

Krzysztof Miecznikowski · Malgorzata Chojak  
Wioleta Steplowska · Marcin A. Malik  
Pawel J. Kulesza

## Microelectrochemical electronic effects in two-layer structures of distinct Prussian blue type metal hexacyanoferrates

Received: 19 March 2004 / Accepted: 25 April 2004 / Published online: 12 August 2004  
© Springer-Verlag 2004

**Abstract** The formation of a rigid bilayer structure from two metal hexacyanoferrates: Prussian blue (PB) and nickel hexacyanoferrate (NiHCNFe), as inner and outer films, respectively, has been demonstrated. To avoid intermingling of the granular cyanometallate microstructures, namely of the outer film (NiHCNFe) into the inner film (PB), the morphology of outer film material was changed by forming a polymeric hybrid (composite) of NiHCNFe with poly(*N*-methylpyrrole). The outer NiHCNFe film is physically separated from the electrode surface, and it undergoes redox reactions at potentials characteristic of the inner PB film. This arrangement leads to the reversible charge state trapping and bistable switching during voltammetric potential cycling. Under solid-state voltammetric conditions in the absence of contact with the liquid electrolyte phase, when the bilayer structure of PB and the oxidized NiHCNFe was formed between two sandwich-forming carbon electrodes, unidirectional rectifying current flow has been observed.

**Keywords** Prussian blue · Nickel hexacyanoferrate · Hybrid structure · Poly(*N*-methylpyrrole) bilayer films · Bistable switching · Charge trapping

### Introduction

Preparation and characterization of zeolite-like Prussian blue (PB) type cyanometallates with identifiable and fixed mixed-valent metal ionic (redox) centers is currently of great interest. The versatility and relative ease of preparation and experimentation has prompted the increased interest in the application of metal hexacyanoferrates to advanced materials fabrication. Attention is focused onto the systems' electrochromism [1, 2, 3, 4], capability to store cations [5, 6, 7, 8], membrane and ion-exchange selectivity [2, 9, 10, 11, 12], ability to mediate and electrocatalyze various reactions [13, 14, 15, 16, 17, 18, 19], molecular magnetism [20, 21, 22], and electronic (rectifying) effects [23]. Metal hexacyanoferrates are well-defined inorganic materials that, from a functional point of view, resemble both  $\pi$ -conjugated conducting polymers [24, 25, 26, 27, 28] and redox conducting polymers in which charge transport occurs by electron hopping between distinct and spatially constrained electron donor–acceptor sites [27, 29]. PB and its analogues [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23], which possess properties permitting their processing into thin films, are characterized by well-defined, reversible and reproducible responses in potassium salt supporting electrolytes. Recent studies indicate the possibility of forming bilayer-type microstructures through ion exchange or insertion/substitution reaction involving PB [30, 31].

One of the attractive targets in the field of modified electrodes is the development of functional films which exhibit potentially useful electrical and optical responses, including current rectification, charge trapping and amplification, electron–hole pair separation, and gates for ion flow [32, 33, 34]. In the present work, we show that bilayers formed by two physically discrete cyanometallate films, iron(III,II) hexacyanoferrate(II,III), i.e., PB, and nickel(II) hexacyanoferrate(II,III) (NiHCNFe), which contain redox centers of distinct formal potential values, can produce arrange-

Dedicated to Zbigniew Galus on the occasion of his 70th birthday

K. Miecznikowski · M. Chojak · W. Steplowska  
P. J. Kulesza (✉)  
Department of Chemistry,  
University of Warsaw, Pasteura 1,  
02-093 Warsaw, Poland  
E-mail: pkulesza@chem.uw.edu.pl

M. A. Malik  
Division of Chemistry,  
Department of Materials Engineering and Applied Physics,  
Technical University of Czestochowa, Armii Krajowej 19,  
42-200 Czestochowa, Poland

ments leading to unidirectional (rectifying) current flow and charge state trapping effects. Previously, both PB and NiHCNFe films were investigated separately, and they were the subject of fundamental studies on solid-state bulk and interfacial charge transfer [2, 5, 11, 35, 36, 37, 38, 39, 40, 41]. When it comes to the formation of two-layer structures, the important issues are the adherence, rigidity, compactness of inner (PB) and outer (NiHCNFe) layers, and the dynamics of charge transfer at their interfaces [42, 43, 44, 45, 46]. To overcome the problem of the granular morphology of cyanometallate films and to assure their physical discreteness within the bilayer structure, we refer here to the recent concept of the preparation of a fairly dense composite film [47] in which metal hexacyanoferrate is introduced into the conducting polymer matrix. Poly(*N*-methylpyrrole) (PMPy) [48] was chosen here owing to its stability in the potential ranges where PB and NiHCNFe are electroactive. Finally, we demonstrate the feasibility of rectifying the operation of the PB/NiHCNFe bilayer under solid-state two-electrode voltammetric conditions [29, 38], i.e., within a sandwich design in the absence of liquid electrolyte.

---

## Experimental

All chemicals were analytical grade materials and were used as received. Solutions were prepared from distilled and subsequently deionized water.

