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Polyaniline–multi-walled carbon nanotube shell-core composite as an electrode material in supercapacitors

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Polyaniline–multi-walled carbon nanotubes (PANI/MWCNTs) composite has been synthesized by *in situ* oxidizing polymerization of aniline in water dispersion of MWCNTs and has been tested as a supercapacitor electrode material. Supercapacitive behaviour of the shell core composite has been investigated by a cyclic voltammetry and galvanostatic charge-discharge tests. In order to obtain information about the composite composition additional thermoanalytical tests have been carried out including mass decrement and heat stream in function of temperature. The research is aimed at utilization of the specific structure of the shell core composite type for designing new materials with promising properties which could find application as supercapacitor electrode materials.

Key words: *supercapacitor; carbon nanotubes; polyaniline; shell core composite*

1. Introduction

The storage of electric energy is a crucial problem which has to be dealt with in the nearest future. Solutions are sought which should permit for a prolonged storage of energy gained from unconventional, renewable energy sources (solar energy, wind power). There is also need for transit stores capable of quick, short-term storage of excess energy and its quick return. In the present paper, we deal with the second type of store-houses. An example of such solution can be emergency power supplies of UPS type, as well as systems used in electric vehicles which are designed to regain and store the energy of braking [1–3]. For this task supercapacitors are perfectly suited because they have a relatively high power and can provide much energy in a short time. There are two basic types of supercapacitors which differ in mechanisms of collecting charges. The first type capacitors use an electrical double layer which is created mainly on activated carbon materials. The other type are the so-called pseudocapacitors in which the collecting of charges is related with a transport of electric charge in metal oxides [4] and conducting polymers [4, 5].

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From a simple notation of the energy W:

$$W = \frac{1}{2}CU^2 = \frac{1}{2}\frac{\varepsilon S}{d}E^2d^2 = \frac{1}{2}\varepsilon E^2 V$$

where: $\varepsilon = \varepsilon_r\varepsilon_0$ – electric permittivity [F/m], E – electric field strength [V/m], $V = Sd$ – dielectric volume in which energy is contained [m^3] it results that the amount of the collected energy is limited by the spatial energy density $(1/2)\varepsilon E^2$ and the volume between electrodes. This leads to the idea, tested and applied in practice, to produce electrodes of a materials with high porosity and high value of physical area, even up to several thousand of m^2/g, such as e.g. activated carbons. In this case, a dependence is fulfilled that the bigger the physical area of carbon electrode, the higher is its capacity and energy. It turned out, however, that oxides and conducting polymers, having relatively small physical area (several dozen to one hundred m^2/g) have also high values of capacity and energy. This phenomenon is not fully clarified yet, despite a constantly growing number of papers concerning this issue [7]. Material for electrodes should also possess high mechanical strength as well as high thermal and electrical conductivity. Such properties are characteristic of carbon nanotubes, hence the concept of producing composite electrodes such as conducting polymers reinforced with nanotubes [6–11].

It is proved that addition of carbon nanotubes (CNTs) to polymer matrix diminishes the main disadvantage of electroconducting polymer (ECP), which is poor stability during cycling [12, 13]. CNTs. Since they have been discovered by Iijima et al. [14], play a significant role in nanoscience. Their unique mechanical, electrical and chemical properties made them useful in many fields of science. They are used, among others, as field emmiters [15], nanoelectronic devices [16], nanotube-based composites [17], and else.

Ajayan et al. were first to prepare composite of CNTs and conducting polymer [11]. Such composites were made by mechanical mixing MWCNTs in epoxy resin. CNTs were used as components of many composites: with PPy (polypyrolle)/CNT, PEDOT/CNT (poly(3,4-ethyledioxythiopene)) used as organic light emitting diodes [18], poly(3-octylthionene)/CNT, PPV/CNT (poly(phenylenevenylene)) used in highly efficient photovoltaic cells [19, 20], and PAN (polyacrylonitrile)/CNT, PANI (polyaniline)/CNT used as capacitor electrode materials [21–23].

In this paper, we described synthesis of "shell-core" PANI/MWCNTs composite, fabricated by in-situ oxidizing polymerization and its application as an electrode in a supercapacitor. In such a composite, a semiconducting nanostructure is enclosed in a conductor casing. Such spatial connection of a filler and a polymer matrix gives considerably more possibilities of extrapolating their mutual interaction and controlling the properties of an output composite [24]. The product quality is less influenced by the dispergation degree of cylindrical tubes in comparison to the spherical and lamellar fillers, since dispersion depends mainly on the orientation of the filler particles, and secondly on the separation degree of the particles. In the case of investigated sys-

tem, the most of nanotubes have the orientation along their structure what can be used as an advantage for the composite. The multi-walled nanotubes used in the experiment were chosen with regard to their higher thermal and chemical resistivity in comparison to uni-walled ones [24, 27].

