



# Hybrid electrodes composed of electroactive polymer and metal hexacyanoferrates in aprotic electrolytes

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## ABSTRACT

In this work hybrid materials composed of electroactive polymer poly(3,4-ethylenedioxythiophene) (pEDOT) and metal hexacyanoferrates (*Mehcf*) (Me = Fe, Co, Ni) were tested in ethylene carbonate (EC):propylene carbonate (PC) electrolytes containing 0.5 M KPF<sub>6</sub> or 0.5 M LiPF<sub>6</sub> salts. The hybrid materials pEDOT/*Mehcf* were examined by using: cyclic voltammetry (CVA), potentiometry and impedance spectroscopy (IS). The materials pEDOT/*Mehcf* exhibit electrode activity, good stability and high electrical capacity in tested nonaqueous electrolytes and they are considered to be suitable active materials for supercapacitors or for positive electrode of secondary cell with lithium and potassium salts. Contrary to the solid Prussian Blue “PB” analogues, hybrid pEDOT/*Cohcf* electrodes work with good efficiency in contact with nonaqueous electrolyte containing lithium salts.

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## 1. Introduction

A demand for energy storage devices such as electrochemical capacitors is now rapidly growing due to the solar batteries, small-wind power stations or electric vehicles [1–3]. Electrochemical capacitors in general make use of three main classes of materials: carbons (hybridization sp<sup>2</sup> of C in graphite type structures), electroactive polymers EP, and metal oxides. Metal oxides and EP utilize a pseudo-Faradaic reaction, unlike carbon materials which exploit the double layer capacitance between the solid electrode and an electrolyte.

Composite nanostructure materials, are also proposed for a construction of electrochemical capacitors [4–6]. Among them there are electroactive polymers modified by inorganic redox networks such as e.g. polyoxometallate [7,8], or metal hexacyanometallates *Me'hcMe'* [9,10]. Recently, a new type of nanostructured composites has been proposed for an application in electrochemical capacitors [11]. They are organic inorganic hybrid materials. Polymer poly(3,4-ethylenedioxythiophene) (pEDOT) can be used for an inner-matrix synthesis of the metal hexacyanoferrate *Mehcf* forming stable composite (hybrid) system (pEDOT/*Mehcf*). Such produced electrochemically systems exhibit an attractive electric capacity (up to 70 F cm<sup>-3</sup>) and stability under multicyclic polarization in contact with aqueous solutions [11]. Both components of the hybrid materials: pEDOT and *Mehcf* are electroactive and both

require ionic contribution in a charge propagation process. This process is restrained in respect to ions' size and electrode material structure. Solvent molecules, contributing to an ion hydrating sheath are also involved in the sorption/desorption during polarization and may hinder electrode reactions. Composite films of iron(III) hexacyanoferrate and poly(3,4-ethylenedioxythiophene) were tested in aqueous electrolytes and their enhanced stability in comparison with pure inorganic films was proved [11].

Need for high power, high energy and robustness of energy storage technology requires materials able to act in a broad potential range [12]. Hybrid materials in aprotic electrolytes may provide needed broader potential range of its activity on the condition that electrode and electrolytes are compatible. The use of nonaqueous electrolyte for pEDOT/*Mehcf* (Me = Fe, Co, Ni) films may offer workable construction of asymmetric supercapacitors made of pEDOT/*Mehcf* as positive electrode and high-negative materials as a counter electrode. However, at a first stage, compatibility between hybrid films pEDOT/*Mehcf* and aprotic electrolytes should be examined. Randriamahazaka et al. describe existing synergic behaviour between poly(3,4-ethylenedioxythiophene) and *FehcFe* which was observed for each part of the composite layer–layer pEDOT-*FehcFe* material tested in aqueous and acetonitrile electrolyte. The authors reported an electrochemical behaviour of the composite as a new prospect for electric charge storage [13]. The main difference between the composite and mentioned above hybrid pEDOT/*Mehcf* systems comes from a direct interaction between both components forming the hybrid bulk material. This direct interaction has been proved by XPS and EXAFS methods [11,14,15].

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This work provides information about electrochemical behaviour of hybrid systems pEDOT/*Mehcf* (Me = Fe, Co, Ni) in propylene carbonate (PC):ethylene carbonate (EC) (1:1) with 0.5 M KPF<sub>6</sub>, 0.5 M LiPF<sub>6</sub> electrolytes.

