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Conducting polymer films of 4(5-chloro-2-pyridylazo)-1,3-diamino benzene and its cobalt complex
Part I: Anodic polymerization in aqueous solutions

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New electroactive polymer films of 4(5-chloro-2-pyridylazo)-1,3-diaminobenzene and its cobalt complex (abbreviated as PL and $PCoL_2$) have been prepared on glassy carbon in 1.0 M HCl by oxidative polymerization. Cyclic voltammetry, potential step chronoamperometry, SEM and IR spectroscopy were used to characterize the polymer films. The films were found to be thin and insoluble in aqueous solutions and common organic solvents. The electroactivity of the polymers in acidic solutions is attributed to a proton + electron addition/elimination process at -NH- sites in the polymer backbone. The diffusion coefficient for the charge propagation through $PCoL_2$ films was found to be higher than for PL formed under identical conditions. No reversible electrochemistry due to the cobalt complex could be detected in the potential range −600 to 800 mV vs SCE in HCl solutions. The electronic conductivity of $PCoL_2$ is much higher than for PL and it was found to decrease with increase in the film thickness.

1. Introduction

Modification of electrodes made from cheap carbon materials such as carbon felt, pyrolytic graphite and glassy carbon by coating the surface with films of redox polymers is of interest in electrocatalysis [1–9]. Many transition metal complexes incorporated in conducting polymers have been studied as electron transfer mediator catalysts [10–15]. Incorporation of the metal complex into the polymer can be achieved in different ways, possibly the simplest being the electropolymerization of the complex itself [14–22]. Pyrrole-based polymers containing cobalt complexes were prepared in this way and they are to date the only known electropolymerized cobalt complexes [23–26].

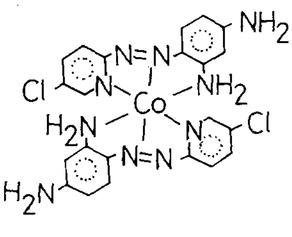
In the present work the anodic polymerization of a new monomer, 4(5-chloro-2-pyridylazo)-1,3-diaminobenzene and its cobalt complex in 1.0 M HCl are presented. Part I (this paper) characterizes the backbone of the polymers themselves; Part II deals with the redox behaviour of the cobalt complex in the polymer formed in acetonitrile and its mediation catalysis.

2. Experimental details

Tacussel glassy carbon disc electrodes (area 0.07 cm^2) were used. The electrodes were mechanically polished successively using finer grades of emery paper down to 4/0, followed by alumina (0.05 μm) to a mirror finish and then cleaned in distilled water in an ultrasonic bath. The monomer 4(5-chloro-2-pyridylazo)-1,3-diaminobenzene was prepared and purified according to the recommended method [27, 28] and all solutions were prepared from AR grade chemicals and triply distilled water. Conventional three-electrode one-compartment electrochemical pyrex glass cells and auxiliary platinum sheet electrodes were employed. The potentials were measured against a saturated calomel electrode (SCE). All electrochemical experiments were conducted in deaerated solutions at 30 ± 0.2°C.

Cyclic voltammetry and potential step chronoamperometry were carried out using a potentiostat/galvanostat (EG&G PAR, Model 362) and an *xy*-recorder and a storage oscilloscope (Nicolet, Model 3091). Morphology, thickness and structure were investigated by scanning electron microscopy (SEM, Hitachi Model S-530) and i.r. spectroscopy (in KBr pellets) for polymer films prepared on indium-tin oxide coated glass electrodes (ITO, surface resistance = 10 Ω).

The polymer films, poly-4(5-chloro-2-pyridylazo)-1,3-diaminobenzene (abbr. PL) and the polymer of the cobalt complex CoL_2 (abbr. $PCoL_2$), were prepared by potential sweep voltammetry at a scan rate 0.1 V s^{-1} in the potential range from 150 to 1200 mV vs SCE in deaerated 1.0 M HCl containing 2 mM L or 1 mM CoL_2. The complex CoL_2 (shown below) was prepared as follows. The L was dissolved in a small amount of ethanol then added to the $CoCl_2$ solution (pH 6.0) to give a violet solution due to complex formation. Concentrated HCl was added dropwise to give a red-violet solution containing 1 mM CoL_2 + 1.0 M HCl.



