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FLEXIBLE POLYANILINE COATED CARBON CLOTH AS BINDER - FREE ELECTRODE MATERIAL FOR SYMMETRIC SUPERCAPACITOR APPLICATION

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Abstract. Nano-structured polyaniline (PANI) containing composite electrodes based on Busofit T-040 carbon cloth (CC) with high specific surface area have been developed for symmetric supercapaitor devices by one-step chemical polymerization of aniline. The capacitive performance of the CC as well as the PANI/CC composites was characterized by the cyclic voltammetry (CV) and the galvanostatic charge-discharge in H_2SO_4-based aqueous electrolyte. A PANI/CC composite demonstrates significant capacitance enhancement up to 222 F g^{-1} and 6.7 F cm^{-2} (vs. 120 F g^{-1} and 3,1 F cm^{-2} for CC). The coulomb efficiency of the composites has been measured to be about 97–99 %. The technological simplicity, easy to scale up and the electrochemical performance of the flexible binder-free PANI/CC electrodes demonstrate the significance of this work for industrial application.

1. Introduction

In view of the current energy scenario and a pursuit of alternative energy sources, the supercapaitors (SCs) with excellent power density and superior cycling durability has positioned itself as the smartest choice for clean and efficient back up power sources and energy storage devices. The specific capacity of SC per unit volume is 20-200 times higher than one of conventional capacitors and batteries [1]. Accumulation and storage of charge in electrochemical capacitors occurs in the electric double layer emerging at the interface of the electrode and electrolyte. So electrode materials for SC must meet a row of criteria, including high electrical conductivity, a developed surface area, availability of a porous structure for electrolyte ions and molecules, a low density, etc. Porous carbon materials, such as activated carbons, carbon fibers and felts, aerogels and so on meet almost all of these criteria [2,3].

To increase the capacitance characteristics and specific energy of SC substances capable of reversible redox transitioning in a potential range of work SC are used in electrode materials which leads to development of so-called pseudocapacity. For this purpose, oxides of transition metals [4,5] as well as conducting polymers (polyaniline, polypyrrole, polythiophene) are used. Among conducting polymers PANI is considered the most promising material for supercapacitor applications due to the fast oxidation-reduction reaction, synthesis simplicity and low cost [6-9]. However, the application of PANI in commercial devices is limited because of deficient chemical reversibility and stability of charge/discharge cycles. A possible solution of this problem can be development of composites which include thin PANI layers deposited on a conductive substrate, such as nanostructured carbon materials - nanotubes, graphene and

various combinations thereof [10-14]. The resulting composites have high capacitance and efficiency, but its application is limited because of the considerable cost.

Carbon fiber materials - fabrics and felts – are used as a conductive substrate less often, despite the fact that they do not require a polymer binder and provide ease of technology [15-19]. In most cases, carbon fibers that do not have their own porosity and capacity are used as the substrate.

The aim of this work was to develop PANI containing composites based on commercially available carbon cloth with high porosity and large surface area and to study the electrochemical behavior of prepared composites. In this case, we can expect an increase in resulting capacitance characteristics of composites due to a combination of the capacity of the CC electrical double layer and pseudocapacity of PANI.

2. Experimental method

For preparation PANI-containing composite carbon fiber cloth Busofit T-040 with thickness 0.37 mm produced by "SvetlogorskKhimvolokno", Belarus was used.

The PANI/CC composites were prepared using chemical oxidation polymerization of aniline in the presence of carbon cloth. Aqueous solutions of aniline (Labtech, Russia) and ammonium persulfate (APS, Merck) with concentrations 0.2 M in 1M HCl were used. The CC samples were soaked into the aniline solution for 0.5 h to complete adsorption of aniline monomer. Then an equal volume of APS solution was added drop wise for 15 min and the mixture was kept without stirring for 2 h to complete the reaction. Finally, the composites were washed with distilled water and acetone and dried in air at the room temperature.

