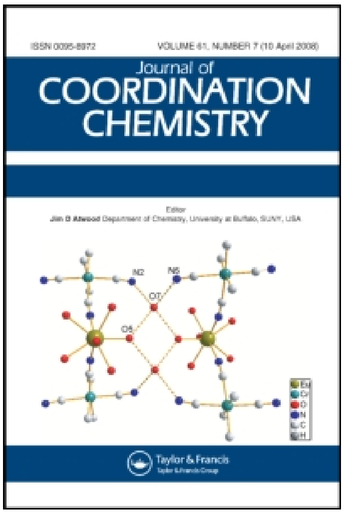

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THE CYANIDE PHOTOISOMERIZATION IN ZINC HEXACYANOFERRATE (II) SUPPORTED ON TITANIUM DIOXIDE-SILICA GEL COMPOSITE: A MATRIX EFFECT

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THE CYANIDE PHOTOISOMERIZATION IN ZINC HEXACYANOFERRATE (II) SUPPORTED ON TITANIUM DIOXIDE-SILICA GEL COMPOSITE: A MATRIX EFFECT

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Zinc hexacyanoferrates(II), ZnHCF, were supported on the surface of titanium(IV) oxide grafted on a silica gel surface, SiO_2/TiO_2. The adsorbed complex species SiO_2/TiO_2/ZnHCF was characterized by cyclic voltammetry, differential pulse polarography and Mössbauer spectroscopy. The pentacyanoferrate (II) species would also be formed by an isomerization of one of the cyano groups, which forms a Zn-CN-Fe bond. The effect of supporting electrolyte in the electrochemical behavior of cyanoferrates was investigated using modified carbon paste electrodes. The modified electrode exhibits a *quasi*-Nernstian response showing the involvement of alkaline metal cations in the electrochemical process. The electrode prepared with the composite ≡TiHCFZn also exhibits electrochemical behavior dependent on acetate anion concentration selectively.

Keywords: Matrix effect; Photoisomerization; Hexacyanoferrate; Titanium dioxide; Silica gel; Zinc cyanoferrates

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INTRODUCTION

In the last years great effort has been devoted to develop chemically modified electrodes [1–5]. Modified electrodes use the specific interactions of the electrode's modifying materials with solution species in order to achieve higher selectivity and catalytic effect [2]. Another approach has been to modify electrodes with ion-exchange materials to adsorb electroactive species. The ion-exchange materials used have been polymers, transition metal oxides and clays [1].

In our laboratory, transition metal oxides grafted on a silica gel surface have been prepared [6, 7]. The titanium dioxide composite is especially interesting because of its high chemical stability, photochemical reactivity and amphoteric character [9]. This amphoteric character has been used, successfully, to immobilize electroactive anionic species on the SiO_2/TiO_2 surface [10, 11].

Several spectroscopic and electrochemical studies have been conducted with isolated and supported [12–16] transition metal cyanoferrates (II). These materials show a wide range of interesting chemical and physical properties, including alkaline metals sorption [17], electrocatalytic activity [18] and electrochromic [19] behavior. In this work the preparation of zinc cyanoferrates supported on the surface of titanium (IV) dioxide- silica gel composite as well as their characterization by Mössbauer spectroscopy and cyclic voltammetry are reported.

EXPERIMENTAL

Reagents

Deionized water was used throughout all the experiments. All the reagents but silica gel (Merck) were purchased from Aldrich. Except tetrabutyl orthotitanate, 98%, all the other reagents were of analytical grade.

Silica Functionalization with Titanium (IV)

Silica gel having a specific surface area $S_{BET} = 500 \pm 76\ m^2g^{-1}$, an average pore diameter of 0.6 nm, and a particle size of 0.023 ± 0.03 mm was activated by heating at 423 K under vacuum (0.13 Pa) before use. Tetrabutyl orthotitanate monomer 24 mL was added to 70 g of this activated material suspended in previously dried toluene (150 mL). The following reaction does occur when the mixture was refluxed for 6 h under argon atmosphere.

$$n(\equiv SiOH) + Ti(OR)_4 \rightleftharpoons (\equiv SiO)_nTi(OR)_{4-n} + n\ HOR$$

where ≡SiOH stands for the silanol groups and R = n-butyl

The solid was filtered and washed with previously dried toluene (350 mL), and then dried at 373 K under vacuum. Afterwards the solid was hydrolyzed and washed with demineralized water, 18 MΩ:

$$(\equiv SiO)_nTi(OR)_{4-n} + (4-n)H_2O \rightleftharpoons (\equiv SiO)_nTi(OH)_{4-n} + (4-n)ROH$$

For the sake of brevity, the chemically modified silica $(\equiv SiO)_nTi(OH)_{4-n}$ will be hereafter denoted as ≡TiOH.

