Electrochemistry of Chromium(II) Hexacyanochromate(III) and Electrochemically Induced Isomerization of Solid Iron(II) Hexacyanochromate(III) Mechanically Immobilized on the Surface of a Graphite Electrode

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Immobilized on the surface of a graphite electrode, solid chromium(II) hexacyanochromate exhibits the reversible reduction–oxidation response of the hexacyanochromate system. The reduction is accompanied by intercalation of alkali metal ions. At room temperature, iron(II) hexacyanochromate(III) undergoes an electrochemically induced isomerization to chromium(III) hexacyanoferrate(II), when the compound is immobilized on the surface of a graphite electrode. This isomerization is a pseudo zero-order reaction within an initial period. The rate constant is 4×10^{-9} mol/s at 22 °C. The isomerization results from ligand labilization, caused by the reduction of chromium-(III) to chromium(II), and involves fast exchange between water molecules and cyanide ions.

Introduction

The study of the electrochemistry of solid compounds is of great importance both for the development of a fundamental understanding of interfacial reactions and for applied science, as, e.g., in battery and fuell cell research. The development of abrasive stripping voltammetry by Scholz et al.[1] has allowed a convenient method to be found which enables electrochemical studies to be undertaken of almost any solid compound. The principle of this technique is a mechanical immobilization of micrometer size particles of a sample on the surface of a suitable solid electrode. Since the transfer is mostly accomplished by abrasion, the term abrasive stripping voltammetry is used. In cases of electronic insulators, it is not trivial to study the electrochemistry because, previously, there were only a few techniques available for such research.[2] Many solid compounds, e.g., several insoluble hexacyanoferrates, have been studied with electrochemical methods, after their synthesis as a film on an electrode surface.[3-11] Bocarsly at al. introduced a technique of chemically modifying oxidatively unstable metal electrodes via irreversible chemisorption of coordination complexes. This technique has proved useful in the study of cyanide complexes of Fe, Ru, and Mn on the surface of a nickel electrode.[12-17] All these techniques, while valuable, suffer from the drawback that not many compounds can be synthesized on an electrode surface and from the fact that the films are not easily characterized by any desired analytical method, primarily because of the very small amount of synthesized compound.

The mechanical attachment of small sample particles on an electrode surface allows the study of the electrochemistry of such unstable solid compounds as iron(II) hexacyanochromate-(III), which can be synthesized chemically but not at an electrode surface. It has been long known that this iron compound undergoes thermal isomerization to chromium(III) hexacyano-ferrate(II) at a temperature around 100 °C.[18-20] Here we report that this isomerization can also be performed at room temperature at an electrode interface when electrochemical reduction of the hexacyanochromate(III) to hexacyanochromate(II) is performed. The isomerization product of iron(II) hexacyano-chromate(III), chromium(III) hexacyanoferrate(II), shows in the accessible potential range in aqueous solution only the volt-ammetric response of the hexacyanoferrate(II/III) system. The reduction of the iron(III) to iron(II) is accompanied by intercala-tion of alkali metal cations. Recently it has been shown that mixed valence chromium hexacyanochromates exhibit high magnetic-ordering temperature of 190 upto 240 K.[21] These results prompted an electrochemical study of their behavior in our laboratory. Chromium(II) hexacyanochromate(III) gives the reversible response of the hexacyanochromate system. Also in this case the reduction is accompanied by intercalation of alkali metal cations.

Two recent publications deal with the modification of the surface of solid electrodes by electrochemical deposition of a film of chromium(III) hexacyanoferrate.[22,24] Our results support the data given by these authors and additionally allow a more detailed understanding of film formation and film properties.

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Experimental Section

Chemicals. Iron(II) hexacyanochromate(III) was prepared according to refs 18 and 20. Anal. Found: Fe, 20.43; Cr, 12.75; C, 17.17; N, 19.44; H, 3.39; K, 2.00. From these data the following formula can be derived: $Fe_{1.6}[Cr[CN]_6](OH)_{0.2}$. The same composition has been found by Brown et al.[18]

Chromium(II) hexacyanochromate(III) was synthesized according to ref 21. Anal. Found: Cr, 28.8; C, 15.99; N, 17.87; K, 5.3; H, 2.69. These data are in agreement with the formula $K_{0.62}Cr^{II}_{1.55}[Cr^{III}(CN)_6]$-$(H_2O)_n(OH)_m$. All electrolyte solutions were prepared with twice distilled and previously ion exchanged water. The electrolyte salts were all of the analytical grade: KNO_3 (VEB Laborchemie Apolda, Apolda, East Germany), KCl (Baker). The following chemicals were used for the experiments: $CrCl_2$ (Merck, Darmstadt, Germany), $K_4[Fe(CN)_6]$ and $Fe(NH_4)_2(SO_4)_2·6H_2O$ (VEB Laborchemie Apolda, Apolda, East Germany), $K_3[Cr(CN)_6]$ was synthesized according to ref 25. Solutions were purged with high-purity nitrogen for at least 10 min prior to the voltammetric measurements. Chromium(III) hexacyanoferrate(II) was synthesized according to ref 18. Anal. Found: Cr, 13.1; Fe, 12.19; N, 18.03; C, 16.5; K, 12.7; H, 3.59. This corresponds to the composition $KCr(III)_{1.07}[Fe(CN)_6]·13.5H_2O$. Equipment: All measurements were performed with the following instrumentation: Autolab (ECO-Chemie, Utrecht, Netherlands), electrode stand VA 663 (Metrohm, Herisau, Switzerland), and a 386 personal computer. The reference electrode (Metrohm, Herisau Switzerland) was a Ag/AgCl electrode with 3 mol/L KCl (E = 0.208 V vs NHE).