The weight fraction of PANI was estimated in accordance with Eq. 1

$$W_{PANI} = \frac{m_1 - m_0}{m_1}, \quad (1)$$

where m_0 is the weight of CC (g); m_1 is the weight of PANI/CC composite (g).

Scanning electron microscopy (SEM) was performed using JSM-6700F instrument (JEOL, USA). Specific surface area was determined by low-temperature nitrogen adsorption in dynamic mode, using the QSurf Series device (Thermo Fisher Scientific Corporation, USA).

To prepare the working electrodes, the CC and the PANI/CC samples were cut into circular dishes of 25.2 mm diameter. Using these working electrodes, symmetric supercapacitor devices were fabricated, where a 25 μm thick polypropylene mono-layer membrane (Celgard, USA) was used as a separator and 3M H_2SO_4 as electrolyte. The electrochemical performance of the CC and the PANI/CC composites were evaluated by cyclic voltammetry (CV) and the galvanostatic charge/discharge technique using a potentiostat-galvanostat Elins P30S (LLC "Elins", Russia). The capacitance values were calculated by the results of galvanostatic discharge according to Eq. 2:

$$C = \frac{I\Delta t}{\Delta U}, \quad (2)$$

where C is measured capacitance of the active materials (F); I – stands for discharging current (A); Δt is discharging time (s), represents the discharging potential range (V).

Weight- and area-normalized specific capacities Cm and Cs of the materials were calculated according to Eq. 3 and Eq. 4 [20]:

$$C_m = \frac{4C}{M}, \quad (3)$$

$$C_s = \frac{2C}{4.9cm^2}, \quad (4)$$

where M stands for mass of working electrode (g). For PANI/CC composites, mass of working electrodes were calculated based on mass of the cloths and mass of the deposited PANI.

The coulombic efficiency $\eta(Q)$ was calculated from Eqn. 5:

$$\eta_{(Q)} = \frac{Q_d}{Q_c} \times 100\%, \quad (5)$$

where Qd is a charge, returned in discharging by a capacitor, C; Qc is a charge, obtained in

charging to a capacitor, C.

The value of charges Qd and Qc were determined by numerical time integration of the effective values of the current, flowing through a cell at the discharging and the charging time respectively. Impedance spectroscopy measurements were carried out using two-electrode device with frequency range from 100 kHz to 0,1 Hz.

3. Results and discussion

Figure 1 illustrates typical SEM images of carbon fiber cloth Busofit T-040 at different magnifications. Carbon cloth consists of individual carbon fibers of 7-8 μm diameter which are sufficiently tightly packed but randomly oriented. Such porous structure of carbon fiber cloth is expected to facilitate the diffusion of electrolyte into an electrode material as well as to provide more channels for rapid ion transport. Open pores can be seen on the surface of carbon fibers with a visible pore size about 0.5 μm. It is important that CC has high own porosity and a high specific surface area - 900 m^2g^{-1}.

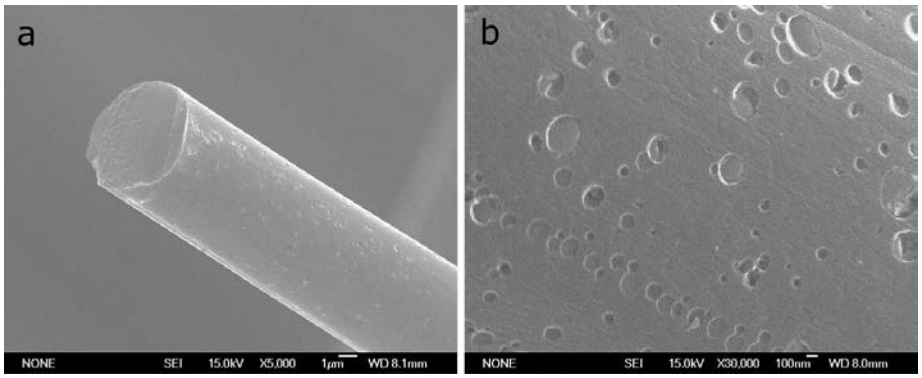


Fig. 1. SEM images of the carbon fiber cloth Busofit T-040 at the magnifications of 5000× (a) and 30000× (b).

