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Synthetic Metals

Electrochemical synthesis and characterization of nanocomposites based on poly(3,4-ethylenedioxythiophene) and functionalized carbon nanotubes

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ABSTRACT

This work is focused on new composite materials consisting of poly(3,4-ethylenedioxythiophene) (pEDOT) and functionalized multi-walled carbon nanotubes synthesized electrochemically. Three types of composites were synthesized: the first one containing carbon nanotubes with carboxyl groups (covalent functionalization), the second one containing oxidized carbon nanotubes ox-MWCNTs (with different oxygen-rich polar groups) (covalent functionalization) and the third one containing carbon nanotubes dispersed using surfactant (non-covalent functionalization). The presence of oxygen moieties attached to carbon nanotubes decreases their hydrophobicity and helps to suspend them more uniformly in a solution used for electrosynthesis than the surfactant addition. Homogenous dispersion of carbon nanotubes and their amount in the synthesis solution is crucial for reproducibility and electrochemical properties of the composite layers. Thin nanocomposite films were tested electrochemically for supercapacitor application. Detailed surface investigation of the electrode layers by X-ray photoelectron spectroscopy shows differences in the chemical composition between the composites and the pure polymer. Moreover, electrochemical results show that the presence of carbon nanotubes with carboxyl groups in the polymer matrix may double the capacitance values compared to pure pEDOT.

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1. Introduction

Due to population growth, harvesting of energy has become the focus of intensive research. The most popular energy storage devices – batteries – can achieve high values of energy density (approximately $250\,Wh\,kg^{-1}$), but relatively low power density (about $1\,kW\,kg^{-1}$). Electrochemical capacitors (ECs), also called supercapacitors, which are relatively new energy storage systems, bridge the gap between conventional capacitors and batteries. ECs feature high specific power ($\sim10\,kW\,kg^{-1}$), great reversibility (about 90–95%), long cycle-life ($>10^5$) and compared to batteries low specific energy ($\sim5\,Wh\,kg^{-1}$) [1–6]. In addition, ECs can operate in a wide temperature window and may be charged in less than $60\,s$ [7]. According to the charge storage mechanism, electrochemical capacitors can be classified in two types: (i) electrochemical double-layer capacitors (EDLCs) – that accumulate energy by non-faradaic charging of an electrochemical double layer (at the interface between the porous electrode and electrolyte), and (ii) pseudocapacitors – if the capacitance originates from a charge-transfer process [8,9].

In order to achieve higher values of energy density and capacitance research has been focused on new electrode materials and electrolytes. It is worth noting that electrode materials are the most significant factor influencing electrochemical performance [10]. The most widely used materials for ECs are carbon materials (e.g. activated carbon, graphene, carbon nanotubes). However, pseudocapacitive materials such as electroactive polymers, exhibit many advantages e.g. high conductivity (~100–$10000\,S\,m^{-1}$) and specific capacitance values (~500–$3400\,F\,g^{-1}$) in the doped state, facility of easy switching between reduced and oxidized states [8,11–13].

Carbon nanotubes, which are allotropic crystalline forms of carbon consisting of C sp^2 hybridizations [14], are often used as the filler material of composites investigated for supercapacitors, because of their excellent electrical properties and high mechanical strength. However, fabrication of high performance CNTs composite requires homogenous dispersion of the filler (efficient load transfer from matrix to the carbon material). Due to a π-conjugated skeleton and binding energy of tube–tube contact

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reaching 500 eV μm^{-1}, CNTs are not easily dispersible [15,16]. This problem can be fixed by covalent (acid oxidation, halogenation, cycloaddition, ozonolysis, etc.) or non-covalent functionalization of carbon nanotubes (addition of surfactants, nucleic acids, peptides, etc.) [16].

It was found that the combination of pseudocapacitive polymers with materials showing electric double-layer capacitance may bring benefits in the form of increased capacitance [10,17–19]. Moreover, the mesoporous structure of carbon nanotubes can adapt to the volume change of CPs [10,19,20]. An approach to combine particularly carbon nanotubes with conducting polymers is not new. However, most of the work has been focused on chemical polymerization. Far less literature reports concern electrochemical way of synthesis [21–23]. During electrodeposition polymer layer is grown directly on the electrode substrate, so there is no need to use any binding material and the contact resistance between polymer and current collector is lower compared to chemically prepared composite. Moreover, polymer chains grown electrochemically should be better connected to each other (comparing to polymers obtained by chemical polymerization) resulting in higher conductivity of the film. Another advantage is that electrodeposition allows to control the layer thickness by controlling the charge passed through the working electrode. If carbon nanotubes are well dispersed in the synthesis solution composite layers obtained electrochemically should be more homogenous and reproducible than in the case of the chemically prepared samples. Therefore, electrode layers prepared by electrodeposition are perfect for the basic research to investigate the relations between the chemical composition, morphology and the electrochemical behaviour of composites for their application as supercapacitors, sensors, electrocatalysis etc.

The aim of this work is to combine multi-walled carbon nanotubes (MWCNTs) and electroactive polymer poly(3,4-ethylenedioxythiophene) (pEDOT) through electrochemical synthesis in order to achieve a composite material of increased capacitance and improved cycle life. We focus here on the influence of covalent and non-covalent functionalization of MWCNTs on the homogeneity of carbon nanotubes dispersion in the synthesis solution and its subsequent impact on the properties of composite electrode layers. The morphology, structure and electrochemical properties of electrodeposited thin films have been thoroughly investigated by several techniques.