Electrode Preparation for Measurements. A very convenient electrode for abrasive stripping voltammetry is the paraffin-impregnated graphite electrode. The preparation of these electrodes is described elsewhere.[1] A small amount (milligrams) of the finely ground sample was placed on a glazed porcelain tile. Small amounts of the sample were transferred onto the electrode surface by gentle rubbing of the circular lower surface of the electrode rod on the sample spot on the tile. Excessive sample can be gentle wiped off with tissue. Then the electrode is dipped into the electrolyte solution and raised until the point at which only the lower circular surface of the electrode, i.e. the electrode surface with the immobilized sample, is in contact with the electrolyte solution. Now the voltammetric measurements can commence after deaeration of the solution.

Results and Discussion

Prussian blue is the prototype of a large group of solid polymeric cyanides of the general formula $M'_i[M''_m(M'''_n(CN)_p)]$-$(H_2O)_q$, where M' may be a metal cation like K^+ or Na^+; M'' can be Fe, Ni, Cr, Co, Ag, Cu, Cd, etc.; and M''' may be Fe, Cr, Co, Ru, etc. The common feature of these compounds is their zeolithic structure with cubic units of the type shown in Figure 1. These cubes are large enough that they can accomodate small cations and water molecules. Usually, these compounds do not have a well-defined stoichiometry, but differ in their composition in a fairly wide range; e.g., the amount of cations in the cages differs from experiment to experiment. This variability is not a factor for the electrochemistry because, after some cyclic polarizations, different varieties of one compound equilibrate with the solution and the electrochemical response becomes identical. The high stability of the metal cyanide framework and the ability to exchange cations between a solution and the cages of the framework gives rise to a very interesting electrochemistry. Electrochemical reactions, i.e. oxidations or reductions by an electron flux, are always associated with an ion flux to balance the charges. The polymeric cyanides offer the possibility that electrochemical reactions can proceed without a dissolution of the solid because an ion flux into or out of the solid can balance the electron flux; a unique property they share only with a small number of other compounds, such as certain oxides.[26]
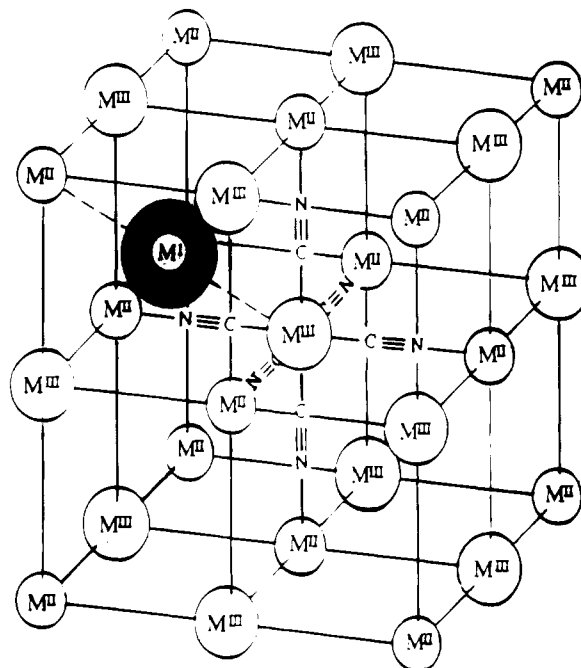

Figure 1. Crystal Structure of Prussian blue analog metal cyanide complexes of the general formula $M'_i[M''_m(M'''_n(CN)_p)](H_2O)_q$, where M' may be a metal cation like K^+ or Na^+, M'' can be Fe, Ni, Cr, Co, Ag, Cu, Cd, etc., and M''' may be Fe, Cr, Co, Ru, etc.

Chromium(II) Hexacyanochromate(III). Figure 2 shows cyclic voltammograms of chromium(II) hexacyanochromate-(III). Only one reversible redox system can be observed at relative negative potentials (peak potentials and formal potentials, see Table 1). This response is clearly associated with the intercalation of electrolyte cations which can be seen from the dependence of formal potentials on cation activity, (cf. Figure 3) which follows the Nernst equation for the reaction

$$K^+ + e^- + [Cr^{2+}(Cr^{3+}(CN)_6)] \rightleftharpoons K[Cr^{2+}(Cr^{2+}(CN)_6)]$$
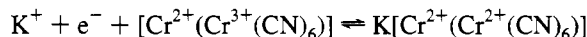
The slope of $E_f = f(\log a_{cation})$ is 57 mV for potassium and 61 mV for lithium. Table 1 gives the formal potentials of this system for different alkali metal cations. The formal potential of the observed system is very near to that of hexacyanochromate $[Cr(CN)_6]^{3-}$ ions dissolved in aqueous solution, which is -1.38 V vs SCE.[27] Later it will be shown that the voltammogram of chromium(III) hexacyanoferrate(II) shows only the response of the hexacyanoferrate system and no signal for the chromium ions coordinated to the nitrogen of the cyanide ions. Therefore we conclude that in case of the chromium hexacyanochromate we observe the reversible redox system of the chromium ions coordinated to carbon. The chromium ions coordinated to nitrogen give a very weak signal of irreversible oxidation at about $+1.0$ V vs Ag/AgCl (see Figure 2). This signal is fully obscured by the hexacyanoferrate system in the case of chromium hexacyanoferrate (cf. Figure 4b,c). Whereas in Prussian blue the $+3$ metal ion is coordinated to nitrogen and the $+2$ metal ion to carbon, the situation is reversed in chromium(II) hexacyanochromate(III).

