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Carbon Nanofibers Fabricated from Electrospun Nano-sized Boron oxide/Polyacrylonitrile Nanofibers as Electrode for Supercapacitors

Ümran KURTAN*[1]

Abstract

Porous carbon nanofiber (CNF) composites are promising electrode materials for supercapacitor (SC) applications. In this research, to investigate the effect of nano-sized boron oxide (B_2O_3) to CNF, PAN solutions introduced with nano-sized boron oxide (B_2O_3) were electrospun then thermal treatment was applied at high temperature. The best electrochemical performance was found for the sample which was doped 1 wt% nano-sized boron oxide and a gradual decrease was seen when the content was increased from 1 to 5 wt%. 1BCNF electrodes prepared from 1 wt% nano-sized boron oxide with PAN show a remarkable specific capacitance of 146 Fg^{-1} at 1Ag^{-1} compared to the pure CNF which is 46 Fg^{-1}. Also, 1BCNF composite has an excellent cycle life which is more than 90 % capacity retention after 6500 cycles. The results showed that 1BCNF composite is a promising potential electrode for supercapacitor applications due to the optimized pore structure and enhanced electrical conductivity.

Keywords: Electrospinning, nano-sized boron oxide, carbon nanofiber, supercapacitors.

1. INTRODUCTION

Supercapacitors are the subject of intense research in energy storage sector due to their high power density, rapid charge-discharge and superior cycle stability [1-4]. A supercapacitor (SC) has the electrical charge capacitance up to hundreds of times compared to the conventional capacitors and it stores energy electrostatically by charge accumulation at the electrode-electrolyte interface. As the key part of SCs, active electrode material is critical for high performance. To date, conductive polymers, transition metal compounds and carbon-based materials have received extensive attention as electrode materials. Carbon based nanomaterials such as activated carbon, graphene, carbon nanotube and carbon nanofibers (CNFs) are commonly used as electrode materials for supercapacitor applications [5–7]. Graphene and CNTs are extensively investigated by the researchers but their close packing, entanglement and agglomeration problems can inhibit the practical applications in energy storage [8-11]. With respect to these considerations, carbon nanofibers with exceptional one dimensional (1D) nanostructure can have many inherent advantages for an electrode of a supercapacitor such as small number of defects low cost, excellent conductivity, ultrahigh power density and compact structure to construct flexible devices compared to graphene and CNTs [12]. On the other hand, pure CNFs still have disadvantages such as low hydrophilicity and low energy density

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thus it is still needed to be improved to enhance the properties of CNFs. Fortunately, modification the surface of CNFs such as heteroatom doping or surface activation is an alternative way to eliminate these disadvantages. Recently, heteroatoms doping is generally focused on to enhance the electrochemical properties and hydrophilicity of the carbon materials [6-8]. This study discusses design, fabrication and application of nano-sized B_2O_3 loaded PAN nanofibers followed by carbonization for supercapacitor applications. The energy storage efficiency can be altered for the optimization of the electrochemical performance.

1. EXPERIMENTAL

1.1. Chemicals

Polyacrylonitrile (PAN), which has a molecular weight of 150,000 $gmol^{-1}$) and N,N-Dimethylformamide (DMF) were supplied from Sigma-Aldrich; boron oxide (B_2O_3) nanoparticles from SSNano, USA.

1.2. Fabrication of CNF composite electrodes

Firstly, 8 wt% of PAN polymer was dissolved in DMF by stirring. After, nano-sized boron oxide powder (1 and 5 wt% relative to PAN) were added into polymer solution and mixed together overnight at 50°C to obtain a uniform solution. The precursor solutions were electrospun with a 10-ml plastic syringe at an electrostatic voltage of 18 kV and the rate was 1 mlh^{-1}. Polymeric fibers were placed into a tube furnace and then stabilization was performed at 250 °C (5 $°Cmin^{-1}$) for 2h. After, carbonization was carried out by heating to 800 °C (2 $°Cmin^{-1}$) for 2 h under N_2 flow to obtain CNFs. The activated samples, denoted as 1BCNF and 5BCNF, indicate concentrations of 1 and 5% nano-sized B_2O_3 relative to PAN, respectively. Pure CNF without nano-sized B_2O_3 was also prepared as shown in Figure 1.

