



# sp<sup>2</sup>–sp<sup>3</sup> Hybrid Porous Carbon Materials Applied for Supercapacitors

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Abstract: Carbon materials have gained considerable attention in recent years due to their superior properties. Activated carbon has been used in supercapacitors due to its density and rapid adsorption capability. The sp<sup>2</sup>–sp<sup>3</sup> hybrid porous carbon materials are synthesized using herringbone-type carbon nanofibers (CNFs) and carbonized spherical phenol resins, with KOH as the activating agent. The morphology of the hybrid porous carbon facilitates the formation of ribbon-like nanosheets from highly activated CNFs wrapped around spherical resin-based activated carbon. The etching and separation of the CNFs produce a thin ribbon-like nanosheet structure; these CNFs simultaneously form new bonds with activated carbon, forming the sp<sup>2</sup>-sp<sup>3</sup> hybrid porous structure. The relatively poor electrical conductivity of amorphous carbon is improved by the 3D conductive network that interconnects the CNF and amorphous carbon without requiring additional conductive material. The composite electrode has high electron conductivity and a large surface area with a specific capacitance of 120 F g $^{-1}.\,$  Thus, the strategy substantially simplifies the hybrid materials of sp $^2$ hybridized CNFs and sp<sup>3</sup>-hybridized amorphous spherical carbon and significantly improves the comprehensive electrochemical performance of supercapacitors. The developed synthesis strategy provides important insights into the design and fabrication of carbon nanostructures that can be potentially applied as electrode materials for supercapacitors.

Keywords: supercapacitor; carbon materials; energy storage system; carbon nanofiber; activated carbon

# 1. Introduction

Over the past few decades, carbon materials have gained widespread attention in the field of energy storage due to the high chemical stability of their C–C covalent bonds, high diversity in terms of crystallinity, morphology, porosity, and texture, as well as the ease of utilization of these characteristics to meet specific application requirements [1-3]. Among the various types of carbon materials, activated carbon has been analyzed extensively for application in supercapacitors owing to its density and rapid adsorption capability [4,5]. However, its amorphous and porous structure significantly reduces the electrode density and the volumetric specific capacitance. Activated carbon exhibits wide pore distribution and contains micropores and macropores, along with random pore connections [6]. Typically, micropores are not accessible to the electrolyte ions because they are closed or the passages between them are narrow, thus completely preventing or drastically decelerating the ion transport [7]. Consequently, the intrinsically irregular pores of activated carbon limit its accessibility to electrolyte ions during the charge/discharge process in case of organic ions in non-aqueous systems. Therefore, new materials are required to overcome the drawbacks of activated carbon electrode materials and to improve the performance of supercapacitors [8].

The sp<sup>2</sup>-hybridized carbon nanomaterials, such as one-dimensional (1D) and twodimensional (2D) nanostructured carbon, exhibit exceptional mechanical strength, electrical



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). conductivity, and adaptability to various interfacial processes [9,10]. Carbon nanomaterials, especially carbon nanotubes (CNTs), carbon nanofibers (CNFs), and graphene, are promising candidates to replace activated carbon as electrode material in high-performance supercapacitors owing to their large surface area, high mesoporosity, electrolyte accessibility, and desirable electrical properties [11]. In most of the studies conducted thus far, CNTs and CNFs exhibit limited capacitance in non-aqueous electrolytes, even with nanostructures, because it is difficult to fabricate the CNTs and CNFs individually and separately owing to their tendency to form bundles due to the high van der Waals attraction [12,13]. The inherent tendency of the restacking of the graphene layers also limits the actual surface area. The poor capacitance of these nanocarbon materials in non-aqueous electrolytes is attributed to their limited specific surface area. Hence, it is extremely difficult to maintain the carbon layers of the nanocarbons separated and thus achieve the maximum surface area required for enhanced electrolyte interaction [14–17].

In this study, the sp<sup>2</sup> and sp<sup>3</sup> hybridizations refer to atoms in carbon materials (e.g., in CNFs and amorphous carbon) that were used to improve the electrochemical performance of supercapacitor. The sp<sup>2</sup>–sp<sup>3</sup> hybrid carbon materials were synthesized from herringbone-type CNF and carbonized spherical phenol resin using KOH as the activating agent shown in Figure 1. The relatively poor electrical conductivity of the amorphous carbon can be significantly improved by the 3D conductive network by interconnecting CNFs with amorphous carbon. Considering an alternate perspective, a large number of CNFs were thoroughly etched to ensure that the fiber walls are significantly thinned and that the edges are completely broken, consequently forming ribbon-like nanosheets. Furthermore, the ribbon-like nanosheets of the CNFs were anchored by amorphous carbon surfaces, which can alleviate their aggregation to some extent. The resultant sp<sup>2</sup>–sp<sup>3</sup> hybrid porous carbon presented an exceptionally high ion-accessible surface area, high electrical conductivity, and low ion diffusion.



