Preparation and Electrochemistry of a New Bilayer Electrode, Pt/poly[Ru^{II}(4-vinyl-4′-methyl-2,2′-bipyridine)$_3$$^{2+}$·2(ClO$_4$$^-$)]/polypyrrole

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Mediated redox reactions of a polypyrrole film were observed at a new bilayer electrode, the title system, which was prepared by the anodic oxidation of pyrrole in acetonitrile at a Pt electrode modified with the Ru complex followed by repeated potential scans (−2.10 to +1.15 V *vs.* Ag/Ag$^+$ reference electrode).

While the electrochemistry of anodically deposited polypyrrole films has been the subject of much recent interest, such studies have been based on polypyrrole films deposited on the surfaces of metallic[1—3] or inorganic semiconductor[4] electrodes. We now report the first study of the preparation and electrochemistry of a bilayer electrode in which a polypyrrole film is deposited on a metallo-organic system, poly-[Ru^{II}(4-vinyl-4′-methyl-2,2′-bipyridine)$_3$$^{2+}$·2(ClO$_4$$^-$)] (**1**). The structure of the bilayer electrode can be expressed as Pt/(**1**)/polypyrrole.

poly[Ru^{II}(4-vinyl-4′-methyl-2,2′-bipyridine)$_3$$^{2+}$·2(ClO$_4$$^-$)]

(**1**)

Pyrrole was oxidised potentiostatically at +0.56 V† at a Pt/(**1**) anode immersed in argon-purged anhydrous acetonitrile containing 0.1 M TBAP (tetra-n-butylammonium perchlorate). The charge passed for polypyrrole deposition was typically 4 × 10^{-2} C cm^{-2}. The Pt/(**1**) electrode was prepared according to the reported method[5] (coverage: 5.6 × 10^{-9} mol cm^{-2}).

The c.v. (cyclic voltammogram) for polypyrrole deposited directly on a platinum substrate (by passing the same amount of charge as above) is depicted together with the c.v. for the above Pt/(**1**) electrode in Figure 1, (a) and (b), respectively. C.v.s obtained in MeCN containing 0.1 M TBAP for the doubly deposited electrode, *i.e.*, (**1**) and polypyrrole deposited on a platinum substrate, initially showed current increase at every potential scan between −2.10 and +1.15 V†

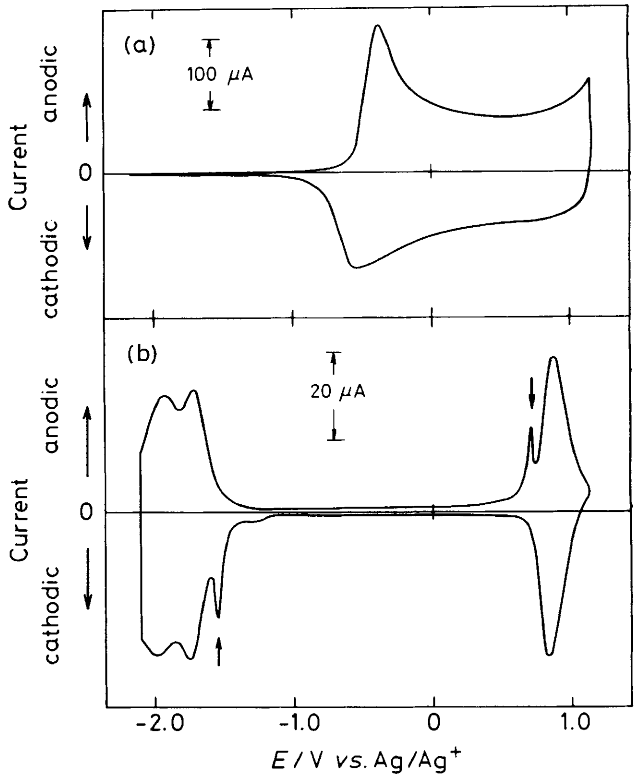

Figure 1. C.v. in 0.1 M TBAP–MeCN at a scan rate of 0.1 V s^{-1}: (a) Pt/polypyrrole electrode prepared by passing 4 × 10^{-2} C cm^{-2}; (b) Pt/(**1**) electrode coated with 5.6 × 10^{-9} mol cm^{-2} of electropolymerised (**1**). Sharp peaks at arrows have been noted as a bilayer mimicking phenomenon (ref. 7).

