High Energy and High Power Lithium-Ion Capacitors Based on Boron and Nitrogen Dual-Doped 3D Carbon Nanofibers as Both Cathode and Anode

Qiuying Xia, Hai Yang, Min Wang, Mei Yang, Qiubo Guo, Liming Wan, Hui Xia,* and Yan Yu*

1. Introduction

With the rapid development of portable electronic devices, electric vehicles, and large-scale grid storage, energy-storage devices are required to provide high energy and power densities as well as long cycle life.[1] Among the current energy-storage systems, Li-ion batteries (LIBs) and supercapacitors (SCs) are attracting more and more attention due to their wide application in our daily life.[2] The LIBs commonly can deliver high energy density (150–200 W h kg⁻¹) but at the expense of low power density and poor cycling stability. In contrast, SCs can provide high power density (2–5 kW kg⁻¹) and longer cycle life (over 1 × 10⁵ cycles) while suffer from low energy density.[3] Thus, developing new energy storage techniques that can combine the advantages of both LIBs and SCs has become an important research direction in the field of energy storage.

Recently, lithium-ion capacitors (LICs) have been proposed to be one of the promising candidates to bridge the gap between LIBs and SCs. The LICs are generally composed of a capacitor-type cathode with fast charge/discharge capability, a LIB-type anode with large capacity, and a nonaqueous lithium containing electrolyte that provides wide working voltage window.[2,3] Until now, several configurations of LICs with different cathode and anode materials have been reported with exciting results.[4] However, how to realize a high-performance LICs with both high energy density and power density remains a great challenge, which requires further exploration of proper cathode and anode materials. Active carbon (AC) is the mostly employed cathode material, which, however, has relatively low specific capacity owing to its physical charge-storage mechanism. The small capacity (30–35 mA h g⁻¹) of AC will compromise the large capacity of the battery-type anode and result in low energy density of LICs.[4] For anode materials, the insertion-type materials (such as graphite, Li₄Ti₅O₁₂, and Nb₂O₅) have good structural stability, while their low specific capacities (<400 mA h g⁻¹) restrict the high energy density of LICs.[5] The conversion-type (such as Fe₂O₃ and MnO) or alloy-type (such as Si and Sn) materials can provide large specific capacities but suffer from poor cycling stability and poor rate capability.[6] In general, the electrode kinetics of anode based on Li⁺ intercalation/deintercalation is much slower than that of cathode based on physical adsorption/desorption. Because of the kinetics mismatch between cathode and anode, high energy densities...
(30–90 W h kg\(^{-1}\)) can only be obtained with trade-off of low power performance (<3 kW kg\(^{-1}\)). Therefore, it is still a great challenge to develop appropriate cathode and anode materials with large specific capacities and matchable electrode kinetics to fully utilize the hybrid system design toward the high energy and power density LICs.

Porous carbon materials are promising electrode materials for both SCs and LIBs due to their large surface area, good electrical conductivity, excellent cycling stability, and superior rate performance.\(^7\) In this work, we developed a facile and controllable synthesis of boron (B) and nitrogen (N) dual-doped 3D porous carbon nanofiber networks (BNC) using the commercial bacterial cellulose (BC) membrane as the starting material. It was demonstrated that the B, N dual doping can significantly enhance the surface area, enlarge the carbon interlayer distance, increase the active sites, and improve the electrode kinetics of the carbon nanofibers. Interestingly, the BNC electrodes exhibit large specific capacity and ideal double-layer capacitive performance as cathode for SCs, while they also exhibit large specific capacity, excellent rate capability, and improved cycling stability as anode for LIBs. For the first time, BNC was successfully employed as both binder-free cathode and anode for high-performance BNC/BNC LICs, which greatly outperform the previously reported LICs with other configurations. In particular, the present symmetric “dual carbon” LICs can achieve a high energy density of 220 W h kg\(^{-1}\) at the power density of 225 W kg\(^{-1}\) and a high power density of 22 500 W kg\(^{-1}\) at energy density of 104 W h kg\(^{-1}\). The outstanding energy density and power capability of the present BNC/BNC LICs indicate that porous carbon modification and symmetric cell configuration are promising for developing high-performance LICs.

