Electrochemistry and detection of some organic and biological molecules at conducting polymer electrodes.
Part 3. Evidence of the electrocatalytic effect of the heteroatom of the poly(hetetroarylene) at the electrode/electrolyte interface [1]

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Abstract

The electrocatalytic effect of the conducting poly(3-methylthiophene) film (3-PMT) electrode on the redox behavior of catechol compounds has been examined. The nature of the electrode material substrate had no effect on the peak potentials in the cyclic voltammograms (CVs) of different redox systems of biological interest: p-aminophenol, dopamine, catechol and ascorbic acid. The nature of the heteroatom of 3-PMT, polypyrrole, polyfuran and polyanaline had a very large effect on their electrokinetic properties. The adsorption of molybdenum ion results in the blocking of 'the active sites' at the interface, as indicated by the disappearance of the electrochemical activity of the 3-PMT film electrode. The surface examination by X-ray photoelectron spectroscopy (XPS) of the molybdenum exposed polymer suggests the possibility of a chemical bonding between the metal ions and the sulfur heteroatom of the polymer surface. The 'apparent' diffusion coefficients D_{app} were determined from the effect of the scan rate dependency of CVs of the catechol, etc. The results showed that the electron transfer is predominantly diffusion controlled at the polymer|solution interface and probably involves the sulfur heteroatom specifically.

Keywords: Organic polymer electrode; Electrocatalysis; Neurotransmitters; Ascorbic acid; XPS; Diffusion coefficients; Electropolymerization

1. Introduction

Conducting polymers represent a class of new materials that have electronic conductivity. The most important polymers of this class are poly(acetylene), poly(pyrrole), poly(thiophene), poly(p-phenylene), poly(aniline) and their derivatives [1]. The polymers are now being compared with the classical electrode materials, such as metals and glassy carbon, in electroanalytical applications [2,3]. The concept of chemically modified electrodes was developed to fulfil the need for controlling the reactivity, sensitivity and selectivity of the electrode reactions in many applica-tions. This approach usually involved the attaching of monomolecular and multimolecular layers of electroactive substances and/or specific functional groups to semiconductors, metal, metal oxide, and carbon electrodes [4–9]. Recently, the conducting polymeric films, such as poly-thiophene, polypyrrole, etc., have acquired wide popularity as they are easy to generate at the surface of the electrode when compared with the usual chemical immobilization techniques [10–12]. As these films are electron conductors, they can be employed as an electrode material directly. Moreover, by employing monomers containing redox functional group substituents, the electrogrown conducting polymers can have a very high density of electrocatalytic sites, thereby increasing the efficiency of other electrochemical processes at its surface or within the polymer matrix itself. This class of polymer has been used to 'entrap' electrocatalysts such as phthalocyanines [13] and enzymes [14], as in the case of polypyrrole.

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In addition, the development of electrochemical sensors using polymer coated electrode surfaces can improve the selectivity of such sensors for practical analysis of clinical and environmental samples. Permselective electrode coatings offer the assurance of bringing higher selectivity and reduced fouling compared with the corresponding bare electrochemical sensor [15,16]. For example, Wang et al. [17] showed that a microelectrode array, each coated with a different polymer possessing a different analytical function (based on differences in size, porosity charge or polarity, etc.), can be employed for simultaneous multispecies analyses. In contrast, modified electrodes based on the immobilization of redox mediators onto the electrode surface are also commonly used. The function of the mediator is to increase the reversibility and/or the selectivity of the charge-transfer between the electrode and the species in solution [18,19].

With respect to conducting poly(3-methylthiophene) (3-PMT) electrodes, previous studies of (i) the electrochemical response of different conducting polymer electrode sensors for many of the biologically important organic molecules in the FIA and HPLC–EC systems, (ii) the electrochemical behavior of these compounds at the conducting polymer electrode surface, (iii) the effect of varying the nature and pH of the supporting electrolyte on the electrochemical nature of the conducting polymer itself, and (iv) the possibility of applying these electrodes for the simultaneous determination of multicomponent mixtures of analytes have been presented in the literature by our group [20–23] and others [24–26]. In addition, electrochemical kinetic parameters of various conducting polymer electrodes have been previously reported [27] using double potential step coulometry, and the results indicate a predominant limiting dependence of the rates of diffusion of the doping anion in the polymer. However, similar measurements have not yet been performed on poly(heteroarylene) electrodes in electrolytic solutions containing organic and biological redox molecules. This is especially important as the redox potentials of species such as the catechol amines is well negative of the oxidation potential of the 3-PMT. Thus, the CV redox peaks observed for the catechol compounds are in the potential region where the polymer is an insulator [28]. It is not known if the electron transfer process for such redox species involves diffusion through pores to the metal electrode substrate, within the polymer matrix itself or occurs at the organic|solution interface.