Before modifications, a glassy carbon disk substrate (geometric area 0.071 cm<sup>2</sup>) was activated by polishing it with successively finer grades of aqueous alumina slurries (grain size 5–0.5 μm) on a polishing cloth. The inner PB film was fabricated on glassy carbon by electrodeposition from the solution (50 cm<sup>3</sup>) formed following mixing 40 cm<sup>3</sup> 1.0 mol dm<sup>-3</sup> KCl with 5 cm<sup>3</sup> 0.1 mol dm<sup>-3</sup> K<sub>3</sub>[Fe(CN)<sub>6</sub>] and 5 cm<sup>3</sup> 0.1 mol dm<sup>-3</sup> FeCl<sub>3</sub> (in 0.1 mol dm<sup>-3</sup> HCl). The procedure involved controlled potential electrolysis at 0.5 V for 120 s and produced a PB film of 150–200-nm thickness. The outer NiHCNFe composite film that contained PMPy was electrodeposited onto the inner PB film through the application of 15 full voltammetric cycles at 50 mV s<sup>-1</sup> in the potential range from 0.85 to -0.4 V in the solution obtained by mixing 48.5 cm<sup>3</sup> 1.0 mol dm<sup>-3</sup> KCl with 0.5 cm<sup>3</sup> 0.1 mol dm<sup>-3</sup> K<sub>3</sub>[Fe(CN)<sub>6</sub>], 0.5 cm<sup>3</sup> 0.1 mol dm<sup>-3</sup> NiCl<sub>2</sub>, and 100 μl PMPy (final concentration 0.02 mol dm<sup>-3</sup>). In the procedure, the conducting polymer (PMPy) was generated on the electrode surface during positive potential scans [24, 25, 26, 47], whereas NiHCNFe was electrodeposited during negative potential scans [39, 41, 49]. The microstructures of the polymer (PMPy) and the polynuclear inorganic compound (NiHCNFe), that were alternately generated and deposited during positive and negative potential scans, are expected to interact electrostatically with each other because partially oxidized PMPy is positively charged and NiHCNFe is anionic. The thickness of the resulting (outer) NiHCNFe–PMPy film was estimated

to be around 200–250 nm. Finally, a simple (single component) PMPy film was obtained by potential cycling as described earlier except that no nickel and hexacyanoferrate salts were present in the solution for modification.

Loadings (in moles per square centimeter) of metal hexacyanoferrate films on electrode surfaces were estimated upon determination of charges under the system's voltammetric peaks (oxidation) recorded at a slow scan rate, 5 mV s<sup>-1</sup>. Film thickness was determined using profilometry (Talysurf 50, Rank Taylor Hobson).

The solid-state (i.e., in the absence of an external phase of supporting electrolyte) voltammetric experiments were executed with two inert glassy carbon slide electrodes that had been mounted in a sandwich configuration [29, 38] (spacing between electrodes around 0.6 mm; effective geometric area 0.3 cm<sup>2</sup>). Approximately 10 mg PB or oxidized NiHCNFe well-ground cyanometallate powder was introduced onto each sandwich-forming glassy carbon electrode. When using a three-electrode potentiostat, the operation of a cell in two-electrode mode implied that one of these two electrodes was connected as a working electrode and the second one acted as reference and counter electrodes simultaneously. To assure good contact of electrodes with the material, a pressing weight was used. The assembly was enclosed in Teflon tubing and sealed to protect the material from dehydration.

Glassy carbon slides modified with metal hexacyanoferrate and composite films were examined *ex situ* using a Digital Instruments (Santa Barbara, CA, USA.) Nanoscope II atomic force microscope (AFM) in Tapping Mode (intermittent contact) with the standard silicon nitride (Si<sub>3</sub>N<sub>4</sub>) probe tips. The AFM probe tip was attached to an insulating cantilever; resonant frequencies in the range 150–180 kHz were applied. The use of the AFM to examine the surface morphology of organic–inorganic hybrid materials was established earlier [48]. The presence of metallic elements (Fe and Ni) in the films was confirmed with the use of an energy dispersive X-ray spectroscopy unit for elemental analysis (coupled with a JEOL model JSM-5400 scanning electron microscope).

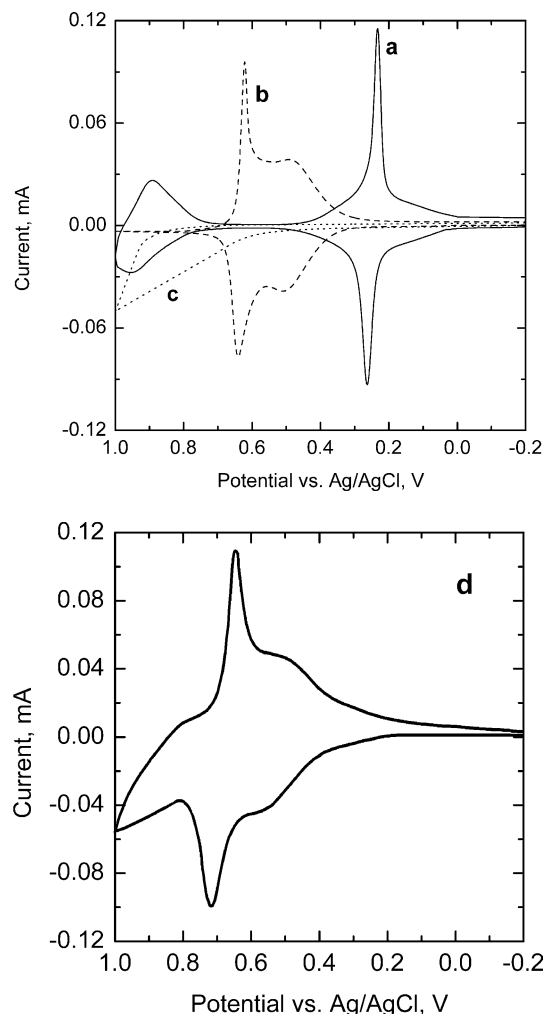
Experiments were carried out at room temperature (22 °C). All potentials were expressed versus the KCl saturated Ag/AgCl reference. Electrochemical measurements were done with a CH Instruments (Austin, TX, USA) model 660 analyzer.

