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The electrodeposition of metals onto polypyrrole films from aqueous solution

G. K. CHANDLER*, D. PLETCHER

Department of Chemistry, The University, Southampton SO9 5NH, UK

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It is demonstrated that several metals may be electrochemically deposited onto polypyrrole films from aqueous solutions. Palladium, platinum and lead may be deposited even on thick films of the polymer (c. 0.5–2.0 μm) but ruthenium only deposits on much thinner films. The effect of the polypyrrole film on the kinetics of nucleation and growth is described and the influences of the deposition potential and the thickness of the polypyrrole layer on the characteristics of the deposition reactions are discussed.

1. Introduction

Since the initial report [1] in 1979 that thick, uniform and adhesive films of polypyrrole could be produced by the anodic oxidation of pyrrole, many papers have appeared which discuss the preparation, properties and application of this conducting polymer [2]. In the more fundamental studies, much interest has centred on the structure of the film, its conductivity and its electrochemistry, especially its ability to cycle between conducting and insulating states by oxidation and reduction. On the other hand, the applications envisaged for polypyrroles have included modified electrodes, the protection of photoelectrodes from corrosion, display devices, the controlled release of anions and as charge storage media for batteries.

It has been suggested that, since polypyrrole type polymers may be switched in a controlled way between conducting and poorly conducting states, the films might make useful components of microelectronic devices. An example was recently described by White *et al.* [3]. The possibilities would be increased substantially if metal layers could be deposited onto the polypyrrole film and in an earlier paper [4], we reported that lead could, indeed, be electroplated onto polymethylpyrrole. This paper reports studies intended to examine metal deposition reactions onto polypyrrole in more detail; the metals investigated were lead, palladium, platinum and ruthenium.

We are aware of no other literature covering the electrodeposition of metals onto polypyrrole. Some studies have, however, been reported using other types of polymers, for example redox polymers [5, 6] and polyvinylacetate [7, 8].

2. Experimental details

The cells and electrochemical instrumentation have been described previously [9]. Solutions were prepared from triply-distilled water and were deoxygenated with N_2 prior to every experiment. The pyrrole (Aldrich Chemicals) was twice distilled at reduced pressure and then stored under N_2 in a refrigerator. The base electrolytes and $Pb(NO_3)_2$ were Analar grade reagents while the palladium, platinum and ruthenium salts were obtained from Johnson Matthey Ltd.

The working electrode was either a Pt disc (area 0.2 cm^2) or a vitreous carbon disc (Tokai Carbon Co., area 0.07 cm^2), and these could be used almost interchangeably for the deposition of metals on the polypyrrole films. Before each experiment the electrodes were polished with 1,

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* *Present address*: Sensors Department, THORN EMI Central Research Laboratories, Dawley Road, Hayes, Middlesex UB3 1HH, UK.

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0.3 then 0.05 μm aluminium powder (Banner Scientific Co.) on a Metron polishing cloth. The electrodes were then placed in distilled water in and ultrasonic bath for about 30 s to remove polishing powders from the surface. The rotating vitreous carbon disc electrode, area 0.38 cm^2, was prepared in the same way.

The polypyrrole films were deposited from a solution of pyrrole (50 mmol dm^{-3}) in a base electrolyte chosen to have the anion common with that in the metal deposition solution. The films were deposited at constant potential, the charges being measured with an electronic integrator. All experiments were carried out at room temperature and potentials were all measured versus the saturated calomel electrode.

3. Results

At the commencement of these studies it was envisaged that multilayer structures or intimate mixtures of metal and polypyrrole might be prepared by pulse electrolysis of an aqueous solution containing both pyrrole and a metal ion. (Clearly the metal would have to be chosen so that it did not redissolve rapidly at the potential for the polymerization of pyrrole.) To our surprise, however, when solutions of pyrrole and metal ions (including Ag(I), Cu(II), Ni(II), Pd(II), Pt(II), Ru(II) and Pb(II)) were prepared, spontaneous homogeneous polymerization occurred and a black precipitate was observed. Moreover, stringent deoxygenation of the solutions prior to mixing did not prevent the polymerization. While the mechanism of polymerization is not clear, it clearly prevents the use of such solutions.

