Polish J. Chem., **78**, 1183–1193 (2004)

Two-Layer Structures of Ultra-Thin Metal Hexacyanoferrate Films: Charge Trapping and Possibility of Application to Corrosion Protection[*]

by K. Miecznikowski[1], M. Chojak[1], W. Steplowska[1], O. Makowski[1], P.J. Kulesza[1], L. Adamczyk[2], M.A. Malik[2], M. Galkowski[2] and H. Bala[2]**

[1]*Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland*
[2]*Division of Chemistry, Department of Materials and Process Engineering and Applied Physics, Czestochowa University of Technology, Armii Krajowej 19, PL-42-200 Czestochowa, Poland*

(Received May 25th, 2004)

The possibility of fabrication of ultra-thin films of metal hexacyanoferrates, Prussian Blue, PB, and nickel hexacyanoferrate, NiHCNFe, by multiple sequential attachment of metal cations (self-assembled on 4-aminobenzoic acid monolayer) and hexacyanoferrate anions, has been demonstrated. These films can form a bilayer arrangement on glassy carbon when PB and NiHCNFe are deposited as inner and outer films, respectively. To avoid mixing of the NiHCNFe and PB redox sites, we introduce an polymer interlayer from poly(4-vinylpyridine) and Nafion. Since the outer NiHCNFe film is physically separated from the electrode surface, and it undergoes redox reactions at potentials characteristic of the inner PB film, an effect of the reversible charge state trapping (bistable switching) is observed. A stable bilayer structure can also be deposited on stainless steel. The whole concept may be of importance to corrosion protection since charge accumulated in the oxidized bilayer film tends to stabilize corrosion potential within passive range.

Key words: Prussian Blue, nickel hexacyanoferrate, ultra-thin films, bilayer films, voltammetry, bistable switching, charge trapping, corrosion protection

Zeolite-like Prussian Blue type metal hexacyanometalates, that contain identifiable and fixed mixed-valent metal ionic centers, have attracted recent attention due to their ability to form polymer-like highly-functionalized thin inorganic films on electrodes. Among technologically promising properties, the systems' electrochromism [1–4], capability to store cations [5–8], membrane and ion-exchange selectivity [2,9–12], the ability to mediate and electrocatalyze various reactions [13–19], molecular magnetism [20–22], and electronic (rectifying) effects [23] shall be mentioned. Semiconducting films of metal hexacyanoferrates resemble those fabricated from π-conjugated conducting polymers [24–28] and redox conducting polymers in which charge transport occurs by electron hopping between mixed-valent sites [27,19]. Prussian Blue and its analogues [2–23] are characterized by well-defined, reversible and reproducible responses in potassium salt supporting electrolytes.

---

[*] Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.
[**] Corresponding author: pkulesza@chem.uw.edu.pl

It has been recently demonstrated that bilayer type microstructures can be produced during ion exchange or insertion/substitution reactions involving Prussian Blue [29,30].

An attractive area of research in the field of modified electrodes concerns the development of functional multilayer films that exhibit such microelectronic effects as current rectification, charge trapping and amplification, electron-hole pair separation, and gates for ion flow [31–33]. In this context, metal hexacyanoferrates fabricated in a form of ultra-thin films (by multiple sequential adsorption or attachment of metal cations and hexacyanoferrate anions) [34–38] could also be of interest. To anchor the first layer of metal cations or hexacyanometalate anions, the self-assembled layer of a proper precursor should be applied [37]. Such a layer serves as precision spacer between the electrode and the redox centers. In principle, the layer-by-layer method [39] engages alternating immersions of an ionized substrate to dilute aqueous solutions of polycations and polyanions. After deposition of each polyion layer, the surface charge is reversed, and a subsequent layer of the opposite charge can then be attached. By the repetition of these two steps the amount of material on the electrode surface can be increased systematically in a controlled fashion leading to stable multilayer assemblies.

Very recently, we have demonstrated [40] the possibility of fabrication of bilayer microstructures from two distinct metal hexacyanoferrates [2,5,11,40–46]: Prussian Blue, PB, and nickel hexacyanoferrate, NiHCNFe, as inner and outer films, respectively. 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. Having in mind the fact that very thin films offer the advantages of short electrolysis times and large electric field strengths, we address the possibility of fabrication of utrathin ("two-dimensional" type) PB and NiHCNFe films. The resulting bilayer structure has occurred to be particularly stable on stainless steel, it has exhibited a useful charge storage characteristics and stabilized the substrate's potential within passive range. The latter observation may be of importance to corrosion protection.