## 2. Experimental

Electrochemical experiments have been performed using the potentiation–galvanostat system AutoLab PGStat10 under GPES 4.9 software control. Three electrode one-compartment cell was used in all experiments. Glassy carbon disc (diameter 1 mm) served as a working substrate electrode. Platinum mesh (10 cm<sup>2</sup>) was used as a counter electrode and Ag/AgCl served as reference electrode. Platinum plate electrodes of geometric surface area of 0.5 cm<sup>2</sup> and 1.5 cm<sup>2</sup> were used for preparation of the hybrid material in the symmetric and asymmetric electrochemical capacitor, respectively.

Electrode materials were obtained in two step procedure from aqueous electrolyte on GC substrate [16]. Materials obtained from aqueous solution in the form of pEDOT/*Mehcf* ~ 0.7 μm thick films were dried and then transferred into nonaqueous electrolyte (0.5 M KPF<sub>6</sub> or 0.5 M LiPF<sub>6</sub> in ethylene carbonate (EC):propylene carbonate (PC) 1:1 and kept in it for 12 h. The electrolyte was replaced for the fresh sample 3 times. The electrodes were examined using: cyclic voltammetry (CVA), potentiometry and impedance spectroscopy (IS). The cell was kept under Ar atmosphere at 22 ± 1 °C in a glove box. All electrode potentials given here are recalculated against Ag/AgCl (0.1 M KCl)<sub>aq</sub>.

### 2.1. Chemicals

Salts LiPF<sub>6</sub>, KPF<sub>6</sub> of electrochemical grade from Aldrich were used as received. Ethylene carbonate was dried using molecular 4 Å sieves at 45 °C. Propylene carbonate (sure seal, 99.7% anhydrous) were used as received. The amount of traces of water was kept below 50 ppm and determined by CVA polarization of glassy carbon electrode and the current density was compared with literature data [17]. Monomer 3,4-ethylenedioxythiophene (EDOT) and inorganic compounds: K<sub>4</sub>Fe(CN)<sub>6</sub>, K<sub>3</sub>Fe(CN)<sub>6</sub>, KCl, NiCl<sub>2</sub>·6H<sub>2</sub>O were supplied Fluka–Aldrich, CoCl<sub>2</sub>·6H<sub>2</sub>O and FeCl<sub>3</sub> anhydrous were supplied by Riedel-de Haën, Germany. All chemicals were of analytical grade and used without further purification. Aqueous electrolytes used for the synthesis of the hybrid materials pEDOT/*Mehcf* were prepared using triply distilled water.

## 3. Results and discussion

Studies performed by Itaya proved that potassium cation size is suitable for ion insertion process of pure inorganic iron hexacyanoferrate (Prussian Blue analogue) [18]. A similar situation was established for hybrid system consisting of pEDOT and *Mehcf* in aqueous electrolytes containing potassium salts [11,19].

Electrodes made of solid Prussian Blue were also tested in organic electrolytes containing potassium salts and potassium secondary cell based on the PB cathode and potassium metal anode was proposed [20]. Eftekhari tested pure iron hexacyanoferrate films in contact in 3:7 EC/EMC electrolyte containing potassium salt KBF<sub>4</sub>. The author established that Stokesian radius of solvated K<sup>+</sup> ion in studied mixed solvent electrolyte guarantees good reversibility for more than 500 reversible cycles [20]. However, inorganic material cannot be used for Li<sup>+</sup> intercalation/deintercalation as is presented by Imanishi et al. [21,22]. The BP-based electrodes lost 30% of its capacity after only 10 cycles and degradation proceeded [21,22].

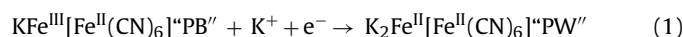
The pure pEDOT film in its oxidized form exhibits reversible capacitive and Faradaic current [e.g. 23]. This phenomenon was qualitatively and quantitatively analysed in respect to exploitation

of the polymer in electrochemical devices for energy storage and conversion namely supercapacitors and lithium batteries [24–28]. Table 1 presents literature data characterising specific capacitance of pEDOT films. The capacitance values are recalculated from original data accessible in cited articles [24–28]. Data presented in Table 1 are obtained for the fresh samples and do not take into account the stability of the polymer during multi-cyclic polarization. The thickness size of each film was estimated using particular charge density data given by the authors. Thus, 16.6 mC cm<sup>-2</sup> for 0.1 μm for pEDOT/PSS film in aqueous electrolytes [24], 140 mC cm<sup>-2</sup> for 1 μm of pEDOT/Cl films obtained both in aqueous and in acetonitrile electrolytes [26].