Hence this investigation has been limited to the deposition of metals on preformed polypyrrole films. As far as possible, however, the film of polypyrrole was prepared in a solution with the same anion as the bath for deposition of the metal. Moreover, the films were always prepared at constant potential in an aqueous solution [9] of pyrrole (50 mmol dm^{-3}). It seems reasonable to expect the characteristics of the metal deposition process to depend to some extent on:

(a) the state of conductivity of the polypyrrole film and hence the potential of the metal deposition reaction with respect to the reduction of the polypyrrole film. The conducting–insulating transition depends on electrolyte, but in aqueous solutions the cyclic voltammetry suggests the transition to be smeared out over a broad range +0.6 V to −0.5 V vs SCE;

(b) the thickness of the polypyrrole film.

As a result we have studied the depositions of four metals (palladium, platinum, lead and ruthenium), which at Pt and C cathodes take place over the range +0.6 V to −1.0 V at polypyrrole films of thickness up to 2 μm. The films are continuous and show only minor features when examined by electron mciroscopy.

3.1. *Palladium*

Fig. 1 shows cyclic voltammograms run between +0.9 V and −0.8 V vs SCE at 100 mV s^{-1} for a Pt disc electrode both uncovered (Fig. 1a) and covered by polypyrrole films of thickness 55 nm and 1.1 μm (Fig. 1b and 1c respectively). The solution is $PdCl_2$ (10 mmol dm^{-3}) in aqueous KCl (1 mol dm^{-3}) at pH 3.5. Throughout the paper, the thickness of the polypyrrole films are estimated by assuming that a charge of 8 mC cm^{-2} during the anodic polymerization leads to a layer 20 nm thick [1, 10]. The *I–E* curve at the bare Pt surface shows a cathodic peak at +25 mV vs SCE and a coupled anodic stripping peak at +532 mV. The reduction of Pd(II) is apparently diffusion controlled ($I_p \propto v^{1/2}$) and the stripping efficiency approaches 100%. There is also a small anodic peak at −220 mV probably due to hydrogen desorption. When the Pt is covered by a layer of polypyrrole, the deposition peak is shifted to −140 mV and the peak becomes somewhat sharper suggesting that a larger overpotential is essential for nucleation. Otherwise, the features of the Pd(II)–Pd couple remain similar and the anodic stripping peak remains at about +530 mV. As the thickness of the polypyrrole film increases, it is clear that the observed currents contain contributions from another process. Certainly with the 1.1 μm layer, there is an additional envelope of charge extending from +0.7 V to −0.3 V and this is due to the reduction and reoxidation of the polypyrrole

