

Metal hexacyanoferrate network synthesized inside polymer matrix for electrochemical capacitors

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Available online 21 May 2007

Abstract

Poly(3,4-ethylenedioxythiophene) (pEDOT) films have been modified by iron, cobalt and nickel hexacyanoferrate analogues (*Mehcf*). Synthesis of these materials was performed using multicyclic polarisation of pEDOT/ $\text{Fe}(\text{CN})_6^{3-/4-}$ films in aqueous electrolytes containing nickel, cobalt and iron salts. Resulting materials are electroactive and show good reproducibility during hundreds of polarisation cycles. Specific capacitance of hybrid materials is equal to 70, 70 and 50 F cm^{-3} for pEDOT/*Cohcf*, pEDOT/*Nihcf* and pEDOT/*Fehcf*, respectively. Scanning electron microscopy shows that obtained films are homogenous and compact on the micrometer scale.

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Keywords: Electroactive polymers; Redox network; Electrochemical capacitors; Prussian Blue analogue

1. Introduction

Hybrid materials (HM) consisting of electroactive polymers and redox inorganic compounds such as metal hexacyanometalates attract attention because of their potential use in electrocatalysis, sensors and energy storage and conversion devices [1–3]. Particularly, HM are considered as materials for electrochemical capacitors [4–6]. Such films are capable of accumulating charge efficiently and exhibit high current density.

Organic–inorganic nanocomposites of a new type are attractive because of their potential to combine the electric capacity of both components under the condition that the inorganic network redox process lies in the potential range where the polymer is conductive. A chemical bond between components is desired, because it may maintain good electrochemical properties of the composite system, an ability to efficiently accumulate the charge and ensure a high current density discharge. Kulesza et al. studied composites containing nickel hexacyanoferrate and polyaniline (*Nihcf*/PANI). The composite (hybrid) exists as a fairly stable system due to interaction between both components, and for the *Nihcf*/PANI hybrid this interaction is reported as electrostatic attraction between polymer (positive) and *Nihcf* (negative) parts [7]. Direct interaction between ferrous/ferric

hexacyanoferrate and polyaniline in *Fehcf*/PANI films was reported as an iron–nitrogen chemical bond by Sawant et al. [8]. It is likely that poly(3,4-ethylenedioxythiophene) (pEDOT) used as a matrix for synthesis of a Prussian Blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) analogue forms direct chemical bonds with the inorganic network, indicated by XPS analysis and micro-Raman spectroscopy as Fe–S interaction [9,10].

The electrochemical deposition process, which leads to formation of metal hexacyanoferrate within pEDOT, makes use of an ionic sorption de-sorption process during potentiodynamic polarisation of the polymer with $\text{Fe}(\text{CN})_6^{3-/4-}$ counter-ions (pEDOT/ $\text{Fe}(\text{CN})_6^{3-/4-}$, has been reported in refs. [11,12]). A three-dimensional composite with uniform distribution of both inorganic and organic parts can be formed by that method.

Choice of pEDOT comes from the fact that the polymer is very stable and chemically resistant [13]. This compound attracts attention also as a material for supercapacitors [14–16]. Specific capacitance of the pEDOT film in 0.1 M LiClO_4 acetonitrile (7000 Å thick) is reported as 3 mF cm^{-2} [15].

In this work, films containing an iron, nickel and cobalt hexacyanoferrate redox network within the poly(3,4-ethylenedioxythiophene) matrix are presented, their synthesis and electrochemical character described. We expected, that charge accumulated in polymer and in redox centres could be utilised in a coupled way giving high current densities, as the polymer is electroactive in the potential range covering activity of every *Mehcf* under study. Composite films were tested in

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aqueous electrolytes to show the cycle life and specific capacitance of composite systems.

2. Experimental

2.1. Apparatus and electrodes

Electrochemical experiments were carried out using the potentiostat–galvanostat system AutoLab PGStat10 and Scanning Potentiostat EG&G, Model 362 (for potentiodynamic step of restructuring of the films, see below). A three-electrode one-compartment cell was used in all experiments. A platinum disc (0.002 or 0.03 cm²) served as a working substrate electrode. Platinum was polished on alumina slurry (Buhler 0.05 μm) and rinsed thoroughly using an ultrasonic bath. Platinum plates of 0.5 cm² surface area served as a support for material deposition for energy-dispersive X-ray (EDX) measurements. Scanning Electron Microscopy (Philips-FEI XL 30 ESEM) (SEM) with EDX Spectrometer–EDAX Sapphire[®] was used for quantitative analysis of elements in the films, a 10 kV voltage was applied. Samples for EDX analysis were prepared by electrodeposition of pEDOT/Fe(CN)₆^{3-/4-} followed by potentiodynamic restructuring of materials on platinum foil (0.5 cm²), average thickness of films—(a) 0.7 μm and (b) 15 μm ± 10%. EDX measurements were taken directly from platinum samples covered with hybrid film. Composites were also analysed by Atomic Absorption Spectrophotometry (AAS) analysis. A Profilometer Hommel Tester T8000 (Hommelwerke, GmbH, Germany) was used for thickness measurements.

All potentials were measured versus Ag/AgCl (0.1 M KCl) used as reference electrode. The cell was kept under Ar atmosphere at 22 ± 1 °C.

2.2. Chemicals

Monomer 3,4-ethylenedioxythiophene (EDOT) (Bayer Co.) was used as received. All inorganic chemicals: KCl (POCH Gliwice), K₂SO₄ (POCH Gliwice), K₄[Fe(CN)₆] (POCH Gliwice), K₃[Fe(CN)₆] (POCH Gliwice), FeCl₃ (Sigma–Aldrich), CoCl₂·6H₂O (Sigma–Aldrich), NiCl₂·6H₂O (Sigma–Aldrich) were of analytical grade and used as received without further purification.