Iron(II) Hexacyanochromate(III) and Its Isomerization to Chromium(III) Hexacyanoferrate(II). For the iron(II) hexacyanochromate(III) a thermal isomerization is known to occur at about 100 °C within a few hours.[18] Figure 4a shows that this isomerization occurs at room temperature when the hexacyanochromate(III) is reduced to hexacyanochromate(II). Iron(II) hexacyanochromate(III) is brick red, whereas chromium(III)

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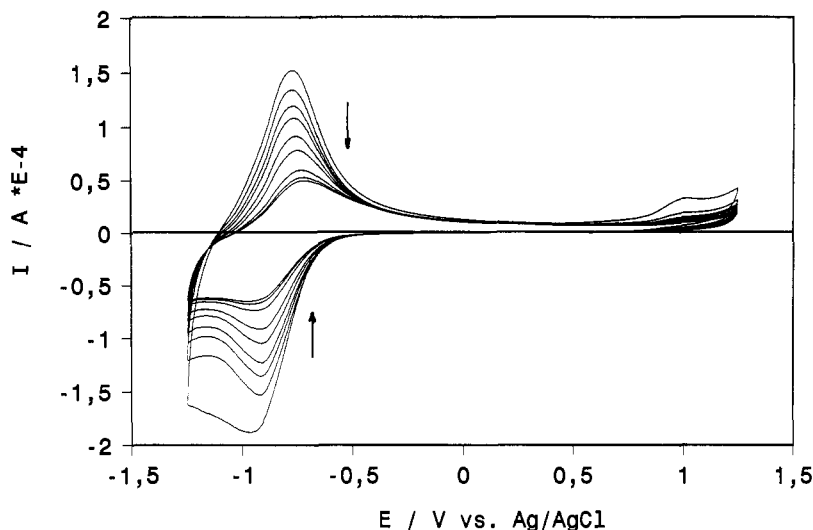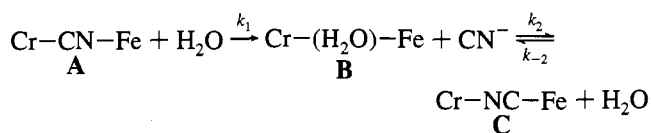
Figure 2. Cyclic voltammograms of chromium(II) hexacyanochromate(III) immobilized on the surface of a paraffin-impregnated graphite electrode. Electrolyte 0.1 M KCl, scan rate 0.1 V/s.

Table 1. Anodic and Cathodic Peak Potentials, Peak Separations, and Formal Potentials of Chromium(II) Hexacyanochromate(III) (Potentials in V vs Ag/Ag/Cl)

electrolyte, 0.1 mol/L	$E_{p,a}$	$E_{p,c}$	$\Delta E_{p,a,c}$	$E_f = (E_{p,a} + E_{p,c})/2$
LiNO₃	−0.835	−1.063	0.228	−0.949
NaNO₃	−0.761	−1.060	0.299	−0.910
KCl	−0.760	−0.978	0.218	−0.869
RbCl	−0.665	−0.912	0.247	−0.788
CsCl	−0.559	−0.873	0.314	−0.716

hexacyanoferrate(II) is green. This change of color can be observed by in situ light microscopy in a specially designed electrochemical cell, in which the graphite electrode is inserted from the bottom and the solution is covered with a thin glass plate above which the objective is situated. Figure 4b shows cyclic voltammograms of chromium(III) hexacyanoferrate(II), which was synthesized by thermal isomerization of iron(II) hexacyanochromate(III). It is identical with the final cyclic voltammogram of iron(II) hexacyanochromate(III) as well as with the cyclic voltammograms of chemically precipitated chromium(III) hexacyanoferrate(II) (see Figure 4c). The isomerization of iron(II) hexacyanochromate(III) is the result of the reduction of hexacyanochromate(III), which allows the labile hexacyanochromate(II) to be formed. This enables a fast exchange of the coordination sites of the cyanide ions in a way that iron becomes coordinated to carbon and chromium becomes coordinated to nitrogen. When this reaction occurs in the solid iron(II) hexacyanochromate(III), due to a finite reaction rate, an intermediate mixed coordinated iron and chromium is formed. Figure 5a shows the dependence of the anodic peak current of the hexacyanoferrate system on the time of cycling of the hexacyanochromate system. This plot is linear during an initial period of about 40 s (cf. Figure 5b). After that time the reaction rate decreases remarkably. Obviously, the reaction is of pseudo-zero-order within this initial period. The peak current measured in the first cycle can never be used for a kinetic evaluation, because it was observed here, as always with these polymeric cyanides, that the first cycle deviates more or less strongly from all following cycles. This is probably because the first cycle finds the compound in a form which has still to be converted to the electrochemical equilibrium form, which is the form of the compound which has intercalated the equilibrium amount of the electrolyte cation. This will not necessarily be the same form which was prepared by chemical synthesis. House and Bailar[20] have found for the thermal isomerization of iron(II) hexacyanochromate(III) a second-order reaction for cyanide,