The capacitive performance of CC was characterized by cyclic voltammetry (CV) (Fig. 2) and galvanostatic charge-discharge (Fig. 3) in the two-electrode configuration.

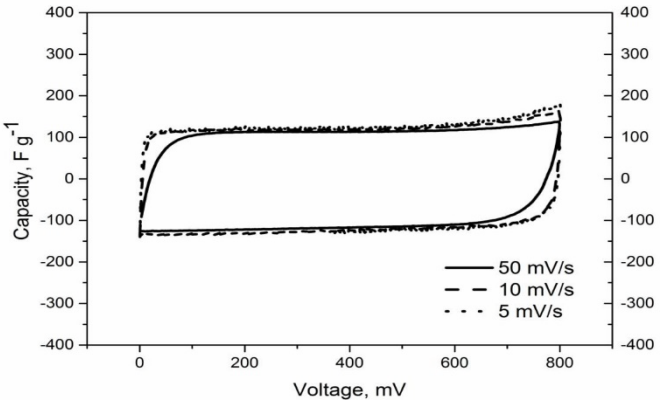


Fig. 2. CV curves of the carbon fiber cloth Busofit T-040 at the different potential sweep rate.

Due to the porous structure with the high specific surface area CC demonstrates good electrochemical performance.

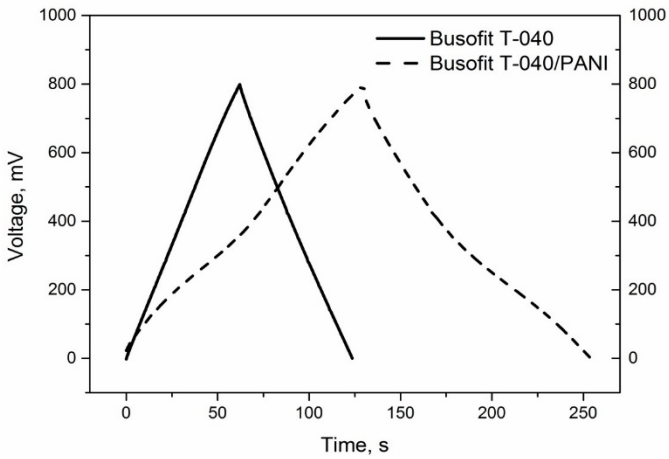
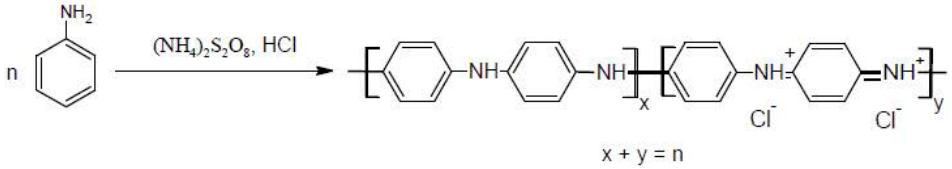


Fig. 3. Charge/discharge curves of carbon cloth Busofit T-040 and the PANI/CC composites in an operating voltage of 0.8 V at 25 mA/cm^2.

The rectangular shape of CV curves (Fig. 2) and the almost constant slope of the potential-time curves during galvanostatic charge/discharge (Fig. 3) demonstrates that the source CC have excellent electrochemical reversibility and capacitive characteristics which are needed for symmetric supercapacitor applications. The weight-normalized and the area-normalized specific capacitances of the CC are 120 F g^{-1} and 3.1 F cm^{-2} respectively.

To enhance electrochemical capacitance of electrode materials we prepared PANI-containing composites based on CC using the one-step chemical method with APS as oxidizer in hydrochloric aid media:



The weight fraction of PANI in the prepared PANI/CC composites was 25 %.