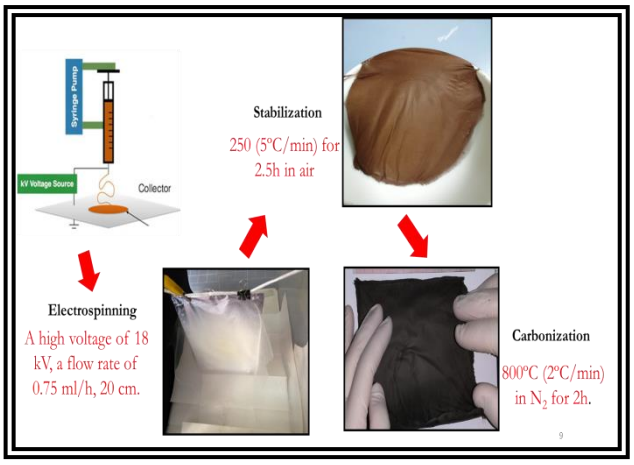

Figure 1 Schematic diagram of carbon nanofiber (CNF) formation.

1.3. Characterization

Fourier Transform Infrared (FTIR, Bruker) spectra of the nanofibers were taken by using a Bruker FTIR-ATR spectrometer in the range from 4000 to 400 cm^{-1}. The morphology of the carbonized fiber samples were observed by scanning electron microscope (JEOL JSM-7001F SEM). Electrochemical performance was evaluated with a two-electrode system. For this, the self-supported CNF electrodes were firstly cut into two pellet discs of 10 mm in diameter and sandwiched a Whatman glass fiber separator in a coin cell (CR2032). The electrolyte was 6M KOH solution. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a Gamry potensiostat-galvanostat-ZRA Interface 1010B. The EIS test was performed with frequency rate from 20 kHz to 0.1Hz. Galvanic charge-discharge (GCD) measurements of the full cells were carried out using a battery test system (MTI).

In two-electrode model, the specific capacitance (Csp, Fg^{-1}) could be estimated from GCD tests using the below formula [9-10]:

$$Csp = (2 \times I \times \Delta t) / (m \times \Delta U) \quad (1)$$

where I is the constant current in GCD, t is the discharge time, ΔU is the potential window and m is the mass of single electrode. Specific energy (E, $Whkg^{-1}$) and specific power (P, Wkg^{-1}) are calculated according to the following equations.

$$E = \frac{1}{3.6} \times \frac{1}{8} \times Csp \times \Delta U^2 \qquad (2)$$

$$P = \frac{3600E}{\Delta t} \qquad (3)$$

2. RESULTS AND DISCUSSION

Chemical characteristics of all CNFs are firstly investigated by FT-IR spectra and shown in Figure 2. Two main absorption peaks at ~1100 and 1556 cm^{-1} are observed due to the stretching band of C-C and C=C bonds, respectively. This implies that cyclization of nitrile groups of PAN takes place during stabilization and carbonization process. This phenomenon is similar to the previously reported articles in literature [18-19]. A new peak is appeared in the FT-IR spectrum of both 1BCNF and 5BCNF composites at around 800 cm^{-1} which is related to the activity of (O)BN functional groups. These results are evidence that CNF composites are synthesized successfully.

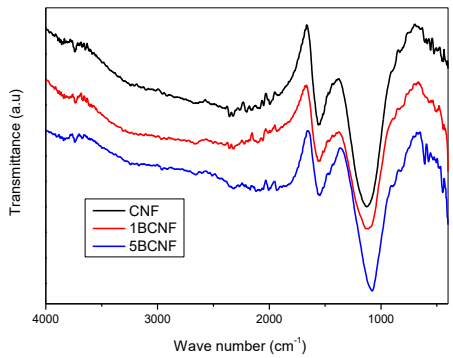

Figure 2 FT-IR spectra of pure CNF, 1BCNF and 5BCNF.