EXPERIMENTAL

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

Before modifications, glassy carbon and stainless steel (containing in wt % C, 0.17; Cr, 12.61; and Ni, 0.25) disk substrates of geometric area, 0.071 and 1 cm^2, respectively, were activated by polishing with successively finer grade aqueous alumina slurries (grain size, 5–0.5 μm) on a polishing cloth.

A glassy carbon electrode (or a stainless steel substrate) modified with 4-aminobenzoic acid (ABA) was obtained in a manner described earlier [47]. The procedure involved 4 voltammetric cycles from 0.4 to 1.0 V in absolute ethyl alcohol solution of 3 mmol dm^{-3} ABA + 0.1 mol dm^{-3} LiClO$_4$. The measurement system utilized Pt flag electrodes as counter and semireference electrodes. Irreversible oxidation of ABA was accompanied by the formation of the system's monolayer type film on glassy carbon. To produce ultra thin films of metal hexacyanoferrates, we utilized the ability of –COO$^-$ groups within ABA to attract iron(III) and nickel(II) ions. PB films were self-assembled by exposing the ABA-modified electrode to 3 mmol dm^{-3} $Fe_2(SO_4)_3$ at pH = 2 for 30 min followed by performing 5 potential cycles from 0 to 0.9 V in 3 mmol dm^{-3} $K_3[Fe(CN)_6]$ + 0.25 mol dm^{-3} K_2SO_4. The latter procedure can be repeated at least 10 times to produce thicker (multilayer) self-assembled PB films. As a rule, the electrode was rinsed with 0.25 mol dm^{-3} K_2SO_4 after each step. Ultra thin (monolayer type) and multilayer films of NiHCNFe were obtained similarly to PB ones except that instead of iron salt $NiSO_4$ was used. ABA-based PB/NiHCNFe bilayer structures were self-assembled on glassy carbon and stainless steel substrates. Fabrication of the inner PB and outer NiHCNFe films involved three consecutive soaking and potential steps in the respective metal ion and $K_3[Fe(CN)_6]$ solutions. To assure physical discreteness of PB and NiHCNFe films, the inner PB film was overcoated first by dipping in a 0.4% (wt) solution of poly(4-vinylpyridine), PVP, in methanol, followed by drying, and, subsequently, by dipping in 5% (wt) Nafion 117 alcoholic solution (from Aldrich).

Conventional PB film (inner) was fabricated on a glassy carbon substrate by electrodeposition from the solution formed following mixing 40 cm^3 1.0 mol dm^{-3} KCl with 5 cm^3 0.1 mol dm^{-3} $K_3[Fe(CN)_6]$ and 5 cm^3 0.1 mol dm^{-3} $FeCl_3$ (in 0.1 mol dm^{-3} HCl). The procedure involved controlled potential electrolysis at 0.5 V for 120 s. To avoid its intermingling into the inner (PB) film, the outer NiHCNFe film was in the polymerized form by forming a hybrid (composite) of NiHCNFe with poly(N-methylpyrrole), PMPy. Conventional NiHCNFe was electrodeposited onto the inner PB film through the application of 15 full voltammetric cycles at 50 mV s^{-1} in the potential range from 0.85 to –0.4 V in the solution obtained by mixing 48.5 cm^3 1.0 mol dm^{-3} KCl with 0.5 cm^3 0.1 mol dm^{-3} $K_3[Fe(CN)_6]$, 0.5 cm^3 0.1 mol dm^{-3} $NiCl_2$ and 100 μl PMPy (final concentration, 0.02 mol dm^{-3}).

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

Fabrication of ultra thin metal hexacyanoferrate films. For some applications, the most attractive bilayer systems would be nanostructured and produced from ultra thin (monolayer type) films of metal hexacyanoferrates. Obviously they must be fairly dense and free of large pores. We have developed an approach that permits fabrication of ultrathin PB and NiHCNFe films on glassy carbon and stainless steel. Our concept refers to the recent report [47] in which preparation of organic negatively charged monolayer on glassy carbon was described and accomplished by voltammetric potential cycling in 4-aminobenzoic acid (ABA) solution. Such ultra thin film covalently grafted on GC was used to attach large inorganic cations (complexes) [47].