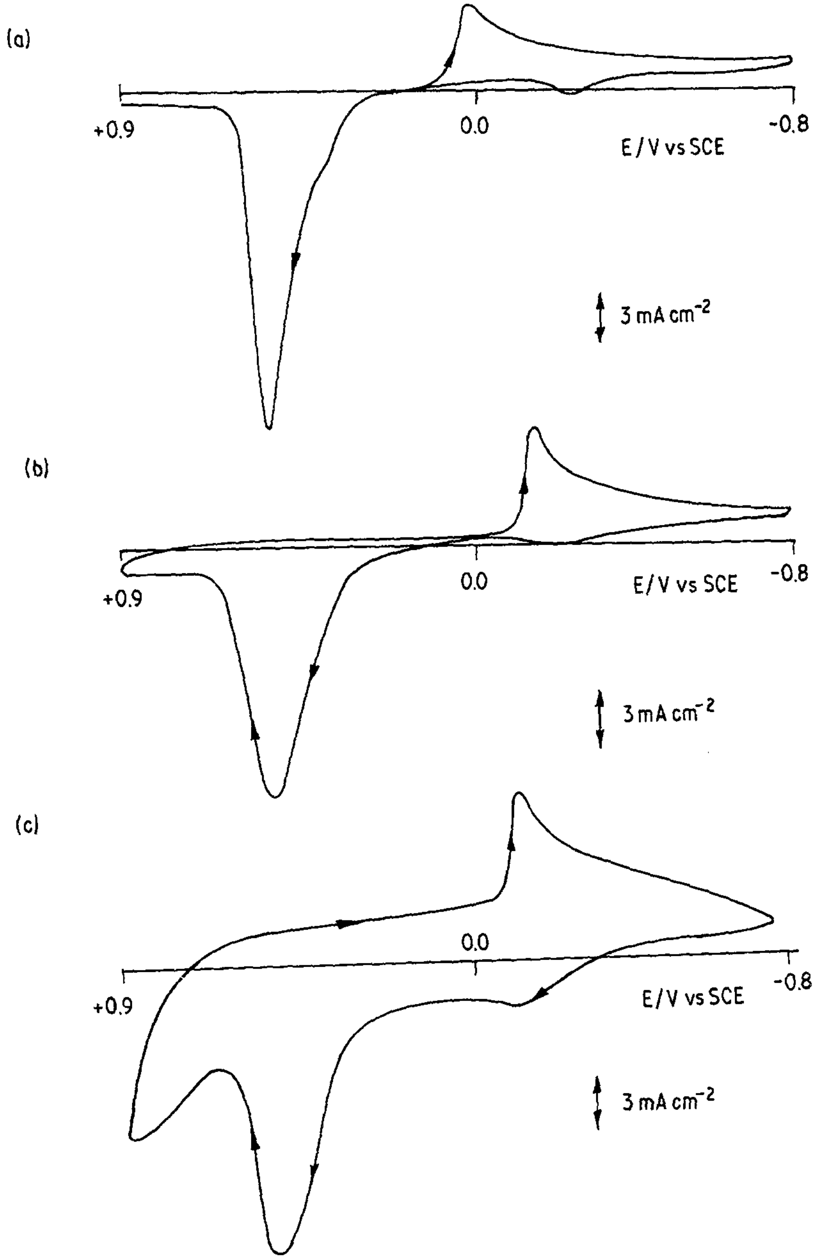

Fig. 1. Cyclic voltammograms for a solution of $PdCl_2$ (10 mmol dm^{-3}) in aqueous KCl (1 mol dm^{-3}), pH 3.5, at a Pt disc electrode (a), and a Pt disc electrode covered by a polypyrrole film of thickness (b) 55 nm, (c) 1.1 μm. Potential scan rates 100 mV s^{-1}. Polypyrrole films formed at +0.9 V vs SCE using a solution of pyrrole (50 mmol dm^{-3}) in aqueous KCl (1 mol dm^{-3}).

layer. Hence palladium deposition and dissolution occur at potentials where the polypyrrole film is in a partially oxidized state and there appears to be no limitation in the rate of deposition of palladium due to the film even when it is above 1 μm thick.

3.2. *Platinum*

Platinum deposition was studied from a bath of K_2PtCl_4 (10 mmol dm^{-3}) in H_2SO_4. The cyclic voltammograms for this process are more complex because hydrogen adsorption peaks overlie