Exemplary SEM micrographs showing typical fiber morphologies are presented in Fig. 3a-c. The SEM images of the all CNFs display long and continuous interconnected morphologies. Fig. 3a shows the images of neat PAN-based CNFs which are a unique hierarchical porous network structure. When the nano-sized boron oxide amount is 1 wt%, more macropores are formed within the nanofibers, leading to a decrease in fiber diameter without any collapsing the fibrous morphology (Fig. 3b). But, when the nanosized boron oxide amount increases from 1 to 5 wt%, the fiber diameter decreases and shows a curved morphology (Fig. 3c). From these results, we can hypothesize that the porosity is strongly dependent on the amount of added material and the nano-sized boron oxide can effectively create suitable pores during thermal treatment [19-20].

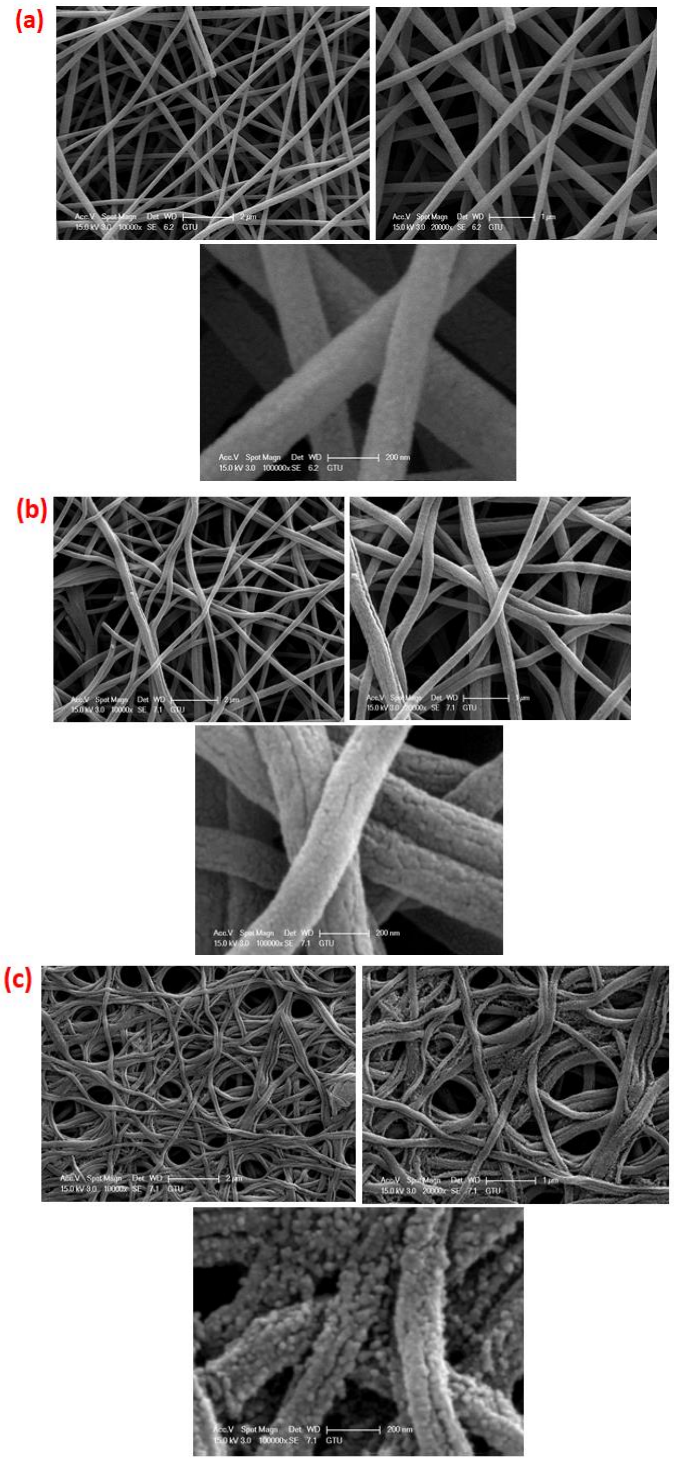

Figure 3 SEM images of (a) pure CNF, (b) 1BCNF and (c) 5BCNF.

