

Supercapacitors Based on Composite Polyaniline / Reduced Graphene Oxide with Network Nanocomposite Polymer Electrolyte

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The paper describes investigation on new types of supercapacitors based on composite polyaniline/reduced graphene oxide with network nanocomposite polymer electrolyte. Its prototypes are all solid state. The new network polymer electrolytes based on polyethylene glycol diacrylate and nanoparticle SiO₂ was synthesized by reaction of radical polymerization in the environment of liquid organic electrolyte. The work is aimed to obtain a polymer electrolyte that is compatible with the electrode materials of supercapacitors. For these purposes the method of FTIR spectroscopy, a.c. electrochemical impedance and galvanostatic cycling were used.

Keywords: Supercapacitor, Polymer Electrolyte, Nanocomposite, Polyaniline, Reduced Graphene Oxide.

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1. INTRODUCTION

Polymer electrolytes are an important component of various electrochemical devices (lithium and lithium-ion batteries, supercapacitors, etc.) [1-2]. Of particular interest are electrochemical capacitors. They can provide quick energy supply in case of peak loads (high-speed charge and discharge). The most promising their use in combination with lithium-ion batteries (LIB) in transport, with solar batteries in space and even in the aviation. Structurally supercapacitors similar to the LIB. The principal difference is the use of electrode materials with the highest possible surface so promising in this respect supplement the reduced graphene oxide in the electrodes based on conjugated polymers (such as polyaniline) [3-4].

In this paper, prepared and tested all-solid supercapacitors with network nanocomposite polymer gel electrolyte based on polyethylene glycol diacrylate with the introduction of 10 wt.% nanopowder SiO₂.

2. EXPERIMENTAL

2.1 Preparation of electrodes of supercapacitors

Synthesis of graphite oxide and reduced graphene oxide. Graphite oxide was prepared Hummers modified method as described in [5]. The reduction of graphite oxide was carried by microwave radiation in a microwave oven (2450 MHz, 900 W). Reduced graphene oxide (RGO) was obtained as a fluffy powder.

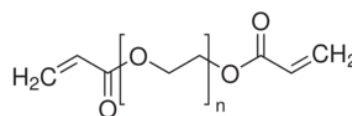
Synthesis of polyaniline composite/RGO. Synthesis of composite polyaniline (PAni) - RGO (55:45 wt.%) by the oxidative polymerization of aniline was performed *in situ* in the presence of RGO. The calculated amount of aniline RGO suspended in distilled water in an ultrasonic bath. Concentrated sulfuric acid was added until pH of the reaction mixture not exceeding 2. Then the mixture was cooled in an ice bath to -2 ± 2°C. Upon cooling an aqueous solution of ammonium persulfate slowly added dropwise in an equimolar ratio

with aniline. The reaction was conducted for 4 hours in the above temperature range. Further, the resulting precipitate was centrifuged and washed repeatedly with distilled water, isopropyl alcohol and acetone to remove low molecular weight PAni. The washed and dried at 60°C for 24 hours composite was a fine powder of black color. Synthesis of pure PAni was carried out in the same manner.

Preparation of the electrodes of supercapacitors. The composition of 70 wt.% PAni-RGO mixed with 20 wt.% of the copolymer polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) as a binder and 10 wt.% conductive carbon black VULCAN® XC72 and treated 15 minutes in the ultrasonic bath. The resulting mass was applied to a glassy carbon plate (SU-2000 grade) 1 × 1 cm. The electrodes were dried in air at 60 °C for 24 hours.

2.2 Synthesis of nanocomposite polymer electrolyte

The components of the polymer electrolyte. Polyethylene glycol diacrylate (Dac-PEG), M_w=575, Aldrich:



The liquid electrolyte - 1M LiBF₄ in gamma-butyrolactone (GBL).

Benzoyl peroxide is a radical initiator.

