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Effect of additives on the anodic codeposition of lead dioxide and polypyrrole

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The influence of acetate, Pb^{2+} species and pyrrole on the electrodeposition of lead dioxide and polypyrrole on a glassy carbon electrode in 1.0 M potassium nitrate medium was studied using cyclic voltammetry, double potential step chronoamperometry and controlled potential electrolysis techniques. In the presence of acetate ion the deposition of lead dioxide initiates at least 200 mV less positive compared to nitrate ions alone. At lower acetate ion concentration (< 0.4 M) two anodic peaks are observed due to the oxidation of acetate and nitrate complexed Pb^{2+} species. Pyrrole totally inhibits the lead dioxide formation at more anodic potentials due to an insulating polypyrrole film formation. At higher concentrations (> 20 mM) acetate ions are found to inhibit polypyrrole formation. The following is the decreasing order of inhibition of polypyrrole formation. Sodium acetate > lead nitrate > lead acetate. Acetate in the form of lead acetate is found to favour simultaneous deposition of lead dioxide and polypyrrole with minimum inhibition on polypyrrole formation.

1. Introduction

The electrodeposition of any new phase in a particular solvent can be influenced by complexing agents, neutral organic molecular species or even by the nature of the supporting electrolyte cation or anion. For example Pb^{2+} can exist as a $PbNO_3^+$ complex or uncomplexed Pb^{2+} species in nitrate media [1–3]. In acetate media Pb^{2+} may be in the form of $PbOAc^+$, $Pb(OAc)_2$, $Pb(OAc)_3^-$ [4] and any other hydrated complex of the acetate [5]. Hence, the acetate ion can play a significant role in the deposition and dissolution of lead dioxide as established by the recent work of Campbell and Peter [6]. Miwa *et al.* [7] recommend electrodeposition of lead dioxide in perchlorate medium and cathodic stripping in acetate medium thus highlighting the effect of the supporting electrolyte anion on the deposition/dissolution behaviour.

The effect of the supporting electrolyte anion on the electropolymerization of pyrrole (Py) has been more extensively investigated [8]. A wide range of supporting electrolyte anions from fluoborate to trifluoroacetate in acetonitrile [8–11], as well as in water [11–13], have been examined as counter ions for improved electronic conductivity of polypyrrole (PPy) films. Recently benzene sulphonate, substituted benzene sulphonates [14–17] and dodecyl sulphate [18] have been shown to be the best candidates for preparing highly conducting polypyrrole films.

Preliminary results relating to the preparation of PPy/PbO_2 composite electrodes was published from this laboratory [19]. In this work it became necessary to choose an anionic species which will not have a substantial negative impact on either of these processes. For example, nitrate is the well known counter ion for polypyrrole synthesis [12, 20], but in neutral media lead nitrate alone would require a very high anodic potential (around +1.6 V vs SCE) when compared to the polypyrrole deposition potential (around +0.65 V vs SCE). Acetate ion can reduce the electrodeposition potential of lead dioxide [21] but this ion has been shown to have a negative effect on conducting PPy formation [22]. Addition of pyrrole can influence the deposition rate of lead dioxide, and addition of lead acetate or lead nitrate can influence the electropolymerization of pyrrole. In this paper these effects are analysed using cyclic voltammetric (CV), double potential step chronoamperometric (CA) and controlled potential electrolytic (CPE) techniques.

2. Experimental details

A BAS-100A electrochemical analyser was employed for the cyclic voltammetry, double potential step chronoamperometry and controlled potential electrolysis measurements. Analar grade pyrrole obtained from E. Merck was vacuum distilled just before use.

The GC working electrode and other electrodes, cell assembly, electrode pretreatment and other experimental details are discussed elsewhere [19, 21].

