Contents lists available at ScienceDirect

# Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

# Influence of boron content on the structure and capacitive properties of electrospun polyacrylonitrile/pitch-based carbon nanofiber composites

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ABSTRACT

Electrospun boron-enriched PAN/pitch-based CNF composites (PPB) are developed by combining $B_2O_3$ as the boron source, and pitch and polyacrylonitrile as the carbon precursor, to introduce surface boron heteroatoms and enhance the electrical conductivity in CNF composites. PPB-10 electrodes prepared from 10 wt% $B_2O_3$ added to the PAN/pitch solution exhibit a high specific capacitance of 180 $Fg^{-1}$ at a discharge current density of 1 $mAcm^{-2}$ and energy density of 22.0–15.8 $Whkg^{-1}$ in the power density range of 400–10,000 $W\,kg^{-1}$ in 6 M KOH aqueous electrolyte, owing to the larger amount of heteroatoms such as boron and the addition of the pitch, thereby inducing fast and reversible surface redox reactions in aqueous electrolyte. Furthermore, the highly mesoporous PPB-10 composite offers 92% capacity retention of the initial current density and a low equivalent series resistance through quick pathways for ion transport and charge diffusion. Hence, these PPB composites exhibit a very promising potential as electrode materials for supercapacitor electrodes due to boron incorporated into the carbon framework, suitable porosity, and good electrical conductivity.

## 1. Introduction

Porous carbon nanofibers (CNFs) have attracted a great deal of attention in the development of electric double-layer capacitors for the application in consumer electronics and hybrid electric vehicles, due to their high specific surface areas and chemical stability. In general, porous CNFs have mainly exhibited double-layer capacitive behaviors which are an electrostatic attraction with charge accumulation at the porous carbon/electrolyte interfaces, leading to high power density and durability of electrochemical capacitors [1–6]. Even so, the surface chemistry, geometrical nanoarchitecture, and electronic structure of porous CNFs are urgent considerations for supercapacitor optimization by using functional groups, large surface areas, and well-developed mesoporosity to enhance the pseudocapacitive effects [7–17] because the charge-storage capacity and the specific energy density of pure CNFs are still low compared to those of batteries.

Therefore, this work focuses on the fabrication of boron-enriched polyacrylonitrile(PAN)/pitch-based CNF composites with high electrical conductivity, large specific surface area, and suitable pore structure with large mesopores. Especially, the added boron acts as the hydrophilic polar site and electron-acceptor on the surface of CNFs, and can thus introduce redox reactions related to ions chemisorption on CNF surface. In other words, the boron-enriched CNFs can improve the electric double-layer capacitance due to the pseudocapacitive effect

induced by the enhanced wettability of the interface between electrolyte and electrodes in aqueous electrolyte. Although the boron-enriched CNF materials offer enhanced accessibility of electrolyte ions, their rate capability and capacitive performance remain unsatisfying because of the large portion of micropores in the CNF surface. To overcome this problem, we used pitch as a CNF additive because of its high electrical conductivity, high carbon yield, and relatively low-cost fabrication compared with PAN [18–20]. Here, we develop a facile approach for preparing boron-enriched PAN/pitch-based CNF composites (PPB) by combining $B_2O_3$ as the boron source and pitch as the carbon precursor. The influences of porosity, wettability, and electric conductivity of the porous PPB on the electrochemical capacitance performance are discussed in this paper.