2. Results and Discussion

The free-standing BNC membranes were prepared via a facile method as illustrated in Figure 1a, using commercially available BC membranes as starting material and NH\(_4\)HB\(_4\)O\(_7\) aqueous solution as N and B sources. BC membranes were firstly immersed into the NH\(_4\)HB\(_4\)O\(_7\) solution to realize uniform impregnation. After freeze-drying, the resulting samples were annealed in a tube furnace under Ar/H\(_2\) atmosphere to obtain black free-standing 3D carbon nanofiber networks. During the annealing process, BC was pyrolyzed to form highly porous carbon nanofibers, while NH\(_4\)HB\(_4\)O\(_7\) decomposed to generate B and N dual doping in the carbon materials. Importantly, the doping concentrations of the B and N can be easily tuned by controlling the concentration of NH\(_4\)HB\(_4\)O\(_7\) in the aqueous solution (see Experimental Section for more details). In convenience, the BNC samples prepared from 0, 0.05, 0.1, and 0.15 m NH\(_4\)HB\(_4\)O\(_7\) solutions are defined as 0-BNC, 0.05-BNC, 0.1-BNC, and 0.15-BNC in the following text.

The morphology and microstructure of the obtained BNC samples were first characterized by field emission scanning electron microscopy (FESEM). As presented in Figure 1b and Figure S1 (Supporting Information), all the BNC samples show a 3D network nanostructure with coadjaunt nanofibers and abundant pores with various sizes. The pristine carbon nanofibers (0-BNC) without B and N doping are about 20–50 nm in diameter, and the diameter increases to 30–80 nm for the 0.05-BNC, 0.1-BNC, and 0.15-BNC samples. The increase in diameter for the doped BNC samples can be attributed to the doping of B and N atoms and the generation of micropores in the carbon nanofibers.\(^8\) In addition, it is noted that the pores between nanofibers of the BNC samples enlarge with the increase of the concentration of the NH\(_4\)HB\(_4\)O\(_7\) aqueous solution. Possible reason to that is high concentration intensifies the decomposition of NH\(_4\)HB\(_4\)O\(_7\) and results in more rapid gas evaporation with large pores. Figure S2 (Supporting Information) shows the cross-section FESEM images of the BNC samples, and the thickness of the BNC samples is in the range between 300 and 500 µm.

To gain further insights into the crystalline phase and pore structures of the BNC samples, X-ray diffraction (XRD), Raman, and nitrogen adsorption/desorption measurements have been carried out. Figure 1c shows the XRD patterns of different BNC samples. Two broad peaks at around 25° and 41° can be observed from the XRD patterns for all the BNC samples, which can be attributed to (002) and (101) reflections of graphite.\(^9\) The (002) peak shifts to lower diffraction angle as the concentration of NH\(_4\)HB\(_4\)O\(_7\) increases, indicating that interlayer spacing is increasing with B, N codoping.\(^10\) At the meantime, the peak intensity decreases with increasing doping level, which suggests that B, N codoping could lower down the degree of crystallinity of the BNC samples.\(^10\) Raman spectra of all the BNC samples are shown in Figure 1d, where the D band at 1350 cm\(^{-1}\) is assigned to disordered carbon or defective graphitic structures, while the G band at 1600 cm\(^{-1}\) corresponds to the graphitic layers and the tangential vibration of the carbon atoms.\(^10\) The ratios of I\(_D\)/I\(_G\) are 0.84, 0.86, 0.87, and 0.88 for 0-BNC, 0.05-BNC, 0.1-BNC, and 0.15-BNC, respectively, indicating more defects and structural distortion in the BNC samples with increasing doping levels.\(^11\) The N\(_2\) adsorption–desorption isotherms and pore size distributions of all the BNC samples are shown in Figure 1e. All isotherms can be classified as type I, suggesting microporous structure for all the BNC samples.\(^12\) The detailed information about the microstructure is summarized in Table S1 (Supporting Information). Inset in Figure 1e shows the pore size distributions of all BNC samples, demonstrating the coexistence of micropores and mesopores. Brunauer–Emmett–Teller-specific surface areas of the 0-BNC, 0.05-BNC, 0.1-BNC, and 0.15-BNC samples are 616, 961, 1076, and 805 m\(^2\) g\(^{-1}\), respectively. The 0.1-BNC sample exhibits the largest specific surface area, which is beneficial to achieve large specific capacity and better rate performance in LICs.

