JOURNAL OF APPLIED ELECTROCHEMISTRY **22** (1992) 922–926

Electrocatalytic oxidation of methanol on platinum microparticles in polypyrrole

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Received 10 October 1991; accepted 21 January 1992

The oxidation of methanol on gold electrodes modified with polypyrrole and platinum is reported. These electrodes were characterized by cyclic voltammetry and by 12 h polarizations in methanol solutions. They were found to give higher currents and lower rates of drift than electrodes of platinum and platinized gold. The effect of varying the amount of platinum deposited is also discussed.

1. Introduction

Although polypyrrole (PPy) was first prepared at the beginning of the century [1] it was not until the synthesis of continuous films by anodic oxidation was reported in 1979 [2] that interest in PPy began to expand, prompting a large body of literature relating to the various properties of this conducting polymer.

PPy has found particular utility in the rapidly expanding field of chemically modified electrodes [3]. Polymer films are frequently more effective than monolayers of adsorbed or covalently bound catalysts since they display better stability and a higher active site concentration. Furthermore, anodic deposition allows the polymers to be prepared as a uniform coating over irregular surfaces and offers easy control over the film thickness. The catalysts may be incorporated as counter ions balancing the positive charge on the oxidized polymer, or as pendant groups attached to the polymer backbone, either by utilizing functionalized monomers or through chemical modification of an already deposited PPy film.

Since the first report [4] PPy has been modified with a variety of metals, including Pd, Pt, Pb, Cu, Ni, Sn and Au [4, 5]. Pt deposited in PPy has received attention as a catalyst for the reduction of oxygen [6, 7, 8] and the oxidation of hydrogen [7] and hydrogen peroxide [9]. In this report the oxidation of methanol on gold electrodes serially modified with PPy and platinum will be described. This reaction was chosen for two reasons. First, under the conditions used for methanol oxidation it will occur at significant rates only on Pt and not on the Au substrate and secondly, it is known to cause considerable electrode poisoning due, it is generally accepted, to adsorption of CO species [10]. Promising results have been reported for the anodic oxidation of methanol on Pt particles in ion-exchange membranes [11], polyaniline [12] and a copolymer of pyrrole and dithiophene [13]. These film modified electrodes have shown some protection of the electrocatalytic properties of the metal particles from poisoning. Here we will describe the oxidation of methanol at gold electrodes serially modified with PPy and Pt in both acidic and neutral media, characterized by cyclic voltammetry and polarizations up to 12 hours duration at constant potential. Several different types of electrode were used. The principle electrodes were thin film gold electrodes modified with PPy and then with platinum. The platinum was deposited either at a constant potential or using a pulse train and these electrodes are referred to as Au/PPy/Pt [Pot] and Au/PPy/Pt [Pul], respectively. The estimated PPy film thickness and platinum loading as given in brackets so, for example, Au/PPy/Pt (200 nm/230 $\mu g\,cm^{-2}$) [Pot] refers to a gold electrode modified with about 200 nm of PPy and 230 $\mu g\,cm^{-2}$ of platinum, which was deposited at a constant potential. To facilitate comparison, platinum electrodes and gold electrodes modified with platinum were also used. This latter type are referred to as Au/Pt [Pot] and Au/Pt [Pul] depending on whether the platinum was deposited at a constant potential or by a pulse train and as above the platinum loading is given in brackets.

2. Experimental details

2.1. *Materials*

H_2PtCl_6 was obtained from Fluka; KCl, KNO_3, H_2SO_4 and pyrrole were obtained from Merck; p-toluenesulphonic acid monohydrate was obtained from Aldrich; methanol (MOS pur élec, electronic grade) was obtained from Soprelec SA. The electrochemical experiments were performed using an EG&G Potentiostat Galvanostat model 273A connected to either a BBC Se 120 *y-t* recorder, or a Kipp & Zonen *x.y* recorder. The measurements were performed in a glass titration vessel, surrounded by an integral water jacket. The temperature was controlled at 25° C by a Lauda RC6 circulator. All solutions were saturated with nitrogen prior to use and were maintained under an inert blanket during the experiment. The pyrrole was always distilled at atmospheric pressure prior to each experiment. The reference electrode used was either an SCE for the neutral electrolyte, or $Hg/Hg_2SO_4/K_2SO_4$ (saturated) for the acid electrolytes, both electrodes were obtained from Metrohm AG. The counter electrode was a piece of platinum foil of geometric area about $10\,cm^2$. The working electrodes were either platinum or gold evaporated on a silicon wafer. A 200 nm thick titanium adhesion layer between the metal and the silicon was used. The wafer was diced into fragments which were glued onto a support and electrical contact was made using conducting epoxy. The electrodes were encapsulated with epoxy resin to give planar electrodes of geometric area about $0.16\,cm^2$. Surface profile measurements were made with an Alpha-step 200 surface profiler from Tencor Instruments.