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3. Results and discussion

3.1. *Medium effects on the electrodeposition of lead dioxide*

The voltammetric behaviour of the electrodeposition of lead dioxide in 1.0 M nitric acid has recently been discussed in detail [21]. Some further voltammetric experiments were carried out in 1.0 M potassium nitrate solution to see if the electrodeposition potential moves closer to the deposition potential of polypyrrole. Figure 1(a) shows such a voltammetric response in 1.0 M potassium nitrate containing 0.1 M lead nitrate. It is seen that the nucleative process in the first sweep initiates around +1.4 V vs SCE in this medium. But in subsequent sweeps the growth process is noticed around +0.9 V, along with a second peak corresponding to fresh nucleation around +1.4 V. For a comparison, a CV recorded in 1.0 M acetic acid/sodium acetate containing 0.1 M lead acetate is given in Fig. 1(b). In this medium the nucleation process starts around +1.2 V. The subsequent growth process once again starts around +0.9 V. The decrease in the nucleation overvoltage in the second and subsequent anodic sweeps is due to the presence of residual lead oxide (PbOx) remaining at the electrode surface as pointed out by Beck *et al.* [23]. Thus, compared to nitrate medium the nucleation process in acetate medium can be initiated at least 200 mV less positive. The cathodic reduction of lead dioxide shows multiple peaks [Fig. 1a]. A similar multipeak reduction response in neutral media has recently been reported in the literature [24] and attributed to the formation of lead monoxide. Hence it appears that acetate containing media are more effective for the electrodeposition of lead dioxide.

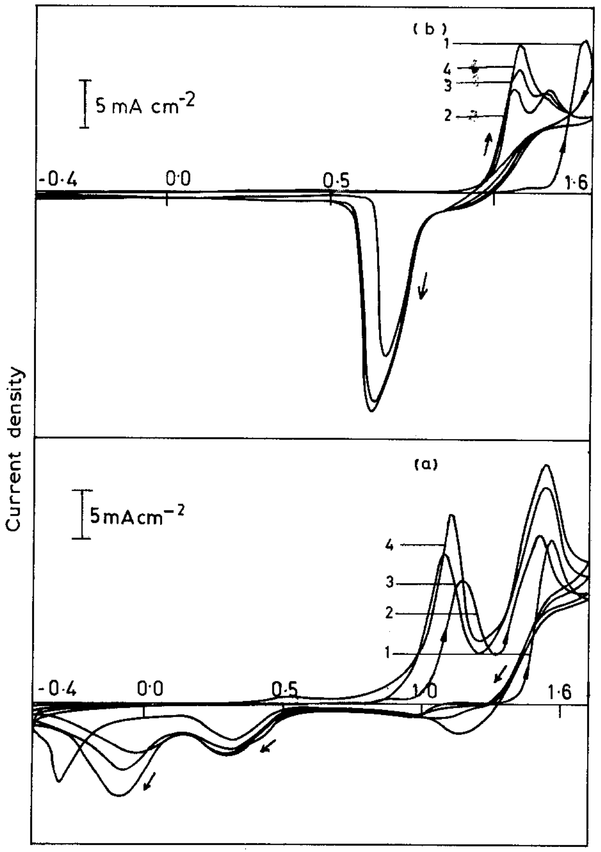

Fig. 1. Cyclic voltammograms showing the deposition/dissolution of PbO_2 on GCE from (a) 1.0 M KNO_3/0.1 M $Pb(NO_3)_2$ (pH 4.5); (b) 1.0 M HOAc/1.0 M NaOAc/0.1 M $Pb(OAc)_2$ (pH 4.7) 1–4 represents cycle number. $V = 10\,mV\,s^{-1}$.

However, it is apparent from Section 3.2 that acetate ions have a negative effect on polypyrrole electrodeposition. Hence, further experiments were carried out to ascertain if the addition of acetate ions in nitrate containing Pb^{2+} species would have the desired effect of shifting the electrodeposition potential to a less positive region. Figure 2 clearly shows that this is possible. In fact the nucleation process in the first sweep starts around 1.0 V itself in the presence of acetate ion [Fig. 2b–d] compared to 1.4 V in nitrate medium [Figs 1a and 2a] and 1.2 V in acetate medium alone [Fig. 1b]. It is thus clear that the presence of acetate, as well as nitrate, has a synergistic effect on the nucleation process of lead dioxide. At this stage it is difficult to establish the actual cause of such a synergistic effect. However it appears that acetate exerts a positive effect on electrodeposition by complexing with the Pb^{2+} species, as well as a less a negative effect by adsorbing onto the GC substrate electrode. The presence of excess nitrate ion and much smaller concentration of acetate ion [compare Fig. 1b and Fig. 2] possibly minimizes acetate adsorption on the electrode surface and, hence, inhibition of the nucleation.

