macrocyclic compounds in direct methanol fuel cell components

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Abstract

Electropolymerized Co(III) and Ru(II)(CO)(2-aminophenyl)porphyrins (poly[Co(III)] and poly[Ru(II)]) were used as catalysts in a direct methanol fuel cell for the reduction of oxygen at the cathode and the oxidation of methanol at the anode, respectively. Although the half-wave potentials for oxygen reduction are +0.3 and +0.55 V when using poly[Co(III)]/C and Pt/C, respectively, as catalysts, higher limiting currents can be obtained with the non-noble metal catalyst. Moreover, the macrocyclic catalyst is 10-fold less prone to methanol poisoning than the one based on Pt. The H_2O_2 yields obtained during oxygen reduction, as measured by the RRDE technique, were 1.9, 4.1 and 2.3% for poly[Co(III)]/C, Pt/C and for a commercial heat-treated Co(III)porphyrin. Methanol oxidation with a catalyst consisting of Pt and poly[Ru(II)] was characterized by a higher limiting current ($i_L = 13$ mA/cm^2, $E_{1/2} = +0.6$ V) than that obtained with a commercial Pt-Ru catalyst ($i_L = 4$ mA/cm^2, $E_{1/2} = +0.5$ V) although the same Pt content was used in the two cases (1 mg/cm^2). Experiments conducted in a fuel cell configuration confirmed the half-cell results and indicated that better distribution of the catalysts in the porous structure of the electrodes and reduction of methanol crossover through the membrane are necessary in order to improve the performance of the cell.
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1. Introduction

Polymer electrolyte fuel cells (PEFC) such as direct methanol fuel cells (DMFC) are particularly attractive for transportation and other small-scale power source applications because of their theoretical high power density at low temperature operation. Since Pt is an expensive metal with a relatively limited abundance, much effort has been aimed to reduce Pt loadings. These are needed at the cathode because of the slow kinetics of oxygen reduction and at the anode due to the relatively poor efficiency of catalysts, such as Pt-Ru, for the oxidation of methanol. Moreover, platinum supported in carbon suffers from the disadvantages of gradual loss in catalytic activity as the surface area of the active platinum particles decreases because of sintering, physical dislodgment, and adsorption of impurities.

There have been several reports describing the use of transition macrocyclic compounds for the catalytic reduction of molecular oxygen [1,2]. Although heat-treated porphyrin compounds adsorbed on carbon have been revealed to exhibit higher activity towards oxygen reduction compared to non-heat-treated ones, the structure and the mechanism of the catalytic processes are not yet clear [3]. Chemically modified electrodes are under extensive study because of their great promise for improving the efficiency and selectivity of a wide variety of electrochemical processes and various macrocyclic complexes have been attached by adsorption [4,5] and covalent attachment [6]. Although electrodes coated with films of electroactive polymers containing macrocyclic compounds have been an intensively researched topic, instability problems of the films, low efficiency of the catalysts, high overpotentials, as well as high H_2O_2 yields have been reported [7]. However, we have shown that electropolymerized (as well as chemically polymerized) macrocyclic catalysts are stable, adherent, and electroactive at a broad potential range [8,9]. Some applications of electropolymerized metalloporphyrin films have been reviewed by Bedioui et al. [10]. In this work, we describe the use of electropolymerized Co(III) and Ru(II) porphyrins as catalysts for oxygen reduction and methanol oxidation at the cathode and anode, respectively, of direct methanol fuel cells.

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2. Experimental

All potentials in this paper are with respect to the saturated calomel electrode (SCE). The electrochemical including the rotating ring disk electrode (RRDE) apparatus were described elsewhere [9].

The electrolyte was 1 M H_2SO_4 for the half-cell experiments of oxygen reduction as well as for the oxidation of methanol.

Commercial catalyst powders containing various amounts of Pt in Vulcan XC-72 carbon (Pt/C) or heat-treated Co(III). Tetramethoxyphenyl porphyrin (Co(III)TMPP) in carbon (Pt/C and Co(III)TMPP/C) were supplied by E-TEK. Electrodes were prepared by mixing the catalyst with a 5% Nafion solution (Aldrich) and applying on carbon paper substrates (E-TEK). The electrodes were dried at room temperature for at least 5 h.

The metalloporphyrins were used as obtained by Midcentury, Posen, Il Films of electropolymerized Co(III)(2-amino-phenyl)porphyrin (poly[Co(III)]) on carbon electrodes were obtained by applying a constant potential of +1.2 V in a solution of 1 M H_2SO_4 at room temperature.

