Electrochemical Coating of an Electrode by a Poly(pyrrole) Film containing the Viologen (4,4′-Bipyridinium) System

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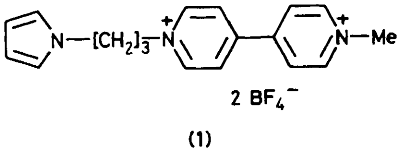
The electro-oxidation of a pyrrole *N*-substituted by an aliphatic chain bearing the viologen (4,4′-bipyridinium) group (V^{2+}) produces a film of electroactive poly(pyrrole) containing the V^{2+} redox centre on the electrode surface.

The straightforward anodic electrodeposition together with its chemical stability and electroconductivity makes poly(pyrrole) a convenient material for the elaboration of polymer-modified electrodes containing a specific redox centre. One approach consists of electrochemical incorporation of an ionic redox species such as Co^{2+}, RuO$_4^{2-}$, Co porphyrin, or Fe phthalocyanine in poly(pyrrole) films.[1] Recently, we have shown that polymer films containing an electroactive centre such as a poly-pyridinyl-Ru^{II}-complex[2] can be otained by direct electropolymerization of a pyrrole covalently bonded to this electroactive centre. Using this alternative method, we report here the electrochemical preparation and behaviour of a poly(pyrrole) film containing the viologen (4,4′-bipyridinium) group (V^{2+}). Electrodes modified with this electroactive group have been demonstrated to be very useful in electrocatalysis and photoelectrocatalysis of redox reactions and in electrochromism.[3]

A cyclic voltammetric study of the 1-methyl-1′-(3-pyrrol-1-ylpropyl)-4,4′-bipyridinium tetrafluoroborate salt (**1**)† shows the formation of an electroactive poly(pyrrole) matrix containing V^{2+} centres.

As seen in Figure 1(a), the cyclic voltammogram of (**1**) (2 × 10^{-3} M in argon-purged anhydrous acetonitrile containing 0.1 M Et$_4$NBF$_4$) at a platinum electrode (3 × 10^{-2} cm^2) in the anodic region shows one peak Pm due to the irreversible oxidation of the monomeric pyrrole unit, E(Pm) = 1.06 V.‡ This value is in agreement with the range of oxidation potentials of *N*-alkylpyrroles.[4] The peaks in the cathodic region are associated with the two well-known successive reversible one-electron reductions of the V^{2+} group [E^0(V^{2+}/V$^{\cdot+}$) = −0.75 V; E^0(V$^{\cdot+}$/V) = −1.16 V, Figure 1(a)].



(**1**)

Films of poly(**1**) were grown on the Pt electrode by controlled potential oxidation at 0.9 V. Increasing the charge considerably enlarged the anodic and cathodic peak currents (i_{pa} and i_{pc}) corresponding to the V^{2+} redox system, and a redox couple appeared in the anodic region [Figures 1(b—f)]. The potential of the latter is *ca.* 0.3 V which is also in good agreement with the reported E^0 values for poly(*N*-alkylpyrroles).[4] Moreover, a prepeak Pp appears, the origin of which will not be discussed here.§ Similar prepeaks have been observed for other electrodeposited films containing redox species.[2,5,6] After deposition, the polymer-modified electrode was transferred, with thorough rinsing, to clean electrolyte. The modified electrode is fairly stable and shows a persistent electrochemical response. Cycling the electrode between 0 and −0.9 V caused a 15% drop in the integrated cathodic V^{2+}/V$^{\cdot+}$ peak current after 450 cycles [scan rate v = 100 mV s^{-1}, Γ(V^{2+}) initial = *ca.* 5 × 10^{-9} mol cm^{-2}].¶ For thicker films [Γ(V^{2+}) = 3.2 × 10^{-7} mol cm^{-2}] the V^{2+} system remains well-behaved (Figure 2) [$E^{0\prime}$(V^{2+}/V$^{\cdot+}$) −0.69 V, (ΔE_p = 40 mV); $E^{0\prime}$(V$^{\cdot+}$/V) = −1.15 V (ΔE_p = 12 mV)] at low sweep rate (v = 5 mV s^{-1}). The i_{pa} and i_{pc} values for the two successive one-electron transfers of V^{2+} vary linearly with sweep rates between 2 and 20 mV s^{-1} as expected for the

