

SHORT COMMUNICATION

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Preparation and characterisation of monomeric molybdate(VI) anion-doped polypyrrole electrodes

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Abstract Stable monomeric molybdate(VI) anion-doped polypyrrole composites [P_{py}(Mo)] have been prepared from sulfuric acid solution containing Mo(VI) by an electrochemical potential cycling method. P_{py}(Mo) films exhibit redox waves inherent to the polypyrrole moiety only, and the built-in Mo(OH)₅O⁻ is found to be electroinactive. X-ray photoelectron spectroscopic examination of oxidised and reduced P_{py}(Mo) films confirms this phenomenon.

Key words Polypyrrole · Monomeric molybdate(VI) anion · X-ray photo electron spectroscopy · Electroinactive anion

Introduction

The basic formation of electroactive polypyrrole (P_{py}) films by anodic oxidative polymerisation of the pyrrole monomer is rather complex. This involves several electrochemical and chemical steps [1]. Compared to this, the processes that accompany the redox transformation between the insulating (neutral) and conducting (oxidised) forms of these films are understood clearly, to some extent. During the redox switching of, for example, neutral P_{py} to its cationic form, the anions of the supporting electrolyte are incorporated into the P_{py} film as counter ions to balance the positive charges in the polymer backbone. The anodic doping process of the anion is an extremely useful procedure for preparing P_{py}-functional anion composite electrodes by simply incorporating the electroactive/electroinactive material as a counter ion into the polymer [1]. Thus the electroactive anion-doped polypyrrole films not only behave

as redox electrodes but also display the electroactivity of the dopant anion. Some of them have shown good catalytic activity towards many dissolved substrates [2, 3]. Since the monomeric molybdate(VI) ion in solution shows very good catalytic activity towards the mediated reduction of various anions [4], we have attempted to prepare Mo(VI)-doped P_{py} composite film electrodes [P_{py}(Mo)]. In the present work the electrochemical preparation and characterisation of these composites are reported. The results show interestingly that monomeric molybdate(VI), although electroactive in a dissolved state in 0.1 M H₂SO₄ [5] and also in an adsorbed state at a glassy carbon electrode (GCE) [6], loses its electroactivity when incorporated into the P_{py} matrix.

Experimental

Electrochemical experiments were carried out with a GCE (area 0.07 cm²), an SCE and a Pt foil as working, reference and counter electrodes, respectively. The GCE was polished and pretreated by potential cycling in deaerated 0.1 M H₂SO₄ for 20 times between +700 to -1000 mV (SCE) at a scan rate of 20 mV s⁻¹. The cyclic voltammetry (CV) set-up contained a potentiostat (ST 72) and a scan generator (VSG 83) from Wenking and a Graphtech X-Y recorder (WX 2300). X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ESCALAB MK II spectrometer and scanning electron microscopy (SEM) measurements were recorded with a JEOL instrument.

Results and discussion

Electrochemical preparation and characterisation of P_{py}(Mo) composites

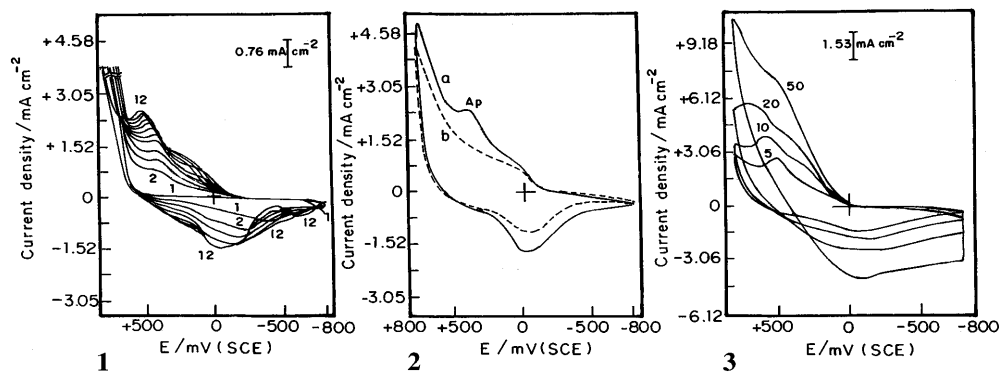
Figure 1 shows the CV of 57 mM pyrrole and 2 mM Mo(VI) in 0.1 M H₂SO₄ at a scan rate of 5 mV s⁻¹. In the first cycle the pyrrole oxidation starts around

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Fig. 1 Cyclic voltammogram (CV) of a glassy carbon electrode in 0.1 M H₂SO₄ with 57 mM pyrrole + 2mM Mo(VI)

Fig. 2 a CV of Ppy(Mo) film electrode in 0.1 M H₂SO₄; b CV of Ppy(Su) film electrode in 0.1 M H₂SO₄

Fig. 3 Scan rate effect on CV of Ppy(Mo) film electrode in 0.1 M H₂SO₄



+650 mV with a sharp current rise and during the reverse scan a higher current compared to the forward scan (current loop), which is characteristic of the nucleation process, is observed. When the potential sweep is terminated at 800 mV or below, increase in the current is noticed in successive scans, indicating conducting P_{py}(Mo) composite formation. When the potential limit is extended beyond 800 mV, no current is found in the subsequent scans owing to the insulating nature of the overoxidised composite film formed in the first scan. The Tafel plot of the first oxidation scan in the presence of molybdate(VI) yields a slope of 130 mV. This can be contrasted with pyrrole monomer oxidation in pure base electrolyte (H₂SO₄), which has been shown to give two different Tafel slopes (≈ 60 and 120 mV) at different potential regions [7]. This is the indication that P_{py} is formed in a single step in the presence of Mo(VI), unlike its formation in pure supporting electrolyte where it proceeds by two steps [7].

