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Electrochemical Study of Microcrystalline Solid Prussian Blue Particles Mechanically Attached to Graphite and Gold Electrodes: Electrochemically Induced Lattice Reconstruction

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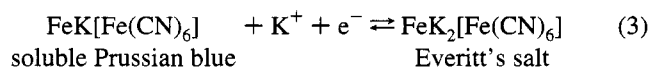
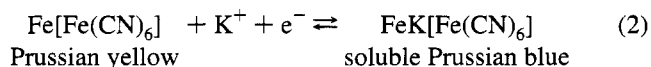
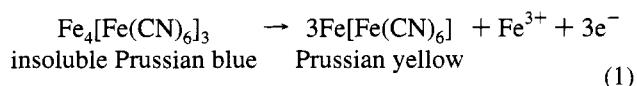
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The voltammetric behavior of solid Prussian blue mechanically attached to graphite, glassy carbon, or gold electrodes as an array of microscopically small particles is extremely well defined when the electrode is placed in aqueous media containing suitable electrolytes. Electron microscopy, electron microprobe analysis, and in situ electrochemical quartz crystal microbalance techniques have been used in addition to the voltammetric data, to characterize the redox and ion-transport processes of solids attached to the electrode. The results compare favorably with published studies based on electrogenerated films, although, as expected, the scan rate dependence is different when solid particles are used. Ion-exchange reactions accompanying redox processes have been examined in K^+ and Cd^{2+} containing aqueous electrolyte solutions, and two types of ion exchange can be distinguished. These are based on replacement of interstitial positions and replacement of lattice positions. An overall reaction scheme based on electrochemically initiated lattice reconstruction is presented to explain the generation of cadmium hexacyanoferrate when oxidation or reduction of Prussian blue occurs at the electrode–solid– K^+/Cd^{2+} containing aqueous electrolyte interface.

Introduction

Prussian blue and related metal cyanometalate compounds belong to a family of polymeric complexes that have been studied extensively for many years.¹ Interesting properties which have led to continuous interest in these compounds include the nondaltonian stoichiometry and ionic as well as electrical conductivity through zeolite molecular pores.

The structure of solid Prussian blue has been determined by both X-ray² and neutron diffraction³ methods and may be described in terms of a rock salt type lattice with a Fe^{3+} and $Fe(CN)_6^{4-}$ framework filled with approximately 14–16 water molecules per unit cell. Lattice defects in the forms of vacancies and interstitial sites initially led to contradicting results concerning the description of the solid as either “soluble” Prussian blue, $FeK[Fe(CN)_6]$, or “insoluble” Prussian blue, $Fe_4[Fe(CN)_6]_3$. This apparent anomaly was resolved by the work of Rosseinsky et al.⁴ and Feldman et al.,⁵ who suggested that a structural change occurs upon electrochemical oxidation of “insoluble” Prussian blue (eq 1) and that on reduction of the oxidized form in



potassium-containing electrolyte solution, potassium insertion

occurs to give “soluble” Prussian blue (eq 2) or Everitt's salt (eq 3).

The volume accessible after potassium expulsion seems to be occupied by water molecules entering the lattice, although a minor change in unit-cell dimension has also been reported.^{4c} Other investigations related to the chemistry summarized by eqs 1–3 have been reported using UV/vis,⁶ photothermal,⁷ electroreflectance,⁸ Mössbauer,⁹ and conductivity measurements.¹⁰

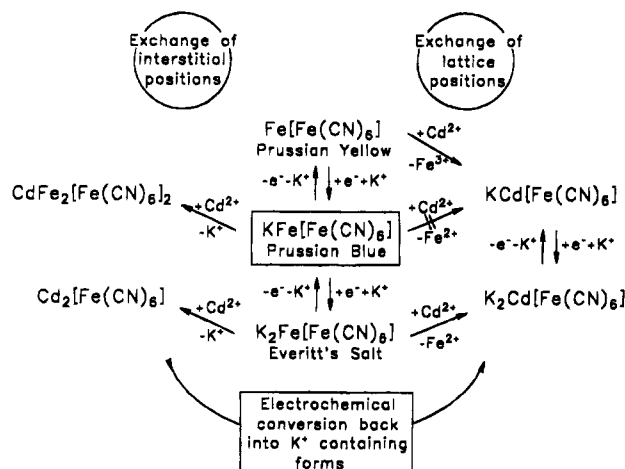
In view of the extensive redox chemistry associated with Prussian blue and related compounds and several unusual properties it would be expected that detailed electrochemical investigations would be available. This is indeed the case. Interest in the electrochromic behavior,¹¹ electrocatalytic properties,¹² photoelectrochemical behavior,¹³ and the development of new ion- and electron-conducting materials and methods for their characterization¹⁴ have provided a focus for these works.

In previous electrochemical studies, films of Prussian blue¹⁵ generally are prepared by deposition on the surface of metal or semiconductor disks,¹⁶ interdigitated arrays,¹⁷ and microelectrodes.¹⁸ In contrast, in the present study, Prussian blue is mechanically attached to carbon electrodes using a technique initially developed by Scholz and co-workers.¹⁹ The new method provides an array of microcrystalline particles on the electrode surface rather than the traditional thin film and because of this feature a large range of solid and insoluble materials may be investigated by electrochemical methods.²⁰ Of particular interest in the present work was the comparison of data obtained by the new approach relative to that when a film is produced, particularly with respect to transport of ions within the microcrystals. For this purpose electrochemical measurements coupled with quartz crystal microbalance experiments are reported and a range of Prussian blue samples are investigated in potassium-containing aqueous electrolytes. Finally, voltammetric studies,

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SCHEME 1. Ion-Exchange Process Accompanying Redox Switching of Prussian Blue Particles in Aqueous Electrolyte Environment Containing K^+ and Cd^{2+} Electrolyte Cations



which demonstrate that lattice reconstruction (Scheme 1) may be achieved rapidly via electrochemical methods when cadmium salts are added into the electrolyte, are described.

Experimental Section

Preparation. All chemical operations were carried out using deionized water and analytical or reagent grade chemicals. Prussian blue was prepared in five different forms using the general procedure described below. All samples were obtained as insoluble dark blue powders by using an excess of the iron cation.