The ≡TiOH titanium content as equal to 0.82 $mmol \cdot g^{-1}$ was determined by x-ray fluorescence (XRF) analysis.

Hexacyanoferrate (II) Adsorption

The oxide (SiO_2/TiO_2) strongly adsorbs anionic species at pH values under the isoelectric charge point, above this value cation adsorption takes place.

The hexacyanoferrate (II) was adsorbed from an acid aqueous solution with pH 3.0. In a typical experiment 50 mL of $K_4[Fe(CN)_6]$ (Aldrich) 0.1M is mixed with 0.50 g of ≡TiOH and the suspension shaken for 30 min. The resulting pale yellow material, hereafter designated as ≡TiHCF, is filtered, washed with 1.0×10^{-3} M nitric acid solution and dried under vacuum (10^{-2} Torr).

It is well known that cyanides in $[Fe(CN)_6]^{4-}$ exchange very slowly [20] and that Ti(IV) (d^0) ion behaves as a labile metal center for water substitution reactions in solution [21]. Therefore, it is reasonable to assume that the ≡TiOH material in acidic aqueous suspension (1.0×10^{-3} M HNO_3) adsorbs $[Fe(CN)_6]^{4-}$ following the equation below:

$$\equiv TiOH_{(solid)} + H^+_{(aq)}\ [Fe(CN)_6]^{4-}_{(aq.)} \rightleftharpoons \equiv\{TiNCFe(CN)_5\}^{3-}_{(solid)} + H_2O_{(aq)}$$

Formation of Zinc Cyanoferrates (II) on the ≡TiOH Surface

After the $\equiv\{TiNCFe(CN)_5\}^{3-}$ was immersed into 100 mL of 0.1 M zinc acetate or zinc chloride solutions, pH 5.5, and stirred for 30 min., the pale yellow color of $\equiv\{TiNCFe(CN)_5\}^{3-}$ species disappeared. The resulting materials, hereafter designated as ≡TiHCFZn were filtered, washed with 1×10^{-3} M aqueous nitric acid solution and dried under vacuum (10^{-2} Torr). The ≡TiHCF iron (0,050 mmol·g^{-1}) and the zinc (0.051 mmol·g^{-1}) contents were determined by atomic absorption.

Formation of Pure $Zn_2[Fe(CN)_6]$

$Zn_2[Fe(CN)_6]$, hereafter designated as ZnHCF, was prepared following the procedure already described [22].

Electrochemical Measurements

The cyclic voltammetric and differential pulse polarography (DPP) experiments were performed as described elsewhere [23]. The saturated calomel electrode (SCE) was used as reference, platinum wire as counter electrode, and the composite ≡TiHCFZn modified carbon paste electrode as the working electrode. The carbon paste was prepared by mixing 2:5≡TiHCFZn:graphite (mass/mass) with a few drops of mineral oil as binding element. All the measurements were carried out under nitrogen on the potentiostat/galvanostat from EG&G Princeton Applied Research, model 273A equipment.

The DPP experiments used the same electrodes as for cyclic voltammetry. The scan rate was 5 mV·s^{-1} and the pulse height was 25 mV. The mid-point potential, $E_{1/2}$ was calculated as $[E_{1/2} = (E_{pa} + E_{pc})/2]$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively.

Mössbauer Spectroscopy

The Mössbauer spectra were obtained at room temperature, using a 24 mCi ^{57}Co/Rh source and detected by a Kr-CO_2 proportional counter (Reuter Stokes) coupled to a multichannel analyzer (EG&G Ortec). The isomer shifts were calibrated against α-iron foils and referenced against sodium nitroprusside (line width at one half maximum of 0.25 mms^{-1}).

