Polyaniline / mesoporous carbon composites as promising materials for supercapacitors

I V Gutnik, T P Dyachkova, E A Burakova and I A Gavrilov

Tambov State Technical University, 106 Sovetskaya Street, 392000 Tambov Russian Federation

E-mail: anosowa_i_w@mail.ru

Abstract. The surface modification of mesoporous carbon with polyaniline was carried out by the method of oxidative polymerization of aniline. It was found that the initial conditions for the synthesis and the percentage of carbon template in the reaction mixture have little effect on the course of temperature dependencies. However, these parameters affect the yield of the target product and the electrically conductive characteristics of the resulting materials. Composites with a polyaniline / mesoporous carbon mass ratio of 1:1 have better electrical conductivity. The electrical capacity of these samples in the aqueous electrolyte is 299.6 F/g, which is 3.5 times higher than in the organic electrolyte. Information on the polyaniline in the modifying layer on the surface of the mesoporous carbon was obtained by the method of Raman spectroscopy.

1. Introduction

Recently, due to the fast-growing market of portable electronics, there is a growing demand for energy storage systems, including due to durability (100,000 charge-discharge cycles), a fast charge process and low self-discharge, ability to work at low temperatures without a significant reduction in performance are supercapacitors (SC) [1]. An important role in the operation of devices that serve for the accumulation and transformation of energy is played by electrode materials, in which carbon nanomaterials (CNM) and electrically conductive polymers can be used [2–5].

The use of CNMs (carbon nanotubes, graphene, graphene oxide, mesoporous carbon) in this area is due to their high electrical conductivity and electrochemical stability. A significant drawback of such materials is the relatively low specific capacity. In contrast, conductive polymers, for example, polyaniline (PANI), are characterized by higher capacitance values. However, the instability of the polymer during the charge-discharge cycle imposes a restriction on their use in the SC.

An effective approach to solve this problem is to obtain hybrid polyaniline / carbon nanostructure composites [6–8]. When a polymer is combined with carbon nanomaterials, an increase in the stability of PANI and an increase in the electrical capacity of carbon nanomaterials is observed. Consequently, supercapacitors with electrode materials of this type will have a longer service life.

An effective approach to solve this problem is to obtain hybrid polyaniline / carbon nanostructure composites. When a polymer is combined with carbon nanomaterials, an increase in the stability of PANI and an increase in the electrical capacity of carbon nanomaterials is observed. Consequently, supercapacitors with electrode materials of this type will have a longer service life.

To create electrode materials with the best performance (stability during charge / discharge, high electrical capacitance), it is advisable to modify the CNM polyaniline with the most developed surface. Mesoporous carbon (MC) satisfies this requirement, the specific surface area of which exceeds the analogous parameter of carbon nanotubes. This opens up broad prospects for obtaining a composite with a high specific electrical capacity.

For example, in [9] it is reported about an increase in the electrical capacity of polyaniline 2.5 times when applied to the surface of porous carbon with a specific surface equal to 422 m²/g. The resulting
composite is characterized by a high electrical capacity (up to 700 F/g) and retains up to 93.6% of the initial capacity after 10,000 charge-discharge cycles [10].

In connection with the promise of using polyaniline-based composites, the purpose of this work was to study the laws of the oxidative polymerization process of aniline on the surface of mesoporous carbon and to study the most important electrochemical properties of the composites obtained.

2. Materials and methods
Mesoporous carbon (manufactured by Nanotechcenter LLC, Tambov, Russia) was used with the following characteristics: specific surface area – 2640 m²/g (according to BET); pore volume – 1.8 cm³/g; pore diameter – 3.6 nm.

PANI/MC composites were obtained by the method of oxidative polymerization of aniline. For this purpose, the MC was introduced into an aqueous solution of H₂SO₄ with a given pH value (1 or 3). Aniline sulfate (0.04 M; 0.05 M) and ammonium persulfate (0.05 M; 0.07 M) were added to the reaction mixture with stirring. During the process, the temperature and pH of the reaction mixture were measured.