In the present work, the ABA-modified electrode was exposed to the Fe^{3+} solution (pH = 2), and the $–COO^-$ groups of ABA were capable of attracting positively charged species (Fe^{3+}). In the next step, the electrode covered with the iron(III)-containing monolayer was subjected to potential cycling in the $K_3[Fe(CN)_6]$ + K_2SO_4 (pH = 2) solution. Consequently, a monolayer type ("two-dimensional") self-assembled ultra-thin film of PB (loading, 4×10^{-10} mol cm^{-2}) has been produced on glassy carbon (Figure 1A, curve a). The latter two steps can be repeated to produce subsequent "two-dimensional" layers of PB. As a rule, the produced surfaces have been thoroughly rinsed with 0.25 mol dm^{-3} K_2SO_4 solution (pH = 2) in between steps.

Figure 1 A shows cyclic voltammetric responses of three consecutive layers of PB recorded in 0.50 mol dm^{-3} K_2SO_4. Two sets of voltammetric peaks that originate from reactions: the oxidation of PB (Equation 1) to iron(III) hexacyanoferrate(III), Prussian Yellow, at about 0.9 V, and the reduction of PB to iron(II) hexacyanoferrate(II), Prussian White (Equation 2) at about 0.2 V are analogous to the peaks of

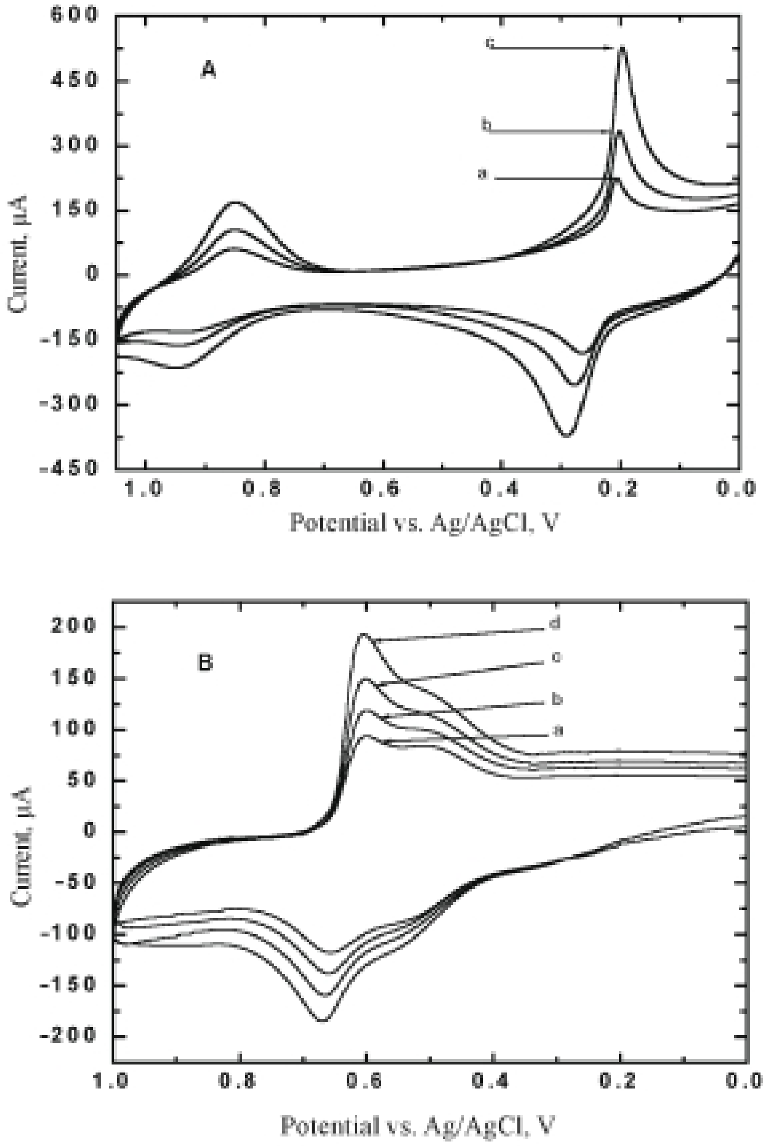

Figure 1. Cyclic voltammetry of ultra thin films: (A) PB and (B) NiHCNFe PB/NiHCNFe deposited on glassy carbon through self-assembling onto ABA monolayer. Letters a, b, c, and d refer to consecutively deposited layers. Electrolyte, 0.50 mol dm^{-3} K_2SO_4. Scan rate, 50 mV s^{-1}.