Samples of Prussian blue were prepared by dropwise addition of a solution of the hexacyanoferrate salt (20 mmol in 100 mL of water) into a stirred solution of the iron solution (25 mmol in 200 mL of 0.1 M aqueous acid). The precipitate was filtered off and washed with water (5×100 mL). The solid was then dried for 15 h in vacuo (0.1 mbar) at ambient temperature and stored in air. Prussian blue I was prepared from $FeCl_3 \cdot 6H_2O$ in hydrochloric acid and $K_4[Fe(CN)_6]$, Prussian blue II from $Fe(ClO_4)_3$ in perchloric acid and $K_4[Fe(CN)_6]$, Prussian blue III from $Fe_2(SO_4)_3$ in sulfuric acid, and $K_4[Fe(CN)_6]$, Prussian blue IV from $FeCl_3 \cdot 6H_2O$ in hydrochloric acid and $H_4[Fe(CN)_6]$ (obtained by ion exchange on a column packed with Amberlite IR 120 resin), and Prussian blue V from $Fe(SO_4) \cdot 7H_2O$ in sulfuric acid and $K_3[Fe(CN)_6]$. Preparation of cadmium hexacyanoferrate(II) and (III) was performed according to the literature method²¹ by addition of a $CdSO_4$ solution to a solution of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$, respectively.

Electron Microscopy and Electron Microprobe Analysis. For scanning electron microscopy measurements an ETEC Autoscan system (20 kV accelerator voltage) was used. Samples were prepared by cutting off a slice (ca. 1 mm thick) from the paraffin-impregnated graphite rod used as the working electrode and attaching it to a metal holder. The samples obtained in this way were then gold plated in a Balzers sputter coating unit. For electron microprobe analysis samples had to be attached to a graphite bead and were analyzed on a scanning electron microscope (JSM 840) coupled to a TN 5500 X-ray analyzer at an acceleration voltage of 15 kV with a probe monitor current ranging from 0.3 to 0.6 nA, a detector dead time of 25–35%, and a collection time of 100 s.

Voltammetry. Unless otherwise specified, all reagents were of analytical or electrochemical grade purity. Millipore water was used for the preparation of the electrolyte solutions. The reference electrode was $Ag/AgCl$ (3 M NaCl) and the auxiliary

electrode was a platinum sheet. Voltammetric experiments were performed at 20 ± 2 °C with either a BAS 100 A electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN) or an AUTOLAB (Eco-Chemie Utrecht, Netherlands) instrument used in conjunction with an Metrohm VA 663 electrode stand (Metrohm, Switzerland) and a 386 personal computer. All solutions were degassed with high-purity nitrogen for 15 min prior to electrochemical measurements.

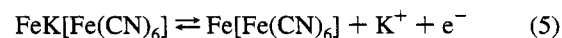
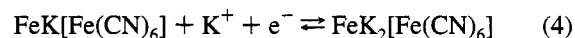
Electrodes used in this study are (i) paraffin-impregnated graphite electrodes prepared from graphite rods sold commercially for spectrographic analysis (VEB Elektrokohle Lichtenberg, Germany), (ii) basal plane pyrolytic graphite electrodes (5 mm diameter fitted into a Teflon holder), (iii) glassy carbon electrodes (3 mm diameter), and (iv) gold electrodes (1 mm diameter). Impregnation of graphite electrodes with molten paraffin (mp 70 °C) was achieved as described elsewhere.¹⁹ Solid samples were attached as follows: Sample amounts of 1–3 mg of Prussian blue powder were placed on coarse grade filter paper and the electrode was gently rubbed over the material causing some of the compound to adhere to the electrode surface. The electrode surface of graphite electrodes can be renewed after each experiment by removing the electrode surface with a razor blade or more simply by vigorously rubbing the electrode surface on clean filter paper.

Electrochemical Quartz Crystal Microbalance Experiments. An ELCHEMA electrochemical quartz crystal Nanobalance system (Potsdam, NY) was used with 10 MHz AT-cut quartz crystals (Bright Star Crystal Pty. Ltd., Vermont, Vic 3133, Australia) coated with 5 mm diameter gold electrodes. The method developed by Deakin and Melroy²² was employed to calibrate the quartz crystal microbalance using a 0.01 M $CuSO_4$ solution in 0.1 M HNO_3 . Prussian blue I applied to the gold electrode by attaching a small amount of solid with a cotton bud achieved a uniform distribution of the solid and was employed for all microbalance experiments. The electrochemical experiments were performed in a three-electrode cell using Pt wire auxiliary and $Ag/AgCl$ (saturated KCl) reference electrodes.

Results

All previous studies on the electrochemical properties of Prussian blue used films deposited onto the electrode surface.¹⁵ These films are readily prepared. However, spectroscopic and analytical investigations are limited because of the need to use an in situ deposition method. Mechanical transfer of microcrystalline solids leads to new possibilities for the investigation of the redox behavior of solid Prussian blue.

A typical cyclic voltammogram obtained when a paraffin-impregnated graphite electrode containing mechanically attached Prussian blue is placed in aqueous 0.1 M KNO_3 is shown in Figure 1a. Two well-defined processes are observed consistent with the known behavior of Prussian blue films. Signals for the reduction process which correspond to the reaction given in eq 4 and which occur at about 165 mV vs $Ag/AgCl$ are



sharper than for processes associated with the oxidation response (eq 5) which occur at about 830 mV vs $Ag/AgCl$.

During the first 20 continuous cycles of the potential a pronounced decay in peak currents is observed with each cycle. Deposition of a Prussian blue film onto a paraffin impregnated carbon electrode surface is possible using the procedure by Itaya et al.^{15a} which requires the cycling of the electrode potential between 1100 mV and 500 mV vs $Ag/AgCl$, in a solution