The obtained samples were washed with distilled water to a neutral pH of the filtrate and isopropyl alcohol until the color of the filtrate disappeared. The sample was dried in an inert atmosphere at a temperature of 80 °C to constant weight.

The content of PANI in the composite and its output from the theoretically possible was determined by the increase in the mass of the MC after the modification. Raman spectra of the samples were recorded using a DXR Raman Microscope instrument (Thermo Scientific, USA) at an excitation laser wavelength of 633 nm.

The specific electrical conductivity of the samples was also determined, and comparative electrochemical studies were carried in a standard three-electrode cell out in aqueous (3M H₂SO₄) and organic (1M tetraethylammonium tetrafluoroborate solution in acetonitrile) electrolyte solutions.

3. Results and discussion
The effect of the pH of the reaction mixture and the concentration of carbon material on the patterns of the oxidative polymerization of aniline on the surface of the MC was studied. The experimental data were used to plot the temperature (t) changing during the process (Figure 1). They turned out to be similar to dependences obtained earlier in the modification of carbon nanotubes with polyaniline [11,12].

![Figure 1. Temperature profiles of the reaction of oxidative polymerization of aniline in the presence of MC at initial pH = 1 (1) and initial pH = 3 (2). The content of PANI in the composite is: 75 wt.% (a), 50 wt.% (b).](image-url)
Table 1 shows the PANI yield during the oxidative polymerization of aniline. The initial conditions of the reaction ambiguously affect the yield of the target product ($\eta$). During the synthesis of polyaniline without a dispersed template, the yield of PANI decreases with decreasing pH. The introduction of mesoporous carbon into the reaction mixture promotes an increase in $\eta$. However, during the synthesis of the PANI composite (75 wt.%)/MC (25 wt.%)(pH = 3), PANI yield decreases by 6%.

**Table 1.** Characterization of the reactions of oxidative polymerization of aniline.

| Sample                  | pH (initial) | $t_{\text{max}}$, °C | PANI yield ($\eta$), % |
|-------------------------|--------------|-----------------------|------------------------|
| PANI                    | 1            | 29.5                  | 78.3                   |
|                         | 3            | 29.3                  | 86.6                   |
| PANI (75 wt.%)/MC (25 wt.%) | 1            | 26.3                  | 98.6                   |
|                         | 3            | 25.6                  | 80                     |
| PANI (50 wt.%)/MC (50 wt.%) | 1            | 27.1                  | 88                     |
|                         | 3            | 26.3                  | 99                     |

The Raman spectra of PANI and its composites with MC contain peaks at 1490 cm$^{-1}$ ($\text{C} = \text{N}$ stretching vibrations in quinoid ring) [13], 1389 cm$^{-1}$ ($\text{C} - \text{N}^+$ ring-stretching vibrations of N-phenylphenazine units) [14], 1161 cm$^{-1}$ ($\text{C}-\text{H}$ bending vibration of the semiquinonoid rings) [13], characteristic of the emeraldine salt of PANI (Figure 2). These peaks are particularly intense in the spectra of pure polyaniline and composites PANI (75 wt.%)/MC (25 wt.%)(Spectra 1-4, Figure 2). Consequently, under the chosen conditions a conductive form of polyaniline is formed.

![Figure 2. Raman spectra of PANI (1, 2) and PANI / MC composites containing 75 (3, 4) and 50 (5, 6) wt.% of polyaniline. The initial pH is 1 (1, 3, 5) and 3 (2, 4, 6).](image)

The value of electrical resistivity ($\rho$) depends on both the mass content of PANI in the composite and the initial pH value (Table 2). Polyaniline synthesized without a dispersed template has the highest electrical resistivity ($\rho$). The conductivity of a PANI sample synthesized in a more acidic medium (at
pH = 1) is 1.5 times higher than that of the sample obtained at pH = 3. The combination of PANI with mesoporous carbon significantly reduces the electrical resistivity of the material. An increase in the electrical conductivity of the composite is promoted by synthesis in a more acidic medium and an increase in the content of MC. The fact that the substrates coated with conducting polymers have higher conductivity than the individual components can be explained by improved ordering of the polymer chains grown on substrates compared with random chain-aggregation produced in the absence of substrate [15].