First data come from experiments done almost a decade ago for the pEDOT film doped with small anion in the acetonitrile electrolyte containing 0.1 M LiClO<sub>4</sub>. The polymer pEDOT was also studied many times in propylene carbonate containing lithium perchlorate [e.g. 24,30]. Data presented by Randriamahazaka show impedance spectroscopy results, unfortunately due to lack of electrode film thickness results are not comparable with other gathered in Table 1. A dielectric permittivity constant of propylene carbonate is high considering organic solvents and is equal to ε<sub>r</sub> = 64.4, thus observed differences in capacitive properties of the materials being in aqueous and propylene carbonate electrolytes are not affected by this parameter to high extent. Observed differences in capacitance values are rather attributed to the salt type and its concentration and predominantly to the porosity of the material. Polymer doped with polyelectrolyte PSS is very smooth and compact [31,32]. On the other hand porosity of the polymer pEDOT may be stimulated by potentiostatic growth of very thick pEDOT films doped with small counter ions e.g. ClO<sub>4</sub><sup>-</sup> [25]. The highest capacitance is recorded for specially grown films of as named by the authors “micro-nanoporous” polymer [25]. Materials achieved very high capacitance values in both aqueous and acetonitrile electrolytes. As it is shown in the data gathered in Table 1, a substantial increase of the capacitance may be achieved by introducing changes in the structure. Thus, many attempts towards improving electrochemical characteristics of the pEDOT are still reported. Another direction in this field is based on combining carbon-nanomaterials with polymers (see Table 1). Results are reported in relation to mass of used porous solids and simple comparison of these composites with pure polymeric films of restricted geometry is not directly obtainable. Thus, following other authors we also highlight the importance of using electrode specific capacitance in respect to geometry F cm<sup>-3</sup> to evaluate tested materials for supercapacitor applications.

As it has already been mentioned in Section 1, the method of growth of the capacitance of the polymer which we suggested bases on an insertion of the inorganic redox network into the polymer matrix [11,19]. The hybrid electrodes pEDOT/*Mehcf* make use of electric charge coming from both an inorganic and organic part. Moreover they exhibit lower diffusional resistance in comparison with pure inorganic films [19]. Thus, one may expect that non-aqueous media also may be used, especially concerning synergism observed for a layered composite pEDOT-*Fehcf* [13].

Fig. 1 shows typical CVA curves obtained for pEDOT/*Fehcf*, pEDOT/*Chcf* and pEDOT/*Nihcf* electrodes of ~0.7 μm thick (thickness measured for the dry films). The measurements demonstrate redox activity of studied films coming from polymer and from inorganic *Mehcf*. As can be seen, broad hump is recorded for pEDOT/*Fehcf* at about +0.1 V/Ag/Ag/Cl. At the same potentials range ~0.1 V current growth is observed in the case of pure inorganic *Fehcf* and the hybrid material pEDOT/*Fehcf* in contact with aqueous media [11]. Besides, Eftekhari recorded redox activity of Prussian Blue transfer to Prussian White “PW” in contact with KBF<sub>4</sub> solution in EC:DME according to reaction:



**Table 1**  
Literature data of capacitance values of pEDOT films and pEDOT composite materials.

Material	Thickness [ $\mu\text{m}$ ]	Electrolyte	Capacitance	E [V] vs. Ag/AgCl/0.1 M KCl	Method	Ref
pEDOT/PSS	2	0.2 M LiClO <sub>4</sub> ; PC	$C_A = 19.75$ [ $\text{F cm}^{-3}$ ], $C_C = 18.1$ [ $\text{F cm}^{-3}$ ]; measured at $5 \text{ mV s}^{-1}$ $C_A = 23.2$ [ $\text{F cm}^{-3}$ ], $C_C = 19.7$ [ $\text{F cm}^{-3}$ ]; measured at $10 \text{ mV s}^{-1}$	-0.5–0.5	CVA <sup>a</sup>	[24]
“Micro-nanoporous” pEDOT/ClO <sub>4</sub>	2.7	0.5 M LiClO <sub>4</sub> ; ACN	94 [ $\text{F cm}^{-3}$ ]	0.1, 0.3	CVA <sup>b</sup>	[25]
“Micro-nanoporous” pEDOT/Cl	2.7	0.5 M KCl; H <sub>2</sub> O	105 [ $\text{F cm}^{-3}$ ]			
pEDOT/PSS	22.5	0.5 M KCl; H <sub>2</sub> O	120 [ $\text{F cm}^{-3}$ ]			
pEDOT/ClO <sub>4</sub>	500	0.5 M KCl; H <sub>2</sub> O	98 [ $\text{F cm}^{-3}$ ]			
pEDOT/PSS	0.8	0.1 M KCl; H <sub>2</sub> O	40 [ $\text{F cm}^{-3}$ ]	0.1	CVA <sup>b</sup>	[26]
pEDOT/ClO <sub>4</sub>	0.7	0.1 M LiClO <sub>4</sub> ; ACN	50 [ $\text{F cm}^{-3}$ ]	-0.8–0.8	CVA <sup>a</sup>	[27]
85% CNT <sup>c</sup> /15% pEDOT	–	1 M H <sub>2</sub> SO <sub>4</sub> ; H <sub>2</sub> O	95 [ $\text{F g}^{-1}$ ]; measured at $2 \text{ mV s}^{-1}$	-0.2–0.6	CVA <sup>a</sup>	[28]

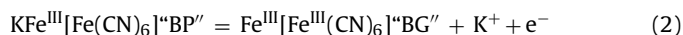
<sup>a</sup>  $C = \text{d}t/\text{d}E$ .

<sup>b</sup>  $C_L = i/v$ ,  $C_L$ —limiting capacitance,  $i$ —current,  $v$ —voltage scan rate [29].

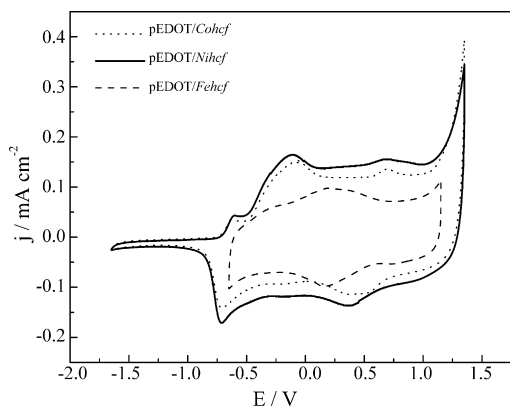
<sup>c</sup> Carbon nanotubes.

Thus, it is very likely that observed current growth on CVA curve (Fig. 1) comes from the redox reaction related to high spin iron centre from Fe<sup>II/III</sup>(CN)<sub>6</sub>Fe coordinated via nitrogen atoms [33].

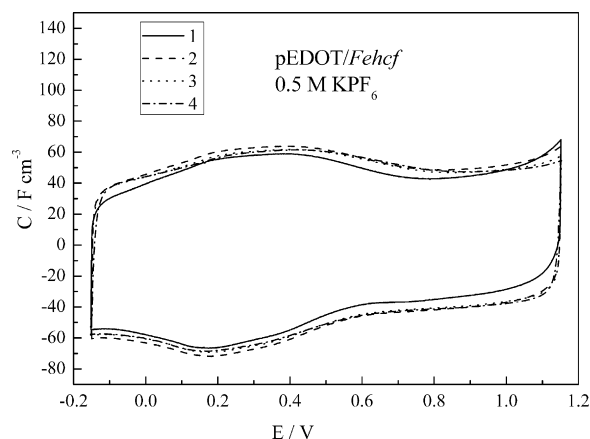
As it is known, the low spin iron atom centre is active at a higher potential range according to reaction taking place during transformation of PB to Berlin Green “BG” [18]:



The reaction presented above is recorded for pure PB studied in aqueous and also in organic electrolytes in the same potential range. However, the hybrid electrodes pEDOT/*Mehcf* (Me = Fe, Co, Ni) exhibit the low spin iron atoms activity only for Me = Ni and Co [8]. In the case of pEDOT/*Fehcf* activity of Fe atoms coordinated by a carbon atoms occurs above 1 V where the polymer decomposition takes place. The same reaction Fe<sup>II/III</sup> in aqueous electrolytes causes the catalytic oxygen evolution from water molecules oxidation [11]. Potential range of Fe<sup>II/III</sup> activity is shifted towards cathodic side when Fe (high spin, coordinated via nitrogen) is replaced by Co or Ni atoms. As can be seen on Fig. 1, the low current rise on anodic and cathodic side of the CVA curve is observed at  $\sim +0.4 \text{ V}$  for pEDOT/*Cohcf* (II/III) and pEDOT/*Nihcf*. Figs. 2–4 show whole runs of the capacitance changes during polarization of the tested electrodes: pEDOT/*Fehcf*, pEDOT/*Cohcf*, pEDOT/*Nihcf*. The electric capacity shown as a function of the electrode potential was estimated using a simple relation  $C = i/v$  (where  $v$  is a sweep rate  $v = \text{d}E/\text{d}t$ ). As can be seen, at the redox peak potential the difference between  $C$  values is negligible expressing the fact that charge propagation follows polarization of the material in the region

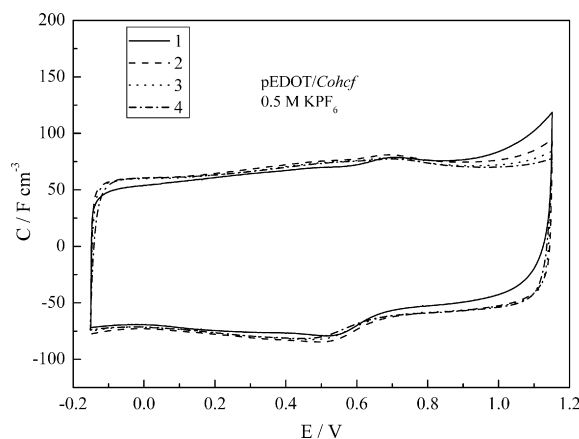


**Fig. 1.** Cyclic voltammograms obtained for pEDOT/*Cohcf*, pEDOT/*Nihcf*, pEDOT/*Fehcf*; outer electrolyte 0.5 M KPF<sub>6</sub> in EC:PC; sweep rate  $20 \text{ mV s}^{-1}$ .

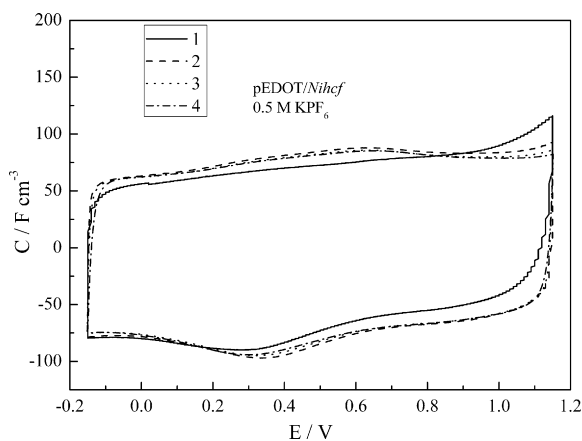


**Fig. 2.** Capacitance values as a function of potential calculated from CVA measurements for the pEDOT/*Fehcf* at different scan rates: (1)  $20 \text{ mV s}^{-1}$ , (2)  $50 \text{ mV s}^{-1}$ , (3)  $100 \text{ mV s}^{-1}$ , (4)  $200 \text{ mV s}^{-1}$ , outer electrolyte 0.5 M KPF<sub>6</sub>.

where a Faradaic current from inorganic part of the hybrid and a capacitive/Faradaic current from the pEDOT are not hindered [34]. However, small discrepancies are recorded at the potential range of the plateau, where a capacitive/Faradaic current from electroactive polymer is dominating. The situation is similar for all the hybrid materials. The source of these discrepancies is difficult to resolve as



**Fig. 3.** Capacitance values as a function of potential calculated from CVA measurements for the pEDOT/*Cohcf* at different scan rates: (1)  $20 \text{ mV s}^{-1}$ , (2)  $50 \text{ mV s}^{-1}$ , (3)  $100 \text{ mV s}^{-1}$ , (4)  $200 \text{ mV s}^{-1}$ , outer electrolyte 0.5 M KPF<sub>6</sub>.

