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The effect of electro-polymerization method on supercapacitive properties of poly (*o*-Anisidine)/CNT nanocomposites

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ABSTRACT

The aim of this work refers to study the effect of electro-polymerization method on supercapacitive properties of a known polymer nanocomposite. Herein, poly (*o*-Anisidine)/multi-walled carbon nanotube (POA/CNT) nanocomposites for supercapacitor applications are prepared by various electrochemical techniques including potentiodynamic, potentiostatic and galvanostatic. The electrochemical response of the prepared POA/CNT by potentiostatic method, is higher than those which are prepared by other methods. The scanning electron microscopy images show that as the preparation method changes from galvanostatic to potentiostatic, the nanocomposite possesses more pronounced porosity. Also, electrochemical impedance spectroscopy shows that with changing the electro-polymerization method from galvanostatic to potentiostatic, the charge transfer resistance decreases. The obtained specific capacitances by galvanostatic charge-discharge measurements for the nanocomposites which are prepared by potentiodynamic, potentiostatic and galvanostatic methods at 0.6 A g^{-1} are evaluated at about 177, 323 and 81 F g^{-1}, respectively. Moreover, energy densities for the composite which are prepared by potentiostatic, potentiodynamic and galvanostatic methods at 0.6 A g^{-1}, are calculated at about 16, 8.8 and 4 Wh kg^{-1}, respectively. The results indicate that the electrode material prepared by the potentiostatic method, exhibits a better supercapacitive performance.

1. Introduction

Supercapacitors also known as ultra-capacitors or electrochemical capacitors as novel energy storage devices are receiving considerable attentions due to excellent properties including fast charge/discharge rate, high electrical power density, long cycle life, environmental friendliness, excellent reversibility, bridging function for the power and energy gaps between batteries and conventional capacitors and low cost maintenance [1–5]. Supercapacitors are generally classified into three classes based on their charge storage mechanism. These include the electrical double-layer capacitor (EDLC), pseudo-capacitor (PC), and hybrid capacitor (HC). Table 1 summarizes the properties of each class of supercapacitors along with an example. Among the materials mentioned in Table 1, conducting polymers (CPs) due to low production costs, good intrinsic conductivities, suitable morphologies, relatively large pseudo-capacitances as well as fast kinetics of charge/discharge processes have been intensively studied as electrode materials in the electrochemical energy storage devices [6–9].

On one hand, the π-conjugated double-bonds in the CP backbone transfer electrical charge from the current collector to the electrolyte [10]. However, the drawback associated with the CP is that it is prone to quick degradation upon repetitive cycles (charge/discharge process) due to its swelling and shrinkage [11].

On the other hand, CNT is also attractive for supercapacitor electrodes due to its large surface area, high chemical stability, low resistivity as well as remarkable mechanical property [12]. However, CNTs don't exhibit satisfactory capacitance values. In order to lessen the restriction of poor cycle stability of CPs as well as maximize the capacitance value, combination of the CPs with CNTs has been evidenced [13–16]. Among all CPs which were investigated, PANI is the most promising candidate for the supercapacitor [17–20]. However, because of rigid structure of PANI, its process ability is limited and hence its C_s is restricted. While, electron donating $-OCH_3$ group at the *o*-Anisidine (OA) by producing a better polymer network, improves the process ability. However, it should be noted that the poly (*o*-Anisidine) has lower conductivity than the original PANI [21]. The presence of a highly conductive carbon based nanomaterial could be effective in the charge transport inside the composites [22,23]. Basnayaka et al have synthesized a graphene-POA nanocomposite by a chemical oxidative polymerization method. The obtained results showed that the C_s increased due to the fasil charge transport of the composite which was caused by highly conductive graphene and electron donating of

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Table 1
Classification of supercapacitors.

Supercapacitor type	Charge storage mechanism	Electrode materials	Example	Advantages	Disadvantages
Electrical double-layer capacitor (EDLC)	non-faradaic process (physical, adsorption, electrostatic)	carbonaceous materials	graphene, carbon nanotubes (CNT), activated car bon	low cost, large surface area, good conductivity, chemical stability	low specific capacitance (C_s)
Pseudo-capacitor (PC)	faradaic process (redox reaction)	CPs, metal oxides	PANI, RuO_2, MnO_2	high specific capacitance, excellent intrinsic conductivity	low cyclic stability
Hybrid capacitor (HC)	both faradaic and non-faradaic processes	carbonaceous materials/CPs, carbonaceous materials/metal oxides	PANI- graphene, RuO_2-CNT	superior cyclic stability, high power density	–

methoxy groups. The C_s in 2 M H_2SO_4 solution was estimated to be 380 F g^{-1} [24,25].

