

## Metal ion incorporation in the conducting polymer electrode matrix using an 'active' metal substrate

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### Abstract

The incorporation of free transition metal cations (potential redox catalyst centers) into conducting organic films by electrodeposition is relatively rare due to the repulsive nature of the positive cation radicals of the polymer itself during polymerization. This paper shows that such metal cations can be trapped in the polymer matrix as it is being electrodeposited on a metal substrate electrode, which itself simultaneously electro-oxidizes (corrodes). The electropolymerization of 3-methylthiophene on Mo(0), Ni(0) and Fe(0) substrate electrodes ('active electrodes') is reported. SEM, EDXRF, and XPS were used to demonstrate the amount of metal cations in and/or on the polymer matrix and to determine the valence states. The rates of diffusion of the incorporated metal ions into an LiClO<sub>4</sub> electrolyte solution were also studied. The presence of trace amounts of all three metal cations were sufficient to destroy the electroactivity of the polymer film electrodes for the oxidation of catechol. © 1997 Elsevier Science S.A.

**Keywords:** Electrocatalysis; 3-Methylthiophene; Metal incorporation; XPS; Metallic substrate; Corrosion; Conducting organic polymer

### 1. Introduction

The advantages gained from employing electrode surfaces modified with conducting polymers have led to a great deal of interest among electrochemists during the last few decades [1–3]. This new class of electrode materials has been found to improve the electrode sensitivity, selectivity and to reduce fouling effects in many applications. These modified electrodes have in some cases also been found to have electrocatalytic properties. Normally, a thin film of a conducting polymer such as polypyrrole, polyphenylene, poly(3-methylthiophene), etc., is deposited on the surface of the substrate metal or carbon electrode [3–6]. Several methods of polymerization have been reported, including plasma, chemical and electrochemical; however, the results have been quite similar with respect to improvements in electrode selectivity and sensitivity [7–13]. Regardless of which polymerization method is utilized, the stability of the film on the substrate is still an open area for improvement.

In an attempt to improve the conductivity, stability and electrocatalytic properties of the films, a number of research groups have investigated the effectiveness of incorporating a metallic species within the polymer film matrix. Tourillon and Garnier [14], were successful in including metallic Ag and Pt aggregates in conducting organic polymers by immersing the film electrode in a solution containing the metal ion. From their studies, they concluded that different metal ions interact with the polymer films in a different manner. Also, they found that the presence of metallic aggregates not only improved the stability of the polymer film but also enhanced its electrocatalytic activity. Other workers [15–18] were able to include metallic compounds, such as WO<sub>3</sub> and SnO<sub>2</sub>, and metal, such as Pd, by co-electrodeposition with the organic monomer. Some workers have reported on the electrodeposition of polypyrrole on 'active' metal substrates, but have not examined incorporation of metal ions in the film [19–21]. Beck and Hülser did observe Al<sub>2</sub>O<sub>3</sub> + polypyrrole inter-layers between the Al substrate and the polymer film [22].

Poly(3-methylthiophene) (P-3MT)-modified electrodes have been widely investigated as sensors for the detection

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of electroactive species such as catecholamines. Such polymeric films are conductive in the positive charged (oxidative) state [23]. It is accepted that counter anions from the supporting electrolyte enter the polymer film to neutralize the matrix charge. Therefore, from an electrostatic point of view it is quite unusual to incorporate cations in the film matrix. In the P-3MT case, it is believed that the sulfur heteroatom serves a twofold purpose. It participates in charge conductivity, and, at the same time, serves as the active site for redox chemistry [23]. The immediate objective of this research is to develop electrodes containing transition metal cations to be tested for the electrolytic reduction of  $C_2H_2$  and  $N_2$  [24].

This paper describes an effective method using 'active' metal substrates for the inclusion of metallic species, in cation form, such as molybdenum, nickel and iron in the electrogenerated poly(3-methylthiophene) thin films. The long term lability of the metal ion incorporation within the polymer was studied utilizing inductively coupled plasma mass spectrometry (ICP-MS) for the measurement of the metallic species leached into solution phase by diffusion. Interface concentrations and morphology determinations were carried out using scanning electron microscopy (SEM) coupled with energy dispersive X-ray fluorescence (EDXRF) and X-ray photoelectron spectroscopy (XPS) techniques. These results were then related to the electrocatalytic activity of the polymer electrodes with metallic inclusions by carrying out the oxidation–reduction of catechol in acidic solution using cyclic voltammetry.