P_{py}(Mo) films for CV and spectral characterisation were deposited on a pretreated GCE from 0.1 M H₂SO₄ containing 57 mM pyrrole and 2 mM Mo(VI) ions under cyclic potential sweeping conditions (-800 to $+800$ mV at a scan rate 5 mV s^{-1}).

Figure 2 illustrates the CV of molybdate(VI)-doped polypyrrole film in pure base electrolyte (0.1 M H₂SO₄). Included in the same figure is the CV of sulfate-doped P_{py} film [P_{py}(Su)]. A comparison of the two voltammograms shows a well-defined anodic peak at $E_p = 420$ mV in the case of the P_{py}(Mo) film. The peak potential at 420 mV does not correspond to any of the E_p of the multiple redox peaks observed for monomeric molybdate(VI) anion on a GCE in 0.1 M H₂SO₄ [5, 6]. Thus the observed peak at 420 mV is more likely due to the redox process of the P_{py} backbone in the P_{py}(Mo) film, facilitated by the entrapped molybdate anions, viz., Mo(OH)₅O⁻.

The scan rate dependence of the peak of the P_{py}(Mo) composite is shown in Fig. 3. Increase in the scan rate shifts the peak potential to positive values and the peak becomes broader and finally disappears when the scan rate exceeds 50 mV s^{-1} . The scan rate dependence of the anodic peak current and peak potential is consistent with a diffusion-limited irreversible electron transfer process.

XPS characterisation of P_{py}(Mo) composites

Following the survey spectrum which shows signals for S 2p, C 1s, O 1s, and Mo 3d, the high-resolution spectra have been recorded for these energy levels. The presence of S 2p and Mo 3d signals indicates that the P_{py}(Mo) composites contain both sulfate and molybdate(VI) as dopants. The S 2p spectrum shows a maximum around binding energy (BE) = 169 eV due to S in the higher +6 oxidation state [8]. The C 1s spectrum is deconvoluted into three different contributions, corresponding to the β carbons, α carbons and disordered carbons of the P_{py} ring at BE 283.6, 284.5 and 286.9 eV [9]. The N 1s high-resolution spectra of P_{py}(Mo) (Fig. 4) could be deconvoluted into three components: 397.4 eV due to Mo 3p; 399.5 eV for the unoxidised N atom; and 401.5 eV due to the oxidised N atom [9].

The Mo 3d level of the P_{py}(Mo) film shows a doublet for Mo 3d_{5/2} and Mo 3d_{3/2} (Fig. 5). They are separated by 3.0 eV with the ratio 3:2 as expected [10]. It is in-

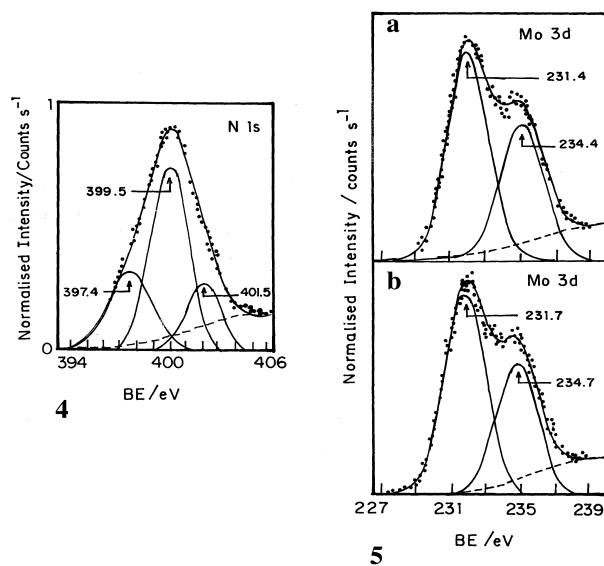


Fig. 4 High-resolution XPS spectra for N 1s of oxidised Ppy(Mo) film

Fig. 5 High-resolution XPS spectra for Mo 3d of Ppy(Mo) film: a oxidised; b reduced

interesting to note that the oxidised $P_{py}(\text{Mo})$ film (prepared by cycling terminated at +800 mV) and the reduced $P_{py}(\text{Mo})$ film (prepared by cycling terminated at -800 mV) both have been found to give deconvoluted Mo 3d peaks at the same BE values. This, suggests that (1) the molybdate(VI) anion doped into the films as the dopant ion does not become involved in any redox reaction of its own, and (2) Mo(VI) is not de-doped on reduction of film and acts as an "immobile" dopant with charge compensation via cation incorporation instead of anion release.

