Electrodeposition of catalytically active mixed solid films of hexacyanoferrate and decavanadates

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Abstract

Novel solid films of a mixed polynuclear hexacyano iron(III) and decavanadates have been electrochemically prepared. The colour of these solid thin films ranged from yellow to blue depending on the thickness. The cyclic voltammograms (CVs) of these solid films indicate the involvement of both vanadium and iron redox centres in performing the electrochemical activities. Evidence of the catalytic activities of these films towards the reduction of some small oxoanions has been reported.

1. Introduction

Solid films of some polynuclear transition metal cyanides and/or oxoanions (with two or more metals) maintaining their redox behaviour have been previously prepared and investigated [1–11]. Some cyanometalates have been anodically immobilized on electrode surfaces [1–5] as insoluble mixed valence polynuclear compounds. The general formula of these cyanometalates 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 heterogenous catalytic properties of these films require that the substances be immobilized in an insoluble form. The catalytic behaviour of some immobilized hexacynaometalates [12–16] has been reported. Furthermore, some polyoxometalates have been immobilized and used as catalytically active substances. The cathodic deposition of some insoluble tungstodicobaltoate aggregates on electrode surfaces has been observed [6, 8]. Recently, we reported electrodeposition of mixed valence solid films of insoluble phosphomolybdates and hexacyanoferrate [17]. Such films show evidence of catalytic activity for the reduction of some small oxoanions. Immobilization of some catalytically active vanadium-based hexacyanometalates has been reported [18–20]. However, no record exists of cathodic deposition of insoluble vanadate-based compounds from their stable solutions (e.g., cyclic ether–water mixtures). The work reported in this paper is a continuation of an earlier study [17] on the formation of a new class of mixed insoluble polynuclear cyanometalates and vanadium-based oxides solid films.

2. Experimental details

All reagents used were at least of analytical grade. All solutions were freshly prepared in deionized water.

All electrochemical experiments were carried out in a low volume, three-electrode cell consisting of a Pt wire counter electrode, an Ag/AgCl reference electrode, and a Pt or GC working electrode of a 0.07 cm^2 geometrical area. Prior to use, each electrode was polished with 2 μm alumina which offered better reactivation than did diamond paste. Electrochemical experiments were performed with either a BAS 100B electrochemical analyser (Bio-analytical Co.) or a PAR 364 scanning potentiostat. All experiments were performed at room temperature (25 °C). X-ray photoelectron spectra (XPS) were recorded using a Perkin Elmer 5500 ESCA (aluminium filament source), with a typical depth analysis of 0.5–5 nm. XPS were calibrated using silver line standards. Scanning electron micrographs of the deposited films on the electrode surfaces were obtained using an Amray 1000A scanning electron microscope at an accelerating voltage of 10 kV. Infrared spectra were carried out using a thremo Nicolet 4100s FTIR. The formation of these mixed polynuclear hexacyano iron(III), and decavanadate films took place in a room temperature bath of 25 mM of $(NH_4)_6V_{10}O_{28}$ and $K_3Fe(CN)_6$, each dissolved in an aqueous solution of 50 mM KCl (pH 2). The electrochemical deposition of this film was carried out via the successive sweeping of the GCE potential between 1.0 and −0.10 V vs Ag/AgCl at 200 mV s^{-1} for 20 scans. In each case, following the deposition, the GCE electrode was removed, rinsed with deionized water, and air dried. Catalytic activities of the formed

film were investigated by comparing the CVs (at 20 mV s^{-1}) of native and modified GCE in aqueous KCl (pH 2) electrolytes in the absence or presence of the studied anions.

3. Results and discussion

3.1. *Electrodeposition of mixed hexacyano iron(III) and decavanadates films*

Figure 1 illustrates the resulting CVs of GCE in the electrodeposition bath. The first scan shows a reduction peak at ~0.550 V and an oxidation peak at 0.790 V. The reduction peak decreased in the second and third scans, after which the peak started to increase again. The anodic peak increased as the number of scans increased. Figure 1 also shows that at the third CV a second reduction wave was initiated at ~0.400 V and continued to grow as the number of scans increased. Furthermore, Figure 1 indicates that, even for anodic scans, a cathodic current was generated between –0.10 to 0.60 V. Such observations indicate that the product of the reduction process, which took place at 0.550 V, not only compensated the double layer, but also reversed the charge order at the electrode–electrolyte interface. The film produced after the successive CVs shown in Figure 1 had a yellowish appearance, whereas thicker films yielded a blue colour.