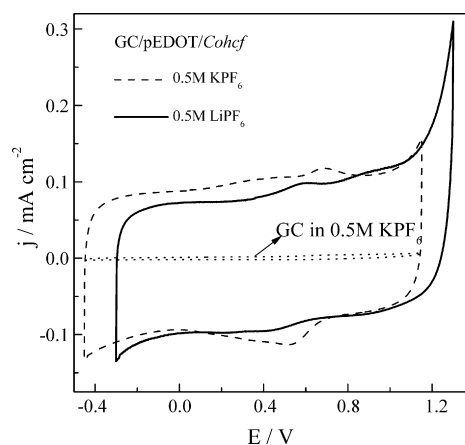


**Fig. 4.** Capacitance values as a function of potential calculated from CVA measurements for the pEDOT/Nihcf at different scan rates: (1)  $20 \text{ mV s}^{-1}$ , (2)  $50 \text{ mV s}^{-1}$ , (3)  $100 \text{ mV s}^{-1}$ , (4)  $200 \text{ mV s}^{-1}$ , outer electrolyte  $0.5 \text{ M KPF}_6$ .

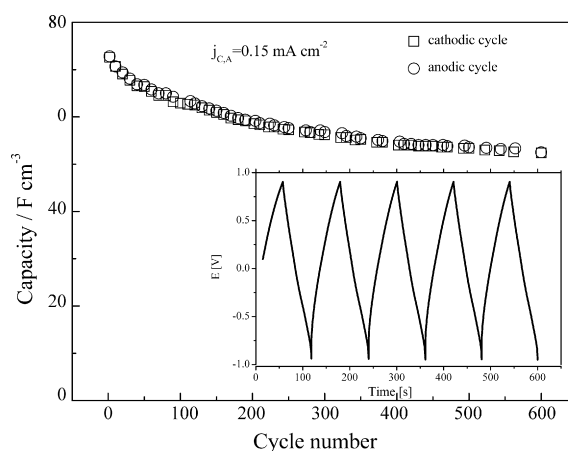
the hybrid materials are not yet described in a sense of its capacitive currents and a redox switching in respect to the polymer chain of its own.

In general, the capacity values are slightly lower in aprotic solvent electrolytes comparing to those obtained for these materials in contact with aqueous electrolytes [11]. Nevertheless they are still attractive. The pEDOT/Fehcf film shows the lowest capacitance value among studied materials. The same observation was found for the materials tested in aqueous electrolytes, pEDOT/Fehcf exhibits lower  $C$  value in comparison with the hybrids containing nickel and cobalt atoms. A comparison of the capacitance values obtained from CVA curves at the redox potential with these obtained at the potentials of plateau shows that Faradaic reaction of Fe centre gives 15–20% rise to capacitance in order: pEDOT/Nihcf < pEDOT/Cohcf < pEDOT/Fehcf. Taking above into account, and the fact that capacitance for pEDOT/Fehcf is the lowest, the pEDOT/Cohcf electrode was chosen for further investigations in electrolyte containing  $\text{LiPF}_6$ .

Fig. 5 shows CVA curves obtained for pEDOT/Cohcf in two electrolytes containing different salts ( $\text{KPF}_6$  or  $\text{LiPF}_6$ ). As can be seen the small current responding to the iron centre activity in pEDOT/Cohcf is observed in both cases. The chronopotentiometry tests for pEDOT/Cohcf electrode material in both electrolytes  $0.5 \text{ M KPF}_6$  and  $0.5 \text{ M LiPF}_6$  were performed. Fig. 6 presents the chronopotentiometric polarization curves and a dependence of the capacitance values of pEDOT/Cohcf on the number of polarization cycles performed in the  $\text{LiPF}_6$  electrolyte. The shape of a chronopotentiometric curve is typical for a capacitive fast charging/discharging process essential for the electrochemical capacitors employing organic electrolytes [9]. Both, anodic and cathodic branches are symmetrical in the applied potential range. The chronopotentiometry results are gathered in the Table 2. The capacitance values calculated from charge–discharge cycles for pEDOT/Cohcf are higher in the case of  $\text{LiPF}_6$  electrolyte comparing to  $\text{KPF}_6$  electrolyte. The pEDOT/Cohcf



**Fig. 5.** Cyclic voltammetry curves obtained for pEDOT/Cohcf; outer electrolyte  $0.5 \text{ M KPF}_6$  or  $0.5 \text{ M LiPF}_6$  in EC:PC; sweep rate  $20 \text{ mV s}^{-1}$ .