3. Results and discussion

3.1. Electrochemical preparation of films

Composite films were synthesized electrochemically on a platinum disc electrode. Synthesis of material proceeded in two steps. The first step was polymerisation of EDOT giving a polymer called here the “prime” film. The second step was potentiodynamic restructuring of “prime” films.

Preparation of the “prime” polymeric film is described in article [9]. Preparation was based on potentiostatic synthesis of pEDOT from 0.015 M EDOT aqueous electrolyte containing ferrous and ferric hexacyanoferrate at +1.0 V versus Ag/AgCl. The electrolytic bath was conditioned for 24 h before film

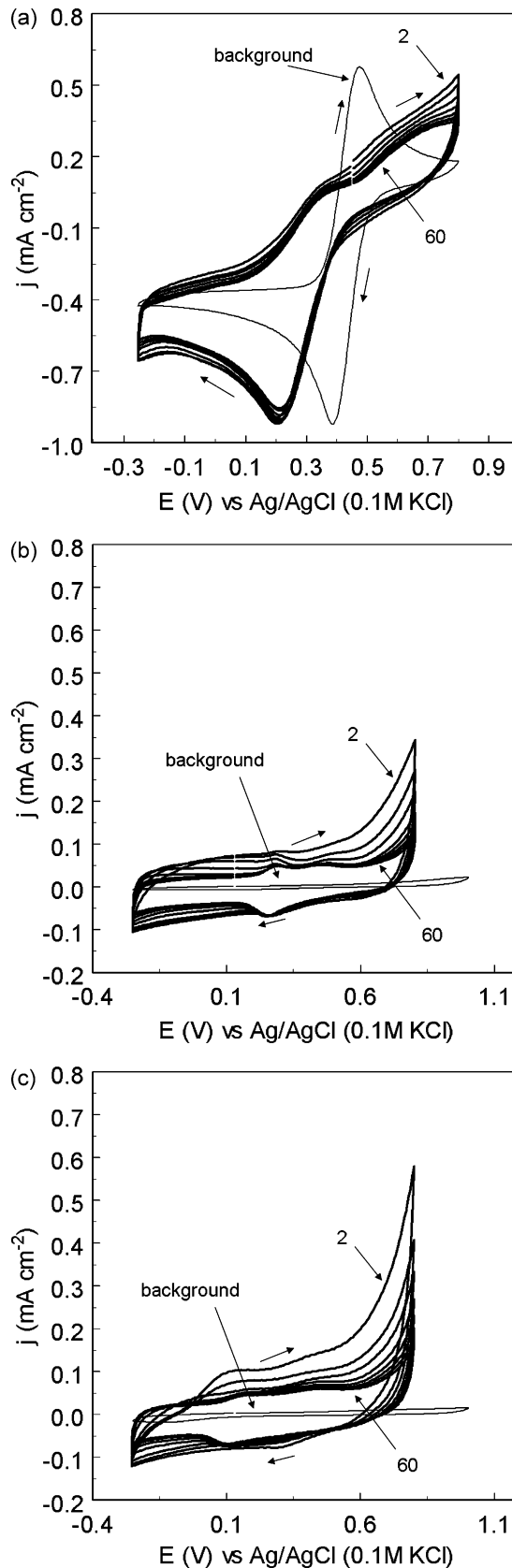


Fig. 1. (a) Cyclic voltammograms obtained for pEDOT/Fe(CN)₆^{3-/4-}; sweep rate 20 mV s⁻¹; outer electrolyte 0.01M FeCl₃. (b) Cyclic voltammograms obtained for pEDOT/Fe(CN)₆^{3-/4-}; sweep rate 20 mV s⁻¹; outer electrolyte 0.05 M CoCl₂. (c) Cyclic voltammograms obtained for pEDOT/Fe(CN)₆^{3-/4-}; sweep rate 20 mV s⁻¹; outer electrolyte 0.05 M NiCl₂.

preparation. The total charge during electropolymerisation was 0.941 C cm^{-2} . Average thickness of film was $0.7 \mu\text{m}$.

Films obtained as the “prime” show redox activity typical for an $\text{Fe}(\text{CN})_6^{3-/4-}$ couple polarised in KCl aqueous electrolyte [9]. Hence, the obtained material was a poly(3,4-ethylenedioxythiophene) electroactive polymer with $\text{Fe}(\text{CN})_6^{3-/4-}$ acting as counter-ions balancing positive charge of oxidised pEDOT.

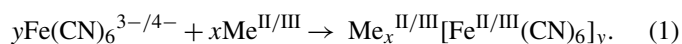
In the second step “prime” pEDOT/ $\text{Fe}(\text{CN})_6^{3-/4-}$ films were transferred into an appropriate electrolyte for further nano-restructuring preceded by careful rinsing with re-distilled water. The multicyclic potentiodynamic reordering of the films was performed in: (a) 0.01 M FeCl_3 , (b) 0.05 M NiCl_2 and (c) 0.05 M CoCl_2 . Electrolytes were prepared directly before the experiment and fresh samples were used for each experiment.

Fig. 1a–c illustrates current changes during subsequent potential cycles of a Pt/pEDOT electrode in the potential range between -0.25 and $+0.8 \text{ V}$ versus Ag/AgCl (0.1 M KCl) in (a) iron, (b) cobalt and (c) nickel electrolytes. All three cases show a common tendency to develop stable patterns of cyclic voltammetry (cv) curves after 50–60 cycles. Activity of films decreases during subsequent cycles, the oxidation current density recorded above 0.6 V significantly diminished. This type of behaviour is common for all studied films and was observed also for polymers modified by cycling in KCl [9]. According to previous studies, the diminishing current is connected with oxidation of free Fe^{2+} ions emerging from decomposition of $\text{Fe}(\text{CN})_6^{4-}$.

