

Application of Polymer Nanowires for Storing Electric Energy in Supercapacitors

Streszczenie. Przedstawiono opis prac badawczych nad wykorzystaniem technologii otrzymywania nanodrutów polianiliny do wytwarzania elektrod superkondensatorów. Elektrody badano w modelowej celce kondensatora elektrochemicznego określając zdolność do gromadzenia energii elektrycznej wykorzystując zjawisko tzw. pseudopojemności. Określono wpływ parametrów technologicznych otrzymywania nanodrutów na właściwości elektrochemiczne związane z gromadzeniem ładunku elektrycznego. **Zastosowanie nanodrutów polimerowych do gromadzenia energii elektrycznej w superkondensatorach.**

Abstract. The paper presents the the research work on preparation of polyaniline nanowires (PANI) in order to produce supercapacitor electrodes. The electrodes were tested in the cell model of supercapacitor specifying the ability to store electrochemical energy in the electrical way of pseudocapacitance phenomenon – the charge storing in the activated electroconducting polymer. The results of the influence of technological parameters on electrochemical properties associated with the storing of electric charge of obtained nanowires are presented.

Słowa kluczowe: superkondensatory, polimery elektroprowadzące, nanodruły, pseudopojemność

Keywords: supercapacitors, electroconducting polymers, nanowires, pseudocapacitance

Introduction

The intrinsically conducting polymers have been intensively studied during last decades because of their ability to behave like insulators, semiconductors or conductors depending on the doping level and the nature of the dopants. Due to some redox reactions and the dopants, the electrical conductivity of such polymers can vary by several orders of magnitude. The most common conducting polymers are polyacetylene (PA), polyaniline (PANI), polypyrrole (Ppy), poly(phenylenevinylene) (PPV), polyfuran (PF), polythiophene (Pth) and poly(para-phenylene) (PPP). In general, all of these polymers are macromolecules that possess a backbone chain of alternating single and multiple C - C bonds forming an extended linear π -system. In this class of polymers, polyaniline (PANI) seems to be the most promising one. It has a relatively high conductivity (the most common green protonated emeraldine has conductivity on a semiconductor level of the order of 100 S cm^{-1}), one of the greatest stability (among the conducting polymers) and a low cost of production. Its unique electronic properties and a large surface area have attracted great attention. The polyaniline has many potential applications in various fields of science: it can be used as a material for modified electrodes [1-4], as an electrochromic material [5, 6], as a corrosion inhibitor for semiconductors in photo-electrochemical assemblies [7], in electrooptics as corrosion protection coatings, molecular and nanoelectronic devices for microwave absorbing. The capability of the reversible doping–dedoping properties provides them for the applications in sensors, actuators, separation membranes and, in electronic devices (as nanowires) [7-10].

However, all of these applications have to deal with one of the biggest disadvantages of conducting polymers, which is still their insufficiently low conductivity and poor stability. It was found out that the addition of various fillers into the polymer matrix can improve mechanical, electrical and chemical properties of composites. The carbon nanotubes have great potential in fabricating such new multifunctional composites because of their great electrical, mechanical and chemical properties [11,12]. The composites of PANI and carbon nanotubes are promising because of their high stability in the air but also due to their electrical and mechanical properties, which change significantly [13].

The nanocomposites of intrinsically conducting polymers and carbon nanotubes were found out to be very promising multifunctional material with a wide range of possible applications. Although intensive studies have been carried

out, the phenomena of the interactions at the boundary of phases between polymer and CNTs are very complex and still have not been clearly explained [14,15]. There are still two main limitations of the composites that need to be deal with: the electrical conductivity must be further enhanced as well as its stability needs to be improved [16,17]. In some publications [18-21] it was shown that due to the strong π - π interactions between polymer and CNTs, the aniline polymerizes along the CNTs. Those interactions influence the structure of composite, which causes simultaneously alignment of the CNTs in polymer matrix. By introducing covalent bonding to the system, e.g. by functionalizing the surface of nanotubes with various functional groups, the interactions between conducting polymers and CNTs could be increased. The strength of those interactions will strongly affect the structure of resulting composite [22-26].