which they interpreted as a result of a coupled flipping of two cyanide ions due to cis- or trans-influence. In our experiments, the isomerization occurs with hexacyanochromate-(II) but not with hexacyanochromate(III); it is not thermally initiated but is the result of labilization of cyanide ions. In the solid iron(II) hexacyanochromate(II) (the reduction product), which is immobilized on the electrode surface, the flipping of single cyanide ions can be the result of fast exchange reaction between cyanide and water in the coordination sphere of chromium(II). Thus, water is a reaction partner, and due to its high concentration, a zero-order reaction rate results for the initial period of reaction:

$$Cr-CN-Fe + H_2O \xrightarrow{k_1} Cr-(H_2O)-Fe + CN^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$$
$$\underset{A}{} \qquad \underset{B}{}$$
$$Cr-NC-Fe + H_2O$$
$$C$$

The exchange of a cyanide ion in the system Cr−CN−Fe by water can be viewed as an irreversible reaction because the backward reaction rate will be very small compared with all other reaction rates. When a cyanide ion joins the system Cr−(H₂O)−Fe, it will prefer the thermodynamically favoured position Cr−NC−Fe. The latter reaction can be reversible with a finite backward reaction rate K_{-2}. Thus, we can describe the reaction with the following set of equations:

$$d[C]/dt = k_2[B][CN^-] - k_{-2}[C][H_2O]$$

$$d[B]/dt = k_1[A][H_2O] - k_2[B][CN^-] + k_{-2}[C][H_2O]$$

According to the Bodenstein pseudo stationarity principle, it follows that d[B]/dt = 0, hence

$$d[C]/dt = k_2[B][CN^-] - k_{-2}[C][H_2O] = k_1[A][H_2O]$$

In the initial period of reaction the concentrations of both A and H₂O are almost constant, and d[C]/dt = k'. The reaction between iron(II) hexacyanochromate(II) and water is not a heterogeneous chemical reaction because the water is present in the interstitial space of the crystal lattice in high amounts. Every cube of the lattice (see Figure 1) houses six to seven molecules of water. Thus the situation is in principle the same as in a very concentrated solution where the dissolved ions form a rigid network through which the water molecules can diffuse. The concentrations [A], [B], [C], and [H₂O] refer to the number
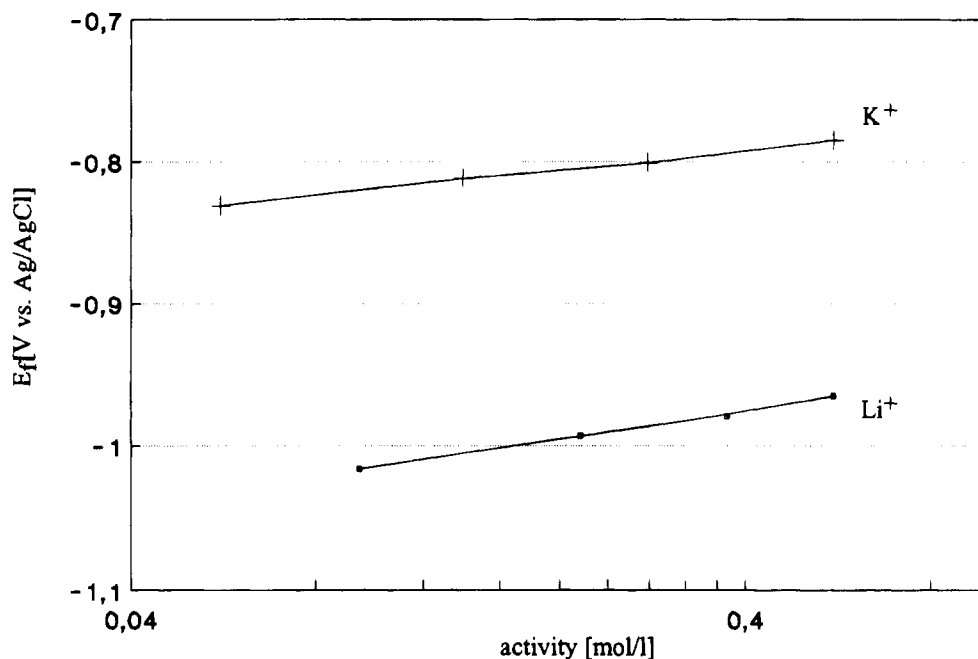
Figure 3. Plot of formal potentials $E_f = (E_c + E_a)/2$ of the Cr(II)/Cr(III) system of chromium(II) hexacyanochromate(III) as a function of the activity of potassium and lithium ions in the electrolyte. Activities were calculated according to Debye—Hückel theory. No additional electrolyte was added to buffer the ionic strength.