In evaluating the effect of acetate ions on the electrodeposition of lead dioxide in nitrate media (Fig. 2), great care was taken to ensure complete absence of memory effect from previous experiments. Figure 2(a) to (d) were thus recorded in totally independent experiments on thoroughly cleaned glassy carbon substrates after measuring the background levels.

The first oxidation peak in the presence of acetate ions in Fig. 2(b) to (d) are ascribed to the nucleative

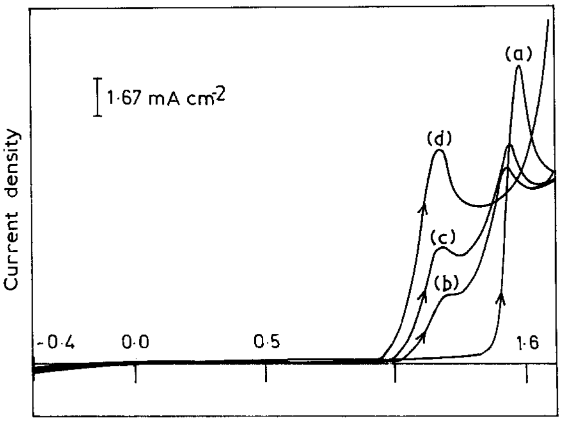

Fig. 2. Linear sweep voltammograms showing the effect of acetate ion on the deposition of PbO_2 on GCE from (a) 1.0 M KNO_3/0.1 M $Pb(NO_3)_2$, (b)–(d) in presence of 0.1, 0.2 and 0.4 M sodium acetate, respectively. $V = 10\,mV\,s^{-1}$.

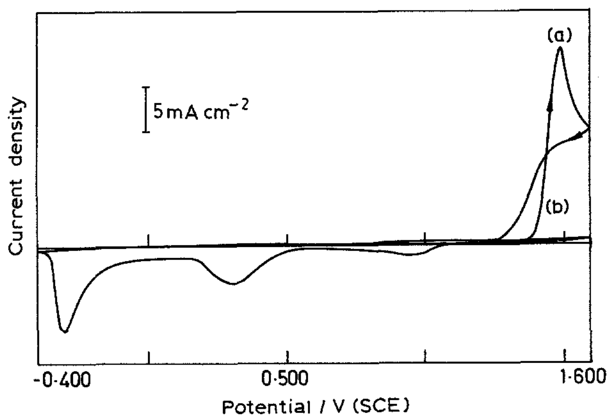

Fig. 3. Cyclic voltammograms showing the effect of pyrrole on PbO_2 deposition on GCE (a) 1 M KNO_3/0.1 M $Pb(NO_3)_2$, (b) a + 2 mM pyrrole, $V = 10\,mV\,s^{-1}$.

oxidation of acetate complex of Pb^{2+} species on the following grounds. The oxidation potential of this peak lies quite close to the first oxidation peak of Pb^{2+} in acetic acid/sodium acetate medium [Fig. 1b]. In earlier work also this favourable impact of acetate complexes of Pb^{2+} species when compared to uncomplexed Pb^{2+} species has been conclusively established [21, 25]. In the absence of Pb^{2+} species no distinct oxidation peak due to the acetate anion alone is noticed on a GC electrode or on a PbO_2 coated GC electrode. Hence acetate oxidation cannot be assumed under the present experimental conditions. Finally CPE at +1.1 V in the solution used obtaining Fig. 2(b) for 5 min results in visible PbO_2 deposits confirming this process in the first oxidation potential itself [19].

Figure 3(a) shows the typical CV obtained in 1.0 M potassium nitrate containing lead nitrate. By adding 2 mM pyrrole under identical experimental conditions a totally different picture is obtained [Fig. 3b]. Even this small level of pyrrole in the electrolyte medium can lead to the formation of a completely inhibiting PPy layer above +0.85 V which totally inhibits the electrodeposition of lead dioxide at more anodic potentials. The present investigation is an effort to overcome this problem.

