

Effective charge propagation and storage in hybrid films of tungsten oxide and poly(3,4-ethylenedioxythiophene)

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Abstract Hybrid (composite) electroactive films consisting of such an organic conducting polymer as poly(3,4-ethylenedioxythiophene), PEDOT, and such a polynuclear inorganic compound as amorphous tungsten oxide, $\text{WO}_3/\text{H}_x\text{WO}_3$ were fabricated on carbon electrodes through electrodeposition by voltammetric potential in acid solution containing EDOT monomer and sodium tungstate. Electrostatic interactions between the negatively charged tungstic units (existing within WO_3) and the oxidized positively charged conductive polymer (oxidized PEDOT) sites create a robust hybrid structure which cannot be considered as a simple mixture of the organic and inorganic components. It is apparent from scanning electron microscopy that hybrid structures are granular but fairly dense. Because PEDOT and mixed-valence tungsten oxides are electronically conducting, the resulting hybrid films are capable of fast propagation. The reversible and fast redox reactions of tungsten oxide component lie in the potential range where PEDOT matrix is conductive. Furthermore, the hybrid films exhibit good mediating capabilities towards electron transfers between model redox couples such as cationic iron(III, II) and anionic hexacyanoferrate(III,II). Since the films accumulate effectively charge and show high current

densities at electrochemical interfaces, they could be of importance to electrocatalysis and to construction of redox capacitors.

Keywords Poly(3,4-ethylenedioxythiophene) · Tungsten oxide · Hybrid organic–inorganic films · Charge storage and propagation · Redox supercapacitor · Redox probing

Introduction

Redox polymers, in particular, organic conducting polymers [e.g., polyaniline, polypyrrole, and poly(3,4-ethylenedioxythiophene) (PEDOT)] [1] are objects of growing interest due to prospects of their wide application in various systems including charge storage devices [2], sensors [3], gas separating membranes [4, 5], molecular electronic [6], displays and light emitting diodes [7], corrosion protection [8], and materials for electrochromic devices [9, 10]. PEDOT is known to form porous but stable, highly conductive and electroactive polymer films [11–19]. PEDOT films can be n- and p-doped [14–16], and its conductivity can reach values as high as 200 S cm^{-1} [20]. It has been recently reported that PEDOT can form in aqueous solutions robust composite films with such inorganic polynuclear species as heteropolytungstates and molybdates, and the resulting materials are characterized by fast dynamics of charge propagation [21]. The polyoxometallate species are stabilized due to existence of electrostatic attraction anionic molybdate or tungstate units and positively charged conducting polymer in the potential range where PEDOT is conductive.

Among stable electroactive transition metal oxides, WO_3 has found application in electrochromic devices, semiconductor gas sensors, catalysis including electrocatalysis, and

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in photocatalysis [22–26]. Films of partially reduced WO_3 , namely hydrogen tungsten oxide bronzes (H_xWO_3), contain mixed-valence redox centers of tungsten(VI,V), and they are characterized by fast electron transfer capabilities, good proton mobility, high porosity, and electronic conductivity as well as high reductive activity towards such inert molecules as bromate or hydrogen peroxide [22, 27, 28].

In the present work, we describe preparation and characterization of a novel hybrid (composite) film consisting of a conducting polymer (PEDOT) and a metal oxide (WO_3). Because PEDOT is positively charged in its conducting state, it attracts electrostatically and stabilizes anionic tungstate units existing within WO_3 . Combination of such two insoluble well-behaved electroactive components leads to fabrication of a robust material characterized by high dynamics of charge propagation and fast redox reactions. Thus this organic–inorganic hybrid material has promising properties for efficient accumulation of charge, particularly with respect to the construction of high density charge storage redox capacitors [29–32]. Both components, PEDOT and WO_3 , exhibit sizeable pseudocapacitive (Faradaic-type) effects, and they can act as effective charge (redox) mediators.

Experimental

All chemicals were commercial materials of highest available purity (analytical grade), and they were used as received. In particular, $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ and 3,4-ethylenedioxythiophene (EDOT) monomer were obtained from Aldrich, $\text{K}_3\text{Fe}(\text{CN})_6$ from POCh (Gliwice, Poland), and $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$ from Fluka. Electrochemical measurements were done using CH Instruments (Austin, TX, USA) Model 660B workstation. All solutions were prepared using doubly-distilled and subsequently de-ionized (Millipore Milli-Q) water. Experiments were run at room temperature ($20 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$).