PB obtained by conventional method [2,5,11,35,36]. They can be described as follows:

$$KFe^{III}[Fe^{II}(CN)_6] - e^- - K^+ \Leftrightarrow Fe^{III}[Fe^{III}(CN)_6] \qquad (1)$$

$$KFe^{III}[Fe^{II}(CN)_6] + e^- + K^+ \Leftrightarrow K_2Fe^{II}[Fe^{II}(CN)_6] \qquad (2)$$

Ultra thin films of NiHCNFe (Figure 1B) can be produced in a similar way except that instead of Fe_2SO_4 the nickel salt ($NiSO_4$) has been used. The electrochemical behavior of self-assembled NiHCNFe films on ABA strongly resembles the characteristics of the respective conventionally electrodeposited metal hexacyanoferrate films. Indeed, the response of NiHCNFe film (Figure 1B) is characterized by overlapping redox reactions at about 0.4–0.6 V [16,44,46]. The following approximate formulas, $KNi_{1.5}[Fe^{II}(CN)_6]$ and $K_2Ni[Fe^{II}(CN)_6]$, can be assigned to two predominant forms (reduced) of electrodeposited NiHCNFe films. As in the case of PB, electron transfers in NiHCNFe are supported predominantly with the flux of cations [44–46]:

$$KNi_{1.5}[Fe^{II}(CN)_6] - e^- - K^+ \Leftrightarrow Ni_{1.5}[Fe^{III}(CN)_6] \qquad (3)$$

$$K_2Ni[Fe^{II}(CN)_6] - e^- - K^+ \Leftrightarrow KNi[Fe^{III}(CN)_6] \qquad (4)$$

We also attempted preparation of bilayer PB/NiHCNFe system by using the above concept of fabrication of PB and NiHCNFe as self-assembled films. The PB film of Figure 1A (curve c) served as an inner layer, and it was covered first with poly(4-vinylpyridine), PVP, and subsequently with Nafion by dipping the modified electrode in the solutions of 0.5% the commercially available PVP in methanol and Nafion (from Aldrich) each time for 15 min. While the cation exchange Nafion layer served to attract Ni^{2+} ions necessary to form the outer layer, the positively charged protonated PVP aimed at stabilizing PB and blocking the access of nickel cations to the electrode surface through the pores (pinholes) in the inner layer. The further treatment was identical to that used to produce self-assembled films of NiHCNFe on glassy carbon and involved potential cycling in hexacyanoferrate solution. The anion exchange properties of protonated PVP helped to attract and stabilize negatively charged NiHCNFe. Figure 2 shows the response of the resulting bilayer system. For comparison and to facilitate interpretation of the data of Figure 2, we provide a typical steady-state voltammetric behavior of a two-layer structure produced by electrodeposition of conventional PB (inner layer) and NiHCNFe (outer layer) films (Figure 3).

The bistable character of the bilayer system, that is composed of two distinct metal hexacyanoferrate layers [40], can be understood as follows. During the reduction cycle starting from 0.7 to 0.35 V (Figure 3A), NiHCNFe in the outer layer remains oxidized because the hexacyanoferrate(II) redox centers of the inner PB are not strong enough reductants to transfer electrons to hexacyanoferrate(III) sites of the oxidized NiHCNFe (compare Figures 3B and 3C). Upon application of potentials more negative than 0.35 V (Figure 3A), the reduction of the inner PB to Prussian White,

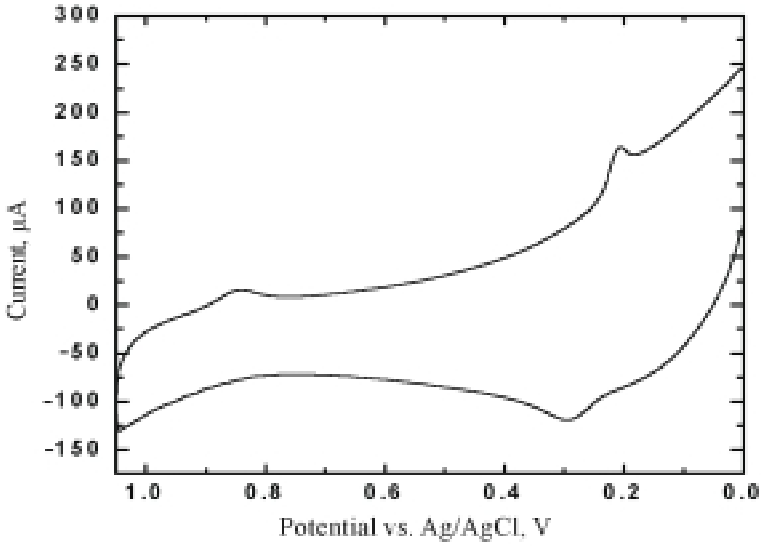

Figure 2. Cyclic voltammetry of a bilayer structure composed of PB (inner) and NiHCNFe (outer) films deposited on glassy carbon through self-assembling onto ABA monolayer. Other conditions as for Figure 1.

