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Removal of toxic chromate ions by the films of poly(1,8-diaminonaphthalene)

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Abstract

Poly(1,8-diaminonaphthalene) films, p(1,8-DAN), were electrosynthesized on a Pt electrode to study their utility in extracting Cr(VI) (as dichromate ions) from acidic aqueous solution. The electrodeposition procedure was improved by acidification of the acetonitrile electropolymerisation bath with CCl_3COOH. Possible molecular structures of electrosynthesized poly(1,8-diaminonaphthalene) were determined by means of IR spectroscopy. The mechanism of dichromate ion removal was studied by potentiometric measurements in the system $Ag/AgCl/Cl^-_{(std)}/0.1$ M $HClO_4$/p(1,8-DAN)/Pt, upon addition of $K_2Cr_2O_7$ solution. The presence and oxidation state of chromium in the polymer matrix was explored by means of energy dispersive X-ray (EDX) spectrometry.

1. Introduction

Practical applications of polymer-modified electrodes have been significantly developed over the past decade. Two examples are the utilisation of conducting polymer films as sensors or extraction devices for heavy metal ions such as chromium. In spite of its harmful effects, Cr(VI) is still used in many industrial applications, including electrodeposition, steel production, dye manufacturing and metal finishing. Consequently, in order to meet environmental protection requirements, there is a need for means of removing hexavalent chromium from solution. As we shall show, p(1,8-DAN) in thin film form shows considerable promise as a material for achieving this goal.

The mechanism of metal ion extraction from solution depends on the structure and the electrochemical properties of the polymer. Poly(1,8-diaminonaphthalene), p(1,8-DAN), contains amine groups capable of complexing heavy metal ions, such as Cu^{2+}, Hg^{2+}, Pb^{2+}, and VO^{2+} [1–4]. This is an alternative to the extraction of heavy metal ions from solution based upon a spontaneous redox reaction between the polymer and metal ion (Me^{z+}/Me^{y+}) redox couples, previously illustrated for the case of Ag^+ [5], in which the neutral form of the polymer reduces the oxidized metal ion.

In this work we describe optimisation of (1,8-DAN) polymerisation conditions to obtain electroactive polymer films of high capacity for metal ions. Issues of primary interest were the effects of acidification of the electrodeposition bath on the deposition and subsequent electroactivity of the resulting p(1,8-DAN) films, and their ability to extract chromium(VI) species from solution. The mechanism of the extraction process was determined by measurements of open circuit potential changes of the system $Ag/AgCl/Cl^-$(std.)/0.1 M $HClO_4$/p(1,8-DAN)/Pt upon addition of $K_2Cr_2O_7$. The presence of chromium in the polymer matrix was detected by energy dispersive X-ray (EDX) spectroscopy.

2. Experimental details

Poly(1,8-diaminonaphthalene) films were prepared by cycling a Pt working electrode in the potential range −0.5 V to 1.2 V vs Ag/AgCl, Cl^- (std.) reference electrode at a sweep rate of 40 mV s^{-1} in acetonitrile (ACN) and acetonitrile acidified with $HClO_4$ or CCl_3COOH, containing 0.01 M 1,8-diaminonaphthalene (Aldrich) and 0.1 M $LiClO_4$ (Aldrich) as the supporting electrolyte. A large area Pt gauze was used as the counter electrode.

The electrochemical properties of p(1,8-DAN) films were studied in aqueous 0.1 M $HClO_4$ solution. Electrochemical measurements were carried out by means of an Autolab (Ecochemie, The Netherlands) potentiostat. Chromium ion sorption by p(1,8-DAN) was studied potentiometrically in 0.1 M $HClO_4$ solution, by successive additions of 0.2 ml portions of 0.001 M $K_2Cr_2O_7$ to a known volume of solution.

The composition of the film after chromium treatment was examined using a scanning electron microscope (LEO 435VP) with a Roentec EDX analyser (model M1). Quoted elemental ratios are the mean of 6 values acquired by probing the film in different locations. Vibrational spectra of p(1,8-DAN) samples, removed from the electrode and pressed in KBr pellets, were recorded using an FTIR spectrometer (Nicolet 550).