The Mössbauer spectroscopy measurements were carried out as described elsewhere [23]. In order to know the acetate influence on the material isomer shift (δ), 0.5 g of ≡TiHCFZn was immersed in an acetate buffer solution, pH 4.5, during 30 min. The solid was filtered off, without washing, and dried under air.

RESULTS AND DISCUSSION

Mössbauer Spectroscopy

Figure 1A shows the Mössbauer spectra for ≡TiHCFZn and Table I presents the calculated parameters. Figure 1A, shows two asymmetric peaks. After fitting, these peaks were assigned to two different contributions: a singlet at $\delta_1 = -0.136\,\mathrm{mm\cdot s^{-1}}$ and a doublet at $\delta_2 = +0.120$ with Δ (quadrupolar coupling) $= +0.570\ \mathrm{mm\ s^{-1}}$ *vs.* α-iron. By comparison with the value found for bulk phase zinc hexacyanoferrate(II) (see Fig. 1B) the singlet was assigned as due to the iron (II) nucleus in zinc hexacyanoferrate (II) [24]. The doublet presents an isomeric shift δ_2 which is higher than those reported for Fe(II) and Fe(III) in hexacyanoferrate complexes (low spin) but

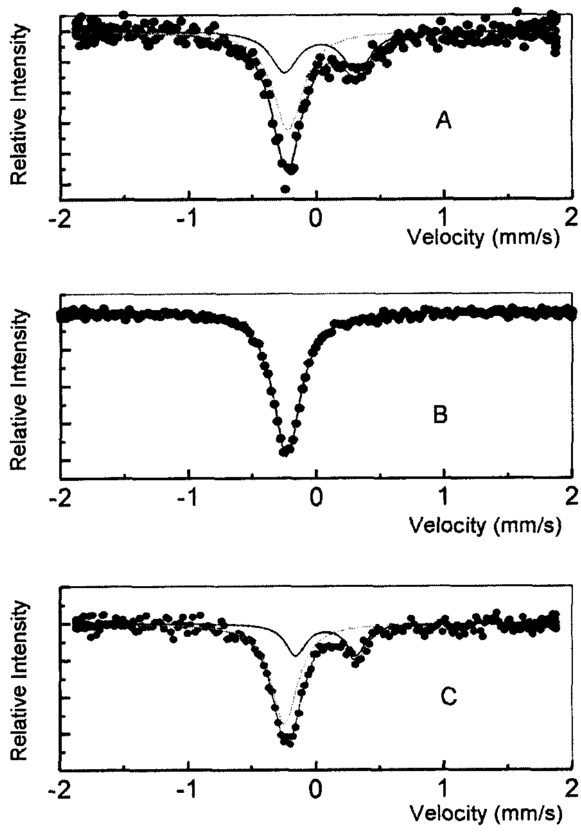

FIGURE 1 Mössbauer spectra at 300 K of (A)≡$Zn_2[Fe(CN)_6]$, (B)≡TiHCFZn and (C)≡TiHCFZn treated with acetate buffer.

TABLE I Mössbauer parameters, isomer shift (δ) and quadrupole splitting (Δ), of $\equiv$TiHCFZn, $Zn_2[Fe(CN)_6]$, and related cyanoferrates(II) and (III). All the isomer shifts are referenced to α-Fe

Samples	$\delta_1/mm/s$	$\Delta_1/mm/s$	$\delta_2/mm/s$	$\Delta_2/mm/s$	$\Delta_2/mm/s$	*Ref.*
$\equiv$TiHCFZn	−0.136	0	+0.120	+0.570	+0.570	Our data
$Na_2Fe^{III}(CN)_5(NH_3)$	–	–	−0.279	+1.78	+1.78	30
$Na_3Fe^{II}(CN)_5(NH_3)$			+0.043	+0.694	+0.694	30
$Na_3Fe^{II}(CN)_5(H_2O)$	–	–	+0.063	+0.795	+0.795	31
$FeCl_3 \cdot 6H_2O$	+0.452	0				31
$ZrFe^{II}(CN)_6$	−0.148	0	–	–	–	31
$Zn_3[Fe^{III}(CN)_6]_2$	–	–	−0.27	+0.25	+0.25	29
$Zn_2Fe^{II}(CN)_6$	−0.14	0	–	–	–	29
$Zn_2Fe^{II}(CN)_6$	−0.136	0	–	–	–	Our data

considerably lower than those reported for other complexes of these ions exhibiting high spin electronic configuration [25] (Tab. I). Indeed, as shown in Table I, the value of $\delta_2 = +0.120$ agrees with those reported for low spin Fe(II) of pentacyanoferrate complexes [26].