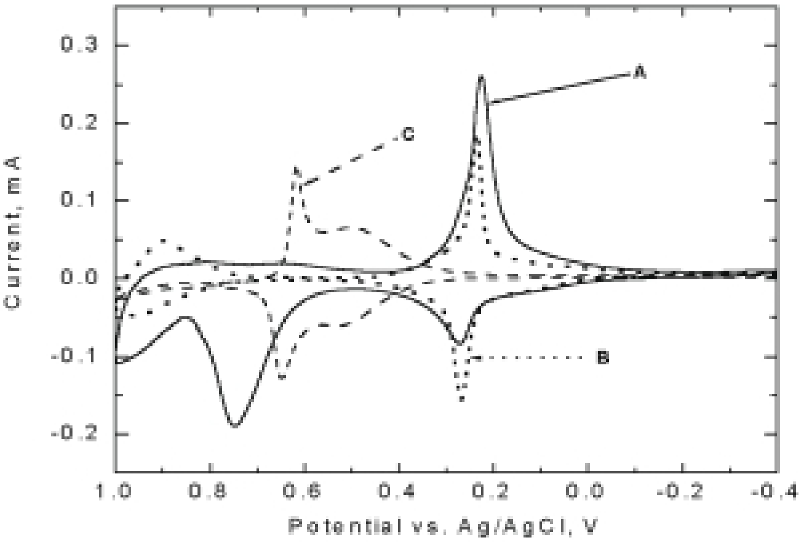

Figure 3. Cyclic voltammetric responses of (A) a bilayer PB(inner)/NiHCNFe(outer), (B) PB, and (C) NiHCNFe films conventionally electrodeposited on glassy carbon substrate. Other conditions as for Figure 1.

iron(II) hexacyanoferrate(II), mediates the reduction of the hexacyanoferrate(III) ionic sites of NiHCNFe to form the reduced nickel hexacyanoferrrate(II). On the other hand, during the oxidation cycle up to 0.7 V, only Prussian White is reoxidized to PB in the inner layer. It can be judged from the data of Figures 3B and 3C, that PB does not have sufficient oxidizing power and cannot act as a mediator towards oxidation of nickel hexacyanoferrrate(II). Consequently, NiHCNFe remains still reduced, and there is a metastable entrapment of charge in the outer film. One has to apply potentials higher than 0.7 V to observe effective mediation (oxidation of both layers). The oxidation process continues until both films are fully oxidized at the positive limit of 1.0 V. The data of Figure 3 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.

It can be expected that, under conditions of the experiment of Figure 2, where ultra-thin "self-assembled" PB and NiHCNFe layers were considered, the inner PB layer (which was overcoated with PVP and Nafion) was dense and uniform enough to prevent intermingling of outer film redox sites into PB film and to preclude direct electroactivity of NiHCNFe in the outer layer. While the ability of the inner PB layer to mediate NiHCNFe redox reactions was clearly apparent during the system's reduction at potentials more negative than 0.35 V (Figure 2), the oxidative mediation capabilities of self-assembled PB towards NiHCNFe were much poor. This observation could originate from the limited stability of the bilayer system composed of "self-assembled" PB and NiHCNFe. It is reasonable to expect that the system's decomposition (dissolution) was the most pronounced during positive potential scans.

PB/NiHCNFe bilayer system on stainless steel. We also found that ultra thin PB films could be fabricated on stainless steel using the approach of self-assembling onto ABA monolayer. Formation of well defined interface between substrate and protective layer is of big importance in the corrosion protection area. In our case as precision linker between the electrode and the redox centers serves self-assembled ABA monolayer.

The actual procedure was identical to that developed for a glassy carbon substrate (Figure 1A). The inner PB film (produced by sequential attachment of three ultra thin PB layers) on stainless steel was subsequently overcoated with NiHCNFe in a manner described in the previous section. Figure 4 illustrates voltammetric responses of (a) bare and (b) modified with a PB/NiHCNFe bilayer film steel substrates recorded in 1 mol dm^{-3} H_2SO_4 + 0.25 mol dm^{-3} K_2SO_4. An important issue is the existence of charge trapping due to the presence of PB/NiHCNFe bilayer film on stainless steel (Figure 4b). In this case, the overall voltammetric behavior is analogous to that presented in Figure 2. It is also noteworthy that the bilayer film showed very good stability during repetitive voltammetric cycling within the potential limits of Figure 4. This observation prompted us to consider the film for protection of stainless steel against general corrosion in acid media.