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† All potentials were measured *vs.* an Ag/Ag$^+$ reference electrode, which showed a potential of +0.290 V *vs.* a saturated calomel electrode in acetonitrile containing 0.1 M TBAP.

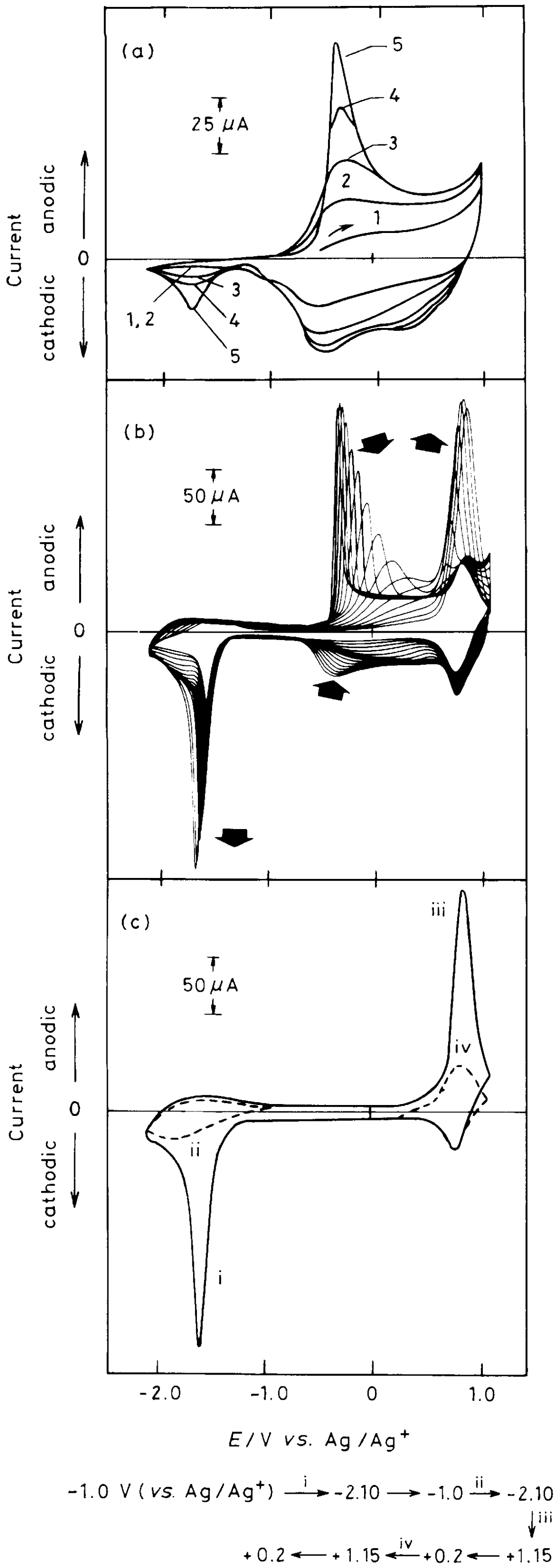

Figure 2. Changes in c.v.s of the bilayer electrode, Pt/(**1**)/polypyrrole, upon repeated scans in acetonitrile containing 0.1 M TBAP (scan rate 0.1 V s^{-1}): (a) after the initial 5 scans; (b) another subsequent 45 scans following the 6th scan [not shown in (a)], recorded after every two cycles. Arrows indicate the direction of the change; (c) the final waveform obtained in (b). Scans were performed as shown below the figure.