3. Results and discussion

3.1. *Influence of acidification of polymerization bath on electrodeposition and electroactivity of p(1,8-DAN)*

Figure 1(a) shows representative cyclic voltammetric data for the electrodeposition (by ten consecutive voltammetric sweeps) of p(1,8-DAN) from an acetonitrile solution of 0.01 M 1,8-DAN/0.1 M $LiClO_4$. Monomer oxidation in the first scan is associated with a sharp peak at 0.45 V, followed by two further peaks at 0.7 and 1.2 V. The reactions underlying these responses lead to modification of the working electrode by a polymer layer of rather low conductivity ($\sigma \approx 10^{-2}$ S cm^{-1}) [6]. Oxidation and reduction of this polymer in the electrodeposition bath are seen as small, broad peaks at $E \approx 0.3$ V and $E \approx -0.15$ V, respectively, that is, at the foot of the monomer oxidation peak.

As with polyaniline and its derivatives, p(1,8-DAN) is electroactive in acid media. The low monomer solubility in aqueous solutions dictates that electropolymerization be carried out from an organic solvent. However, the low H^+ concentrations typical of such media may be suspected as one reason for the low conductivity of the growing polymer film, manifested as a progressive shift of the first oxidation peak to more positive potentials, as seen in Figure 1(a). The compromise strategy adopted to optimise the polymerization efficiency was to acidify the acetonitrile solution of the monomer, with concentrated $HClO_4$, to pH 1. Surprisingly, addition of $HClO_4$ did not increase the polymerisation yield, but resulted in a substantial decrease of the first oxidation peak current, as shown in Figure 1(b).

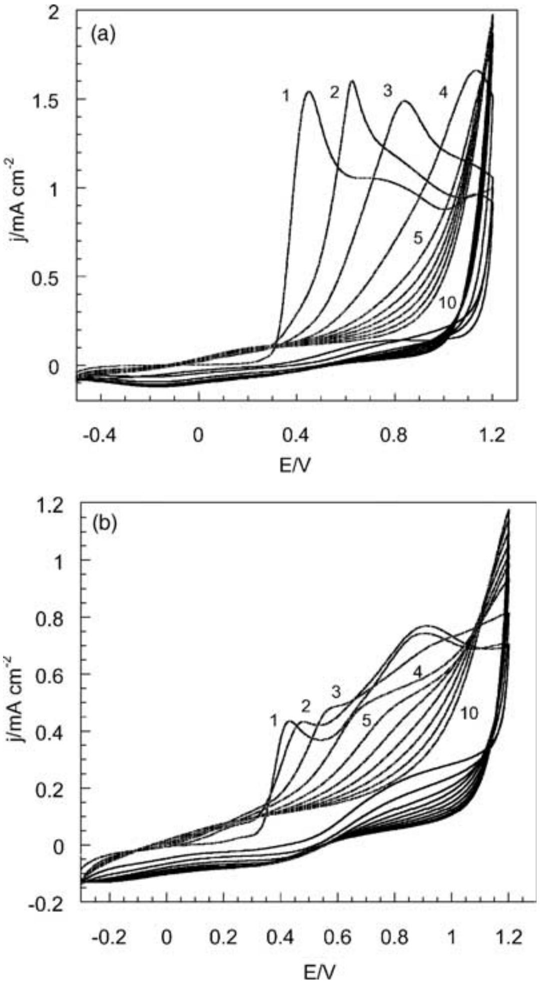

Fig. 1. Cyclic voltammograms for polymerization of 1,8-DAN in the solution containing 0.01 M monomer and 0.1 M $LiClO_4$ in: (a) acetonitrile and (b) acetonitrile acidified with $HClO_4$ to pH 1.