2.1. Electrochemical Measurements

The electrochemical activities of the prepared electrodes were firstly investigated by CV analysis. Fig. 4 illustrates the CV plots of pure CNF, 1BCNF and 5BCNF with the potential window of 0-1V and ranging a scan rate of 10, 25, 50, 75, 100 and 200 mVs^{-1} obtained by two-electrode cell measurement. The rectangular shape of CV curves was observed for 1BCNF and 5BCNF, which suggests a potential capacitive behavior comparing to pure CNF. High scan rates caused to decrease in specific capacitance since electrolyte cannot access the full surface of electrode [22, 23]. Notably, the shape of the CV graphs of 1BCNF are well maintained even at the scan rate of 200 mVs^{-1}, indicating the good rate ability among all CNFs. 1BCNF electrode has highest current density which indicates a large increase in capacitance. These results indicate that 1BCNF electrode shows a typical SC behavior.

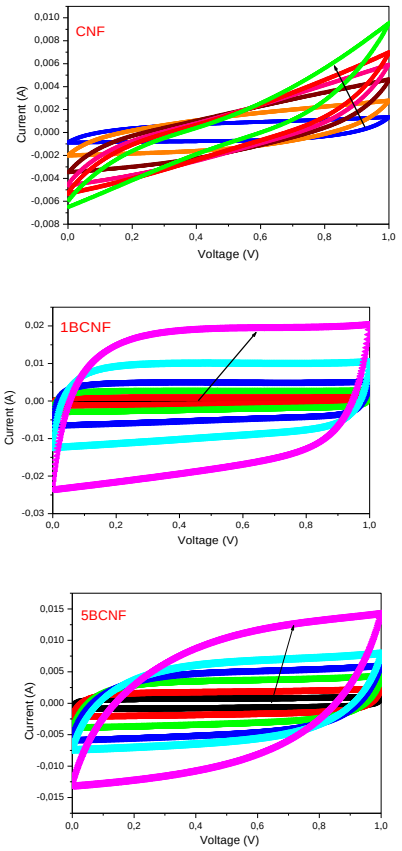

Figure 4 CV of CNF, 1BCNF and 5BCNF at different scan rates. The arrows mean the trend in CV with the increasing scan rates (from 10 to 200 mVs^{-1}).

Figure 5a-c shows GCD curves of CNF, 1BCNF and 5BCNF at a current density of 0.5-5 Ag^{-1}. It was noticed that there is a common trend in specific capacitance while current density increases, the specific decreases. Compared to the pure CNF, there is a big increase in the discharging time meaning that the introduction of nano-sized boron oxide enhances the electron mobility between carbon nanofibers. The discharge time is the longest for 1BCNF thus the highest specific capacitance it has. The lines are almost linear and symmetrical. It should be also noted that there is an IR drop in pure CNF electrodes but there is no such IR drop observed for 1BCNF and 5BCNF. This difference is due to the electrode microstructure.