Polyaniline (PANI) is a very stable conducting polymer with good damping and antistatic properties, resistant to most of organic solvents. However, its mechanical strength is low and its processing is difficult, because the use of too strong cutting forces or too high temperatures may lead to the loss of conductive properties. The conductivity of polyaniline depends on its oxidation degree. This can be improved by choosing an appropriate method and conditions of synthesis (oxidizing polymerization, electrochemical polymerization, synthesis of conducting salt PANI-HCl) or modification of the ready polymer (doping with sulfonic acid) [10].

Conductivity in polyaniline takes place along the main chain, statistically placed perpendicularly to nanotubes (by the "shell core" structure), which may give interesting results due to the spatial orientation of CNTs. The polyaniline conductivity can be controlled in the phase of polymerization or processing. Polyaniline in a glassy state can be easily pulverized and combined with other polymers as dry blendes for easier processing or plastics refining [9, 25].

The total covering of a nanotube with a polymer is a difficult task. Polyaniline is a good material for such purpose due to its environmental stability and due to the fact that its conductivity can be controlled by doping. In the process of nanocomposite creation it is helpful to make use of a compatibilizer which increases the efficiency of covering the nanotube surface with a polymer. The role of such an agent can be played by non-ionic surfactants of co-polymerizing monomers. Non-ionic surfactants additionally raise the degree of nanotube dispersion, thus helping to break up their aggregations [10, 24, 25, 28].

2. Experimental

The *in situ* method of polymerization was used in which anilines are oxidized in water dispersion of multi-walled nanotubes. The initial amounts of all components were calculated to give a composite with of the weight composition 0.75 PANI/0.25 MWCNT. MWCNT was introduced into an aqueous solution of a block co-polymer of ethylene oxide and propylene oxide (PEO-PPO, non-ionic surfactant) and exposed to ultrasound action. A non-sedimenting dispersion was obtained which was then cooled down to ca. 0 °C. Further, cooled down aniline (ANI) was instilled and the solution was stirred with mechanical mixer at this temperature. A polymerizing agent (oxidant – ammonium persulfate) was introduced into the cold solution which was then left to enable the reaction to proceed. The raw product was transferred onto a soft quantitative drain and washed several times with distilled water and ethanol to remove residues of the compatibilizer and excessive amount of polymerizing agent. The composite purified in this way was dried 8 h at 60 °C in vacuum and next 12 h in the ambient air. The ready composite had a form of a black, compact but brittle sediment.

The following materials have been used: multi-walled nanotubes, MWCNT 90%, Aldrich, block co-polymer PEO-PPO, Pluronic F-68, Sigma, aniline, ACS reagent ≥99.5%, Sigma-Aldrich and ammonium persulfate, APS reagent grade 98%, Sigma-Aldrich. Electrochemical tests were carried out in a model supercapacitor cell in which electrodes have been formed of the described composite, comminuted to the fraction <100 μm. The electrolyte was 1 M solution of H_2SO_4, and cellulose served as the separator. The measurements were made using a device ATLAS 0531 Electrochemical Unit & Impedance Analiser.

3. Results and discussion

3.1 Characterization of the PANI/MWCNT composite

The data on the composite structure and degree of MWCNT dispersion in aniline was obtained based on photographs made with electron scanning microscope VEGAII from TESCAN. Figure 1 shows a disordered, porous surface of the composite, with visible longitudinal structures of maximum length of 6 μm and the diameter >100 nm. These structures are single carbon nanotubes, some of which are not fully covered with a polymer. Spherical aggregates of various sizes, with diameters ranging from 0.5 μm to 2 μm are other visible elements of the composite. These are polyaniline particles which cover nanotubes to various degrees or appear in concentrations independent of MWCNT.