Following this idea, the authors of this paper proposed a modified in-situ method of producing PANI/CNT composite [27]. The further works on optimisation of the polymerisation process and electrode layer preparation for the research resulted in obtaining a composite with specific capacitance 170 F/g and ESR (Equivalent Series Resistance) at $1 \text{ kHz } 0,4 \Omega$ (Fig.1).

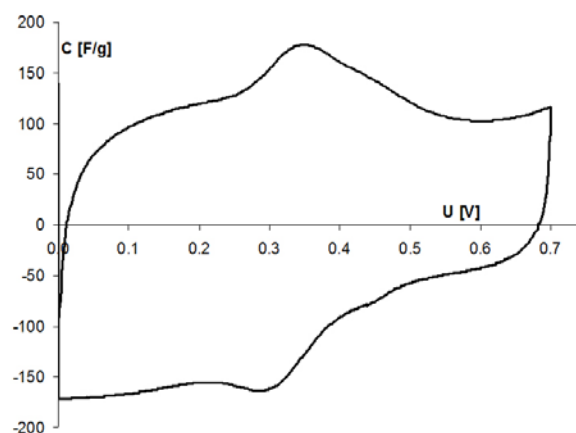


Fig.1. Voltammogram of PANI/CNT composite in electrolyte $1\text{M H}_2\text{SO}_4$ at scanning speed 10 mV/s

The above result can be treated as very promising also due to the persistence of properties after many-cycle trials over several weeks. However, literature reports state that PANI composite may show specific capacitance

theoretically even up to 1300 F/g [28]. The basic problem, which must be solved in order to increase the ability to accumulate charges, is to provide simultaneously good electric contact of the current supplying collector and to provide good access of the electrolyte to the thin layers of PANI. The following three techniques of the polymerisation process are mostly used in the production of polymer nanowires:

- **Electrochemical method.** In this method the ability to initiate polymerisation under influence of external electric field is used. In this process, a carrier - electrolyte is used, in which there are dispersed particles of the monomer. As a result of electrochemical phenomena caused by electric current conduction, polymer chains are produced on one electrode. Control of electric parameters of the system enables controlling the polymer structure. A direction of the polymer chain growth results from the applied matrix, which is the material with a specific structure allowing for the formation of the new polymer chain, for example, in its pores or around the elements of its structure.
- **Oxidative polymerisation with rapid mixing.** External electric field constitutes a factor which initiates the reaction. The nanofibrous structure is obtained thanks to the mechanisms of oxidative polymerization – where in the first phase of polymerization nanowires are produced which in the successive phases of the reaction are branched by the next monomer particles losing their original structure. In order not to allow for the phase growth and branches of the structure with new particles, the method of quick mixing is used, which does not allow for the further structure growth, at the same time keeping the original form.
- **Oxidative polymerisation on the border of phases.** Here, two non-mixing liquid phases with various densities are used. In one of the phases monomer particles are dispersed, while the other phase constitutes a polymerization initiator. In such conditions, polymerization takes place only on the border of phases where monomer particles are subjected to the influence of the initiator. Under the influence of gravitation, original structures fall to the bottom and depending on the phase density choice they do not have access to the monomer particles or initiator. This prevents a further growth of the structure keeping its original nanofibrous form.

Experimental

In the discussed studies, polyaniline in the form of nanowires was produced by means of the oxidating polymerisation method on the border of phases. The organic phase with lower density than water constituted a monomer solution – aniline in toluene. An oxidating factor APS (Ammonium PeroxydiSulfate) dissolved in the water solution of acid constituted the inorganic phase. Two inorganic acids HCl and HNO₃ were used to produce the water phase (Table 1). Both solutions were carefully transferred to the reaction vessel placing the phases according to their densities and producing the reaction environment – interface between two layers.