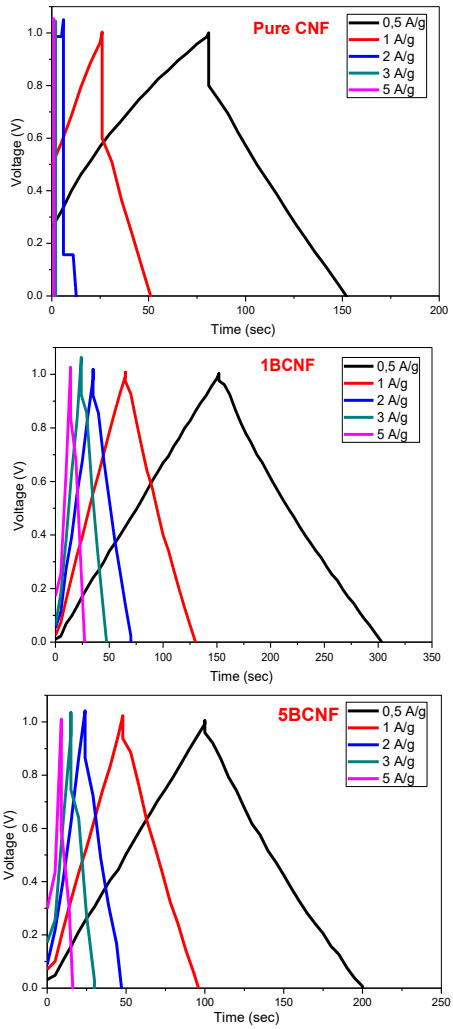

Figure 5 GCDs curves of SCs using CNF, 1BCNF and 5BCNF in 6M KOH electrolyte at different current densities.

The CV graphs of CNF based SC devices acquired at 50 mVs^{-1} scan rate are presented in Fig. 6a. Nano-sized boron oxide added nanofibers, 1BCNF and 5BCNF, show a larger rectangle shape compared to the pure CNF, which means the expansion of the electrical double-layer area implying an ideal capacitive behavior. Specifically, 1BCNF has the largest integral area among all CNFs. This is ascribed to rapid diffusion of electrolyte within the electrode, 1BCNF, and the quick charge-discharge cycles.

Figure 6b shows specific capacitance values obtained at various current densities (0.5 to $5Ag^{-1}$). Among them, SC cell assembled with 1BCNF electrode showed the best specific capacitance. The specific capacitance value of 1BCNF was found as 150 Fg^{-1} for at $0.5Ag^{-1}$ and it still maintained by 86.7 % at $5Ag^{-1}$, providing an exceptional retention ability.

Fig. 6c indicates that the specific capacitances of CNF, 1BCNF and 5BCNF at 1 Ag^{-1} are 46, 146 and 96 Fg^{-1}, respectively (Table 1). The gravimetric specific capacitance value of 1BCNF is enhanced by a factor of about 3 compared to pure CNF which are comparable reported in the literature [14, 24, 25]. As expected from the results of the CV and GCD measurements, the specific capacitance increased as follows: CNF < 5BCNF < 1BCNF suggesting that lower amount of nano-sized boron oxide addition may provide fast ion channels and ion mobility.

Table 1 Gravimetric electrochemical performance of symmetric electrodes in 6M KOH electrolytes.

	Specific Capacitance of the Electrode (F/g)		Energy and Power Density for the device		
Sample	CV at 50mV/s	GCD at 1A/g	EIS (ohm) 0.1Hz to 1MHz	E(Wh/kg)	P(W/kg)
CNF	47	46	38	1.6	250
1BCNF	120	146	2.9	5.1	252
5BCNF	91	96	9.4	3.3	248

In order to better understand the electrochemical performance of the studied samples, EIS was employed. Fig. 6d presents the Nyquist plots for the studied electrodes. All impedance spectra of CNF, 1BCNF and 5BCNF showed almost similar behavior, presenting a half semicircle at high frequencies and a straight line at low frequencies. SC from pure CNF exhibited a highest semicircle indicating a poor capacitive performance. For the device made of 1BCNF electrodes, the semicircle decreased clearly, suggesting the lower charge transfer resistance. In the presence of more nano-sized boron oxide addition, it is better than pure CNF but worse than 1BCNF, which is consistent with the little IR drop of the discharge curve. Based on these results, it is worth mentioning that the small amount of nano-size boron oxide doped interconnected carbon network can provide a continuous conducting paths for electron transfer as well as excellent structural stability during electrochemical process.