## 2. Experimental

### 2.1. Materials and fabrication

PAN, $B_2O_3$, petroleum pitch (*Hanwha Chemical Co.*, Korea), and dimethylformamide (DMF) were used for the fabrication of PPB composites. A solution of pitch in THF was added to PAN in DMF solution to achieve a PAN/pitch weight ratio of 70/30 wt%, after which a given amount of $B_2O_3$ (5 and 10 wt% to PAN and pitch combined) was added and the solution was vigorously stirred at 60 °C for 4 h to obtain a

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homogeneous solution for electrospinning. The PAN/pitch/$B_2O_3$ spinning solution was electrospun into nanofibers (NFs) by using an electrospinning machine (NTPS-35 K, NTSEE Co., Korea). The electrospun fiber web was stabilized in air at 280 °C for 1 h and then carbonized in $N_2$ atmosphere at 800 °C for 1 h at a heating rate 5 °C min$^{-1}$ using an electrical furnace. The three composite samples were denoted as PPB-0, PPB-5, and PPB-10, where the numbers represent the weight ratio of $B_2O_3$ to the combined PAN/pitch component. PB-10 without pitch was also prepared as a control sample to identify the effect of $B_2O_3$ and pitch on the structure and capacitive behavior.

### 2.2. Characterization

The surface morphologies of the three composites were examined using a scanning electron microscope (SEM; Hitachi, S-4700, Japan) equipped with an energy dispersive X-ray spectroscopy (EDX) detector. The microstructures were investigated by a transmission electron microscopy (TEM) instrument equipped with selected area electron diffraction (SAED) micrographs with a Tecnai-F20 system operated at 200 kV. The chemical state of the surface of the materials was examined by X-ray photoelectron spectroscopy (XPS) with a VG Scientific ESCALAB 250 spectrometer equipped with a monochromatized Al Kα X-ray source (15 mA, 14 kV). The specific surface area and the micropore size distribution of the samples were evaluated by using the Brunauer-Emmett-Teller (BET) theory and the micropore plot method. Pore volume fraction was calculated using the T-plot using carbon black with BET surface area of 109 m$^2$g$^{-1}$ as reference. The bulk electrical conductivity of the CNFs was measured using a four-point probe method at room temperature. The electrical conductivity, σ was calculated using:

$$\sigma = L/(wtR) \qquad (1)$$

where R is the electrical resistance of the web in Ω, w the sample width in cm, t the sample thickness in cm, and L the distance between the electrodes in cm. The water vapor adsorption/desorption isotherms were measured at 298 K using a constant volume adsorption apparatus (BELSORP-max, Bel Japan).

### 2.3. Cell fabrication and measurement

The electrochemical performances of the PPB-0, PPB-5, PPB-10, and PB-10 composite electrodes were investigated in two-electrode capacitors using a 6.0 M KOH aqueous electrolyte. Supercapacitor cells were built by assembling twin electrodes weighing 10.3 mg with rectangles (1.5 cm × 1.5 cm) and compressed into a Ni foam current collector without adding any conducting agent or polymer binder for electrochemical measurements. The weight of two electrodes of PPB was 0.0012 g in the fabrication of the symmetric supercapacitor. The capacitance of the electrodes was galvanostatically measured with a VSP multi potentiostat/galvanostat system in the potential range of −0.2 to 0.8 V and at a current density of 1–20 mAcm$^{-2}$. The unit cell was subjected to cyclic voltammetry (CV) testing in the potential range of −0.2 to 0.8 V at a scan rate of 10–100 mVs$^{-1}$. The ac impedance measurements were performed in the frequency range of 100 kHz–100 MHz using an electrochemical impedance analyzer (Jahner Electrik IM6, Germany).

## 3. Results and discussion

Fig. 1 shows FE-SEM images of the three composites. The average diameters of the composites were estimated to be about 950–1000 nm for PPB-0 (Fig. 1a), 680–738 nm for PPB-5 (Fig. 1b), and 280–315 nm for PPB-10 (Fig. 1c). In particular, more and bigger agglomerated lumps were evident in the CNFs with increasing $B_2O_3$ concentration because $B_2O_3$ hinders dispersion of pitch in PAN solution. In the corresponding

EDX spectrum (Fig. 1d), the individual fiber of PPB-10 was composed of B, C, and O and the elementary composition of B, C, and O were estimated to be 7.90, 87.45, and 4.65%, respectively.