Table 1. Comparison of materials made within the scope of presented works

| Designation of Material | Solvent of water phase | Ratio Aniline/APS | Surfactant of water phase |
|-------------------------|------------------------|-------------------|---------------------------|
| NW-1 | 1M HCl | 1/1.25 | - |
| NW-2 | 1M HNO ₃ | 1/1.25 | - |
| NW-3 | 1.5M HCl | 1/1.25 | - |
| NW-4 | 1.5M HCl | 1/1.25 | AOT 0.05M |

Initially, polymer fibres were produced in the inter-phase boundary layer and as the reaction progressed they gradually migrated to the water phase where lack of a monomer did not allow for branching of the chain. The process continued till complete filling of the water phase with homogenous nanowires PANI. After separating phases, the fibres were separated through filtration and washed.

The purpose of the research was to produce a material of the electrochemical capacitor electrodes; therefore, the programme assumed conducting a series of examinations which were supposed to test electrochemical properties of electrodes made of these materials in the supercapacitor model. Two electrodes were made from each of these materials using titanite foil as the material of current collectors. The examinations were carried out in the two-electrode system, using 1M H₂SO₄ as an electrolyte, on the specialist device ATLAS 0531 Electrochemical Unit & Impedance Analyser. Each test consisted of:

- cyclic voltammetry test carried out at a rate of potential 5 mV/s to the value of -0.8 to 0.8 V;
- impedance spectroscopy, sinusoidal impulses 50 mV with frequency from 1 mHz to 10 kHz;
- galvanostatic charging and discharging to the value of 0.7 V current intensity 0.5 A/g.

Two initial aging examinations of the produced materials were carried out. In order to achieve this, the material of PANI designated as NW-3 was divided into two parts after the synthesis. The first part was used to produce electrodes and for electrochemical examinations immediately after the synthesis. The second part was placed in oxygen-free conditions in the argon chamber for 10 weeks. After this time, the examinations were carried out in the same way as in the case of all samples.

The electrodes for examinations were made by means of ironing saturated with the electrolyte PANI nanowires under pressure of 1,5 MPa. Taking advantage of the previous research in PANI/CNT composite preparation, we conducted the examination which tested applicability of this technique in relation to nanofibres. With this end in view, the material designated as NW-4 was divided into two parts. The first part was used for examining electrochemical properties according to the method of electrode preparation which was applied in all of the remaining samples. The second part was combined with the suspension of carbon nanowires in the weight ratio 1:1 and mixed. 90+% purity multiwall carbon nanotubes Aldrich was applied. After saturating the composite with an electrolyte, it was ironed with 1,5 MPa pressure and subjected to electrochemical examinations.

Results and Discussion

A comparison of chosen electrochemical examination results are presented in Table 2. Values of electrochemical properties of each of the materials produced in the framework of the research were compared. Electric capacitance, energy and power values come from examinations conducted by means of the galvanostatic charging and discharging to the potential of 0.7 V, by current 0.5 A/g. ESR and EDR (Equivalent Distributed Resistance) were obtained from measurements of impedance spectroscopy.

The comparison of results shows the influence of particular technological factors on electrochemical properties of PANI nanowires in such applications. The comparison of results of NW-1 and NW-2 materials makes it possible to determine applicability of both inorganic acids used in the research as the basic component of the water phase.

Table 2. Results of electrode electrochemical examinations of each of the produced materials in the electrochemical capacitor in 1M H₂SO₄ environment

| Designation of materia | Specific capacitance [F/g] | ESR 1kHz [Ω] | EDR [Ω] | Energy density [J/kg] | Power density [kW/kg] |
|------------------------|----------------------------|--------------|---------|-----------------------|-----------------------|
| NW-1 | 356 | 1.45 | 1.7 | 45.1 | 0.73 |
| NW-2 | 297 | 1.37 | 2.0 | 34.0 | 0.66 |
| NW-3 | 312 | 1.31 | 1.6 | 36.4 | 0.53 |
| NW-3 after 10 weeks | 60 | 1.49 | 3.2 | 0.5 | 0.01 |
| NW-4 | 380 | 1.29 | 1.8 | 44.5 | 0.71 |
| NW-4-CNT | 112 | 3.35 | 3.4 | 4.6 | 0.10 |