## 2. Experimental

### 2.1. Reagents and materials

The 3-methylthiophene (3MT) monomer was obtained from Aldrich (Milwaukee, WI) and was used after fractional distillation. Supporting electrolytes tetrabutylammonium tetrafluoroborate (TBATFB) and tetrabutylammonium hexafluorophosphate (TBAHFP), were purchased from Aldrich and dried for about 1 h at 100°C before use. Acetonitrile, methanol (HPLC grade) and sulfuric acid (A.C.S. reagent) were obtained from Fisher Scientific company and were used as-received. Electropolymerization solutions were prepared fresh for each experiment and were deaerated with argon for about 10 min before the polymerization step. Distilled deionized water (DI water) with an 18 M $\Omega$  resistance (Nanopure 4C unit, Fisher) at room temperature was used throughout.

### 2.2. Electrode materials and preparation

Electrochemical polymerization was carried out in a one-compartment three-electrode glass cell (25 or 50 ml) containing argon-deaerated acetonitrile, 0.1 M supporting electrolyte and 0.05 M 3MT. The reference electrode was

Ag|AgCl|3 M KCl (MF-2074, BAS, Inc. West Lafayette, IN, USA). The auxiliary electrode was a coiled Pt wire. The Mo, Ni and Fe working electrodes were constructed by sealing metal rods (diameters 4.8 mm, 2 mm and 6.35 mm respectively) in Kel-F. All electrodes were roughly polished on a nylon cloth with 2  $\mu$ m diamond paste. They were fine polished on a microcloth using a 0.05  $\mu$ m alumina + water suspension until no visible scratches were observed. All polishing materials were purchased from Buehler. After polishing, the electrodes were ultrasonicated in a methanol bath for 15 min, rinsed with DI water, and dried in a stream of  $N_2$  gas. For the XPS experiments metal foils 0.1 mm thick (Goodfellow, Berwyn, PA) were cut to form flat circular disc electrodes with an area of approximately 1 cm<sup>2</sup>.

### 2.3. Techniques and instrumentation

The electropolymerization step was performed using an EG&G model 173 potentiostat–galvanostat (Princeton Applied Research, Princeton, NJ, USA). A BAS-100 electrochemical analyzer was employed in the cyclic voltammetric studies. A Perkin-Elmer 5300 spectrometer was used to obtain XPS spectra and chemical compositions of the polymer films. Calibration was performed using the C 1s component (binding energy is 284.6 eV). An Mg K $\alpha$  X-ray source was used with 300 W applied to the anode. Metal ion concentrations in the solution phase were determined by use of a VG Plasma Quad PQ 1 (VG Elemental, Winsford, Cheshire, UK) inductively coupled plasma mass spectrometer. All standards and samples for ICP-MS analysis were prepared with 0.1 M LiClO<sub>4</sub> solution. Calibration curves were constructed using four standards with concentrations 50, 100, 200 and 400 ppb for each element. The standards were blank subtracted to correct the matrix effect. A Cambridge 90 electron microscope coupled with a Princeton Gamma Tech (System 4 Plus) energy dispersive spectrometer were used for determination of film morphology and elemental analysis.

## 3. Results and discussion

Cyclic voltammograms (CVs) at a bare Pt electrode (Fig. 1(A)) and at a polymer (Pt) electrode (Fig. 1(B)) for catechol show a very large difference in the electrocatalytic activity between the two electrodes. On the other hand, the performance of the organic film was greatly changed after including a metal ion in the matrix, for example by dipping the electrode in a molybdate solution (Fig. 1(C)). The incorporation of the metallic species in the polymer film matrix was carried out in two different fashions for this investigation. Two different experiments (SEM/EDXRF and XPS) were used to examine the incorporation of metal ions in the polymer film matrix.