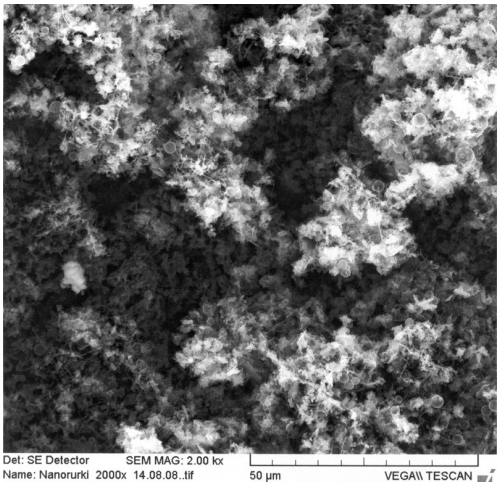

Fig. 1. SEM images of PANI/MWCNT composite (1:2000)

Thermoanalytical investigations provide information on mass alterations (TG) and energy variation during processes (DSC) taking place while heating up the sample. The results are particularly helpful for the improvement of the technology of fabrication of composites, showing a real proportion of components and degree of contami-

nation. They also provide practical data (for example thermoresistivity). The measurements were made with use of a thermoanalyzer DCS/TGA1 from the Mettler Toledo, with the air flow of 50 cm^3/min and the rate of increasing the temperature of 10 °C/min.

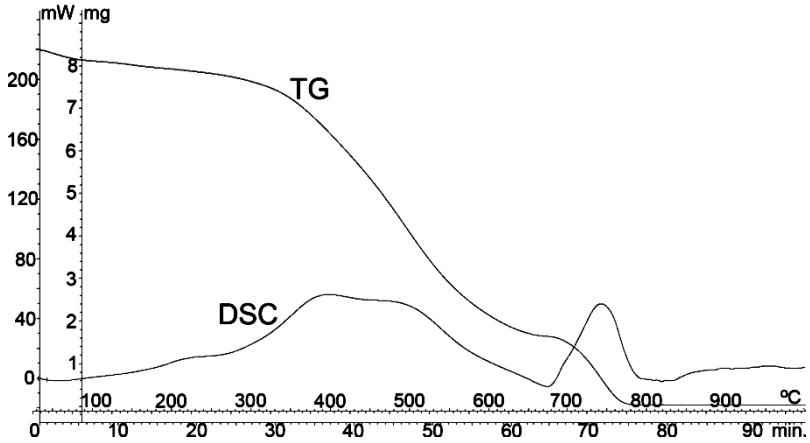

Fig. 2. Thermogram PANI/MWCNT

In the curve of mass diminution (TG) for the composite PANI –MWCNT (Fig. 2) two inflexions are visible. The first one at ca. 325 °C corresponds to decomposition of polyaniline, and the other one, narrower, above 700 °C, to decomposition of nanotubes. Temperature 325 °C is a limit of thermal stability of the composite (thermoresistivity). From the TG curve, the composition of the composite PANI:CNT = 0.7:0.2 was determined. Hence, the remaining 10% of the composite mass are contaminations removed during matrix degradation. The presence of PANI does not influence the resistivity of nanotubes, and neither brings about side effects. This is confirmed by the course of comparative curves for pure nanotubes. Based on those curves, it is possible to determine the purity of MWNTs (98%) as well as to learn that degradation occurs as a result of carbon oxidization to CO and CO_2, because almost 100% of the substance vanishes.

3.2. Capacitative properties of PANI/MWCNT

Cyclic voltammetry test was carried out at the rate of potential increase 1 mV/s to the value of 1.1 V. From the shape of the voltammetric curve (CV) it results that the capacity of a condenser is composed of the capacitance of a double electrical layer and the so called pseudocapacitance, related with the transfer of electric charge – expected for ECP. In experimental conditions, the Faraday process shows the largest exchange of charges for the cell potential 500 mV and is practically closed for the potential 600 mV (Fig. 3a).