In the present work, we will present the effect of the metal substrate in the polymer electrode on its electrocatalytic activity. The nature of the heteroatom in the heterolyne ring and the effect of adsorption of molybdenum ion on the surface on the electrode kinetics are examined. Surface analysis experiments (X-ray photoelectron spectroscopy (XPS)) conducted at polymer films exposed to molybdate are also given and discussed.

2. Experimental

2.1. Reagents and materials

The 3-methylthiophene (3MT) monomer was obtained from Aldrich (Milwaukee, WI, USA) and was used after fractional distillation. The tetrabutylammonium tetrafluoroborate (TBATFB), (Aldrich, Milwaukee, WI, USA) was recrystallized and dried. Potassium and sodium salts of chloride, nitrate, sulfate and phosphate, all organic and biological salts and catechols were used as-supplied (Aldrich). All other salts, buffer solutions, HPLC-grade solvents, and reagents were purchased from Fisher Scientific Company and were used as-received. Solvents used in the electropolymerization were distilled, purified according to standard methods [29–31], and kept over molecular sieves type A4 for at least 48 h prior to use. Aqueous solutions were prepared by dissolving a preweighed sample or by dilution from a stock solution using conductivity water obtained through a Nanopure 4C unit (Fisher).

2.2. Electrode materials, preparation, and mounting

Electrochemical polymerization was carried out in a one compartment cell containing argon deaerated acetonitrile, 0.1 M TBATFB and 0.05 M 3MT. Film growth was achieved by applying a constant potential of +1.70 V vs. a $AgCl|Ag|KCl_{(sat)}$ reference electrode. Following the electropolymerization step, all films were kept at −0.20 V for 30 min in a monomer free deaerated electrolyte solution. The film thickness was estimated from the amount of charge passed during the electropolymerization and assuming 100% efficiency during the conversion. The following empirical equation was used to roughly estimate the film thickness

$$t = sL/m_e j$$

where t is the time (s), s is the density (g cm^{-3}), L is the thickness (cm), m_e is the electrochemical equivalent (mg C^{-1}), and j is the current density (mA cm^{-3}). The thickness was calculated to be about 100 nm. As 100% current efficiency may not be obtained, this represents the maximum film thickness possible. Even, in the event that the efficiency is not 100%, it is a good assumption that it is constant in all experiments. The working electrode was a platinum disc electrode having a surface area of 0.031 cm^2; model Paroz-series 2001 Pt (American Micro Products, Inc., Cincinnati, OH, USA) and glassy carbon electrode model MF2013 (BAS, Inc. West Lafayette, IN, USA). The auxiliary electrode was a 4 × 4.2 cm^2 platinum sheet. All electrodes were polished mechanically prior to the electropolymerization step using metallurgical papers of successive different grades 600 to 1200 and an alumina + water suspension (10 μm) until no visible scratches were observed. For the purpose of specimen preparation

for the XPS experiments, a platinum sheet was cut in the form of flat circular disc electrode of approximately 1 cm^2.

2.3. Techniques and instrumentation

The electrosyntheses of the polymers were performed using an EG&G model 173 potentiostat–galvanostat mounted with a plug-in EG&G model 176 current-to-voltage convertor and equipped with an EG&G 179 digital coulometer (Princeton Applied Research, Princeton, NJ, USA). A model BAS-100 Electrochemical Analyzer (BAS, West Lafayette, IN, USA) was employed in the cyclic voltammetric studies. A Perkin–Elmer ESCA-5300 spectrometer was used to obtain the spectra and the chemical composition of the polymer film. The molybdenum attachment on the polymer film was carried out by cycling the film in a 0.5 M NaMoO$_4$ buffer solution under conditions which were similar to those described above.