The use of K$_4$[Fe(CN)$_6$] and K$_3$[Fe(CN)$_6$] in the electrodeposition bath was explored; however, concurrent electroless deposition of the yellowish film in the cell was observed with K$_4$[Fe(CN)$_6$] but at a very slow deposition rate. Therefore, the electrodeposition process was limited to the use of K$_3$[Fe(CN)$_6$] to ensure 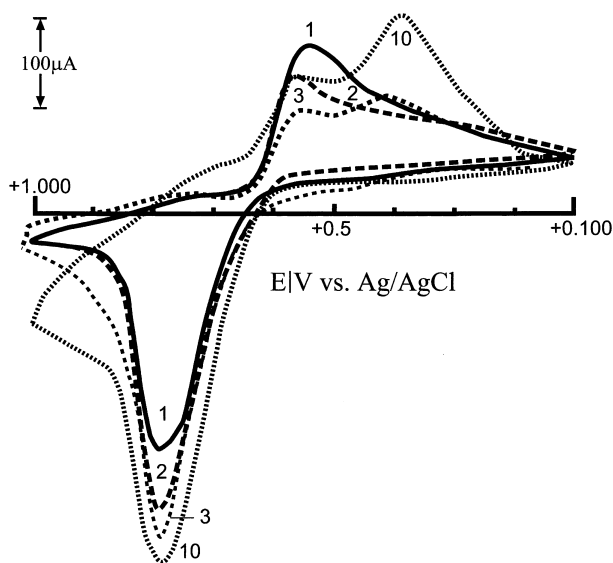that only the electrochemical process took place during film formation. The acidic medium is very important to the chemical or electrochemical formation of this mixed film. Furthermore, no insoluble film was formed under the same conditions in aqueous acidic solution of either decavanadates or a mixture of decavanadates and FeCl$_3$. These observations suggest that the decavanadate anion (in which V$^{(v)}$ occupies the centre of octahedral structure where it coordinates with six O atoms), and the octahedral structure of Fe(CN)$_6^{3-}$ are essential to the formation of this insoluble film. Further investigations show that the film shows better adherence to Pt than to GCE surfaces.

3.2. *Spectroscopic characterization*

Figure 2 represents the scanning electronic micrograph of the film formed on the GCE substrate. The XPS spectrum for the film shown in Figure 2 is displayed in Figure 3. In Figure 3, the peaks corresponding to the vanadates are identifiable. The three peaks between 510 and 530 eV correspond to pentavalent vanadium. In particular, the signals at 516–525 support the V—O bonding that can be V(v) surrounded by six O atoms. On the other hand, signals appearing between 705 and 725 eV indicate a mixed valence iron coordinated with oxygen (Fe—O). This is evidence for the coexistence of Fe(II)—O and Fe(III)—O. Furthermore, the signal at 709 refers to Fe—CN of octahedral structure Fe(CN)$_6^{3-}$. The peak at 290 eV corresponds to C in the CN group, while the N peak was at 400 eV. It has been previously reported [1, 3] that multivalent oxides of transition metals can be co-deposited from cyano-metalate solutions at pH 2.

Figure 4 shows the infrared spectra of the solid film formed on the electrode surface. The band at 2100 cm^{-1} corresponds to the –CN group, while bands at 580, and 630 cm^{-1} is characteristic of Fe(II/III) cyanides. Bands at 924 and 894 cm^{-1} correspond to the mixed valence oxovanadate cluster. This surface analysis suggests that