The experiment suggests that the photoisomerization of the complex on $\equiv$TiOH surface may occur similar to that previously observed for hexacyanoferrates in aqueous solution [27]. Exchange of labeled cyanide between $[Fe(CN)_6]^{4-}$ and free cyanide is reported to be extremely slow in the dark, but under light or acids reversible aquation [27] takes place. When aqueous $[Fe(CN)_6]^{4-}$ is irradiated with ultraviolet light [28] ($\lambda_{ir} = 254\,nm$ and $\Phi_{max} = 0.67 \pm 0.01$) pentacyanoferrate and HCN are formed according to the reaction:

$$[Fe(CN)_6]^{4-} + 2H_2O \rightleftharpoons [Fe(CN)_5(H_2O)]^{3-} + HCN + OH^-$$

In alkaline or acid solutions, hexacyanoferrate photodecomposes into pentacyanoferrate which undergoes subsequent reactions leading to the Prussian blue complex.

Partial photodecomposition may occur [27] when photoirradiation is not sufficient and we would observe instead of the product of total photoisomerization, Prussian blue, the pentacyanoferrate (II).

In the solid state CN^- dissociation is more difficult than in solution therefore, as a matrix effect, an isomerization of the complex can take place [29]. In the present case, formation of pentacyanoferrate can be favored by the presence of zinc on the surface since zinc has high affinity for the CN^- ion, ($\log K_1 = 5.3$ for $[ZnNC]^+$) [30]. Therefore it is likely that in presence of Zn(II) photoisomerization could occur partially:

$$\text{Zn-NC-Fe} \overset{h\nu}{\rightleftharpoons} \text{Zn-CN-Fe (Scheme 1)}$$

As reported for other metallocyanides [29], the above isomerization can be envisaged as a flipping of the CN^- ligand.

As pointed out before, the isomerized cyanocomplex (zinc pentacyano-N-cyanoferrate) is expected to exhibit an isomeric shift and quadrupolar coupling more similar to those of pentacyanoferrate complexes than the immobilized hexacyano species, since the sixth coordination position is occupied by the nitrogen atom and not by the carbon atom. Due to the kinetic lability of zinc (II) center [31], a d^{10} transition metal, the existence of the linkage isomers Zn-CN and Zn-NC could be possibly observed in ZnHCF adsorbed on the ≡TiOH. This assumption is in agreement with the observed Mössbauer spectra, which suggest about 50% abundance for both species (58% for ZnCNFe and 42% for ZnNCFe).

In order to test the photodecomposition of ≡TiHCF, a conveniently dried sample was irradiated under the same conditions as used for ≡TiHCFZn. The freshly prepared ≡TiHCF has a maximum absorption at 400 nm [32]. Slowly the material starts to develop a blue color, with a maximum absorption at 800 nm, indicative of the Prussian Blue complex [27]. Therefore, it is possible to observe the CN^- photodissociation for both supported complexes, ferrocyanide and zinc ferrocyanide.

Electrochemistry

Carbon paste electrodes prepared by using ≡TiOH and ≡TiHCFZn were employed as working electrodes and the electrochemical properties studied by means of cyclic voltammetry between 0 and 1.1 V *vs.* SCE in different supporting electrolyte solutions.

The voltammograms obtained in alkaline metal chloride solutions (KCl, NaCl, and LiCl presented two redox midpoint potentials (Fig. 2). The presence of the two electrochemical processes $(E_{1/2})_1 = 0.70$ and $(E_{1/2})_2 = 0.85$ V, provides additional support to our hypothesis for the existence of two different iron centers on the composite surface. The peak at 0.85 V attributed to the Fe^{III}/Fe^{II} couple is in agreement with the reported value for zinc hexacyanoferrate wax impregnated graphite electrode (WIPG) [32] and the $E_{1/2}$ is directly proportional to log $[C^+]$, where C^+ is the cation supporting electrolyte concentration. The modified electrode showed a *quasi* Nernstian response for K^+ (43 mV) and Na^+ (72 mV) (see Figs. 3 and 4) which clearly shows the involvement of alkaline metal cations in the electrochemical process. The dependence of the mid-point potential on the supporting electrolyte concentration, explained by the equilibrium of the cation with the surface of the material, has been previously reported [16].