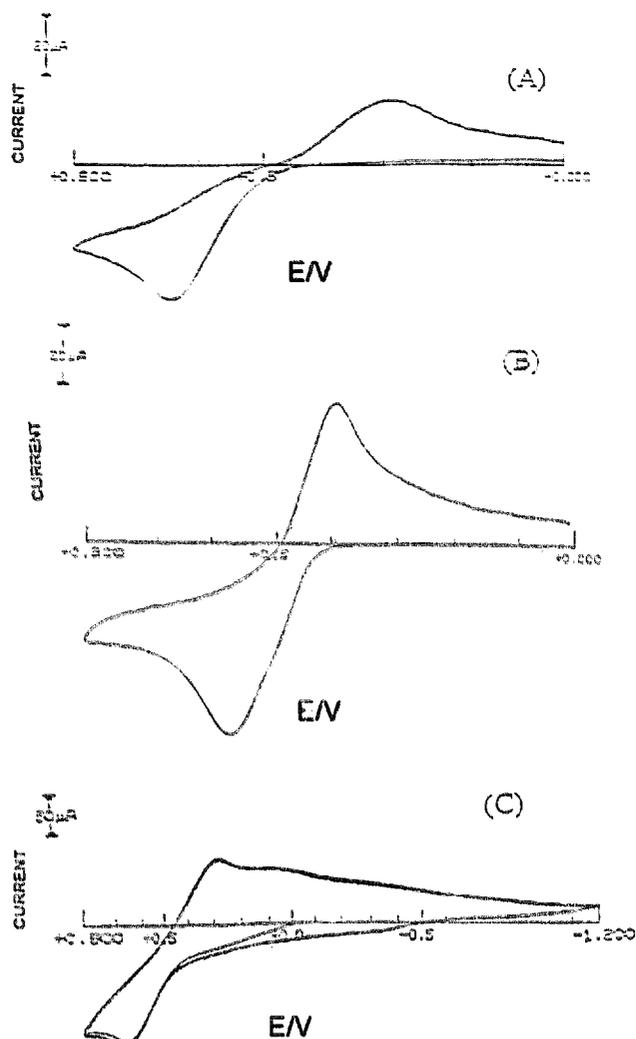


Fig. 1. A CV of 0.01 M catechol at a Pt electrode: (A) bare electrode; (B) P-3MT-modified electrode; (C) modified electrode dipped in 0.1 M  $\text{Na}_2\text{MoO}_4$ . Scan rate  $100\text{ mV s}^{-1}$ ; electrolyte aqueous 0.01 M  $\text{H}_2\text{SO}_4$ .

In the first case, the polymer film was prepared by polymerizing 3MT on Pt substrate, as described previously [1], for 90 s, soaking for 5 days in 0.1 M  $\text{Na}_2\text{MoO}_4$  dissolved in Sorensen buffer solution ( $\text{pH} \approx 7$ ), and washing repeatedly with DI water. The purpose of this experiment was to determine whether the  $\text{Mo}^{6+}$  ions diffuse from the solution into the polymer matrix. The morphology of the film surface was examined by SEM. As shown in Fig. 2(A), cluster-shaped formations of molybdate salts were deposited on the surface. These probably form during the drying process in preparation for the SEM measurements as water and salts diffuse out of the polymer matrix to the surface. Before dipping, the surface morphology appeared the same as in Fig. 2(B) (see below). Optical photomicrographs ( $1000\times$ ) also showed a uniform polymer film deposited on the Pt substrate [25].

The other approach for metal incorporation within the polymer film was to polymerize the film directly on an 'active' metal substrate of interest. For example, if Mo was the metal ion to be incorporated, then the substrate used

for electrodeposition was a Mo metal disk. Presumably, with this technique, the corroding metal ions of the metal substrate would be trapped within the polymer matrix while it was being formed by electropolymerization. Fig. 2(B) is the SEM picture which shows P-3MT film formed on the Mo substrate. It is important to note that no observable pores or holes were found in the Mo substrate film, and nor were any found in the Pt substrate film. A polymerization time of 90 s was chosen for this part of the study. This film was well formed with a sufficient thickness that it can be peeled off at a negative potential of about 3 V vs.  $\text{Ag}|\text{AgCl}$ . Concurrent with the SEM experiment, an EDXRF study of both surfaces was carried out on both the P-3MT (Pt) molybdate-dipped and the P-3MT (Mo) electrodes. These results revealed that a certain amount of molybdenum was incorporated on or within the polymer films in both cases. Minimal differences in the EDXRF spectra were observed for the two films.