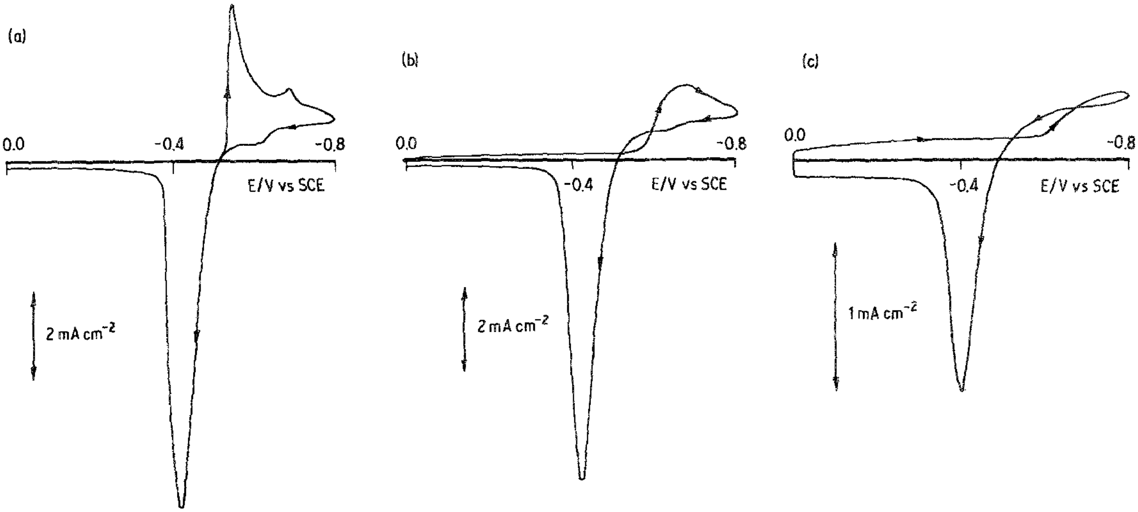

Fig. 2. Cyclic voltammograms for a solution of $Pb(NO_3)_2$ (12 mmol dm^{-3}) in KNO_3 (1 mol dm^{-3}) run at 100 mV s^{-1}. (a) Bare Pt; (b) Pt covered by a 57 nm polypyrrole layer; (c) Pt covered by 0.19 μm polypyrrole. Polypyrrole film prepared at 0.8 V in a solution of pyrrole (50 mmol dm^{-3}) in KNO_3 (1 mol dm^{-3}).

the peaks for platinum deposition and there are no peaks for the dissolution of the metal. On a polypyrrole surface, a well-formed peak for Pt deposition is observed at −210 mV and this peak is largely unchanged as the polypyrrole layer is prepared thicker, at least up to 0.5 μm. With even thicker films, the deposition peak begins to broaden.

3.3. *Lead*

From a solution of $Pb(NO_3)_2$ (10 mmol dm^{-3}) in KNO_3 (1 mol dm^{-3}), the deposition of lead on Pt occurs at $E_p = -0.54$ V, a potential where cyclic voltammograms of a polypyrrole film would indicate that it is almost completely reduced. The curve in Fig. 2a also shows that only a small nucleation potential is required and the Pb–Pb^{2+} couple is very rapid. With a relatively thin film of polypyrrole, i.e. 57 nm, see Fig. 2b, the nucleation and growth of the lead is inhibited and the peak potential is shifted to −0.64 V. Hence the nucleation loop becomes more apparent and the charges associated with both deposition and stripping during the cycle between 0.0 V and −0.8 V vs SCE become smaller. The anodic peak potential is not shifted. Fig. 1c shows the cyclic voltammogram at a 0.19 μm film of polypyrrole. With the thicker layer the nucleation and growth processes are further retarded and the deposition process is seen only as a wave close to the negative limit. The anodic stripping peak still occurs at −0.40 V although there is again less lead to be dissolved. On this figure, some current for the oxidation–reduction of the polypyrrole film is also observed. If the experiments are repeated on thicker polypyrrole films, the trends shown by Fig. 2a–c continue. The thickest film investigated was 1.6 μm and deposition of lead was observed, but only as a slow process. These results are very similar to those reported earlier for polymethylpyrrole films [4].

3.4. *Ruthenium*

The experiments with ruthenium employed a solution of $RuCl_3$ (10 mmol dm^{-3}) in aqueous KCl (1 mol dm^{-3}). Fig. 3 compares the deposition of ruthenium onto bare vitreous carbon and carbon with 14 nm polypyrrole film. With this metal, deposition occurs at $E_p = -0.70$ V vs SCE on the film free surface and even a thin film of polypyrrole inhibits the deposition process. The 14 nm film shifts the deposition to $E_p = -1.0$ V and with thicker films ($>$ 50 nm), there is no evidence for nucleation or growth on a voltammogram run at 100 mV s^{-1}.