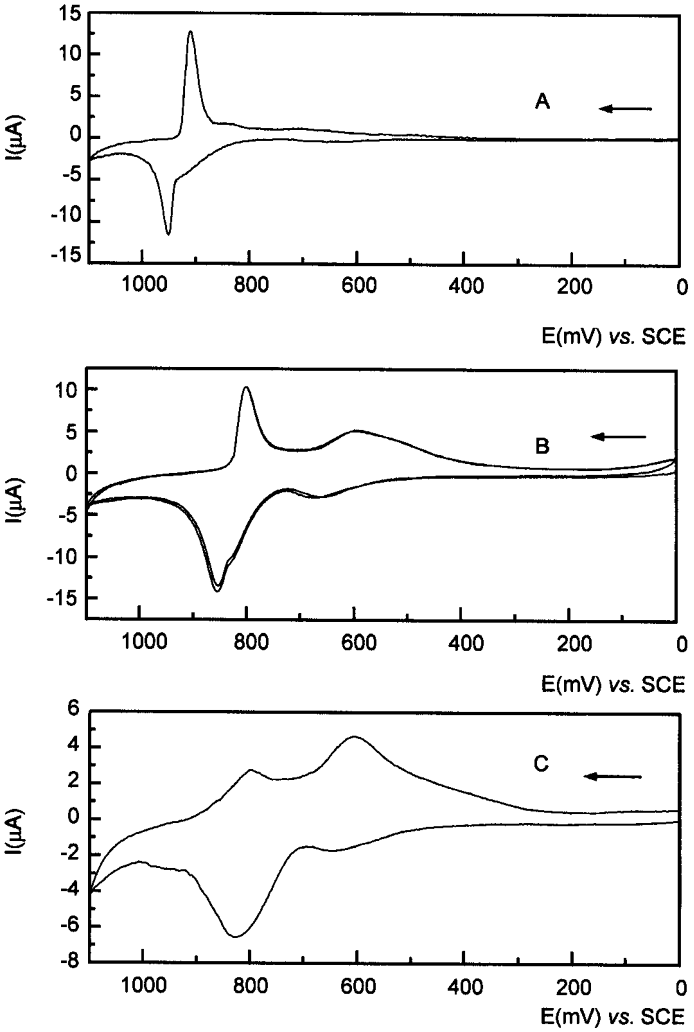

FIGURE 2 Cyclic voltamogram of ≡TiZnHCF in 1 M solutions; (A) KCl, (B) NaCl and (C) LiCl.

Based on the above observations, the following scheme is proposed for the $(E_{1/2})_2$ redox process of the ZnHCF modified electrode in XCl, were $X = K^+, Na^+$

$$ZnC_2[Fe^{II}(CN)_5(NC)] \rightleftharpoons ZnC[Fe^{III}(CN)_5(NC)] + C^+ + e^-$$

The different $E_{1/2}$ values and the shape of cyclic voltammograms exhibited for two different cations (K^+, Na^+) in the same experimental conditions