Analysis by XPS provided valuable qualitative and quantitative information regarding the surface elemental composition (7.0 to 20.0 nm depth profiling). Additionally, the oxidation state of the element was determined and the shift in binding energy of the metal species provided

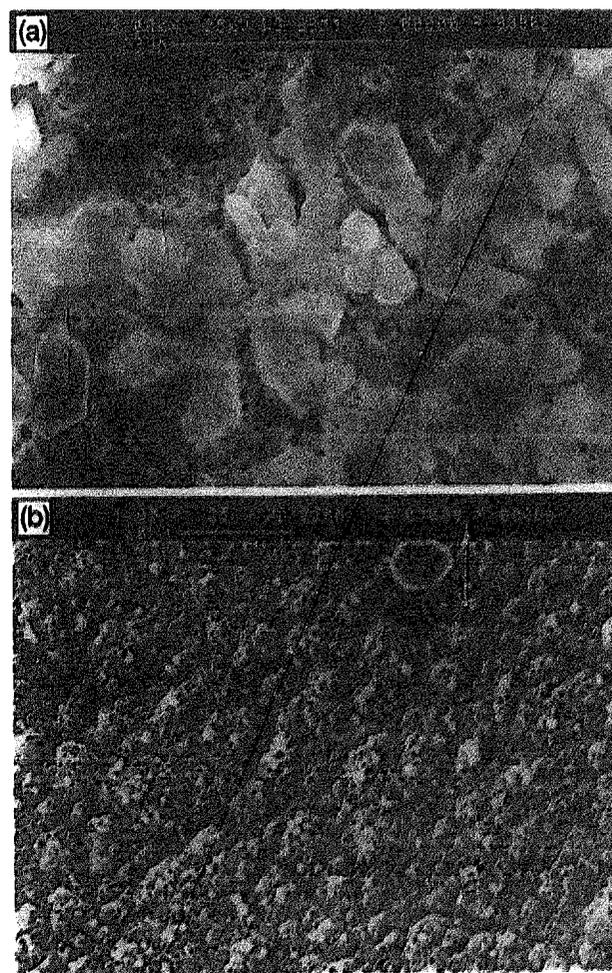


Fig. 2. Scanning electron micrograph of: (A) Pt electrode dipped in Mo solution; (B) Mo-modified electrode.

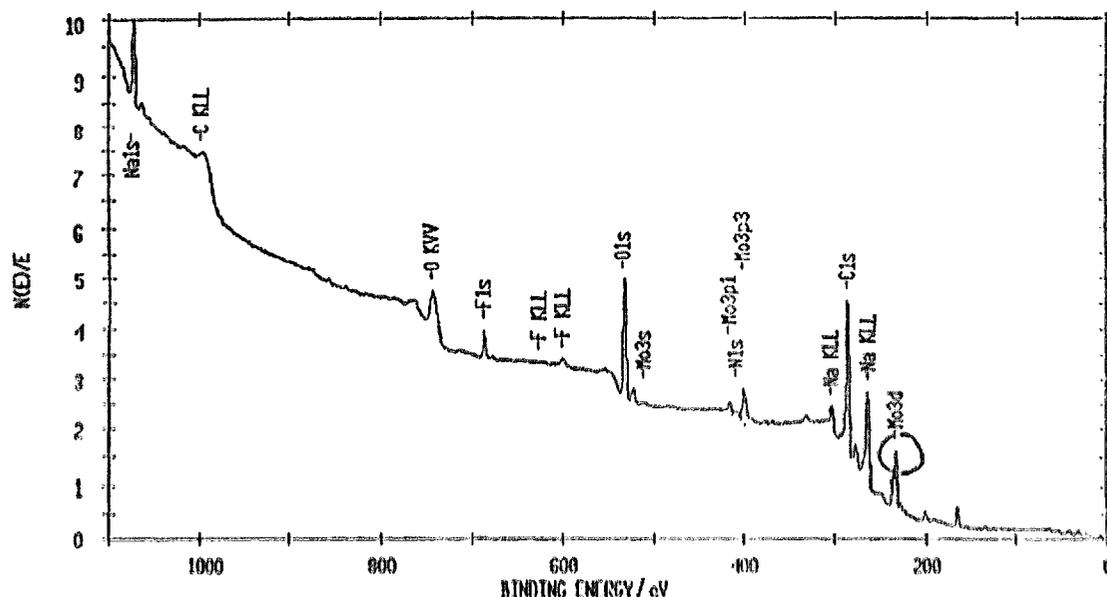


Fig. 3. X-ray photoelectron survey spectrum of a Pt-modified electrode dipped for 5 days in Mo solution. Polymerization time 45 s; take-off angle  $45^\circ$ .