2. Experimental

2.1. Chemicals

3,4-Ethylenedioxythiophene (EDOT) monomer, multi-walled carbon nanotubes–MWCNTs ($\geq$98 carbon basis; O.D. $\times$ I.D. $\times L$ 10 nm $\pm$ 1 nm $\times$ 4.5 nm $\pm$ 0.5 nm $\times$ 3 $-$ $\sim$6 μm) were purchased from Sigma–Aldrich, Germany and used without purification. Functionalized multi-walled carbon nanotubes–COOH-MWCNTs (O.D. $\times$ I.D. $\times L <$ 8 nm $\times$ 2–5 nm $\times$ 10–30 μm; 3.8% COOH-groups) were supplied by Cheap Tubes Inc., USA. Oxidized multi-walled carbon nanotubes (ox-MWCNTs) were obtained by acidic oxidation of MWCNTs (Sigma–Aldrich) (120 ml of 65% HNO_3 per 1 g of MWCNTs, 120 °C, 24 h reflux). Poly(sodium 4-styrenesulfonate (PSS) and surfactants: 4-(1,1,3,3-tetramethylbutyl) phenyl-polyethylene glycol (Triton^{TM} X-100), sodium dodecylbenzenesulfonate (SDBS), sodium dodecyl sulfate (SDS), hexadecyltrimethylammonium bromide (CTAB) were supplied by Sigma–Aldrich. Acetonitrile, HNO_3 (65 wt%) and salts KCl, Na_2SO_4 (Avantor Performance Materials Poland S.A.) were of analytical grade and used as received.

2.2. Characterization techniques

The electrochemical properties of the layers were investigated by cyclic voltammetry (CV) chronopotentiometry and electrochemical impedance spectroscopy (EIS) using the AUTOLAB 302N potentiostat-galvanostat (AUTOLAB, Eco Chemie, B.V., Netherlands) under Nova software. All electrochemical tests were performed in a one-compartment three-electrode electrochemical cell. The working electrodes were: glassy carbon electrode (0.0314 cm^2) and fluorine-doped tin oxide (FTO) coated glass (area of 0.25 cm^2). Pt mesh and the Ag|AgCl|0.1 M KCl electrode served as the counter and reference electrode, respectively. The electrolyte was initially purged with argon for 40 min in order to remove oxygen and all the investigations were carried out under argon atmosphere. X-ray photoelectron spectroscopy (XPS) spectra were measured using an Escalab 250Xi spectroscope (Thermo-Fischer Scientific) with monochromatic Al Kα source. Charge compensation was implemented. Spectra were acquired at constant analyser pass energy of 10 eV with 0.1 eV steps. Samples before measurement were etched with an ion gun for 5 s in the case of electrode layers: pEDOT/ox-MWCNTs, pEDOT/COOH-MWCNTs/PSS, pEDOT/MWCNTs0.2/PSS/TrX, pEDOT/PSS and for 10 s in the
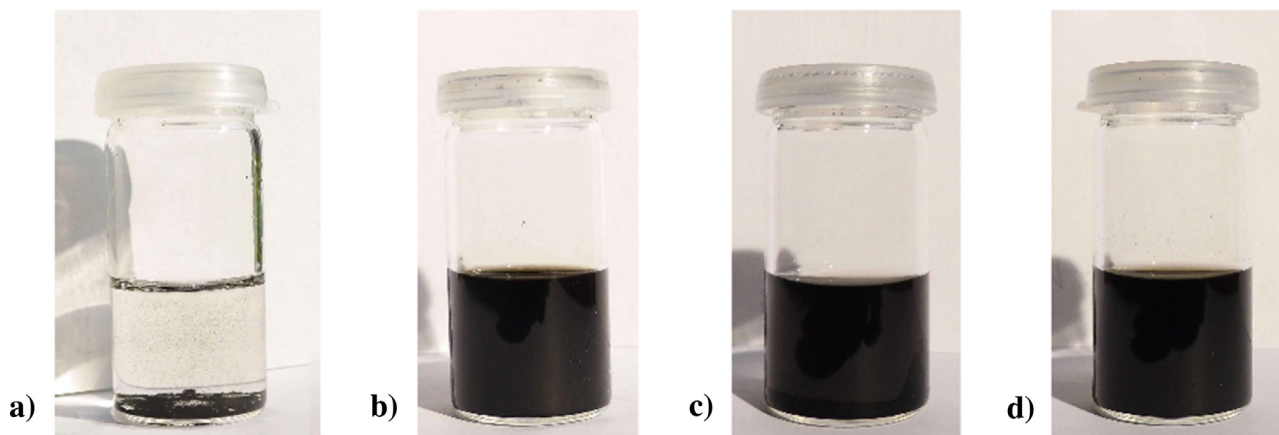

Fig. 1. Aqueous suspensions of: (a) 0.2 mg ml^{-1} MWCNTs and 0.005 M SDBS, (b) 0.2 mg ml^{-1} MWCNTs and 0.005 M TrX-100, (c) 3.0 mg ml^{-1} COOH-MWCNTs and 0.1 M PSS, (d) 3.0 mg ml^{-1} ox-MWCNTs and 0.1 M PSS.