---

## Results and discussion

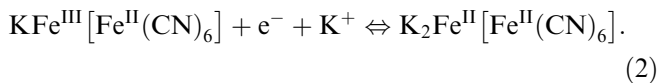
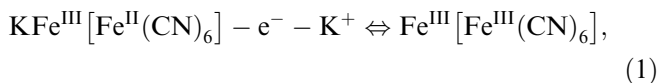
Electrochemical identity of PB, NiHCNFe, PMPy, and bilayer films

Typical cyclic voltammetric responses of PB, NiHCNFe, and PMPy films recorded in 0.50 mol dm<sup>-3</sup> K<sub>2</sub>SO<sub>4</sub> are shown in Fig. 1. The electrochemical behavior of PB (Fig. 1, curve a) is dominated by two sets of voltammetric peaks that originate from the reactions of the



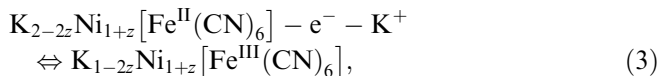
**Fig. 1** Cyclic voltammetric responses of films of Prussian blue (PB) (a), nickel hexacyanoferrate (NiHCNFe) (b), poly(*N*-methylpyrrole) (PMPy) (c), and NiHCNFe–PMPy (d) on glassy carbon recorded in  $0.50 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$ . Scan rate  $50 \text{ mV s}^{-1}$

oxidation of PB to iron(III) hexacyanoferrate(III), Prussian yellow, at about 0.9 V (Eq. 1), and the reduction of PB to iron(II) hexacyanoferrate(II), Prussian white, at about 0.2 V (Eq. 2) [2, 5, 11, 35, 36]:



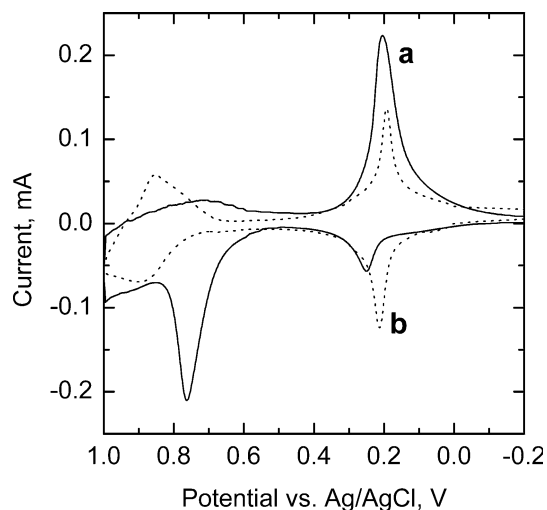
The response of NiHCNFe film (Fig. 1, curve b) is characterized by overlapping redox reactions at about 0.4–0.6 V. Although the approximate formulas  $\text{KNi}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]$  and  $\text{K}_2\text{Ni}[\text{Fe}^{\text{II}}(\text{CN})_6]$  are usually assigned to two predominant forms of the reduced NiHCNFe films, in reality the films are electrodeposited (in the presence of  $\text{K}^+$  ions) in the form of solid solutions rather than homogeneous phases [16, 39, 41]. As in

the case of PB, electron transfers in NiHCNFe require the flux of cations [39, 40, 41]:



where  $0 \leq z \leq 0.5$ . It is noteworthy that the voltammetric response of NiHCNFe (Fig. 1, curve b) lies between two sets of voltammetric peaks of PB (Fig. 1, curve a). Under the same experimental conditions (electrolyte, scan rate), PMPy is oxidized to its electronically conductive form at potentials more positive than 0.6 V (Fig. 1, curve c). Because NiHCNFe is electroactive in the potential range (Fig. 1, curve b) where PMPy is basically in a nonconducting state, the latter polymer would act as an inert matrix in the case of the PMPy–NiHCNFe composite film (Fig. 1, curve d). The presence of PMPy results only in the increase of voltammetric currents at potentials where NiHCNFe is already oxidized, i.e., at potentials higher than 0.7 V. PMPy is expected to assure the physical separation between granular NiHCNFe and PB films within the bilayer structure described in the following.

The steady-state voltammetric behavior of a two-layer structure made of PB (inner layer) and PMPy-containing composite film of NiHCNFe (outer layer) is shown in Fig. 2, curve a. For comparison, we provide the voltammetric responses of a PB film (Fig. 2, curve b) onto which the NiHCNFe-based composite film (as for Fig. 1, curve d) had been introduced. The bistable character of the two-layer cyanometallate structure can be understood as follows. The inner PB layer is designed to act as a mediator for NiHCNFe in the outer layer. Suppose an experiment starts at 1.0 V, i.e., with PB (inner layer) and NiHCNFe (outer layer) in their fully oxidized, iron(III) hexacyanoferrate(III), i.e. Prussian yellow, and nickel(II) hexacyanoferrate(III) forms.



**Fig. 2** Steady-state voltammetric behavior of a bilayer PB/NiHCNFe–PMPy film on glassy carbon (a). Response of the inner PB film (b). Other conditions as for Fig. 1

When the potential is scanned negatively down to 0.7 V, hexacyanoferrate(III) centers within Prussian yellow are reduced to hexacyanoferrate(II) according to Eq. (1), and PB is formed in the inner layer. At the same time, NiHCNFe in the outer layer remains oxidized because the hexacyanoferrate(II) redox centers in PB are not strong enough reductants to transfer electrons to hexacyanoferrate(III) sites of oxidized NiHCNFe. When the potential is further scanned down to 0.35 V, no redox reaction is operative in the inner layer, and NiHCNFe still remains oxidized in the outer layer. In other words, the inner film blocks the needed charge transfer and, hence, there is a metastable entrapment of charge in the outer film over the potential range from 0.7 to 0.35 V. At potentials more negative than 0.35 V, the iron(III) centers of PB become reduced to iron(II), and so-called Prussian white, iron(II) hexacyanoferrate(II), is formed, which in turn is capable of passing charge into the hexacyanoferrate(III) ionic sites of NiHCNFe, which would be finally reduced to nickel hexacyanoferrate(II) (Eqs. 3, 4). During the oxidation cycle up to 0.35 V, Prussian white is oxidized to PB in the inner layer but the iron(III) sites of PB are not strong enough oxidants to produce nickel hexacyanoferrate(III). In the potential range from 0.35 to 0.7 V, the inner PB film does not act as a mediator, NiHCNFe still remains reduced, and there is a metastable entrapment of charge in the outer film. When the potential is scanned further in a positive direction, iron(III) hexacyanoferrate(III), or Prussian yellow, which is produced in the inner layer acts as a sufficiently strong oxidant to remove electrons from nickel hexacyanoferrate(II) and to produce nickel hexacyanoferrate(III). Hence, the oxidation process continues until both films are fully oxidized at the positive limit of 1.0 V.