Electrodeposition of the catalyst containing Pt and Ru(II)(CO)(2-aminophenyl)porphyrin (Pt + poly[Ru(II)]) onto porous (average pore diameter: 10 μm) aerogel carbon paper electrodes (Marketech, Port Townsend, WA) was performed in solutions of 1 M H_2SO_4 by alternating the potential between −0.3 V (to introduce Pt) and a positive potential in the range +0.8 to +1.3 V (to electropolymerize the Ru(II) compound) each 2 h for a period of 24 h.

Membrane-electrode assemblies (MEAs) were made by pressing electrodes onto Nafion 117 membranes at room temperature. The cell was composed of a pair of graphite plates with serpentine flow-fields. The anode was a porous aerogel carbon electrode coated with Pt + poly[Ru(II)] with a Pt loading in the range 0.25–1 mg/cm². The cathode was a commercial electrode made of Pt/C on carbon paper (E-TEK) with higher Pt loading (2 mg/cm²) in order to minimize the effect of cathode on performance. The effective electrode area was estimated to be ~0.5 cm². The anode was supplied with a water + methanol (1 v/o) mixture and the cathode with a continuous air flow (100 cc/min). The temperature was kept at 80 °C for all the tests.

3. Results

Linear sweep voltammograms for oxygen reduction at 80 °C in an air saturated 1 M H_2SO_4 solution at carbon paste electrodes coated with various catalysts are shown in Fig. 1. The performance of the catalyst that we are developing (poly[Co(III)], curve (a)) is compared to that of two commercially available catalysts Co(III)TMPP/C and Pt/C (curves (b) and (c), respectively). It can be seen from the figure that the commercial Pt/C and Co(III)TMPP/C catalysts reduce oxygen at relatively high positive potentials
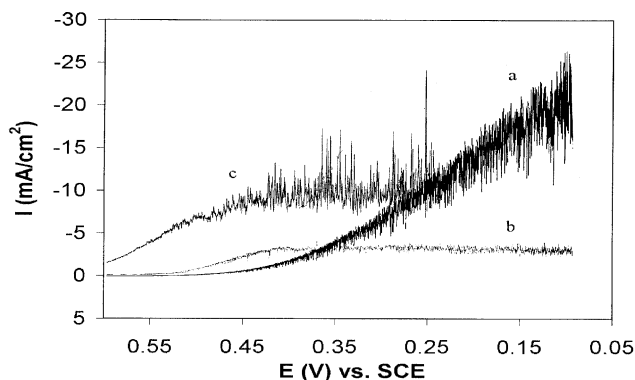

Fig. 1. Polarization curves at a scan rate of 1 mV/s for oxygen reduction in a 1 M H_2SO_4 solution at 80 °C with continuous air bubbling (100 cc/min) at carbon paper electrodes coated with (a) 0.5 mg/cm² poly[Co(III)]/C, (b) 2 mg/cm² commercial Co(III)TMPP/C, and (c) 1 mg/cm² commercial Pt/C.

($E_{1/2}$ = +0.55 and +0.46 V, respectively) as compared to the poly[Co(III)]/C catalyst ($E_{1/2}$ = +0.3 V). However, the limiting current obtained with the poly[Co(III)]/C catalyst is ~2- and 8-fold higher than that obtained with the commercial Pt/C and Co(III)/C catalysts. This effect is observed although the concentration of the poly[Co(III)] catalyst is lower than that of the commercial Pt/C and Co(III)/C catalysts (0.5, 1 and 2 mg/cm², respectively). Efforts are continuing in order to increase the concentration of poly[Co(III)] in the carbon substrate.

Methanol crossover from the anode through the electrolyte membrane in DMFC poisons the cathode catalyst, lowers the operating potential of the oxygen electrode and results in the consumption of fuel and generation of heat without the production of useful electrical energy [11]. Hence, the development of catalysts less prone to methanol poisoning is desirable. The poisoning effect was determined from linear sweep voltammograms as those shown in Fig. 1 by calculating the ratio: (current without methanol)/(current with 2% methanol) at +0.25 V. This ratio is low for the cobalt ion-based catalysts: 2.7 for poly[Co(III)]/C, 3.2 for Co(III)TMPP/C and high for Pt/C: 26.9, clearly indicating that the Co(III) macrocyclic catalysts are much less prone to methanol poisoning than the ones based on Pt.