The Table 2 results show that application of HCL gives better results. The obtained material NW-1 is characterized by a distinctly higher capacitance, while low internal resistance of the capacitor model built on the basis of this material allowed for obtaining – from all of the examined materials – the best values of usable energy and power. This conclusion is proved by the voltammetric curve presented in Fig. 2. What is worth noticing is the fact of easier formation of a double layer on the material from HNO₃ - NW-2 (Table 1), which is seen in the form of faster growth of the voltammetric curve and lower ESR value. The analysis of the impedance spectroscopy curve in the Nyquist plot (Fig. 5) also proves that; however, it can be seen that total internal resistance of the model was clearly higher for MW-2 in comparison with NW-1. This occurred due to a significantly higher value of the electrode through resistance as well as the resistance on the current collector contact, which can be observed as a longer semicircle chord occurring at higher frequencies of the measurement signal. Moreover, the inclination angle of the straight section of the graph, at lower frequencies, is more acute for NW-2 material; therefore, also resistance of ion transport is higher. PANI nanowires, NW-3 and NW-4 electrode materials produced with the use of HCl but with higher concentration than in the case of NW-1, were characterized by lower ESR values and comparable resistances of ion transport in the pore volume, whereas resistances of the electrode materials themselves and their contact with the current collector were higher (Fig. 5).

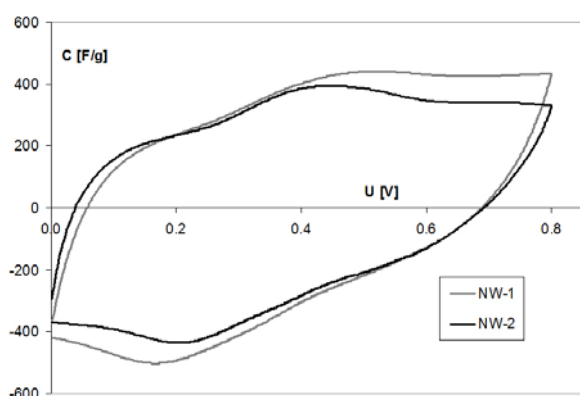


Fig.2. Cyclic voltammogram curve from nanowire electrochemical examinations made with the use of HCl as the water phase environment - NW-1 and z HNO₃ - NW-2

NW-4 material, for whose production a surfactant in the water phase was used in order not to allow for the fibre width growth, was characterised by the greatest ability to accumulate the charge – electric specific capacitance 380 F/g (Table 2). The result comes from the measurement of galvanostatic current discharge 0.5 A/g.

As it can be seen in Fig. 3 and 4, the research results obtained by means of the cyclic voltammetry method at a scanning speed of 10 mV/s can be even higher and significantly exceed 400 F/g. A difference between these values results from charging dynamics and constitutes the result of the aforementioned various factors of which object impedance consists.

Fig. 3 shows the material aging effect and a basic drawback of conducting polymers, which is particularly troublesome in applying these materials in the production of supercapacitor electrodes. Specific capacitance of the material measured before and after ten weeks decreases over five times (Table 2). Impedance spectroscopy curves, which can be seen in Fig. 6, show a significant value increase of each of the previously discussed resistance components of the supercapacitor model.

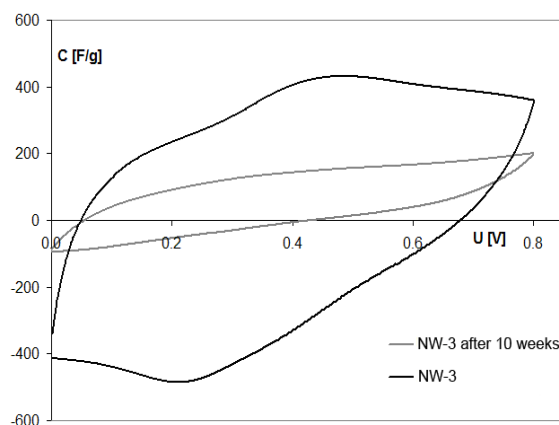


Fig.3. Cyclic voltammogram curve of NW-3 nanowires from electrochemical examinations before and after 10 weeks since the synthesis