2.2. *Deposition of polymeric films*

The PPy films were deposited by cyclic voltammetry, sweeping at $25\,mV\,s^{-1}$ in 0.1 M potassium chloride containing 0.1 M of freshly distilled pyrrole and saturated with nitrogen, between 0.1 and 0.825 V/SCE. The thickness of the films was adjusted by varying the number of sweeps.

2.3. *Deposition of platinum particles*

Two procedures (see below) were mainly used for the deposition of the platinum microparticles. Both utilized the electrochemical reduction of a solution of 0.04 wt% hexachloroplatinic acid dissolved in 50 mM KCl at −0.2 V/SCE. In the first procedure the electrode was polarized at a constant potential of −0.2 V, while in the second procedure a repeated pulse sequence composed of a 5 s open circuit period followed by 1 s polarization at −0.2 V/SCE, was used. Prior to the reduction the electrode was soaked in the hexachloroplatinic acid solution for 15 min. The total charge passed was measured and by assuming that the reduction of the Pt^{4+} is 100% efficient the amount of platinum deposited was estimated. It was found that charge passed in the absence of the Pt^{4+} was negligible when compared to that passed when the acid was present.

2.4. *Determination of the thickness of the PPy films*

The film thickness was determined using a surface profiler. The equipment required a flat area on the sample to act as a reference. This was obtained by masking half of the electrode surface.

3. Results

3.1. *Characterization of the polymer films*

Using the films as prepared above, it was possible to measure the film thickness using a surface profiler. The measured film thickness was plotted against the total charge passed during the deposition and fell on a straight line of slope $2400 \pm 300\,nm\,(C\,cm^{-2})^{-1}$. This value, which was used to estimate the thickness of other PPy films deposited under the same conditions, is comparable with the value of about $2200\,nm\,(C\,cm^{-2})^{-1}$ given by the literature for galvanostatically grown films [6].

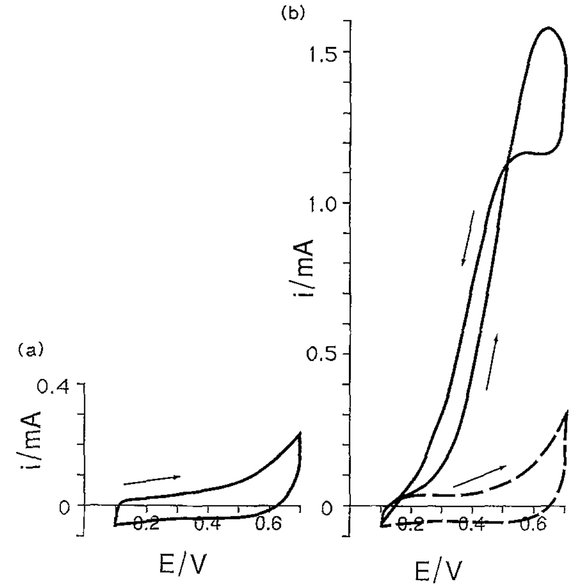

Fig. 1. Cyclic voltammetry of 1.0 M methanol in 1.0 M H_3PO_4 on (a) an Au/PPy electrode (300 nm PPy), (b) an Au/PPy/Pt (300 nm PPy, $200\,\mu g\,cm^{-2}$ Pt) [Pot]. The temperature was 25° C and the scan speed $25\,mV\,s^{-1}$. The potential is given against SCE. The response in the absence of methanol is shown by a broken line, which for the Au/PPy electrode is hidden by the solid line recorded in the presence of methanol.