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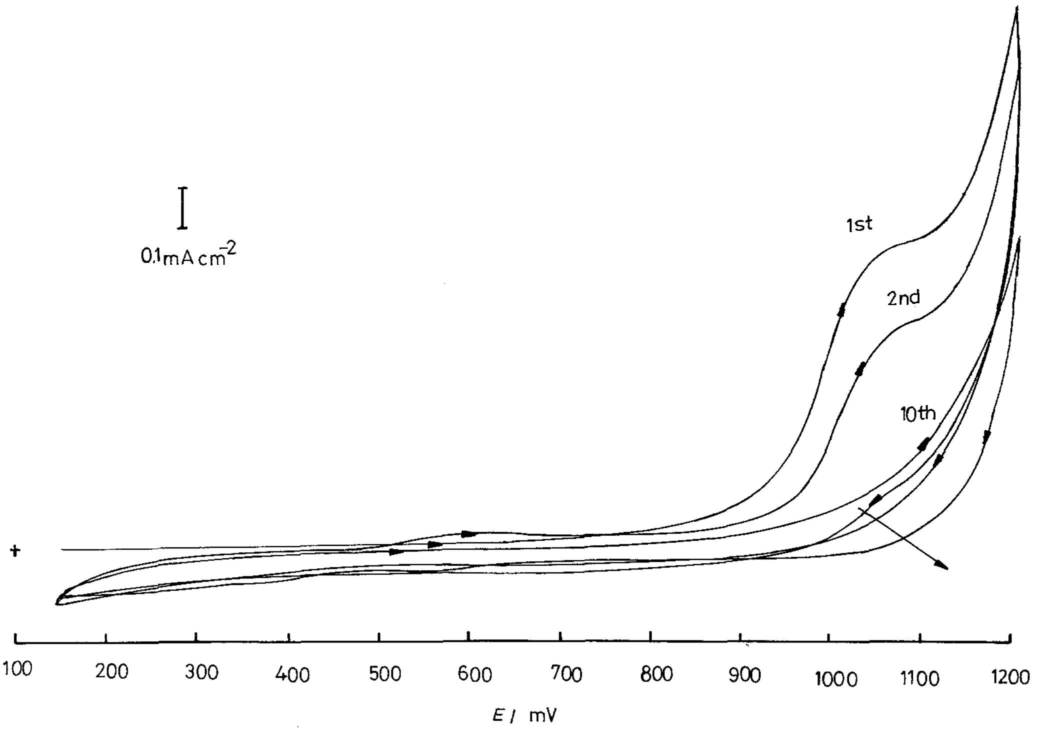


Fig. 1. CVs for oxidative polymerization of 1 mM CoL_2 in 1.0 M HCl. Scan rate = 100 mV s^{-1}.

3. Results and discussion

3.1. *Polymer film preparation*

Thin polymeric films of PL and $PCoL_2$ were prepared by potential sweep voltammetry (150 → 1200 → 150 mV at 0.1 V s^{-1}). Figure 1 shows illustrative cyclic voltammograms (CVs) for the oxidative polymerization of CoL_2 in 1.0 M HCl. The oxidation peak at 1050 mV is attributed to the oxidation of the primary aromatic amine [29–33]. The absence of a corresponding reduction peak indicates that the oxidation products are involved in a fast following chemical reaction, i.e. EC mechanism. On the following scans the peak magnitude decreases with increasing scan number due to blocking of the electrode surface by a growing barrier film. Similar CVs were recorded for L in 1.0 M HCl where the oxidation peak was at 1100 mV. The surface investigation after the electrolysis showed that the surface was covered by thin coloured films (orange–red for L and violet for $PCoL_2$). The films were found to be insoluble in aqueous solutions and many organic solvents, e.g. ethanol, methanol, carbon tetrachloride, chloroform, acetone, acetonitrile, benzene, diethyl ether and ethyl acetate, but soluble in dimethyl formamide and tetrahydrofuran.

3.2. *Morphology, thickness and i.r. spectra*

Scanning electron micrographs of PL and $PCoL_2$ films (Fig. 2) show that the polymer films are fibrous and porous and that the homogenity and compactness of PL films are higher than those of $PCoL_2$. The thickness of different samples of the films were estimated relative to the ITO surface from SEM and it was found that the thicknesses of PL and $PCoL_2$ films formed by 100 scans were approximately 0.3 and 0.2 μm, respectively. Generally the film thickness increases with an increase in the number of polymerization scans.