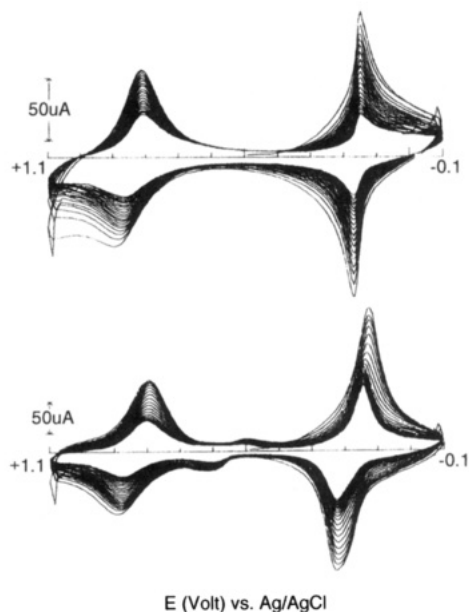


Figure 1. Cyclic voltammograms of (a) Prussian blue particles mechanically attached to a paraffin-impregnated graphite electrode and (b) a Prussian blue film electrochemically deposited (from FeCl_3 0.02 M/ $\text{K}_3[\text{Fe}(\text{CN})_6]$ 0.02 M in hydrochloric acid at pH 2 onto a paraffin-impregnated graphite electrode and rinsed) immersed in 0.1 M KNO_3 at 22 °C and cycled with a scan rate of 20 mV s^{-1} over 20 potential cycles.

containing FeCl_3 and $\text{K}_3[\text{Fe}(\text{CN})_6]$ in hydrochloric acid at pH 2. If the modified electrode is rinsed and transferred into KNO_3 solution (0.1 M), then the voltammogram shown in Figure 1b is obtained. The characteristic signals for the reduction and the oxidation processes are also observed from this film and again signal intensity also decays with cycling the potential. The major differences are that the measured currents are higher due to the larger amount of compound attached to the electrode and additional signals discussed by Vicente et al.²³ are observed.

An investigation of the electrode surface by scanning electron microscopy before mechanical attachment of Prussian blue reveals the structure of the paraffin-impregnated graphite electrode (Figure 2a). The gray areas are likely to be paraffin, although a film of graphite could be present on the surface. Examination of the surface after mechanical attachment of Prussian blue (Figure 2b) shows that small agglomerates of Prussian blue I (diameter $< 1 \mu\text{m}$) adhere mainly to the harder carbon ridges. They are observed as white traces on the dark pattern. The roughness of the carbon surface is ideal for mechanical transfer of microcrystalline solid onto the surface.

Ideally, the electrode material should have only a minimal influence on the faradaic aspects of the electrochemistry of the solids, although changes in background current are to be expected. The faradaic response for mechanically attached Prussian blue was in fact found to be indistinguishable at paraffin-impregnated graphite, basal plane pyrolytic graphite, glassy carbon, and gold electrodes. However, the adherence of Prussian blue is superior at the graphite electrodes, and the mechanical transfer to gold or glassy carbon electrodes requires a roughening of the surface which irreversibly damages the electrode surface. Furthermore, regeneration of the surface after measurements is not readily achieved at these surfaces as is the case with graphite.

To investigate any possible influence of the preparative method on structural or compositional properties and therefore on the voltammetry, five samples of Prussian blue were prepared using different counterions in the solution from which the material is precipitated. The Prussian blue materials prepared by the different methods were characterized by electron micro-

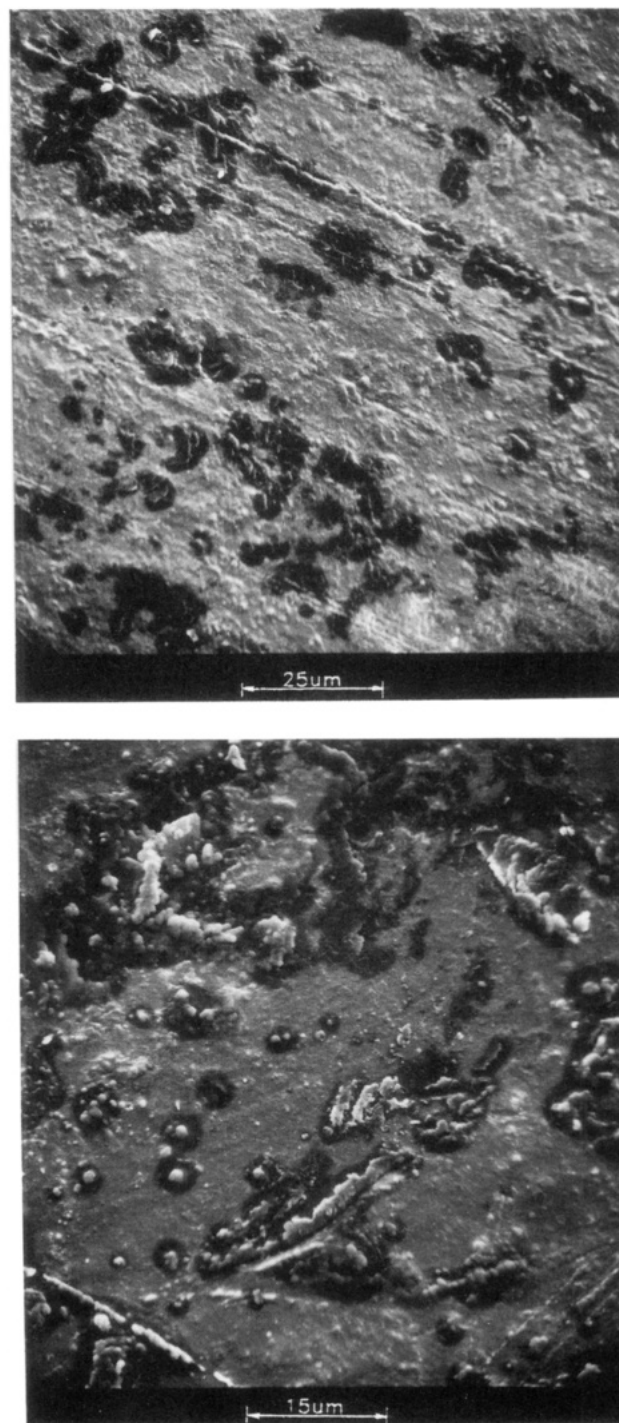


Figure 2. (a, top) SEM micrograph of a paraffin impregnated graphite electrode. (b, bottom) SEM micrograph of Prussian blue I mechanically attached to a paraffin-impregnated graphite electrode.

probe analysis in conjunction with electrochemical measurements. Prussian blue I, prepared in presence of chloride anions and examined by electron microprobe analysis, clearly reveals the presence of iron and potassium but no chloride. Thus, it can be concluded that chloride is not incorporated into the lattice. In Figure 3a–c, the variation of the potassium X-ray signal after different forms of electrochemical treatment of microcrystalline Prussian blue prepared by method I is shown when the electrode is placed in 0.1 M KNO_3 . In contrast, samples of Prussian blue II (Figure 3d) and III (Figure 3e) give additional X-ray analysis signals for chlorine and sulfur which have to be interpreted in terms of incorporation or coprecipitation of perchlorate and sulfate into the lattice. Prussian blue IV, prepared from $\text{H}_4[\text{Fe}(\text{CN})_6]$, as expected gives no signal for