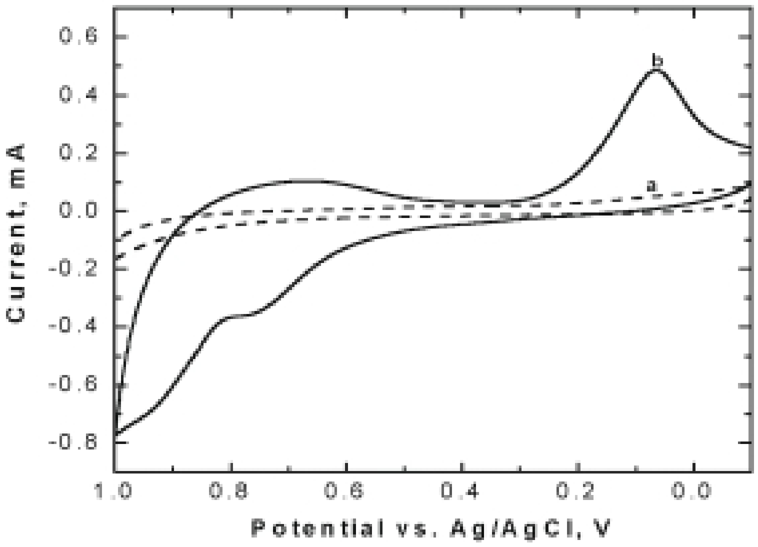

Figure 4. Voltammetric examination of stainless steel: (a) bare, and (b) modified with PB/NiHCNFe. Electrolyte, 1 mol dm^{-3} H_2SO_4 + 0.25 mol dm^{-3} K_2SO_4. Scan rate, 50 mV s^{-1}.

Recently, it has been established that modification of stainless steel with conducting polymer based films can stabilize the system's potential within limits of stability of the passive oxide layer on a metal surface [48–52]. But the charge stored in the polymer layer (used to oxidize base metal and to produce passive layer) can be irreversibly consumed during the system's redox reactions. Consequently, protective properties of the polymer coating may be lost with time. It can be expected that these processes can be significantly suppressed by overcoating a passive layer with a bilayer film capable of charge trapping [53]. It comes from preliminary potentiodynamic measurements (Figure 5A) that our bare stainless steel sample is characterized by corrosion potential of –0.55 V, undergoes passivation from –0.45 V to 0 V, and it exists in the passive state (*i.e.* it is covered with the passive oxide layer) from *ca*. 0 to 0.75 V. Current fluctuations are consistent with the dynamic character of passive state [52]: apparently two contrasting mechanisms depassivation and repassivation coexist. Open circuit (Figure 5B, curve a) measurements imply that the protective properties of a passive layer (on bare steel) are lost in acid medium (in 1 mol dm^{-3} H_2SO_4 + 0.25 mol dm^{-3} K_2SO_4). After approximately 2.5 minutes of exposure of the bare steel sample to acid medium its open circuit potential drops to the value of corrosion potential, and active dissolution proceeds. In the case of stainless steel covered with a bilayer film composed of ultra thin PB and NiHCNFe films, the open circuit potential increases up to the value (*ca*. 0.3 V) where the stable passive layer exists as evidenced from the lowest observed currents (Figure 5B, curve b). Finally, the PB/NiHCNFe modified stainless steel has kept its potential constant under open circuit conditions for at least 11 h (after this period the measurement system was dismantled).