I.r. spectra of PL and $PCoL_2$ showed weak absorption peaks relative to the monomer L. The peaks could be assigned to the appropriate vibration modes as follows [34–36]: peaks at 3050 cm^{-1} (weak), 1600 cm^{-1} (strong), 1500–1510 cm^{-1} (strong), 945–920 cm^{-1} (medium), 855–840 cm^{-1} (medium) and 775 and 700 cm^{-1} (strong) are characteristic for the various vibration modes of the C–H and C–C bonds of the benzene ring. For the pyridine ring, peaks at 3080–3010 cm^{-1} (weak; C–H stretching), 1995–1430 cm^{-1} (medium; $C\overset{\cdots}{=}C\overset{\cdots}{=}N$ ring stretching) and 745 and 700 cm^{-1} (strong; C–H out-of-phase bending) were identified. Weak fused peaks at 3440–3320 cm^{-1} correspond to the stretching of the N–H bond. The azo group manifests itself by medium peaks at 1450–1430 cm^{-1} corresponding to the stretching of this group. More significant medium peaks at 1305–1235 and 1630–1620 cm^{-1} were identified. The former are attributed to the stretching of the C–N bond of secondary amines while the others correspond to the stretching of the C=N bond. This agrees with the published work on polyanilines which suggests that the polymerization occurs via the formation of C–N=C and C–NH–C bonds [29, 38, 39, 41, 43].

3.3. *Mechanism of polymerization*

Many primary aromatic amines have recently been polymerized successively in nonaqueous and aqueous acidic solutions by anodic polymerization [29–34, 37–44]. The oxidation of the molecule in a one electron step gives the radical cation, which may add a

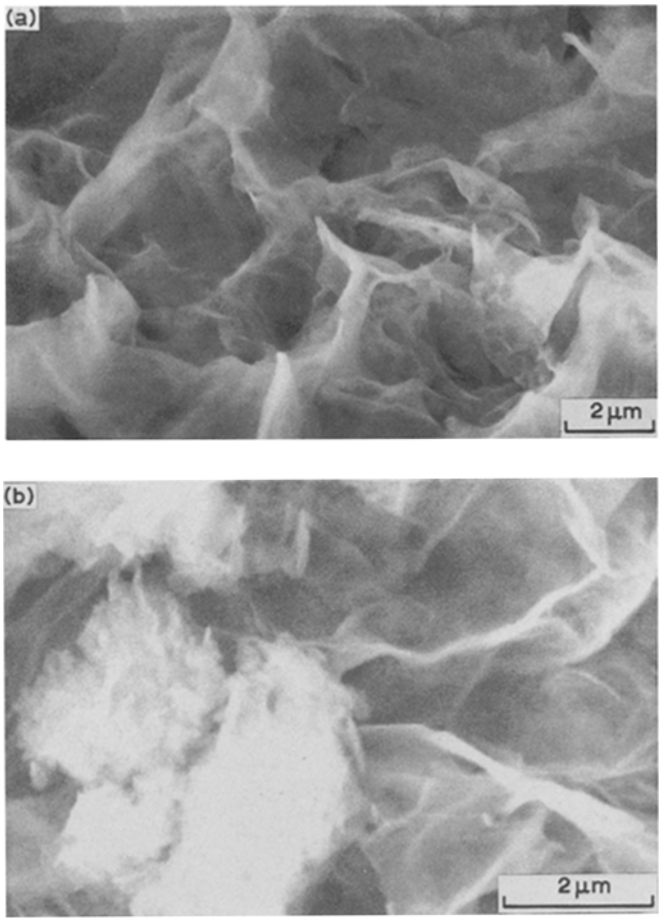
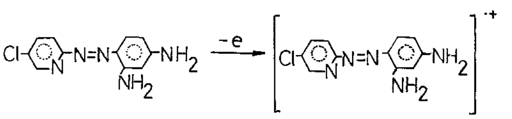


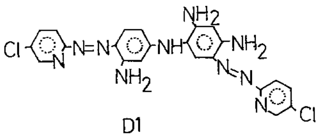
Fig. 2. SEMs for films (a) PL and (b) $PCoL_2$. The films were prepared on ITO electrodes by 200 polymerization scans.

new molecule or other radical cation (head to tail), to form the dimer after deprotonation. Energetically the dimer is easier to oxidize than the monomer [45]. The oxidation of the dimers and the subsequent addition of new molecules or dimers give the trimers, tetramers, . . . etc. The process continues until the polymer is formed. The polymerization of L is assumed to occur as follows:

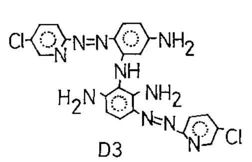


(1)