The morphologies and microstructures of the BNC samples were further investigated by transmission electron microscopy (TEM). Figure 2a,b shows the TEM images of the 0.1-BNC sample at low and high magnifications, revealing the nanofiber morphology and highly porous structure (also see Figure S3 in the Supporting Information for other BNC samples). Under close observation from high-resolution TEM (HRTEM) image in Figure 2c, ultrasmall graphite particles of 2–3 nm are interconnected with numerous micropores and mesopores in between. As shown in Figure 2c and Figure S3 (Supporting Information), the interlayer spacing of graphite increases from 0.38 to 0.49 nm with increasing doping level, agreeing well with the XRD results. Figure 2d shows the typical...
scanning transmission electron microscopy (STEM) image and corresponding elemental mapping images of 0.1-BNC, showing uniform distribution of B and N atoms throughout the entire body of nanofibers.

X-ray photoelectron spectroscopy (XPS) measurements were performed to further confirm the incorporation of heteroatoms in the porous carbon nanofibers. The survey-scan XPS spectra in Figure S4 (Supporting Information) clearly show the B and N signals in the doped carbon samples. Specifically, Table S1 (Supporting Information) summarizes the B and N contents in different BNC samples based on XPS analysis. In the high-resolution C1s spectra (Figure 2e, also see Figure S5 in the Supporting Information), the sharp peak at around 284.8 eV corresponds to the sp²-C with C=O bonds, and the other three weaker peaks can be attributed to C=O/C=C–O–B/C=N bonds (285.3 eV), C=O bonds (286.2 eV), and O–C=O/O–C=N bonds (289.0 eV), respectively. The high-resolution B1s spectrum (Figure 2f) can be deconvoluted into two components at 191.0 and 192.3 eV, corresponding to B–N/BC3 and B–C/O/ B=CO₂ bonds, respectively. The high-resolution asymmetric N1s spectrum can be deconvoluted into four peaks, which can be assigned to pyridinic N at 398.8 eV, C=N/B/BC at 399.2 eV, pyrrolic N at 401.1 eV, and quaternary N at 402.1 eV, respectively. The XPS analysis confirmed that the present synthesis method is efficient for introducing B and N heteroatoms into the carbon frameworks. The distribution diagrams of different B and N species in all BNC samples are shown in Figure S6 (Supporting Information). The 0.1-BNC sample exhibits the highest atomic ratios of pyridinic N, pyrrolic N, and B–C functionalities, which can provide a large number of active sites to improve the surface charge storage according to previous reports.