These results raised the question as to whether it was the acid itself or the associated water which had the primary influence over film formation and structure. To separate these two effects, $HClO_4$ was replaced with an organic acid, CCl_3COOH, which could be added with or without accompanying water (typically by deliberate addition of a few drops of water). As shown in Figure 2(a), addition of CCl_3COOH (alone) did not

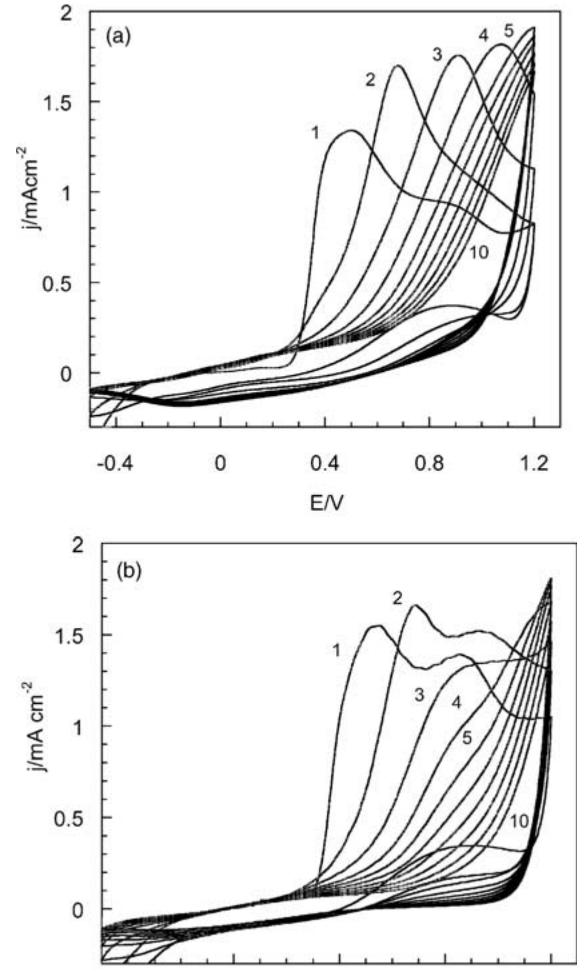

Fig. 2. Cyclic voltammograms for polymerization of 1,8-DAN in the solution of 0.01 M monomer and 0.1 M $LiClO_4$ in: (a) acetonitrile acidified with CCl_3COOH to pH 1 and (b) acetonitrile acidified with CCl_3COOH to pH 1 with a few drops of water.

cause suppression of the first oxidation peak, merely a little broadening. The additional presence of a small amount of water also did not depress the main oxidation peak; in fact, in the first and second scans, it slightly enhanced the height of the second oxidation peak at $E \approx 0.8$ V (see Figure 2(b)). In this latter experiment, there was a general lowering of the current density in the third and subsequent scans and the resultant film was less electroactive than that obtained from the water-free medium (as judged by the decrease of polymer oxidation/reduction currents). We make the reasonable speculation that this decrease is a consequence of nucleophilic attack by water molecules on the radical cations formed along the polymer chains at the positive end of the polarization range, $E \approx 1.1$ V.

Comparison of the data in Figures 1 and 2 led us to the hypothesis that the differences in peak current for monomer oxidation in $HClO_4$ and CCl_3COOH are primarily attributable to the different strengths of the two acids. Polymerization via an amine group requires that it not be protonated. It has been reported in the literature [7], that one of the two amine groups in 1,8-DAN is easily protonated ($pK_a = 4.61$, [8]), whereas the second one is only protonated in strong acids, such as $HClO_4$. Protonation of one amine group in 1,8-DAN in the presence of CCl_3COOH, which is a weaker acid than $HClO_4$, would not prevent the electrooxidation of the second group; therefore, formation of the polymer would not be inhibited. Additionally, the hydrogen atoms of $-NH_3^+$ groups can interact with oxygen atoms of the anions present. There is precedent for this in that formation of relatively stable complexes between the protonated monomer and anions have been also reported for other aromatic amines, such as polyaniline [9] and *o*-methoxyaniline [10]. Polymer formed in the solution acidified with CCl_3COOH revealed higher electroactivity, that is, larger peak currents, than that obtained in pure CH_3CN (cf. Figures 1 and 2).

3.2. *Identification of the molecular structure of electrosynthesized p(1,8-DAN) by IR spectra*

The molecular structure of the monomer and several possible structures of p(1,8-DAN) are illustrated in Figure 3. Evidence for these candidate structures in the polymer electrodeposited from acetonitrile solution was sought by comparison of IR spectra of the polymer and monomer, shown in Figure 4. Spectral assignments of the vibration modes for the monomer and p(1,8-DAN) are summarized in Table 1.