The first step is the oxidation of the molecule (at positions 1 and/or 3) to give the radical cation; where the protonation of the $-NH_2$ group is neglected for simplicity. Since position 4 is blocked, the best position for coupling with a new molecule or other radical cation is position 6 followed by position 2. Hence dimers, D1–D4, may be formed. Head to tail coupling is also probable [38] and gives dimers D5–D6. Further oxidation of the dimer is expected to yield numerous trimers and tetramers. As the polymerization proceeds a polymer of a complicated structure is formed and crosslinking occurs. Actually the recorded CVs indicated the formation of an insulating layer, probably due to crosslinking. Naturally the structure of $PCoL_2$ is expected to be more complicated. According to the present data the formed polymer films are characterized by the presence of –NH– connecting the aromatic nuclei of the polymer. The electroactivity, discussed later, is attributed to a proton + electron addition/elimination process at these sites [30, 31, 46, 47].



D1



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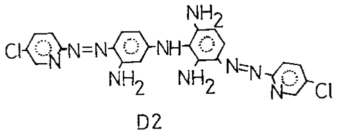

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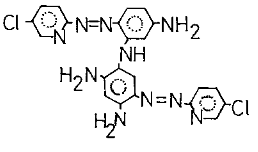
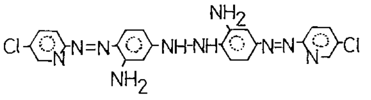
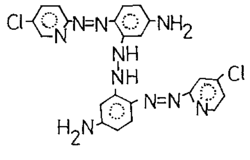


D4



D5



D6

3.4. *Electroactivity of the polymer films*

Figure 3 shows the electroactivity of $PCoL_2$ films deposited on glassy carbon electrodes in 1.0 M HCl in comparison to the monomers L and CoL_2. The first CV (curve a) shows reversible redox peaks at about 350 mV followed by a large irreversible peak at about − 10 mV. The latter peak diminished quickly as the number of scans increased and it disappeared completely after about 10 scans (curve b). The irreversible reduction peaks of the monomers occur at potentials