3. Results and discussion

3.1. Effects of electrode substrate on the peak potential

The anodic peak potentials obtained for catechol and other organic molecules with biological significance on a 3-PMT electrode were found to be independent of the substrate material. In this study the polymer film was grown electrochemically on two different substrates: platinum and glassy carbon. The results obtained from the CVs carried out utilizing these 3-PMT electrodes showed that the E_{pa} values for each catechol, etc., were constant and independent of the substrate material. Table 1 lists the E_{pa} values obtained for dopamine, p-aminophenol, ascor-

Table 1

Oxidation peak potentials of some organic compounds with biological significance; experiments were carried out with three different electrode materials

Compound	E_{pa} /mV [a]		
	3-PMT	Pt	GC [b]
Dopamine	510	690	849
Ascorbic Acid	296	[c]	981
Catechol	520	689	849
p-Aminophenol	471	620	900

[a] Values were obtained from the positive scan of the first voltammetric cycle.

[b] GC, glassy carbon. [c] No peak was observed in the potential window studied.

bic acid and catechol, from CVs which were carried out on 3-PMT polymer film which was grown on platinum and glassy carbon substrates and on bare platinum and glassy carbon electrodes. These values were obtained from the positive scan of the first voltammetric cycle at a scan rate of 50 mV s^{-1}. Also, the electrocatalytic activity of the 3-PMT polymer film can be seen from the fact that these E_{pa} values were consistently more negative than those obtained from the bare platinum and glassy carbon electrodes. Similarly, Table 2 gives the E_{pa} values for ascorbic acid at bare platinum and glassy carbon, and 3-PMT films on Pt and glassy carbon substrates for various electrolytes; again E_{pa} values at the 3-PMT film electrodes are the same regardless of substrate.

3.2. Electrocatalytic behavior

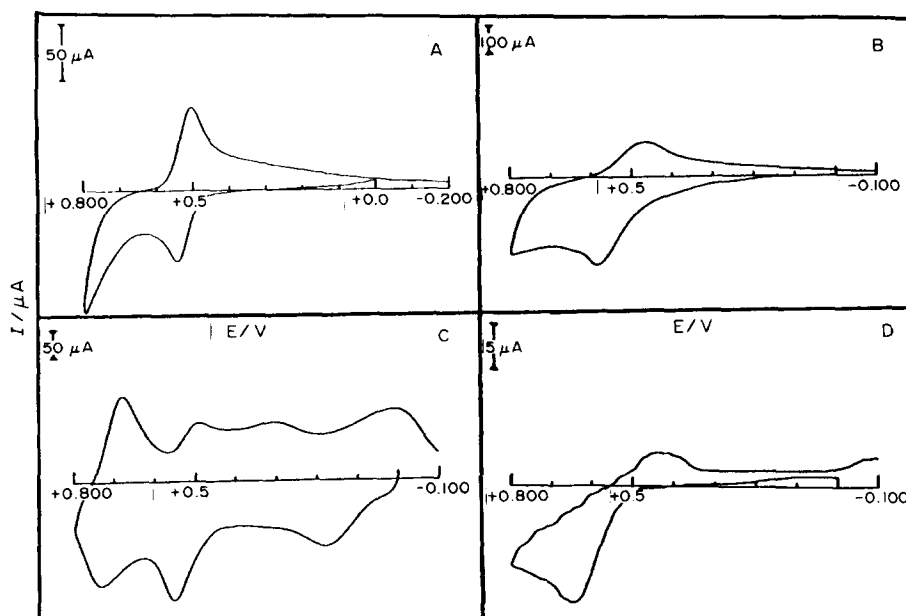The electrocatalysis of various polymer film electrodes was determined by carrying out cyclic voltammetry experi-

Fig. 1. Cyclic voltammetry of 5 mM catechol in 0.1 M H$_2$SO$_4$, at 3-PMT (A), PNMP (B), PAn (C), and PF (D) electrodes. Scan rate 50 mV s^{-1}. All films were prepared under similar conditions.

