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STRUCTURE AND ELECTROCHROMIC PROPERTIES OF FERRIC AQUAPENTACYANOFERRATE—A NEW ANALOGUE OF PRUSSIAN BLUE

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Abstract—A new electrode material of ferric aquapentacyanoferrate (FAPCF) film was fabricated. Its structure, optical, electrochemical and electrochromic properties were studied. In comparison with Prussian blue FAPCF exhibits a moderate contraction of the cubic lattice and a different texture of film. The maximum of optical absorption is shifted by 100 nm towards the long wavelength region for FAPCF relatively to Prussian blue.

Key words: electrochromic effect, ferric cyanoferrates, optical properties, structure, ligand.

INTRODUCTION

Prussian blue (PB) or ferric hexacyanoferrate ($Fe_4[Fe(CN)_6]_3$) has received much attention as a promising electrochromic material[1, 2]. While many PB analogues are known, only a few have been fabricated as film-modified electrodes acceptable for electrochemical studies and applications[3–6]. In these compounds Fe cations in the outer sphere are replaced typically by ions of other transition metals.

An alternative means is substitution of different ligands for some of the CN ligands in the Fe coordination sphere. The aim of the present paper is to examine the influence of the ligand changes on the structure, electrochemical and electrochromic properties of ferric cyanoferrates in the case of ferric aquapentacyanoferrate (FAPCF).

EXPERIMENTAL

The electrochemical deposition was performed from a freshly prepared mixture of equal values of equimolar ($5{\cdot}10^{-4}$ M) solutions of sodium aminopentacyanoferrate(III) $Na_2[Fe(CN)_5NH_3]\ 2H_2O$, prepared in accordance with[7], and $FeCl_3$ in 1 M KCl. The films studied were deposited at 0.2 V vs. Ag/AgCl saturated KCl reference electrode on glass plates covered with conducting SnO_2 or In_2O_3 200–400 nm layers. The deposited films were placed in HCl solution (pH 2) for 18 h, then rinsed in water thoroughly and dried in vacuum. For comparison PB films were deposited at 0.4 V (vs. Ag/AgCl) by a similar procedure from a freshly prepared mixture of equimolar ($5{\cdot}10^{-4}$ M) solutions of $K_3[Fe(CN)_6]$ and $FeCl_3$ in 1 M KCl.

Powder samples for X-ray studies were prepared by a slow addition of $FeCl_3$ solution to an equivalent amount of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ solution. After filtration and water washing the samples obtained were placed in HCl solution (pH 2) for 18 h.

The substance structure was examined by X-ray diffraction and *ir* spectroscopy. Film morphology was tested with a scanning electron microscopy (SEM). Electrochemical investigations were performed in a 1 M KCl solution (adjusted to pH 4 with HCl) by use of a standard three-electrode scheme with a graphite counter electrode and Ag/AgCl saturated KCl reference electrode.

RESULTS AND DISCUSSION

Film composition

We assume that the mechanism of film growth is the same as in the case of PB. Thus we can suppose the formula for the composition of deposited material: $Fe[Fe(CN)_5NH_3]$. Pentacyanoferrates like this can be modified chemically by substitution of different molecules for NH_3 ligands. We assume that in our case the deposited substance transforms to a compound like $Fe[Fe(CN)_5H_2O]$ after exposure to acidified water (a partial replacement with H_2O molecules probably occurs during the deposition

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Table 1. Interplanar spacings, d (Å) and intensities, I (relative units) of base diffraction peaks for PB and FAPCF samples

	PB			FAPCF		
		I			I	
hkl	d*	powder*	film	d	powder	film
200	5.10	100	68	5.06	100	62
220	3.60	32	100	3.58	36	67
222				2.92		100
400	2.55	48	32	2.54	30	27
420	2.28	32	26	2.27	15	20
422	2.07	3	13	2.06	6	15

* Data from [6].

process). This supposition is confirmed indirectly by *ir* spectroscopy (Fig. 1). For the deposited material *ir* spectra exhibit bands at 1390 1240 cm^{-1} attributed to vibrations of co-ordinated NH_3 molecules. After exposure to acidic solution these bands disappear. Supplementary research is still needed to determine the correct formula of this compound.