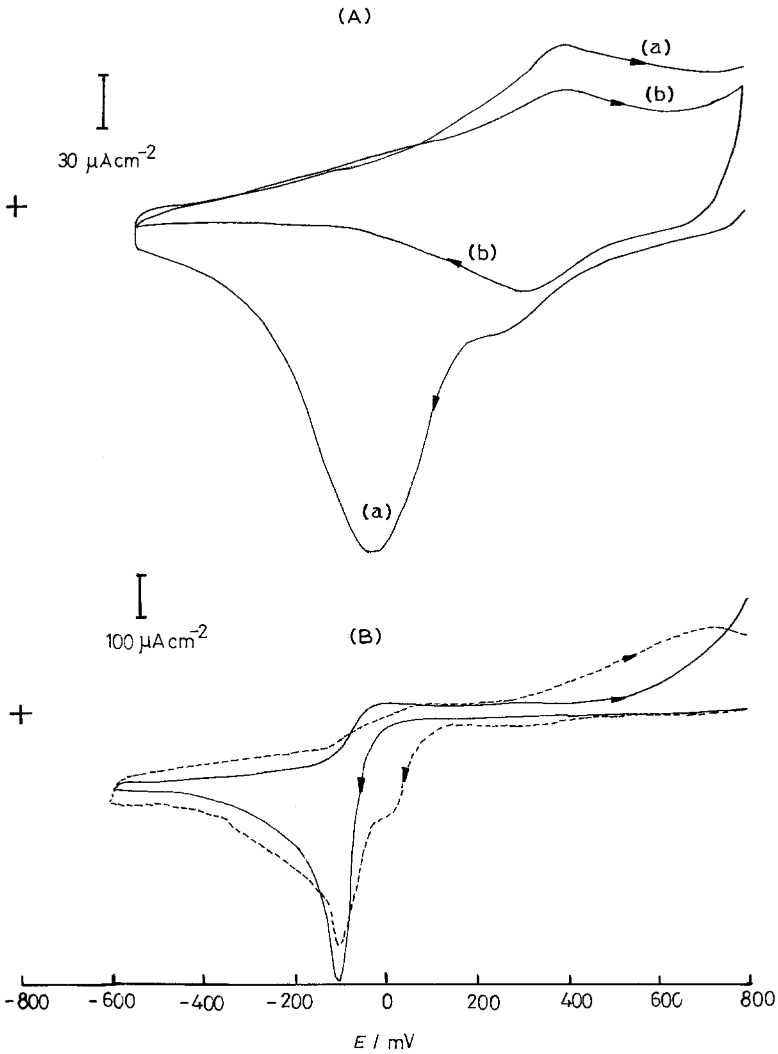


Fig. 3. (A) CVs of glassy carbon electrodes covered by $PCoL_2$ films in 1.0 M HCl. Curves (a) and (b) refer to the first and the steady state scans, respectively. The films were prepared by 50 polymerization scans. Scan rate = 100 mV s^{-1}. (B) CVs of glassy carbon electrodes in 1.0 M HCl containing 2 mM L (——) and 1 mM CoL_2 (- - -). Scan rate = 100 mV s^{-1}.

close to that peak. The large reduction peak at − 100 mV is attributed to the irreversible reduction of the azo group [48] while the smaller one (only for CoL_2) at about 0 mV may be connected to the reduction of the cobalt complex. The reversible redox peaks are very stable in the potential range − 800 to + 800 mV but at higher potentials the films may suffer degradation. A similar response was observed for PL in 1.0 M HCl. The redox peaks are attributed to a proton + electron addition (reduction)/elimination (oxidation) process at -NH- sites. They occur in a potential region close to that of polyaniline [46].

The effect of pH on the redox peaks is shown in Fig. 4. At pH > 3 (not shown) the response was very weak and cannot be distinguished from the large capacitive current. The peak potential, E_p, shifts to less positive values as pH increases while the peak current, i_p, decreases. The dependence of E_p on pH for $PCoL_2$ and PL is shown in Fig. 5 and $dE_p/d(pH)$ values (60 mV) were determined in agreement with the expected Nernstian value for a 1 : 1 proton : electron reversible process. The peak separation, ΔE_p, for PL film at 80 mV s^{-1} (ΔE_p = 200 mV) is four times that for $PCoL_2$ film (ΔE_p = 50 mV). Theoretically ΔE_p for surface-attached species is 0 V [1] but, experimentally, higher ΔE_p is observed due to the film resistance. As the film resistance increases the ohmic drop increases and, consequently, the peak separation increases [49]. Thus it may be concluded that PL film is more resistive than $PCoL_2$ film.

The effect of scan rate, v, on the redox peaks of $PCoL_2$ and PL films in 1.0 M HCl was investigated in the range 5–500 mV s^{-1}. The correct peak current was determined by subtracting the large background (mainly capacitive) current from the apparent peak current. Since the CVs were recorded by scanning the potential in the anodic direction first it is easier to estimate the anodic i_p (using linear base lines) than the cathodic i_p. Thus, only the anodic i_p against v and $v^{1/2}$ is given in Fig. 6. As can be seen, i_p varies linearly with v up to 0.1 V s^{-1} but it varies linearly with $v^{1/2}$ at higher scan rates. This behaviour is characteristic for thin polymer films where the linear i_p–v relation is characteristic for a surface-attached redox species [1] while the linear i_p–$v^{1/2}$ region illustrates the classic linear diffusion of soluble species. Since the peak separation decreases as the scan rate decreases, E_p was estimated