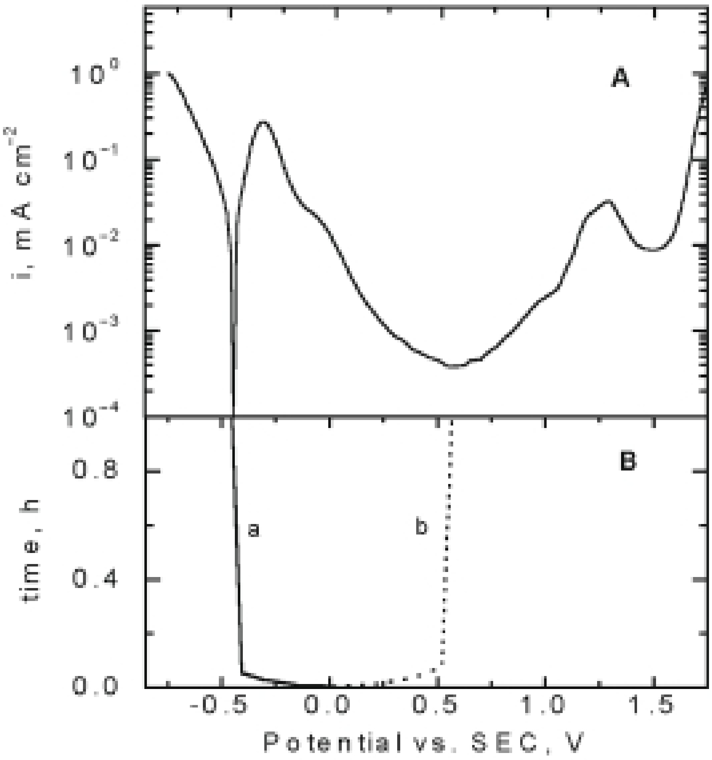

Figure 5. (A) Potentiodynamic curve recorded (at 5 mV s^{-1}) for bare stainless. (B) Changes of open circuit potentials for (a) bare and (b) PB/NiHCNFe modified stainless steels substrates. Samples were preconditioned at 1.0 V for 10 s. Electrolyte as for Fig. 4.

CONCLUSIONS

We describe a novel approach to fabrication of ultra thin metal hexacyanoferrate films by multiple sequential attachment of metal cations (self-assembled on 4-aminobenzoic acid monolayer) and hexacyanoferrate anions. Although stability of ultra thin films is poorer in comparison to conventional ones, it is possible to assemble them in a rational way to observe electronic effects, such as reversible charge state trapping (bistable switching), analogous to those recently reviewed elsewhere [54]. In this context, bilayer structures of metal hexacyanoferrates resemble two-layer films of redox and conducting polymers. An important issue is that our bilayer films can be produced on stainless steel to get protective coatings capable of maintaining a stationary potential of the metal in the passive range.

Acknowledgments

This work was supported by Ministry of Science, Poland under the Polish State Committee for Scientific Research (KBN) grant 4T08C02425. K.M. was supported in part by the University of Warsaw under BW-1602/09/03. M.Ch. appreciates the stipend from Foundation for Polish Science, FNP.