3.2. Medium effects on the electrodeposition of polypyrrole

The nitrate, acetate and pyrrole additives were found to exert a profound influence on the electrodeposition of lead dioxide (Section 3.1). Similar experiments were also carried out to establish the effect of free acetate ions, lead acetate and lead nitrate additives on the voltammetric behaviour of pyrrole in 1.0 M potassium nitrate solution.

In the absence of the above additives, the CV corresponding to the electropolymerization of pyrrole is similar to those reported in the literature under identical conditions [10]. Pyrrole oxidation starts around +0.65 V. The peak is noticed at about +0.80 to + 0.85 V If the multisweep experiments are carried out with an anodic limit of +0.8 V, the PPy growth current in subsequent sweeps continues to increase with sweep number [Fig. 4a]. Addition of 20 mM sodium acetate into the 1.0 M potassium nitrate medium containing 0.1 M pyrrole leads to a small anodic shift of the pyrrole oxidation potential [Fig. 4b]. However, the magnitude of the anodic peak current is not affected significantly. In multisweep experiments, growth currents are found to increase with cycle number [Fig. 4b] as noted above in the absence of sodium acetate [Fig. 4a].

When the concentration of sodium acetate was increased to 40 mM the inhibiting effect of acetate on PPy formation and growth became significant. Both the peak potential and peak current values are significantly affected [Fig. 4c]. In 80 mM and 100 mM sodium acetate the current decreases very significantly and the forward and reverse sweep currents retrace each other in multisweep experiments [Fig. 4d and e]. In these experiments an anodic limit of +0.8 V, which lies before the peak potential region, was deliberately chosen. Since it is well known that PPy growth beyond the peak potential region would lead to insulating film formation [12]. It should also be noted that a significant inhibiting effect of acetate is noticed, in spite of the fact that

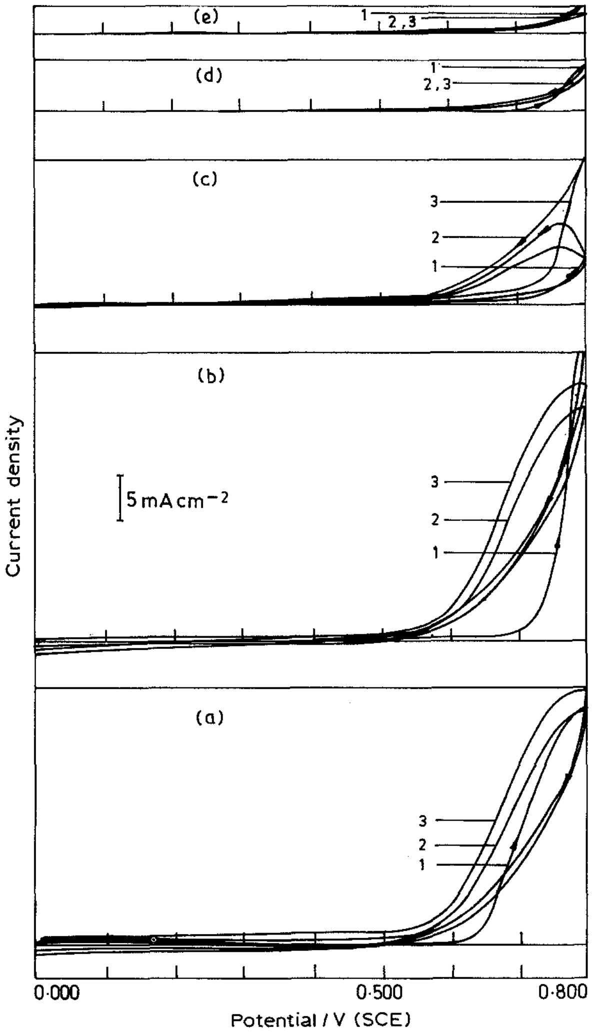

Fig. 4. Cyclic voltammograms of PPy formation on GCE from 1.0 M KNO_3/0.1 M pyrrole showing the effect of acetate ion. (a)–(e) = 0, 20, 40, 60 and 80 mM sodium acetate, respectively. 1–3 represents cycle number. $V = 10\,mV\,s^{-1}$.