From SEM (Fig. 4) observations it was found that the composites have an unusual morphology: PANI forms individual granules on the carbon fiber surface whose diameter is about 30-50 nm. PANI granules located predominately near the walls of CC pores and some part of the CC surface remains uncovered.

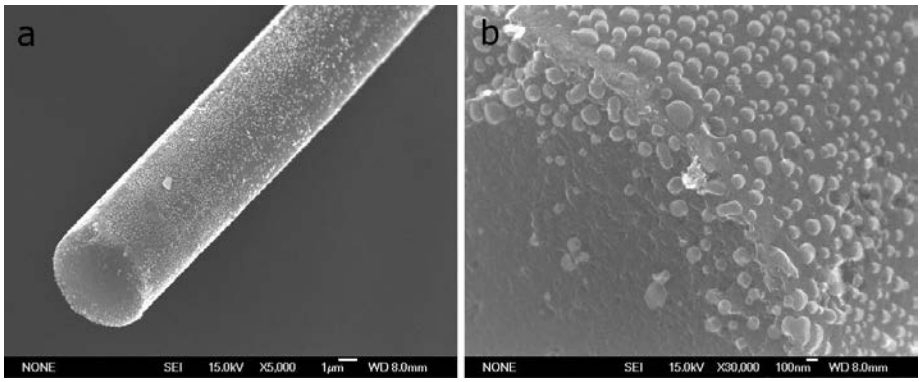


Fig. 4. SEM images of the PANI/CC composites with weight fraction of PANI 25 % at the magnifications of 5000× (a) and 30000× (b).

The galvanostatic charge/discharge curves of the PANI/CC composites (Fig. 3) reveals high specific capacity. In order to explore the capacitive properties of PANI/CC composites,

cyclic voltammetry was carried out at the different scan rates in the potential range of 0-0.8 V (Fig. 5).

The increase in CV current for PANI/CC composites in compare to CC (Fig. 2), indicates an increase in capacitance value. The distinct shape of CV curve and the enhancement in capacitance value PANI the redox conversion of leucoemeraldine/emeraldine and faradic transformation of emeraldine/pernigraniline is associated, as evidenced by many previous publications [12-16].

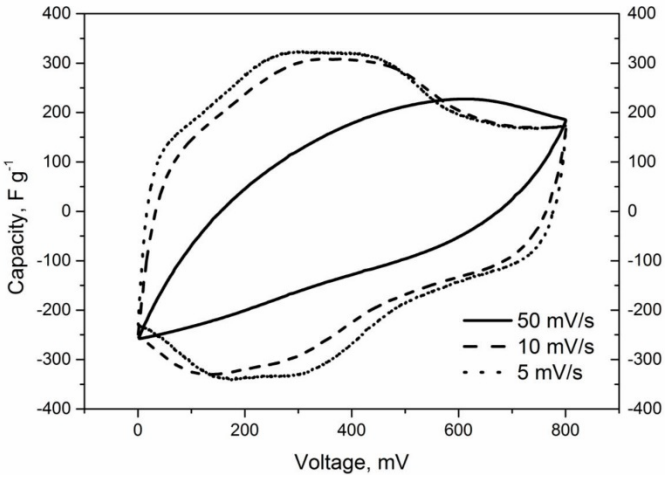


Fig. 5. CV curves of the PANI/CC composites at the different potential sweep rate.

So, the resulting composites show approximately twofold increase in the area-normalized capacity in comparison with the source carbon materials. A CC/PANI composite has the area-normalized specific capacity as high as 6.7 F cm^{-2} and weight-normalized specific capacitance as 222 F g^{-1}. Furthermore, the CC/PANI composite with weight fraction of PANI 25 % retains coulombic efficiency as high as 96-99 %.

Figure 6 is the Nyquist plot of impedance for CC and PANI/CC composite.