The data are reported versus the saturated (KCl) Ag/AgCl electrode. The counter electrode was from graphite rod. A glassy carbon disk electrode (geometric area, 0.071 cm^2) was used as the working electrode substrate for the deposition of composite films. Before modification, surface of the glassy carbon electrode was activated by polishing (on a piece of cloth) with aqueous alumina slurries (grain sizes from 5 to $0.5 \text{ }\mu\text{m}$). Electrodepositions of the following films: conducting polymer (PEDOT), tungsten oxide, and hybrid organic–inorganic material, was achieved on the electrode surface by application of typically 25 full voltammetric potential cycles at 50 mV s^{-1} scan rate in the range from -0.4 to 0.9 V . Both single-component (PEDOT or tungsten oxide) and composite/hybrid (PEDOT–tungsten oxide) films were deposited on

glassy carbon electrode by potential cycling in the appropriate solutions containing either a single compound or their mixture, namely solutions of 7.5 mmol dm^{-3} EDOT monomer, 10 mmol dm^{-3} WO_3 , or 7.5 mmol dm^{-3} EDOT with 10 mmol dm^{-3} WO_3 , respectively, in 2 mol dm^{-3} H_2SO_4 as a supporting electrolyte. Chronocoulometric experiments were performed in 0.5 mol dm^{-3} H_2SO_4 upon application of 1 s pulses from the initial potential of 0.9 V down to -0.2 V .

Composite films for capacitor electrodes were prepared electrochemically in a standard three-electrode cell using carbon foils (from Goodfellow Cambridge Limited, UK). The films were electrodeposited from solutions containing EDOT monomer and $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$ (in 2 mol dm^{-3} H_2SO_4) in a manner described above except that the applied voltammetric potential ranges were from -0.5 to 1.0 V . Typically, 150 full potential cycles at 50 mV s^{-1} were applied. Furthermore, the capacitor electrodes (half-cells) were utilized as a two symmetric disks (geometric area, 0.95 cm^2), and they were mounted within the Swagelok holders. The Nafion membrane (semi-solid electrolyte) was used a separator. The membrane thickness was approximately $183 \text{ }\mu\text{m}$ with conductivity of 0.083 S cm^{-1} . Capacitors were tested on ATLAS Model 0461 Multichannel Battery Interface (Atlas-Sollich, Poland) under galvanostatic conditions in the potential range from -0.2 to 0.8 V .

Scanning electron microscopy (SEM) images were obtained using the LEO 435 VP microscope (Germany) equipped with EDX analyzer. Film thicknesses were determined using profilometry (Talysurf 50, Rank Taylor Hobson).

Results and discussion

Preparation and general characteristics of films

Controlled deposition of the following films: (a) PEDOT, (b) WO_3 , and (c) WO_3 /PEDOT was achieved by voltammetric potential cycling (Fig. 1) in the respective mixtures for modification as described in **Experimental** section. It is noteworthy that, in all three situations, currents systematically increased during potential cycling. In view of earlier reports [21, 23], it is reasonable to expect that, while during positive potential cycles conducting polymer (PEDOT) sites are generated, the inorganic metal oxide (WO_3) centers are formed during negative potential scans. Voltammetric generation of the hybrid (composite) film (Fig. 1c) is compared with the generation of single-component coatings of PEDOT (Fig. 1a) and tungsten oxide (Fig. 1b). In the latter case (and in the case of Fig. 1c), the peaks occurring at potentials lower than 0.3 V correspond to redox reactions of deposited (sparingly soluble) tungsten oxide species [22, 23]. The definite current increases observed in positive

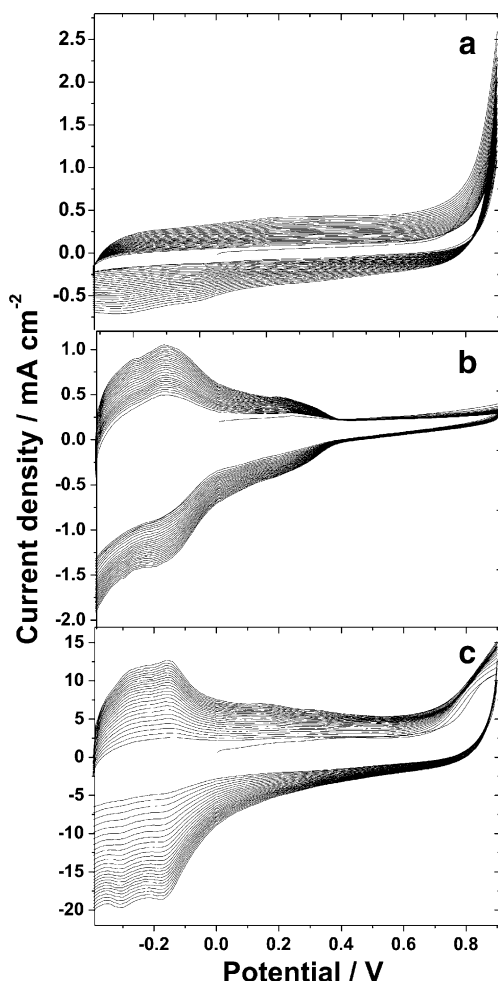
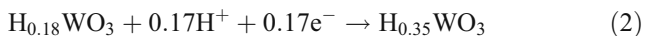
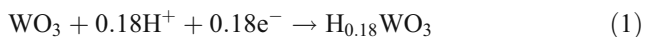


Fig. 1 Cyclic voltammetric monitoring of the growth of **a** PEDOT; **b** WO₃; and **c** PEDOT-WO₃ films on glassy carbon. Scan rate, 50 mV s⁻¹. Electrode geometric area, 0.071 cm². Electrolyte, 2 mol dm⁻³ H₂SO₄

potential scans at potentials higher than 0.7 V (Fig. 1a, c) reflect oxidation of EDOT monomer leading to the system electropolymerization and deposition.

