

# Electrode materials for electrochemical capacitors based on poly(3,4-ethylenedioxythiophene) and functionalized multi-walled carbon nanotubes characterized in aqueous and aprotic electrolytes

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## ABSTRACT

Within this work, we report a facile one-stage synthesis of nanocomposites based on functionalized carbon nanotubes (CNTs) and electroactive polymer poly(3,4-ethylenedioxythiophene). Three different composites are investigated as potential electrode materials for the electrochemical capacitors. Two of the composites contain carbon nanotubes (ox-CNTs), functionalized by acid oxidation process (65% HNO<sub>3</sub>, 120 °C). The third composite comprises of non-covalently functionalized carbon nanotubes, modified by surfactant addition. The functionalization process provides a uniform distribution of carbon nanotubes in water, what in turn helps to synthesize homogenous and reproducible composite materials. The composites are synthesized by chemical polymerization of EDOT in the solution of dispersed carbon nanotubes. The goal of such synthesis is to obtain polymer chains directly on CNTs. For comparison, one composite is prepared by simple dispersion of ox-CNTs in the commercially available pEDOT/polystyrene sulfonate (PSS) solution. The composite layers are tested electrochemically in aqueous and aprotic electrolytes for electrochemical capacitor application. The electrochemical results reveal that the presence of oxidized carbon nanotubes improves the conductivity and increases the capacitance values of the composites layers. The best electrochemical performance (capacitance of approx. 80 F g<sup>-1</sup> in the aqueous and aprotic electrolyte) is exhibited by the composite obtained by chemical polymerization of EDOT in the solution of ox-CNTs.

## 1. Introduction

In recent years, nanocomposites based on electrically conducting polymers (ECPs) have attracted considerable interest as electrode layers for energy storage devices such as electrochemical capacitors. ECPs in a neutral form are insulators. However, oxidation or reduction of electroactive polymers is always connected with the incorporation of different species, mostly ions but also peptides or hyaluronic acid *etc.* [1], into polymer chains. The process is called doping. Conducting polymers (e.g. polyaniline (PANI), polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (pEDOT)), demonstrate high metal-like conductivity (up to 10<sup>4</sup> S cm<sup>-1</sup> [2]) in their doped state. Furthermore, they show high specific capacitance, high chemical stability, low environmental impact and comparably low cost. Moreover, they can be easily switched

between reduced and oxidized states (fast charge-discharge behaviour) by switching applied potentials. Furthermore, ECPs have good affinity to many other materials [2–5], what makes them an excellent conducting matrix for hybrid and composite materials [6–11]. Among ECPs pEDOT deserves particular attention due to the high reversibility, fast ion diffusion, broad electrochemical window and low oxidation potential [12–16]. However, electroactive polymers in their pure form often exhibit poor mechanical and cyclic stability. Due to the volume changes during charge/discharge processes, the capacitance of the majority of pPy and PANI electrodes retains less than 50% after 1000 cycles [17–19]. On the other hand, carbonaceous materials (CM) are an important component of composite materials for electrochemical capacitor applications, due to their unique properties such as high surface area, high electrical conductivity, long life-cycles, very good

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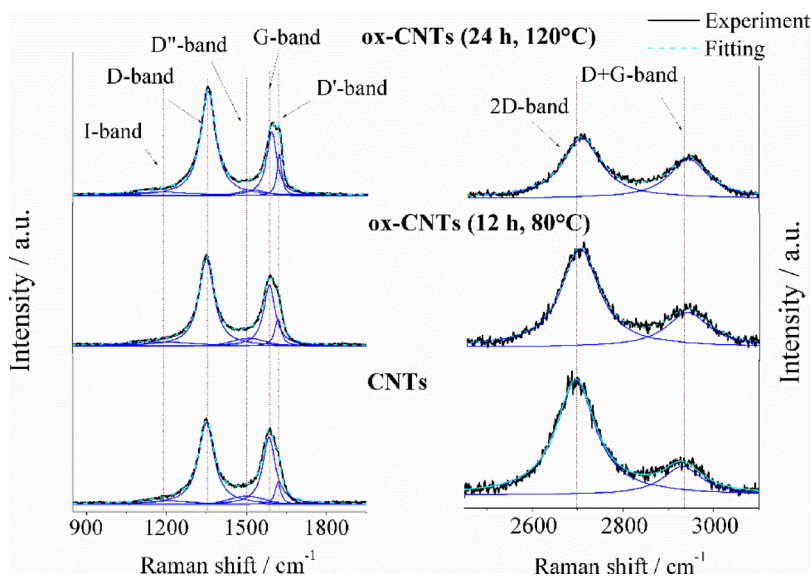


Fig. 1. Raman spectra of pristine CNTs, oxidized CNTs (12 h, 80 °C), ox-CNTs (24 h, 120 °C), a) experiment, b) fitting. Characteristic vibration modes are observed at:  $\sim 1200\text{ cm}^{-1}$  (D4-band),  $\sim 1350\text{ cm}^{-1}$  (D-band),  $\sim 1500\text{ cm}^{-1}$  (D'-band),  $1580\text{--}1590\text{ cm}^{-1}$  (G-band),  $\sim 1620\text{ cm}^{-1}$  (D'-band), and second-order region:  $\sim 2700\text{ cm}^{-1}$  (2D-band),  $\sim 2940\text{ cm}^{-1}$  (D + G-band).