The H_2O_2 yields obtained during oxygen reduction were assessed using the RRDE technique. Voltammograms obtained for reduction of oxygen at the disk electrode and for oxidation of H_2O_2 at the ring electrode with various catalysts coated on the disk electrode are shown in Fig. 2. Two waves are observed in the ring voltammograms for the cobalt macrocyclic catalysts ($E_{1/2}$ = +0.38 and +0.17 V for poly[Co(III)]/C and $E_{1/2}$ = +0.47 and +0.13 V for commercial Co(III)TMPP/C) while only one wave ($E_{1/2}$ = +0.28 V) appears for Pt/C. However, most of the H_2O_2 for the three catalysts is produced at very negative potentials at which the limiting current of oxygen reduction at the disk is attained. The maximum H_2O_2 yields, as calculated by the ratio of the ring/disk currents at these potentials, are: 1.9,
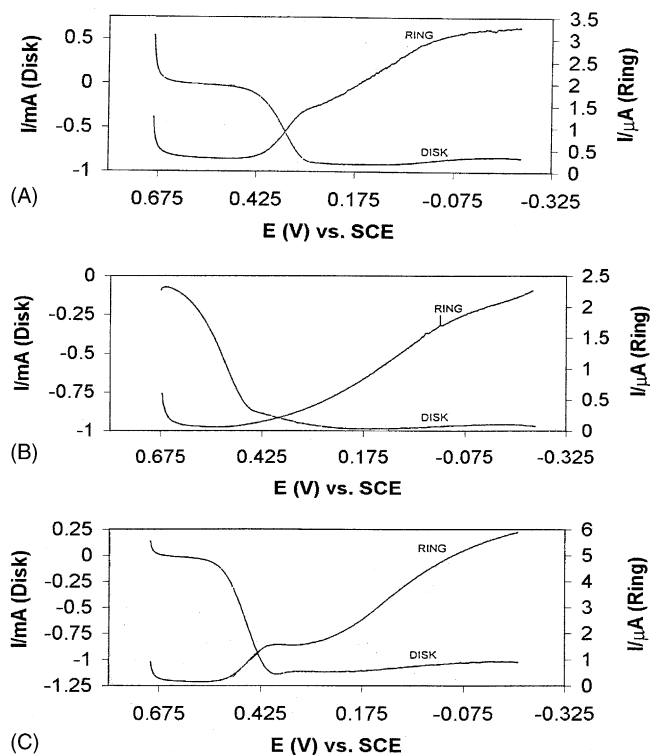
(A)

(B)

(C)

Fig. 2. RRDE voltammograms obtained at a rotation velocity of 4000 rpm, a disk potential scan rate of 5 mV/s and ring potential of +1 V in oxygen saturated 1 M H_2SO_4 solution for the various catalysts applied on the GC disk electrode: (A) 0.5 mg/cm² poly[Co(III)]/C; (B) 0.6 mg/cm² commercial Pt/C; (C) 1 mg/cm² commercial Co(III)TMPP/C.

4.1 and 2.3% for the poly[Co(III)]/C, Co(III)TMPP/C and Pt/C, respectively. The relatively low H_2O_2 yield obtained with the poly[Co(III)] catalyst can be attributed to its peroxide dismutase activity [12].

The catalyst for the anodic oxidation of methanol consists of two components: Pt and poly[Ru(II)], both introduced into the electrode substrate as described in Section 2. Fig. 3 depicts the linear sweep voltammogram obtained for methanol oxidation at a carbon paper (non-porous) electrode coated with this catalyst (Pt + poly[Ru(II)]) as compared to those obtained for electrodes coated with commercial Pt/C and Pt-Ru/C catalysts. It can be seen that methanol oxidation at a commercial Pt-Ru/C catalyst (curve (b)) occurs at a less anodic potential and the current is higher than that (curve (a)) of a Pt/C catalyst ($E_{1/2} = 0.5$ V, $i_{max} = 4$ mA/cm², and $E_{1/2} = +0.6$ V, $i_L = 1.2$ mA/cm², respectively). Methanol oxidation at an electrode coated with a catalyst consisting of Pt and the electropolymerized Ru(II) macrocyclic compound (curve (c)) is characterized by a higher limiting current ($i_L = 13$ mA/cm², $E_{1/2} = +0.6$ V) than obtained with the commercial catalysts although all contain approximately the same Pt surface coverage (∼1 mg/cm²).