Figure 2 illustrates cyclic voltammetric responses of the resulting (a) PEDOT, (b) tungsten oxide, and (c) hybrid PEDOT-WO₃ films. It is apparent upon comparison of the above results that both components, WO₃ and PEDOT, are present in the hybrid film. Tungsten oxide deposits undergo reversible electroreduction to nonstoichiometric tungsten oxide bronzes, H_xWO₃ (0 < x < 1) and/or substoichiometric lower tungsten oxides, WO_{3-y} (0 < y < 1) [22, 23]. The appearance of two peaks at potentials lower than 0.3 V (Fig. 2b, c) should be attributed to formation of two main phases of hydrogen bronzes, H_{0.18}WO₃ and H_{0.35}WO₃:



These redox transitions overlap more irreversible simultaneous electroreduction of tungsten oxide to WO_{3-y}. The latter process is responsible for increased background currents at potentials lower than 0 V in Fig. 2b, c. The fact that the tungsten oxide redox reactions start to appear in the composite film (Fig. 1c) at potentials ca. 150 mV more negative in comparison to conventional WO₃ (Fig. 1b) may reflect the existence of specific interactions between the organic and inorganic components. Because the polymer backbone is positively charged in conducting state [21] and hydrated tungsten oxide (WO₃×H₂O or H₂WO₄) possesses interfacial anionic (tungstate) charge in moderately acidic medium [28], it is likely that the generated organic and inorganic structures interact electrostatically with each other. It is also possible that mechanisms of proton insertion and hydrogen mobility in tungsten oxides are somewhat different in the presence of hydrophobic conducting polymer domains.

The stability of composite PEDOT-WO₃ film was diagnosed by subjecting the system to the long-term voltammetric potential cycling in 0.5 mol dm⁻³ H₂SO₄

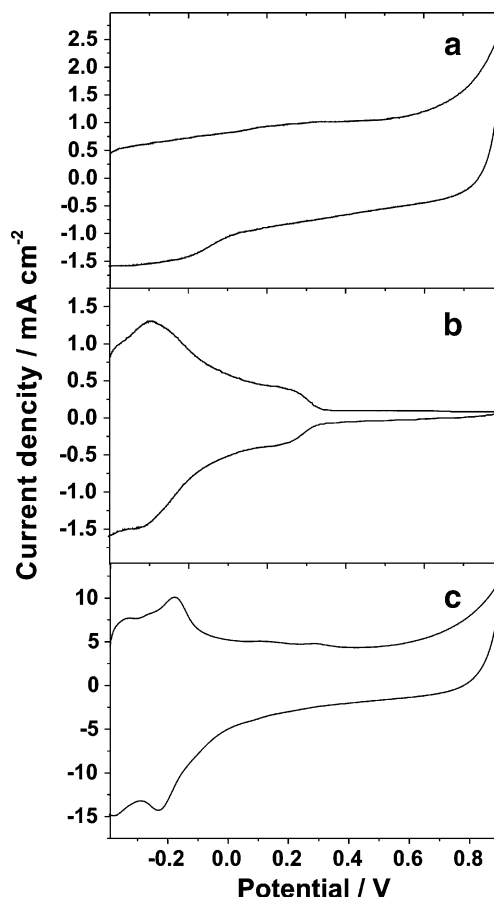


Fig. 2 Cyclic voltammetric responses of **a** PEDOT; **b** WO₃; and **c** PEDOT-WO₃ films electrodeposited on glassy carbon as for Fig. 1. Scan rate, 50 mV s⁻¹. Electrolyte, 0.5 mol dm⁻³ H₂SO₄

electrolyte within the potential limits of Fig. 2c. For example, following potential cycling for 1 h, the decrease of the voltammetric peak currents characteristic of tungsten oxide did not exceed 10%. The result is consistent with moderately good stability of the composite system. No attempt has been made to improve stability of the system, though, application of a Nafion membrane as separator in capacitor cell should preclude physical dissolution of WO_3 or PEDOT.

SEM examination of (a) PEDOT, (b) WO_3 , and (c) PEDOT- WO_3 films indicate that the conducting polymer-based films are granular grain size on the 100 nm level, dense, and free of cracks or large pores contrary to morphology of the inorganic oxide. In the latter case (Fig. 3b), micrometer cracks are clearly visible. It is apparent from Fig. 3c, that the excessive amounts of tungsten oxide exist as sub-micrometer random deposits overlaying the composite film. Independent determinations of film thicknesses using profilometry have shown that PEDOT-based films are much thicker than the simple metal oxide one: while the WO_3 film is typically approximately 0.2- μm thick, the composite PEDOT- WO_3 film is on the level of 1.5–2 μm .