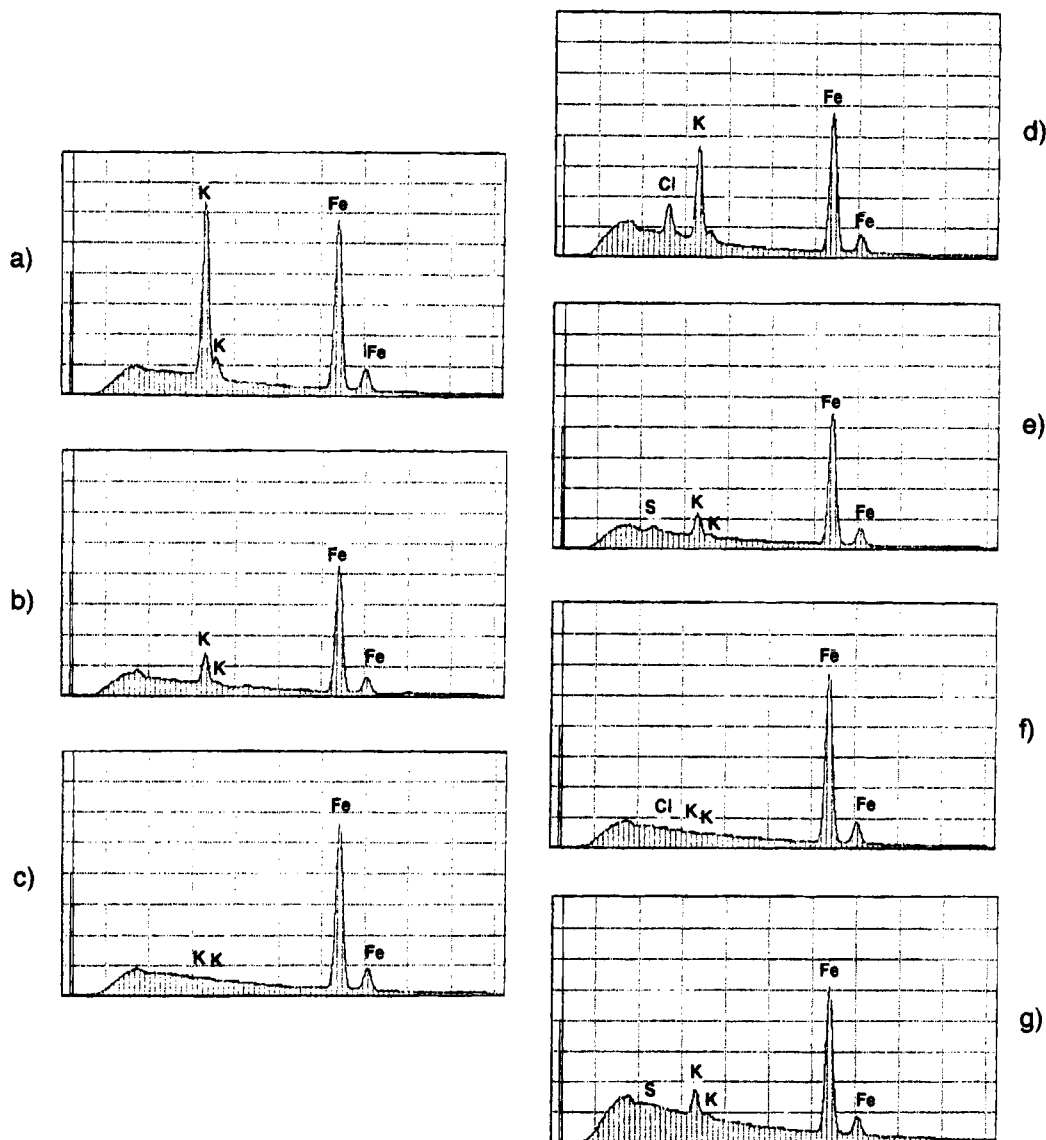


Figure 3. Typical examples for single particle electron microprobe analyses of various Prussian blue samples mechanically attached to a paraffin-impregnated graphite electrode: (a) Prussian blue I electrochemically reduced in 0.1 M KNO_3 at -100 mV vs Ag/AgCl for 5 min, (b) without treatment, and (c) electrochemically oxidized in 0.1 M KNO_3 at $+1100$ mV vs Ag/AgCl for 5 min; (d) Prussian blue II containing traces of ClO_4^- ; (e) Prussian blue III containing traces of SO_4^{2-} ; (f) Prussian blue IV prepared without K^+ ; (g) Turnbells blue.

potassium (Figure 3f), and the sample of Turnbells blue V gives only signals for iron and potassium (Figure 3g). It needs to be noted that changes in the precipitation or drying procedure may lead to gross changes in the composition and in electrochemical behavior.

The electrochemical behavior of all Prussian blue samples, except Prussian blue IV, are very similar. Obviously slight changes in composition and the type of anionic guest species has no great effect on electrochemical properties. In Figure 1 the potential was cycled over wide potential ranges allowing both the reduction and oxidation of Prussian blue to be detected. In Figure 4, the first 10 potential cycles for oxidation and for reduction of Prussian blue I attached to a paraffin-impregnated carbon electrode (0.1 M KNO_3) are shown when the potential is cycled only over the oxidation region (Figure 4a) and the reduction region (Figure 4b). This different potential cycling format modifies the response in the sense that the reduction process is now stable and only a progressive decrease in signal intensity can be observed for the oxidative Prussian blue—Prussian yellow couple (Figure 4b). This loss of current intensity can be attributed to a loss of electroactive compound presumably resulting from the proposed solubilisation.²³

A significant change in electrochemical behavior is observed for Prussian blue IV. In this case no potassium cations are initially available for expulsion from the solid and the observed voltammetric oxidative response in the first cycle is broad and ill defined. However, in the second and subsequent potential cycles a peak can be observed and subsequently two responses develop (Figure 4c). The transformation has been described in literature as a conversion from “insoluble” to “soluble” forms of Prussian blue.^{4,5} In contrast electrochemical reduction prior to the oxidation leads to a well-defined process even in the first cycle. Thus, electrochemical oxidation as well as reduction of Prussian blue IV appears to cause a change in composition which allows potassium to intercalate. For the oxidation process, this structural change readily can be understood in terms of expulsion of excess iron and electroinsertion of potassium into the lattice. The nature of the reduction process will be elucidated on the basis of additional experiments described later.