Polarisation curves taken in $\text{FeCl}_{3\text{aq}}$ electrolyte exhibit activity of ferrous/ferric couples from the electrolyte, Fig. 1a. The background cv curve, taken for Pt electrode, shows symmetrical anodic and cathodic current peaks. Different kinds of Fe(III/II) hydrated iron ions are active in the potential window of interest [17]. The cathodic branch of the cv curve, obtained for the film modified in FeCl_3 , has a slight slope in comparison with the background curve, very likely due to resistivity of the film. On the anodic branch of the cv curve two waves have been recorded. The first one may be related to iron oxidation inside the polymer, e.g. $\text{Fe}^{\text{II/III}}(\text{CN})_6^{3-/4-}$ and/or $\text{Fe}^{\text{II/III}}$ in Prussian Blue. The second wave, positioned more anodically, may be ascribed to Fe(II) oxidation from the outer electrolyte.

The cv curves taken for electrodes modified in $\text{CoCl}_{2\text{aq}}$ and $\text{NiCl}_{2\text{aq}}$ mainly show changes of film activity, as the outer electrolytes are not active in the studied potential range. Fig. 1b and c reveals changes during formation of Co and Ni derivatives of *Mehcf*. Activity of the films changes, average current density slightly diminishes and new anodic and cathodic humps appear. New redox processes which emerge under the cyclic procedure will be shown and interpreted in the next paragraph describing behaviour of hybrid materials in KCl electrolyte (compare to Fig. 3).

Multicyclic polarisation is carried out for the purpose of introduction of metal ions into films which already contain $\text{Fe}(\text{CN})_6^{3-/4-}$ counter-ions. During cathodic polarisation the polymer loses the positive charge. The $\text{Fe}(\text{CN})_6^{4-}$ counter-ions may be desorbed from the film to maintain electroneutrality and/or (a) Fe(II,III), (b) Ni(II) and (c) Co(II) ions may be inserted into the film polarised in FeCl_3 , NiCl_2 and CoCl_2 electrolyte, respectively. Insertion of iron, cobalt and nickel ions from outer electrolyte should result in the formation of an inorganic redox network of the respective metal hexacyanoferrate. $\text{Me}_x[\text{Fe}^{\text{II/III}}(\text{CN})_6]_y$ according to simplified scheme:



Precise indication of the mechanism is not possible without further studies. It is very likely that formation of insoluble compounds is a driving force of the observed changes. The new compound formed in the film exhibits its own redox activity. This change can be observed on cv curves, see Fig. 3. Dashed line curve shows electroactivity of “prime” pEDOT/ $\text{Fe}(\text{CN})_6^{3-/4-}$ film in KCl. Broad humps indicate oxidation and reduction of counter-ions $\text{Fe}(\text{CN})_6^{3-/4-}$ in the film. cv curves (solid lines) of final films prove that composites created during subsequent multicyclic polarisation exhibit new redox couples and their probable origin is discussed in Section 3.3.

3.2. Composition of films

EDX analysis was employed to estimate the composition of films. Two sets of samples were analysed: (a) $0.7 \mu\text{m}$ and (b) $15 \mu\text{m}$ thick samples. Moreover, metal atom quantity was

Table 1
EDX data and empirical formula of the materials; film thickness— $0.7 \mu\text{m}$

Element	Material (at.%)		
	pEDOT/ <i>Fehcf</i>	pEDOT/ <i>Cohcf</i>	pEDOT/ <i>Nihcf</i>
C	70.02	70.04	73.54
N	5.63	8.89	5.61
O	15.06	11.86	12.2
S	7.55	5.83	6.07
K	0	0	0.55
Fe	1.74 1.46 ^a	1.51 1.35 ^a	0.92 1.17 ^a
Co	0.00	1.87 1.85 ^a	0
Ni	0.00	0.00	1.11 1.41 ^a
Empirical formula	$\text{FeFe}(\text{CN})_6, \text{Fe}_4[\text{Fe}(\text{CN})_6]_3, \text{Fe}_4[\text{Fe}(\text{CN})_6]_3^{\text{a}}$	$\text{Co}_{2.5}[\text{Fe}(\text{CN})_6]_2, \text{Co}_3[\text{Fe}(\text{CN})_6]_2^{\text{a}}$	$\text{K}_{0.6}\text{Ni}_{1.2}[\text{Fe}(\text{CN})_6], \text{Ni}_{1.2}[\text{Fe}(\text{CN})_6]^{\text{a}}$

^a AAS analysis.

Table 2
EDX data and empirical formula of the materials; film thickness—15 μm

Element	Material (at.%)		
	pEDOT/ <i>Fehcf</i>	pEDOT/ <i>Cohcf</i>	pEDOT/ <i>Nihcf</i>
C	68.13	73.84	67.74
N	5.93	5.49	6.41
O	15.71	12.24	15.14
S	7.93	6.15	7.67
K	0.00	0.00	0.00
Fe	2.3	0.91	2.01
Co	0.00	1.37	0.00
Ni	0.00	0.00	1.03
Empirical formula	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$	$\text{Co}_3[\text{Fe}(\text{CN})_6]_2$	$\text{NiFe}[\text{Fe}(\text{CN})_6]$

established by AAS for samples prepared as films of the same thickness as samples tested electrochemically ($\sim 1 \mu\text{m}$). Tables 1 and 2 contain data and empirical formulas resulting from EDX and AAS analysis.