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† The new compound (**1**) was synthesized by monoquaternisation of excess of 4,4′-bipyridine with *N*-alkylpyrrole, followed by methylation. ^{1}H N.m.r. data for (**1**) in MeCN, δ *vs.* Me$_4$Si, J in Hz: 8.88 (4H), 8.39 (4H), 6.66 (t, 2H, 4.5), 5.99 (t, 2H, 4.5), 4.63 (t, 2H, 6.7), 4.44 (s, 3H), 4.07 (t, 2H, 6.7), and 2.5 (q, 2H, 6.7).

‡ All potentials were measured *vs.* an Ag/10^{-2} M Ag$^+$ reference electrode.

§ The amount of charge corresponding to this prepeak may be deduced by subtracting the integrated current for the reduction of the poly(pyrrole) from the integrated current for the oxidation of the poly(pyrrole). This value is identical (within 10%) to the difference between the charge for the reduction of V^{2+} and the charge for oxidation. This data indicates that prepeak Pp is associated with the first reduction peak of V^{2+}. Similar results have been observed in the electropolymerization of pyrrole substituted with a complex of ruthenium(II) (ref. 2).

¶ The apparent surface concentration of electroactive species Γ(V^{2+}) is determined from the charge under the two anodic peaks associated with the viologen group, assuming 2 F per mol.

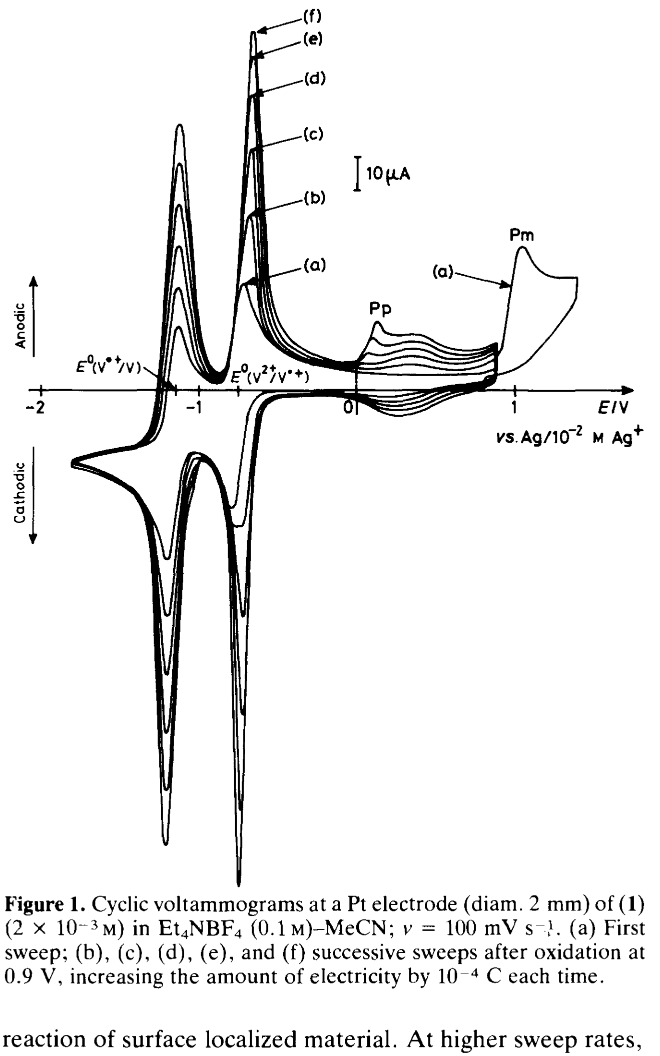

Figure 1. Cyclic voltammograms at a Pt electrode (diam. 2 mm) of (**1**) (2×10^{-3} M) in Et_4NBF_4 (0.1 M)–MeCN; v = 100 mV s^{-1}. (a) First sweep; (b), (c), (d), (e), and (f) successive sweeps after oxidation at 0.9 V, increasing the amount of electricity by 10^{-4} C each time.