The phenomenon of charge compensation in the conducting P_{py} polymer via cation incorporation instead of anion release is extensively discussed in the literature [1]. However, direct evidence for the incorporation of cations in a P_{py} film during its reduction was demonstrated only recently by Arca et al. [11] by the use of scanning electrochemical microscopy. In the present case the charge compensating cation is H^+ . This is demonstrated from the fact that the CV trace of $P_{py}(\text{Mo})$ film is found to be independent of the nature of the anion of the electrolyte [when the $P_{py}(\text{Mo})$ film electrode was potential cycled in various acids, e.g., 0.2 M HNO_3 , HCl or HBr], and also independent of other cations of the electrolyte (when potential cycled in 0.1 M H_2SO_4 solution containing 0.1 M of salts like Na_2SO_4 , K_2SO_4 or Bu_4NHSO_4).

Unlike the results with monomeric Mo(VI) species in acid solution at a Pt electrode, where catalytic reduction of various anions was detected [4], in the present case it is experimentally observed that the P_{py} -immobilised Mo(VI) species does not catalyse the mediated reduction of these anions. In fact, the dissolved Mo(VI) species does not show any electroactivity on the $P_{py}(\text{Mo})$ film. All these findings substantially prove that the immobilised redox dopant loses its electroactivity once it is inside the P_{py} film. The loss of electroactivity by the redox dopant, i.e., $\text{Mo}(\text{OH})_5\text{O}^-$, may arise owing to its strong binding to the polymer and, therefore, cannot be reduced or oxidised electrochemically while inside the film. In this respect the dopant molybdate(VI) anion in P_{py} behaves similar to the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox anion which was reported to show [12] that only a portion of these built-in anions displayed reversible electrochemistry; the majority of the doping anions are non-electroactive, when present as exclusive dopants in a P_{py} matrix. We believe that the relative population of electroinactive anions (sulfate) and Mo(VI) anions as dopants in P_{py} determines the electroactivity of the redox anions. As it is possible to calculate the ratio of the (Su) doping to (Mo) doping since the S 2p peak is also observed in XPS, further work is planned to vary the relative quantities of sulfate/Mo(VI) and study its electrochemical behaviour. In this context, electropolymerisation in sulfate-free acid solution to give a P_{py} matrix with exclusive $\text{Mo}(\text{OH})_5\text{O}^-$ dopant will be of considerable value.

In view of the observed experimental fact that an exclusively cathodically pretreated GCE is highly acti-

vated towards monomeric Mo(VI) ion adsorption and its electroreduction, compared to other surface pretreated GC electrodes [13], $P_{py}(\text{Mo})$ films were deposited on different pretreated GCE surfaces, like cathodically pretreated, anodically pretreated, mechanically polished (with no electrochemical pretreatment), etc. The loss of electroactivity of the immobilised Mo(VI) dopant in the P_{py} film was found to be a general phenomenon independent of the GCE surface pretreatment. This is reasonable, since the activity of the precathodised GC electrode to Mo(VI) ion adsorption and its reduction is connected with the creation of specific surface groups ($>\text{C-O}-$) on the electrode surface following precathodisation and its activating effect on the adsorbed Mo(VI) monolayer [13]. On the other hand, the loss of electroactivity of the redox dopant in P_{py} film is related to the P_{py} matrix stabilising effect on the three dimensionally distributed Mo(VI) ions. Thus the two cases represent two different situations.

In order to assess the extent of Mo(VI) doping in $P_{py}(\text{Mo})$ composites, the depth profile of Mo(VI) ion distribution has been studied using angle-resolved XPS in order to eject photoelectrons from different depths. A linear correlation is noticed between the peak intensity and the take-off angle with respect to the sample surface. Thus uniform distribution of Mo(VI) penetration to a considerable depth in the $P_{py}(\text{Mo})$ composite can be inferred. However, it must be mentioned that on repetitive cycling of the $P_{py}(\text{Mo})$ composite in pure 0.1 M H_2SO_4 , its CV trace reverts back to that of the $P_{py}(\text{Su})$ film, suggesting exchange of solution ions (Su) with immobilised ions (Mo).

SEM characterisation

SEM micrographs of $P_{py}(\text{Su})$ and $P_{py}(\text{Mo})$ composites grown on GCE show significant differences. $P_{py}(\text{Su})$ film shows cauliflower structured crystallites of different size as reported on Pt [14], Ta and GCE electrodes [15]. The maximum size of the crystallites is $7.4 \pm 0.3 \mu\text{m}$. $P_{py}(\text{Mo})$ composite, on the other hand, shows needle-shaped microstructures in the midst of the cauliflower structure. The creation of highly ordered structure in polymer chains of $P_{py}(\text{Mo})$ film on monomeric molybdate(VI) anion doping is quite interesting and further studies confined to structural changes of $P_{py}(\text{Su})$ and $P_{py}(\text{Mo})$ composites are being pursued.

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