mechanical properties, chemical and thermal stability, low cost and non-toxicity [4,5,20]. Many literature reports show that addition of carbon materials (carbon nanotubes, graphene, carbon nanorods, etc.) results in higher capacitance values and better stability of composites [9,19–30]. Such an improvement of electrochemical properties may be achieved due to: *i*) direct interaction between carbon material and the delocalised electrons on the conjugated polymer chains; *ii*) formation of pathways for electrons and ions through CM and pore network; *iii*) faster ion transport across the electrolyte/polymer interface and inside the polymer layer; *iv*) the development of the specific surface of polymers and their less compact structure by creating a three-dimensional carbon nanotexture; *v*) reversible redox reactions of functional groups or/and introduced into carbon matrix heteroatoms providing additional capacitance [26,31–37]. In addition, the presence of carbonaceous material in the composite ensures good material conductivity in the potential range where the polymer is in its neutral state [20].

In this regard, a preparation of electrode materials based on the electroactive polymers and various carbon materials is a popular approach [9,20–23,26,29,30,38]. As reported by Peng et al. [39], the presence of CNTs in various polymer matrices (pPy, PANI and pEDOT) significantly improved mechanical integrity, increased electronic and ionic conductivity, increased capacitance values and enhanced stability upon charge-discharge cycles of composites in comparison with pure polymers. Nevertheless, this topic is still drawing attention due to a huge potential of composite materials for energy storage application. Moreover, many factors influence the electrochemical behaviour of composite electrode layers: e.g. type of polymer, the structure of carbon material, synthesis method, type of counterions in the polymer matrix, electrode substrate or electrolyte [21,40]. Thus, it is important to appropriately tailor chemical composition and structure of composite materials to achieve electrodes of improved electrochemical properties for the reversible, stable and reliable accumulation of energy.

Herein, we report a facile one-stage synthesis of nanocomposites based on oxidized carbon nanotubes (ox-CNTs) and poly(3,4-ethylenedioxythiophene) with different counter-ions: PSS<sup>-</sup> and Cl<sup>-</sup>. The goal was to investigate the influence of the composites' synthesis method on their electrochemical properties. The hypothesis was that polymerization of the monomer in the homogenous suspension of CNTs should result in obtaining polymer chains directly on the carbon nanotubes' surface, resulting in the uniform and reproducible composite materials. In general, conducting polymers are synthesized *via* oxidative coupling of monomers by electrochemical and chemical methods. In this work, the chemical method was used due to its simplicity and lower costs in large-scale production in comparison with electrochemical

polymerization. Preparation of the pEDOT/CNTs composites required homogenous dispersion of CNTs in the aqueous synthesis solution. To achieve this goal, highly hydrophobic CNTs were functionalized in two ways: *i*) non-covalently (by addition of a surfactant) and *ii*) covalently (by acidic oxidation of CNTs). Functionalization of CNTs improved the dispersibility of CNTs and enabled synthesis of nanocomposites. Chemical composition, structure and electrochemical performance of nanocomposites were thoroughly examined by a number of techniques.

## 2. Experimental

### 2.1. Chemicals

3,4-ethylenedioxythiophene (EDOT) monomer, multi-walled carbon nanotubes – CNTs – used without purification ( $\geq 98$  carbon basis; O.D.  $\times$  I.D.  $\times$  L  $10\text{ nm} \pm 1\text{ nm} \times 4.5\text{ nm} \pm 0.5\text{ nm} \times 3\text{--}6\text{ }\mu\text{m}$ ), 4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol (Triton™ X-100) and 1 M LiPF<sub>6</sub> in ethylene carbonate (EC)/dimethyl carbonate (DMC) were supplied by Sigma-Aldrich (Germany). FeCl<sub>3</sub>, KCl, Na<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> (65 wt%) and H<sub>2</sub>SO<sub>4</sub> (95 wt%) were purchased from Avantor Performance Materials Poland S.A. All chemicals were of analytical grade and used as received.

### 2.2. Characterization techniques

The electrochemical properties of the materials were investigated by chronopotentiometry (ChP), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using two potentiostats/galvanostats: the AUTOLAB 302N (AUTOLAB. Eco Chemie. B.V., Netherlands) under Nova software and VersaSTAT 4 (Princeton Applied Research, USA). under VersaStudio software. Electrochemical investigations were carried out under an argon atmosphere (the electrolyte was deoxygenated by purging with Ar for 40 min). All electrochemical tests were performed in a three-electrode electrochemical cell: platinum disc electrode (area of  $0.0177\text{ cm}^2$ ) or platinum wire as the working electrode, platinum mesh as the counter electrode and Ag|AgCl|0.1 M KCl or Ag|AgCl|3.0 M KCl as the reference electrodes.

The electrochemical impedance spectroscopy was recorded in the frequency range from 0.1 Hz to 100 kHz at 25 °C in 1.0 M KCl. The potential amplitude was equal to 10 mV.

Raman spectra were recorded by a confocal micro-Raman spectrometer (InVia. Renishaw) with an argon ion laser (514 nm) within the wavenumber range of  $100\text{--}3200\text{ cm}^{-1}$ .

X-ray photoelectron spectroscopy (XPS) spectra were measured

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