The data in Fig. 2, curve a are consistent with the view that the oxidation or reduction of the outer film containing NiHCNFe occurs indirectly at potentials where oxidizing or reducing states of the inner PB film are generated. The fact that the reduction hexacyanoferrate(III) ionic sites in the outer NiHCNFe film at potentials lower than 0.3 V attenuate the Prussian white to PB oxidation peak at about 0.2 V supports the hypothesis about the mediation capabilities of inner PB toward outer NiHCNFe. The same comment applies to the attenuation of the Prussian yellow to PB reduction peak at about 0.9 V.

The charge trapping within the PB/NiHCNFe bilayer system is impressively long and virtually complete, and such behavior implies the quality of electrical and chemical isolation imposed on the outer film by the inner one. Fabrication of a composite film of NiHCNFe with PMPy is an important factor in this context. Recently, it has been established that NiHCNFe microstructures are stabilized by introduction of a conducting polymer [47]. It can be expected that PMPy occupies the void space between metal hexacyanoferrate granules, provides physical separation between layers, and it prevents the appearance of any possible reorganization or insertion/

substitution reactions [30] at the interface formed between PB and NiHCNFe.

Using the AFM, we examined the morphologies of single component, PB (Fig. 3a), and bilayer PB/NiHCNFe–PMPy (Fig. 3b) films. Previously [47], we described results of the AFM investigation of polymer-free NiHCNFe film (for simplicity not included here): the granular morphology of NiHCNFe was virtually identical to that of PB (Fig. 3a). Although the size of the grains in a single component metal hexacyanoferrate film (Fig. 3a) is comparable to that of a bilayer system (Fig. 3b), the distribution of NiHCNFe granules seems to be much denser in the latter system in comparison with simple PB. Further, the data in Fig. 3b are also consistent with the existence of the PMPy polymer in the free space between cyanometallate granules.

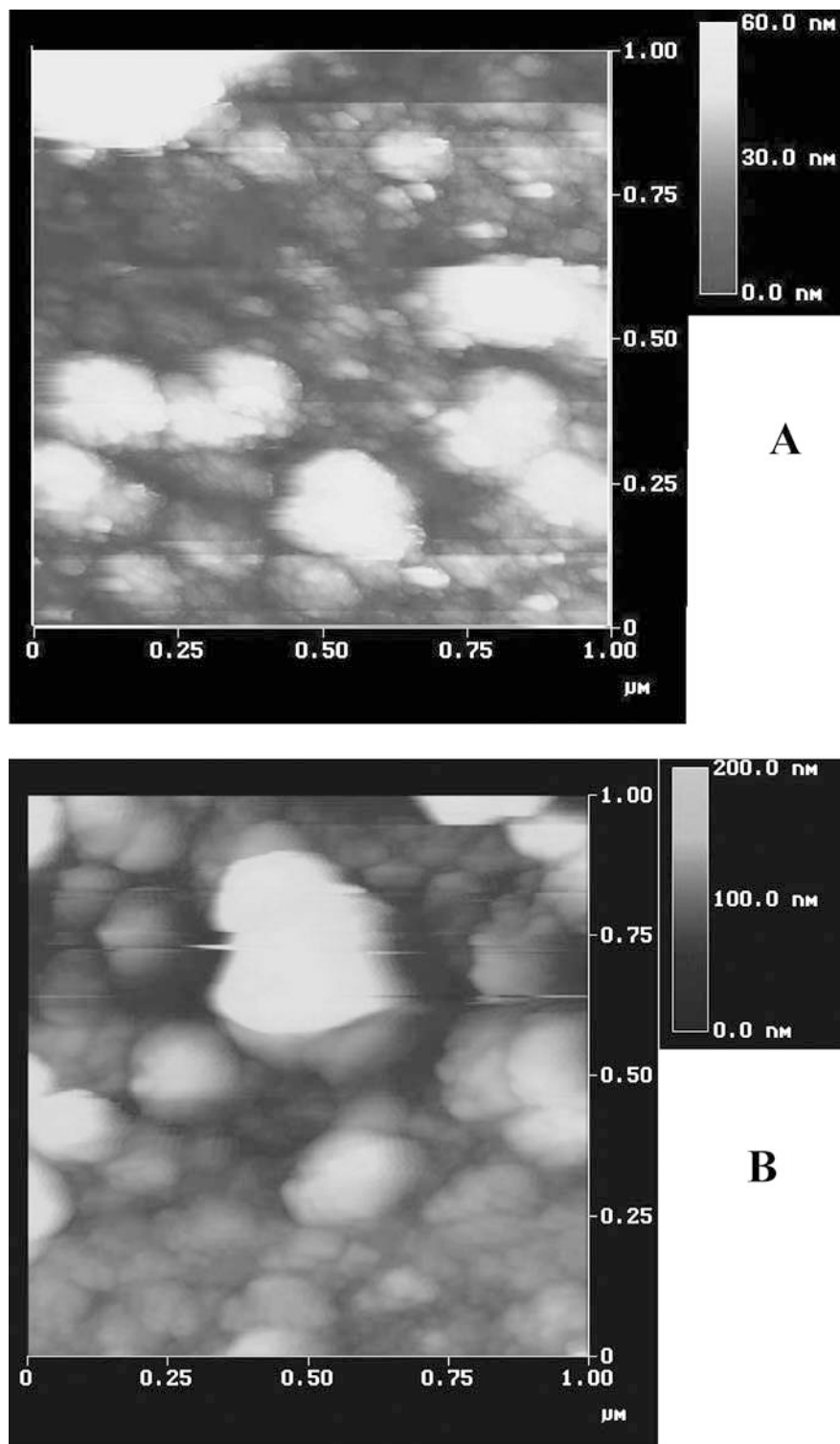
The PB/NiHCNFe bilayer systems can be produced in the absence of PMPy. The results are, however, very irreproducible, and the trapping effect is not always observed. It is likely that simple (PMPy-free) metal hexacyanoferrate films are too porous to assure the principal condition that the outer film is not in physical contact with the electrode substrate. On the contrary, introduction of larger amounts of PMPy does not improve conditions for charge trapping in a bilayer system. The voltammetric response of the bilayer structure where electrodeposition of both PB and NiHCNFe was performed in the presence of methylpyrrole is shown in Fig. 4, curve a. The large baseline currents, that appear at potentials more positive than 0.6 V, originate from the oxidation of PMPy, which is now present in larger amounts. Thus the oxidative charge trapping effect is somewhat hindered. Finally, by reversing the sequence of deposition of metal hexacyanoferrate films to form a bilayer structure composed of NiHCNFe and PB as inner and outer films, respectively, the charge trapping effect is completely lost regardless of the presence of the stabilizing PMPy matrix. The cyclic voltammogram of this bilayer system is characterized by the overlapping responses of PB, NiHCNFe, and PMPy (Fig. 4, curve c). The result is not surprising because NiHCNFe does not have appropriate mediating capabilities toward either oxidation or reduction of PB.