Dynamics of charge transport and redox probing of films

To get insight into dynamics of charge transport, we have recorded dependencies (Fig. 4) of the chronocoulometric charge (Q) on the square root of time ($t^{1/2}$). Figure 4 illustrates chronocoulometric (potential step) measurements performed on electrodes modified with the films of (a) conducting polymer (PEDOT), (b) tungsten oxide, and (c) hybrid material (prepared as for Fig. 1). In terms of slopes of Q versus $t^{1/2}$, the dependence characteristic of the hybrid film comprised of polymer and inorganic metal oxide seems to be superior in comparison to the simple layers of polymer or tungsten oxide layers. The appearance of linear portions in the chronocoulometric plot implies existence of the diffusional (linear) type patterns. Under such conditions, the dependence of Q on $t^{1/2}$ can be described in terms of the integrated Cottrell equation [33, 34]:

$$[Q/t^{1/2}] = 2nF\pi^{1/2}r^2[D_{\text{app}}^{1/2}C_0] \quad (3)$$

where r , D_{app} , C_0 stand for the radius, apparent diffusion coefficient for charge propagation, concentration of redox centers, and other parameters either have been discussed above or have their usual significance. Obviously, it would be difficult to elucidate the value of C_0 in a case of mixed composite organic–inorganic films. But, from the slope $[Q/t^{1/2}]$, which is determined from the linear portion of the dependence of Q on $t^{1/2}$, the kinetic parameter $[D_{\text{app}}^{1/2}C_0]$, can be estimated. The linear portion of the plot in Fig. 4c is

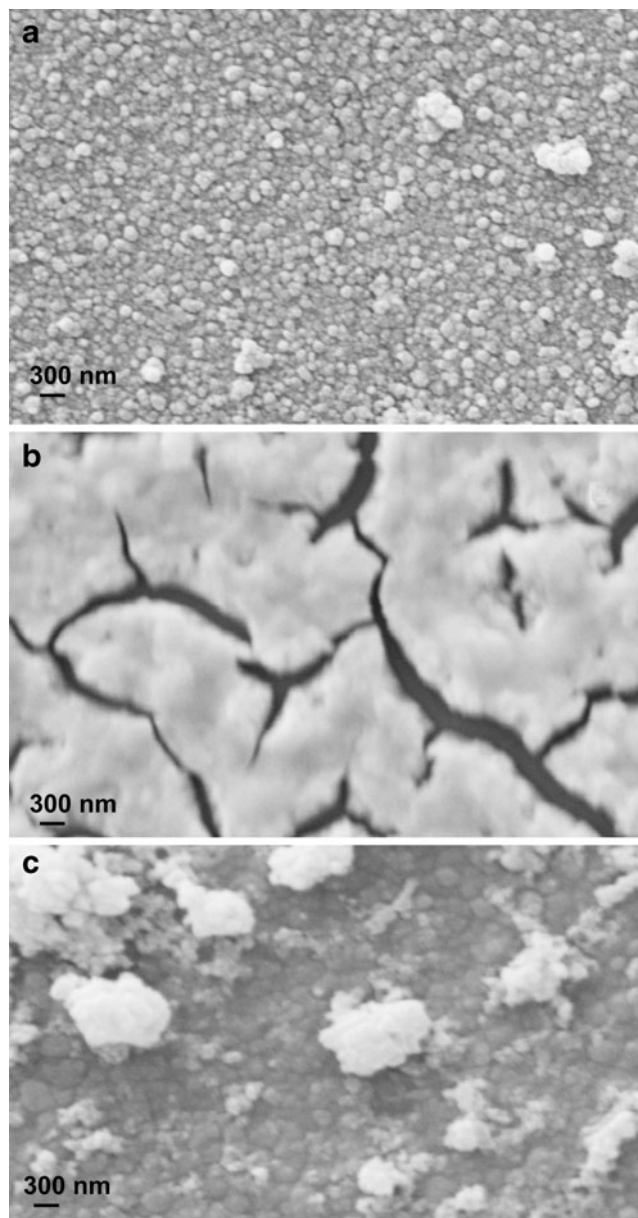


Fig. 3 Scanning electron micrographs of **a** PEDOT; **b** WO_3 ; and **c** PEDOT- WO_3 films electrodeposited on glassy carbon (see Figs. 1 and 2)

characterized by the highest slope ($10.3 \text{ mC s}^{-1/2}$) relative to those of Fig. 4b, a ($4.1 \text{ mC s}^{-1/2}$ and $8.1 \text{ mC s}^{-1/2}$, respectively). Using Eq. [3], the values $[D_{\text{app}}^{1/2}C_0]$ are equal: (a) 1.0×10^{-6} ; (b) 5.3×10^{-7} ; and (c) $1.3 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1/2}$ upon assumption of the existence of redox centers involving one-electron transfers. The value of $1.3 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1/2}$ (for Fig. 4c) is consistent with the view that the overall dynamics of charge transport in the hybrid (composite) film is high. For comparison, typical redox conducting films and solids on electrodes [11, 33], that are characterized by D_{app} 's and C_0 's ranging from 1×10^{-10} to $4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and from 0.2 to 1.5 mmol cm^{-3} , respec-