of moles of these compounds per volume of 1 mol of iron(II) hexacyanochromate(III). Since there is considerable uncertainty with respect to the exact value of the latter, we calculated with [C] and [A] in moles because this is measurable by coulometry. Therefore, the unit of k' is mol/s (or exactly, mol/s·v^*, if v^* is the molar volume). We determined k' in several experiments and obtained $k' = 4 \times 10^{-9}$ mol/s at 22 °C. For six experiments the span of results was $(2.9-5.0) \times 10^{-9}$ mol/s. The absolute amount of formed chromium(III) hexacyanoferrate(II) was determined by integration of the anodic voltammetric peak of the hexacyanoferrate system. The reaction rate was found to be independent of the scan rate within the limits of 50 and 500 mV/s. This is a strong indication that the isomerization is not influenced by the electrical field, but that the isomerization is a chemical followup reaction in relation to the electrochemical reaction. If the scan rate is further increased, the reduction peak of Cr(III) is fully obscured by the ascending end of the voltammogram but the anodic peak is still observable. In accordance with the proposed reaction mechanism, and also in accordance with the determined rate constant, the anodic peak current of the process $Cr(CN)_6^{4-} \rightarrow Cr(CN)_6^{3-} + e^-$ becomes constant at scan rates above 5 V/s in cyclic voltammetry. Because the voltammograms are rather drawn out at this scan rate, an exact evaluation of them is not possible. Using the theory of irreversible follow-up reaction of the first order,[23] calculating the amount of reacting chromium from the voltammmogram, one can estimate k' to be on the order of 10^{-9} mol/s. This is in agreement with the above-given calculation. The chemical isomerization reaction is considerable slower than the electrochemical reduction of chromium(III) sites and the associated potassium intercalation. Therefore, the kinetics of the electrochemical reduction, i.e. the diffusion regime of electrons and K^+, cannot influence the kinetics of isomerization. The observed pseudo-zero-order reaction rate is observed over a surprising long period of the overall reaction time, i.e. within half of the entire reaction time. After that period the reaction rate changes rapidly from zero-order via first-order until the reaction fully stops. This behavior can be explained by the unusual high concentration of both reactants in the solid material.

In accordance with the proposed mechanism, the isomerization does not occur if the only species being oxidized and

reduced during cyclic voltammetry of iron(II) hexacyanochromate(III) is nitrogen-coordinated iron, i.e. in the potential range -0.6 to $+1.4$ V (cf. Figure 6a). In this experiment a continuous decrease of peak currents is observed, which is due to a slow dissolution of the immobilized compound. This dissolution can only lead to dissolved hexacyanochromate(III) and iron aquo complexes, because of the kinetic inertness of the chromium-(III). The observed iron(II)—iron(III) couple of iron hexacyanochromate is practically identical with the couple which occurs in a solution of iron aquo complexes (cf. Figure 6b), and, is far away from the couple of nitrogen coordinated iron in Prussian blue. Additionally, evidence for the formation of an iron aquo complex during dissolution of the iron(II) hexacyanochromate(III) comes from the dependence of the formal potential of the iron system on activity of alkali metal ions. This formal potential is fully independent of the alkali metal activities, because the electrode reaction does not occur with the solid compound and intercalation can not play a role.

When the iron(II) hexacyanochromate(III) is cycled in a potential range such that chromium(III) is reduced to chromium-(II), the final product is insoluble chromium(III) hexacyanoferrate(II). The iron system exhibits the typical behaviour for a coupled intercalation of alkali metal ions. The experimental plots of formal potential vs metal alkali ion activities (Figure 7) supports the following equation:

$$KCr^{III}[Fe^{II}(CN)_6]\cdot 13.5H_2O \rightarrow$$
$$Cr^{III}[Fe^{III}(CN)_6]\cdot 13.5H_2O + e^- + K^+$$
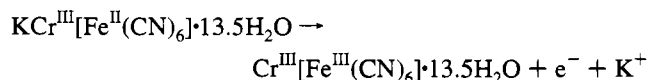
The slope of these graphs is 58 mV for potassium and 56.5 mV for lithium.