Table 2. Electrical resistivity of PANI and PANI / MC composites.

| Sample                  | pH (initial) | Specific electrical resistance, ohm-cm |
|-------------------------|--------------|----------------------------------------|
| PANI                    | 1            | 29.74                                  |
|                         | 3            | 50.2                                   |
| PANI (75 wt.%)/MC (25 wt.%) | 1            | 7.6                                    |
|                         | 3            | 21.76                                  |
| PANI (50 wt.%)/MC (50 wt.%) | 1            | 1                                      |
|                         | 3            | 1.05                                   |

In the course of the study, the electrochemical properties of composites PANI (50 wt.%)/MC (50 wt.%) were studied. In Figure 3 shows cyclic current-voltage curves.

![Figure 3](image)

**Figure 3.** Cyclic current-voltage curves of the composite PANI (50 wt.%)/MC (50 wt.%): electrolyte is: 3M H₂SO₄ (a); 1M solution of tetraethylammonium tetrafluoroborate in acetonitrile (b).

The cyclic current-voltage curves (CCVC) in the aqueous electrolyte have pronounced peaks due to the Faraday process (Figure 3). The current values for CCVC in the aqueous electrolyte are much higher than in acetonitrile. This is due to the fact that in the latter case only the charge of the electric double layer occurs without an additional flow of the Faraday process.

On the basis of the obtained CCVC curves, the specific capacity (designation) by formula (1) was found using the method of integration in the Origin 8 Pro program:

\[
C_s = \frac{1}{m\nu(E_f - E_i)} \int_{E_i}^{E_f} I(E) dE
\]  

(1)
where \( m \) – electrode mass; \( \nu \) – potential sweep rate; \( E \) – electrode potential; \( I(E) \) – current strength on the current-voltage curve; \( E_i \) and \( E_f \) – integration limits on the current-voltage curve.

The results of the calculations are presented in Table 3. A decrease in the capacitance of the studied samples by 79.7% (in the aqueous electrolyte) and by 86.6% (in the organic electrolyte) is observed with an increase in the sweep rate to 100 mV/s. Capacity decreases due to increased kinetic difficulties during the course of the electrochemical reaction.

**Table 3.** Specific capacitances of the studied electrode in aqueous and organic electrolytes at different potential scan rate.

| Sample | Specific electrical capacitance \( C_s \), F/g at potential sweep rate \( \nu \), mV/s |
|--------|---------------------------------|
|        | 5     | 10    | 20    | 50    | 100   |
| 3M aqueous solution H\(_2\)SO\(_4\) | | | | | |
| PANI (50 wt.%) / MC (50 wt.%) | 299.6±4.8 | 281.6±7.9 | 256.6±16.7 | 146.8±32.3 | 60.9±16.9 |
| 1M solution of tetraethylammonium tetrafluoroborate in acetonitrile | 80.8±5.8 | 68.7±8.7 | 51.1±10.8 | 22.3±11.4 | 10.8±5.0 |

In Figure 4 shows the dependences obtained by the method of electrochemical impedance. Comparing the impedance hodographs in an aqueous and organic electrolyte, one can see that the studied electrodes in an organic electrolyte have a much greater resistance compared to an aqueous electrolyte, therefore the specific capacitance in an aqueous electrolyte is much higher.

**Figure 4.** Dependences obtained using alternating current tests in 3M H\(_2\)SO\(_4\) (a); in 1M tetraethylammonium tetrafluoroborate solution in acetonitrile (b).

### 4. Conclusion

The conditions of the oxidation polymerization of aniline in the presence of mesoporous carbon are slightly affected by the reaction conditions and the mass ratio of polymer and MC in the composite. However, these factors determine the electrically conductive properties of the samples. So the best electrically conductive properties have materials PANI (50 wt.%)/MC (50 wt.%) obtained at pH = 1. With a potential sweep rate of 5 mV/s in a 3M aqueous solution of sulfuric acid, this composite has a rather high specific electrical capacity (299 F/g).