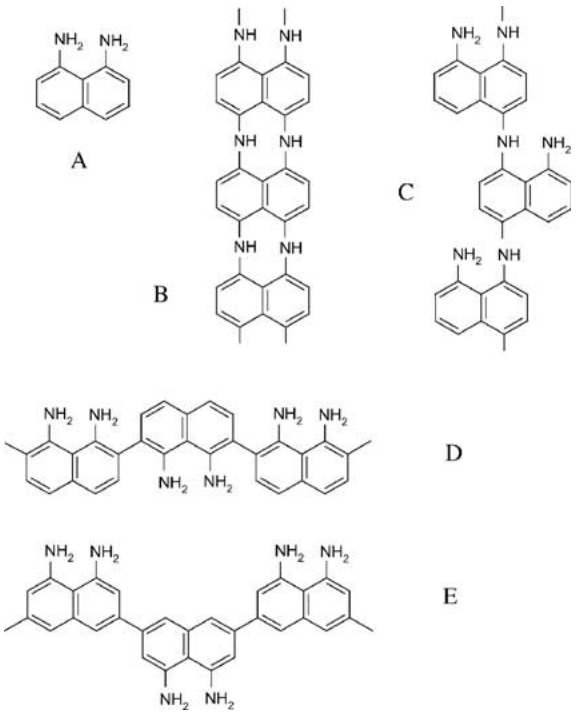

Fig. 3. Molecular structure of 1,8-DAN (A) and possible structures of p(1,8-DAN) (B-E).

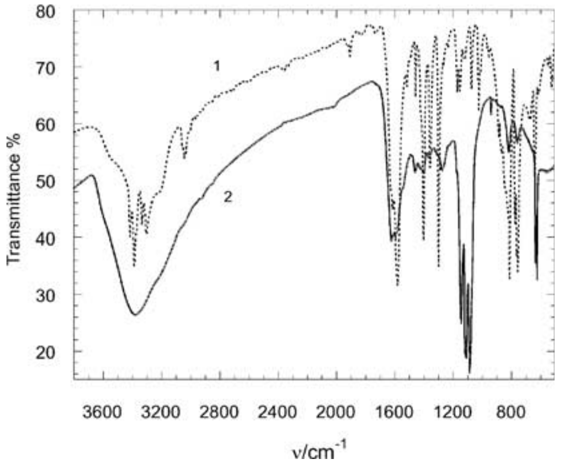

Fig. 4. FTIR transmittance spectra of 1,8-DAN (curve 1) and p(1,8-DAN) (curve 2).

Crucial information about the linkages between monomer units in the polymer chains may be obtained from the γ_{C-H} out-of-plane bending modes, found in the spectral region between 700 and 900 cm^{-1}. Bands observed in the polymer spectrum at 820 cm^{-1} and 763 cm^{-1} indicate the presence of 2 and 3 adjacent CH groups [11], respectively. This indicates that the polymer film contains a mixture of structures B, C and D (Figure 3). Absence of a band located between 860 and 900 cm^{-1}, typical of C–H vibration of isolated CH group, excludes the presence of structure E. The presence of C–C linkages between monomer units (structure D) is confirmed by the observation of a strong band at 1145 cm^{-1}; this is assigned to inter-ring stretching vibrations [12], and is not visible in the monomer spectrum. The existence of C–NH–C bonds (structures B and C) is suggested by the appearance of the bands between 1256 cm^{-1} and 1280 cm^{-1}, assigned to CN stretching vibrations of secondary amine groups [11, 12]; again, these are not present in the monomer spectrum. Another region characteristic of amine groups is the N–H stretching region between 3800 and 3000 cm^{-1}. In this range, the spectrum of the monomer

Table 1. Possible assignments of main IR bands (cm^{-1}) of 1,8-DAN and p(1,8-DAN) film

Possible assignments	1,8-DAN	p(1,8-DAN)
N–H stretching		3420 (broad)
ν_{asym} (NH_2)	3417	
ν_{sym} (NH_2)	3389, 3335, 3304	
C–H stretching	3040	2970
def. δ (NH_2)	1616	1625 (s)
$(C{=}C)_{Ar}$ stretching	1587, 1459 (w)	1580 (w), 1462 (w)
C–N stretching (primary amino group)	1359, 1300	1320
C–N stretching (secondary amino group)		1280
C–C inter-ring		1146 (s)
C–H out-of-plane		
3 H	810, 776	763
2 H		820
ClO_4^- dopant anion		1088, 626

shows bands attributable to a primary amine, but the spectrum of the polymer shows only a very broad multicomponent band. This probably results from a mixture of primary and secondary amine, consistent with structures B and C of Figure 3.

