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Carbon/polypyrrole composites for electrochemical capacitors

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ABSTRACT

Composite materials made of electrically conductive polymer–polypyrrole (PPy) and carbon materials have been prepared and characterized. Oxidative chemical polymerization has been selected as the synthesis method. $FeCl_3$ was used as oxidizing agent. Process was carried out in aqueous acidic medium. Composites were prepared by immersion of selected carbon materials in the solution of monomer and followed by addition of oxidant specimen to subjected solution under vigorous stirring. Obtained composite materials were characterized by three electrochemical methods (cyclic voltammetry, galvanostatic charging/discharging, electrochemical impedance spectroscopy) to determine capacitive parameters for further applications in the electrochemical capacitors. Capacitance of the materials varied in the range of 90–135 $F g^{-1}$ and has been retained during 5000 cycles of galvanostatic charging/discharging, working in the acidic medium (1 mol L^{-1} H_2SO_4 aqueous solutions). Moreover, the measurements confirmed a very high electrochemical stability of polypyrrole supported by carbon materials with a current load of up to 50 $A g^{-1}$.

1. Introduction

Development of energy storage systems designed for supplying portable electrical devices requires enhancement of the energy and/or power release, indeed. Devices which presently focused scientific attention as a promising solution for efficient energy storage are electrochemical capacitors. Mechanism of energy storage in these devices can be considered as two phenomena: fundamental one utilizes electrostatic accumulation of charge in electrical double layer and involves carbon materials with a well-developed surface area; thus, charge storage takes place at the electrode/electrolyte interface. The second mechanism is based on reversible redox reactions occurring on electrode materials. Example of such materials are metal oxides and conducting polymers [1–4]. Different carbon materials with their microtexture, degree of graphitization, dimensionality (from 0 to 3D) or form of occurrence (powder, fibers, foams) have been studied as a potential electrode materials in electrochemical capacitors [5]. Much attention has been focused also on conducting polymers such as polypyrrole (PPy), polyaniline, polythiophene, and their derivatives [6]. Most studied among the conducting polymers is polypyrrole because of its high conductivity, high storage ability, good thermal and environmental stability, high doping/dedoping rates and biocompatibility [7–10]. Conductive polymers can be synthesized by a number of methods, for example by chemical polymerization, chemical vapor deposition or electrochemical polymerization [11]. However, regardless of the method of preparation, in comparison to the carbon materials, their main disadvantages include reduced mechanical strength and a shorter cycle life caused by gradual deterioration of the conductive properties originating from volumetric changes during the process of doping/dedoping [12,13]. In order to improve a cycle performance and to enhance the electrical conductivity, use of PPy composites with carbon materials, which will provide a flexible skeleton adaptable to any mechanical stress seems to be a reasonable approach. Several studies reporting on the use of PPy/carbon material composites as an electrochemical capacitor electrodes can be found in the literature [12–20]. Mainly, authors reports different electrochemical characteristic of the composites originating from the different routes of synthesis and type of carbon material used. Briefly, Lee et al. [21] fabricated PPy/carbon nanotubes (CNTs) on a ceramic fabric; the specific capacitance of this composite was 152 $F g^{-1}$ at 1 mA cm^{-2}. 1 mol L^{-1} of $LiClO_4$ in propylene carbonate solution was selected as electrolyte, giving operating voltage of 2 V. The ceramic material was a substrate for the growth of carbon nanotubes and chemical polymerization. Good stability even after 5000 cycles was also achieved. Ternary composites like CNTs/PPy nanofibers core shell decorated with titanium dioxide nanoparticles demonstrated the capacitance values of 282 $F g^{-1}$ in 1 mol L^{-1} KCl electrolyte solution after few cycles. Unfortunately, the same material charged/discharged with the current load of 0.5 $A g^{-1}$ after 1000 cycles showed capacitance

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retention at the level of 64% [22]. CNTs/PPy/hydrous MnO_2 gave 88% of the initial capacitance after 10,000 voltammetry cycles. For the galvanostatic charging/discharging method, specific capacitance value was of 146 F g^{-1} during initial cycles at current load of 1 mA cm^{-2} and decrease rapidly after 2000 cycles reaching 35 F g^{-1}. Applied electrolyte was 1 mol L^{-1} aqueous solution of Na_2SO_4 [23]. Zhu et al. [24] investigate materials composed of PPy and multiwalled carbon nanotubes (MWCNT) combined in various proportions. Obtained composites were examined as electrodes in coin- and pouch-type cells at various current regimes. During galvanostatic charging/discharging of coin cell an increase of capacitance was observed and were attributed by authors to microstructure changes of the active material. Capacitance retention after 5000 cycles was close to 100%. In case of pouch cell assembly, capacitance retention was 90% after 5000 cycles with values in the range of 30–40 F g^{-1} at current load of 1–33 mA cm^{-2}.