information about the chemical environment in which it resided. The XPS results for the Mo(VI)-dipped electrode showed that Mo was incorporated at and within the film (Fig. 3). A high resolution XPS spectrum (Fig. 4) showed that the oxidation state of Mo within the film was +6 (a doublet at 232.70 and 235.80 eV; Mo  $3d_{3/2}$  and  $3d_{5/2}$  respectively). Therefore, the Mo ions were adsorbed on and in the electrode surface without change in valence state. The binding energy difference between  $3d_{5/2}$  and  $3d_{3/2}$  electrons of  $\text{Na}_2\text{MoO}_4$  compound should be 3.20 eV [26], while in this study, the value obtained was about 3.10 eV. Thus, it appeared that there was no strong com-

plexation process accompanying interaction between Mo(VI) and the thiophene moiety. No evidence for formation of Mo(IV) at 231 eV was obtained [27,28]. The less intense peak at 228.00 eV was identified as a sulfur 2s peak, not an Mo(0)  $3d_{3/2}$  peak, based on: (i) the absence of the second peak of the Mo(0) doublet,  $3d_{5/2}$ ; (ii) the ratio of this peak to the sulfur 2p peak at 164 eV corresponded to the reported value [26]. The Mo/S mole ratio calculation based on the Mo/S atomic concentration ratio (Table 1) gave a value of 0.7 mol of Mo per mole of S.

Another P-3MT film was polymerized on the Mo substrate for further XPS study. Two different polymerization

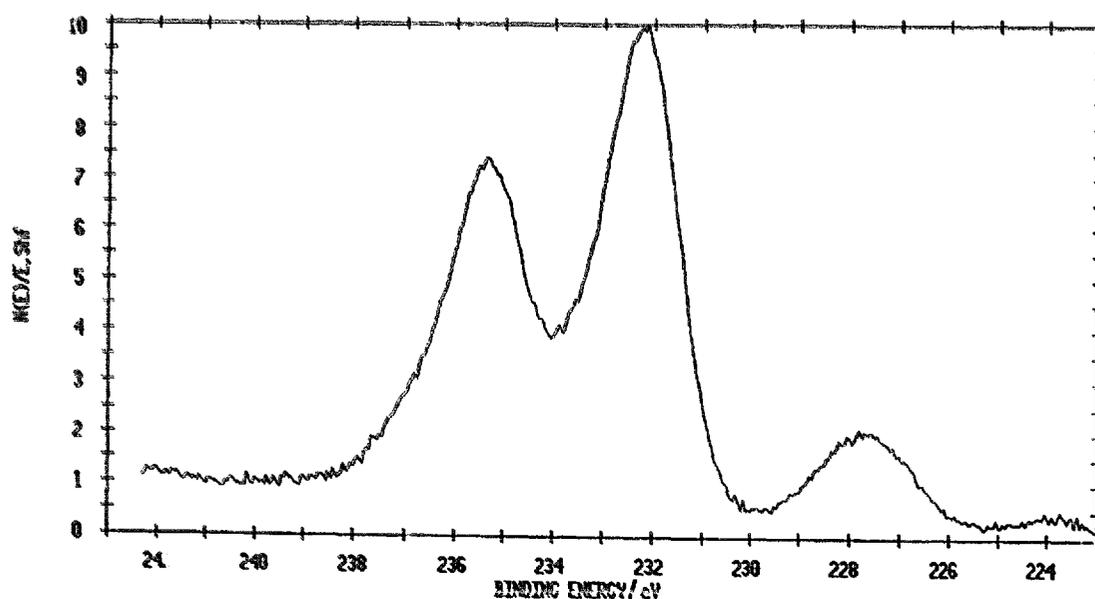


Fig. 4. High resolution Mo 3d X-ray photoelectron spectra of a Pt-modified electrode dipped in Mo solution. Polymerization time 45 s; take-off angle  $45^\circ$ .