The influence of the polypyrrole layer on the deposition of ruthenium was also studied by potential step methods. At bare vitreous carbon, well-formed, rising *I–t* transients were recorded

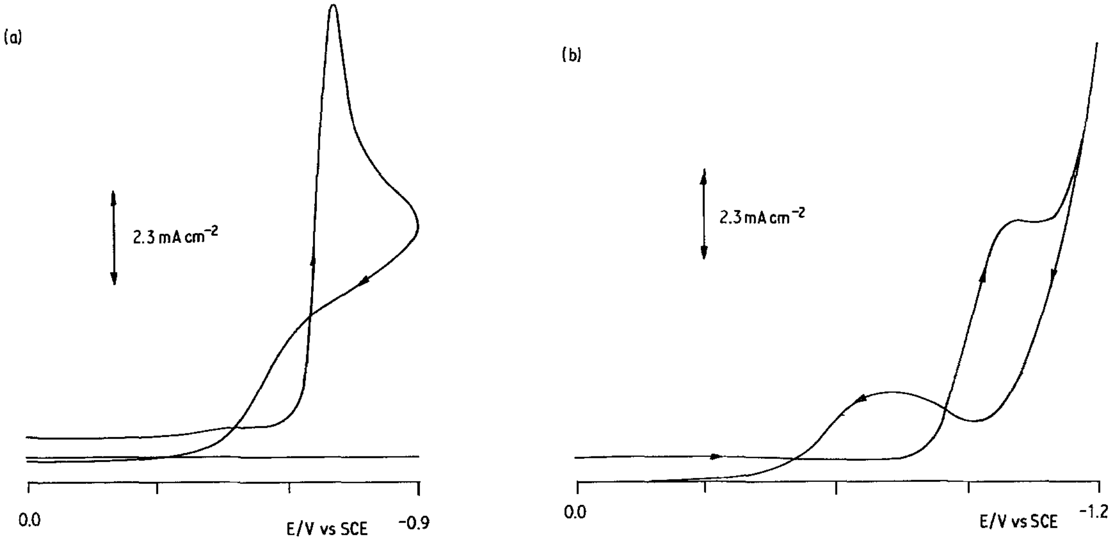

Fig. 3. Cyclic voltammograms for a solution of $RuCl_3$ (10 mmol dm^{-3}) in KCl (1 mol dm^{-3}) run at 100 mV s^{-1}. (a) Bare vitreous C; (b) C covered by 14 nm film. Polypyrrole film prepared at +0.9 V in a solution of pyrrole (50 mmol dm^{-3}) in KCl (1 mol dm^{-3}).