**Fig. 6.** Capacity of pEDOT/Cohcf as a function of a cycle number; outer electrolyte  $0.5 \text{ M LiPF}_6$ . Inset: cathodic and anodic branch of a chronopotentiometric curve.

material was polarized in the ranges: 1.5 and 1.7 V in  $\text{KPF}_6$  and 1.8 V in the case of  $\text{LiPF}_6$ . The loss of capacity reaches a high value at the beginning, probably due to a complete electrolyte exchange in the polymer matrix. Further cycles up to 6 hundreds are not decreasing in the same degree. Differences between capacitance after 300 and 600 cycles is about 7%, which is acceptable for the device. The material obtained by preliminary cycles in aprotic solvent should be treated as a starting substrate for the electrode formation in electrochemical capacitors. Based on the CVA measurements and the chronopotentiometry tests in electrolyte containing  $\text{LiPF}_6$  salt one may conclude that lithium ions (similarly to potassium ions) are suitable for the ion insertion process of the hybrid material pEDOT/Cohcf.

The symmetric cell has been made of two identical Pt|pEDOT/Cohcf electrodes immersed in  $0.5 \text{ M LiPF}_6$  electrolyte.

**Table 2**

Capacitance values of the pEDOT/Cohcf calculated from charge–discharge plots.

Material	Electrolyte	Potential range E/V	Number of cycles	Capacity/ $\text{F cm}^{-3}$	
pEDOT/Cohcf	0.5 M $\text{KPF}_6$ EC:PC	0.85–0.65	300	55.7	Start
				44.5	After 300 cycles
		0.95–0.75	600	52.4	Start
				38.1	After 300 cycles
	LiPF <sub>6</sub> EC:PC	1.17–0.63	600	31.4	Final
				72.2	Start
				56.6	After 300 cycles
				52.5	Final



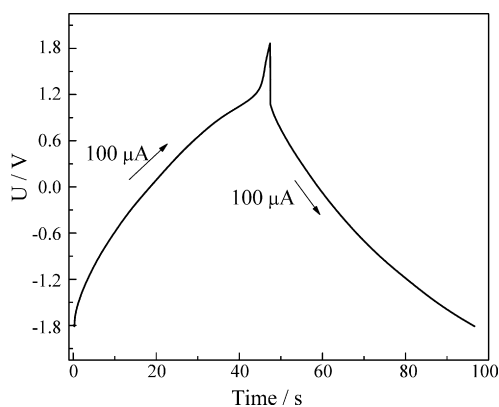


Fig. 7. Examples of chronoamperometric charge–discharge plots; current  $100 \mu\text{A}$ ; area of each pEDOT/Cohcf electrode  $0.5 \text{ cm}^2$ .

Fig. 7 presents an example of a chronopotentiometry curve. At a positive voltage amplitude limit is achieved at  $+1.2 \text{ V}$ , negative range is limited to  $-1.8 \text{ V}$ , thus voltage  $U$  of the symmetric system is equal to  $3 \text{ V}$  at discharging current of  $100 \mu\text{A}/45 \text{ s}$  which gives  $0.018 \text{ Wh cm}^{-3}$  for the material pEDOT/Cohcf ( $0.7 \mu\text{m}$  thick).

Impedance spectroscopy measurement was obtained for the symmetrical cell at OCV (0) with frequency range of AC signal from  $100 \text{ kHz}$  to  $0.1 \text{ Hz}$ , amplitude  $0.01 \text{ V}$ , see Fig. 8. The shape of spectrum indicates that the finite length diffusion impedance to the blocking electrode (Pt) is the main element of the electrical equivalent circuit of the symmetric cell at zero DC current condition. At a higher frequency range small  $R$  and  $C$  in parallel element ( $R \sim 10\text{--}12 \Omega$ ,  $C \sim 2 \cdot 10^{-5} \text{ F}$ ) is recognised as a semicircle. The measurement was repeated for separated one Pt/pEDOT/Cohcf electrode and fitting procedure were performed similarly to the procedure presented in the previous paper [16]. Two different charge fluxes were observed and the apparent diffusion constant ( $D_{\text{app}}$ ) was estimated. The values of  $D_{\text{app}}$  were in the range of  $10^{-6}$  and  $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ . These values are lower than those obtained for pEDOT/Cohcf in contact with aqueous electrolytes [19].