Different compounds were obtained depending on the modifying electrolyte. Modification of iron chloride enables obtaining of “soluble” ($\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$) or “insoluble” ($\text{Fe}_4^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$) Prussian Blue (PB) analogues. In the case of “soluble” PB both iron atoms are in the oxidised Fe(III) form.

Two forms of *Cohcf* are known from previous studies [18,19]. In our case, only one form of *Cohcf* can be proposed on the basis of EDX data for thin and thicker films, see Tables 1 and 2.

Results obtained for pEDOT/*Nihcf* material were different for thin and thicker film complexes. In most cases, *Nihcf* appears as inorganic material with composition given

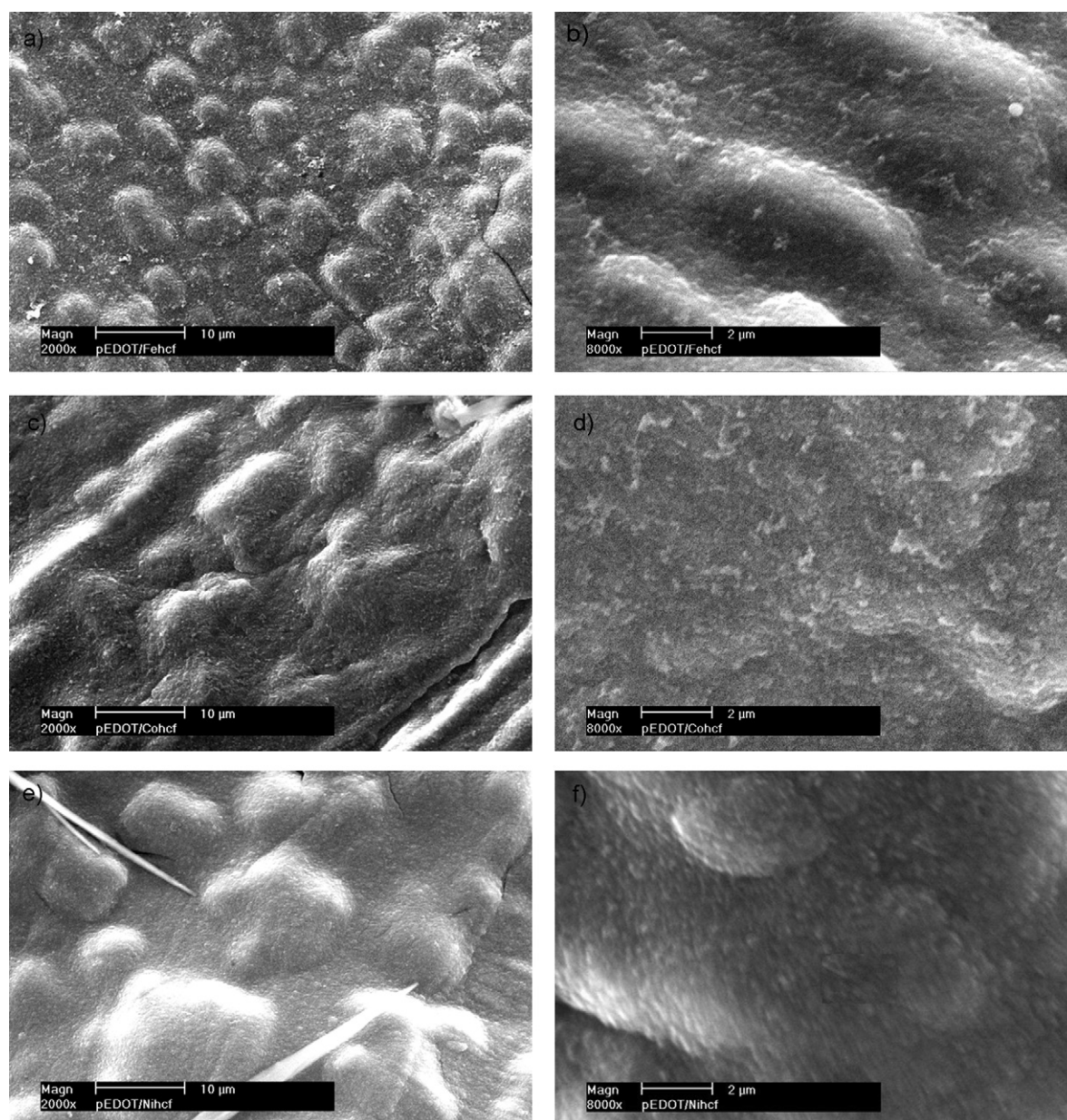


Fig. 2. (a–f) SEM image of pEDOT/*Me hcf* material; (a) pEDOT/*Fehcf*, magnitude 2000 \times , (b) pEDOT/*Fehcf*, magnitude 8000 \times , (c) pEDOT/*Cohcf*, magnitude 2000 \times , (d) pEDOT/*Cohcf*, magnitude 8000 \times , (e) pEDOT/*Nihcf*, magnitude 2000 \times and (f) pEDOT/*Nihcf*, magnitude 8000 \times .