reaction of surface localized material. At higher sweep rates, limitations arise owing to the motion of ions in the film, and the kinetics of the electron transfer between V^{2+} pendant groups. As a matter of fact, in the potential range for the reduction of V^{2+}, poly(pyrrole) is in its neutral insulating form[7] and the polymer film acts as a polymer with pendant groups. This redox behaviour compares well with the results reported for the electropolymerisation of *N*-*p*-nitrophenylpyrrole.[6]

Taking into account the prepeak phenomena in the thick film,§ the ratio of the integrated currents for the V^{2+} centres and the poly(pyrrole) redox system is about 6.8. This value indicates that the oxidation reaction of the poly(pyrrole) chains involves 1 charge for 3.4 pyrrole rings, as expected.[8] The integrated current for the reduction of poly(pyrrole) is 7% of the total charge involved in the preparation of the film (1.3×10^{-1} C cm^{-2}). This value is less than expected as the polymerization reaction requires (2 + 1/3.4) F mol^{-1}, where charge in excess of 2.0 F mol^{-1} (12%) is associated with the oxidation of the poly(pyrrole) chains.

In the study of the electropolymerization of the complex $[Ru(bpy)_2L_2]^{2+}$ (bpy = 2,2′-bipyridine), where L is a pyrrole-substituted pyridine[2] a redox couple does not appear in the potential range of poly(*N*-alkylpyrrole). One hypothesis is that steric hindrance inhibits the formation of conjugated and, consequently, electroactive poly(pyrrole) chains. On the other hand, the similar electrochemical behaviour of poly(**1**) and poly(*N*-alkylpyrroles) suggests a polymer film consisting of an electroconducting matrix with pendant redox V^{2+} groups. This difference may be explained by the smaller size of the V^{2+} group compared with the Ru^{II} complex, and also by the presence of a longer aliphatic chain which reduces steric interactions. The influence of chain length will be discussed in a separate paper.

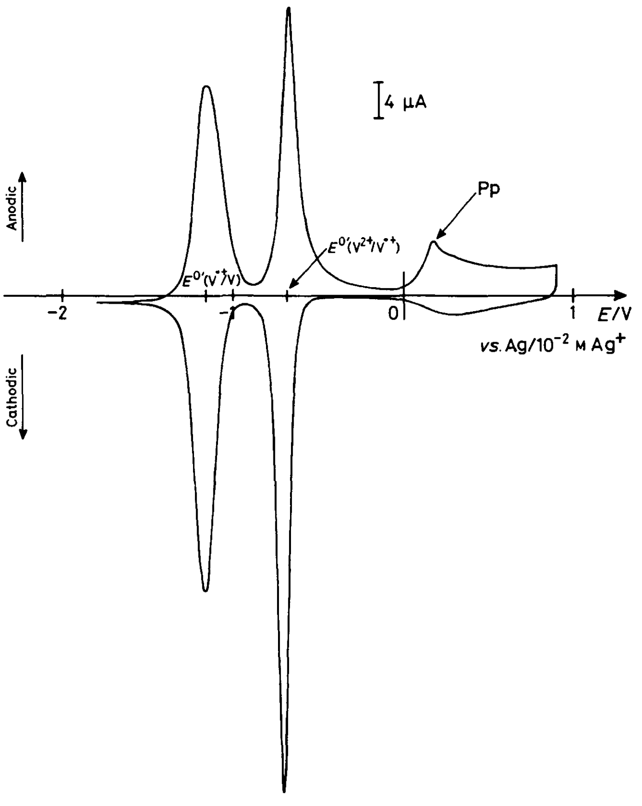

Figure 2. Cyclic voltammogram of a Pt–poly(**1**) electrode in Et_4NBF_4 (0.1 M)–MeCN after 4×10^{-3} C deposition; v = 5 mV s^{-1}; $\Gamma(V^{2+}) = 3.2 \times 10^{-7}$ mol cm^{-2}.

With regard to the stability and redox properties of the V^{2+}-poly(pyrrole)-modified electrode, we believe that electropolymerization of suitable *N*-alkyl-substituted pyrroles opens a new field in the coating of electrodes by electroactive and photo-sensitive centres.

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