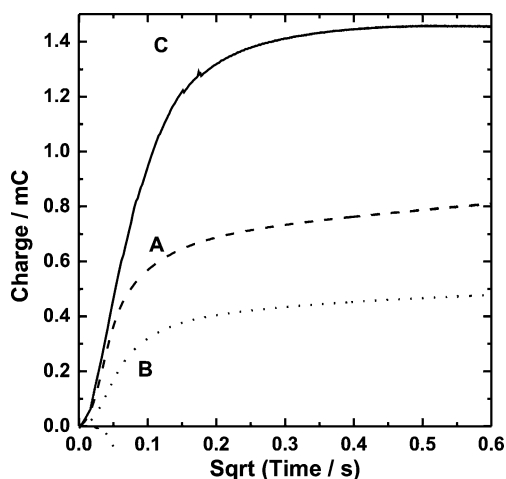


Fig. 4 Chronocoulometric responses of glassy carbon electrodes modified with **a** PEDOT; **b** WO_3 ; and **c** PEDOT- WO_3 films. Potential steps (1.0 s) were from 0.9 to -0.2 V. Electrolyte: $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$

tively, would yield values of $[D_{\text{app}}^{1/2}C_0]$ typically from 2×10^{-9} to $1 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1/2}$.

Both single-component and composite (hybrid) films were also subjected to voltammetric potential cycling in the presence of such model redox systems as hexacyanoferrate (III,II) and iron(III,II) ions. The results are summarized in Figs. 5 and 6. It is not surprising that redox behavior of the anionic hexacyanoferrate system was reversible and well-defined at the PEDOT film (Fig. 5a). The latter polymer is conductive in the investigated range of potentials and, because it is positively charged, it can attract (certainly not block) anionic species including hexacyanoferrates. Redox characteristics of hexacyanoferrates were more complex when the system was investigated at the glassy carbon electrode modified with tungsten oxide. Here, two overlapping phenomena can be observed: direct reduction of hexacyanoferrate(III) at the oxidized WO_3 film (at about 0.4–0.5 V in Fig. 5b) was followed by the mediated reduction of hexacyanoferrate(III) by nonstoichiometric partially reduced tungsten oxides that exist at potentials lower than 0.3 V. Electrochemical behavior of hexacyanoferrate(III,II) redox couple was definitely very well-defined at the composite film (Fig. 5c). Apparently, the composite film was well-conducting, and it produced the largest hexacyanoferrate(III,II) voltammetric peak currents, as well as the smallest separation between peaks. On the other hand, the single-component WO_3 film (Fig. 5b) that was semiconducting and anionic in nature, occurred to be relatively less facile to electron transfers (unless partially reduced) to the hexacyanoferrate(III,II) redox couple. We also considered the cationic redox couple (probe), namely the iron(III,II) system (Fig. 6). Due to repulsive interactions between the positively charged iron ions and the PEDOT polymer backbone (Fig. 6a), the separation between the

system's voltammetric peaks was fairly large (ca. 260 mV), and the voltammetric peak currents were somewhat lower. When the iron(III,II) system was investigated at the negatively charged tungsten oxide film, only the iron(III) reduction currents were observed (Fig. 6b) in the investigated range of potentials. Both the initial well-defined peak and the further more drawn-out iron(III) reduction currents should be attributed to the strong mediating (reductive) capabilities of partially reduced tungsten oxides. The fact that no oxidation of the resulting iron(II) ions was possible until 0.8 V (for simplicity, not shown here) reflects limited conductivity of tungsten oxide film at potentials higher than 0.3 V (where hydrogen tungsten oxide bronzes do not exist and WO_3 itself is believed to be semiconducting [23]). Only at the composite PEDOT- WO_3 film (Fig. 6c), the iron (III,II) couple behaved reversibly and produced the largest voltammetric peak currents. The later film seems to be non-blocking and well-conducting, i.e., supporting unimpeded electron transfers to the iron(III,II) system.

Finally, it should be mentioned that out of all systems studied (Figs. 5 and 6), only single-component films, PEDOT and tungsten oxide, exhibited some anion and cation exchange properties, and they were capable to