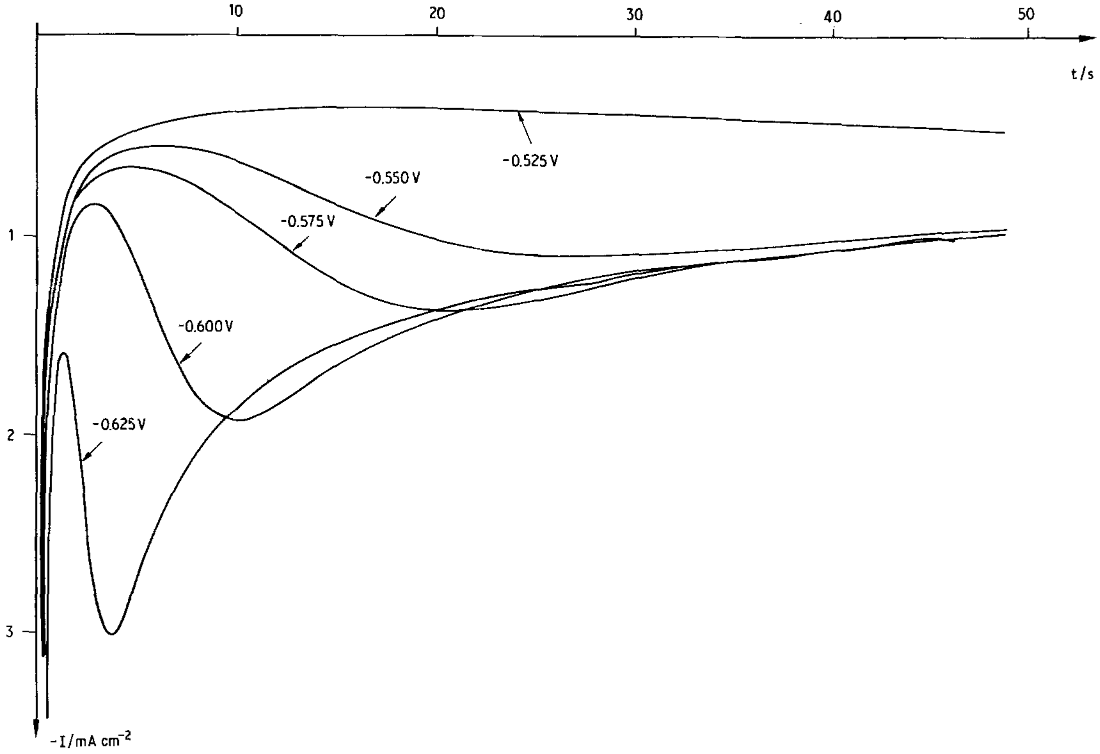

Fig. 4. I–t transients in response to potential steps from 0.0 V to the potential shown. Vitreous carbon electrode in $RuCl_3$ (10 mmol dm^{-3}) + KCl (1 mol dm^{-3}).

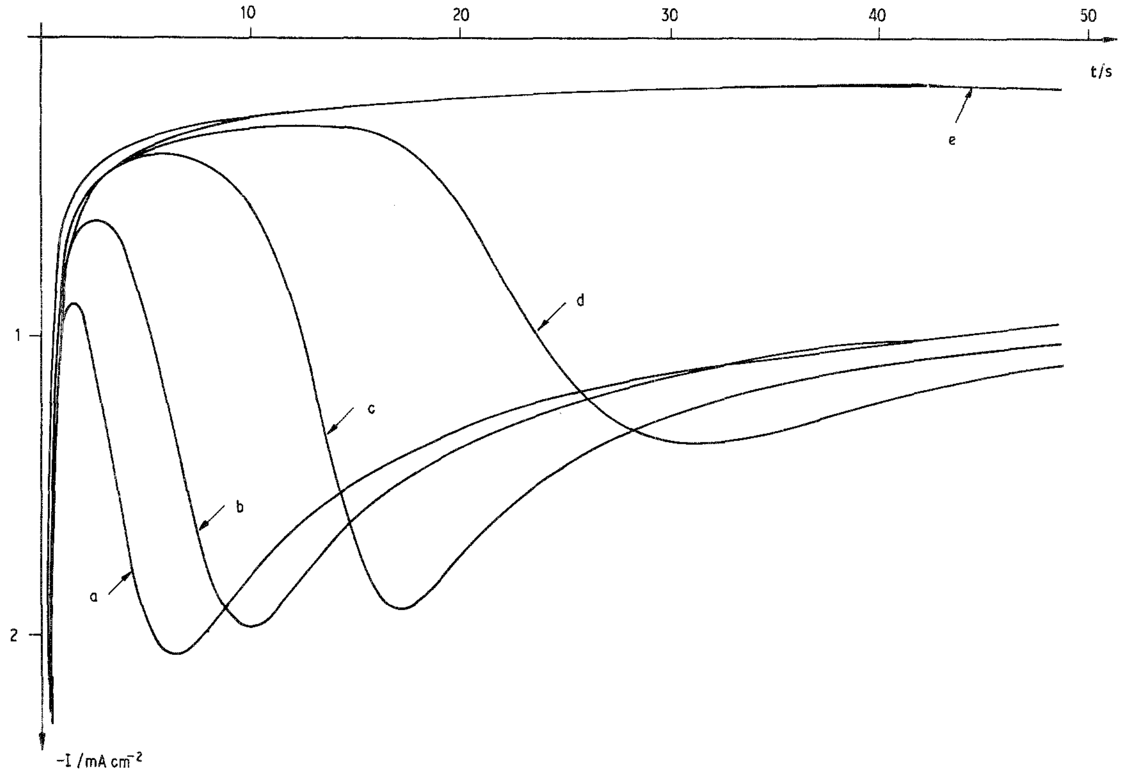

Fig. 5. I–t transients in response to potential steps from 0.0 V to −0.6 V. Solution is $RuCl_3$ (10 mmol dm^{-3}) + KCl (1 mol dm^{-3}). Vitreous carbon covered by polypyrrole thickness: (a) 0 nm; (b) 1.4 nm; (c) 2.4 nm; (d) 4.7 nm; (e) 140 nm. Polypyrrole deposited at +0.7 V from pyrrole (50 mmol dm^{-3}) in KCl (1 mol dm^{-3}).