SiO₂ nano-powder grade Aerosil 380. BET surface area of 380 ± 30 m²/g. The average primary particle size is 7 nm (Fig. 1).

Preparation of gel-electrolyte solution. Weighed sample of Dac-PEG was dissolved in a liquid electrolyte. Then benzoyl peroxide (BP) was added. After complete dissolution of BP 10 wt.% SiO₂ was introduced.

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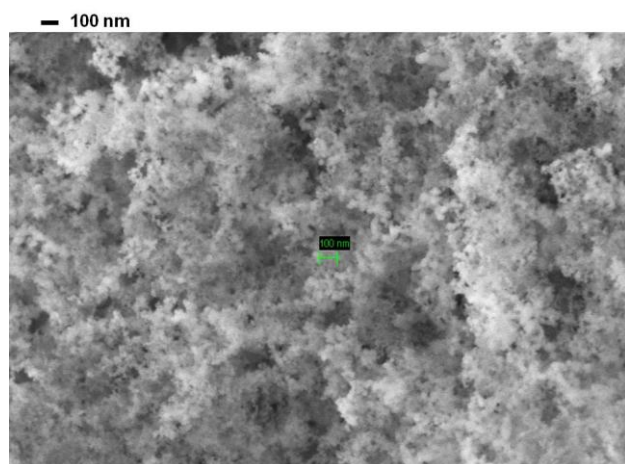


Fig. 1 – Micrographs of nano-powder SiO₂ grade AEROSIL 380

Gel electrolyte solution was filled into a glass reactor. The thermal curing of polymer electrolyte by reaction of radical polymerization was carried out for 3 hours at 80 °C.

2.3 The assembly of supercapacitors prototypes

The assembly of laboratory samples of supercapacitors (SC) was carried out in a soft laminated case, such as a "package". SC consisted of two plates of glass carbon (grade SU-2000), measuring 1 × 1 cm, which was smeared a layer of electrode paste. The dried mass of the electrode before assembly to SC was soaked in 1 M LiBF₄ GBL. The nanocomposite polymer electrolyte film was placed between the electrode plates. The size of the electrolyte film on a 1 mm greater than the size of the electrode plates to eliminate the possibility of the electrodes circuit.

2.4 The measurements techniques

The a.c. impedance was measured in the frequency range of 20 to 500,000 Hz at amplitude of the measurement signal 10 mV, using Impedancometry Z-2000 from Elns (Russia) in symmetric cells made of stainless steel with an area of 0.2 cm².

FTIR spectra of polymer electrolytes and SiO₂ nanoparticles were measured at room temperature by Fourier transform infrared spectrometer of Perkin-Elmer Spectrum 100 of "Perkin-Elmer" the USA, by the range 500 ÷ 4000 cm⁻¹ with a spectral resolution of up to 0.5 cm⁻¹.

Lifetime tests of SC samples were performed on computerized stand "Charge-8K" (produced by IPCP RAS) in galvanostatic mode. Model allows testing of up to 8 electrochemical cells.

3. RESULTS AND DISCUSSION

3.1 Characterization of network polymer electrolyte

Synthesis of thin film gel electrolytes based on 15 wt.% DAC-PEG with the introduction of 10 wt.% SiO₂ and without nanopowder (for comparison) was carry out. Figure 1 shows a view of the film nanocomposite polymer electrolyte.