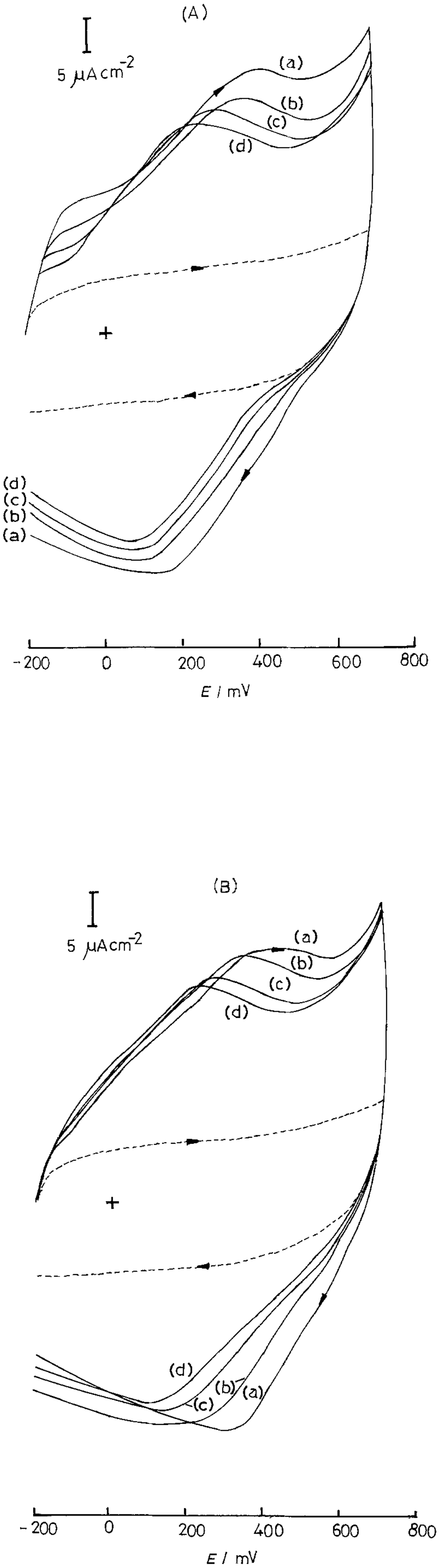


Fig. 4. CVs of glassy carbon electrodes covered by PL (A) and PCoL$_2$ films (B) in acidic chloride solutions of different pH: (a) 0.0, (b) 0.4, (c) 1.4 and (d) 2.4. [Cl$^-$] = 1 M. The films were prepared by 50 polymerization scans. Scan rate = 80 mV s^{-1}. The dashed curves refer to bare glassy carbon electrodes.

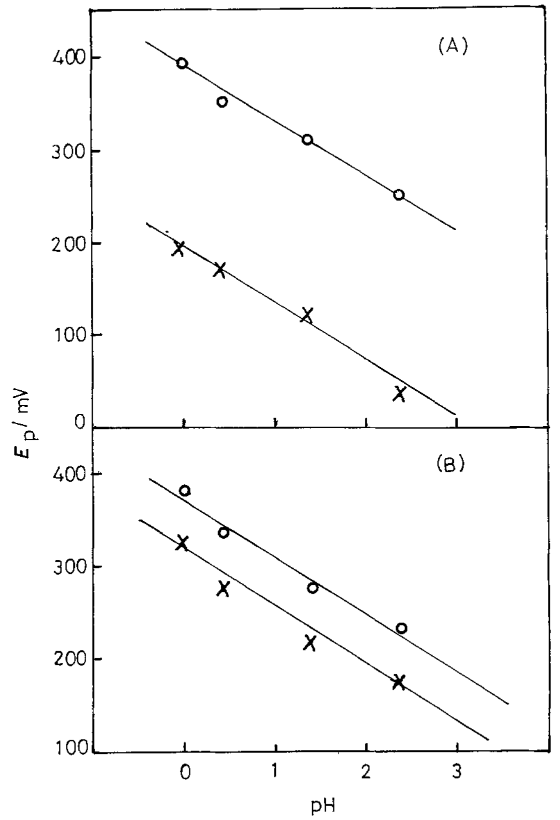


Fig. 5. The dependence of the peak potential, E_p, on pH for PL (A) and PCoL$_2$ films (B). (○) Anodic and (x) cathodic. Details are given in Fig. 4.

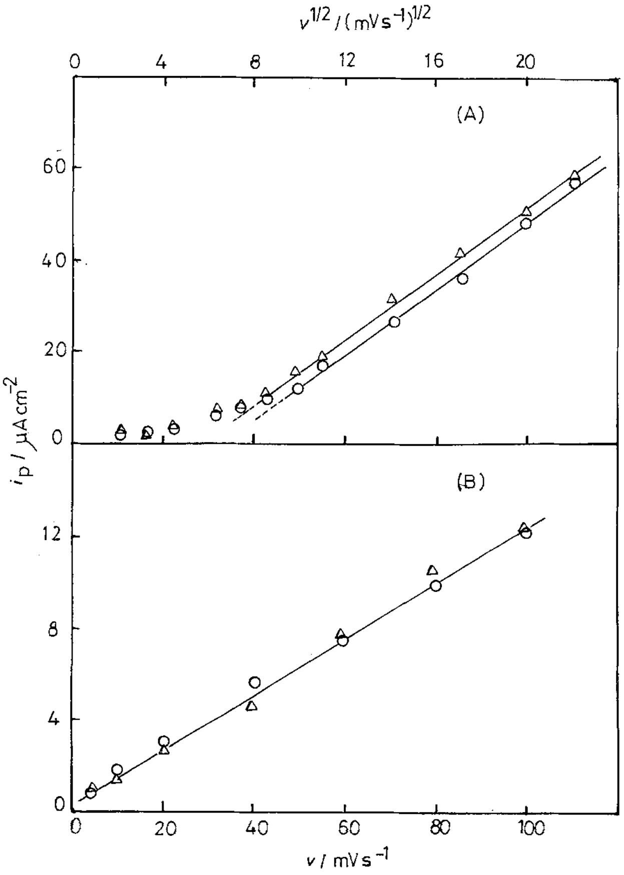


Fig. 6. The dependence of the peak current, i_p, on $v^{1/2}$ (A) and v (B) for (△) PL and (○) PCoL$_2$ films in 1.0 M HCl. The films were prepared by 100 polymerization scans.