in response to potential steps from 0.0 V to potentials in the range −0.5 V to −0.8 V (see Fig. 4). Fig. 5 shows the effect of polypyrrole film thickness on the I–t response to a potential step from 0.0 V to −0.6 V. Again it can be clearly seen that even the thin films of polypyrrole retard nucleation and growth of the metal phase although interestingly, if nucleation occurs, the current always reaches the mass transport limit at long times. In fact, when the film was thicker than 30 nm it was never possible to deposit the ruthenium metal. On the other hand, using a RDE where the vitreous carbon disc was covered with 20 nm polypyrrole, it was possible to show that the deposition of ruthenium proceeds at a mass transport limited rate. Indeed, the diffusion coefficienct for Ru(III) calculated from the slope of the I–$\omega^{1/2}$ plot using a C–polypyrrole–Ru electrode was 0.9×10^{-5} cm^{-2} s^{-1}, the same value as when the electrode was C–Ru; both experiments were carried out at −0.8 V vs SCE. Hence it appears that the problem in depositing ruthenium onto thicker polypyrrole films must lie in the nucleation step, since once a ruthenium layer is formed the polymer film can carry the electrons necessary for the mass transport controlled reduction of Ru(III).

4. Discussion

The literature [2] would lead one to expect that polypyrrole undergoes a conductor-to-insulator change due to reduction and, although cyclic voltammograms for this process show broad peaks and some structure, it appears to be complete by −0.4 V. Hence it is to be expected that no reductions would be possible at potentials negative to this value at the polypyrrole surface. This is certainly not the case as both ruthenium and lead may be electrodeposited at potentials negative to −0.4 V, the former even at polypyrrole films 1.6 μm thick. Perhaps one should also consider the possibility that metal deposition occurs, at least initially, within pores in the film and that subsequently electrons are conducted through dendrites within the pores. Such a mechanism is quite unlikely at thicker films and such a conclusion is supported by the sharp shape, independent of film thickness, of the anodic stripping peaks observed for both lead and palladium. Even in the case of ruthenium, where deposition is only possible on quite thin films, the currents for the Ru(III)–Ru process rapidly reach values expected for deposition under planar diffusion control to the total geometric area of the electrode. Moreover it is the nucleation rather than the growth process which is most affected by the film.

The metals, palladium, platinum and lead, can certainly be deposited onto thick polypyrrole films, and metal layers several microns thick can readily be formed on polymer films 1–2 μm thick. The first influence of the polymer film is always to inhibit the initiation of metal deposition and the nucleation overpotential is increased by 50–300 mV; this change occurs even with quite thin films of polypyrrole and is not surprising for the substantial change in the surface properties represented by a transition from metal or carbon to conducting polymer. Whether the growth of the metal layer is also affected seems to depend on the potential of the metal deposition reaction. With platinum and palladium, the deposition occurs at potentials where the polypyrrole is quite conducting and there appears to be no limitation in the growth rate due to the film. On the other hand, the curve for lead deposition on the 0.19 μm film clearly shows that the deposition of lead is retarded by the presence of the film, even when nucleation has occurred. Probably the restriction on the maximum film thickness where nucleation of ruthenium is possible is so severe that limitations in its growth rate are not apparent. The data is, however, compatible with a situation where the polypyrrole becomes less conducting as the potential is made more negative but where this change is less severe than previously considered, so that some conductivity is retained at -0.8 V vs SCE.

From the viewpoint of technology, we believe that Pt–polypyrrole–Pt or Pd–polypyrrole–Pd sandwiches could be manufactured with controlled variation of both metal and polymer layers.

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