Fig. 1. Repetitive CV at 200 mV s^{-1}. Of GCE in equi 25 mM of each of (NH$_4$)$_6$V$_{10}$O$_{28}$ and K$_3$Fe(CN)$_6$ dissolved in aqueous solution of 50 mM KCl (pH 2). Scan numbers are reported on the CVs.
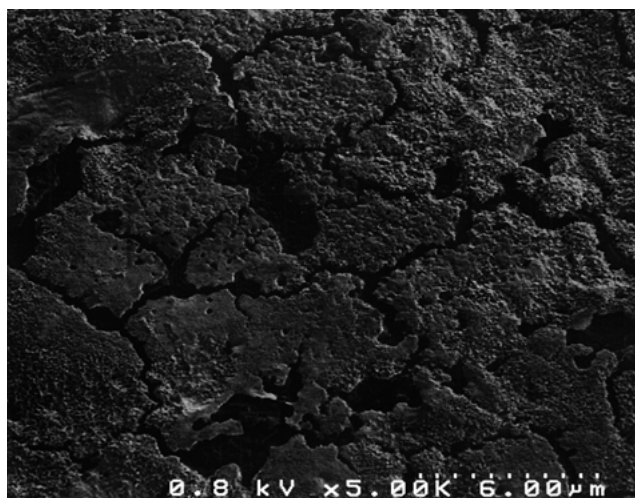

Fig. 2. Scanning electron micrograph of mixed polynuclear hexacyano iron(III), and decavanadates films on GCE surface. Accelerating voltage was 0.8 kV.
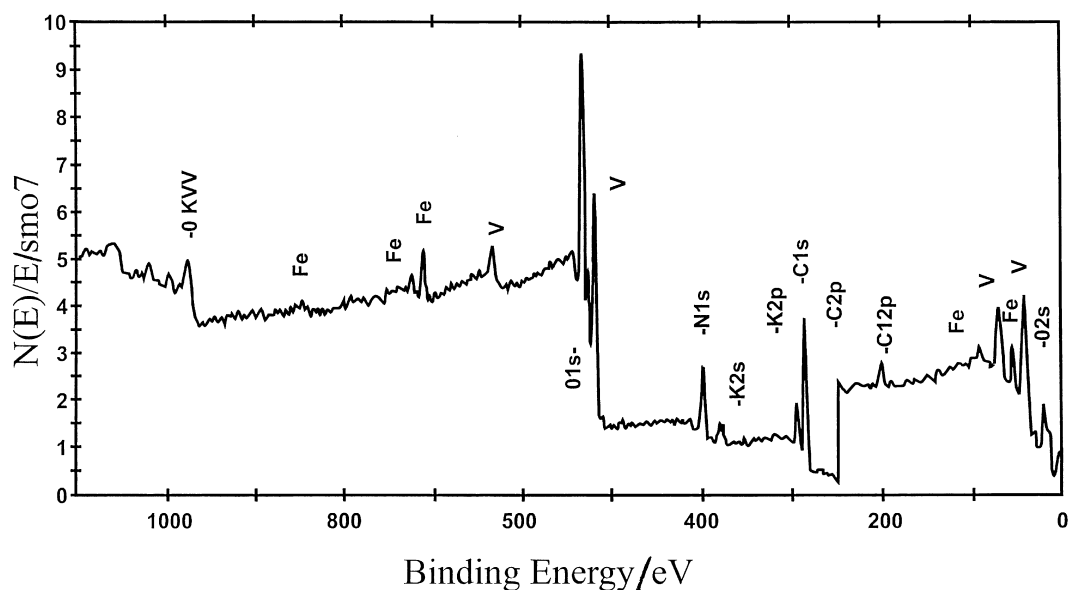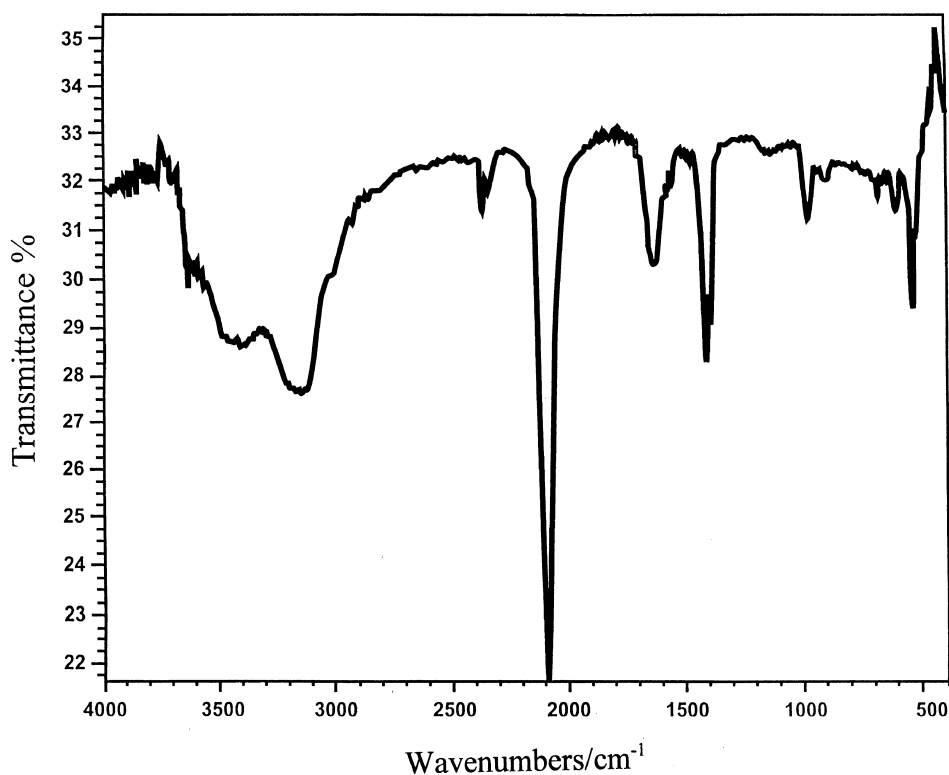
Fig. 3. XPS of the aggregates shown in Figure 2.