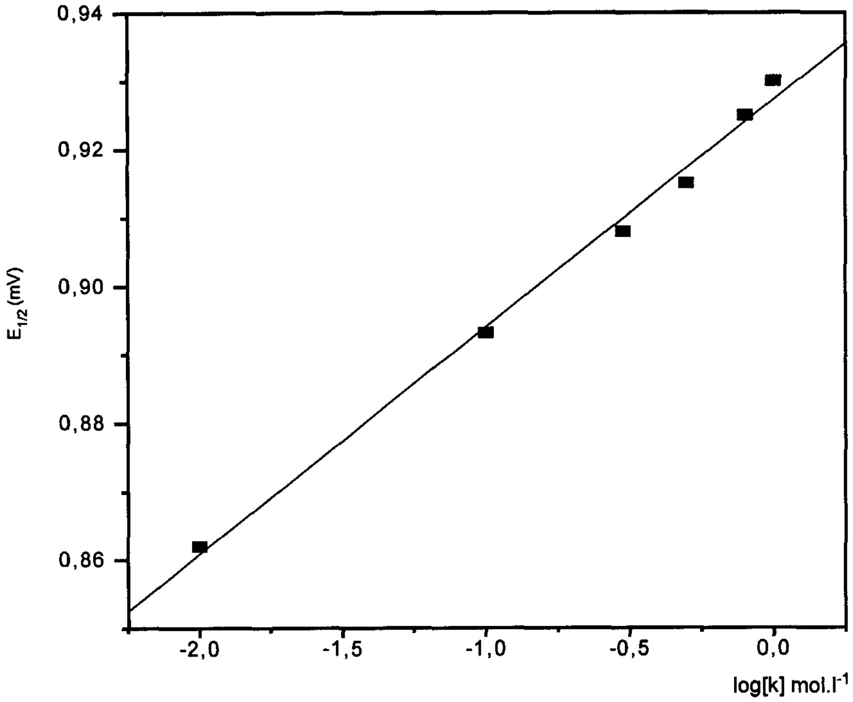

FIGURE 3 Plot of the logarithm of potassium ion concentration *vs.* potential.

could not be attributed to ionic strength or liquid junction potential effect (estimated as 0.005 V per decade of concentration) [33]. Therefore, it is reasonable that the hydrated cation ionic radius ($K^+ = 0.24$ nm and $Na^+ = 0.36$ nm) would account at least in part for the observed $E_{1/2}$ difference [32, 34] due to diffusional capacity to get and move inside the ZnHCF channel structure.

The assignment of this process to the pentacyano species is in agreement with the expected $E_{1/2}$ values of these species [25].

The anodic peak profile (peak A in Fig. 5) in 1.5 M $NaClO_4$ supporting electrolyte solution changes after addition of sodium acetate solution. The intensity of peak A $(E_{1/2})_2$(0.85 V *vs.* SCE) decreases while that of peak B $(E_{1/2})_1$ (0.75 V *vs.* SCE) increases during the various redox cycles (Fig. 4). The insert in Figure 5 shows that Ipc decreases as a function of time. The anion sorption (Cl^-, SO_4^{2-}, and NO_3^-) has already been verified in the case of zinc and nickel hexacyanoferrates [35], however, the anions Cl^-, SO_4^{2-} and NO_3^- did not show similar behavior. Our results indicate that the chloride, sulfate and nitrate sorptions are weaker than for acetate.

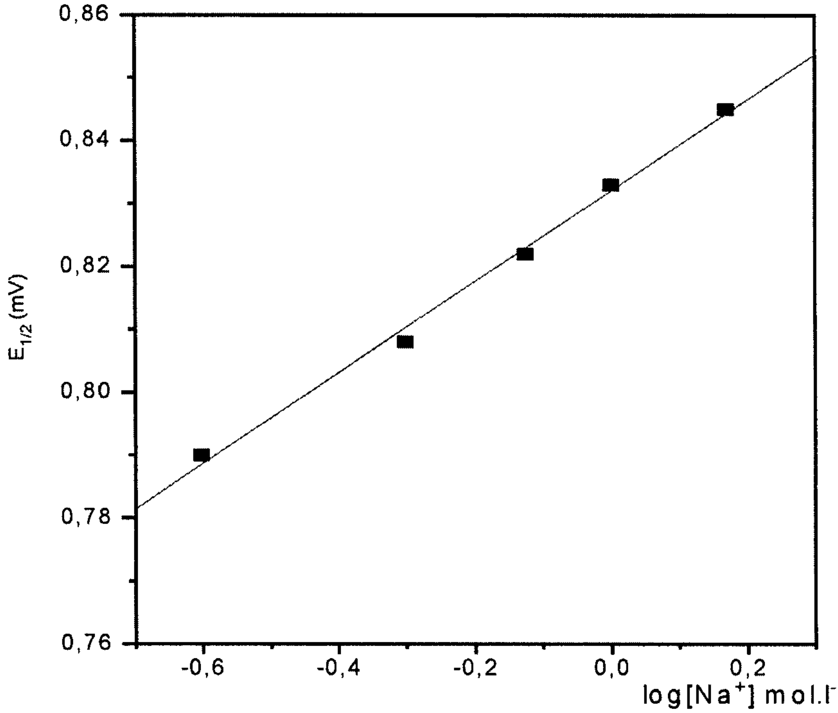

FIGURE 4 Plot of the logarithm of sodium ion concentration *vs.* potential.