The microstructure of the PPB-10 composite was investigated using TEM with corresponding SAED. The low-resolution TEM image for PPB-10 (Fig. 2a) shows a rough surface with larger clusters on the fiber surface. In the high-resolution TEM image (Fig. 2b), the cluster with red dotted circle line shows multilayers of with an interplanar distance of 0.34 nm corresponding to the (002) planes of the BN [21], while the section below the green dotted line is poorly crystallized CNF with nanopores between the nanocrystalline domains [22–25]. From these results, the $B_2O_3$ transform to BN during carbonization process with the release of CO and $CO_2$ by the following reaction: $B_2O_3 + C + N_2 \rightarrow BN + CO_2$ (CO) [18]. Furthermore, the corresponding SAED patterns show the surface characteristic of the PPB-10 composite. The SAED of the section below the green dotted line exhibits diffuse ring patterns without a distinct lattice fringe, confirming the surface amorphous carbon. Furthermore, the distinct diffraction rings increases in the cluster with red dotted circle line exhibiting the development of the graphitic structure.

The binding energy peak and composition of PPB-5 and PPB-10 were studied by XPS. The XPS high-resolution survey of the B 1 s spectrum (Fig. 3a) has only one peak at 191.25 eV, which can be assigned to C−B−N or C−B−O [7,26,27]. In the high- resolution C 1 s spectrum (Fig. 3b), three peaks indicates the presence of active species of carbon corresponding to the graphite peak (C=C, 284.7 eV), C−O (286.0 eV), and C=O (288.7 eV). The chemical state of nitrogen atoms could be assigned to two categories of N−B bond (397.9 eV) and M−C bond (400.7 eV), as shown in Fig. 3c. The relative amounts of B, O, and N increased as the $B_2O_3$ concentration increased from 5 to 10 wt% in Fig. 3b, suggesting that heteroatoms were responsible for the PPB composites' pseudocapacitive effect. Scheme 1 presents the formation mechanism of porous CNF with heteroatoms. Electrospun NF with $B_2O_3$ was stabilized in air to form an oxygen-enriched ladder polymer structure to prevent melting at high carbonization temperature. During the subsequent carbonization process, CO, $CO_2$, $H_2$, $CH_4$, $H_2O$ or other volatile compounds were released resulting in a porous carbon network structure. In addition, the incorporation of boron also introduced other heteroatom functional groups such as nitrogen and oxygen because the electron deficiency of the boron atoms attracts the strongly electronegative nitrogen and oxygen, resulting in C−B−O and/or C−B−N functional groups [28–30]. These functional groups can strengthen the interfacial wettability of the electrolyte ions and electrode surfaces, thereby enhancing the capacitive behaviors by providing pseudocapacitance.

Nitrogen sorption isotherms of the three composites are shown in Fig. 4a. All samples show typical type IV isotherms with capillary condensation steps at higher relative pressure, which are typical mesopore characteristics. Moreover, the hysteresis loops based on the IUPAC guideline shows H4 type loops at $p/p_o = 0.45$ for all composites, which indicate the presence of large mesopores embedded in a matrix with micropores [31–33]. The texture properties such as the BET surface area and the fraction of micro- and mesopores of the three composites are summarized in Fig. 4b. The micropore volume fraction of the PPB composites was calculated using $V_{micro}\% = (V_{micro}/V_{(micro + meso)}) \times 100\%$. The specific surface area and the faction of mesopores increased in the following order: PPB-0 (408 m$^2$g$^{-1}$, 37%) < PPB-5 (568 m$^2$g$^{-1}$, 49%) < PPB-10 (641 m$^2$g$^{-1}$, 57%). The porous composites exhibited an improved microstructure with increasing $B_2O_3$ content, suggesting that $B_2O_3$ plays a key role in developing porosity with a larger proportion of mesopores on the surface of fibers by the thermal decomposition of $B_2O_3$. These results were in good agreement with the type IV isotherms with H4 hysteresis loops because the hysteresis loop of the PPB-10 composite had a bigger area than that of PPB-0 and PPB-5, revealing the more developed mesoporosity in the PPB-10 composite.