**Figure 1.** Schematic diagram of the hybrid porous carbons (HPCs) induced by KOH activation. (a) sp<sup>2</sup>–sp<sup>3</sup> HPCs exhibit 3D spherical morphology covered with a thin carbon nanosheet. (b) Structural change of herringbone-CNFs by KOH activation process. The resultant CNFs form ribbon-like nanosheets.

#### 2. Materials and Methods

#### 2.1. Material Preparation

A commercial herringbone-type carbon nanofiber (Vina Tech Co. Ltd., Jeonju-si, Korea) and a spherical phenolic resin carbonized at 600 °C were thoroughly mixed with 300 mL

Darmstadt, Germany) was added to the dispersion after ultrasonication and stirred for 2 h to obtain a mixture. The KOH and H-CNF/carbonized spherical phenol resin were gravimetrically mixed at various ratios (carbon:KOH 1:2, 1:6, and 1:10). The mixture was heated at 120 °C to evaporate the ethanol and then dried at 120 °C for The nitrogen adsorption was carried out for 12 h to completely remove moisture. Subsequently, the dried sample was activated at 900 °C for 1 h under continuous Ar flow. After cooling to the ambient temperature, the resulting powder mixture was collected and washed with diluted hydrochloric acid (HCl) and distilled water. The samples were dried at 150 °C for 12 h to obtain hybrid porous carbon (HPC) denoted as HPC-1/2, HPC-1/6, and HPC-1/10, where the numbers represent the carbon:KOH weight ratio required for activation.

## 2.2. Material Characterization

Field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F, Tokyo, Japan) and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2000EX, Tokyo, Japan) were used to determine the morphologies of the as-prepared composite materials. The nitrogen adsorption–desorption isotherms at 77 K were examined to analyze the pore structure of the samples using a gas analyzer (Belsorp-Max II, BEL, Tokyo, Japan). The specific surface area was obtained from the Brunauer-Emmett-Teller (BET) method. The pore size distribution was estimated using the BELsim software that uses the non-localized density functional theory. X-ray diffraction (XRD, Rigaku D/Max 2500/PC, Tokyo, Japan) with Cu Ka radiation at 40 kV and 200 mA was used to analyze the crystal structure. The surface components of the samples were analyzed using X-ray photoelectron spectroscopy (XPS, ULVAC PHI 5000 VersaProbe, Chigasaki, Japan). The electrical conductivity of the samples in a Teflon cylinder cell filled with the powder was measured using a currentvoltage (I-V) potentiostat (VSP, EC-Lab, Claix, France). Here, 20 mm-diameter electrodes were used as probes, and the conductivities of the samples were calculated from the slope of the I-V curves because the I-V characteristics are ohmic in the measured voltage range (from 0 to 5 mV s<sup>-1</sup>).

# 2.3. Electrochemical Characterization

The electrodes of the HPC samples were fabricated by mixing the active material (95 wt.%) and polytetrafluoroethylene (PTFE, 60 wt.% dispersion in H<sub>2</sub>O, Sigma Aldrich, Darmstadt, Germany) to form a binder (5 wt.%) without separately adding a conductive agent. Tetraethylammonium tetrafluoroborate in acetonitrile was used as the electrolyte. All the components were assembled in a 2032-coin cell using a cellulose separator (TF4035, NKK) in an argon-filled glovebox. Cyclic voltammetry (CV) was performed on a potentio-stat (Biologic VMP3) at voltages ranging from 0 to 2.7 V at a scanning rate of 5 mV/s at room temperature to analyze the electrochemical properties of the samples. Galvanostatic charge-discharge tests were performed at various current densities from 1 mA·cm<sup>-2</sup> to 20 mA·cm<sup>-2</sup> at room temperature. Cyclic stability tests were performed at 1–2.7 V and 5 mA·cm<sup>-2</sup> current density. The specific capacitance of a single electrode in a symmetric two-electrode cell was calculated from the galvanostatic charge/discharge curves by using the following equation [18]:

$$C_g = \frac{I \cdot t}{m \Delta V} \tag{1}$$

where  $C_g$ , *I*, *t*, *m* and  $\Delta V$  represent the specific capacitance of a single electrode, discharge current (A), discharge time (s), mass of active material in single electrode (g), and the potential change during the discharge process (V), respectively. Electrochemical impedance spectroscopy (EIS) measurements were performed between 100 kHz and 100 MHz using a potentiostat (VSP, EC-Lap, Claix, France).

