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Technical Note

Electrodeposition of doped solid films of phosphomolybdates

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1. Introduction

The demand for materials that catalyse heterogenous reactions stimulated the interest in formation of solid films of some polynuclear transition metal cyanides and oxides [1–8]. Some cyano-metalates have been anodically immobilized on electrode surfaces [1–5] as insoluble mixed valence polynuclear compounds. The general formula of these cyano-metalates is $M^A[M^B(CN)_6] \cdot xH_2O$, where M^A and M^B are transition metal ions with different formal oxidation numbers. The cathodic deposition of some insoluble oxometalate aggregates on electrode surfaces has been observed [6–8].

Unlike oxo-tungstate, no record exists of cathodic deposition of insoluble molybdate-based compounds from their stable solutions such as that in dioxane–water mixture. This note reports the electrodeposition of insoluble mixed valence solid films of phosphomolybdates doped with multivalence iron centres.

2. Discussion

The formation of these doped polyphosphomolybdates took place from a room temperature bath of 10 mM of each of $H_3PMo_{12}O_{40}$ and $K_3Fe(CN)_6$ dissolved in a 50% dioxane–water mixture containing 0.5 M H_2SO_4. A conventional three-electrode cell consisted of a Pt counter electrode, Ag/AgCl reference electrode, and a GCE (glassy carbon electrode) working electrode. The electrochemical deposition of this film was carried out both by bulk electrolysis at 0.400 V vs Ag/AgCl for 30 s, and by successive sweeping of the GCE potential between 1.0 and −0.10 V vs Ag/AgCl at 100 mV s^{-1} for twenty CV scans. In each case, after the deposition time, the GCE electrode was removed and rinsed with deionized water and air dried. Figure 1 shows the scanning electronic micrograph of the film formed over the GCE substrate.

Figure 2 is the XPS spectrograph from which the peaks corresponding to the molybdates are identifiable. The two peaks at about 708 and 721 (Fig. 2, inset) correspond to the mixed valence iron that coordinated with oxygen (Fe–O). This is evidence for the co-existence of Fe(II)–O and Fe(III)–O. The peak at 290 eV corresponds to C in the CN group, while the N peak is overlapped by a Mo 3p^3 peak at 400 eV. The detected Fe(II/III)–O signals may also indicate the coexistence of Fe_3O_4 that occupies the octahedral interstitial sites. It has been previously reported [1, 3] that multivalent oxides of transition metals can be codeposited with their cyano-metalates at pH 2. The infrared spectra of the solid film formed on the electrode surface, shown in Figure 3, shows a band at 2100 cm^{-1} corresponding to the –CN group, while bands at 450, 580, 630 cm^{-1} are characteristic of Fe(II/III) cyanides. Bands in the 650 to 1200 cm^{-1} range are related to a mixed valence oxomolybdate cluster. Such surface analysis indicates that an inorganic constellate has been made between octahedrally structured $Fe(CN)_6^{3-}$ and the Keggin anion $PMo_{12}O_{40}^{3-}$. These surface data are limited and are not sufficient to conclude whether this solid film is a mechanical mixture of Prussian Blue, iron oxides and a mixed valence oxomolybdates. However, the formation of a mixed iron oxide at this very low pH is thermodynamically and kinetically unlikely.

Figure 4 is a display of the CV for the GCE modified with this mixed Fe/Mo insoluble compound in 50% dioxane–water mixture containing 0.5 M H_2SO_4. This figure clearly shows two surface redox waves at 0.250 V and at 0.370 V vs Ag/AgCl due to immobilized polymolybdates, while two irreversible anodic peaks at about 0.550 and 0.850 V correspond to immobilized iron centres (oxo and cyano). Figure 4 also indicates that the redox wave that characterizes Prussian Blue is not well developed, as the a cathodic peak is barley seen at about 0.500 V while the anodic peak is broadened.