By analogy to the previous work [39], we performed potential step experiments and plotted dependencies of chronocoulometric charge ( $Q$ ) versus  $t^{1/2}$  to get some insight into the dynamics of charge propagation during charge trapping. They are described in terms of the integrated Cottrell equation [29]:

$$[Q/t^{1/2}] = 2nF\pi^{1/2}r^2C_o[D_{app}]^{1/2}, \quad (4)$$

where  $r$ ,  $D_{app}$ ,  $C_o$  stand for the radius of a disk-type electrode, the apparent diffusion coefficient for charge propagation, and the concentration of redox centers, and the other parameters have either been discussed already or have their usual significance. From the linear portion of the dependence of  $Q$  on  $t^{1/2}$ , one can determine the slope,  $[Q/t^{1/2}]$ , and, indirectly, the charge

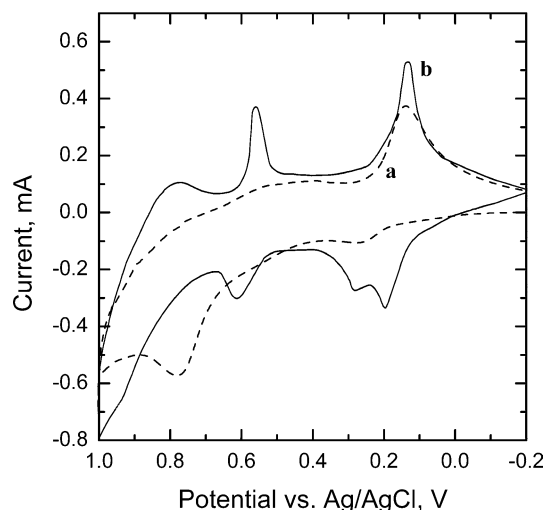
**Fig. 3** Atomic force microscopy examination of **a** PB (as for Fig. 1, curve a) and **b** PB/NiHCNFe-PMPy (as for Fig. 2, curve a) films



transport parameter,  $[D_{app}]$ . The concentration ( $C_o$ ) of hexacyanoferrate(III,II) redox centers was estimated (around  $0.6 \text{ mol dm}^{-3}$ ) upon consideration of such parameters as loading of the cyanometallate film and its thickness. The value of  $C_o = 0.6 \text{ mol dm}^{-3}$  is in agreement with the data reported previously for PB [50].

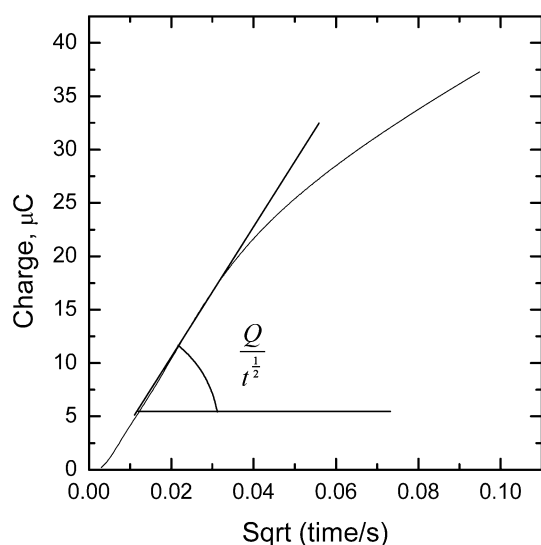
Two types of chronocoulometric experiments were executed on a bilayer system: with potential steps from

(1) 0.5 to  $-0.2 \text{ V}$ , and (2) 0.5 to  $1.0 \text{ V}$ . They were performed following the oxidative (case 1) and reductive (case 2) charge trapping voltammetric cycles under the conditions of Fig. 2 (curve a). For simplicity, we only present here (Fig. 5) the chronocoulometric response characteristic of case 1. Care was exercised to apply sufficiently short potential steps to assure a sufficiently large region where diffusional charge transport occurs