On the other hand, all aforementioned materials provide good capacitance values but their cycle life as well charge propagation (power performance) is rather moderate. Hence, the aim of the present study was to obtain a composite material (PPyC) composed of polypyrrole and carbon materials such as carbon nanotubes (CNTs) and carbon black (CB). Such combination allowed us to benefit from good pseudocapacitive properties of polypyrrole and enhancement of charge propagation due to carbon nanotubes or carbon black addition. Composites were obtained by chemical polymerization of pyrrole in suspension of carbon material and tested as electrodes for the electrochemical capacitor. For comparison, pure PPy was produced and subjected to electrochemical analysis. Performed electrochemical tests showed enhancement of the charge propagation in composite materials with a current load above 10 A g^{-1}.

2. Experimental

2.1. Materials preparation and characterization

Pyrrole (Py) (Aldrich), hydrochloric acid (HCl) (POCh), iron(III) chloride ($FeCl_3$) (POCh), carbon black P 1042 (Kohlenstoff), multiwalled carbon nanotubes of two different size, O.D. × L 110–170 nm × 5–9 μm and O.D. × I.D. × L 10–15 nm × 2–6 nm × 0.1–10 μm (Sigma–Aldrich) were used as received from suppliers. The polymerization of pyrrole was carried out by a chemical reaction at 0 °C directly on the surface of the carbon material. The specified amount of carbon material (carbon nanotubes, carbon black) was suspended in 0.1 mol L^{-1} aqueous solution of HCl. Subsequently, cooled liquid pyrrole was added to the suspension, kept all time under intensive stirring. An aqueous solution of $FeCl_3$ was used as oxidizing agent; the solution was gradually added in the initial ratio of 1:2.33 (pyrrole:$FeCl_3$) to ensure an excess of oxidant. The synthesis was carried out for 1 h. Obtained composite materials were filtered, thoroughly washed with distilled water and dried at 65 °C for 24 h. For comparison, pure polypyrrole was synthesized the same way but without the addition of carbon material. Finally, 9 composite materials from three carbon materials (multiwalled carbon nanotubes with two outer diameters and carbon black) in the three different percentages was obtained. The content of carbon in the composite material was adjusted to be approximately 15, 20 and 40%. Detailed composition and sample labeling are given in Table 1. The proportion of components was estimated by weighing composite materials in the dried state.

Morphology of the obtained materials was observed by scanning electron microscope (SEM EVO®40 ZEISS).

2.2. Electrochemical measurements

The electrochemical performance of obtained materials in symmetric capacitors were studied in two and three electrode Swagelok® systems using 1 mol L^{-1} H_2SO_4 aqueous solutions as electrolyte. The type of electrolyte has been chosen taking into account the properties of selected polymers; in case of neutral or alkaline electrolytes, conductive polymers can undergo irreversible change to the non-conductive state. In this case, the acidic environment preserves good structural stability. The capacitor electrodes were formed as pellets with 85% of active material, 10% of binder (PVDF, Kynar Flex 2801) and 5% of carbon black (to preserve good conductivity). Average mass of the electrodes in the form of pressed pellets was in range 10–12 mg. Glass microfibre paper GF/C (Whatman™) has been selected as a separator. All electrochemical measurements were carried out at room temperature in a voltage range from 0 to 0.8 V. The specific capacitance of electrode materials was investigated by three electrochemical techniques: cyclic voltammetry at scan rates from 1 to 1000 mV s^{-1}, galvanostatic charging/discharging with current load ranged between 100 mA g^{-1} and 50 A g^{-1} and electrochemical impedance spectroscopy in the frequency range of 100 kHz–1 mHz using potentiostat/galvanostat VMP3 (Biologic, France). The capacitance values were expressed per active mass of one electrode.

3. Results and discussion

3.1. Structural characterization

SEM images of composites with the lowest content of the carbon materials (c.a. 15%), and pure polypyrrole are shown in Fig. 1.

From structural observations one can see the presence of PPy particles with spherical shape distributed on carbon surface. Carbon black and carbon nanotubes with O.D. 10–15 nm form a compact skeleton covered with aggregates of polypyrrole. Carbon

Table 1
Composition and labeling of composite materials.

Designation	Type of carbon material	Content of carbon material (%)	Content of PPY (%)
PPyC1-1	Carbon black P 1042	39	61
PPyC1-2		20	80
PPyC1-3		15	85
PPyC2-1	Multiwalled carbon nanotubes OD 10–15 nm	36	64
PPyC2-2		19	81
PPyC2-3		14	86
PPyC3-1	Multiwalled carbon nanotubes OD 110–170 nm	38	62
PPyC3-2		23	77
PPyC3-3		16	87