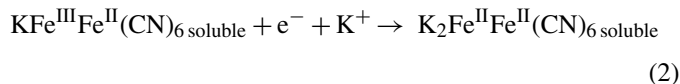
by simplified formula: $K_xNi_y[Fe(CN)_6]$ [20]. Modification of $pEDOT/Fe(CN)_6^{3-/4-}$ films in $NiCl_2$ solution is not expected to produce *Mehcf* containing potassium ions. However, $KNi[Fe(CN)_6]$ may be proposed to be formed in thinner films. The only reasonable explanation is that potassium ions were present in the $pEDOT/Fe(CN)_6^{3-/4-}$ film before modification in $NiCl_2$ solution. Thus, it seems that during polymerisation of EDOT potassium ions from the initial bath are captured by polymer. Insertion of nickel ions (and their transformation to *Nihcf*) prevents expulsion of potassium ions from the film during potentiodynamic modification. *Nihcf* is known to be the best material among *Mehcf* for ionic transport of alkali metal cations [21].

Scanning electron microscopy (SEM) images of platinum plates covered with $pEDOT/Fe_hcf$, $pEDOT/Co_hcf$ and $pEDOT/Ni_hcf$ are presented in Fig. 2a–f. Examined samples were of similar thickness as those studied in electrochemical tests, i.e., $\sim 1 \mu m$. As can be seen, the texture of all three samples does not differ significantly in respect to micro-porosity of the material. The observed surface is creased, covered with “humps” of different sizes. However, higher magnification shows that materials are fairly dense and compact. They look homogeneous in the micro-scale.

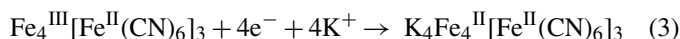
3.3. Electrochemical properties of the *pEDOT/Mehcf* films

New materials were tested in 0.1 M KCl aqueous electrolyte by cyclic voltammetry. cv curves of hybrid material containing metal hexacyanoferrate within the polymer exhibit stable redox couples in 0.1 M KCl electrolyte, Fig. 3. Material obtained by cyclic polarisation in $FeCl_3$ aqueous electrolyte shows sharp anodic and cathodic peaks at $E \cong +0.1$ V. The origin of this current may be disclosed by comparison between activity of the hybrid material and well-known activity of Prussian Blue films [22,23]. It was recognised that inorganic films of Prussian Blue exhibit redox activity from the Fe(II/III) couple belonging to iron coordinated via nitrogen atoms from the CN group (so-

called high-spin iron ions) at the same potential range [24,25]. One may suppose that that peak observed at ~ 0.1 V represents an Fe(II/III) couple of similar coordination in hybrid systems. The second redox couple of Prussian Blue, originating from low-spin iron ions coordinated by carbon atoms, is active at higher anodic potential (above +0.6 V) and in the case studied the wave is overlapped with electrolyte decomposition (not shown here). In the first redox system at 0.1 V cation exchange is involved [26]:

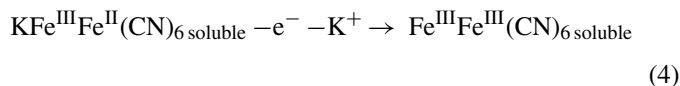


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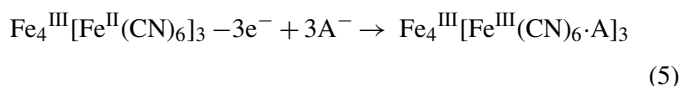


allowing the so-called “soluble” form of Prussian Blue to form. Compounds containing potassium are known as “soluble” whilst others are “insoluble”—they vary with structure [27]. Formation of hybrid material allows keeping inorganic redox networks free from the mass losses, which are known to occur for *Mehcf* films in contact with electrolytes.

In the second redox process (above +0.6 V, not shown in Fig. 3 for *Fe_hcf*), cation and anion exchange may contribute to the reaction [26]:



or



In the studied case it is difficult to gain a precise picture of the type of species undergoing ionic transfer, since both the inorganic and organic part of the system participate in sorption/de-sorption processes. It was established that potassium chloride and potassium sulphate were compatible electrolytes with the electrode material.

The position of the current maxima related to FeII/III (from low-spin iron) depends on the type of the second metal in the inorganic network. Modification in $NiCl_2$ gives maxima which are observed at about +0.39 V, as was already found for nickel hexacyanoferrate [28,29]. The hybrid material with *Co_hcf* reveals redox activity at a slightly more anodic potential ($\sim +0.41$ V). The anodic current in the shape of a plateau, or not clearly defined separate humps (depending on sweep rate) can be seen in Fig. 3 (*pEDOT/Co_hcf*) and Fig. 4.

It is known from the work of Kulesza et al. that cobalt and nickel hexacyanoferrate in aqueous electrolytes may show activity of low-spin iron ion redox centres only [19,29]. High-spin iron ion redox centres are substituted by cobalt and nickel atoms. In the pure inorganic state metal hexacyanoferrates have complex stoichiometry and in the presence of potassium salts form two types of compounds (for cobalt derivative): $KCo_{1.5}[Fe^{II}(CN)_6]$ and $K_2Co^{II}[Fe(CN)_6]$ [19]. Also nickel hexacyanoferrate in contact with potassium electrolyte forms a

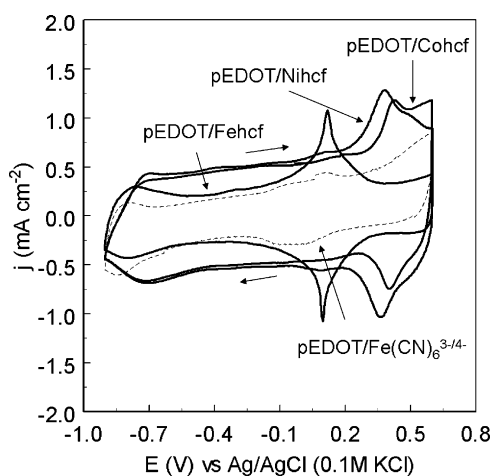


Fig. 3. Cyclic voltammetry curves of the Pt/*pEDOT/Fe_hcf*, Pt/*pEDOT/Co_hcf* and Pt/*pEDOT/Ni_hcf* electrodes in 0.1 M KCl; sweep rate 100 mV s^{-1} (solid lines). Dashed line represents cv curve obtained for not modified “primary” polymer $pEDOT/Fe(CN)_6^{3-/4-}$ film in 0.1 M KCl; sweep rate 100 mV s^{-1} .