**Fig. 4** Voltammetric characteristics of bilayer films: PB-PMPy/NiHCNFe-PMPy (a) and NiHCNFe-PMPy/PB-PMPy (b). Other conditions as for Fig. 1

under semi-infinite conditions (linear portion of the dependence in Fig. 5). To avoid kinetic or ohmic limitations (appearing as a sizeable negative intercept), the potential steps were not too short. The  $Q-t^{1/2}$  dependencies yielded  $D_{app}$  values of  $2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  (case 1)- and  $5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  (case 2). For comparison, we also considered charge transport in simple PB and NiHCNFe films in the same ( $0.5 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$ ) electrolyte. The  $D_{app}$  values found were as follows:  $3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  for the reduction of PB to Prussian white,  $2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  for the oxidation of PB to Prussian yellow, and  $5 \times 10^{-9}$  and  $6 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  for the oxidation and reduction of NiHCNFe, respectively. Since the chronocoulometric



**Fig. 5** Chronocoulometric  $Q-t^{1/2}$  plot obtained for the PB/NiHCNFe PMPy system on glassy carbon. The potential step (9 ms) was from 0.5 to  $-0.2 \text{ V}$ . It was applied following oxidative charge trapping, i.e., upon performing the initial voltammetric scan ( $50 \text{ mV s}^{-1}$ ) from  $-0.2$  via 1.0 to  $0.5 \text{ V}$

potential step from 0.5 to  $-0.2 \text{ V}$  performed on a bilayer system (Fig. 2a) involved transfers of electrons from  $-\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  ions in the PB/Prussian white inner film to  $-\text{Fe}^{\text{II}}(\text{CN})_6/\text{Fe}^{\text{III}}(\text{CN})_6$  ions in the outer NiHCNFe film, it is not surprising that the dynamics of this mediation process was controlled by the somewhat slower charge propagation occurring in the PB film (with respect to NiHCNFe). The obtained  $D_{app} = 2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  is indeed close to the value characteristic of the PB/Prussian white redox transition. On the other hand, the chronocoulometric potential step from 0.5 to 1.0 V performed on a bilayer system was controlled by a relatively slower charge transport in the outer NiHCNFe film (charge propagation during oxidation of PB to Prussian yellow was faster). This result explains why the value of  $D_{app} = 5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  was obtained. Although these kinetics results shall be considered as estimates, the similarity between results determined for simple (single component) metal hexacyanoferrate films and the bilayer structure are consistent with the view that there was neither any appreciable kinetics limitation at the interface formed by PB and NiHCNFe films nor a blocking effect originating from the polymer (PMPy) introduced into NiHCNFe.

#### Rectifying effect under solid-state voltammetric conditions

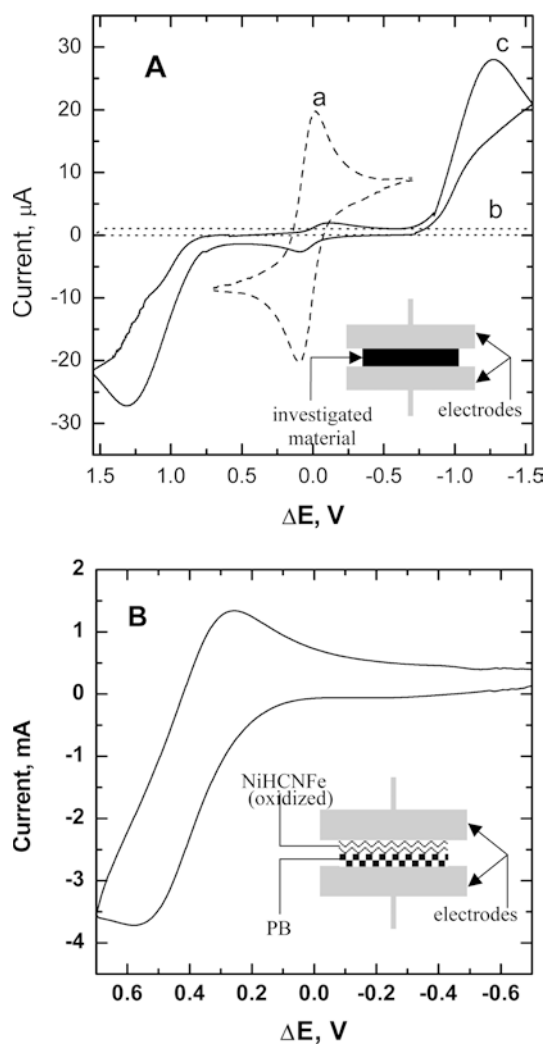
An interesting alternative is to consider a bilayer system that would operate in the absence of external liquid electrolyte. Since metal hexacyanoferrates are ionically and electronically conducting solids that contain fixed mixed-valent redox centers and mobile potassium counter cations, solid-state electrochemical experiments are feasible. In the simplest mode, a solid-state voltammetric experiment utilizes a two-electrode sandwich configuration in which the potential differences applied polarize two electrodes in opposite directions [29, 38, 50, 51, 52].