# 3. Results and Discussion

The microstructure changes of the composite material after the activation process were analyzed according to the KOH content using field-emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM). As observed from Figure S1, the HR-TEM images clearly exhibited structural changes corresponding to the KOH agent. The average diameter and length of pure CNFs were approximately 100 nm and 150 µm, respectively, as shown in Figure 2a,d. The HR-TEM image in Figure 2d illustrates the CNFs with nanocone-shaped tips (marked by the vellow box) and open snake head-like tips (marked by the blue box). The carbonized spherical phenol resins exhibited a spherical morphology with non-uniform spherical particle size and possessed an amorphous microstructure, as shown in Figure 2b,e. The CNF structure was altered following the activation performed at different concentrations of KOH. The change in the morphology was minimal a low KOH content (1:2) when compared with raw CNF, whereas the increase in the KOH weight ratio produced several noticeable grooves on the surface. Some of the fibers were cut short or activated when the weight ratio increased to 1:6, which resulted in the complete etching of the edges, thus creating open channels in the fibers and several ribbon-like nanosheets. The spherical morphology was largely maintained, and the HPC-1/10 was covered by a thin, wrinkled, and crumpled carbon layer having a 2D layer structure similar to that of graphene, as observed in Figure 2c. The HR-TEM image of the HPC-1/10, shown in Figure 2f, establishes that HACs were adequately wrapped by the wrinkled ribbon-like carbon nanosheets (inset), resulting in hybrids with a 3D structure of sp<sup>2</sup> carbons and sp<sup>3</sup> carbon. A previous study has reported that significant structural changes in fibers led to destruction in some parts and probably rearrangements in some parts to form non-fibrous bulky grains, as observed in the conventional activated carbon [19–21].



**Figure 2.** Morphologies and microstructures of (a,d) pure CNFs, (b,e) carbonized spherical phenol resin, and (c,f) hybrid porous carbon (HPC)-1/10. (a,d) Pure CNFs have an approximate diameter of 100 nm and length of 150 um, respectively; they exhibit nanocone-shaped tips (marked yellow box) and open snake head-like tips (marked blue box). (b,e) Pure spherical phenolic resins have a spherical morphology with non-uniform particle size. (c,f) HACs are well wrapped by ribbon-like carbon nanosheets.

The adsorption isotherms of  $N_2$  at 77 K provide significant information related to pore structure. Since changes in isotherms imply changes in pore structure, isotherm measurement is the basis for estimating pore structure parameters. There are six types of adsorption isotherm patterns according to the International Union of Pure and Applied Chemistry (IUPAC) classification [22], and each is indicated by a distinct pore structure. According to the IUPAC standards, all the curves in Figure S2 have Type I shape, largely consisting of micro-pores. Theoretically, the larger the specific surface area of the electrode material, the greater the number of ions adsorbed; therefore, a higher specific capacitance can be observed when applied to a supercapacitor [23]. The activated carbon prepared based on phenolic resin has a specific surface area of approximately 1900 m<sup>2</sup>  $g^{-1}$ , which indicates a high specific capacitance. In contrast, CNF, which has a specific surface area of 100–300 m<sup>2</sup> g<sup>-1</sup>, presents a low specific capacitance [24]. It is difficult to increase the specific surface area of activated CNFs due to their tendency to cause aggregation. Table 1 summarizes the specific surface area (A<sub>BET</sub>), various specific volumes, and average pore sizes of the as-synthesized materials. The amount of adsorption increases substantially after activation by KOH, especially in the low-pressure range, thus presenting an IUPAC type I isotherm [23]. The amount of adsorption in the BET of HPC samples increased with higher KOH weight ratios during the activation process. The A<sub>BET</sub> values of HPC-1/2 and HPC-1/10 were 945 and 1969  $m^2/g$ , respectively, and the total specific volume around the micropores of 86% and 85% was 0.43 and 0.92 cm<sup>3</sup>/g, respectively. Compared with HPC-1/10 and HPC-1/2, the pore ratio was similar but the specific surface area value was almost twice as high. The decrease in the specific surface area of HPC-1/2 is caused by the blocking of pores on the AC surface, as well as inactivated CNF aggregation. Following the severe activation of HPC-1/10, CNFs were completely disassembled since many edge sites and pores were formed, indicating that the composite was induced on the AC surface. This produced a ribbon-like carbon nanosheet with several edges in the exfoliated structure, which can be employed as an ion diffusion pathway for energy-storage materials.