Since the reduction response, when obtained on its own, is stable even after prolonged cycling (Figure 4b), the dependence of peak currents, areas, and potentials on scan rate can be analysed. A plot of $\log(\text{peak current})$ vs $\log(\text{scan rate})$ for cyclic voltammograms shown in Figure 5 exhibits a slope which

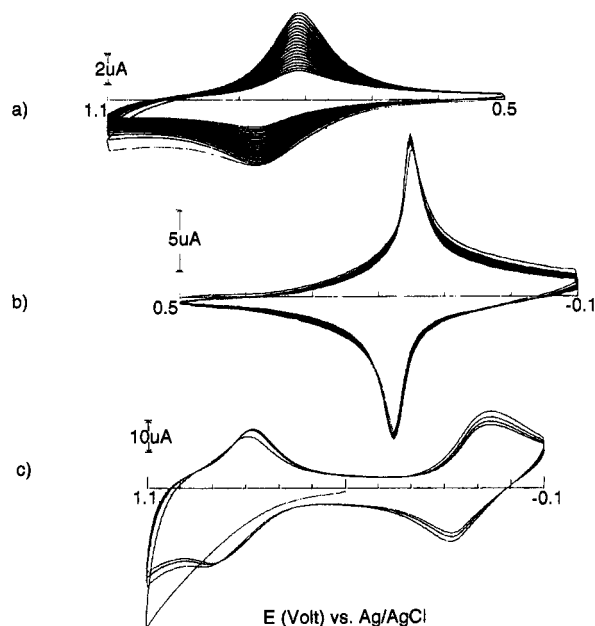


Figure 4. Cyclic voltammograms of (a) Prussian blue I mechanically attached to a paraffin-impregnated graphite electrode and immersed in 0.1 M KNO_3 at 22 °C using a potential range of 500–1100 mV vs Ag/AgCl and a scan rate of 20 mV s^{-1} over 20 cycles, (b) using a potential range of –100 to 500 mV vs Ag/AgCl and a scan rate of 20 mV s^{-1} over 20 cycles, (c) and of Prussian blue IV under the same conditions using a scan rate of 200 mV s^{-1} .

changes from 0.6 at high scan rate to about 0.9 at low scan rates. However, the charge determined by integration of the area under the peak exhibits only a minor decrease with increasing scan rate. This latter result is consistent with almost complete conversion of electroactive material present. A plot of peak current vs peak potential for the Prussian blue–Everitt's salt reduction process is linear (Figure 5d) at high scan rates. The "uncompensated resistance" calculated from the slope increases at lower coverage as shown in Figure 5d. After completion of the first experiment (A), approximately half of the electroactive material was removed with a razor blade and the second data set (B) obtained. After further removal, a third data set (C) was obtained. With loss of electroactive material, the resistance increases. The situation may be compared to resistors switched in parallel, although whether this resistance is caused by a process in the particle²⁴ or whether it is caused by the electrolyte solution cannot be determined from the above set of experiments. The peak potentials of voltammetric responses shift 60 mV/decade change in the K^+ concentration, corresponding to the known Nernstian shift for Prussian blue films.¹ Furthermore, the "uncompensated resistance effect" decreases in magnitude with increasing concentration of K^+ , indicating that the transport of ions in the solution phase may be associated with this effect.

Quartz Crystal Microbalance. A new and very valuable method to investigate electrode processes which are accompanied by mass changes at the electrode–solution interface is the measurement of changes in resonance frequency of a quartz crystal used as an electrode.²⁵ The method has been extensively used for polymer films and adsorbed species and recently for solid microcrystalline particles.²⁶ Here we compare data obtained for Prussian blue I applied to the gold electrode deposited on 10 MHz AT-cut quartz crystals with results obtained for Prussian blue films.⁵ Figure 6b illustrates the mass changes of a Prussian blue modified electrode during a cyclic voltammogram in 0.1 M KNO_3 using a scan rate of 50 mV s^{-1} . The reduction process is accompanied by a simultaneous increase in mass, whereas upon reoxidation there is a reversible

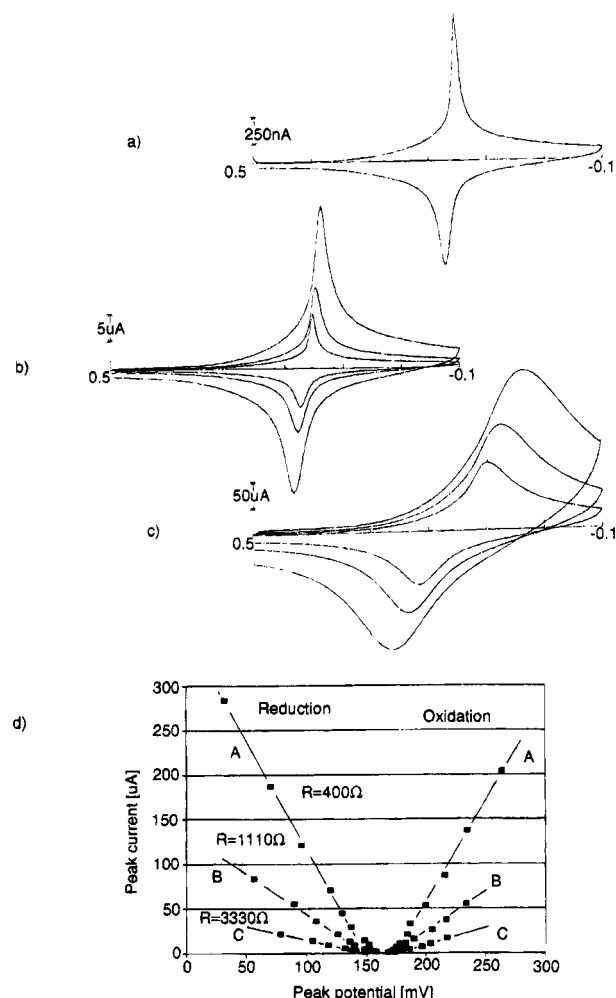


Figure 5. (a) Cyclic voltammogram for Prussian blue I mechanically attached to a paraffin-impregnated graphite electrode and placed in 0.1 M KNO_3 solution at 22 °C using a scan rate of 1 mV s^{-1} . (b) Cyclic voltammograms for Prussian blue I under the same conditions using 10, 20, and 50 mV s^{-1} . (c) Cyclic voltammograms under the same conditions using 500, 1000, and 2000 mV s^{-1} . (d) Plot of peak currents vs peak potentials for the reduction process in cyclic voltammograms of Prussian blue I under conditions described above using scan rates ranging from 1 to 2000 mV s^{-1} . The plot shows three consecutive experiments with removal of approximately half of the electroactive material between them.