The Pt/poly[Ru(II)] catalyst was introduced in a porous aerogel carbon substrate by electroreduction of H_2PtCl_6 and electropolymerization of the Ru(II) porphyrin. Scanning electron microscopy of the substrate surface reveals
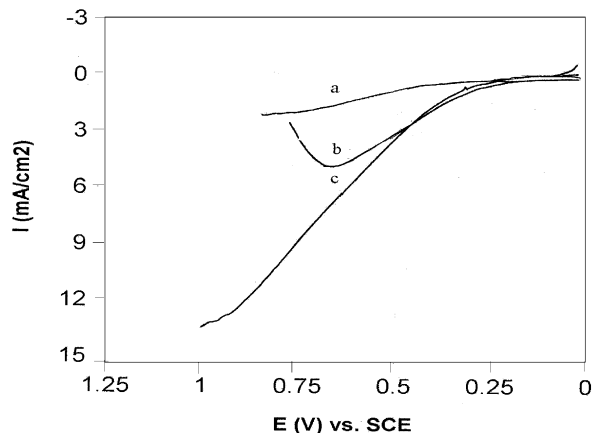

Fig. 3. Polarization plots at a scan rate of 1 mV/s for the oxidation of 0.5 M methanol in 1 M H_2SO_4 and at 25 °C at a carbon paper electrode coated with commercial Pt(10%)/C (a), commercial Pt-Ru (10%)/C (b), and Pt + poly[Ru(II)] (c). The estimated coverage of Pt in all cases is estimated to be ∼1 mg/cm².
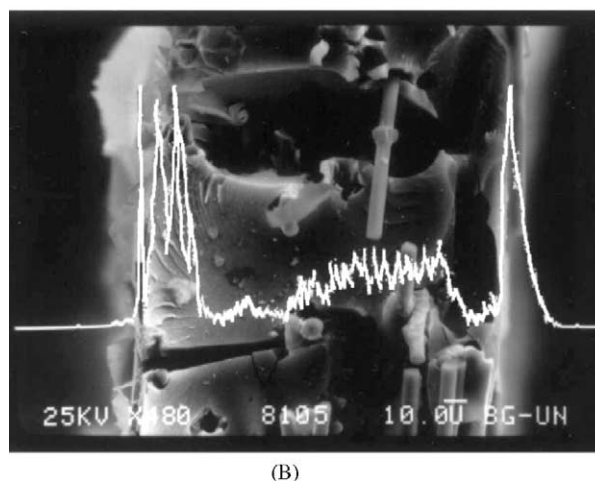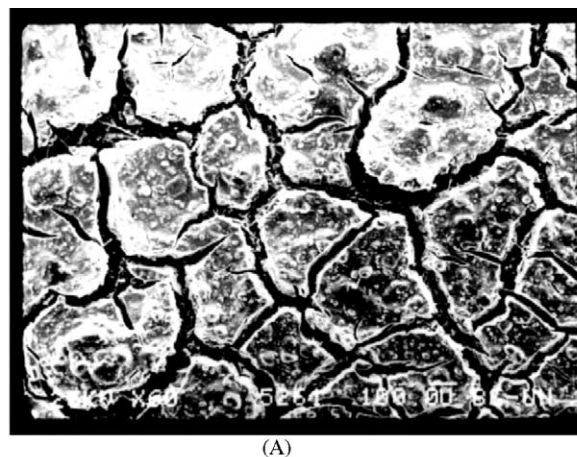

(A)

(B)

Fig. 4. Scanning electron micrographs for an aerogel carbon anode onto which the electrodeposited Pt + poly[Ru(II)] catalyst was incorporated: (A) micrograph of the surface (60×); (B) cross-section micrograph (480×) with Pt EDX signal inserted.
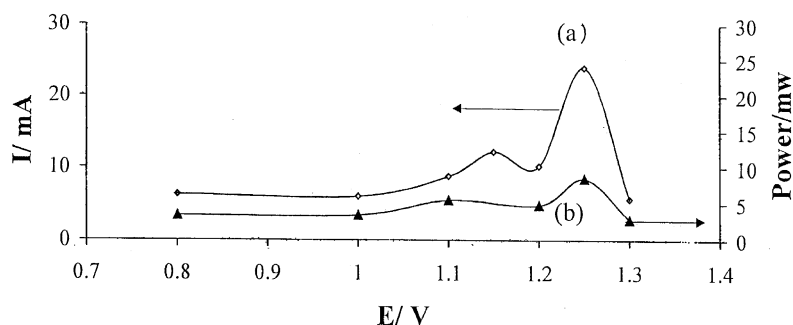
Fig. 5. The activity towards methanol oxidation of aerogel carbon anodes ($A = 1\,cm^2$) onto which the electrodeposited Pt + poly[Ru(II)]catalyst was incorporated. Curve (a) describes the dependence of the current ($A = 1\,cm^2$) obtained in a half-cell configuration on the catalyst electrodeposition potential (1 M H_2SO_4 + 1% methanol, 80 °C), while curve (b) shows the power ($A \sim 0.5\,cm^2$) developed in a fuel cell configuration (water + 1% methanol, 80 °C) as function of this potential.