In agreement with the cyclic voltammetry, the differential pulse polarography results show that the anodic current of the peak at 0.85 V(peak B) also decreases in the presence of acetate solution as shown in Figure 6, thus suggesting an interconversion between them. Based on the above observations and on our Mössbauer results the possible redox reaction may be tentatively proposed as:

$$Ac^- + Zn_2[Fe^{II}(CN)_6] \rightleftharpoons \{Zn_2[Fe^{III}(CN)_6]\}^+Ac^- + e^-$$

where $Ac^- = CH_3COO^-$.

The observed current peak intensity changes were attributed to the acetate ion interaction with Zn (II) of the zinc hexacyanoferrate structure. This assignment agrees with the high affinity of cyanide for Fe(II) and the thermal inertia of the Fe-CN bonds [26, 32, 35]. Additional support to the above considerations was provided by ^{57}Fe Mössbauer spectroscopy which is very sensitive to the chemical environment of the iron nucleus and able to

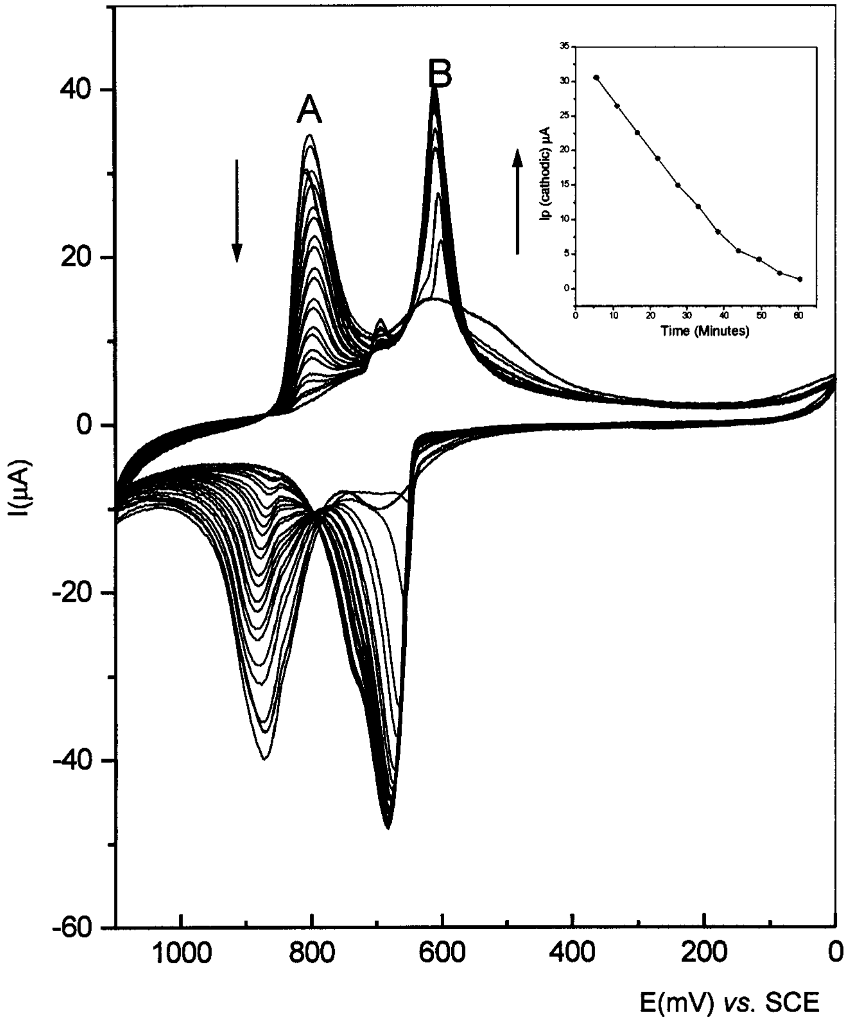

FIGURE 5 Cyclic voltamogram of ≡TiZnHCF in NaCl 1M (A) in absence and (B) presence of 4.7 x 10^{-2} M sodium acetate solution.

detect even small changes in the iron coordination sphere [26]. Also, no noticeable change was observed in the ^{57}Fe Mössbauer spectra of the ≡TiHCFZn after treatment with a solution of H_3COOH/H_3CCOO^- (pH 5.8), Figure 1C, therefore suggesting that it is unlikely the observed changes in the electrochemical behavior arise from alteration in the iron coordination sphere.