decrease in mass. The uptake and expulsion of a potassium cation would require a mass change per charge unit of 39.4 g mol^{-1} but the obtained results averaged over six experiments on different crystals are 22.3 g mol^{-1} upon reduction and 22.9 g mol^{-1} upon oxidation which compares well with results obtained by Feldman et al.⁵ for a film of Prussian blue (reduction 22.3 g mol^{-1} , oxidation 23.5 g mol^{-1}). The values have been interpreted in terms of expulsion of water molecules upon uptake of potassium cations.

Electrochemically Induced Lattice Reconstruction with Cadmium Cations. The influence of redox inert supporting electrolytes on the electrochemical behavior of thin films of Prussian blue has been studied by many authors, although the effect of added salts in the electrolyte solution has only recently been reported.²⁷ In Figure 7, the change of voltammetric behavior of microcrystalline Prussian blue I mechanically attached to a paraffin-impregnated graphite electrode and immersed in aqueous solution containing 0.1 M KNO_3 and 0.1 M $\text{Cd}(\text{NO}_3)_2$ can be followed (Figure 7a). Over 20 cycles of the potential in this cadmium-containing electrolyte, a new redox couple develops and the original two redox couples associated with the reduction and oxidation process become smaller. The

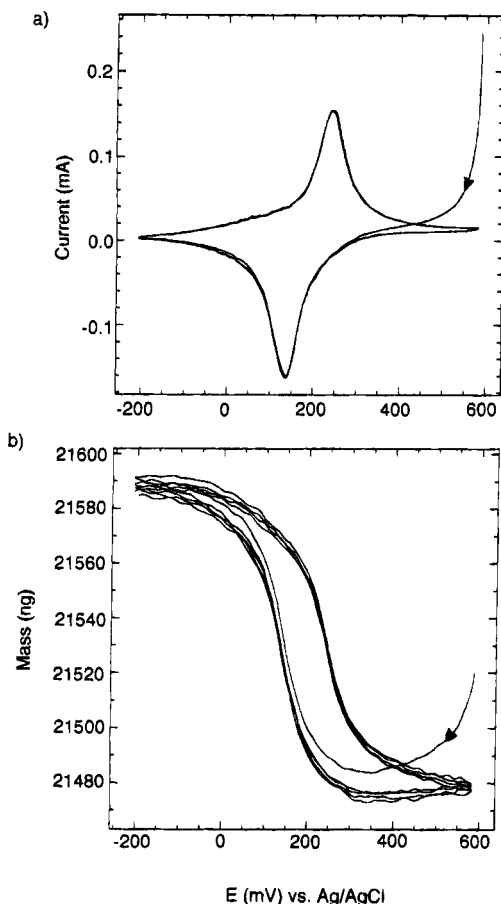


Figure 6. Simultaneous electrochemical quartz crystal microbalance measurement. (a) Cyclic voltammogram for Prussian blue I mechanically attached to a gold electrode (coated on a Quartz crystal) and placed in 0.1 M aqueous KNO_3 solution at 22 °C using a scan rate of 50 mV s^{-1} and (b) mass change accompanying the reduction and reoxidation of Prussian blue as monitored by the quartz crystal microbalance.

peak height for the Prussian blue reduction process at 150 mV vs Ag/AgCl decreases more rapidly than the peak height corresponding to the oxidation of the low-spin hexacyanoferrate iron at about 860 mV vs Ag/AgCl. The new redox couple can be identified as resulting from formation of cadmium hexacyanoferrate by comparison of the voltammetry with a synthetically prepared sample (Figure 7b). The elemental composition as monitored by the electron microprobe analysis confirms via comparison to a synthetically prepared sample of cadmium hexacyanoferrate(III) (Figure 8a) that partial conversion (Figure 8b) of Prussian blue to $\text{K}_2\text{Cd}[\text{Fe}(\text{CN})_6]$ occurs.

The peak height for both the electrochemically generated and the synthetically prepared cadmium compound are stable upon voltammetric cycling provided sufficient cadmium is present in solution. If the electrode, placed in a 0.1 M $\text{Cd}(\text{NO}_3)_2$ solution, is transferred to a 0.1 M KNO_3 electrolyte solution, the electrochemically generated as well as the synthetic cadmium hexacyanoferrate response decreases with each cycle (Figure 7b). The shape of the first cycle of the voltammogram of cadmium hexacyanoferrate(II) (Figure 7c) may be attributed to a change in composition by loss of Cd^{2+} cations from interstitial lattice positions as is the case for Fe^{3+} cations when "insoluble" Prussian blue is converted to "soluble" Prussian blue. The cadmium hexacyanoferrate(III) compound prepared from ferricyanide does not show this behavior (Figure 7b) presumably because sites for potassium uptake are readily available.