During the cyclic voltammetry of iron(II) hexacyanochromate(III), it was observed that, intermediately, cathodic peaks (at -0.11 and at -0.6 V) and an anodic peak ($E_p^{ox} = -0.24$ V) occur. They increase during the first scans and later decrease until they fully vanish. Their overall intensity is small compared to the other voltammetric signals. The same peaks can be obtained when chromium(II) hexacyanochromate(III) is cycled in an electrolyte containing dissolved iron(II) ions (cf. Figure 8). It is assumed that at these peaks the reduction and oxidation
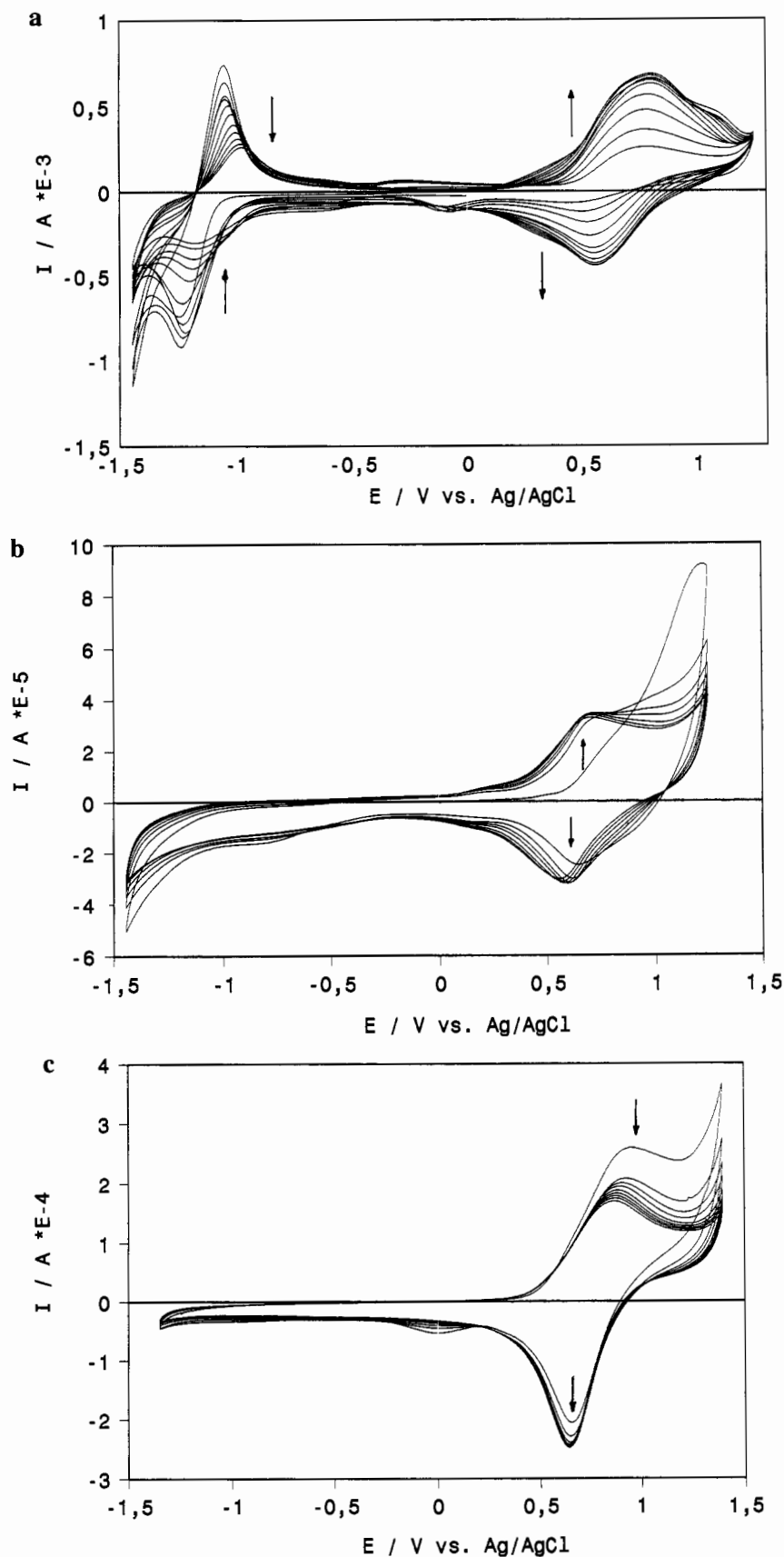
Figure 4. Cyclic voltammograms: (a) iron(II) hexacyanochromate(III) immobilized on the surface of a paraffin impregnated graphite electrode (electrolyte 0.1 M KCl, scan rate 0.1 V/s); (b) chromium(III) hexacyanoferrate(II) obtained by thermal isomerization of iron(II) hexacyanochromate-(III) for 3 h at 90 °C (experimental conditions for CV as in part a); (c) chromium(III) hexacyanoferrate(II) obtained by precipitation from a solution of CrCl$_2$ and K$_4$[Fe(CN)$_6$] (experimental conditions for CV as in part a).

of iron occurs which is partly coordinated to nitrogen and partly coordinated to carbon. In the case of chromium(II) hexacy-anochromate(III) the reaction with dissolved iron(II) ions does not lead to chromium(III) hexacyanoferrate(II), but it stops at