The electrochemical polymerization is widely used for fabrication of the POA films on the electrode surface. In a typical work, POA coatings were electrosynthesized using cyclic voltammetry (CV) on Cu from an aqueous salicylate medium [26]. Also, POA-DBSA coatings were prepared on the stainless steel using CV method [27]. Savale et al. [28] prepared the POA-H_2SO_4-glucose oxidase film on Pt electrode using galvanostatic method. The growth mechanism of the POA coating on the low carbon steel substrates have been suggested by Pawar et al. [29] which was synthesized by electrochemical polymerization under galvanostatic conditions from aqueous solution of oxalic acid. Also, embedding of CNTs into the POA by oxidative polymerization method was reported by Bavastrello et al. [30]. The experimental data of the specific conductivity showed that the presence of CNTs inside the CPs matrix enhances the electrical properties of the polymer. Previously, the effect of the PANI morphology on its super-capacitive performance has been addressed by Zhou et al. [31]. The obtained results showed a superior performance for supercapacitor for the nano-fibrous PANI which was prepared on a stainless steel substrate using pulse galvanostatic method.

Interestingly, there is still no report on the fabrication of the POA/CNT nanomaterials by electrochemical methods and their use as an electrode material in supercapacitor. Thus, in this work, electro-polymerization process of the OA monomer in the presence of CNT by different electrochemical methods including potentiodynamic, potentiostatic and galvanostatic was investigated. The electrochemical characterization for investigation of supercapacitive properties has been carried out by CV, galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) methods.

2. Experimental

2.1. Materials and instruments

Ethanol (99%) and KCl (99%), $K_3Fe(CN)_6$ (99%), $K_4Fe(CN)_6$ (99%), H_2SO_4 (98%) and HNO_3 were purchased from Merck Co., and used as received. Alumina powder (Al_2O_3) and OA monomer (98%) were purchased from Aldrich Co., and Fluka Co., respectively. Doubly distilled water (DDW) was used to wash the glassware, and to prepare all solutions. CNTs with outer diameter of 10 nm, purity of 95% and length of 30 μm were purchased from Neutrino Co., Iran. For the activation and pretreatment of the CNTs, 0.5 g of CNTs was ultra-sonicated in a mixture of H_2SO_4 and HNO_3 (3:1, V/V) solution for 30 min and refluxed for 8 h at 60 °C. Then, it was washed with DDW to neutrality, separated by centrifugation and dried in an oven at 50 °C. 1.0 mg of the CNTs was dispersed in 1.0 mL ethanol and sonicated in an ultrasonic for 15 min to obtain a stable suspension.

Ultrasonic (BANDELIN Co., Germany) bath was used for cleaning the electrode and agitation for preparation of the suspension. The morphology of the electrode surface was checked by scanning electron microscope (SEM). The electrochemical measurements were performed using a potentiostat/galvanostat Autolab (Nova software model PGSTAT 302 N, Metrohm, Netherlands) coupled with a PC. Impedance measurements were performed with a potentiostat/galvanostat Palmsense (PSTrace software version 4.2.2, Netherlands), at the open circuit potential (OCP) with an AC voltage amplitude of 10 mV and a frequency range of 20 kHz to 10 mHz. The conventional three-electrode system was set by a glassy carbon electrode (GCE), Ag|AgCl|KCl (3 M), Pt wire (all from Azar Electrode Co., Iran) as working, reference and auxiliary electrodes, respectively.

2.2. Preparation of the CNT/GCE

An aqueous slurry of alumina powder on a damp smooth polishing cloth was used for manually polishing of the GCE. Adherent alumina powder was removed from the electrode surface by rinsing with DDW. The GCE was then sonicated in the DDW and dried in air. The CNT/GCE was prepared by dropping of 5 μL of the black CNT suspension on the GCE surface using a micropipette and left to dry. The CNT/GCE was activated by 10 successive CVs in a potential range of -0.3 to 1.1 V at $\upsilon = 50$ mV s^{-1} in 0.5 M H_2SO_4 solution until stable CVs were obtained. The electroactive surface area of the CNT/GCE and a bare GCE was measured by CV method using 0.1 M KCl solution containing 1.0 mM $K_4Fe(CN)_6$. The CNT/GCE was used for the study of electro-polymerization of OA monomer in 0.5 M H_2SO_4 solution as supporting electrolyte.

2.3. Preparation conditions of the POA/CNT nanomaterials

To prepare the POA film at the CNT/GCE surface, three polymerization methods including potentiodynamic, potentiostatic and galvanostatic were used. To create the same conditions for the accurate comparison, the active surface in all cases was considered to be same. Also, to reproduce the thickness of the polymeric film, the amount of charge passing during the electrochemical polymerization was controlled at about 51.2 mC. Furthermore, 0.1 M OA monomer in 0.5 M H_2SO_4 was used at all methods. Herein, H_2SO_4 not only acts as a carrier electrolyte in aqueous solution, but also helps to dissolves the organic monomer by protonation of the amine groups at the monomer structure and formation of a salt.

The electrochemical techniques include:

(a)

(a) **Potentiodynamic method**: Consecutive potential cycling between -0.3 and 1.1 V (10 cycles at $\upsilon = 50$ mV s^{-1}).
(b) **Potentiostatic method:** Applying a constant potential of 0.82 V for period of time at about 400 s.
(c) **Galvanostatic method:** Applying a constant current of 0.512 mA for 345 s.

When polymerization was accomplished, the polymer coated electrodes were carefully rinsed with H_2SO_4 solution and the electrode potentials were cycled between -0.3 and 1.1 V (10 cycles at $\upsilon = 50$ mV