On the basis of the experimental data obtained, it can be concluded that composites based on polyaniline and mesoporous carbon can be successfully used in the manufacture of supercapacitors based on aqueous electrolytes.
References
[1] Libich J, Máca J, Vondrák J, Čech O, Sedlaříková M 2018 Supercapacitors: Properties and applications. *J. of Energy Storage* 17 22
[2] Liu L, Niu Z, Chen J 2018 Flexible supercapacitors based on carbon nanotubes *Chinese Chemical Letters* 29 571 https://doi.org/10.1016/j.ccl.2018.01.013
[3] Ding B, Guo D, Wang Y, Wu X, Fan Z 2018 Porous carbon nanotube/graphene composites for high-performance supercapacitors. *J. of Power Sources* 398 113 https://doi.org/10.1016/j.jpowsour.2018.07.063
[4] Li J, Tang J, Yuan J, Zhang K 2018 Porous carbon nanotube/graphene composites for high-performance supercapacitors. *Chemical Physics Letters* 693 60 https://doi.org/10.1016/j.cplett.2017.12.052
[5] Li Z, Jiao X, Li C, Chen D 2018 Synthesis and application of nanocages in supercapacitors. *Chemical Eng. J.* 351 135 https://doi.org/10.1016/j.cej.2018.06.108
[6] Liu J 2018 A high performance all-solid-state flexible supercapacitor based on carbon nanotube fiber/carbon nanotubes/polyaniline with a double core-sheathed structure. *Electrochimica Acta* 283 366 https://doi.org/10.1016/j.electacta.2018.06.158
[7] Aydinli A, Yuksel R, Unalan H E 2018 Vertically aligned carbon nanotube – Polyaniline nanocomposite supercapacitor electrodes. *Int. J. of Hydrogen Energy* 43 18617 https://doi.org/10.1016/j.ijhydene.2018.05.126
[8] Zhang L, Huang D, Hu N, Yang C, Li M, Wei H, Yang Z, Su Y, Zhang Y 2017 Three-dimensional structures of graphene/polyaniline hybrid films constructed by steamed water for high-performance supercapacitors. *J. Power Sources* 342 1 https://doi.org/10.1016/j.jpowsour.2016.11.068
[9] Zhao W 2017 Design and fabrication of flexible supercapacitor devices by using mesoporous carbon/polyaniline. *Surface and Coatings Technology* 320 595 https://doi.org/10.1016/j.surfcoat.2016.10.075
[10] Zhang X, Lin Q, Zhang X, Peng K 2018 A novel 3D conductive network-based polyaniline/graphitic mesoporous carbon composite electrode with excellent electrochemical performance. *J. of Power Sources* 401 278 https://doi.org/10.1016/j.jpowsour.2018.08.091
[11] Dyachkova T P, Anosova I V, Tkachev A G et al. 2018 Synthesis of Composites from Functionalized Carbon Nanotubes and Polyaniline. *Inorg. Mater. Appl. Res.* 9 305 https://doi.org/10.1134/S2075113318020089
[12] Stejskal J, Sapurina I, Trchová M 2010 Polyaniline nanostructures and the role of aniline oligomers in their formation. *Progress in Polymer Science* 35 1420 https://doi.org/10.1016/j.progpolymsci.2010.07.006
[13] Šeděnková I, Trchová M, Stejskal J 2008 Thermal degradation of polyaniline films prepared in solutions of strong and weak acids and in water – FTIR and Raman spectroscopic studies. *Polymer Degradation and Stability* 93 2147 https://doi.org/10.1016/j.polymdegradstab.2008.08.007
[14] Čirić-Marjanović G, Trchová M, Stejskal J 2008 The chemical oxidative polymerization of aniline in water: Raman spectroscopy. *J. of Raman Spectroscopy* 39 1375
[15] Stejskala J, Acharya U, Bober P 2019 Surface modification of tungsten disulfide with polypyrrole for enhancement of the conductivity and its impact on hydrogen evolution reaction. *Applied Surface Science* 492 497 https://doi.org/10.1016/j.apsusc.2019.06.175