Figures 5(a) and (b) indicate that these mixed Fe/Mo insoluble compounds showed catalytic activity towards the reduction of ClO_3^-, and for IO_3^- in acidic medium at very positive potentials. A carbon paste electrode of the same apparent geometrical area was used to confirm that the reduction peak illustrated in Figure 5b was not due to the increase of the electrode's surface area. No evidence for any catalytic activities towards the oxidation of NO_2^- or SCN^- was found within the potential range between 0.0 and 0.5 V vs Ag/AgCl. Such behaviour is anticipated because a Keggin-type structure

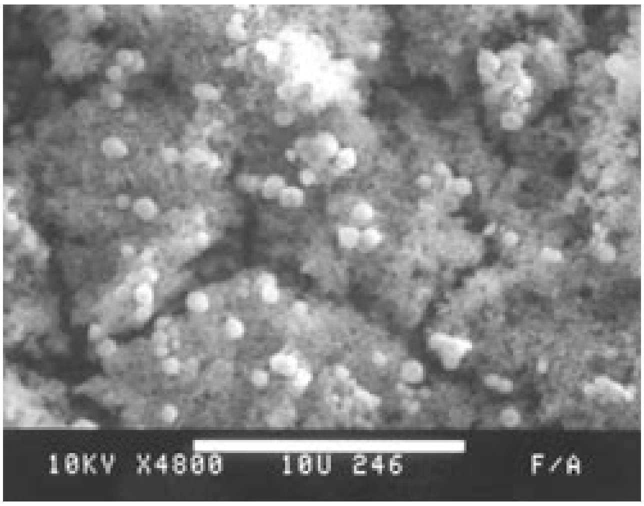

Fig. 1. Scanning electron micrograph of phosphomolybdates aggregates on GCE surface. Accelerating voltage was 10 kV.

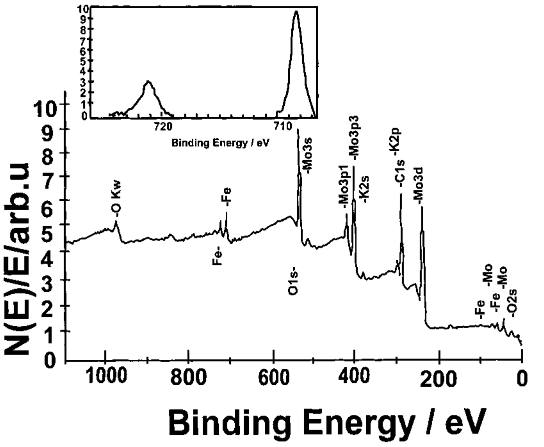

Fig. 2. XPS of the aggregates shown in Figure 1. Inset is the exploded view of Fe peaks at 708 and 721 eV.

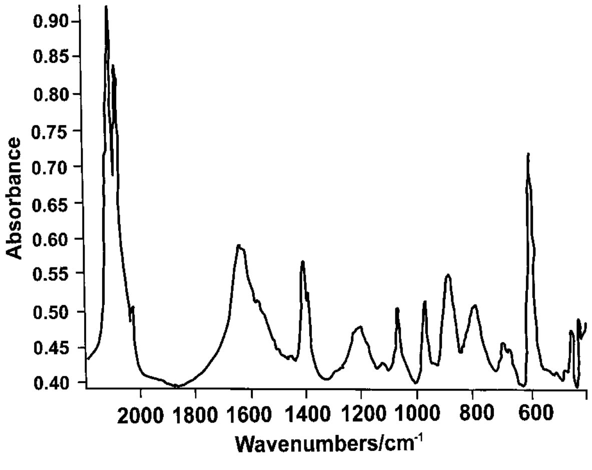

Fig. 3. FTIR of the aggregates after being removed from the electrode surface.