When the PPy films were examined by SEM they displayed the typical nodular morphology of PPy films grown in aqueous electrolytes. After deposition of the platinum a large number of spheres, of diameter about 50 nm, could be seen distributed across the polymer surface. Freshly prepared Au/PPy/Pt electrodes were also examined by XPS, which revealed the platinum to be entirely in the 0 oxidation state.

3.2. *Oxidation of methanol at the Au/PPy/Pt electrodes*

Figure 1 shows that, in the absence of methanol, the Pt does not have a dramatic effect upon the electrochemical properties of the PPy film, as determined by cyclic voltammetry, over the range 0.1–0.7 V/SCE. This is in agreement with previously reported observations [6]. However a considerable difference between the Au/PPy/Pt and Au/PPy electrodes is seen in the presence of methanol. The Au/PPy electrode displays no apparent methanol oxidation under these conditions (Fig. 1a) whilst the Au/PPy/Pt electrode showed the characteristic cyclic voltammogram of methanol oxidation [14]. Similar behaviour was also seen in phosphate buffered saline and 0.1 M H_2SO_4 solutions. It is well known that although platinum electrodes display high initial activity for methanol oxidation this decays due, it is generally accepted, to poisoning by bound CO species [10]. Figure 2 shows

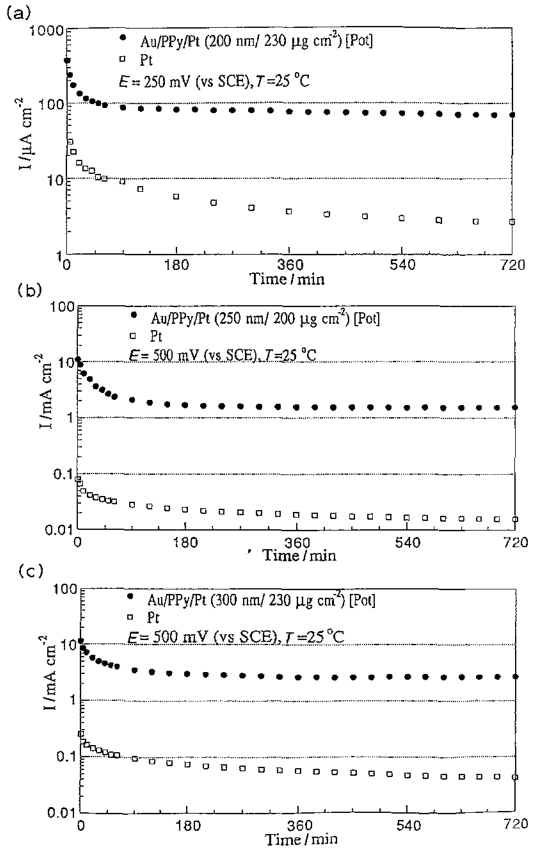

Fig. 2. Comparison of the current density at platinum and Au/PPy/Pt electrodes during the electrolysis of 1.0 M methanol in (a) phosphate buffered saline, pH 7.2, (b) 1.0 M H_3PO_4, and (c) 0.1 M H_2SO_4.

the results of 12 h polarizations of Au/PPy/Pt and platinum electrodes in neutral and acidic methanol solutions. It can be seen that the Au/PPy/Pt electrodes supported current densities of over 10 times higher than any of the other electrodes and seemed less prone to poisoning.

The thickness of the PPy in the range investigated (about 100–700 nm) was not found to have a significant effect upon the behaviour of the Au/PPy/Pt electrodes. It is known that the counter ion can affect the film morphology and conductivity [15]. To investigate the effect of the counter ion, PPy films were deposited from solutions containing Cl^-, NO_3^-, and TsO^-. After platinum deposition the behaviour of these electrodes during 12 h duration polarization in 1.0 M methanol in phosphate buffered saline was investigated. It was found that the current density supported by the films decreased in the order $Cl^- > NO_3^- > TsO^-$. As expected the amount of platinum deposited was found to have considerable influence on the electrocatalytic activity of the Au/PPy/Pt electrodes. Figure 3 shows the current density recorded at the end of a 12 h electrolysis in neutral media displayed against the platinum loading. It can be seen that the final current density increases with rising platinum loading and was greater than that at the Au/Pt electrodes.