Ion-Exchange Reactions in the Prussian Blue Lattice. An important aspect of solid-state electrochemistry is the role of ion-transport processes accompanying the electron-transfer

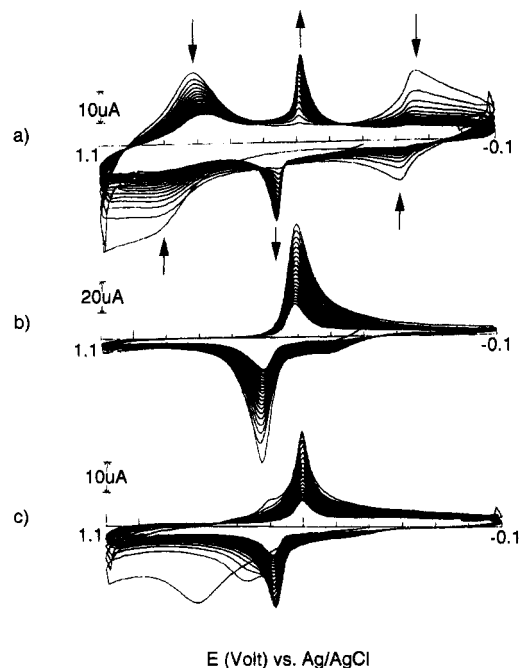


Figure 7. (a) Cyclic voltammogram for Prussian blue I mechanically attached to a paraffin-impregnated graphite electrode and placed in aqueous electrolyte containing 0.1 M KNO_3 and 0.1 M $\text{Cd}(\text{NO}_3)_2$ at 22 °C using a scan rate of 100 mV s^{-1} over 20 potential cycles. (b) Cyclic voltammogram of cadmium hexacyanoferrate(II) mechanically attached to a paraffin impregnated graphite electrode and immersed in 0.1 M KNO_3 at 22 °C using a scan rate of 100 mV s^{-1} over 20 potential cycles. (c) Cyclic voltammogram of cadmium hexacyanoferrate(III) mechanically attached to a paraffin impregnated graphite electrode and immersed in 0.1 M KNO_3 at 22 °C using a scan rate of 100 mV s^{-1} over 20 potential cycles.

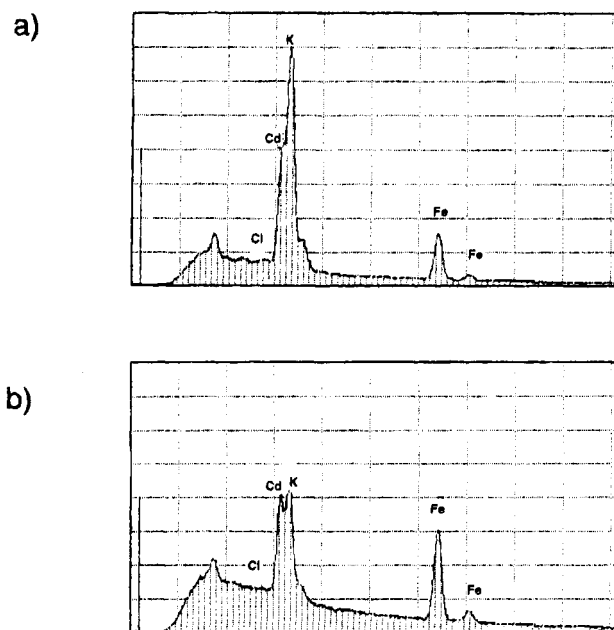


Figure 8. Single-particle electron microprobe analyses of (a) cadmium hexacyanoferrate(II) mechanically attached to a paraffin impregnated graphite electrode, and (b) Prussian blue I mechanically attached to a paraffin-impregnated graphite electrode after 20 potential cycles in aqueous electrolyte containing 0.1 M KNO_3 and 0.1 M $\text{Cd}(\text{NO}_3)_2$ using a scan rate of 100 mV s^{-1} .

processes. Ion transport is necessary to achieve electroneutrality and may in principle also lead to an exchange of interstitial mobile cations or the high spin lattice Fe^{3+} cations. For Prussian blue in the absence of a redox process, ion exchange affects only the interstitial labile cations.²⁸ To confirm this, a graphite

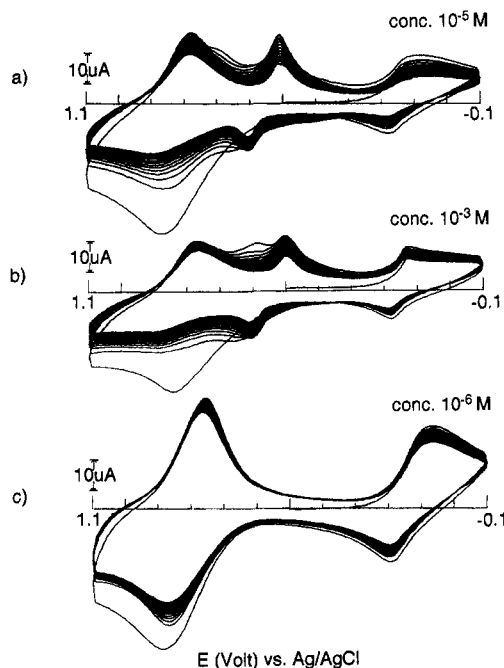


Figure 9. Cyclic voltammograms for Prussian blue I mechanically attached to a paraffin impregnated graphite electrode pretreated by immersion for 15 h in 10 mL of a solution of (a) 0.1 M KNO_3 and 10^{-3} M $\text{Cd}(\text{NO}_3)_2$, (b) 0.1 M KNO_3 , and 10^{-5} M $\text{Cd}(\text{NO}_3)_2$, and (c) 0.1 M KNO_3 and 10^{-6} M $\text{Cd}(\text{NO}_3)_2$, and placed in aqueous 0.1 M KNO_3 solution using a scan rate of 300 mV s^{-1} over 10 potential cycles.

electrode with Prussian blue mechanically attached to the surface was investigated by cyclic voltammetry in KNO_3 electrolyte after immersion in a solution containing 0.1 M KNO_3 and different concentrations of $\text{Cd}(\text{NO}_3)_2$ for 15 h. Figure 9 demonstrates that cyclic voltammograms observed after Prussian blue is immersed in Cd^{2+} solutions are critically dependent on the concentration of cadmium. However, it is especially important to note that no signal due to lattice reconstruction can be found in the first scan. Thus, ion exchange with Cd^{2+} uptake into the solid Prussian blue seems to be a facile process, whereas the lattice reconstruction appears to be initiated by an electrochemical process. In Figure 9a, the voltammogram obtained in 0.1 M KNO_3 after ion exchange in KNO_3 (0.1 M) and $\text{Cd}(\text{NO}_3)_2$ (10^{-5} M) exhibits intermediate redox couples in the first cycle as also is the case after treatment with a higher concentration of Cd^{2+} (10^{-3} M, Figure 9b). The stepwise shift of potential which occurs during the course of the experiment could be related to the number of exchanged cations in the vicinity of the hexacyanoferrate position in the lattice of the solid. Cadmium ion exchange from a 0.1 M KNO_3 solution (10 mL) cannot be detected when the concentration is 10^{-6} M (Figure 9c), although the process may still occur. From these experiments it can be seen that Prussian blue is highly effective in extracting metal cations such as cadmium from solution by ion exchange.

