SHORT COMMUNICATION

Electrocatalytic oxidation of methanol on platinum dispersed in polyaniline conducting polymers

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Received 1 September 1988; revised 31 October 1988

1. Introduction

Electronic conducting organic polymers are known to be very important new materials due to the large field of their potential application [1–3]. The electropolymerization of some organic monomers is particularly attractive, because the deposits obtained are generally homogeneous, strongly adherent to the electrode surface and chemically stable. Some of them, such as polyaniline, polypyrrole and polythiophene, are particularly interesting since they may be formed in aqueous electrolytic solutions and are stable in such media.

Electropolymerized polyaniline may be used in electrochromic displays, organic batteries or ion-sensitive electrodes [4]. Recently the incorporation of catalytic metal particles into polymer-modified electrodes has gained wide interest for electrocatalytic purposes. It is known that highly dispersed platinum catalysts have been widely employed particularly for organic fuel cells such as formic acid or methanol fuel cells [5].

In this preliminary work the electrocatalytic oxidation of methanol at Pt modified polyaniline coated electrodes has been investigated.

2. Experimental details

Solutions were prepared from water (Millipore 'Milli Q' system) and Merck reagents (p.a. for aniline and methanol, 'zur synthese' for H_2PtCl_6, $6H_2O$ and 'Suprapur' for H_2SO_4). Aniline was purified by distillation under vacuum.

All experiments were performed at room temperature under a nitrogen atmosphere in a three-electrode cell with a vitreous carbon counter electrode and a mercury/mercurous sulphate electrode (MSE) as reference. However, the electrode potentials are given on the reversible hydrogen electrode (RHE) scale. Working gold electrodes were used as substrates for the film depositon.

The polyaniline films were grown by electrochemical oxidation of the corresponding monomer from solutions containing 0.1 M aniline in 0.5 M H_2SO_4, using cyclic voltammetry (sweep rate $v = 50\,mV\,s^{-1}$). Polyaniline-coated gold electrodes were modified by potentiodynamic cycling in 0.5 M H_2SO_4 containing 0.01% H_2PtCl_6 at $v = 50\,mV\,s^{-1}$, between 0.08 and 0.78 V/RHE.

The voltammograms were recorded using standard equipment (a Wenking MP-81 potentiostat, a Wenking Model VSG72 waveform generator and a Linseis LY-1700 XY recorder).

3. Results and discussion

Figure 1 shows the electrodepositon of polyaniline using a 0.1 M aniline solution in 0.5 M H_2SO_4 and cycling the electrode potential between 0.08 and 1.13 V/RHE at $50\,mV\,s^{-1}$. During the first cycle the film deposition begins at 0.68 V/RHE, and the polyaniline film grows during continuous potential cycling, as evidenced by the increase of the redox charge at potentials greater than 0.9 V/RHE.

The voltammogram in a blank solution (0.5 M H_2SO_4) shows two main reversible redox systems. The voltammogram is relatively complex, but displays well-defined electroactive regions. The small peak in the middle is attributed to different structures of the polyaniline film resulting from different coupling processes between aniline cation radicals [6, 7].

The electrocatalytic oxidation of 1 M methanol in acid medium at a polyaniline-coated gold electrode was investigated, but no oxidation current was found.

The polyaniline-coated gold electrodes were modified by deposition of platinum particles into the polymer films. This was achieved by potentiodynamic cycling in 0.5 M H_2SO_4 + 0.01% H_2PtCl_6. Under these experimental conditions, it is reasonably expected that the Pt particles grow during the successive sweeps. Different cycling times (5, 10 and 15 min) were used. Voltammograms recorded in the supporting electrolyte alone are shown in Fig. 2 for comparison. In the presence of deposited Pt, the reversible peaks of the polymer are inhibited.

The behaviour of the platinum-modified polymer electrodes towards the electrocatalytic oxidation of 1 M methanol in acid medium is shown in Fig. 3. Clearly, the Pt deposit behaves as a good electro-

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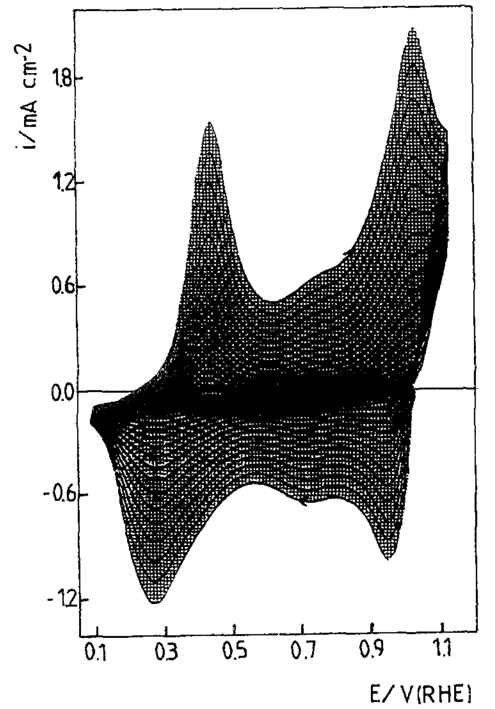

Fig. 1. Cyclic voltammograms, recorded at 50 mV s^{-1}, of a 0.1 M aniline solution in 0.5 M H_2SO_4 on a gold electrode.

catalyst for the oxidation of methanol since the *i–E* polarization curves are strongly modified. Methanol oxidation starts at around 0.48 V/RHE and reaches a maximum rate at $E_p = 0.84$ V/RHE with peak current densities, i_p, of 1.8, 3.5 and 6.3 mA cm^{-2}, respectively for the different amounts of deposited platinum. The current densities of methanol oxidation increase with time during continuous cycling, probably because the catalyst particle size changes with time.