massive electrodeposition (Fig. 4A). The distribution of the catalysts in the porous substrate was followed by SEM/EDX cross-section analysis (Fig. 4B). The EDX signal for Pt shows that although the catalyst is mostly located on the edges, its presence is confirmed throughout the whole cross-section. However, the Ru content in the deposits did not exceed 10% of that of Pt. Fig. 5 shows half-cell limiting currents obtained for methanol oxidation at these electrodes in which the macrocyclic component in the catalyst was electropolymerized at different potentials and Pt electrode-posited at -0.3 V (curve (a)). Maximum activity is attained when the Ru(II) compound is electropolymerized at a potential of $+1.25$ V. Linear sweep voltammograms for these electrodes coated with Pt/poly[Ru(II)] in these conditions are shown in Fig. 6 for various methanol concentrations. Oxidation of methanol occurs at less anodic potentials ($E_{1/2} = +0.25$) than observed for the same catalyst applied on a non-porous substrate ($E_{1/2} = +0.6$ V, Fig. 3, curve (c)). The limiting current increases until a methanol

concentration of 7 v/o is attained. No significant current increase is obtained at higher methanol concentrations.

Experiments conducted in a fuel cell configuration showed the same behavior than that obtained in the half-cell experiments: the maximum power is obtained with films of Pt/poly[Ru(II)] with the macrocyclic compound electropolymerized at $+1.25$ V (Fig. 5, curve (b)). Moreover, for a Ru(II) content of $0.05\,mg/cm^2$ in these films (the Ru(II) content is about one-tenth of that of the macrocyclic compound), the power was independent of the Pt content in the range $0.25–1\,mg/cm^2$. Attempts to increase the maximum power ($\sim15\,mW/cm^2$) were unsuccessful probably due to non-homogeneous distribution of the catalysts in the porous substrate (as evidenced by SEM/EDX analysis) as well as to methanol crossover through the Nafion membrane.

4. Summary and conclusion

Metalloporphyrins containing non-noble metal ions (Co(III) and Ru(II)) have been used as catalysts for the reduction of oxygen and oxidation of methanol which are the reactions occurring at the cathode and anode, respectively, of a direct methanol fuel cell. It has been shown that these catalysts can be introduced as electropolymerized films in carbon-coated carbon paper electrodes as well as in aerogel porous carbon electrodes. The potential of oxygen reduction is lower by 0.25 V for poly[Co(III)]/C compared to commercial Pt/C and that for methanol oxidation is higher by ~0.1 V for Pt + poly[Ru(II)]/C compared to commercial Pt-Ru/C. However, higher limiting currents are obtained with the same or even smaller contents of the metalloporphyrins used as catalysts. Continuation of the research is aimed to improve the catalyst performance by increasing the metalloporphyrin/carbon ratio, searching new techniques for better distribution of the catalysts in porous carbon substrates and for the decrease of methanol crossover through the membrane.
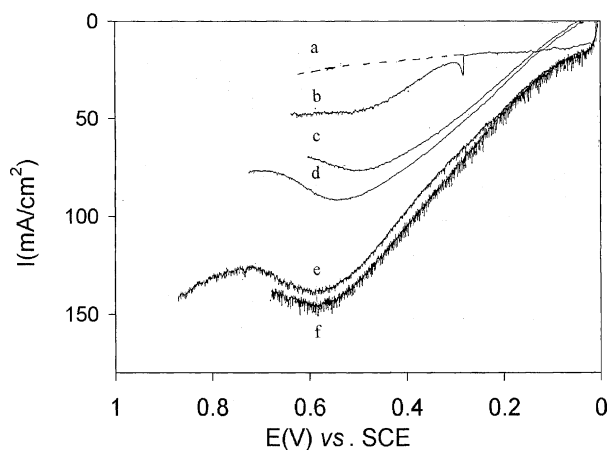

Fig. 6. Polarization curves at a scan rate of 1 mV/s for the oxidation of methanol in 1 M H_2SO_4 and at 80 °C at an aerogel carbon paper electrode electrodeposited with Pt + poly[Ru(II)]. Curves (a)–(f) are for the addition of 0, 0.25, 0.75, 1.75 and 2.5 M methanol, respectively.

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