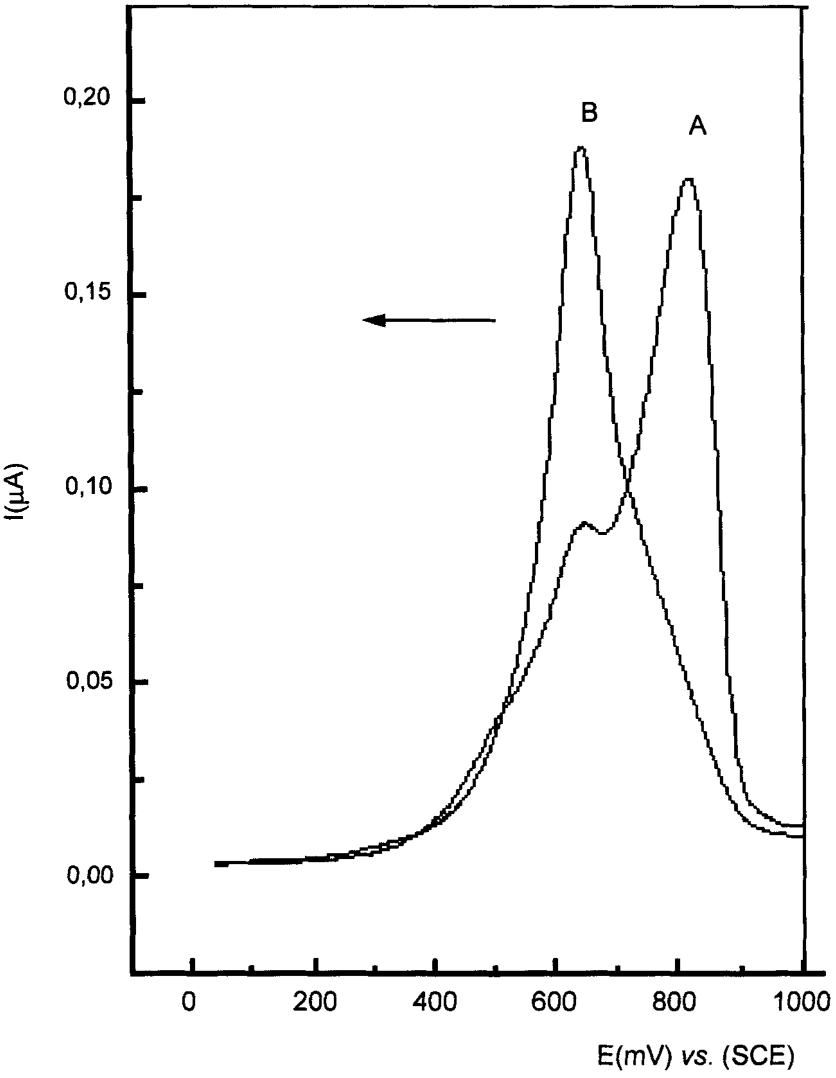

FIGURE 6 Differential pulse polarography of ≡TiZnHCF-Cl in 1 M KCl solutions; (A) in absence of sodium acetate, (B) with adition of 4.7×10^{-2} M sodium acetate solution. Both experiments were carried out at pH 5.8.

CONCLUSIONS

Due to the absence of solvent CN^- photodissociaton is more hindered in ≡TiHCF than in hexacyanoferrate(II) in solution. Therefore, the flipping of the cyanide ligand forming Fe-NC isomer is more likely to occur. The presence of Zn(II), which rapidly reacts with flipped cyanide, acta as a local trap forming a Fe-NC-Zn bond. This process seems to be favored by the high dispersion of the zinc hexacyanoferrate(II) in the SiO_2/TiO_2 matrix since it is faster for the supported species than for the bulk solid. The composite exhibits electrochemical dependence on acetate ion concentrations that can be explored for building up a promising electrochemical sensor.

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