Fig. 4. FTIR of the aggregates after being removed from the electrode surface.

an inorganic constellate was formed with two redox centres, one related to V and the other related to Fe. The structure of this film can be simplified as $[M_2(V^V \cdot O_x)\ Fe^{III}(CN)_6]^{-z}$, where M is an alkaline metal cation and z is the anion charge. Considering the composition of the electrolyte used, and the cation size, the charge balance in this film can be maintained by K^+ ion exchange.

3.3. *Cyclic voltammetric behaviour*

The electrochemical behaviour of GCE modified with these mixed Fe/V compounds solid films was investigated using aqueous 0.1 M KCl solution (pH 2). The results are displayed in Figure 5A. They show one irreversible reduction wave at 0.320 V and one redox wave with formal potential of 0.730 V vs Ag/AgCl. A comparison of
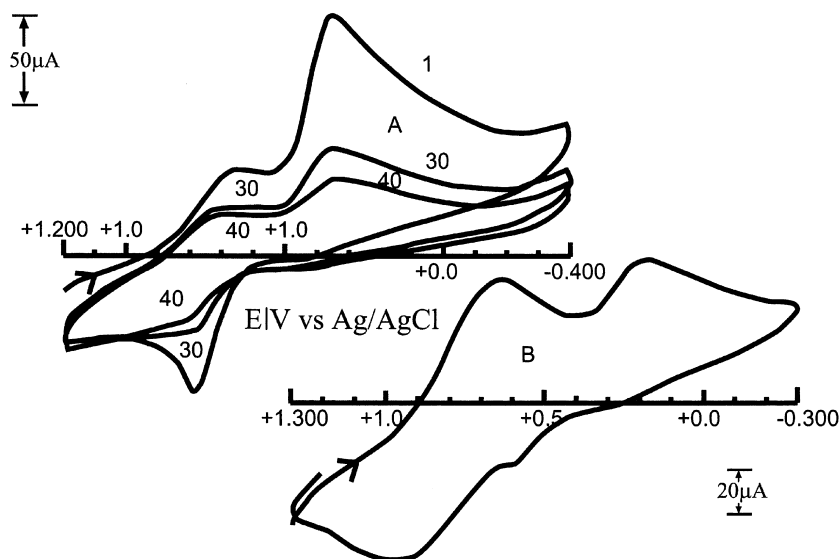
Fig. 5. (**A**) CV for the GCE modified with the mixed Fe/V insoluble compounds in aqueous solution of 50 mM KCl (pH 2). Scan numbers are reported on the CVs. (**B**) CV for the GCE modified with the mixed Fe/V insoluble compounds in aqueous solution of 50 mM KClO$_4$. Scan rate 100 mV s^{-1}.