This should be viewed in conjunction with Fig. 4. Here the percentage change in the current between the 11th and 12th hours of a 12 h electrolysis is shown as a function of platinum loading for several types of electrodes. It can be seen that the Au/PPy/Pt electrodes, particularly when deposited by the potentiostatic technique, showed smaller rates of drift than the other electrodes at comparable platinum loadings.

4. Discussion

In agreement with the published work on other polymers it has been found that platinum dispersed in PPy films displays electrocatalytic activity for methanol oxidation and that the polymer provides some protective effect against the poisoning reactions of methanol oxidation when compared with unmodified platinum or platinized gold. The studies in acidic media may be compared to similar reports on other dispersed metal/polymer systems. Kost *et al.* [12] report current densities of about 1 mA cm^{-2} for 2–5 µm thick polyaniline films modified with 30 µg cm^{-2} of platinum, recorded at 600 mV (Ag/AgCl) and in 1.0 M H_2SO_4 containing 1.0 M methanol, whilst Aramata and Ohnishi [16] report current densities of about 20 µA cm^{-2} (geometric area) for Nafion films about 200 µm thick loaded with 4–8 mg cm^{-2} of platinum, recorded in 1.0 M H_3PO_4 containing 1.0 M methanol at 600 mV/RHE. In the present work current densities of around 2 mA cm^{-2} were obtained after running the electrodes for 12 h, in 0.1 M H_2SO_4 or 1.0 M $HClO_4$ containing 1.0 M methanol at 500 mV/SCE using electrodes composed of a 300 nm PPy film modified with about 200 µg cm^{-2} of platinum.

A feature of the Au/PPy/Pt electrodes may relate to the available electrode area. However with these electrodes the hydrogen adsorption waves were not well defined and so an estimate of the effective surface area of the electrodes could not be made. The absence of well defined hydrogen adsorption waves has previously been reported for platinum in a copolymer of pyrrole and dithiophene [13] and in polyaniline [12]. In the former case it was suggested that this results from the platinum being very well dispersed so there are no platinum islands which would have the same adsorption properties as bulk platinum.

It has been suggested [17] that the high activity of polyaniline films modified with platinum for the oxidation of formate stems from metal–polymer interactions which inhibit the formation of strongly chemisorbed species. An alternative mechanism is that the longevity of platinum microparticles in anion or cation exchange membranes stems from an ability of the membranes to stabilize a surface mediator couple (Pt^0/Pt^{2+}) [16]. From the present results it is unclear which, if either, of these mechanisms applies in the current case.

Although we have not explicitly determined the distribution of the platinum particles within the PPy films it is thought that by using different deposition procedures the distribution of the metal could be altered. To this end several other deposition protocols were investigated. It was found that the electrocatalytic behaviour of the platinum deposited by the pulsed and potentiostatic methods was slightly different perhaps

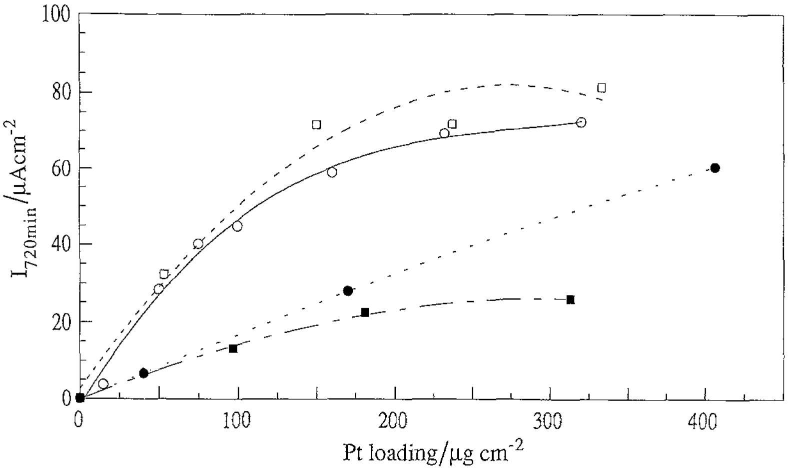

Fig. 3. The current density at the end of 12 h electrolysis of 1.0 M methanol as a function of the platinum loading. Electrolyte was phosphate buffered saline, pH 7.2, the applied potential was 250 mV/SCE and the temperature 25° C. (○) Au/PPy/Pt [Pot], (□) Au/PPy/Pt [Pul], (●) Au/Pt [Pot] and (■) Au/Pt [Pul].