**Table 1.** Specific surface area ( $A_{BET}$ ), various types of pore volume of activated carbon, HPC-1/2, HPC-1/6, and HPC-1/10.

Sample	$\begin{array}{c} \mathbf{A}_{\text{BET}} \\ \text{(m}^2 \ \text{g}^{-1} \text{)} \end{array}$	V <sub>total</sub> (cm <sup>3</sup> /g)	V <sub>Micro</sub> (cm <sup>3</sup> /g)	V <sub>Meso &amp; Macro</sub> (cm <sup>3</sup> /g)
Activated carbon	1902	0.88	0.75 (86.7%)	0.13 (13.3%)
HPC-1/2	945	0.43	0.37 (85.8%)	0.06 (14.2%)
HPC-1/6	1816	0.86	0.72 (84.8%)	0.14 (15.2%)
HPC-1/10	1969	0.92	0.77 (85.1%)	0.15 (14.9%)

XPS spectra were obtained to determine the surface components of the samples. Figure 3a presents the XPS survey spectra, and Figure 3b–e present the C 1s spectra. The main peaks of C1s at 284.4 and 284.8  $\pm$  0.1 eV are attributed to the sp<sup>2</sup> carbon of C=C bonding and the sp<sup>3</sup> carbon of C–C bonding, whereas the four peaks at 288.7  $\pm$  0.2,  $287.5 \pm 0.2$ ,  $286.4 \pm 0.2$ , and  $285.8 \pm 0.2$  eV are attributed to the carbon atoms in the O–C=O, C=O, C–O–C, and C–OH functional groups, respectively [24]. The sp<sup>2</sup> carbon proportion of C=C bonding decreased with the increase in the KOH content in the HPC sample, whereas that of the oxygen-containing functional groups (e.g., C–C, C–O, C–O–C, and C=O) increased. Yoon et al. previously reported that the KOH activation of herringbonetype CNFs first widens the gap between the structural units, while further reactions disrupt the entire fiber structure and rearrange it into accumulated amorphous carbon [24]. It can be inferred that the sp<sup>2</sup> carbon of C=C bonding in CNF changes to a single bond through KOH activation, forming a new bond with activated carbon. The deconvoluted C 1s peaks in Table S1 indicate that the oxidation of the CNF surface occurred through the dissociation of  $\pi$  bonds in C=C, because the relative ratio between the sp<sup>2</sup>- and sp<sup>3</sup>hybridized carbon atoms indicates the partial dissociation of the sp<sup>2</sup> carbon layers. It was observed that the higher the KOH concentration during the activation process, the more pronounced the etching of CNF, ultimately forming a thin ribbon-like nanosheet structure and simultaneously forming new bonds with activated carbon to form an sp<sup>2</sup>-sp<sup>3</sup> hybrid porous structure, which is consistent with the TEM results.



Figure 3. (a) XPS survey spectra and C 1s spectra of (b) activated carbon, (c) HPC-1/2, (d) HPC-1/6, and (e) HPC-1/10.

The electrochemical properties of the HPC electrode samples were evaluated and compared with those of the phenol resin-based activated carbon, as shown in Figure 4. It is evident that the HPC-1/10 electrode exhibited a larger cyclic voltammogram area than other HPC samples and even exhibited higher specific capacitance when compared with pure activated carbon-based on phenolic resin. The activated carbon, i.e., HPC-1/2, HPC-1/6, and HPC-1/10, showed gravimetric capacitances of 103, 28, 73, and 113 F/g, respectively, at 5 mV/s. It can be observed that the CV curves of the electrodes showed a typical rectangular shape, and no distinct Faradaic current was observed in the voltammogram, apart from that of HPC-1/2. The cyclic voltammograms of HPC-1/2 exhibited redox peaks, indicating pseudocapacitive behavior of the electrode materials between the electrolyte and oxygen functional groups, as shown in Table S1.