The specific energy (E) and specific power (P) are important parameters that characterize the performance of supercapacitors. Fig. 6e is a Ragone plot, which correlates the energy density and the power density of all supercapacitor. A symmetric SC based on the CNFs is compatible with the discharging time observed in GCD curves, where a longer discharging time indicates a better specific energy value. As expected, 1BCNF symmetric SC delivers a maximum specific energy of 5.2 $Whkg^{-1}$ at a specific power of 125 Wkg^{-1}, and a maximum specific power of 1245 Wkg^{-1} at a specific energy of 4.5 $Whkg^{-1}$. 5BCNF possessed the specific energy of 3.5-2.8 $Whkg^{-1}$ while pure CNF exhibited a dramatical decrease in specific energy (2.5 $Whkg^{-1}$) in the similar range of specific power range. These are close and even better values reported in previous studies [1, 26].

The long-term cycle stability test is a crucial factor in SC application. In this study, SC stability was evaluated by repeating the GCD measurements for 6500 cycles at a fixed current density of 1 Ag^{-1}. The results are shown in Figure. 6f. The lowest capacitance retention is seen for pure CNF which can be explained by decomposition of electrode during charge/discharge process. On the other hand, 1BCNF shows a good cycling stability with a capacitance loss of 9.4 % after 6500 cycles. It confirms that its porous structure can offer more

channels for the electrolyte ions. Also, high porosity can easily relieve the internal stress during charging and discharging process, protecting the electrode from physical damage. Thus, the more fibrous an electrode, the better cycle stability is [6].

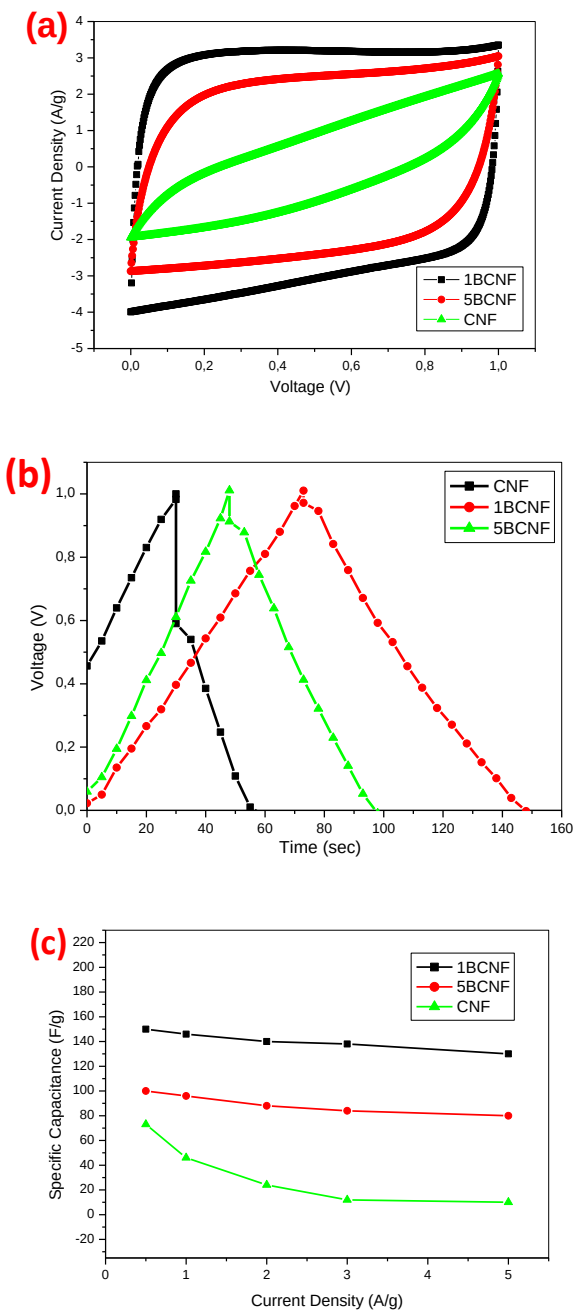

Figure 6 Electrochemical performance of CNF, 1BCNF and 5BCNF based SC cell of (a) CV plots at 50 mVs^{-1}, (b) galvanic charge/discharge graphs at 1 Ag^{-1}, (c) specific capacitance for various current densities, (d) Nyquist plots, (e) cycling performance test for 1 Ag^{-1}, (f) Ragone plot.