Figure 5 with Figure 1 suggests that the irreversible reduction wave at 0.320 V and the oxidation wave at 0.750 V can be used as an indicator of the mixed Fe/V compound film formation.

Although the CV redox wave of formal potential 0.730 V is due to the immobilized redox centre, the ΔE_p of 0.06 V (one electron solution like wave) is reported. This indicates that the electron transfer to the fixed sites required K$^+$ transfer from the solution to the immobilized redox centre. The CV of the same electrode in 0.1 M KClO$_4$, shows two anodic waves at 0.60 and 0.90 V vs Ag/AgCl (Figure 5B). Similar behaviour was also observed in KCl solution. This behaviour cannot be attributed to the anion size effect, because in this study further investigations showed that the anion size had no effect on the redox behaviour and that the difference in the anion size of Cl$^-$ and ClO$_4^-$ was not significant to start with (the hydrodynamic radii of CL$^-$ and ClO$_4^-$ ions are 300 and 350 pm, respectively). The fact that these two anodic peaks combined at low pH (0–2), suggests that this redox behaviour can be attributed to the concentration and the size of H$^+_{aq}$ (radii 900 pm).

Repetitive CVs show that after the third cycle no decrease in the peak current occurs. This indicates the durability of the deposited film during larger numbers of CV scans. Furthermore, the film demonstrates a long
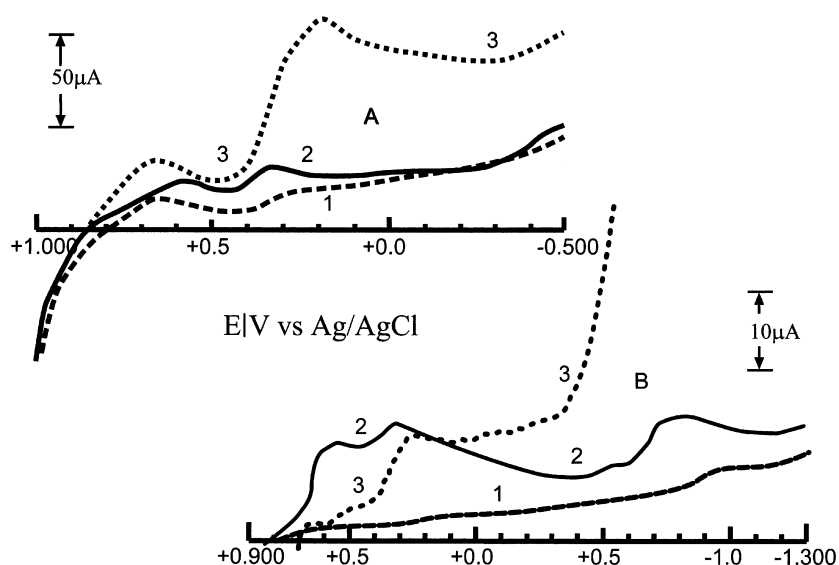

Fig. 6. (**A**) Linear scan voltammetry (at 20 mV s^{-1}) in aqueous solution of 50 mM KCl (pH 2) of: (**1**) native GCE, (**2**) modified GCE with mixed Fe/V insoluble compound, and (**3**) modified GCE with mixed Fe/V insoluble compound in presence of 50 mM KBrO$_3$. (**B**) Linear scan voltammetry (at 20 mV s^{-1}) in aqueous solution of 50 mM KCl (pH 2): (**1**) and (**2**) as described in (**A**); (**3**) modified GCE with mixed Fe/V insoluble compound in presence of 50 mM KNO$_3$.

time stability in air, as the modified electrode with this film give the same CV after being exposed to air for more than two weeks. A comparison of this electro-chemical behaviour with that reported [20] for vanadium hexacyanoferrate (VHF), which shows two reversible redox waves at formal potentials of 0.940 and 0.775 V vs SCE, indicates that $Fe(CN)_6^{3-}$ and $V_{10}O_{28}^{6-}$ assemble differently from VHF.