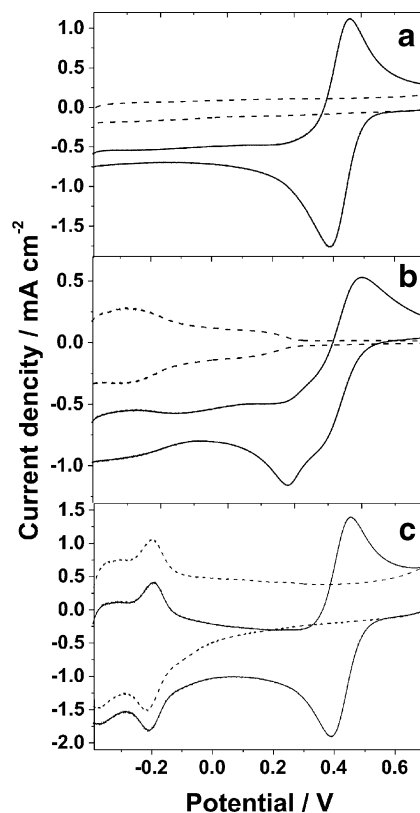


Fig. 5 Voltammetric responses of hexacyanoferrate(III,II) system recorded at glassy carbon electrodes modified with **a** PEDOT; **b** WO_3 ; and **c** PEDOT- WO_3 films. Scan rate, 10 mV s^{-1} . Electrolyte, $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. $\text{K}_3[\text{Fe}(\text{CN})_6]$ concentration, 20 mmol dm^{-3} . Dotted line refers to the behavior in the absence of redox couple

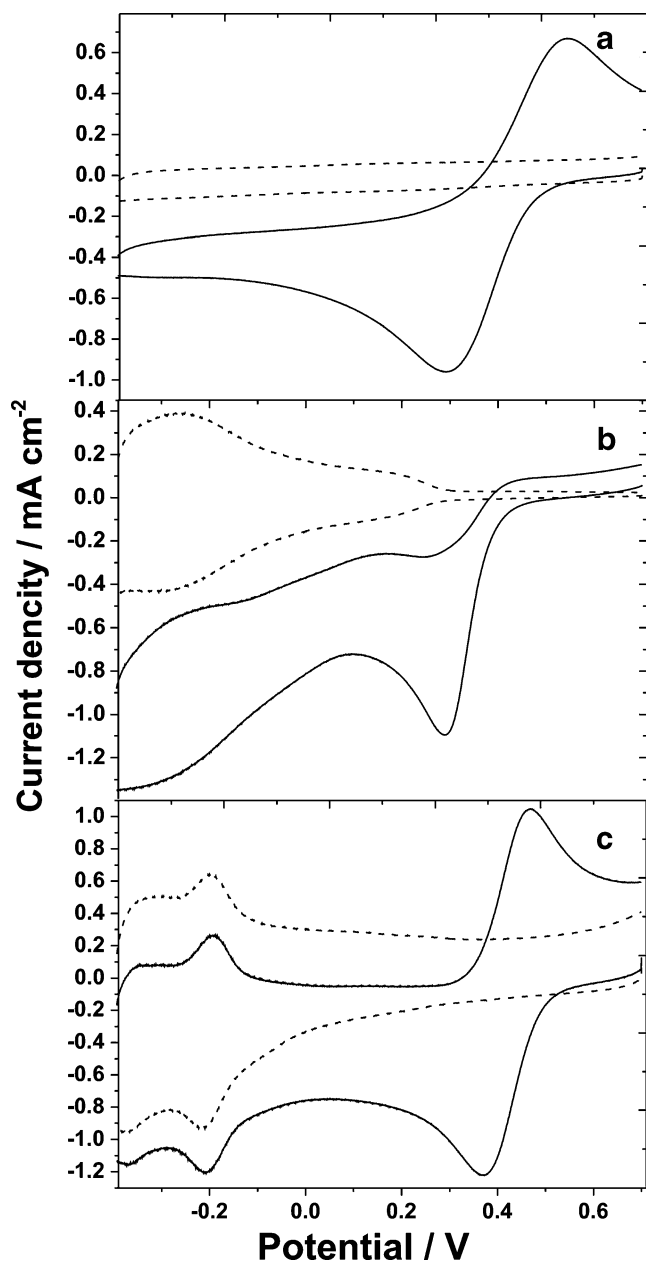


Fig. 6 Voltammetric responses of iron(III,II) system recorded at glassy carbon electrodes modified with **a** PEDOT; **b** WO₃; and **c** PEDOT-WO₃ films. Scan rate, 10 mV s⁻¹. Electrolyte, 0.5 mol dm⁻³ H₂SO₄. FeCl₃ concentration, 20 mmol dm⁻³. Dotted line refers to the behavior in the absence of redox couple

preconcentrate hexacyanoferrate anions and iron cations, respectively (Fig. 7). The actual experiments involved dipping of PEDOT and WO₃-covered electrodes in 20 mmol dm⁻³ Fe(CN)₆³⁻ and Fe³⁺ (in 0.5 mol dm⁻³ H₂SO₄) solutions, respectively, followed by potential cycling upon medium transfer to the supporting electrolyte (Fig. 7a, b). Attachment of the redox systems mentioned was not permanent, because it was found that, after two full voltammetric cycles, the characteristic (refer to Figs. 5a and

6b) hexacyanoferrate(III,II) (Fig. 7a) and iron(III,II) (Fig. 7b) peaks significantly decreased. Nevertheless, the respective preconcentration effects occurred, and the results were consistent with the existence of positively charged sites within the polymer (PEDOT) backbone as well as anionic groups on hydrated tungsten oxide surfaces. Neither hexacyanoferrate(III) nor iron(III) ions underwent preconcentration on PEDOT-WO₃ hybrid (composite) film. Thus, it is reasonable to expect that the latter system was largely neutral provided that positively charged sites of PEDOT were neutralized by anionic interfacial charge of tungsten oxide.