Table 1  
Mo/S molar ratio at different conditions from XPS experiment

Pretreatment	Atomic concentration/%		Mo/S ratio
	Mo	S	
Dipping experiment with Pt P-3MT mediated electrode	2.2	3.2	0.688
Mo substrate, polymerization time 45 s	0.1	3.0	0.033
Mo substrate, polymerization time 90 s	50.05	0.8	0.063

times (45 and 90 s) were used. In both experiments the Mo/S mole ratios were significantly less than found in the dipping experiment (Table 1). It is well known that the P-3MT film usually forms by deposition of consecutive layers [29]. The layers next to the substrate are homogeneous and dense; however, with increasing thickness the polymer becomes less ordered with a 'noodle-like' structure. It was not surprising to find that the relative amount of Mo ions incorporated in the film decreased significantly with longer polymerization times, as shown in Table 1. In this experiment, two species of Mo can be found in the XPS spectra: Mo with oxidation state of zero (elemental molybdenum), and Mo with oxidation state of +6. Both Mo(0) and Mo(VI) were found within the thinner film (45 s polymerization) and in the thicker film (90 s polymerization). As shown in Fig. 5 the XPS spectrum obtained for the 90 s film, the  $3d_{5/2}$  peak of the Mo(VI) at 232 eV was quite asymmetric. The intensity of the peak at 227.7 eV was also much higher than the one observed in the dipping experiment (Fig. 4), while the concentration of sulfur in both experiments remained the same. This would be expected if the doublet of atomic Mo is convoluted with the Mo(VI) doublet.

To determine the depth distribution of the Mo within the 90 s polymer film, an XPS experiment was performed with three different take-off angles (15°, 45°, and 75° with

respect to the sample surface). With higher take-off angles, greater depth probing can be obtained. Table 2 shows the concentration of Mo ions as a function of take-off angle. The highest ratio of Mo/S was at 45°, giving a ratio of 0.1 mol of Mo per mole of S.

A similar take-off angle XPS study was carried out on a P-3MT (Ni) electrode. An example of an XPS survey spectra of P-3MT (Ni) electrode at 45° take-off angle is presented in Fig. 6. Fig. 7 shows the multiplexed peaks obtained for the nickel in the polymer, which are characteristic of a +2 valence state. However, the binding energies were shifted about 2.0 to 3.0 eV higher than expected (ca. 858 eV for the  $2p_{3/2}$  peak compared to 855 eV and 856 eV for NiO and Ni(OH)<sub>2</sub> respectively) [26]. This indicated that Ni(II) was interacting within the polymer matrix. However, due to the complicated composition of the system (i.e. thiophene sulfur, TFB anion, acetonitrile and H<sub>2</sub>O possibly present in the matrix), it was not possible to define its environment from this data. There was no evidence for the presence of any atomic Ni at this surface. A similar distribution as a function of take-off angle was obtained for both Mo and Ni (Table 2). The main difference between Ni and Mo films was that, at a take-off angle of 45°, the ratio was 5.4 mol of Ni per mole of S. A striking difference was realized for the P-3MT (Fe) electrode. Surprisingly, there was no measurable amount of