Table 2

Electrolyte and substrate effect on the E_{pa} response of 3-PMT; solution 5 nM ascorbic acid in 100 mM electrolyte, scan rate 100 mV s^{-1}

Electrolyte	pH	E_{pa} /V			
		Pt	3-PMT–Pt	GC	3-PMT–GC
H_2SO_4	1.6	0.524	0.445	0.663	0.439
Na_2SO_4	3.7	0.367	0.340	0.444	0.335
HCl	1.56	0.590	0.427	0.663	0.435
NaCl	3.23	0.439	0.381	0.512	0.388
HNO_3	1.25	0.568	0.422	0.667	0.430
$NaNO_3$	3.28	0.422	0.317	0.444	0.321
H_3PO_4	3.85	0.385	0.291	0.475	0.298

Fig. 2. Cyclic voltammetry of 5 mM catechol in 0.1 M phosphate buffer pH at 7.5, scan rate 50 mV s^{-1}. Curve A was obtained from an experiment with a 3-PMT film electrode. Curve B was obtained with a 3-PMT film electrode treated with molybdate solution.

ments in 5 mM of catechol, in 0.1 M phosphate buffer solutions (pH = 7.5). Fig. 1 shows that the nature of polymer film has a very large effect on the reversibility of the CVs. This large effect suggests that the 'heteroatom' (3-PMT exhibits by far the greatest electrocatalytic effect) may be involved directly with the electron transfer intermediate.

This hypothesis is supported by a comparison of catechol CVs; curve A, of Fig. 2, obtained on a typical 3-PMT, and curve B were carried out on a similar polymer electrode after treatment with molybdate solution. Obviously, the loss of both the anodic and cathodic peak currents is due to the treatment with the molybdenum.

A possible explanation for this behavior is that the molybdenum ions were chemically bonded, probably at the thiophene surface, which blocks the electron transfer sites. A similar set of experiments with a polypyrrole film electrode showed no effect on the catechol CVs on exposure to Mo(VI). Thus, the sulfur atom might be the 'active site' in the electrocatalytic effect of this electrode. To test this, XPS experiments were carried out on the 3-PMT films exposed to Mo(VI). XPS is an effective method for the determination of surface bonded molybdenum and other metals [32,33]. Fig. 3 shows the molybdenum 3d electron region (223–243 eV) of an XPS measurement of the polymer surface after treatment with molybdate ions.

These peaks are Mo peaks representing different oxidation states [34]. The small Mo peak at 228 eV is one of the doublet peaks due to a Mo(IV) oxidation state. The other peak of this doublet is masked by the larger peak at 232 eV, representing Mo(VI) oxidation state, but accounts for an alteration of the molybdate doublet peak ratio which is supposed to have a 3:2 ratio [35]. This evidence strongly indicates a chemical interaction between the Mo ions and the polymer, as these peaks remained even after prolonged electro-oxidation of catechol. XPS studies of polypyrrole electrodes exposed to molybdenum showed no Mo peaks in this region. It can be expected that the metal ion is bonded to the sulfur atom of the thiophene ring; however, a quantitative determination of the actual chemical bonding would require further investigation.

3.3. Apparent diffusion coefficient

The presence of the polymer film on the surface of an electrode tends to complicate the mathematical treatment required for the diffusion coefficient calculation [36]. It has
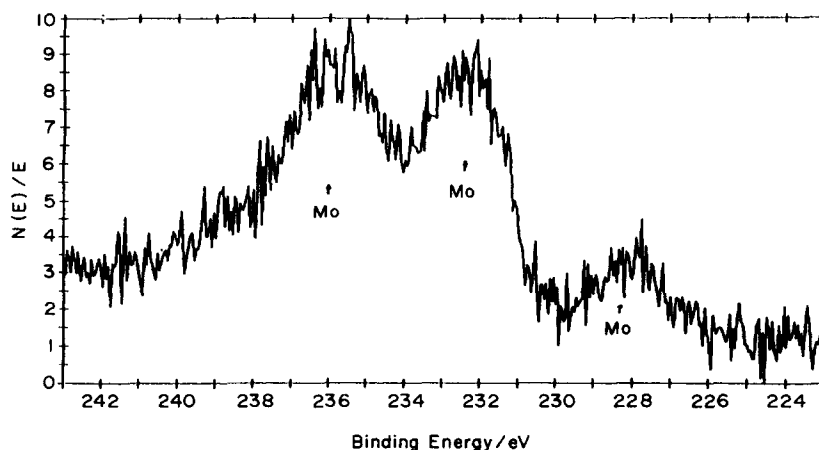