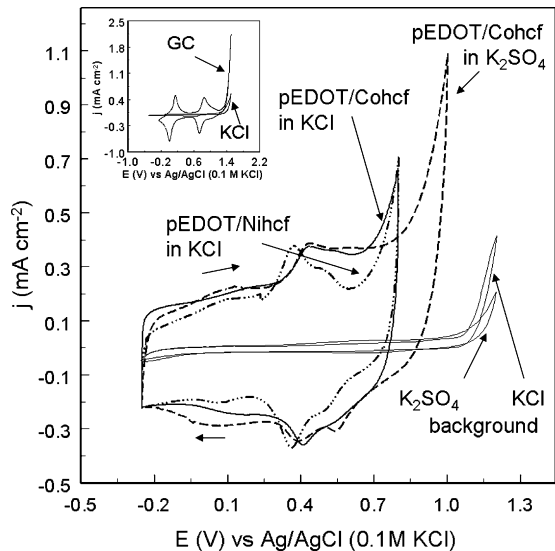
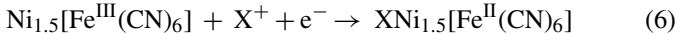
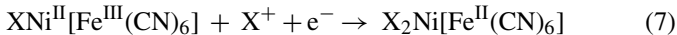


Fig. 4. Cyclic voltammetry curves obtained for Pt/pEDOT/Cohcf and Pt/pEDOT/Nihcf electrode in 0.1 M KCl and 0.1 M K₂SO₄ solutions; sweep rate 50 mV s⁻¹. Inset: cyclic voltammetry curves of glassy carbon (GC) GC/PB electrode in 0.1 M KCl; sweep rate 50 mV s⁻¹.

solid solution of compounds of different stoichiometry. Nickel atoms from *Nihcf* are known to be at valence state (II) in the studied potential range. Hence, the observed plateau in Fig. 3 (pEDOT/*Nihcf*) may be ascribed to the reactions cited below [21]:

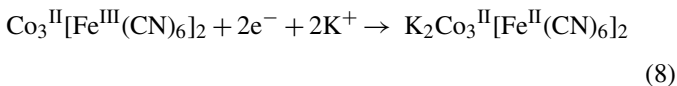


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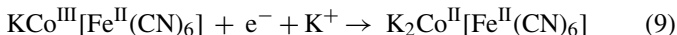


Thus, the observed current on the cv curve (Fig. 3 pEDOT/*Nihcf*) may correspond to a redox process of low-spin iron ions, Fe(II/III). The current maximum is found to be shifted (in comparison with Prussian Blue activity), due to presence of nickel atoms in the network.

Also two redox reactions are possible for the *Cohcf* analogue [18]:



or



Thus, the current plateau observed at potential $E \sim +0.41$ V for hybrid pEDOT/*Cohcf* is very likely to be attributed to Co(II/III) and Fe(II/III) redox reaction, Fig. 3 (pEDOT/*Cohcf*). Introduction of Co(II) ([Ar] 3d⁷4s⁰) and Ni(II) ([Ar] 3d⁸4s⁰) is equivalent to addition of subsequent electrons to the structure of Prussian Blue. Activity of the Fe(II)/Fe(III) couple changed shifting cathodically in the order: pEDOT/*Fehcf* > pEDOT/*Cohcf* > pEDOT/*Nihcf*. Cathodic potential shifts are promoted by a higher number of electrons in the inorganic molecule.

The pEDOT/*Nihcf*, pEDOT/*Cohcf* and pEDOT/*Fehcf* (line not shown) electrodes show evidence of catalytic activity towards oxidation reactions. Fig. 4 presents cv curves obtained for pEDOT/*Cohcf*, pEDOT/*Nihcf* electrodes in aqueous KCl (both electrodes) and K₂SO₄ electrolytes (for pEDOT/*Cohcf*) compared to cv curves obtained on a bare Pt electrode. As can be seen, electrolyte decomposition is taking place at a smaller anodic potential in comparison with the oxidation reaction at the platinum electrode. Reactions which take place at the Pt electrode are water oxidation with oxygen evolution (in K₂SO₄) accompanied by chlorine evolution from chloride oxidation (in KCl electrolyte). Electrocatalytic behaviour of films towards water molecule oxidation reactions seems to rely on redox activity of iron coordinated via carbon atoms (low-spin iron ions). This activity is not reported for inorganic *Mehcf* films. Prussian Blue films polarised to high anodic potential do not act as catalyst for water oxidation, see Fig. 4, inset. Catalytic activity of studied samples diminishes during subsequent cycles, especially in KCl electrolyte. This catalytic feature is disadvantageous considering the available potential window for capacitors working in aqueous electrolytes.

Another redox activity observed already for pEDOT/Prussian Blue hybrid material at -0.65 V [9] appears for all three materials, Fig. 5a–c. In our previous work the peak was interpreted as resulting from a new electronic stage of polymer affected by iron bond with sulphur in pEDOT/Prussian Blue (iron hexacyanoferrate) [9]. Chemical interaction between polymer and inorganic part of pEDOT/Prussian Blue was also traced by micro-Raman spectroscopy [10,30].