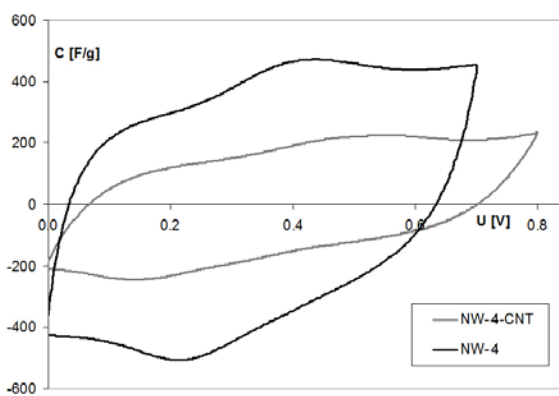


Fig.4. Cyclic voltammogram curve from electrochemical examinations of NW-4 nanowires with addition of carbon nanowires and without this addition

Fig. 4 presents the influence of the applied carbon nanowires and NW-4/CNT composite production on electrochemical properties of supercapacitor electrodes. Specific capacitance of such an electrode decreases over three times (Table 2). The analysis of model resistance components, which is enabled by the graph from Fig. 6, shows an explicit improvement of these components which depend on the addition of a component with significantly higher electric conductivity to the electrodes (including first of all through resistance). However, the influence of difficulties of the charge transfer electrode process electrolyte-polymer which exists in these conditions was much greater, hence the lower quantity of accumulated energy and low power.

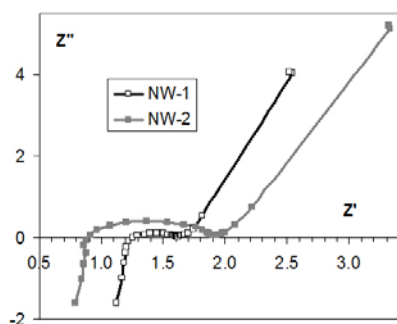


Fig.5. Nyquist chart from electrochemical examinations of impedance spectroscopy of nanowires produced with the use of HCl as the water phase environment - NW-1 and with HNO₃ - NW-2

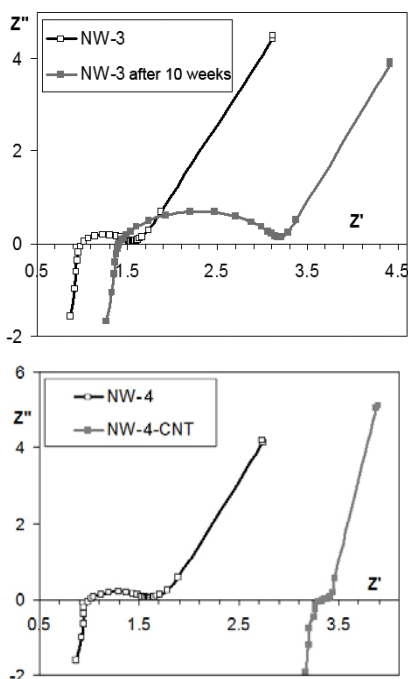


Fig.6. Nyquist chart from electrochemical examinations of impedance spectroscopy of nanowires NW-3 – aging examinations and NW-4 – examinations with the addition of carbon nanotubes

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Conclusions

The application of PANI nanowires as the material of supercapacitor electrodes with pseudocapacitance allows to obtain significantly greater possibilities to accumulate electric charges, than the PANI/CNT nonocomposite method.

The effectiveness of applied oxidative polymerization on the phase border as the method of producing nanowires of conducting polymers was proved.

The influence of PANI nanowires synthesis parameters on electrochemical properties of capacitor electrodes made of them was also confirmed. The impact of the type of the water phase inorganic acid as well as its concentration was observed.

It was noticed that the application of a surfactant in the water phase was conducive to quick absorption of the produced polymer fibre to the water phase, which shortened the time of a possible reaction of its branching. The addition of AOT, which was applied in the examinations, contributed to the improvement of electrochemical properties of the electrode material.

The range of changes of electrochemical properties of the electrode material made of PANI nanowires occurring in the aging process of polymers was initially determined.

The influence of the addition of carbon nanowires with higher conductivity than a polymer to PANI nanowires electrodes on electrochemical properties of the composite produced in this way was also initially determined.

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