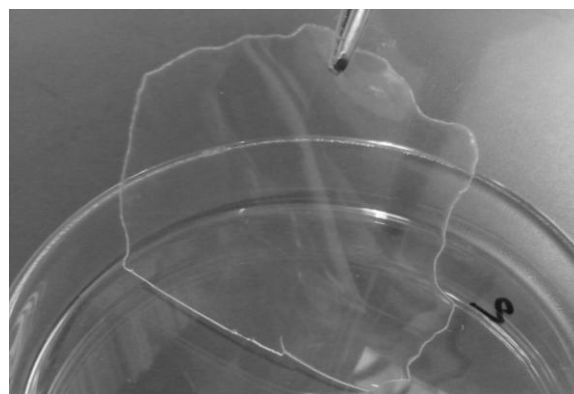


Fig. 2 – The view of the film nanocomposite polymer electrolyte

Six electrochemical cells with blocking electrodes were collected. Then its electrochemical impedance was measured at 20 °C. The hodograph for all cells was a straight line, indicating that a purely ionic conduction mechanism. The angle of slope of the line was 80°. This means that the resistance in series with the equivalent circuit element is describing the double layer capacitance. According to the calculations of the program ZView2 order capacity for all electrolytes is 10⁻⁶ F. The calculated resistances of the electrolyte (R) ZView2 program are shown in Table 1.

Table 1 – Characteristics of the polymer electrolyte without nanopowder (Empty) and with the introduction of 10 wt.% SiO₂ (Nanocomposite)

| Polymer electrolyte | Empty | Nanocomposite |
|------------------------------|----------------------|----------------------|
| The film thickness, cm | 0.035 | 0.050 |
| R ₁ , Ohm | 81.0 | 54.0 |
| R ₂ , Ohm | 71.0 | 57.7 |
| R ₃ , Ohm | 80.0 | 59.1 |
| R average, Ohm | 77.3 | 56.9 |
| Mean square error R, Ohm | 4.5 | 2.2 |
| The ionic conductivity, S/cm | 2.3×10 ⁻³ | 4.4×10 ⁻³ |

Table 1 show that the ionic conductivity of polymer electrolyte with introduction nanopowder SiO₂ increases 2 times. The mechanical strength of the films with SiO₂ nanoparticles increases.

A study of the interaction of SiO₂ nanoparticles with components of the polymer gel electrolyte was carry out by FTIR spectroscopy (Fig. 3).

Fig. 3 shows that the presence of SiO₂ nanoparticles is no noticeable shifts of intense peaks of the polymer matrix. The changes that are observed in the high-frequency part of the spectrum, require further analysis.

3.2 The testing of prototypes supercapacitors

Test of laboratory models supercapacitors was performed with nanocomposite polymer electrolyte which has the highest conductivity and good mechanical properties.

Two prototypes supercapacitors with different electrodes were collected and tested:

- 1) Net polyaniline (PAni).
- 2) The composite of polyaniline (55 wt.%) with reduced graphene oxide (45 wt.%) (PAni-RGO).

The cells were cycled at a constant current of 1 mA. Test results on the charge-discharge shown in Fig.4-5.

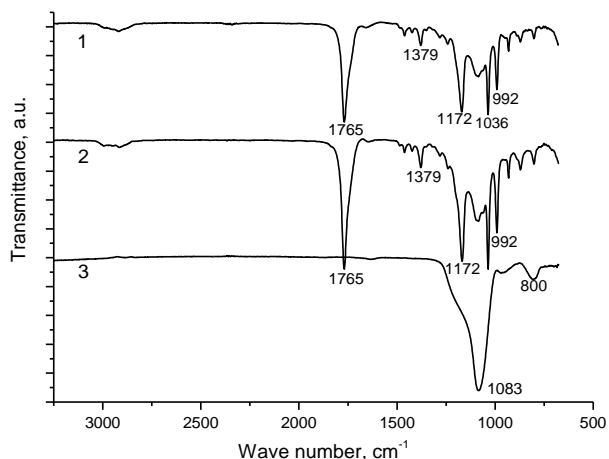


Fig. 3 – FTIR- spectra of empty polymer electrolyte (1), nanocomposite polymer electrolyte (2) and Aerosil 380 (3)