[Figure 2(a)]. The wave forms in Figure 2(a) are consistent with the c.v. in Figure 1(a), except for the current waves centred at −1.68 V.† The current increase for potentials more positive than −1.0 V† can be explained as reflecting the increase in the number of electrochemically accessible sites in the polypyrrole film.[6] It should be noted that no current wave responsible for the redox reaction of (**1**) was observed in Figure 2(a).

Upon further repeated scans between −2.10 and +1.15 V† the c.v. changed markedly, Figure 2(b). The oxidation peak shifted anodically, accompanied by the growth of a spike-shaped current peak at −1.68 V.† The shifts of the oxidation peak were then followed by the onset and growth of an anodic spike-shaped peak at *ca.* 0.88 V.† Eventually, the c.v. as shown in Figure 2(c) was obtained, in which the redox waves of the polypyrrole film are apparently lost.

The spike-shaped current peaks in Figure 2(c) were observed only for virgin scans after the electrode was polarised to the opposite direction of the potential to allow the 'spiky' current flow of the opposite sign. Current waves indicated by broken lines in Figure 2(c) are ascribed to the redox reactions of (**1**) in Pt/(**1**)/polypyrrole, as was confirmed by coulometric comparisons of c.v.s in Figure 2(c). Hence, the electrochemical processes represented by the broken lines in Figure 2(c) could be expressed as reactions $A \rightleftharpoons A^- \rightleftharpoons A^{2-}$ in the cathodic region and $A \rightleftharpoons A^+$ in the anodic region, where A denotes a Ru(2,2′-bipyridine)$_3^{2+}$ redox centre in the (**1**) layer of Pt/(**1**).

The above consideration meant that the 'spiky' current waves should be a consequence of mediated reduction and oxidation of polypyrrole through the redox levels of (**1**). The electrochemical processes of the mediated redox reactions could be explained in the following manner. The A^- centres formed at the platinum electrode surface, diffuse into the layer of (**1**) and reach the (**1**)/polypyrrole interface, where A^- centres are oxidised by polypyrrole. This reaction corresponds to the c.v. wave i of Figure 2(c). In the reverse case, A^+ centres at the interface oxidise the polypyrrole (wave iii). After reduction or oxidation of the polypyrrole layer, a potential sweep to the cathodic or anodic direction causes only reduction or oxidation of A centres (wave ii or iv), respectively.

The wave form in Figure 2(c) persisted for more than 30 scans. The electrochemistry represented in Figure 2(c) is essentially consistent with observed phenomena for other bilayer systems.[5,7] However, it should be noted that in the present study, preparation of the bilayer structure required potential sweeps following the successive electropolymerisations of two different kinds of monomeric precursors.

Preliminary depth profile analyses of the present electrode by Auger electron spectroscopy confirmed the bilayer structure of Pt/(**1**)/polypyrrole.

The results in Figure 2 were obtained only under the oxygen-free, anhydrous conditions used for the deposition of polypyrrole. The changes of the c.v.s in Figure 2(c) can be understood by assuming a localised electrochemical depolymerisation reaction of polypyrrole near the surface of the platinum electrode. This assumption is supported by a separate observation that a polypyrrole film at a Pt/polypyrrole electrode, prepared under the same electrolytic conditions, was lost leaving no insoluble material upon repeated scans in the same region of potential. This observation also explains the relatively small charges involved in the mediated redox reactions of polypyrrole [Figure 2(c), 6.5×10^{-3} C cm^{-2}] compared with the charge passed during the deposition[2] (4×10^{-2} C cm^{-2}).

The polypyrrole film in the bilayer electrode behaved as an electroconductive electron reservoir, separated from the metallic substrate by an electroactive layer, (**1**). This characteristic feature may be associated with the photosensitive nature of (**1**) which should have interesting applications. Mechanistic details will be published in a separate paper.

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