The same redox process at ~ -0.65 V recorded for cobalt and nickel analogues may be interpreted as similar redox transformation, probably of the same origin as that observed already for pEDOT/*Fehcf* composite. However, this assumption requires further spectroscopic studies for all three composites.

All materials were found to work reproducibly for hundreds of subsequent cycles. The loss of charge capacity was less than 15% between cycle 1 and 500 (see Fig. 5a). A higher capacitance was shown by hybrid materials with *Cohcf* and *Nihcf*, up to 70 F cm⁻³ (Fig. 5b and c). It was found for films of average thickness about 0.7 μm. Similar results showing comparable behaviour of composites were obtained by chronopotentiometry. Fig. 6a–c shows typical chronopotentiometric curves, calculated capacitance is given in the inset. Cathodic and anodic current density was 0.15 mA cm⁻². Potential limits in the experiment were fixed at -0.9 to +0.6 V. Capacitance of the polymer pEDOT with poly(2-styrenesulphonate) counter-ions (pEDOT/PSS) in propylene carbonate was found to reach 25 F cm⁻³ [31], about 20 F cm⁻³ in acetonitrile electrolyte [15] and 15–20 F cm⁻³ in aqueous electrolytes [32]. For comparison, polyoxometalate modified polyaniline was found to supply 25 F cm⁻³ [2]. According to technical expectations for electrochemical capacitors [33] specific capacitance of studied materials is sufficient for practical applications, especially for pEDOT/*Cohcf* and pEDOT/*Nihcf* hybrids.

Capacitance of hybrid films was found to be higher, very likely due to presence of inorganic networks. Faradaic reaction of Me(II/III) centres contributes to the whole measured electric

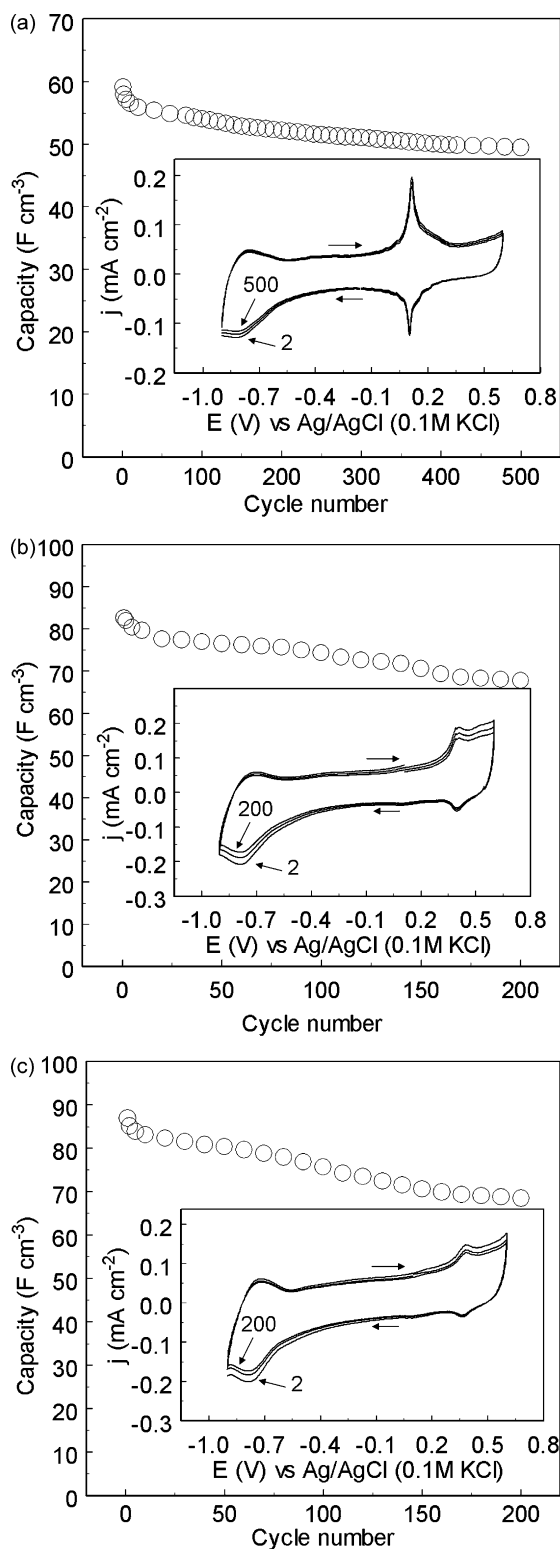


Fig. 5. (a) Capacity of the pEDOT/FeHcf as the function of the cycle number; outer electrolyte 0.1 M KCl. Inset: cyclic voltammograms of Pt/pEDOT/FeHcf electrode obtained in 0.1 M KCl; sweep rate 20 mV s⁻¹. (b) Capacity of the pEDOT/CoHcf as the function of the cycle number; outer electrolyte 0.1 M KCl. Inset: cyclic voltammograms of Pt/pEDOT/CoHcf electrode, 0.1 M KCl; sweep rate 20 mV s⁻¹. (c) Capacity of the pEDOT/NiHcf as the function of the cycle number; outer electrolyte 0.1 M KCl. Inset: cyclic voltammograms of Pt/pEDOT/NiHcf electrode in 0.1 M KCl; sweep rate 20 mV s⁻¹.