the mixed coordination state. When the chromium(III) in chromium(II) hexacyanochromate(III) is reduced to chromium-(II), it can be substituted by dissolved iron(II). Then the iron has nitrogen coordination and an isomerization can occur to
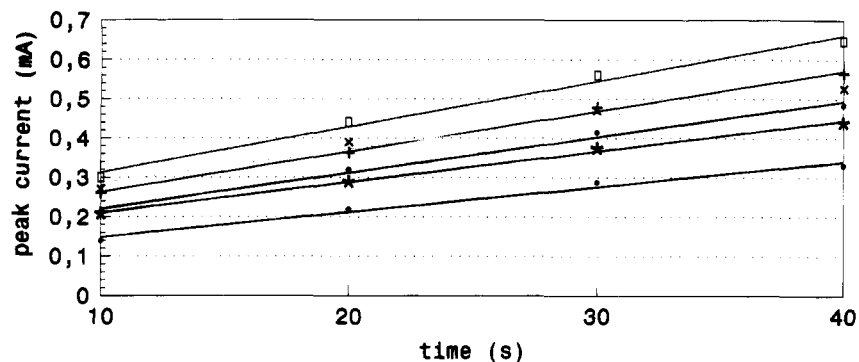
Figure 5. Dependence of anodic peak current of the hexacyanoferrate system on time during the isomerization of iron(II) hexacyanochromate(III) to chromium(III) hexacyanoferrate(II). Conditions: electrolyte 0.1 M KCl; scan rate 0.1 V/s. The six plots represent six separate experiments.
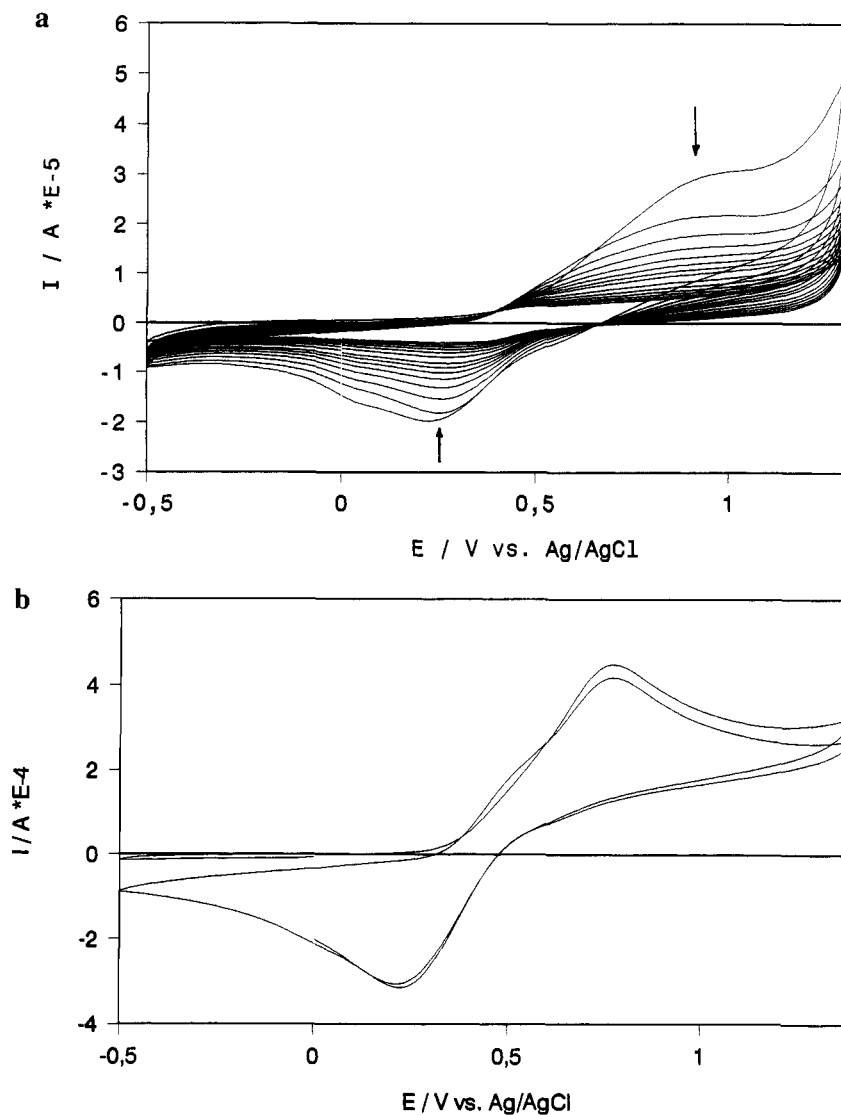

Figure 6. Cyclic voltammograms: (a) iron(II) hexacyanochromate(III) in the restricted potential range of -0.5 to 1.3 V vs Ag/AgCl (electrolyte 0.1 M KCl, scan rate 0.1 V/s); (b) 0.1 M iron(II) solution in 0.1 M KCl (scan rate 0.1 V/s). Electrode: paraffin-impregnated graphite electrode.

form chromium(III) hexacyanoferrate(II). It is very probable that this substitution is a surface-confined process and that therefore the extent of this substitution is limited, leaving the mixed coordinated iron as the final reaction product.

Conclusion

In this study it has been shown that an electrochemical reduction of the hexacyanochromate(III) subunits of polymeric metal hexacyanochromates(III) can prompt lattice reconstructions via substitution or isomerization reactions. The reason