Structure

The X-ray diffraction data are listed in Table 1. The trend is observed for decreasing interplanar spacings in FAPCF in comparison with PB that corresponds to a certain contraction of the cubic lattice for FAPCF. This contraction may be caused by the replacement of the relatively large negatively charged CN ligands with electroneutral H_2O ones, and by a redistribution of electron density at the Fe ions and a gain of the bonds between Fe ions and retained CN ligands. At the same time there is no substantial distortion of cubic symmetry of FAPCF as is evidenced by the good correspondence of the diffraction peak positions of FAPCF with those of PB. The data listed in the table also indicates the presence of textured films—there is a considerable growth of 220 peak intensity for both type of films in comparison with powdered ones, but for FAPCF films the outstanding growth of 222 peak intensity is also observed. The SEM images in Fig. 2 indicate the difference of textures and show that the crystallites in FAPCF films are oriented with [111] direction aligned with the normal to the substrate, whereas directions, aligned predominantly with this normal in PB crystallites, are [100] and [110].

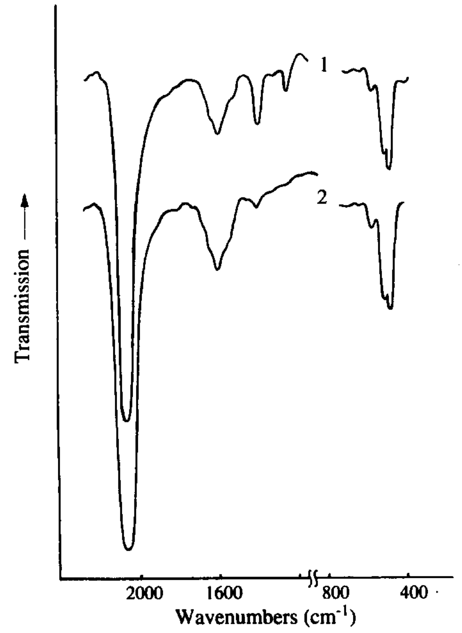

Fig. 1. Infrared spectra of FAPCF films before (1) and after (2) the treatment with HCl.

Electrochemical study

Voltammograms of FAPCF at the first cycle and in a steady state are shown in Fig. 3. Two peaks at 0.26 and 0.82 V (vs. Ag/AgCl) are observed that correspond to reversible electrochemical reactions. The positions of these peaks are close to those of PB films. We suppose that by analogy with PB[8] reversible redox reaction at $0 < \varphi < 0.6$ V region for FAPCF may be describe as:

$$Fe^{3+}[Fe^{2+}(CN)_5H_2O] + K^+ + e^- \rightleftharpoons KFe^{2+}[Fe^{2+}(CN)_5H_2O]$$

At the same time such cyclic variation of potential may also leads to formation of "soluble" (K^+-containing) form of FAPCF, as in the PB case[9]. From Fig. 3 one can determine that total charge involved in reaction at $0 < \varphi < 0.6$ V is twice as large as that for reactions at $0.6 < \varphi < 1.0$ V. The value of charge ratio for these reaction differs from one for PB, which according to ref [8] comprises 3/2. However obtained data do not allow us to describe adequately a mechanism of FAPCF redox reaction at $\varphi > 0.7$ V.

It is interesting to note that this variation of potential does not lead to marked changes either in the texture or in the structure of the film.

Electrochromic properties

The optical absorption spectra of FAPCF are shown in Fig. 4, PB spectrum is also given for comparison. A substance colour depends on the potential φ: at $\varphi < 0$ V FAPCF is practically colourless with the weak yellow hue; at $0.2 < \varphi < 0.6$ V it is green-blue, and at $\varphi > 0.7$ V is yellow-green. The absorption band in FAPCF spectrum ($\varphi = 0.4$ V) is shifted by 100 nm to the long wavelength region in comparison with one of PB (780 and 680 nm, correspondingly).

The electrochromic efficiencies (the ratio of a value of optical density change to a value of surface density of injected charge) of the PB and FAPCF are close at the maxima of the absorption bands and amount near 100 cm^2 C^{-1} ($0.2 < \varphi < 0.3$ V).

According to[10] optical absorption in PB at 700 nm band involves a transfer of the *d*-electrons between sublevels of Fe^{2+} and Fe^{3+} ions. The replacement of CN ligands by water molecule lowers the field strength of ligands that leads to a change of *d*-sublevel positions for these cations. The change of field strength largely affects the *d*-electrons of Fe^{2+}