Fig. 3. The Mo 3d XPS spectra of 3-PMT film treated with molybdate solution.
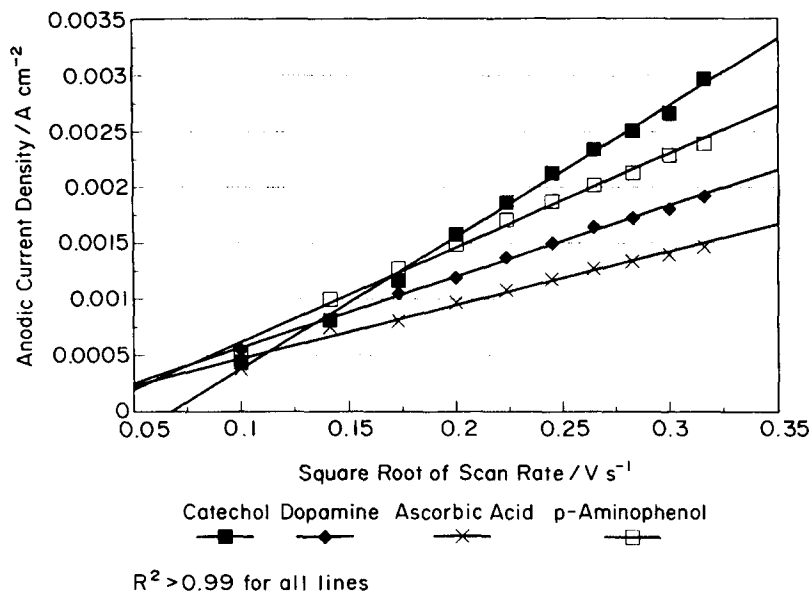
Fig. 4. The effect of the (scan rate)$^{1/2}$ on the anodic peak current density. R^2 values are all better than 0.999.

been assumed, by many researchers, that the polymer film is another layer that the analyte or a counter anion has to penetrate in order for the electron to move through the film for a redox reaction to be observed. This movement of the charges through the polymer layer is known as the 'electron hopping process' [37]. Diffusion coefficients for redox reactions at various polymer films were, as expected, much lower (10^{-10} to 10^{-15} cm^2 s^{-1} [13]) than typically found in aqueous solution (ca. 10^{-5} cm^2 s^{-1} [38]).

In this study, the dependence of the anodic peak current density on the scan rate has been utilized for the estimation of D_{app} for various organic species. Plotting the anodic peak current vs. the square root of the scan rate results in a straight line relationship for a pure diffusion controlled process. Fig. 4, shows that all species tested showed a near linear dependence. From the slopes of these lines, the value of D_{app} can be calculated from [39]

$$I_{ap} = (2.69 \times 10^5) n^{3/2} A D^{1/2} c^o v^{1/2}$$

where n is the number of electrons transferred, F is the Faraday constant (96 484 C mol^{-1}), A is the electrode surface area (0.031 cm^2)^2, c^o is the analyte concentration (0.005 mol cm^{-3}), I_{ap} is the anodic peak current (A), and v is the scan rate (V s^{-1}).

The calculated values for D_{app} ranged between 10^{-6} and 10^{-7} for the different analytes. This relatively high value for D_{app} for a polymer modified electrode indicates

that the electron transfer step of the electrocatalytic reaction takes place at the solution|polymer interface at a predominantly solution diffusion controlled rate.

4. Conclusion

From the results of the electrocatalytic study, the XPS, and the determination of the diffusion coefficients, it can be concluded that the redox electron transfer step is taking place at the polymer/solution interface; neither does the redox species diffuse through pores in the film, nor does it undergo electron transfer after diffusion into the polymer matrix. The 'electron hopping process' is not a rate limiting step, even though the redox reactions of the analyte occur at a potential region where the polymer film is an insulator. Also, it suggests that the site of electron transfer involves the heteroatom of the thiophene ring at the surface.

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[2] This area is the area of the disk platinum electrode substrate, and was used in this calculation. The true surface area is expected (from previous SEM studies) to have considerable surface roughness. However, the approximation of the apparent surfaces will not significantly effect the value of the D_{app} as the magnitude of the surface roughness was very small compared with that of a solution phase diffusion layer in cyclic voltammetry.

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