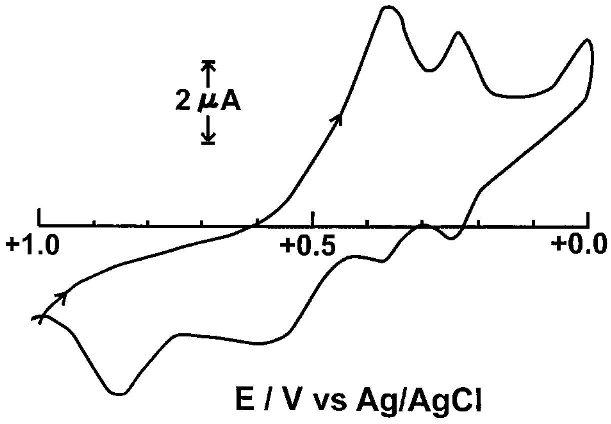

Fig. 4. CV for the GCE modified with the mixed Fe/Mo insoluble compounds in 50% dioxane–water mixture containing 0.5 M H_2SO_4. Scan rate 100 mV s^{-1}.

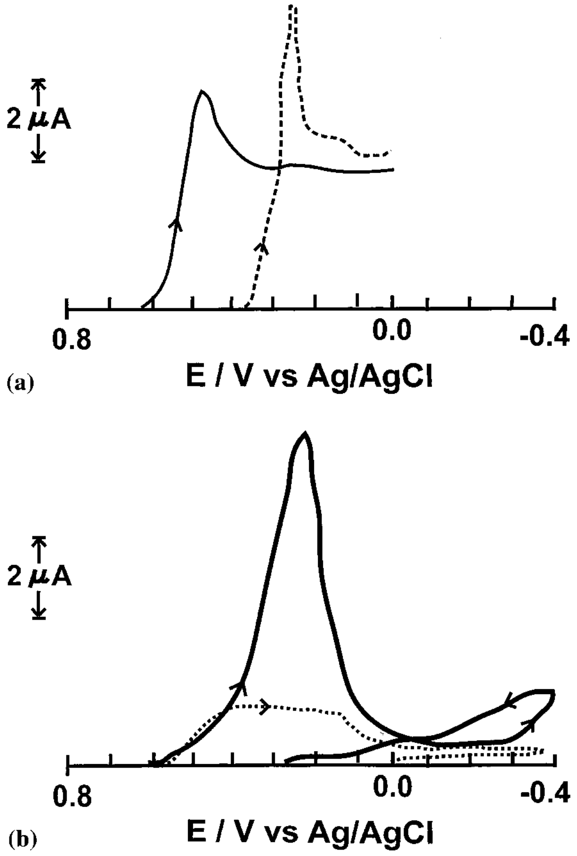

Fig. 5. Voltammograms in 50% dioxane–water mixture containing 0.5 M H_2SO_4, and (a) 0.2 M $KClO_3$, (b) 0.2 M KIO_3. Solid curve for the GCE modified with the mixed Fe/Mo insoluble compounds; Dashed curve for the native GCE electrode. Scan rate 10 mV s^{-1}.

containing 12 Mo(VI) atoms is more stable than one which contains Mo(VI)/Mo(V) mixture. $PMo_{12}O_{40}^{3-}$ undergoes a series of consecutive bi-electron reversible redox waves. After each reduction step 2 Mo(V) are produced at the expense of Mo(VI). The more Mo(V) atoms in the structure, the less stable $PMo_{12}O_{40}^{3-}$. The polyoxomolybdate anion regains its stability by donating electrons from Mo(V) to the electron acceptor substance. This explains why $PMo_{12}O_{40}^{3-}$ is an active catalyst for reduction. The catalytic oxidation will produce a less stable mixed valence polyoxomolybdate. Furthermore, the iron centres which juxtapose to Mo(VI) centres in these insoluble films are more stable in the Fe(III) form than in the Fe(II) form. However, further studies on the solvents' effects on the electrochemical behaviour of these insoluble mixed Fe/Mo compounds are needed, to identify solvent/electrolyte systems that stabilize the mixed Mo(VI/V) polyanion. Stabilization of the mixed Mo(VI/V) will extend the use of immobilized $PMo_{12}O_{40}^{3-}$ for catalytic oxidation.

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