The fact that hybrid PEDOT-WO₃ films form rigid, fairly dense but still porous structures, as well as they are characterized by fairly fast dynamics of charge transport and by the ability to transfer electrons to the redox systems in solution makes them potentially attractive for application in redox capacitors and in electrocatalysis. Our data are also consistent with the combined activity of both organic polymer and inorganic oxide in the hybrid film.

Charging/discharging diagnostic experiments

To comment on the applicability of the hybrid PEDOT-WO₃ system as a material for reversible charging/discharging during anodic and cathodic electrochemical processes, we assembled a symmetrical electrochemical cell consisting

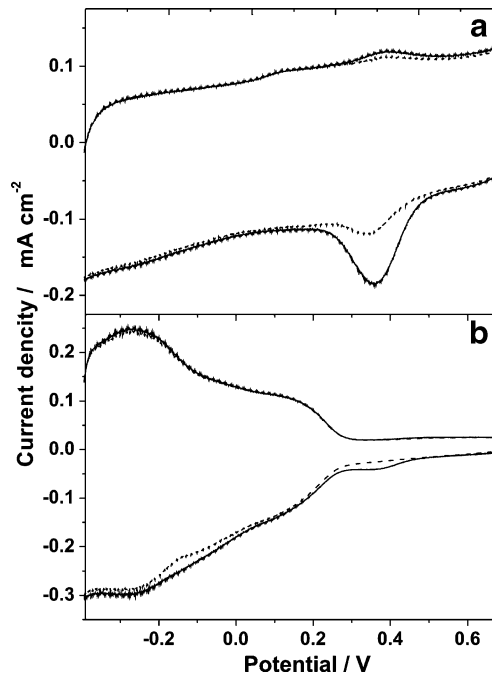


Fig. 7 Voltammetric responses (two first potential cycles) of a PEDOT and **b** WO₃ films containing surface-attached **a** hexacyanoferrate(III) and **b** iron(III). Preconcentration was achieved under potential cycling conditions of Figs. 5a and 6b, respectively. Voltammograms were recorded upon medium transfer to 0.5 mol dm⁻³ H₂SO₄ electrolyte. Scan rate, 10 mV s⁻¹

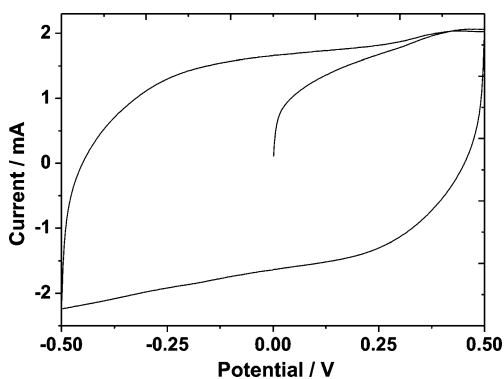


Fig. 8 Voltammetric-type dependence of current on potential difference applied to two opposing carbon foil electrodes of symmetrical capacitor. Electrodes were covered with hybrid PEDOT-WO₃ films and separated with a Nafion membrane. Scan rate, 10 mV s⁻¹

of hybrid film electrodes (electrodeposited as for Fig 1c except that 150 full potential cycles were applied) separated by protonated Nafion membrane, and we subjected it to solid-state diagnostic experiments in which current-potential experiments were performed in two-electrode mode (Fig. 8) in the absence of contact with external liquid supporting electrolyte. Because electrodes were assembled in sandwich-type configuration, application of potential differences to the opposing carbon foil electrodes forced both ions and electrons to flow in response and led to displacement of the electrode potentials in opposite directions. Figure 8 illustrates solid-state voltammetric-type response recorded in two-electrode mode, namely the dependence of current on potential differences applied to two identical carbon paper electrodes modified with the hybrid PEDOT-WO₃ film (prepared as for Fig. 1c except that 150 full voltammetric cycles in the solution for modification were used) and positioned parallel in a capacitor cell. The shape of the resulting current-potential response is similar to that characteristic of a typical double-layer capacitor [35, 36]. The fact that the dependence

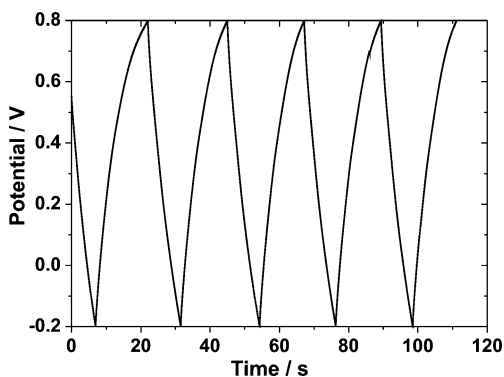


Fig. 9 Galvanostatic charging–discharging curves recorded using the symmetrical capacitor (as for Fig. 8) utilizing electrodes covered with hybrid PEDOT-WO₃ films and separated with a Nafion membrane. Current density, 5 mA cm⁻²