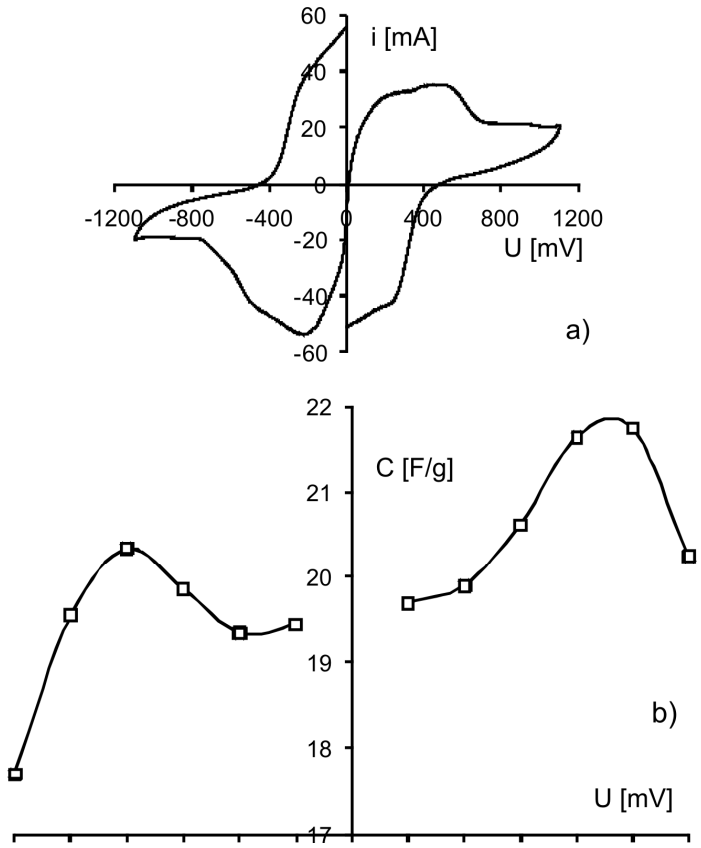

Fig. 3. Diagrams of: a) cyclic voltammetry, scan rate 1 mV/s, b) capacity in the function of electrode potential for the composite PANI/MWCNT in 1M H_2SO_4 electrolyte

This result is confirmed by galvanostatic measurements of the capacitor capacity. In Figure 3b, it can be seen that the capacitor reached its highest capacity when the potential difference was 500 mV. In the experimental conditions, the capacitance value during discharge was then 22 F/g in conversion to the mass of both electrodes. The measurements were taken for the constant value of current intensity for charging and discharging at the capacitor voltage amounting 100–600 mV. The assumed value in this investigation of the current intensity for charging and discharging was different for each voltage, and its value in amperes amounted 1/5 of the voltage value. The characteristics of the capacitor operation obtained in this way were used to calculate its capacitance (Fig. 3b) and to check the repeatability of its properties in sequential cycles (Fig. 4).

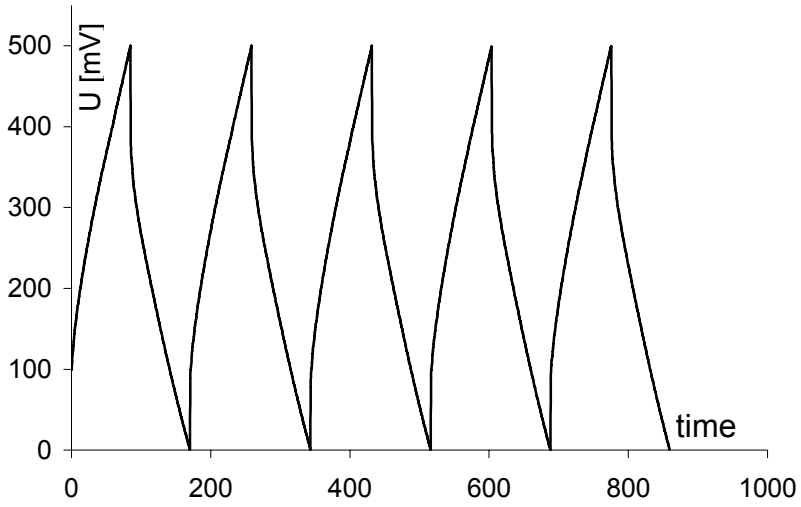

Fig. 4. Diagram of the galvanostatic measurements of the condenser charging and discharging for the composite PANI/MWCNT in 1 M H_2SO_4, i = 100 mA

Resistivity of pure PANI, pure MWCNT and PANI–MWCNT composite was measured with a Keithley electrometer 6517A and HP multimeter 34401A under similar conditions at room temperature. For PANI it equals 2.0×10^8 Ω·cm, for MWCNTs it is 0.9 Ω·cm, and for PANI/MWCNT composite – 5.0 Ω·cm.

4. Conclusions

Based on the TG/DSC measurements, it was concluded that the presence of nanotubes in the composite does not reduce the thermoresistivity of polyaniline. The polymerization of aniline in the presence of carbon nanotubes proceeds with the same efficiency as in the case of a pure monomer.

The degree of covering of nanotubes with polymere matrix, visible in SEM pictures, can be improved in the phase of synthesis of the composite by means of a stronger compatibilization of components. The structure imperfections negatively influence the properties of the composite as far as its supercapacitor applications are concerned by decreasing the participation of capacitance constituent which results from the separation of charges on the electrode/electrolyte boundary.

The capacitor capacitance amounted during the experiment ca. 20 F/g in conversion to the mass of both electrodes, what can be regarded as a very promising value for further investigations. Similarly promising are: stability of properties during consecutive cycles of charging and discharging and low resistivity.

It is shown, as expected, that addition of MWCNTs to PANI increases conductivity of the composite.

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