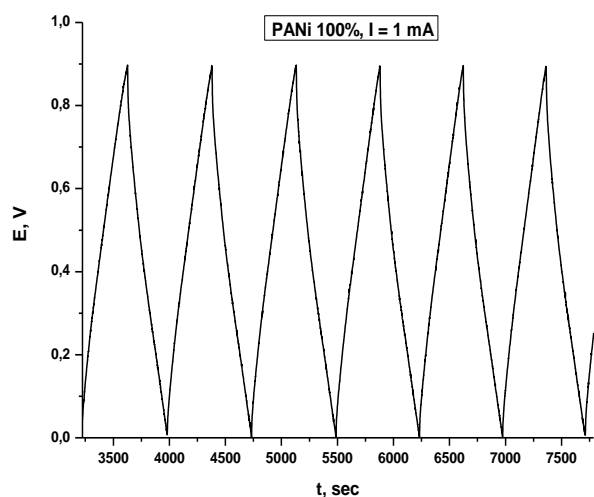


Fig. 4 – The charge-discharge characteristics of a supercapacitor with a nanocomposite polymer electrolyte and the electrodes of polyaniline

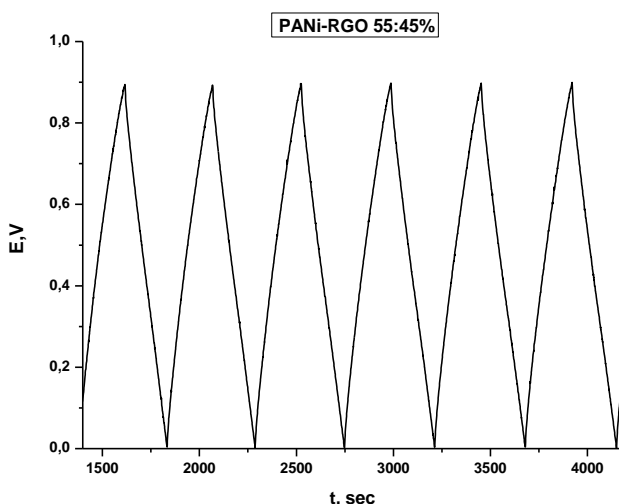


Fig. 5 – The charge-discharge characteristics of a supercapacitor with a nanocomposite polymer electrolyte and the electrodes of composite polyaniline / reduced graphene oxide

Summarized results for cycling supercapacitors are shown in Figure 6. Fig. 6 show that the capacity of supercapacitors practically maintained for 100 charge-discharge cycles. The difference in the initial capacity does not depend on the composition of the electrolyte, and it is determined only by the nature of the electrode materials.

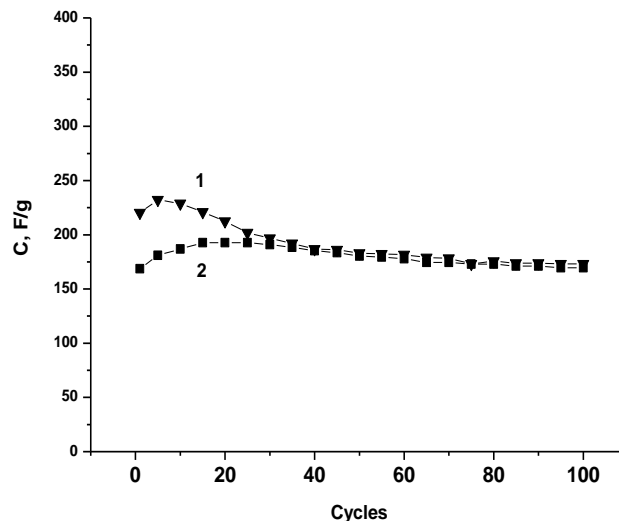


Fig. 6 – The dependence of supercapacitors capacitance with nanocomposite polymer electrolyte and the electrodes of PANi (1) and PANi-RGO composite (2)

4. CONCLUSIONS

Thus, the perspective of use of nanocomposite network polymer electrolyte in supercapacitors with electrodes made of pure polyaniline and its composite with 45 wt.% reduced graphene oxide is shown. A further modification of this system allows obtaining higher performance of the electrochemical device.

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