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# Capacitance properties and structure of electroconducting hydrogels based on copoly(aniline – p-phenylenediamine) and polyacrylamide



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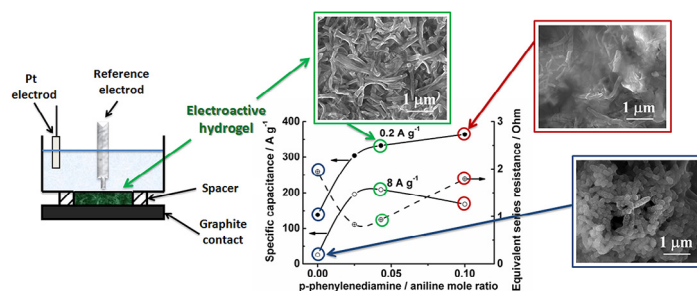
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## HIGHLIGHTS

- Electroactive hydrogels based on PAAM and polyaniline copolymers were prepared.
- Optimal composition for highest properties was found.
- Hydrogels display a high specific capacitance in wide range of current densities.
- After 1000 cycles the hydrogels keep more than 100% of their initial capacitance.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Electroconducting hydrogels (EH) based on copoly(aniline – p-phenylenediamine) grafted to the polyacrylamide for the application as pseudo-supercapacitor's electrodes have been prepared. The influence of preparation conditions on the structure and capacitance properties of the systems were investigated: we determined the optimal amount of p-phenylenediamine to obtain the network of swollen interconnected nanofibrils inside the hydrogel which provides the formation of continuous conducting phase. Structure and morphology of the prepared samples were investigated with UV–VIS spectroscopy, scanning electron microscopy (SEM) and wide-angle X-ray diffraction (WAXD). The maximal value of capacitance was  $364 \text{ F g}^{-1}$  at  $0.2 \text{ A g}^{-1}$ . It was shown that the EH samples demonstrate the retention of 50% of their capacity at high current density  $16 \text{ A g}^{-1}$ . Cycle-life measurements show evidence that capacitance of EH electrodes after 1000 cycles is higher than its initial value for all prepared samples. Changes of the copolymer structure during swelling in water have been studied with WAXD.

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## 1. Introduction

During the last decade the supercapacitors attract considerable attention due to their promising properties [1–3]. A large number of organic and inorganic materials was investigated as candidates for supercapacitor electrodes. Great interest of researches is focused on carbon nanotubes [4], graphene with metal oxides [5,6]

or reduced graphite oxide [7] possessing good electrochemical properties and high stability. However, these materials have significant drawback - namely a high cost [3] in comparison with the organic electroactive polymers such as polypyrrole and polyaniline (PANI) which can be synthesized by relatively simple electrochemical or chemical procedures [8]. Although electroconducting polymers demonstrate cycling stability and specific capacitance lower than the best inorganic materials they have high potential for development [9,10]. Two factors that significantly restrict the properties of polymeric electrodes are: 1) slow diffusion of ions inside the bulk of the electrode [3], and 2) low compatibility of electroconducting polymers with electrolyte phase [11]. The first factor reduces the power density of batteries while the second one restricts its specific capacity. Consequently, thickness of electrode should not be too large for effective charge storage. It was shown in Ref. [12] that an increase in electrode thickness from 300 nm to 6  $\mu\text{m}$  leads to the decreasing of specific capacity by one order of magnitude.

The problem of the limited ion diffusion is very important one for supercapacitors [11] because the storage of charge in the whole volume of electrode would improve its effectiveness [13]. For this purpose authors use porous templates for preparation of conducting polymer electrode: for example, graphene-mesoporous silica nanosheet [14] or three-dimensional cross-linked carbon network [15]. In such systems ions rapidly permeate inside the active material due to its through pore structure. Another approach which is less popular but more simple is to use the cross-linked composite of conducting polymer with water soluble component [11]. Such systems, so called electroconductive hydrogels (EH), swell in water and at the same time act as ionic and electronic conductors [16,17]. This permits to increase both the rate of ion diffusion and the compatibility of conducting polymer with electrolyte.

One else problem of EH electrode materials is the formation of continuous electroconducting phase inside the hydrogel. This is also related to low compatibility of conducting polymers with water solutions. Methods to increase connectivity of electroconducting phase in nonhydrogelic electrode materials are the preparation of electroactive polymers in the form of nanotubes or nanofibers [18–20] or the introduction of different nanocarbon materials into the polymer matrix [21,22]. Preparation of conducting polymer in anisometric form (for example, nanofibers) decreases the percolation threshold for electroconducting phase.