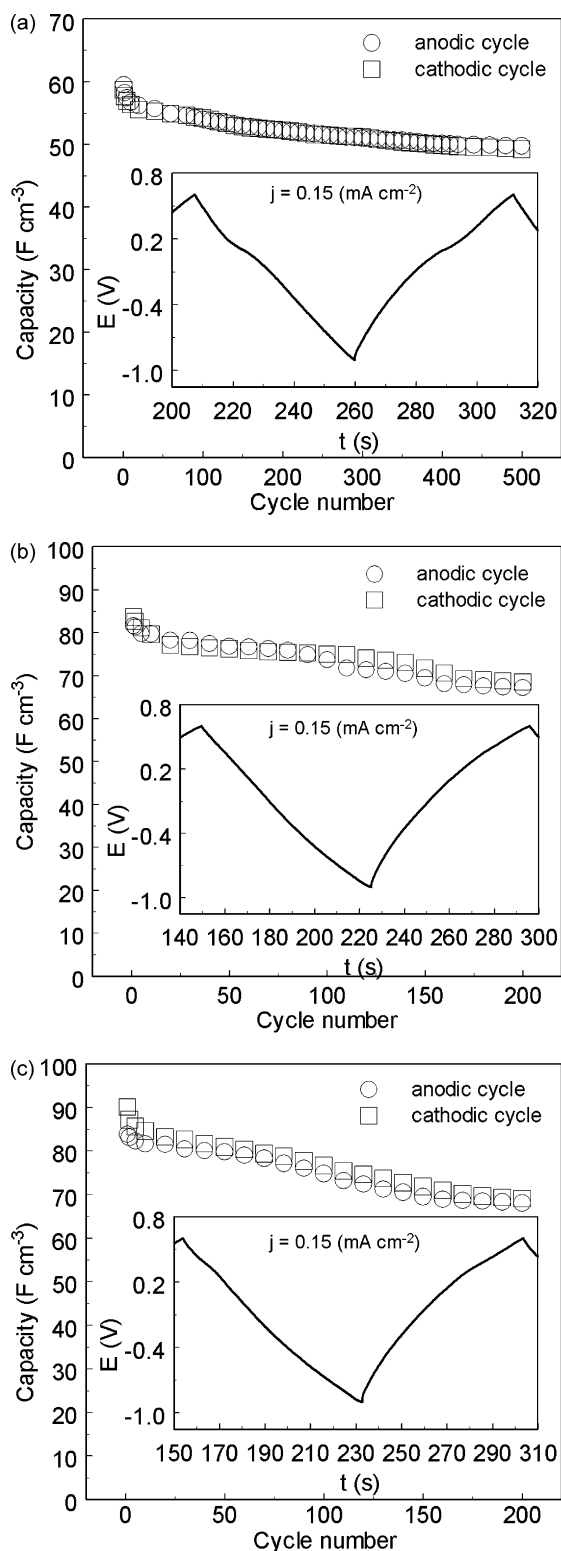


Fig. 6. (a) Specific capacitance of pEDOT/FeHcf as the function of the cycle number; outer electrolyte 0.1 M KCl. Inset: cathodic and anodic branch of the chronopotentiometric curve. (b) Specific capacitance of pEDOT/CoHcf as the function of the cycle number; outer electrolyte 0.1 M KCl. Inset: cathodic and anodic branch of the chronopotentiometric curve. (c) Specific capacitance of pEDOT/NiHcf as the function of the cycle number; outer electrolyte 0.1 M KCl. Inset: cathodic and anodic branch of the chronopotentiometric curve.

capacity. The question is why *Fehcf* modified polymer exhibits the lowest (50 F cm^{-3}) capacitance among studied systems. This material does not exhibit the low-spin iron ions activity. As the Fe(II/III) redox reaction proceeds with simultaneous electrolyte decomposition, low-spin iron ions activity is not achieved in the studied potential range. The other studied materials utilise activity of this centre. It was found that the ability to transport the charge within the whole potential range (from -0.9 to $+0.6 \text{ V}$) is better for pEDOT/*Cohcf* and pEDOT/*Nihcf*. It might be caused by interactions between low-spin iron ions and the polymer chain. Confirmation of existence of these interactions requires further investigation.

It is obvious that specific capacitance calculated per weight will not be so affirmative. Despite this fact, new hybrid materials are attractive because of their stability, uniform three-dimensional structure and simple synthesis from cheap, accessible chemicals.

4. Conclusion

It has been shown that hybrid electrode materials made of electroactive polymer pEDOT and metal hexacyanoferrate (*Mehcf*) can be synthesized in two-step procedures. The process of electro-sorption of outer electrolyte leads to formation of a chosen *Mehcf* inside the polymer pEDOT matrix. Obtained hybrid materials pEDOT/*Fehcf*, pEDOT/*Cohcf* and pEDOT/*Nihcf* exhibit good cycle life stability in aqueous KCl electrolyte. The specific capacitance of films containing *Fehcf*, *Cohcf* and *Nihcf* is higher than for polymer pEDOT without an inorganic multinuclear redox network. Electroactivity of hybrid materials is expected to come from both metal redox centres coupled with polymer pseudo-capacitance. There is no evidence in morphological changes for increase of specific capacitance of the material.

The pEDOT/*Fehcf* film shows the lowest capacitance value among studied materials. Only in this case the redox centre belonging to low-spin iron ions cannot be exploited.

Electrocatalytic decomposition of aqueous electrolytes with oxygen or/and chlorine evolution limits the “potential window” for capacitor application.

High capacitance and good cyclic stability promote the use of these new electrode materials in electrochemical capacitors or other types of energy storage devices.

Acknowledgments

Financial support from Gdańsk University of Technology (DS 014668/003) and State Committee for Scientific Research (KBN), Poland under Grant N205 051 32/3072 is gratefully acknowledged.

Assistance of Mr. J. Stryjewski in matters related to EDX measurements is gratefully acknowledged.

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