Figure 1. a) Schematic illustration of the fabrication process of BNC. b) Typical FESEM image of 0.1-BNC. c) XRD patterns, d) Raman spectra, and e) Nitrogen adsorption/desorption isotherms of the BNC samples with different B and N doping levels. Inset in (e) is the pore size distributions of different BNC samples.
To investigate the effect of the B and N dual doping on the electrochemical properties of the BNC samples as both cathode and anode for LICs, half cell tests were first carried out using coin cells with Li foil as both counter and reference electrodes. Typical cyclic voltammetry (CV) curves of all BNC electrodes between 2.0 and 4.5 V (vs Li/Li\(^{+}\)) at a scan rate of 10 mV s\(^{-1}\) are compared in Figure 3a. All CV curves of BNC electrodes exhibit quasirectangular shapes with small humps, indicating dominating electrochemical double-layer capacitance (EDLC) and subordinate pseudocapacitance. It is noted that the included areas of the CV curves for doped BNC electrodes are much larger than that of the pristine carbon nanofiber electrode (0-BNC), demonstrating improved charge-storage capability with B and N doping. The major EDLC contribution can be attributed to anion (PF\(_{-}\)) adsorption/desorption, while the minor pseudocapacitance can be ascribed to the interaction between the electrolyte and the O, B, and N containing functional groups at the carbon surface.\(^{[3b,12,15]}\) The CV curves of all BNC electrodes retain good rectangular shapes without severe distortion even at a high scan rate of 40 mV s\(^{-1}\) (Figure 3b; Figure S7 in the Supporting Information), indicating good rate capability and small electrode polarization. Linear charge–discharge curves at different current densities from 0.1 to 10 A g\(^{-1}\) can be observed for all BNC electrodes (Figure 3c; Figure S8 in the Supporting Information), indicating ideal capacitive behavior. Figure 3d compares the rate capabilities of all BNC electrodes, showing that the doped BNC electrodes can deliver larger capacities than the pristine carbon nanofiber electrode at all current densities. At a low current rate of 0.1 A g\(^{-1}\), the 0.1-BNC electrode exhibits the highest specific capacity of 113 mA h g\(^{-1}\), which is larger than 83, 107, and 94 mA h g\(^{-1}\) for 0-BNC, 0.05-BNC, and 0.15-BNC electrodes, respectively. The large specific capacity of the 0.1-BNC electrode is also much larger than those of previously reported conventional AC electrodes and other porous carbon electrodes in the similar potential ranges.\(^{[6b,16]}\) Importantly, the 0.1-BNC electrode can still deliver a high capacity of 63 mA h g\(^{-1}\) even at a high current density of 10 A g\(^{-1}\), demonstrating its superior rate performance over other BNC electrodes. In addition to excellent rate performance, the 0.1-BNC electrode also exhibits good cycling stability. As shown in Figure 3e, the 0.1-BNC electrode reveals 87% capacity retention after 5000 charge/discharge cycles at a current rate of 2 A g\(^{-1}\), making it promising cathode for high-performance LICs.
Next, the electrochemical properties of BNC samples were further investigated as anode by using coin-type cells in the potential range of 0.02–3.0 V (vs Li/Li$^+$). Figure S9 (Supporting Information) shows the CV curves for initial three cycles of all BNC electrodes at a scan rate of 0.1 mV s$^{-1}$. Reduction peaks at $\approx$0.75 V can be observed for all the BNC electrodes from the first discharge curves, which can be attributed to decomposition of electrolyte and the formation of solid electrolyte interface (SEI) layers.\textsuperscript{[17]} Another two small reduction peaks at around 1.5 and 2.2 V are probably induced by the irreversible reactions between the electrolyte and the surface functional groups.\textsuperscript{[17,18]} Nevertheless, all these reduction peaks disappear in the subsequent cycles, suggesting stable SEI formation at the initial cycle. Figure 4a shows the CV curves of the 0.1-BNC electrode at different scan rates, revealing similar rectangular shape without obvious redox peaks. Several charge-storage mechanisms could exist for heteroatom-doped carbon materials, including diffusion-controlled process of Li$^+$ intercalation, capacitive surface charge storage associated with ion adsorption/desorption, and the reversible faradaic reactions between electrolyte and surface functional groups.\textsuperscript{[17,19]} The charge-storage behaviors of the BNC anodes can be investigated by analyzing the CV curves at different scan rates.\textsuperscript{[6]} By using the current separation method, the capacitive capacity contribution can be separated from the diffusion-controlled capacity contribution as shown in the shadowed area in the CV curve in Figure 4b (also see Figure S10 in the Supporting Information for all BNC electrodes). It can be found that about 60.6% of the total capacitance of the 0.1-BNC anode is contributed by capacitive mechanism at 0.5 mV s$^{-1}$, which is higher than