for these reactions is the kinetic lability of the hexacyanochromate(II) subunits, in which the cyanide ions are free to react with other metal ions of the adjacent solution, as in case of substitution reactions, or, as a result of ligand exchange reactions they may change the metal partners with which they are coordinated in the framework of the polymer, as is the case of isomerization. In the light of our results it is not difficult to understand why Gao[24] obtained a film of chromium(III) hexacyanoferrate(II) only if he reduced the chromium(III) of a CrCl$_3$ solution to chromium(II). Only chromium(II) can
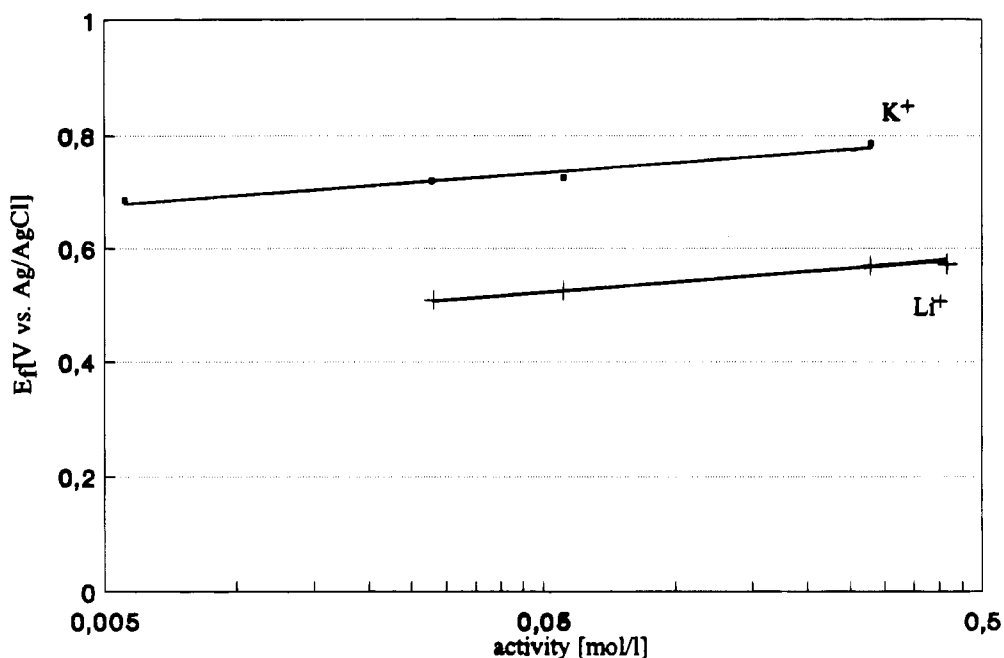
Figure 7. Dependence of formal potentials of the hexacyanoferrate system of chromium(III) hexacyanoferrate(II) on activity of potassium and lithium ions.
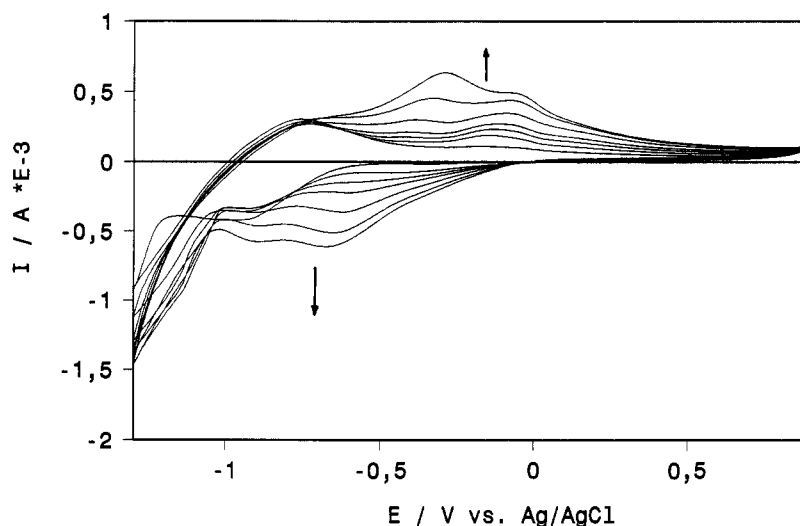

Figure 8. Cyclic voltammograms of chromium(II) hexacyanochromate(III) in a 0.01 M iron(II) solution in 0.1 M KCl. Scan rate: 0.1 V/s.

substitute the coordinated water in a reasonable, short time for the nitrogen coordination site of the hexacyanoferrate(II) ions to form the insoluble chromium hexacyanoferrate. Thus it is not a codeposition of chromium, as described by Gao, but the reduction to dissolved labile chromium(II) ions which is responsible for the film formation. The so-called "break-in" effect discussed by Gao, i.e. the change of voltammetric response after formation of the film when for the first time cycled in NaCl, is nothing but the electrochemically equilibration of the complex solid cyanide with the intercalating cations Na^+. This initial change in response can always be observed when a Prussian blue analogue compound is for the first time cycled in a solution which is different from the solution in which the compound was synthesized, regardless of whether this was done chemically or electrochemically.

The electrochemically induced lattice reconstruction which we recently observed in case of Prussian blue in cadmium solutions[28] can also be rationalized in terms of labilization of ligands by electrochemical reactions. Also in the case of iron-

(II) and iron(III) it is well-known that the iron(II) complexes have a far higher rate of ligand exchange than the corresponding iron(III) complexes. Thus, a reduction of iron(III) to iron(II) can prompt fast subsequent ligand exchange reactions which lead to a reconstruction of the solid iron compound on the surface of the electrode. In the last case, it is the formation of cadmium hexacyanoferrate by reduction—oxidation cycles of Prussian blue in solutions containing cadmium ions.

The described electrochemically induced reactions of solid compounds are believed to be significant also with respect to chemical oxidations and reductions of solid compounds. Thus, it can be expected that Prussian blue which, for the sake of immobilization, is deliberately formed from cyanide ions in contaminated soil, can undergo reactions with mobile metal ions under anaerobic conditions.

(28) Dostal, A.; Meyer, B.; Scholz, F.; Schröder, U.; Bond, A. M.; Marken, F.; Shaw, Sh. J. *J. Phys. Chem.*, in press.