During the negative sweep, no reduction peak appears in the voltammogram but, conversely, an anodic peak is recorded, corresponding to methanol oxidation. The cyclic voltammogram is relatively different from that obtained at a smooth platinum bead electrode under similar experimental conditions (sweep rate of 5 mV s^{-1}, scan limits of 0.08 and 1.08 V/RHE) (Fig. 4) [8, 9]. It is remarkable that for the voltammogram recorded at a 15 min deposition time polymer electrode, the oxidation current during the negative sweep is superimposed on that during the positive sweep. This apparently means that the strongly chemisorbed poisoning species are not formed to any great extent on the Pt-modifed polymer

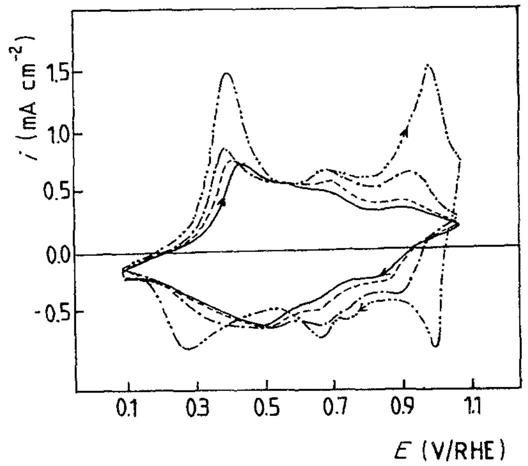

Fig. 2. Voltammograms of a polyaniline film modified by platinum particles in 0.5 M H_2SO_4; 5 mV s^{-1}, 25°C. Time of platinum deposit: (—··—) 0 min; (—·—) 5 min; (– – –) 10 min; (——) 15 min.

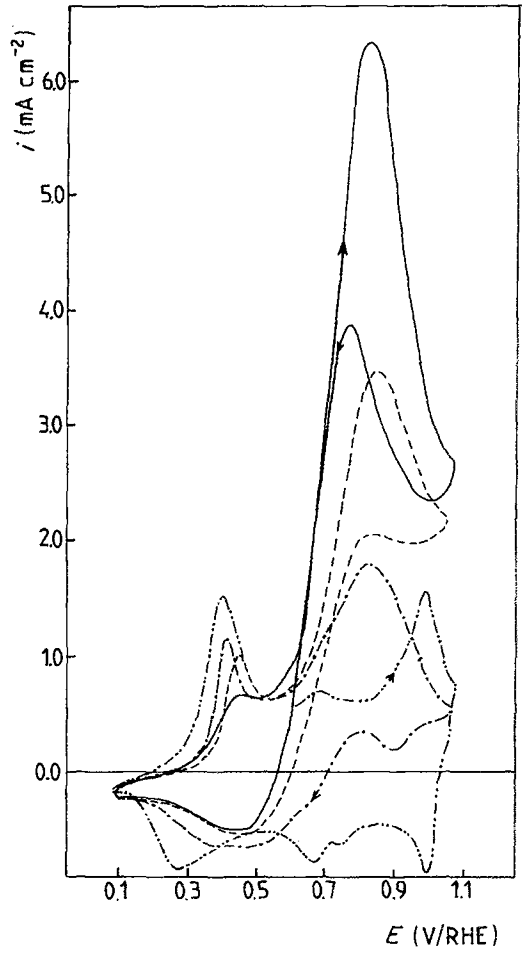

Fig. 3. Voltammograms recorded under the same experimental conditions as in Fig. 2 but with 1 M CH_3OH.

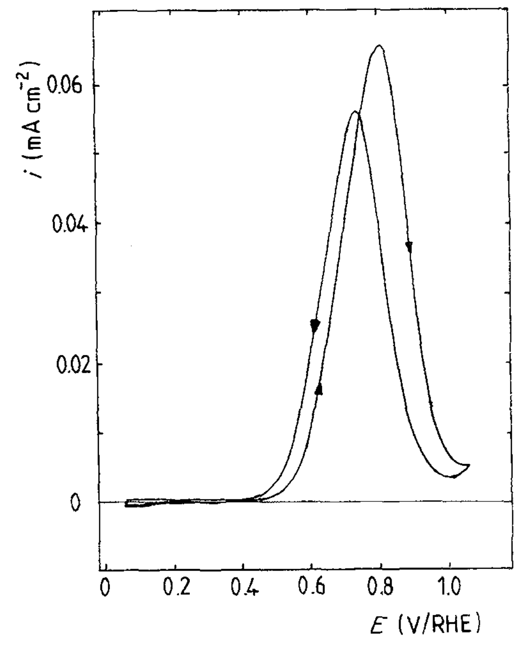

Fig. 4. Voltammogram of a smooth platinum bead electrode in 0.5 M H_2SO_4 + 1 M CH_3OH; 5 mV s^{-1}, 25°C.

electrode. The strongly chemisorbed species require a critical geometrical arrangement of the catalyst sites so that their formation to a significant extent on a small microparticle Pt catalyst is less probable.

Acknowledgements

Part of this work was performed within the framework of the contract AFME No. 7.06.0016 granted to which we are greatly indebted by the 'Agence Francaise pour la Maîtrise de l'Energie'.

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