Figure 3. a) Typical CV curves of the 0-BNC, 0.05-BNC, 0.1-BNC, and 0.15-BNC cathodes at a scan rate of 10 mV s$^{-1}$. b) CV curves of the 0.1-BNC cathode at different scan rates. c) Charge–discharge curves of the 0.1-BNC cathode at different current densities. d) Rate performances of the 0-BNC, 0.05-BNC, 0.1-BNC, and 0.15-BNC cathodes. e) Cycle performance of the 0.1-BNC cathode at a current density of 2 A g$^{-1}$ for 5000 charge/discharge cycles.
35.4%, 55.4%, and 48.6% for 0-BNC, 0.05-BNC, and 0.15-BNC, respectively, demonstrating large pseudocapacitance contribution of the 0.1-BNC anode. The charge–discharge curves of the BNC anodes at different current densities are presented in Figure 4c and Figure S11 (Supporting Information). Interestingly, a very high specific capacity of about 1130 mA h g\(^{-1}\) is obtained for the 0.1-BNC electrode at a current density of 0.1 A g\(^{-1}\), which is about three times larger than the theoretical capacity of graphite (372 mA h g\(^{-1}\)). It is also higher than 768, 1034, and 910 mA h g\(^{-1}\) for 0-BNC, 0.05-BNC, and 0.15-BNC electrodes, respectively. Figure 4d compares the rate performances of all BNC electrodes, showing that the B and N dual-doped electrodes show higher capacities than the pure carbon nanofibers electrode (0-BNC) at the same specific currents. This corroborates the expectation that B and N dual doping is also efficient in improving anode performance of carbon materials. Even at high specific current densities of 5 and 10 A g\(^{-1}\), the 0.1-BNC electrode can still deliver high capacities of 375 and 272 mA h g\(^{-1}\), respectively, demonstrating superior rate performance. Furthermore, the 0.1-BNC electrode possesses superior long cycle life. As shown in Figure 4e, negligible capacity loss can be found for the 0.1-BNC electrode after 5000 charge/discharge cycles at a high current density of 2 A g\(^{-1}\), demonstrating its promising application as anode for high-performance LICs.

The 0.1-BNC samples exhibit outstanding electrochemical performance as both cathode and anode, including large specific

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**Figure 4.** a) CV curves of the 0.1-BNC anode at different scan rates. b) CV curve of the 0.1-BNC anode with shadowed area representing the surface capacitive contribution. c) Charge–discharge curves of the 0.1-BNC anode at different current densities. d) Rate performances of the 0-BNC, 0.05-BNC, 0.1-BNC, and 0.15-BNC anodes. e) Cycle performance of the 0.1-BNC anode at a current density of 2 A g\(^{-1}\) for 5000 charge/discharge cycles. f) Nyquist plots of the 0-BNC, 0.05-BNC, 0.1-BNC, and 0.15-BNC electrodes.
capacity, excellent rate capability, and long cycle life, which can be attributed to the following aspects: (1) The enlarged carbon interlayer spacing due to B and N codoping facilitates diffusion of Li$^+$ ions. (2) The large surface area with ample micropores can greatly increase the electrolyte/electrode interface, resulting in large pseudocapacitance contribution and facile electrolyte penetration into the active material. (3) The 3D interconnected conductive network builds up an expressway for fast electron transfer. (4) The rich pyridinic N, pyrrolic N, and B-C functionalities create a large number of active sites at the surface to enhance the surface capacity contribution. (5) As illustrated by the electrochemical impedance spectroscopy (EIS) results in Figure 4f, the optimized B and N dual doping can greatly improve the electrode kinetics. The small charge transfer resistance of the 0.1-BNC electrode suggests fast and highly efficient faradaic redox reactions at the electrode surface.

By using 0.1-BNC cathode and prelithiated 0.1-BNC anode, a full LIC was constructed using 1 M LiPF$_6$ electrolyte. The proposed charge-storage mechanism is schematically shown in Figure 5a. During the charge process, PF$_6^-$ ions are absorbed