In order to investigate the electrochemical stability of the as-fabricated supercapacitor, the device was cycled for 6500 cycles as depicted in Fig. 7a and 7b. Fig. 7a shows the Nyquist plots

obtained by EIS for the device composed of 1BCNF electrode. As can be seen, the semicircular diameter increased slightly after 6500 cycles which may be caused by the inferior ionic conductivity and ion diffusion rate. Fig. 7b shows the cycling stability of 1BCNF acquired by CV at 200 mVs^{-1}. Excitingly, CV plot did not change significantly and almost overlapped even after 6500 cycles, indicating the capacitance showed a low degradation and superior cycling reversibility. Thus, the cycle stability result reveals that 1BCNF is a suitable electrode for long term stability SC.

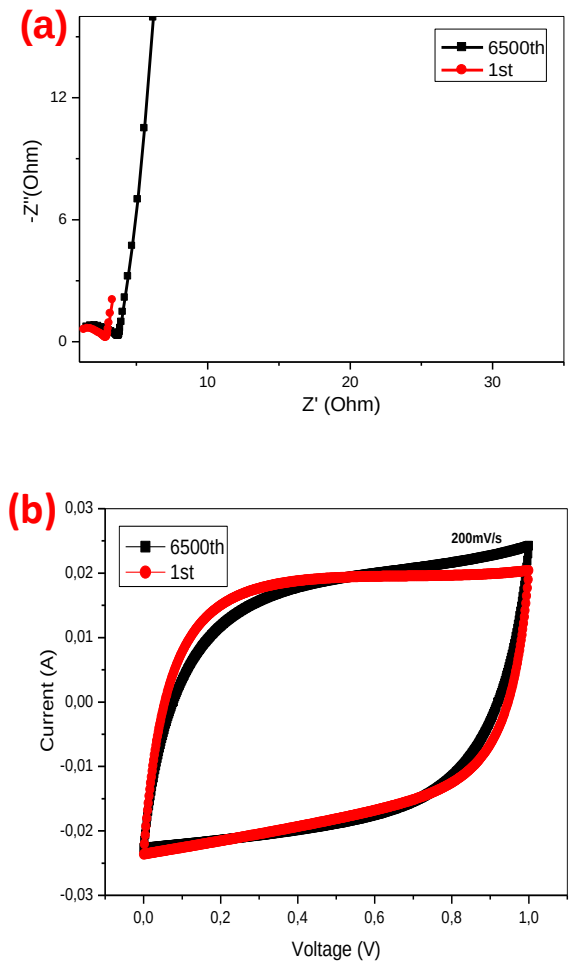

Figure 7 Electrochemical cycling stability test of symmetrical SC cells fabricated with identical 1BCNF electrodes before and after 6500 cycles, (a) EIS plots and (b) CV at 200mVs^{-1}

3. CONCLUSION

In summary, starting from electrospun PAN/nano-sized boron oxide composites, 1BCNF and 5BCNF were fabricated via oxidation and carbonization. CV and GCD results proved that 1BCNF electrode has the best electrochemical performance with respect to specific capacitance and energy density thus the optimum weight percentage of nanoparticles in PAN polymer was found to be 1. Additionally, 1BCNF supercapacitor exhibited an exceptional long cycle lives for at least 6500 charge/discharge cycles. It is expected to be a promising electrode material for application of energy storage.

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The Declaration of Conflict of Interest/ Common Interest

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this paper.

The Declaration of Ethics Committee Approval

This paper does not require any ethics committee permission or special permission

The Declaration of Research and Publication Ethics

This paper has been prepared within the scope of international research and publication ethics. In addition, I declare that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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