In this work we used p-phenylenediamine (pPhDA) as an effective regulator of PANI morphology [23,24]. In addition, it is reasonable to assume that introducing polar  $-\text{NH}_2$  groups will increase the compatibility of conducting polymer with water thus reducing the number of contacts between elements of electroconducting phase. The goal of this work is to investigate the influence of different amounts of additive component (pPhDA) on structure and capacitance of electrode materials.

It should be noted that usual method of electroconducting hydrogels preparation [25–28] which is based on in situ synthesis of electroconducting polymer inside the cross-linked polymer matrix does not allow to achieve homogeneous distribution of its phase. Another way is the preparation of water compatible dispersion of conducting polymer with subsequent cross-linking of the system [11]. The procedure including synthesis of PANI dispersion in polyacrylamide (PAAM) water solution was elaborated in our previous work [17]. It was pointed out in literature [29] that grafting of conducting polymer on-to back-bone of PAAM takes place during oxidative polymerization of aniline in the solution of this polymer. As a result, the compatibility of PANI with water is significantly increased. In present study this method is modified to achieve higher processability of the system and to improve its properties.

## 2. Experimental

### 2.1. Materials

Acrylamide (AAM), ammonium peroxydisulfate (PSA), N,N,N',N'-tetramethylethylenediamine (TMED), and aniline (ANI) hydrochloride were purchased from Sigma–Aldrich and used as received without purification. Para-phenylenediamine (MERK) was recrystallized from water solution prior to use. Methanol and hydrochloric acid were obtained from Vekton (Russia). All solutions were prepared in distilled water.

### 2.2. Preparation of PAAM

PAAM was prepared in 3.75% solution of AAM in deaerated water by radical polymerization with mixed initiator PSA-TMED at 40–50 °C. Molar ratio between monomer and components of initiator was AAM:PSA:TMED = 125:1:1. The polymer was precipitated in methanol and dried under vacuum at 40 °C. Weight-average molecular mass ( $M_w$ ) of PAAM was calculated from characteristic viscosity ( $[\eta]$ ) of polymer solution in 1 M aqueous  $\text{NaNO}_3$  at 30 °C according to equation  $[\eta] = 3.73 \times 10^{-4} M_w^{0.66}$  [30] and was found to be 330 000. The chemical structure of the polymer was confirmed by Raman spectroscopy.

### 2.3. Synthesis of EH

The chemical oxidative copolymerization of ANI and pPhDA was carried out in water solution saturated with nitrogen and containing 5.7% of PAAM and 1 M of HCl. The mole ratio pPhDA/ANI was equal to 0.025, 0.043, and 0.1 (samples EH-0.025, EH-0.043, and EH-0.1, respectively). For comparison the sample without addition of pPhDA (EH-0) was also synthesized. Reaction was conducted at 0 °C in the thermostatic flask connected to refrigeration thermostat and equipped with magnetic stirrer. The solution of oxidant – PSA was cooled till 0 °C and then added to the reaction mixture to start the polymerization. The sum of monomer concentrations was 0.26 M and the oxidant/(ANI + pPhDA) mole ratio was equal to 1. Thus the theoretical mass ratio between conducting polymer and PAAM is equal to 30:70 and the concentration of conducting polymer after polymerization is 2.45% by mass for all prepared samples. Reaction was allowed to proceed for 2 h and then the mixture was precipitated into methanol. Obtained green mass was dried in vacuum without heating and then it was swollen in 1 M HCl water solution. A sample of pure PANI without PAAM and pPhDA was also prepared with the same procedure.

### 2.4. Characterization methods

#### 2.4.1. Measurement of swelling ability

The swelling degree (Q) was measured gravimetrically by immersion of dried EH into the electrolyte (1 M HCl in water) until the constant mass was reached. The equation:  $Q = (m_s - m_d)/m_d$ , where  $m_s$ , and  $m_d$  are the masses of swollen and dried samples respectively, was used for calculation of Q.

#### 2.4.2. Scanning electron microscopy

Morphology of synthesized samples in dry state was investigated by scanning electron microscope ZEISS MERLIN (Germany). The specimens were dispersed in water on the ultrasonic bath. Then the dispersion was cast on the table of microscope and investigated at 10 kV voltage. Due to electroconducting nature of the samples the high quality pictures were obtained without covering of them with metal or carbon layer.

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