Additionally, it exhibited the lowest capacitance, indicating limited charge transfer kinetics due to pore blocking by the non-activated CNFs, as inferred from the BET analysis [25,26]. The electrical conductivity results demonstrate that HPC-1/10 exhibited much higher conductivity  $(4.5 \text{ S cm}^{-1})$  than the phenol resin-based activated carbon  $(2.1 \text{ S cm}^{-1})$ . The high specific surface area, suitable small pore size, and high conductivity of the HPC-1/10 electrode are advantageous for the absorption and transport of electrolyte ions through the porous channels within the ribbon-like nanosheets of HPC-1/10 [27]. Therefore, the highest specific capacitance of the HPC-1/10 electrode is mainly attributed to its high specific surface area and high conductivity. The specific capacitance of the composite electrodes was also tested as a function of the current density; the results are presented in Figure 4c. HPC-1/10 exhibited specific capacitances of 120, 118, 114, 113, and 109 F/g, at 1, 2, 5, 10, and 20 mA·cm<sup>-2</sup> discharge, respectively, demonstrating good rate capability (91% retention at 20 mA $\cdot$ cm<sup>-2</sup> against 1 mA $\cdot$ cm<sup>-2</sup>). In contrast, the activated carbon electrode exhibited a lower rate capability (81% retention at 20 mA·cm<sup>-2</sup>) and lower specific capacitance than HPC-1/10 for equivalent current densities of 106, 104, 99, 95, and 86 F/g, respectively. These results indicate that the HPC-1/10 electrode enabled rapid ion diffusion, which is consistent with the electrical conductivity analysis. Considering the similarity in the surface areas of the HPC-1/10 sample and the phenol resin-based activated carbon, it can be concluded that the nanopores within the nano-network-like structure of HAC-1/10 between the activated carbon and ribbon-like nanosheets could be accessed more readily by electrolytes; thus, these nanopores present a significantly higher utilization rate than those in the phenol resin-based activated carbon [28-32].



**Figure 4.** (a) Cyclic voltammograms at 5 mV s<sup>-1</sup> and (b) electrical conductivity of activated carbon and HPC samples under various compressive pressure values. (c) Rate capabilities at various current densities. (d) Nyquist plots recorded at frequencies between 200 kHz and 100 MHz.

Electrochemical impedance spectroscopy (EIS) was performed using a symmetric system to further evaluate the electrochemical performance. Figure 4c presents the Nyquist plots of the activated carbon and HPC electrode samples within the frequency range of 200 kHz to 100 MHz. In the high-frequency region, the real axis intercept represents the internal resistance, which includes the sum of the contact resistance between the active material and current collector, the intrinsic resistance of the active material, and the ionic resistance of the electrolyte; the semicircle in the middle frequency region corresponds to the charge transfer resistance [33,34]. In the Nyquist plots, all the electrodes of the samples presented a negligible semicircle, indicating a low charge transfer resistance. The real axis intercepts in the Nyquist plots of the activated carbon electrodes HPC-1/2, HPC-1/4, and HPC-1/10 were 0.7, 1.0, 0.9, and 0.5 ohms, respectively. This result indicates that the internal resistance of HPC-1/2 and HPC-1/4 increased due to the generation of oxygen-containing functional groups after activation. It can be observed that the chargetransfer resistance and the Warburg impedance for the HPC-1/10 electrode decreased. This decrease can be attributed to the fact that the KOH activation combines the oxygen functional groups on the ribbon-like nanosheets with activated carbon, thus reducing the oxygen functional groups on the composite materials. Furthermore, HPC-1/10 can provide double-layer capacitance to improve the overall energy storage as well as efficient electron transfer channels to improve the electrochemical performance.

# 4. Conclusions

In summary, this study presented a combination of carbon nanofiber and spherical phenol resin-based activated carbon, which was successfully prepared for sp<sup>2</sup>–sp<sup>3</sup> hybrid porous carbon materials through KOH activation. The structure of the CNFs changed considerably following the carbon:KOH (1:10) weight ratio treatment; consequently, the fiber walls became thin, and most of them were separated, generating pores on the surface or thin ribbon-like nanosheets. The ribbon-like nanosheets were simultaneously wrapped

around the surface of the activated carbon, providing a 3D network by creating a new bond capable of ensuring rapid transfer and diffusion of the electrolyte ions. Furthermore, the activation due the carbon:KOH (1:10) weight ratio treatment significantly increased the specific surface area and decreased the oxygen functional groups, thereby improving the electrochemical properties without a requirement for a conductive material. The developed synthesis strategy provides important insights into the design and fabrication of carbon nanostructures that can be potentially applied as electrode materials for supercapacitors.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/ 10.3390/en14195990/s1, Figure S1: FE-SEM images of samples, Figure S2: BET characterization of different samples, Figure S3: XRD pattern of samples. Figure S4: Equivalent series resistance (ESR) of cells assembled with each sample, Figure S5: Cycle stability for samples at 5 mA·cm<sup>-2</sup> and 1–2.7 V. Figure S6: Charge-discharge profiles, Table S1: Surface contents in samples and curve fitting results of the XPS C1s spectra, Table S2: Electrode density of samples.

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