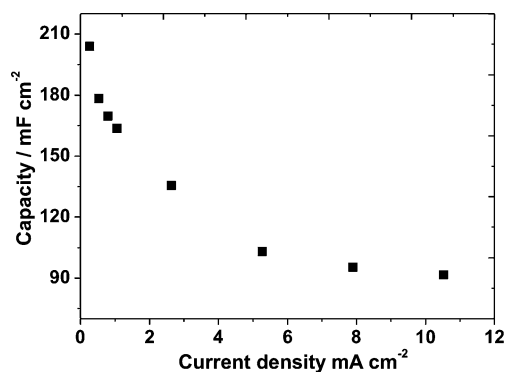


Fig. 10 Dependence of capacity on increasing current density recorded using capacitor of Fig. 9

(Fig. 8) did not exhibit any clear voltammetric peaks may be explained in terms of the absence of well-defined redox transitions in the voltammetric behavior of PEDOT-WO₃ film in the positive range of potentials (Fig. 2c). But, the capacitive-like behavior of PEDOT may be Faradaic in nature and originate from the existence of numerous overlapping redox processes in the polymer matrix. Because measurements were performed in two-electrode mode (without any reference system), it is difficult to make unequivocal conclusion about the nature (capacitive or pseudocapacitive) of electrochemical charging/discharging processes observed in Fig. 8. Having in mind the cardinal requirement of simultaneous occurrence of oxidations and reductions at opposing electrodes, redox reactions of tungsten oxide (e.g., reduction to hydrogen bronzes at the negatively poised electrode) would simultaneously require electrochemical charging/discharging of PEDOT (e.g., oxidation of the polymer at the positively poised electrode).

Figure 9 illustrates typical charging–discharging cycles of the capacitor recorded upon application of the constant current of 5 mA cm⁻². The observed charging profiles were not perfectly symmetrical to the discharging patterns. Furthermore, a shape of the charging profile was not

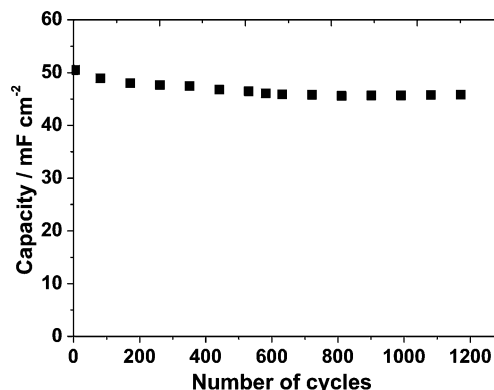


Fig. 11 Dependence of capacity on the number of charging cycles. Current density, 5 mA cm⁻²; other conditions as for Fig. 9

exactly linear presumably due to the existence of overpotentials originating from the system's internal resistance and/or kinetic limitations to charge flow during charging. Under current density of 0.1 mA cm^{-2} , the average capacity determined in repeating cycles was 205 mF cm^{-2} (Fig. 10) which corresponds to energy density of almost 30 mJ cm^{-2} . It is also apparent from Fig. 10 that application of increasing current densities led as usual to the decrease of the effective capacity. Indeed, after an initial rapid decrease, the values of capacitances leveled and oscillated around 80 mF cm^{-2} at current densities exceeding 10 mA cm^{-2} . Another important issue is that the system showed a reasonable cyclability over a fairly long period of time. Figure 11 illustrates the dependence of effective capacity over thousand cycles. Following some initial decrease, which occurred during the first few hundred cycles, capacitance values were basically unchanged upon further cycling.

No attempt was made to optimize construction of the electrochemical capacitor particularly with respect to the thickness and morphology of hybrid PEDOT- WO_3 films. Nevertheless, the present results clearly show the possibility of application of the material for energy storage applications. The results could get further improved by considering asymmetric design of redox capacitor in which the positive electrode would utilize different metal oxide species within polymer matrix. Further research is along this line.

Conclusion

The hybrid organic/inorganic films composed of conducting polymer (PEDOT) matrix and tungsten oxide are described under conditions of aqueous solutions. The systems are electropolymerized by potential cycling to form robust fairly dense films on electrode surfaces. The composite film is apparently porous enough to permit unimpeded flux of protons capable of supporting redox chemistry of WO_3 . The study has been performed in acid medium because both PEDOT and tungsten oxide are stable and sparingly soluble. All diagnostic experiments are consistent with the view that the films are characterized by fast charge propagation in the investigated potential range (-0.4 to 0.9 V). The possibility of application of a new type of a composite (hybrid) material to electrochemical charging/discharging in redox capacitors is also demonstrated here.

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