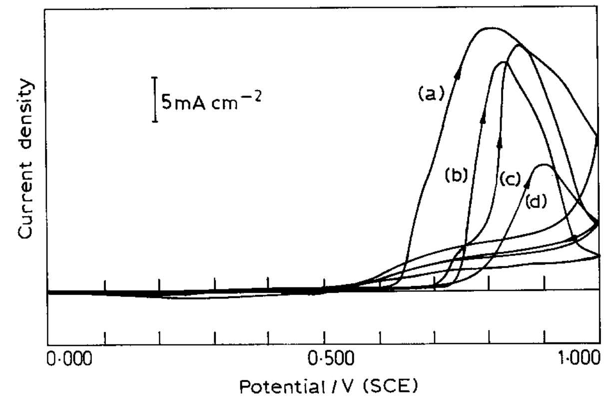

Fig. 5. Cyclic voltammograms of PPy formation on GCE from (a) 1 M KNO_3/0.1 M pyrrole showing the effect of 40 mM, (b) $Pb(OAc)_2$, (c) $Pb(NO_3)_2$ and (d) NaOAc. $V = 10\,mV\,s^{-1}$.

Table 1. Typical results of the effect of lead acetate and sodium acetate on the constant potential electrolysis of 0.1 M pyrrole in 1.0 M potassium nitrate on GCE

C_{OAc^-} mM	*Deposition charge*/C cm^{-2}
0	22.87
60 mM $Pb(OAc)_2$	2.16
60 mM NaOAc	0.079

$E_{dep} = 0.8$ V vs SCE; $t_{dep} = 5$ min.

the nitrate ion concentration (1.0 M) is in substantial excess when compared to acetate ion (≥ 40 mM). Since lead nitrate and lead acetate are not completely dissociated in aqueous solutions [1–4], it was expected that addition of these compounds as such would have different quantitative effects on the electrochemical oxidation of pyrrole. The single sweep CV recorded for the oxidation of 0.1 M Py in 1.0 M KNO_3 solution in the absence of [Fig. 5a] and in the presence of 60 mM lead acetate [Fig. 5b], lead nitrate [Fig. 5c] and sodium acetate [Fig. 5d] confirms this expectation. It is found from this figure that lead acetate with comparatively higher stability constant [4] shifts the PPy deposition potential to the minimum extent [Fig. 5b]. Lead nitrate leads to two distinct electrodeposition peaks during the oxidation of pyrrole [Fig. 5c] indicating the more complicated nature of the inhibiting effect. This figure also shows the maximum inhibiting effect of free acetate ion added in the form of sodium acetate [Fig. 5d].

Further evidence for the inhibiting effect of these additives was also obtained from double potential step chronoamperometry. The PPy deposition current at +0.8 V was found to decrease substantially in the presence of lead acetate and even further in the presence of sodium acetate. The cathodic reduction current at zero potential was also correspondingly lower. Coulometric experiments carried out under similar experimental conditions (Table 1) also show an almost tenfold decrease in the anodic deposition charge in the presence of lead acetate when electropolymerization was carried out in 1.0 M potassium nitrate containing 0.1 M pyrrole. The inhibiting effect further increases by thirty times in the presence of the same concentration of sodium acetate (60 mM).

The exact nature of the inhibiting effect of even small concentrations of acetate ions in the presence of a large excess of nitrate ions is not clear at present. In acetate medium alone Kuwabata *et al.* [22] have noticed the inhibiting effect of acetate anions on ppy formation. They have attributed this effect to the interaction between positive charges of the polymer chain and the doped anions in the film which act as nucleophiles. It appears that acetate ions are more easily attracted towards the polypyrrole cation chain when compared to nitrate ions. It is also possible that the cationic centre in the polypyrrole chain is acetylated, and hence the ionic conductivity of the PPy film is lost. Further experiments are necessary to establish this mechanism of inhibition of polypyrrole film formation.

4. Conclusion

As a first step towards identifying appropriate experimental conditions for the electrodeposition of PPy–PbO_2 composite, the effect of different additives on these two individual electrode processes was evaluated. Acetate ions have a favourable synergistic effect in nitrate media for the electrodeposition of lead dioxide. However, these acetate ions have a profound inhibiting effect on the electropolymerization of pyrrole. Lead acetate appears to be a better choice for the electrodeposition of lead dioxide with minimum inhibiting effect on polypyrrole formation, when compared to free acetate ions and lead nitrate.

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