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Figure 5. a) Schematic illustration of the charge-storage mechanisms for the BNC//BNC LIC. b) CV curves of the BNC//BNC LIC at different scan rates. c) Charge–discharge curves of the BNC//BNC LIC. d) Cycle performance of the BNC//BNC LIC between 0.02 and 4.5 V at a current density of 2 A g$^{-1}$. e) Ragone plots of the present BNC//BNC LIC compared with previously reported LICs. Inset is a demonstration of the LIC device powering 10 green LED panel.
at the porous surface with B and N functional groups and the defects moieties for the cathode, while Li\textsuperscript+ ions are either intercalated into the graphite layer or absorbed at the surface for the anode. And the discharge process is the reverse of the charge process. Before fabricating the LICs, the 0.1-BNC anode was prelithiated for about 6 h to obtain an extended potential window and eliminate the initial irreversible reactions (Figure S12, Supporting Information).\textsuperscript{20}\textsuperscript{20} To balance the charge between two electrodes, the optimized mass ratio of cathode to anode was determined to be about 3 (Figure S13, Supporting Information). The optimized “dual carbon” LIC device can work in a broad voltage window between 0 and 4.5 V. Figure 5b shows the CV curves of the BNC//BNC LIC device at different scan rates from 5 to 40 mV s\textsuperscript{−1}. The CV curves exhibit similar rectangular shape without obvious redox peaks, indicating ideal capacitive behavior. As the sweep rate increases, the rectangular shape of CV curves is still retained without severe distortion (Figure S14, Supporting Information), demonstrating high reversibility and good rate capability. The charge and discharge curves of the BNC//BNC LIC device at different current densities show near-linear slope with negligible internal resistance drops (Figure 5c). The corresponding specific capacitance values (based on total mass of cathodic and anodic active materials) are 78.2, 70.1, 63.3, 58.0, 50.2, 43.3, and 36.8 F g\textsuperscript{−1} at the current densities of 0.1, 0.2, 0.5, 1, 2, 5, and 10 A g\textsuperscript{−1}, respectively. Furthermore, a reasonable cycling stability was obtained with 81% capacity retention after 5000 charge/discharge cycles at a current density of 2 A g\textsuperscript{−1} as well as good coulombic efficiency of nearly 100% (Figure Sd). If the BNC//BNC LIC device was tested in a slightly narrow voltage window of 0.02−4.0 V (Figure S15 and Table S2, Supporting Information), the capacity fading becomes negligible, but with trade-off for its high capacity and energy density. The capacity loss of the present LIC when tested between 0 and 4.5 V could be attributed to the decomposition of the electrolyte at high voltage near the end of charge.\textsuperscript{21} Ragone plot of the present BNC//BNC LIC device is shown in Figure 5e in comparison with previously reported LICs. It is noted that the BNC//BNC LIC can achieve a high energy density of 220 W h kg\textsuperscript{−1} at a power density of 225 W kg\textsuperscript{−1}. Even at a high power density of 22.5 kW kg\textsuperscript{−1}, which is beyond the recommended target for electric vehicles (15 kW kg\textsuperscript{−1}), the LIC can still deliver a high energy density of 104 W h kg\textsuperscript{−1}. The high energy density and high power capability of the present BNC//BNC LIC are superior to previously reported LICs (see detailed comparison in Table S3 in the Supporting Information), such as graphite//AC,\textsuperscript{22} hard carbon//AC,\textsuperscript{23} Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}/graphene//AC,\textsuperscript{24} TiO\textsubscript{2}/graphene,\textsuperscript{25} Nb\textsubscript{2}O\textsubscript{5}/C//AC,\textsuperscript{26} Fe\textsubscript{3}O\textsubscript{4}/Graphene//Graphene,\textsuperscript{27} MnO/CNS//CNS,\textsuperscript{28} VN−RGO//APDC,\textsuperscript{29} TIC//PHPNC,\textsuperscript{30} and NiCo\textsubscript{2}S\textsubscript{4}//AC.\textsuperscript{31} To demonstrate the potential application for the present BNC//BNC LIC, a light-emitting diode (LED) panel was powered by a single BNC//BNC LIC device. As shown in Figure 5e and Figure S16 (Supporting Information), a fully charged LIC device can lighten 10 green LEDs for over 3 min.

### 3. Conclusions

In summary, we have demonstrated the successful synthesis of B and N dual-doped 3D porous carbon nanofiber networks via a facile and controllable strategy, and their superior electrochemical performance as binder-free electrodes for LICs. It has been shown clearly that B and N dual doping results in increased surface area, expanded interlayer distance, improved charge-storage active sites, and enhanced electrical conductivity of the carbon nanofiber networks. With optimized doping conditions, the obtained BNC electrodes simultaneously show large specific capacities, excellent rate capability, and good cycling stability as both cathode and anode. With major capacity contribution from the surface, B and N dual doping can greatly reduce the mismatch of electrode kinetics between cathode and anode, thus resulting in both high energy density and high power density. With a symmetric “dual carbon” configuration, a 4.5 V BNC/BNC LIC device has been successfully constructed, presenting high energy density (220 W h kg\textsuperscript{−1} at 225 W kg\textsuperscript{−1}), high power density (22 500 W kg\textsuperscript{−1} at 104 W kg\textsuperscript{−1}), and reasonably long cycling life (81% capacitance retention after 5000 cycles). This simultaneous manipulation of heteroatoms in 3D carbon materials provides new opportunities to the design of high-performance electrodes to boost the energy and power densities of hybrid SCs.