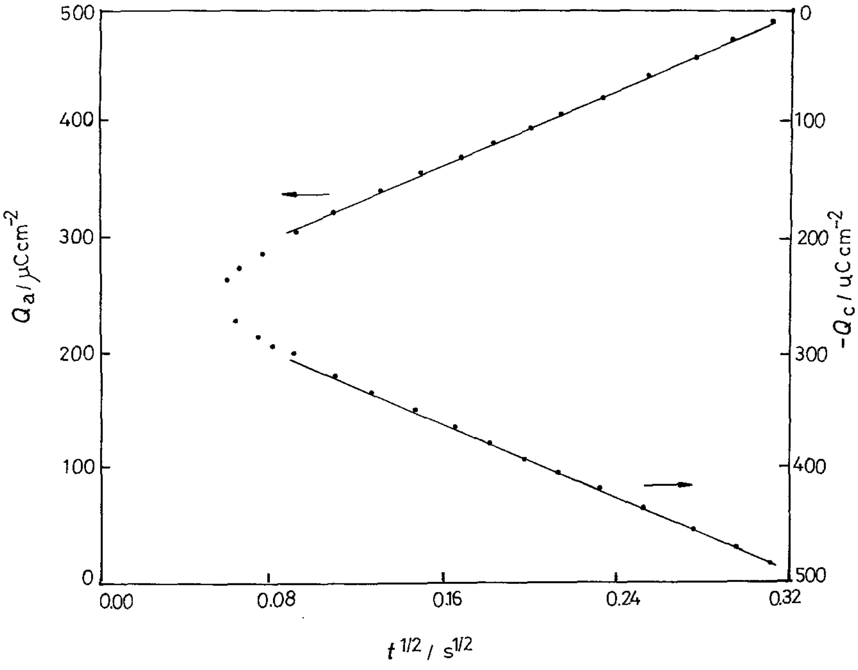


Fig. 7. Charge, Q, against $t^{1/2}$ for glassy carbon electrodes covered by $PCoL_2$ films in 1.0 M HCl. For oxidation the potential was stepped from −300 to 700 mV and for reduction from 700 to −300 mV. The films were prepared by 100 polymerization scans.

at $v \rightarrow 0 \, mV s^{-1}$ by extrapolation of the E_p–$v^{1/2}$ relation to 0 V [50]. The formal redox potential, E^0, at pH 0, was estimated as follows [51]:

$$E^0 = \tfrac{1}{2}(E_p^a + E_p^c)_{v=0} \quad (2)$$

E^0 values for PL and $PCoL_2$ films were found to be 350 and 375 mV, respectively.

The diffusion coefficient, D^0, for the charge transport process through the films was estimated from potential-step chronoamperometry. Sufficiently large potential steps were applied (from −300 to 700 mV for oxidation and from 700 to −300 mV for reduction) to satisfy the condition for application of the Cottrell equation. The integral form of the Cottrell equation is [51, 52]:

$$Q = Q_{dl} + 2nFC^0(D^0 t/\pi)^{1/2} \quad (3)$$

where Q is the total charge, Q_{dl} is the capacitive charge, n is the number of electrons involved in the process, F is the Faraday constant and C^0 is the concentration of the electroactive sites. Figure 7 shows the applicability of Equation 3 for $PCoL_2$ films in 1.0 M HCl. D^0 can be determined from the slope of the linear part of the Q against $t^{1/2}$ relation if C^0 is known. C^0 was calculated as $C^0 = \Gamma/d$, where Γ is the surface concentration of the electroactive sites and d is the film thickness. The thicknesses of the dry films were estimated from SEM and Γ was obtained from the peak charge corresponding to the faradaic process [51]. The corrected peak charge for the oxidation process was found to be equal to that for the reduction process. For films formed by 100 polymerization scans under identical conditions, the average Γ values for $PCoL_2$ film ($d = 0.3 \, \mu m$) and PL film ($d = 0.2 \, \mu m$) were 1.61 and 2.24 nmol cm^{-2} and the average $dQ/dt^{1/2}$ values were 776 and 236 $\mu A s^{1/2} cm^{-2}$, respectively. Thus the average D^0 values for $PCoL_2$ and PL films are 1.8×10^{-8} and $3.7 \times 10^{-10} cm^2 s^{-1}$, respectively.