REFERENCES

1. Monk P.M., Mortimer R.J. and Rosseinsky D.R., Electrochromism, Fundamentals and Applications, VCH Weinheim (1995).
2. Itaya K., Uchida I. and Neff V.D., *Acc. Chem. Res.*, **91**, 162 (1986).
3. Carpenter M.K. and Conell R.S., *J. Electrochem. Soc.*, **137**, 2464 (1990).
4. Kulesza P.J., Malik M.A., Zamponi S., Berrettoni M. and Marassi R., *J. Electroanal. Chem.*, **397**, 287 (1995).
5. Feldman B.J. and Melroy O.R., *J. Electroanal. Chem.*, **234**, 213 (1987).
6. Neff V.D., *J. Electrochem. Soc.*, **132**, 1382 (1985).
7. Lasky S.J. and Buttry D.A., *J. Am. Chem. Soc.*, **110**, 6258 (1988).
8. Kulesza P.J., Malik M.A., Berrettoni M., Giorgetti M., Zamponi S., Schmidt R. and Marassi R., *J. Phys. Chem. B*, **102**, 1870 (1998).
9. Hartmann M., Grabner E.W. and Bergveld P., *Anal. Chim. Acta*, **242**, 249 (1991).
10. Coon D.R., Amos L.J., Bocarsly A.B. and Fitzgerald Bocarsly P.A., *Anal. Chem.*, **70**, 3137 (1998).
11. Kulesza P.J. and Doblhofer K., *J. Electranal. Chem.*, **274**, 95 (1989).
12. Dussel H., Dostal A., Scholz F. and Fresenius J., *Anal. Chem.*, **355**, 21 (1996).
13. Lin C. and Bocarsly A.B., *J. Electroanal. Chem.*, **300**, 325 (1991).
14. Zhou D.M., Ju H.-X. and Chen H.-Y., *J. Electroanal. Chem.*, **408**, 219 (1998).
15. Dong S. and Che Guangli, *J. Electroanal. Chem.*, **315**, 191 (1991).
16. Kulesza P.J., Brajter K. and Dabek-Zlotorzynska E., *Anal. Chem.*, **59**, 2776 (1987).
17. Zhou J. and Wang E., *J. Electroanal. Chem.*, **331**, 1029 (1992).
18. Lin M.S. and Jan B.I., *Electroanalysis*, **9**, 340 (1997).
19. Cataldi T.R.I., De Benedetto G.E. and Bianchini A., *Electroanalysis*, **10**, 1163 (1998).
20. Kahn O., *Nature*, **378**, 667 (1995).
21. Sato O., Einaga Y., Iyoda T., Fujishima A. and Hashimoto K., *J. Phys. Chem. B*, **101**, 3903 (1997).
22. Ohkoshi S., Fujishima A. and Hashimoto K., *J. Am. Chem. Soc.*, **120**, 5349 (1998).
23. Masui H. and Murray R.M., *J. Electrochem. Soc.*, **145**, 3788 (1998).
24. Inzelt G., Electroanalytical Chemistry, Dekker, New York (1994).
25. Inzelt G., Pineri M., Schultze J.W. and Vorotyntsev M.A., *Electrochim. Acta*, **45**, 2403 (2000).
26. Rubinson J.F. and Mark Jr H.B., Interfacial Electrochemistry, Marcel Dekker, New York (1999).
27. Murray R.W., Molecular Design of Electrode Surfaces Introduction to the Chemistry of Molecularly Designed Electrode Surfaces, Wiley (1992).
28. Doblhofer K., The Electrochemistry of Novel Materials Thin Polymer Films on Electrodes: A Physicochemical Approach, VCH Publishers Inc (1994).
29. Hermes M., Lovric M., Hartl M., Retter U. and Scholz F., *J. Electroanal. Chem.*, **50**, 193 (2001).
30. Joseph J., Bharathi S., Gomathi H. and Rao G.P., *Bull. Electrochem.*, **18**, 267 (2002).
31. Chidsey C.E.D. and Murray R.W., *Science*, **231**, 25 (1986).
32. Mannes K.M., Masui H., Wightman R.M. and Murray R.W., *J. Am. Chem. Soc.*, **119**, 3987 (1997).
33. Huang J. and Wrighton M.S., *Anal. Chem.*, **65**, 2740 (1993).
34. Pyrasch M., Toutianoush A., Jin W., Schnepf J. and Tieke B., *Chem. Mater.*, **15**, 245 (2003).
35. Ravaine S., Lafuente C. and Mingotaud C., *Langmuir*, **14**, 6347 (1998).
36. Bharathi S., Nogami M. and Ikeda S., *Langmuir*, **17**, 7468 (2001).
37. Bharathi S., Yegnaraman V. and Prabhakara Rao G., *Langmuir*, **11**, 666 (1995).
38. Saliba R., Agricole B., Mingotaud C. and Ravaine S., *J. Phys. Chem. B*, **103**, 9712 (1999).
39. Decher G., *Science*, **277**, 1232 (1997).
40. Miecznikowski K., Chojak M., Steplowska W., Malik M.A. and Kulesza P.J., *J. Solid State Electrochem.*, in press.

41. Feldman B.J. and Murray R.W., *Inorg. Chem.*, **26**, 1702 (1987).
42. Kelly M.T., Arbuckle-Keil G.A., Johnson L.A., Su E.Y., Amos L.J., Chun J.K.M. and Bocarsly A.B., *J. Electroanal. Chem.*, **500**, 311 (2001).
43. Kulesza P.J. and Galus Z., *J. Electroanal. Chem.*, **323**, 261 (1990).
44. Malik M.A., Miecznikowski K. and Kulesza P.J., *Electrochim. Acta.*, **45**, 3777 (2000).
45. Humphrey B.D., Sinha S. and Bocarsly A.B., *J. Phys. Chem.*, **88**, 736 (1984).
46. Bacskai J., Martinusz K., Czirok E., Inzelt G., Kulesza P.J. and Malik M.A., *J. Electroanal. Chem.*, **385**, 241 (1995).
47. Liu J., Cheng L., Liu B. and Dong S., *Langmuir*, **16**, 7471 (2000).
48. Wessling B., *Adv. Mater.*, **6**, 226 (1994).
49. Ahmad N. and MacDiarmid A.G., *Synth. Met.*, **78**, 103 (1996).
50. Tallman D.E., Spinks G., Dominis A. and Wallace G.G., *J. Solid State Electrochem.*, **6**, 73 (2002).
51. Mengoli G. and Mussiani M.M., *Electrochim. Acta*, **31**, 201 (1986).
52. Malik M.A., Galkowski M.T., Bala H., Grzybowska B. and Kulesza P.J., *Electrochim. Acta*, **44**, 2157 (1999).
53. Dumanska J. and Maksymiuk K., *Corrosion Science*, **44**, 1681 (2002).
54. Fendler J., *Chem. Mater.*, **13**, 3196 (2001).