Solid-state voltammetry of both PB and NiHCNFe pressed powders is well established [35, 38, 50, 51, 52]. The mobility of  $\text{K}^+$  ions is strongly dependent on the presence of structural water molecules in the cyanometallate powders. Under ambient conditions (80–90% humidity), the systems are sufficiently hydrated (around 7–9 molecules per metal hexacyanoferrate molecule) to assure good mobility of potassium ions. The transport of electrons is based on hopping (self-exchange) and, in order to observe redox transitions and to preserve electroneutrality, the process must be coupled to the displacement of counterions (hydrated  $\text{K}^+$ ). To observe any nonohmic (Faradaic) current under the sandwich configuration, two simultaneous redox processes must occur at interfaces formed by the opposing electrodes. Therefore, in our diagnostic experiment, we considered a mixed NiHCNFe system, i.e., containing mixed-valent hexacyanoferrate(III,II) redox centers, or more precisely, in which  $\text{Fe}^{\text{III}}$  and  $\text{Fe}^{\text{II}}$  ions coexist in an

approximate ratio of 1:1. Cyclic voltammograms of such a NiHCNFe powder are shown in Fig. 6a (curve a). As expected, for two-electrode solid-state voltammetry (sandwich configuration) [50, 51, 52], the responses are in a form of voltammetric peaks symmetrical around the point of zero with respect to current and potential. It should be remembered that the cell operates in a manner analogous to classic biamperometry in which potential differences are applied to two identical electrodes and scanned linearly with time. Owing to the existence of CN-bridged iron ions at two different oxidation states, simultaneous oxidation of hexacyanoferrate(II) and reduction of hexacyanoferrate(III) is operative at two opposing electrodes. The fully oxidized NiHCNFe powder does not contain any mixed-valent hexacyano-

ferrate(III,II) redox centers and, therefore, it behaves as an insulator and does not exhibit any voltammetric peaks (Fig. 6a, curve b). When the PB powder was sandwiched between two glassy carbon slides and subjected to potential cycling, the response depicted by curve c was obtained. As described earlier [51], the solid-state voltammetric (two-electrode) pattern of PB is characterized by low currents in the vicinity of 0 V and much larger peaks at about  $\pm 1.0$  V. Prior to  $\pm 0.7$  V, the potential differences ( $\Delta E$ ) applied are insufficient to cause appreciable oxidation and reduction of PB. The low peak currents at about  $\pm 0.1$  V and symmetrical around 0 V originate from the fact that the  $K_4[Fe^{II}(CN)_6]$  used to produce PB was somewhat contaminated with  $K_3[Fe^{III}(CN)_6]$ . Thus, some mixed-valent sites,  $-Fe^{III}(CN)_6/-Fe^{II}(CN)_6$ , must have initially existed, and the  $K^+$ -supported electron self-exchange was possible. The true redox reactions of sandwiched PB start to appear when  $\Delta E$  exceeds 0.7 V, i.e., when it becomes large enough to cause simultaneous reduction of PB to Prussian white and oxidation of PB to Prussian yellow (Eqs. 1, 2).

A possibility of the rectifying effect was demonstrated by sandwiching two distinct pressed powders, PB and oxidized NiHCNFe [nickel(II) hexacyanoferrate(III)] between two glassy carbon slide electrodes mounted in a sandwich configuration. Care was exercised to avoid intermixing of the microcrystalline powders: a few drops of agar sol were introduced onto each material before mounting the sandwich design. The applied potential differences forced both electrons and ions to flow in response. While PB is subject to both oxidation and reduction processes, the fully oxidized NiHCNFe can only be reduced to nickel(II) hexacyanoferrate(II). Consequently, when the potential of the glassy carbon electrode covered with the oxidized NiHCNFe was polarized negatively, the voltammetric peaks appeared at the potential differences where both reduction of NiHCNFe and oxidation of PB were operative (Fig. 6b). The fact that this potential difference was around 0.4 V is in agreement with the data in Fig. 1. When the potential was polarized positively, although PB could have been reduced to Prussian white, the oxidation of NiHCNFe [nickel(II) hexacyanoferrate(III)] was not possible (destruction of the system occurs at potential differences larger than 2 V). Thus the system permitted current flow in one direction and blocked it in the opposite one; in other words, the system behaved like a rectifying microelectrochemical device.



**Fig. 6a,b** Steady-state voltammetric responses recorded in a two-electrode sandwich configuration (as shown in insets) in the absence of liquid electrolyte **a** for the single pressed powders  $K_2Ni[Fe^{II}(CN)_6]$  plus  $KNi[Fe^{III}(CN)_6]$  (admixed at 1:1 ratio) (**a**), oxidized NiHCNFe ( $KNi[Fe^{III}(CN)_6]$ ) (**b**), and PB (**c**) and **b** for the bilayer system composed of two pressed powders—PB and oxidized NiHCNFe (introduced separately onto sandwich-forming glassy carbon electrodes)

## Conclusions

We demonstrated here the technical feasibility to assemble bilayers of metal hexacyanoferrates (PB and NiHCNFe) to display such electronic effects as reversible charge state trapping (bistable switching) or unidirectional (rectifying) current flow. In this context, bilayer electrodes of metal hexacyanoferrates resemble

redox and conducting polymers [27, 28, 53, 54]. To avoid structural reorganizations (e.g., ionic substitutions in cyanometallate lattices) at the inner/outer film interface and to eliminate fatal direct electron transfer between the electrode and the outer film, inner PB and outer NiHCNFe films should be separated with some kind of a polymer interlayer. This step can be achieved by the physical introduction of a thin polymer layer or by subjecting the outer film material to polymerization to form a hybrid organic-inorganic [55] type film of PMPy and NiHCNFe. The positively charged polymer backbone is expected to attract electrostatically and stabilize negatively charged metal hexacyanoferrate films. Finally, owing to good ionic and electronic conductivities, metal hexacyanoferrates seem to be good candidates for solid-state micro- and nanoelectronic devices [56] that could operate in the absence of contact with a liquid supporting electrolyte. Although we have said relatively little about other possibilities, metal hexacyanoferrate based bilayer systems may be considered for display applications, sensing, charge storage, and corrosion protection.

**Acknowledgements** This work was supported by the State Committee for Scientific Research (KBN), Poland, under grant 7 T09 05426. K.M. was supported by the University of Warsaw under the BW-project. M.C. gratefully acknowledges a fellowship from the Foundation for Polish Science (FNP).