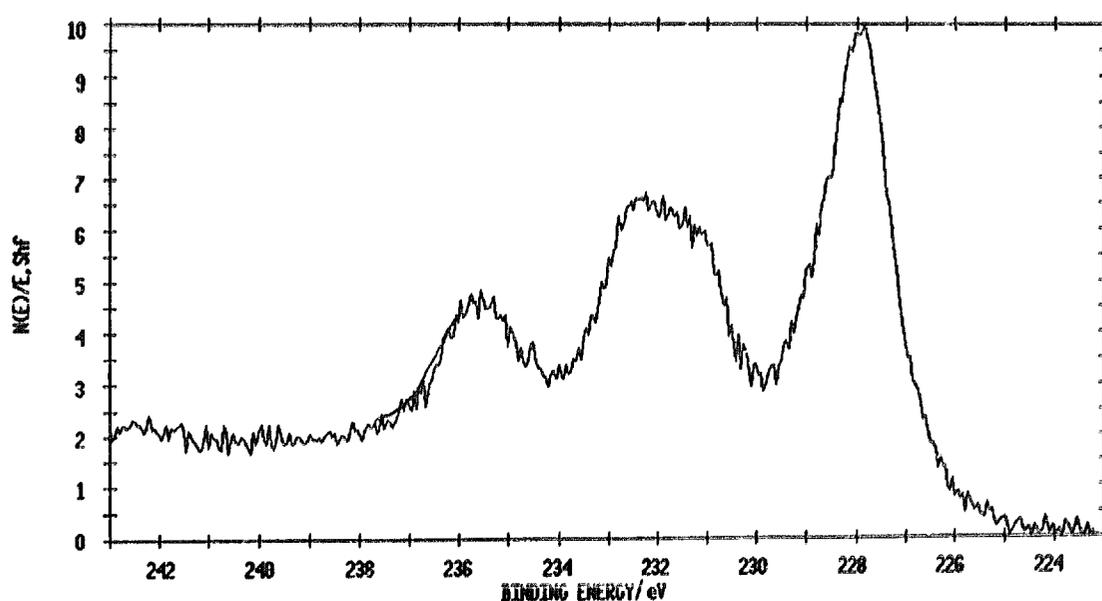


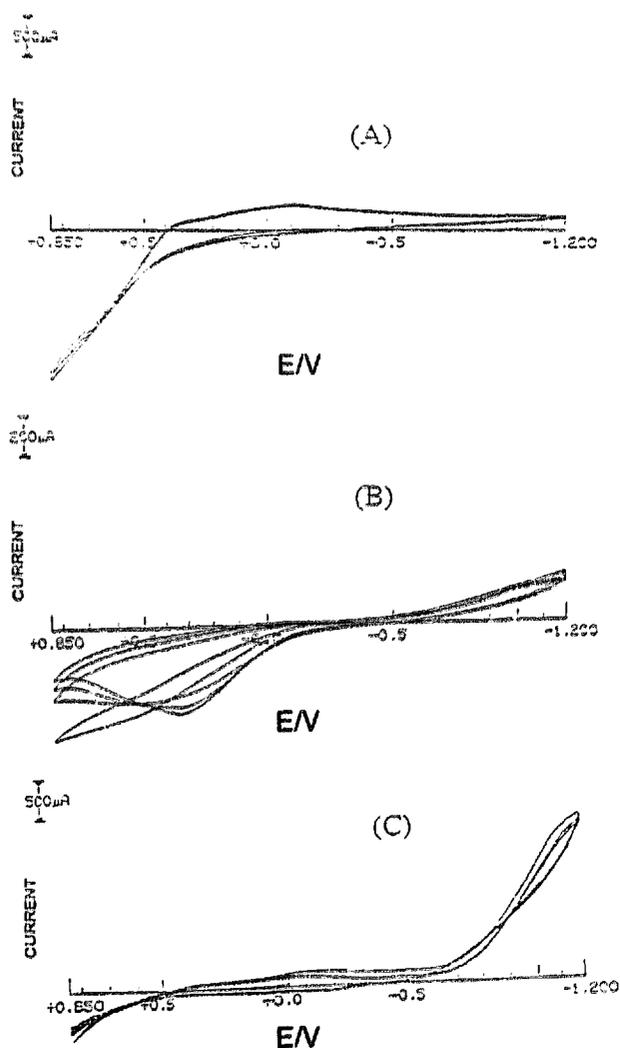
Fig. 5. High resolution Mo 3d X-ray photoelectron spectra of Mo-modified electrode. Polymerization time 90 s; take-off angle 45°.



**Table 2**  
Molar ratios of metal ion to sulfur at the surface of Mo-, Ni-, and Fe-modified electrodes determined by XPS

Take-off angle/deg	Metal/sulfur ratio		
	Mo	Ni	Fe
15	0.004	4.7	0
45	0.1	5.4	0
75	0.01	4.4	0

containing 0.01 M catechol. The voltammograms for the three active metal substrates showed a complete absence of P-3MT electrocatalytic activity for catechol (Fig. 8). The electrodes were tested again in catechol by cyclic voltammetry after immersion in the 0.01 M  $\text{LiClO}_4$  solution for 8 days. The poor electrocatalytic performance shown by all three electrodes supports the belief that metal ions were still present within the polymer film, even though the metal ion concentrations were depleted significantly during