reflecting a different distribution or state of the metal deposited by the two protocols. Platinum was also deposited using a procedure in which a pre-oxidised PPy film was soaked in H_2PtCl_6 solution for 2 min and then transferred to 0.1 M KCl for reduction at −0.2 V. This, it was hoped, would produce a PPy film containing uniformly distributed platinum, similar to that reported by [6]. However, the electrode was found to support very low current densities for methanol oxidation, perhaps resulting from the relatively low platinum loadings that this technique gave. Platinum was also deposited by cyclic voltammetry (sweeping by 0.6 to −0.725 V/SCE, at 25 mV s^{-1}) out of H_2PtCl_6 solution. Surprisingly this electrode displayed poor stability and decayed along approximately the same path as the thin film platinum electrodes. Although in the present study this type of electrode was not investigated, further adjustment of the deposition parameters, in particular sweep rate and potential limits, should allow this type of electrode to be optimized. Another possible variable was the length of time that the electrode was allowed to soak in the H_2PtCl_6 solution prior to the reduction, as well as the composition of that solution. However these variables were not investigated. Following the observations of Vork and Barendrecht (1989) [7] the current density during the metal deposition is also likely to be an important parameter. The effects of adjusting this parameter are currently being investigated.

The results presented in this paper were all made at 25° C. However, preliminary results of 12 h polarizations in 0.1 M H_2SO_4 containing 1.0 M methanol made at temperatures up to 60° C indicate that the electrode is stable at elevated temperatures, where it supported current densities of the order of 30 mA cm^{-2}.

In conclusion the above results show that gold electrodes modified with platinum dispersed in films of PPy display interesting electrocatalytic properties. For the model reaction of methanol oxidation the modified electrodes exhibited both better electrocatalytic activity and an increased resistance to poisoning when compared with bulk platinum.

Acknowledgements

The authors would like to thank Mme S. Pochon and

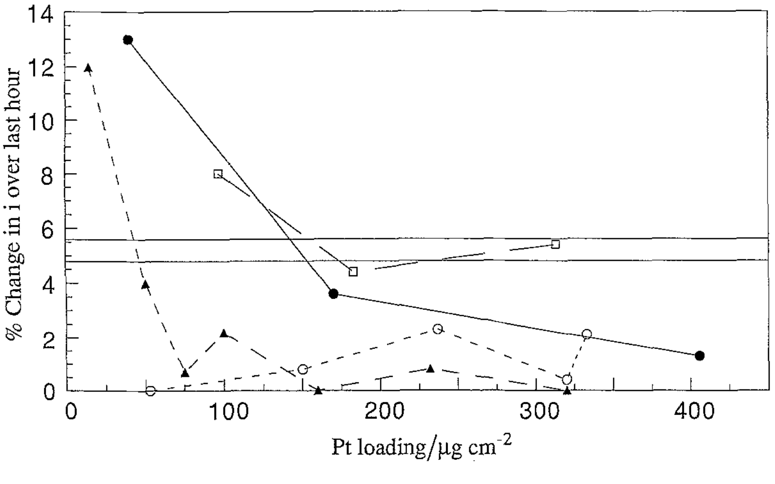

Fig. 4. The rate of decay in the current over the final hour of a 12 h electrolysis of 1.0 M methanol as a function of the platinum loading. Electrolyte was phosphate buffered saline, pH 7.2, the applied potential was 250 mV/SCE and the temperature 25° C. (●) Au/Pt [Pot], (□) Au/Pt [Pul], (▲) Au/PPy/Pt [Pot], (○) Au/PPy/Pt [Pul] and (- - -) thin film Pt.

Mr G. Mondin for their technical assistance and the Office Fédéral de l'Énergie for financial support.

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