3.3. *Extraction of toxic dichromate ions from the solution by p(1,8-DAN) films*

P(1,8-DAN) films for ion extraction studies were deposited on a large area (6 cm^2) Pt flag, from acetonitrile solution acidified with CCl_3COOH. Ten voltammetric deposition cycles were used, for which the deposition charge density $Q_{dep} = 130$ mC cm^{-2}. This corresponds to a polymer surface coverage, Γ, of about 168 nmol cm^{-2}, calculated using the expression $\Gamma = Q_{dep}\eta/zF$, where η is the deposition efficiency (25% [3]), F is the faradaic constant and z is the number of electrons involved in deposition of one polymer unit ($z = 2$).

After deposition the polymer was pretreated by immersion in 0.1 M $HClO_4$ solution and potential cycling in the range $-0.2 < E/V < 0.7$ at a scan rate of 10 mV s^{-1}. It was then oxidized potentiostatically (in the same medium), by holding the working electrode at a potential of 0.6 V for 60 s and then left at open circuit for 500 s, during which the open circuit potential (o.c.p.) was monitored. After that, the polymer was reduced by a potential step to −0.3 V (for 60 s) and then left at open circuit, again with monitoring of the o.c.p. This procedure was repeated twice and very good reproducibility of the potential responses was found. As seen in Figure 5, the open circuit potential of a p(1,8-DAN)-modified electrode relaxes to a value of about 0.19 V after the reduction step and to a value of 0.36 V after the oxidation step.

Finally, the film was reduced and, after a 20 s relaxation period at open circuit, 0.2 ml portions of 0.001 M $K_2Cr_2O_7$ solution were added to the stirred supporting electrolyte until the final concentration was 7.3×10^{-5} mol dm^{-3}. Initially, after addition of first portions of $K_2Cr_2O_7$ the open circuit potential did not change (curve 3 in Figure 5), but later it increased steeply to 0.59 V, that is, higher than that of the oxidized p(1,8-DAN). The change in polymer oxidation state (manifested through the potential) is attributed to the presence of the redox couple in the solution. Introduction of positive charge sites in the polymer then induced anion transfer into the polymer film to maintain electroneutrality. This type of effect and the influences of redox species concentration and of the supporting electrolyte has been modelled for the polypyrrole system [13].

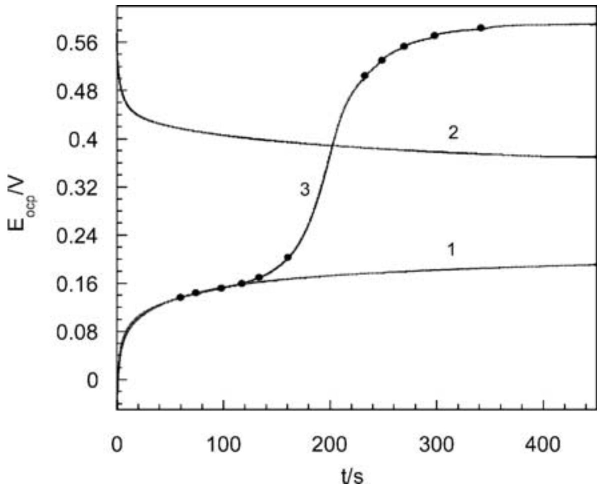

Fig. 5. Open circuit potential responses of p(1,8-DAN) in 0.1 M $HClO_4$ after polymer reduction at −0.3 V (curve 1), after oxidation at 0.5 V (curve 2) and after addition of 0.001 M $K_2Cr_2O_7$ during relaxation of the reduced polymer (curve 3). Black points indicate the time of adding of subsequent portions of $K_2Cr_2O_7$ solution.