Preliminary tests with the asymmetric cell using lithium metal as a negative electrode and pEDOT/Cohcf as a positive one was performed. Electrolyte was  $0.5 \text{ M LiPF}_6$  in 1:1 EC:PC. An open circuit voltage of the cell was  $3.0 \text{ V}$ . The difference in charging/discharging cycles points out that kinetic of the lithium electrode reaction  $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$  and a kinetic of the electrode process at the hybrid pEDOT/Cohcf causes the difference between electric charges dur-

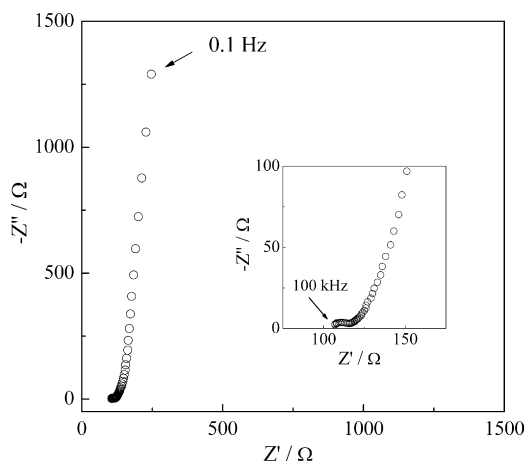


Fig. 8. Complex plane impedance plot of the symmetric cell pEDOT/Cohcf|  $0.5 \text{ M LiPF}_6$ , EC:PC| pEDOT/Cohcf at OCV (0V).

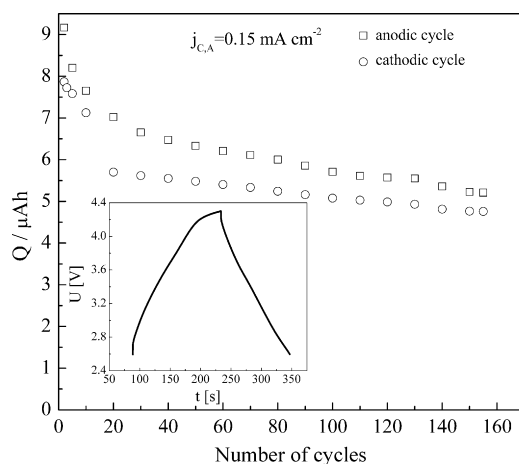


Fig. 9. Charge capacity as a function of a cycle number; outer electrolyte  $0.5 \text{ M LiPF}_6$ . Inset: examples of chronoamperometric charge–discharge plots; current  $0.25 \text{ mA}$ , electrode surface area  $1.5 \text{ cm}^2$ .

ing opposite cycles, see Fig. 9. The average charge capacity after 100 cycles was established as  $5 \mu\text{Ah}$  for  $1.5 \text{ cm}^2$  electrode material.

#### 4. Conclusions

The electrode materials pEDOT/Cohcf, pEDOT/Fehcf and pEDOT/Nihcf can be employed in EC:PC electrolytes containing  $\text{KPF}_6$  and  $\text{LiPF}_6$ . The Faradaic activity of the metal redox centres causes increase in the electric capacity of the materials in comparison with the pure polymer (excluding “micro-nanoporous” one) or the pure inorganic material. Tests in the electrolyte containing lithium ions show that  $\text{Li}^+$  ions, as well as potassium ions, are suitable for the ion insertion process of the hybrid material pEDOT/Cohcf (the insertion of  $\text{Li}^+$  ions was not reversible for the pure inorganic Mehcf).

The high electrical capacity of pEDOT/Cohcf in contact with  $\text{LiPF}_6$  electrolyte allows the application of this material as a positive electrode of the lithium secondary batteries and asymmetric electrochemical capacitors with lithium ion insertion possible to occur.

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