3.4. *Evidence of catalytic activity*

The mixed Fe/V insoluble compounds showed catalytic activity towards the reduction of BrO_3^- (Figure 6A), and NO_3^- (Figure 6B) in an acidic medium. A carbon paste electrode of the same apparent geometrical area was used to confirm that the reduction peaks illustrated in Figure 6 (A and B) were not due to an increase in electrode surface area.

The observed catalytic current in Figure 6A is due to the reduction of bromates to bromide according the following reaction:

$$BrO_3^- + 6\,H^+ + 6\,e^- = Br^- + 3\,H_2O \qquad (1)$$
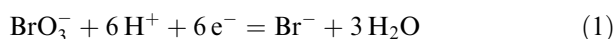
Since the modified electrode scanned to negative poten-tial, the oxidized form of the film assembly can be written as $M_2(V^{(v)}\cdots O_x)\,Fe^{(III)}(CN)_6$, which at ~ 0.7 V undergoes reduction as follows:

$$M_2(V^{(V)} \cdot O_x)\,Fe^{(III)}(CN)_6 + 2\,H^+ + 2\,e^-$$
$$\implies M_2(V^{(IV)} \cdot O_{x-1})\,Fe^{(II)}(CN)_6 + H_2O$$
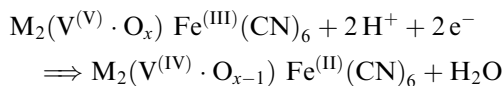
The compound $M_2(V^{(IV)} \cdot O_{x-1})\,Fe^{(II)}(CN)_6$ is unstable as it contains (d^3) vanadium and (d^6) Fe. To restore its stability, $M_2(V^{(IV)} \cdot O_{x-1})\,Fe^{(II)}(CN)_6$ transfers electrons to BrO_3^- according to the following reaction:

$$3\,M(V^{(IV)} \cdot O_{x-1})\,Fe^{(II)}(CN)_6 + BrO_3^-$$
$$\implies Br^- + 3\,M_2(V^{(V)} \cdot O_x)\,Fe^{(III)}(CN)_6$$
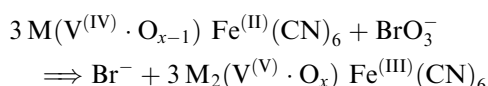
Compound $M_2(V^{(v)} \cdot O_x)\,Fe^{(III)}(CN)_6$ of (d^0) vanadium and (d^5) Fe is more stable than that containing (d^3) vanadium and (d^6) Fe.

Ongoing studies in this laboratory showed that immobilized hexacyanometalates cobalt and/or iron catalysed the reduction of IO_3^-. The fact that some vanadium oxo-compounds are catalytically active can be used to explain the sudden rise in the reduction current started at about -0.4 V. At this potential only the V centres are the sources of catalytic activity. This is because more vanadium atoms in $M_2(V^{(v)} \cdot O_x)$ $Fe^{(II)}(CN)_6$ are reduced to V(IV). These V(IV) are less stable than V(V) and the more V(IV) in $M_2(V^{(v)} \cdot O_x)$, the less stable is the oxoanion. To restore the stability of $M_2(V^{(v)} \cdot O_x)\,Fe^{(II)}(CN)_6$, V atoms must act as electron donors. This behaviour was reported [8, 17] in several polyoxometalates such as $PMo_{12}O_{40}^{4-}$ and SiW_{40}^{4-}. The

results displayed in Figure 6 (A and B) represent examples of the participation of both Fe and V centres in the catalytic behaviour of this mixed Fe/V compound film.

4. Conclusion

The work described presents a new class of stable, solid, insoluble film of mixed hexacyano iron(III) and deca-vanadates. Spectroscopic studies indicate the coexis-tence of an octahedral structure of hexacyanometalate and polyoxometalates. Cyclic voltammograms indicate that the redox centres of both vanadium and iron are electrochemically active under the studied conditions. Catalytic activity of the deposited compound can be explained on the basis of the involvement of both redox centers in the election/proton transfer process.

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