In the reaction between p(1,8-DAN) and $Cr_2O_7^{2-}$ ion, the Cr(VI) acts as an oxidant. It oxidises the polymer and is itself reduced to Cr^{3+}, according to the following scheme:

$$\mathrm{Cr_2O_7^{2-} + 14\,H^+ + 6\,p(1,8\text{-}DAN)^0 + 6ClO^-_{4(S)} \rightleftharpoons 2\,Cr^{3+} + 7\,H_2O + 6\,p(1,8\,DAN)^+ + 6\,ClO^-_{4(P)}} \quad (1)$$

For simplicity, we do not consider the acid–base equilibrium which accompanies the redox reaction of the polymer. At equilibrium, the sum of the electrochemical potentials, $\tilde{\mu}$, on the left side of Equation 1 is equal to the sum of the electrochemical potentials on the right side:

$$\tilde{\mu}_{\mathrm{Cr_2O_7^{2-}}} + 14\tilde{\mu}_{\mathrm{H^+}} + 6\tilde{\mu}_{\mathrm{P}} + 6\tilde{\mu}_{\mathrm{A^-(s)}} = 2\tilde{\mu}_{\mathrm{Cr^{3+}}} + 7\mu_{\mathrm{H_2O}} + 6\tilde{\mu}_{\mathrm{P^+}} + 6\tilde{\mu}_{\mathrm{A^-(P)}}, \quad (2)$$

where the subscripts P and P^+ denote the polymer in the neutral and oxidized states, respectively, whereas A^-(P) and A^-(S) correspond to the anions in the polymer film and in the solution.

By splitting the electrochemical potentials into the chemical and electrical potentials, one obtains the following expression for the difference of the Galvani potentials between the polymer and the solution, $\Phi^{P} - \Phi^{S}$:

$$\Phi^{p} - \Phi^{s} = \frac{1}{6F}\left(\mu^{o}_{Cr_2O_7^{2-}} + 14\mu^{o}_{H^+} - 2\mu^{o}_{Cr^{3+}}\right) + \frac{RT}{6F}\ln\left(\frac{a_{Cr_2O_7^{2-}}a^{14}_{H^+}}{a^{2}_{Cr^{3+}}}\right) - \frac{1}{F}\left(\mu^{\circ}_{P^+} - \mu^{\circ}_{P}\right) - \frac{RT}{F}\ln\left(\frac{a_{P^+}}{a_{p}}\right) - \frac{RT}{F}\ln\left(\frac{a_{A^-(P)}}{a_{A^-(S)}}\right) \quad (3)$$

The potential difference between the polymer and the solution is one of the terms which influences the open circuit potential of the cell Ag|AgCl, $Cl^{-}_{(std)}$|solution|polymer|metal:

$$E = (\Phi^{M} - \Phi^{P}) + (\Phi^{P} - \Phi^{S}) + (\Phi^{S} - \Phi^{ref}), \quad (4)$$

where the difference in the Galvani potentials, $\Phi^{ref} - \Phi^{S}$, corresponds to the potential of the reference electrode, E_{ref}. The potential difference between the metal substrate and the polymer may be expressed as follows:

$$\Phi^{M} - \Phi^{P} = \frac{1}{F}\left(\mu^{o}_{P^+} - \mu^{o}_{P} + \mu_{e(Me)}\right) + \frac{RT}{F}\ln\left(\frac{a_{P^+}}{a_{P}}\right). \quad (5)$$

Inserting Equations 3 and 5 into Equation 4 shows that the open circuit potential measured in the cell after spontaneous reaction between the polymer and chromate depends on the Nernst potential of the redox system $Cr_2O_7^{-}/Cr^{3+}$ and the concentration ratio of the counter ions in the film and in the solution:

$$E = E^{\circ} + \frac{RT}{6F}\ln\left(\frac{a_{Cr_2O_7^{2-}}a^{14}_{H^+}}{a^{2}_{Cr^{3+}}}\right) - \frac{RT}{F}\ln\left(\frac{a_{A^-(P)}}{a_{A^-(S)}}\right), \quad (6)$$

where $E^{\circ} = \frac{1}{6F}\left(\mu^{\circ}_{Cr_2O_7^{2-}} + 14\mu^{\circ}_{H^+} - 2\mu^{\circ}_{Cr^{3+}} + 6\mu_{e(Me)}\right) - E_{ref}$