## References

- Monk PM, Mortimer RJ, Rosseinsky DR (1995) *Electrochromism, fundamentals and applications*. VCH, Weinheim
- Itaya K, Uchida I, Neff VD (1986) *Acc Chem Res* 91:162
- Carpenter MK, Conell RS (1990) *J Electrochem Soc* 137:2464
- Kulesza PJ, Malik MA, Zamponi S, Berrettoni M, Marassi R (1995) *J Electroanal Chem* 397:287
- Feldman BJ, Melroy OR (1987) *J Electroanal Chem* 234:213
- Neff VD (1985) *J Electrochem Soc* 132:1382
- Lasky SJ, Buttry DA (1988) *J Am Chem Soc* 110:6258
- Kulesza PJ, Malik MA, Berrettoni M, Giorgetti M, Zamponi S, Schmidt R, Marassi R (1998) *J Phys Chem B* 102:1870
- Hartmann M, Grabner EW, Bergveld P (1991) *Anal Chim Acta* 242:249
- Coon DR, Amos LJ, Bocarsly AB, Fitzgerald Bocarsly PA (1998) *Anal Chem* 70:3137
- Kulesza PJ, Doblhofer K (1989) *J Electroanal Chem* 274:95
- Dussel H, Dostal A, Scholz F (1996) *Fresenius J Anal Chem* 355:21
- Lin C, Bocarsly AB (1991) *J Electroanal Chem* 300:325
- Zhou DM, Ju H-X, Chen H-Y (1998) *J Electroanal Chem* 408:219
- Dong S, Che G. (1991) *J Electroanal Chem* 315:191
- Kulesza PJ, Brajter K, Dabek-Zlotorzynska E (1987) *Anal Chem* 59:2776
- Zhou J, Wang E (1992) *J Electroanal Chem* 331:1029
- Lin MS, Jan BI (1997) *Electroanalysis* 9:340
- Cataldi TRI, De Benedetto GE, Bianchini A (1998) *Electroanalysis* 10:1163
- Kahn O (1995) *Nature* 378:667
- Sato O, Einaga Y, Iyoda T, Fujishima A, Hashimoto K (1997) *J Phys Chem B* 101:3903
- Ohkoshi S, Fujishima A, Hashimoto K (1998) *J Am Chem Soc* 120:5349
- Masui H, Murray RM (1998) *J Electrochem Soc* 145:3788
- Inzelt G (1994) *Electroanalytical chemistry*. Dekker, New York
- Inzelt G, Pineri M, Schultze JW, Vorotyntsev MA (2000) *Electrochim Acta* 45:2403
- Rubinson JF, Mark HB Jr (1999) *Interfacial electrochemistry*. Dekker, New York
- Murray RW (1992) *Molecular design of electrode surfaces. Introduction to the chemistry of molecularly designed electrode surfaces*. Wiley, New York
- Doblhofer K (1994) *The electrochemistry of novel materials. Thin polymer films on electrodes: a physicochemical approach*. VCH, Weinheim
- Kulesza PJ, Malik MA (1999) *Interfacial electrochemistry*. Dekker New York
- Hermes M, Lovric M, Hartl M, Retter U, Scholz F (2001) *J Electroanal Chem* 50:193
- Joseph J, Bharathi S, Gomathi H, Rao GP (2002) *Bull Electrochem* 18:267
- Chidsey CED, Murray RW (1986) *Science* 231:25
- Mannes KM, Masui H, Wightman RM, Murray RW (1997) *J Am Chem Soc* 119:3987
- Huang J, Wrighton MS (1993) *Anal Chem* 65:2740
- Lundgren CA, Murray RW (1988) *Inorg Chem* 27:933
- Feldman BJ, Murray RW (1987) *Inorg Chem* 26:1702
- Kelly MT, Arbuckle-Keil GA, Johnson LA, Su EY, Amos LJ, Chun JKM, Bocarsly AB (2001) *J Electroanal Chem* 500:311
- Kulesza PJ, Galus Z (1990) *J Electroanal Chem* 323:261
- Malik MA, Miecznikowski K, Kulesza PJ (2000) *Electrochim Acta* 45:3777
- Humphrey BD, Sinha S, Bocarsly AB (1984) *J Phys Chem* 88:736
- Bacskaï J, Martinusz K, Czirok E, Inzelt G, Kulesza PJ, Malik MA (1995) *J Electroanal Chem* 385:241
- Danisevich P, Willman KW, Murray RW (1981) *J Am Chem Soc* 103:4727
- Maksymiuk K (1996) *Electroanalysis* 8:661
- Murao K, Suzuki K (1988) *J Electrochem Soc* 135:1415
- Hillman AR, Mallen EF (1990) *J Electroanal Chem* 281:109
- Ren X, Pickup PG (1993) *J Phys Chem* 97:3941
- Kulesza PJ, Miecznikowski K, Malik MA, Galkowski M, Chojak M, Caban K, Wieckowski A (2001) *Electrochim Acta* 46:4065
- Kulesza PJ, Matczak M, Wolkiewicz A, Grzybowska B, Galkowski M, Malik MA, Wieckowski A (1999) *Electrochim Acta* 44:2131
- Joseph J, Gomathi H, Prabhakara Rao G (1991) *Electrochim Acta* 36:1537
- Kulesza PJ, Cox JA (1998) *Electroanalysis* 10:73
- Kulesza PJ (1990) *J Electroanal Chem* 289:103
- Kulesza PJ, Galus Z (1997) *Electrochim Acta* 42:867
- Majda M (1992) *Molecular design of electrode surfaces*. Wiley, New York
- Forster RJ (1994) *Chem Soc Rev* 289
- Gomez Romero P (2001) *Adv Mater* 13:163
- Fendler J (2001) *Chem Mater* 13:3196