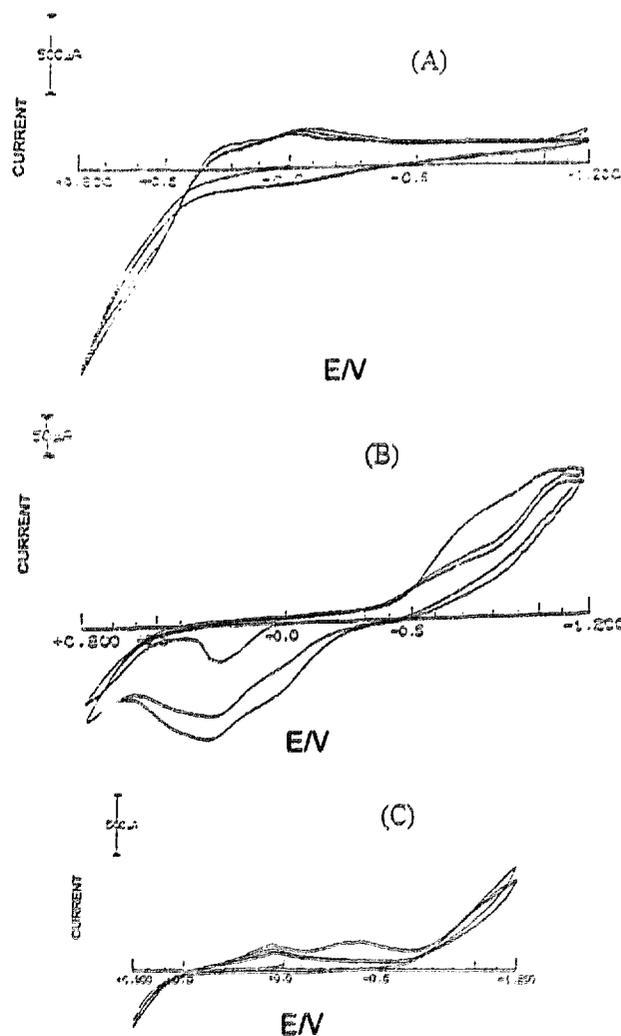


**Fig. 8.** CVs of 0.01 M catechol at fresh modified electrodes: (A) Mo substrate; (B) Ni substrate; (C) stainless steel substrate. Scan rate  $100 \text{ mV s}^{-1}$ ; electrolyte aqueous 0.01 M  $\text{H}_2\text{SO}_4$ .

**Table 3**  
Concentration of metal ions in solution phase determined by ICP-MS

Metal	Concentration/ppb				
	2 days	3 days	5 days	6 days	8 days
Mo	0.83	1.04	2.24	3.32	3.79
Ni	28.31	32.68	48.7	62.52	104.2
Fe	13.11	13.81	20.6	28.79	32.67

the 8 days contact with  $\text{LiClO}_4$  solution. Fig. 9 shows that there were sufficient metal ions or some redox couples in the polymer to give current peaks in the CVs. These results indicate that the electroactivity of the electrodes was not completely inhibited. In the Ni case, a peak at  $+0.33 \text{ V}$  responded to formation of  $\text{Ni}(\text{+2})$  oxide [30]. Furthermore, a P-3MT Mo(VI)-dipped electrode showed no difference in the CVs for ferricyanide with respect to an undipped electrode.



**Fig. 9.** CVs of 0.01 M catechol at modified electrodes after 8 days immersion in 0.1 M  $\text{LiClO}_4$  solution: (A) Mo substrate; (B) Ni substrate; (C) stainless steel substrate. Scan rate  $100 \text{ mV s}^{-1}$ ; electrolyte aqueous 0.01 M  $\text{H}_2\text{SO}_4$ .

#### 4. Conclusion

The reported electropolymerization processes prove to be very convenient for the accumulation of metal cations in a polymer film matrix simultaneous with the active electrode substrate corrosion. Some (a small fraction) of Mo and Ni ions seem to be incorporated in the film, presumably through S heteroatom interaction, as inferred from the 'poisoning' of the catechol oxidation. Investigation will continue in order to determine the mechanism of interaction between metal cations and the thiophene ring. It will also be of interest to determine if the concentrations of metal ions in the polymer matrix can be controlled by variation of deposition potential, concentration of monomer, temperature, etc. The high concentration of Mo(0) in the polymer is puzzling. This suggested that some intermediate valence of Mo was produced by corrosion and then with time or environment it disproportionated inside the polymer. However, no such disproportionation reaction could be found in the literature. Beam-promoted disproportionation has been observed for copper systems on prolonged exposure during XPS measurements [31]. Although beam exposures were on the order of minutes in the Mo case, it could possibly account for the Mo(VI) and Mo(0) results found. It will be important to determine if Mo(0) microclusters are forming. Since the total inhibition of the electro-oxidation of catechol is achieved by relatively small amounts of all three metal ions, this suggests that very specific sulfur configurations (hot spots) are responsible for the electrocatalysis of redox processes for these species [23]. The fact that the Mo(VI)-dipped electrode remains electroactive with respect to the ferrieyanide reduction indicates that only specific sites are inhibited for an inner-sphere electron transfer in the catechol oxidation. Further studies will also be carried out to determine microscopically the chemical nature and morphology of the active sites and their 'poisoning' by the metal ions.

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