According to Equation 1, the oxidation of 3 moles of the electroactive centres in the polymer leads to formation of 1 mole of Cr^{3+} ions. The total number of electroactive centres available within the polymer film for reaction with the solution redox couple may be determined by integration of I/E curve (at a low scan rate, to ensure complete access to all sites) during the redox cycling of the polymer in 0.1 M $HClO_4$. For the film of Figure 6, the value is 740 nmoles. To determine the concentration of the anions in oxidized polymer matrix one should also evaluate the polymer volume. The value of 1.2×10^{-4} cm^3 was obtained by us from the equation:

$$V = \Gamma MS/\rho \quad (7)$$

where M is molar mass of the monomer (156 g mol^{-1}), S is the electrode area and ρ is the polymer film density (about 1.3 g cm^{-3}). The value of Γ, 168 nmol cm^{-2}, was estimated from electrodeposition charge. It is higher than that derived from the reduction charge because not all monomer units deposited are electroactive.

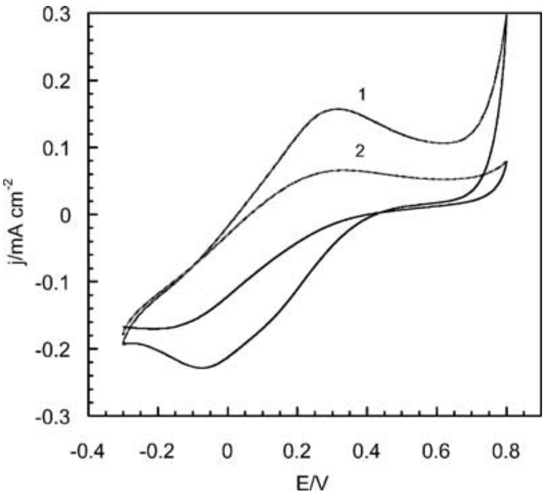

Fig. 6. Study of the electroactivity of p(1,8-DAN) by cyclic voltammetry in 0.1 M $HClO_4$ at $v = 20$ mV s^{-1} before (1) and after (2) reaction between $Cr_2O_7^{2-}$ ions and the polymer film.

Taking $E^{\circ}(Cr_2O_7^{2-}/Cr^{3+}) = 1.1$ V (vs Ag/AgCl,Cl$^-$) the calculated value of the open circuit potential of the cell after redox reaction between the polymer and the solution is 0.95 V, which is markedly higher than the experimental value of 0.59 V. This implies that the process occurring in the polymer film upon addition of dichromate ions is more complicated than that of Scheme 1. This is probably a consequence of relatively high redox potential of the $Cr_2O_7^{2-}/Cr^{3+}$ couple, which may lead to overoxidation of the polymer. To test this hypothesis, the electroactivity of the polymer after dichromate oxidation was determined by redox cycling in 0.1 M $HClO_4$ solution. As seen in Figure 6, the $Cr_2O_7^{2-}$ treatment caused partial loss of polymer electroactivity: from the charge passed during film reduction at slow scan rate (5 mV s^{-1}) we estimated that of about 50% of electroactive centres underwent irreversible oxidation by Cr(VI).

Despite this, we stress that electroactivity and ion extraction rely upon different chemistry. Thus, degradation of the polymer does not necessarily imply degradation of its ability to extract Cr^{3+} ions formed in the solution by the spontaneous reaction between the polymer and Cr(VI) species. There is no apparent reason why the amine groups should not continue to act as effective complexing agents for Cr^{3+}. In such a case, the p(1,8-DAN) matrix could be used in practice to remove $Cr_2O_7^{2-}$ ions from different types of wastes.

To explore this possibility, following the o.c.p. experiments in $Cr_2O_7^{2-}$ solution and subsequent redox cycling in 0.1 M $HClO_4$, the polymer was peeled off the substrate and analyzed by means of EDX spectrometry. EDX spectra were recorded from six locations across the surface, to provide a mean relative elemental composition.