### 4. Experimental Section

**Synthesis of 3D B and N Dual-Doped Carbon Nanofiber Networks:** The BC membranes were provided by Hainan Yeguo Foods Co., Ltd. The BC membranes were first immersed into NH\textsubscript{4}HB\textsubscript{4}O\textsubscript{7} aqueous solution for 24 h with slow stirring at room temperature, and then freeze-dried for 24 h. The obtained sample was then carbonized at 500 °C for 1 h and at 1000 °C for 2 h in Ar/H\textsubscript{2}-mixed atmosphere to obtain 3D B and N dual-doped carbon nanofiber networks. After carbonization, the products were extensively washed in hot deionized water for several times and dried at 80 °C overnight. The concentration of the NH\textsubscript{4}HB\textsubscript{4}O\textsubscript{7} aqueous solution was varied to be 0, 0.05, 0.1, and 0.15 M to control the B and N doping levels in the final products.

**Materials Characterizations:** The morphologies and microstructures of the samples were characterized by FESEM (Quanta 250F), TEM, and HRTEM (FEI Tecnai G2 F30). The structures of the samples were characterized by XRD (Bruker AXS D8 Advance) with Cu K\alpha radiation. The Raman spectra were collected on a Renishaw inVia Reflex Raman Microprobe with a 532 nm wavelength incident laser. Nitrogen adsorption/desorption isotherms were measured at 77 K (ASAP Tristar II 3020 model). XPS measurements were carried out on an X-ray photoelectron spectrometer (Escalab250Xi, Thermo scientific) using monochromatic Al K\alpha X-Ray source.

**Electrochemical Measurements:** All the samples were directly used as the electrodes without any binders or conducting additives. Half cells using Li foil as both counter and reference electrodes were assembled in R2025-type coin cells in a glove box. Celgard 2400 was used as the separator, and 1 M LiPF\textsubscript{6} in ethylene carbonate and diethyl carbonate (EC/DEC, v/v = 1:1) solution was used as the electrolyte. Galvanostatic charge-discharge measurements were performed on a LANDCT2001A battery test system. CV and EIS measurements were conducted on an electrochemical workstation (CHI760D). All the tests were carried out at room temperature. A Santorius Analytical Balance (CPA225D, with resolution of 10 μg) was used to determine the mass loading. The mass loadings of the 0-BNC, 0.05-BNC, 0.1-BNC, and 0.15-BNC electrodes are in the range of 1.5−2 mg cm\textsuperscript{−2}.

Prelithiated 0.1-BNC was used as the anode and 0.1-BNC was used as the cathode with an optimized cathode/anode mass ratio of about 3:1. During the prelithiation process, the anode was directly put in contact with the Li foil in the same electrolyte for 6 h. Then, the anode was washed with DEC and shifted to the assembly of coin cell-type hybrid SCs. The capacities of single electrodes and the capacitance of the LiCs are calculated from galvanostatic charge−discharge curves. The energy...
density and power density were calculated based on the active materials of both cathode and anode using the following equations

\[ P = \Delta V \times i/m \]  
\[ E = P \times t/3600 \]  
\[ \Delta V = (V_{\text{max}} + V_{\text{min}})/2 \]

where \( i \) is the discharge current (A), \( t \) is the discharge time (s), \( m \) is the total mass of active materials including anode and cathode (kg), and \( V_{\text{max}} \) and \( V_{\text{min}} \) are voltages at the beginning and end of the discharge (V), respectively.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

boron and nitrogen dual doping, carbon nanofibers, high energy, high power, lithium-ion capacitors

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