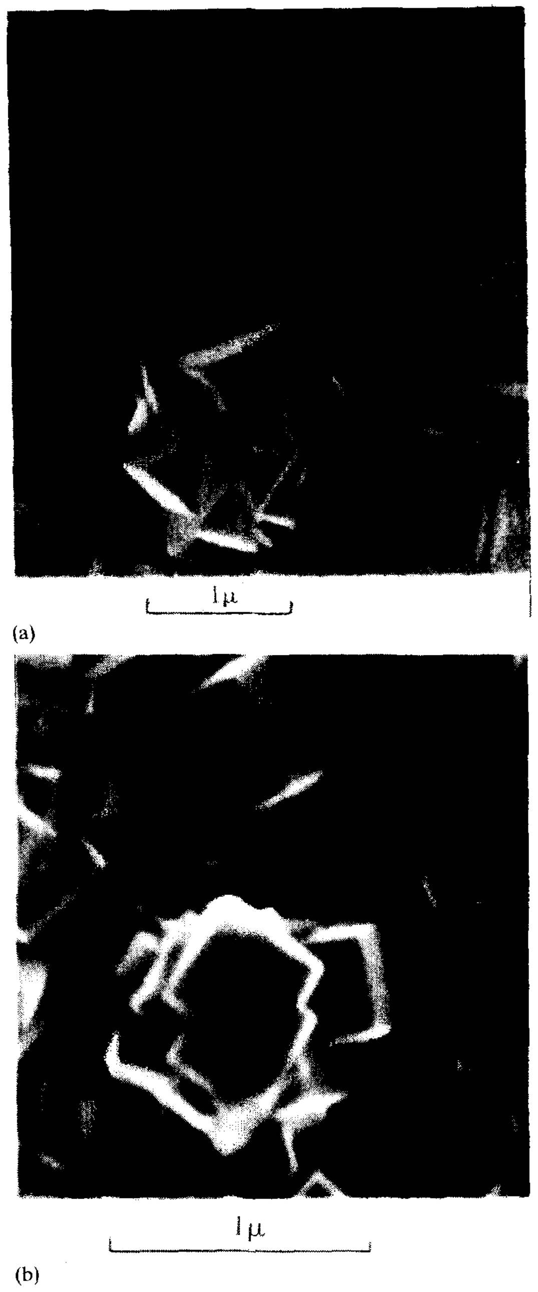

Fig. 2. SEM images of FAPCF (a) and PB (b) films.

which is in the low spin strong field configuration, than those of Fe^{3+} in the high spin weak field configuration. This leads to a decrease in the difference between sublevel energies of the electrons involved in optical transition. Thus the absorption band of FAPCF would shift to the long wavelength region in a comparison with PB that is observed in our study. CN ligand is positioned at the onset of the spectrochemical row[11]. Thus, the replacement of these ligands in the coordination sphere of Fe cations in PB by any weak field ligand whose size is comparable with one of water molecule should shift the absorption band to the long wavelength region of spectra.

By this means a new approach is proposed for a modification of composition and properties of Prussian blue by replacement of ligands in coordination sphere with molecules of a different nature. It has been shown that the insertion of water molecules in the coordination sphere of PB leads to a moderate variation of the structure and to changes of texture, electrochemical behaviour and electrochromic properties of the films.

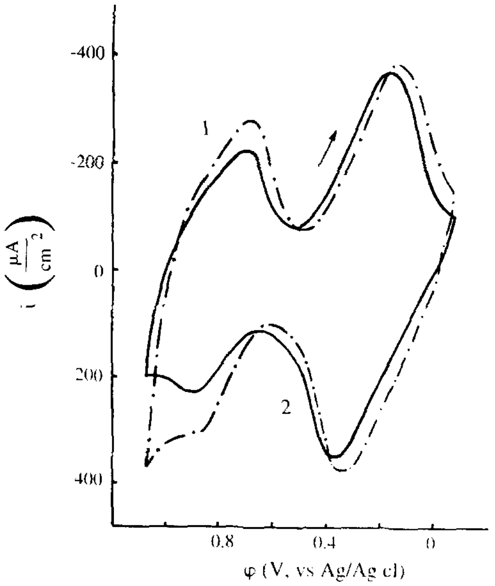

Fig. 3. Cyclic voltammograms of FAPCF in 1 M KCl: 1; first cycle, 2; 25th cycle. The scan rate was $16\,mV\,s^{-1}$.

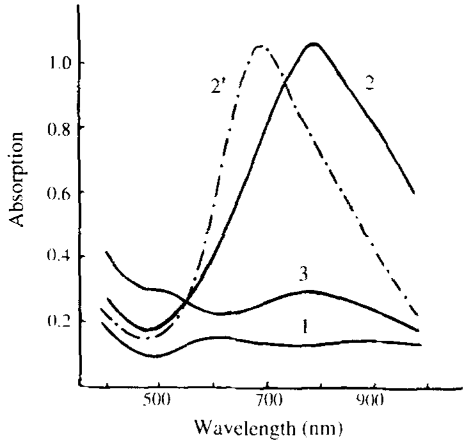

Fig. 4. Optical absorption spectra of the films of FAPCF (1, 2, 3) and PB (2') in 1 M KCl. 1 – $\varphi = 0$ V; 2,2' – $\varphi = 0.4$ V; 3 – $\varphi = 1$ V.

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