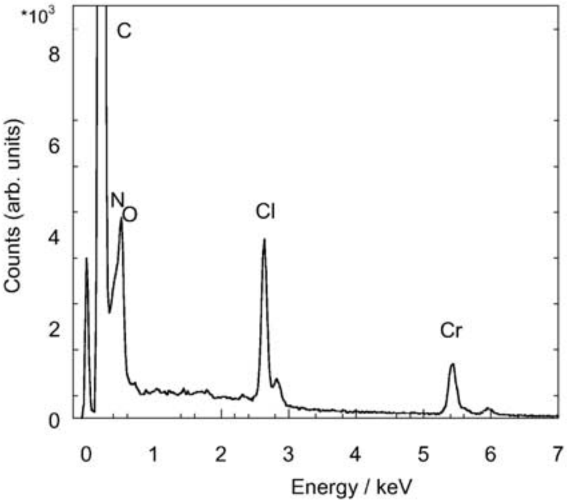

Fig. 7. EDX spectrum of p(1,8-DAN) sample after spontaneous redox reaction between the polymer and $Cr_2O_7^-$ ions.

In line with our hypothesis, the EDX spectrum presented in Figure 7 confirms the presence of Cr in the polymer film. Since polymer oxidation by means of dichromate is accompanied by the incorporation of ClO_4^- ions (to satisfy electroneutrality), the O/Cl ratio may be used to determine the oxidation state of Cr in the polymer. The O/Cl ratio in the polymer is about 5, from which we deduce that the oxygen atoms in the sample mainly originate from perchlorate, not $Cr_2O_7^-$ ions. Thus, we conclude that chromium was sorbed by the sample mainly in the form of Cr^{3+} ions via complexation by the amino groups.

The N/Cl atom ratio was in the range 6 to 8, from which we deduce that on average each positive charge introduced during polymer oxidation is spread over 3–4 monomer units. Although the number of electrons involved in creation of one electroactive center is lower than that reported in [1], it is consistent with our observation above that about 50% of the film was irreversibly deactivated during the redox process between the dichromate and the polymer.

Qualitatively, the EDX results unequivocally demonstrated that the p(1,8-DAN) matrix may be successfully used for removal of Cr^{3+} ions from the bathing solution. Quantitatively, the observed N/Cr ratio of about 12 was higher than anticipated. One possible explanation of this could be crosslinking of the polymer chains brought about during the polymer/dichromate redox reaction. Another possible explanation may be a high content of structure B (Figure 3) in the polymer film, in which adjacent monomer units are coupled by both amino groups, thereby decreasing the availability of the ligand.

4. Conclusions

Our study of the p(1,8-DAN) film system as a candidate for removal of $Cr_2O_7^{2-}$ ions from solutions has lead to three significant conclusions.

First, the efficiency of electrodeposition of p(1,8-DAN) is influenced by the type of acid used in the polymerisation bath. Strong acids, like $HClO_4$, cause the protonation of both amine groups in the monomer. This leads to strong interactions of protonated monomer with oxygen atoms in the anions present. Rather than generate polymer that is deposited on the electrode, these complex species may diffuse away from the vicinity of the electrode. Consequently, the current corresponding to the monomer oxidation in acetonitrile acidified with $HClO_4$ is lower than that in non-acidified acetonitrile or in acetonitrile acidified with the weaker acid CCl_3COOH. CCl_3COOH, as a weak acid, protonates only one amine group of monomer, so that film growth is not inhibited by the process described above.

Second, electrosynthesized p(1,8-DAN) does not have a simple or single structure. IR spectra showed that the films contain a mixture of different structures, presumably randomly distributed along the chains, in which monomer units are linked by C–N–C and by C–C bonds.

Third, p(1,8-DAN) films, whether deposited from acetonitrile or acetonitrile acidified with CCl_3COOH, may be effectively used as the matrices for removing the toxic $Cr_2O_7^{2-}$ ion from different types of liquid wastes. In a spontaneous reaction between the polymer and $Cr_2O_7^{2-}$ ions, the polymer is oxidized and Cr(VI) is reduced to the less toxic Cr(III) species. The high value of the redox potential of the $Cr_2O_7^{2-}/Cr^{3+}$ couple causes partial irreversible overoxidation of the polymer. This leads to decreased electroactivity of the film, but does not seriously inhibit Cr^{3+} ion complexation by free NH_2 groups in the p(1,8-DAN) matrix.

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