The capacity of the film/solution interface, C_{dl}, can be calculated from the relation

$$C_{dl} = Q_{dl}/E_s \quad (4)$$

where E_s is the potential step value and Q_{dl} is obtained by extrapolation of the Q against $t^{1/2}$ lines to zero time. C_{dl} for the previously mentioned samples of $PCoL_2$ and PL were estimated to be 0.24 and 0.22 mF cm^{-2}, respectively. For the cell used ($R = 125 \, \Omega$) a time constant $RC_{dl} \approx 2$ ms is expected. This explains why the Q against $t^{1/2}$ relations (Fig. 7) deviate from linearity at times $\leqslant 6$ ms, where the contribution of the capacitive current cannot be ignored.

3.5. *Electron transfer through the films*

Electron transfer through $PCoL_2$ and PL films was tested by using the redox couple $[Fe(CN)_6]^{3-/4-}$. As can be seen in Fig. 8, $PCoL_2$ film shows some resistance to electron transfer (i_p decreases and ΔE_p increases) while PL film is completely insulating. The higher insulating properties of PL film can be explained in terms of crosslinking. The crosslinking is more probable in PL than $PCoL_2$, since two $-NH_2$ groups are available for polymerization in the monomer of the former polymer while only one $-NH_2$ group is available in the latter. As the thickness of $PCoL_2$ film (in terms of number of the polymerization scans) increased its insulating properties were found to increase. The diffusion coefficient for the electron transfer of the redox couple $[Fe(CN)_6]^{3-/4-}$, D_s, through $PCoL_2$ films was estimated from potential-step chronoamperometry. The potential was stepped from −800 to 800 mV for oxidation and from 800 to −800 mV for reduction. For $PCoL_2$ films formed by 20, 50, 100 and 200 polymerization scans, the average D_s values were 3.3×10^{-5}, 1.2×10^{-5}, 0.7×10^{-5}

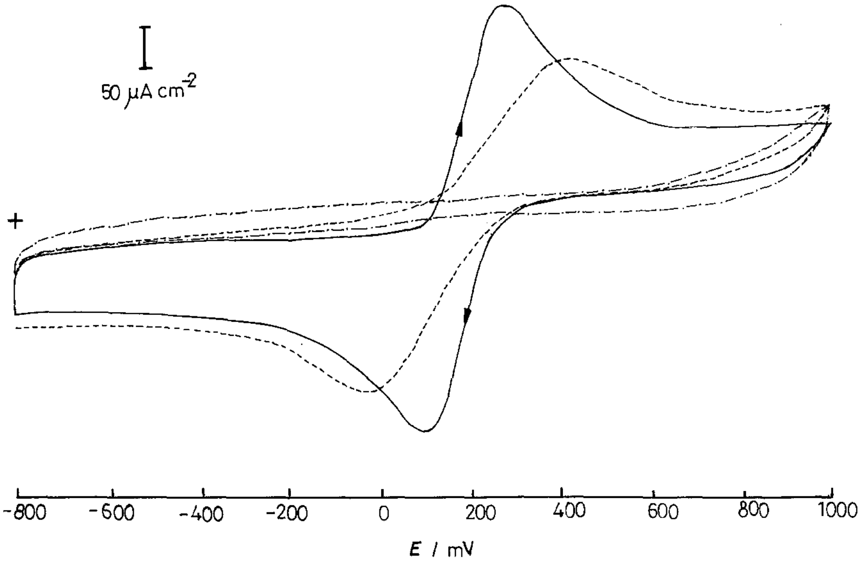


Fig. 8. CVs of glassy carbon electrodes in 1 mM $K_4[Fe(CN)_6]$ + 1 mM $K_3[Fe(CN)_6]$ + 0.2 M $NaClO_4$. (——) bare, (-·-·) covered by PL films and (- - -) covered by $PCoL_2$ films. The films were prepared by 20 polymerization scans.

and $0.3 \times 10^{-5} cm^2 s^{-1}$, respectively, while for bare GC electrodes the D_s value was $4.9 \times 10^{-5} cm^2 s^{-1}$.

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