The growth of the redox couple associated with the presence of cadmium hexacyanoferrate also occurs when the potential is scanned over the range of 600 mV to -100 mV vs Ag/AgCl (switching occurs between the redox couples for Prussian blue and Everitt's salt) as is the case when cycling is undertaken in the oxidation range from 400 to 1100 mV vs Ag/AgCl. Results in Figure 10 demonstrate that the nature of electrochemical pretreatment determines the ion-exchange reactivity of lattice ions and that the highest exchange activity is found in the reduced state, the minimum activity is found for Prussian blue and intermediate activity is found for oxidized Prussian blue. That is, the chemical lattice reconstruction accompany the ion-

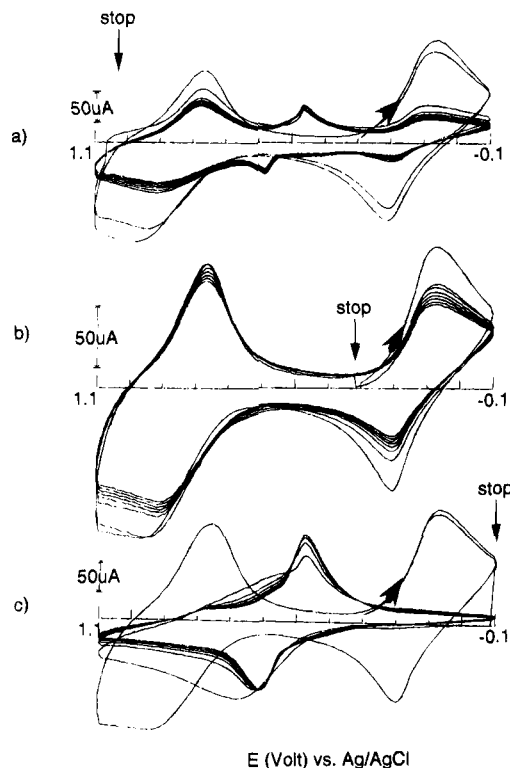


Figure 10. Cyclic voltammograms for Prussian blue I mechanically attached to a paraffin impregnated graphite electrode and placed in aqueous 0.1 M KNO_3 solution at 22°C using a scan rate of 200 mV s^{-1} . (a) After two initial cycles the potential is held for 1 min at ca. 1100 mV vs Ag/AgCl, and the electrode is immersed in a solution containing 0.1 M KNO_3 and 0.1 M $\text{Cd}(\text{NO}_3)_2$ (60 s), rinsed, and cycled again in the original electrolyte. (b) After one initial cycle the potential is held for 1 min at ca. 300 mV vs Ag/AgCl and the electrode is treated as above. (c) After one initial cycle the potential is held for 1 min at ca. -100 mV vs Ag/AgCl, and the electrode is treated as above.

exchange process that occur in the oxidized or reduced state of the solid. However, such processes cannot occur rapidly for Prussian blue which contains high-spin d^5 iron as well as low-spin d^6 iron and both are kinetically inert configurations.

Discussion

The electrochemical investigation of solid Prussian blue particles after mechanical transfer onto an electrode surface provides a convenient method to better understand the processes accompanying oxidation and reduction of these solids. A comparison with the electrochemical behavior of a film attached to the surface of a paraffin-impregnated graphite electrode and immersed in 0.1 M KNO_3 solution reveals related behavior suggesting that the rate-determining processes in both types of solids are the same.

The electrochemical results may be summarized as follows (also refer to Scheme 1): (i) The redox chemistry of solid Prussian blue particles can be investigated conveniently by electrochemical methods after mechanical attachment to various types of electrodes. (ii) In situ measurements of weight changes using a quartz crystal microbalance give reliable results. (iii) The lattice of a rigid solid may undergo substantial rearrangement after electrochemical processes as shown for the cases of Prussian blue and cadmium hexacyanoferrate in the presence of K^+ as well as for Prussian blue in the presence of Cd^{2+} . (iv) Two types of ion exchange of the Prussian blue lattice, which depend on the redox state of the solid, may be distinguished in which an interstitial labile cation or a cation from a framework position is exchanged. (v) Under conditions where a stable reduction response of Prussian blue in KNO_3 electrolyte can

be obtained, the variation of peak with scan rate suggests that almost complete reduction of the solid is possible even at high scan rates. Furthermore, a resistance parameter, which depends on surface coverage can be extracted from current-potential plots.

The fact that different samples of Prussian blue exhibit similar electrochemical behavior can be understood in terms of the compositional changes that occur in the solids after electrochemical reduction or oxidation. Compositional changes are readily monitored in the case of an ion-exchange reaction in which the potential of the electrochemical response is shifted (e.g., by formation of cadmium hexacyanoferrate). The labilization of the Prussian blue lattice after oxidation or reduction is the key factor in understanding the ion-exchange processes.

The linear dependence of peak potential on peak current at fast scan rate corresponds to an "IR-drop" effect. A qualitative interpretation can be given by considering the net of resistors switched in parallel. Removal of material from the electrode surface leads to an increase of the total resistance. An understanding of this resistance effect which has so far not been mentioned in work using Prussian blue film modified electrodes has, however, been reported in investigations of nonconducting solid particles²⁹ mechanically attached to electrodes and could reveal important information about the transport mechanism. The presence of an array of microcrystalline particles on the electrode surface allows parallels to be drawn from investigations in which microelectrodes are used. The theory of resistance effects with semi spherical microelectrodes under steady-state conditions has been described by Oldham.³⁰

Conclusions

The applicability of the voltammetric investigation of solid microcrystalline particles mechanically attached to electrode surfaces to ion-conducting and electrically semiconducting materials such as Prussian blue has been demonstrated in conjunction with in situ quartz crystal microbalance experiments. These techniques offer tools for investigations of many solid materials previously not considered electroactive.

The electrochemical behavior of Prussian blue has been demonstrated to be accompanied by ion-exchange processes not only of interstitial but also of lattice sites and in presence of cadmium cations the conversion from Prussian blue into cadmium hexacyanoferrate could be followed by cyclic voltammetry.

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