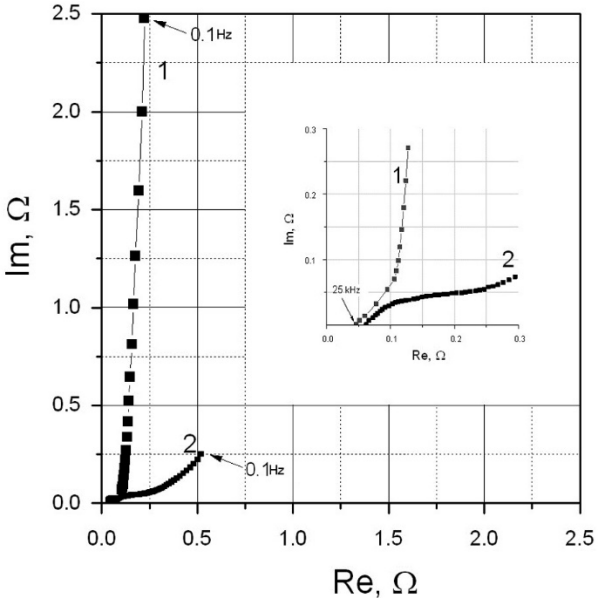


Fig. 6. Nyquist plots for carbon cloth Busofit T-040 (1) and the PANI/CC composites (2) at a frequency range from 100 kHz to 0,1 Hz at potential 0 V.

In the all range of frequencies the actual resistance of the PANI/CC composite is higher than that of the unmodified CC, which is associated with PANI pseudocapacitive

processes. It is evident that the capacity of the composite even in the medium frequency is much higher than the capacity of the carbon cloth, which indicates a high degree of reversibility of PANI pseudocapacity. Such excellent performance is attributed to unusual morphology of PANI/CC composite, when some part of the CC surface remains uncovered, which not only provides pseudocapacitance with high rate capability, but also retains the double-layer capacitance of the underlying CC.

The self-discharge characteristics of a supercapacitor device are important in evaluating its performance and commercial specifications. We charged the CC and PANI/CC capacitors to 0.8 V and then left on open circuit for 25 000 s. We can see that coating of the CC by PANI leads to a significant reduction in self-discharge rate (Fig. 7). Therefore, a PANI/CC composite with a 25 wt.% of PANI possesses the optimal ratio of capacity characteristics and efficiency.

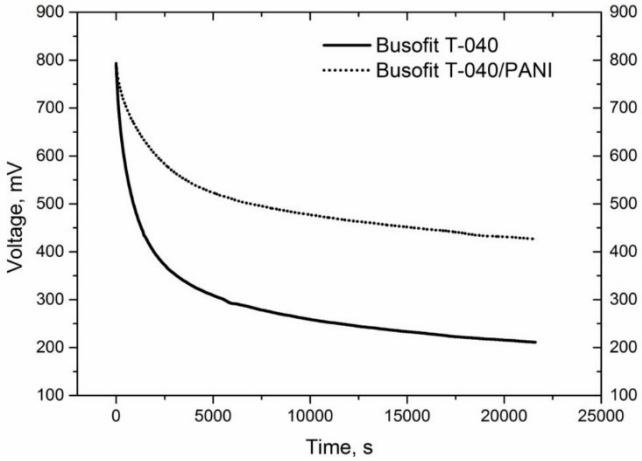


Fig. 7. Self-discharge of the carbon cloth Busofit T-040 and the PANI/CC composites.

4. Conclusions

Nano-structured polyaniline (PANI) containing composite electrodes based on Busofit T-040 carbon cloth with high specific surface area have been prepared by cost effective one-step chemical polymerization of aniline. It has been shown that the PANI/CC composite has both high weight-normalized and area-normalized specific capacitance, which makes them the most promising for practical application. The coulombic efficiency of composites is as high as 97-99 %. Such excellent performance is attributed to an unusual morphology of PANI/CC composite, when some part of the CC surface remains uncovered, which not only provides pseudocapacitance with high rate capability, but also retains the double-layer capacitance of the underlying CC. This encouraging result demonstrates the importance of developed PANI/CC composites as binder free and flexible electrode materials for high-energy symmetric supercapacitor.

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