Highly Compressible Nitrogen-Doped Carbon Foam Electrode with Excellent Rate Capability via a Smart Etching and Catalytic Process

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Supporting Information

ABSTRACT: Freestanding three-dimensional nitrogen-doped carbon foam with large pores is proposed as a promising electrode configuration for elastic electronics. Although it exhibits excellent mechanical performance, the capacitive performances (especially its rate capability) are still unsatisfactory. By using KMnO₄, we demonstrate a smart etching and catalytic process to form highly graphitized and etched nitrogen-doped carbon foam (ENCF) with an exfoliated carbon-shell architecture. These compositional and structural features endow the ENCF electrodes with excellent electron conductivity as well as more ion-accessible electrochemical active sites. Significantly, all-solid-state symmetric supercapacitor devices based on the ENCF electrodes exhibit enhanced specific capacitance and marked high-rate capability. Furthermore, the integrated device has no significant capacity loss under 60% compressive strain.

KEYWORDS: KMnO₄, nitrogen-doped carbon, compressible electrode, symmetric supercapacitor, excellent rate capability

INTRODUCTION

Wearable, flexible, and elastic electronic devices have attracted increasing attention in recent years. To power these devices, flexible and compressible/stretchable power sources with robust mechanical properties are needed. Among the various power sources, lithium-ion, sodium-ion, lithium-air, and lithium-sulfur batteries offer higher energy densities than supercapacitors (SCs); however, concerns regarding their poisonous organic electrolyte and increasing cost have prompted extensive research into using SCs in poisonous organic electrolyte and increasing cost have supercapacitors (SCs); however, concerns regarding their unique features of high safety, long cycling life, and ultrahigh power density.

Numerous previous efforts have shown that three-dimensional porous structures are suitable configurations to prepare compressible electrodes, and great progress has been achieved using materials such as graphene and carbon nanotube (CNT) foams. However, compressible electrodes based on graphene and CNTs were limited by their relatively small pores and low porosity, which hinder the infiltration of the gel electrolytes and lead to many of the inner pores or active sites in the electrode not being fully utilized. Indeed, many excellent studies have shown superior electrochemical performances and mechanical properties in aqueous electrolyte, but similar studies of all-solid-state devices have not been reported. An attractive approach of coating active materials on commercial sponges with large pores was developed to overcome this limitation. For example, Niu et al. first reported compressible all-solid-state SC devices based on PPy/SWCNT (polypyrrrole/single-walled carbon nanotube) sponge electrodes, where the commercial sponges endowed the materials with superior compressibility and polyaniline provided pseudocapacitance. However, the active material (PPy/SWCNTs) was directly deposited on the framework of the sponge through weak binding forces; hence, they are not capable of withstand large deformations over long time periods. Moreover, the inactive mechanical support may deteriorate the rate performance because of its low electron-transport ability.

Within this context, electrode materials with large pores and freestanding structures are desired. Recently, our group has developed a type of freestanding, hydrophilic, and highly compressible nitrogen-doped carbon foam (NCF) that can be used as the electrode material in supercapacitors. An integrated all-solid-state symmetric supercapacitor (SSC) device based on NCF electrodes can be arbitrarily compressed under 60% strain without significant changes in the electrochemical performance. Additionally, a specific capacitance of 343 mF cm⁻² can be achieved without any other active capacitive materials. However, significantly boosting the high-rate capability while maintaining the mechanical performance still remains a big challenge, which is perhaps due to the low degree of graphitization of NCF. If its capacitance and rate performance could be further enhanced while retaining its mechanical properties, it would provide a significantly useful alternative electrode for commercial all-solid-state SC applications. It has been recognized that carbon materials with large specific surface areas and higher degrees of graphitization offer more active sites and superior conductivity, which results in higher capacitances and rate capabilities. Consequently, numerous studies have mainly focused on the two aforementioned aspects to improve the capacitive performance of carbon material electrodes. For instance, Wang et al. demonstrated that the direct use of chemically activated carbon cloth as the electrode material greatly enhanced the areal capacitance. A more efficient electrochemical exfoliation...
Figure 1. (a-1—c-1) Schematic illustration of the formation of ENCF. Structure evolution images: (a-2) MS, (b-2) MS after etching, and (c-2) ENCF.

Figure 2. SEM images of (a) MS, (b) etched MS, and (c) ENCF. (d) Low-magnification TEM image of single ENCF fiber. (e, f) High-resolution TEM images collected at the edge of the single ENCF fiber, as indicated by the cusp in (d). (g) Scanning transmission electron microscopy image and (h) elemental mappings of ENCF.
strategy was proposed by Lu and co-workers, which shows that surface exfoliation of the carbon fibers in carbon cloth enhances the surface area, which could significantly boost the capability while preserving the original mechanical properties. Inspired by this, we hypothesize that if the surface of the carbon fibers in NCF could be exfoliated and transferred to graphitized carbon, remarkable compressible NCF electrode materials with high surface roughness and conductivity could be achieved.

Herein, we reported a smart etching and catalytic process to distinctly enhance the capacitive performances of NCF electrodes using commercial KMnO₄ as the etchant and catalyst precursor, which leads to faultless implementation in highly compressible all-solid-state SSC devices. Our strategy to improve the electrochemical performance by etching the NCF (final product denoted as ENCF) electrode can be described as follows: (i) a melamine sponge (MS) precursor was etched with KMnO₄ solution, yielding an ENCF consisting of exfoliated carbon fibers with more ion-accessible surface-area sites; (ii) MnO₂ (derived from the pyrolysis of KMnO₄) as a graphitization catalyst can improve the degree of graphitization of ENCF and thus contribute to high electric conductivity; (iii) a small quantity of MnO₂ nanoparticles embedded in ENCF can produce extra pseudocapacitance; and (iv) hierarchical micro-, meso-, and macropore channels formed a rapid ion and electron-transport network for further improvement in the rate performance.

RESULTS AND DISCUSSION
The experimental preparation of ENCF electrodes involves two steps, as schematically illustrated in Figure 1 (upper panels), and the digital photos of the respective samples are presented in the lower panels. The etching of MS was achieved by applying a preferential etching process to the preformed ENCF precursor. In this process, the unsaturated hydrocarbons in the MS can be oxidized to hydroxy- or carboxy- derivatives. Next, after the selective removal of redundant KMnO₄ and the subsequent calcination treatment in Ar atmosphere, an ENCF with shaggy carbon fibers was obtained. The scanning electron microscopy (SEM) images in Figure 2a,b show that MS has a rather smooth surface over the whole fiber, and after etching, the surface morphology of the carbon fiber is completely different, indicating that the surface of the fiber was etched, leading to the formation of rough surface morphologies. A subsequent calcining process was carried out to convert the MS to ENCF. As seen in the SEM observations (Figure 2c), the final ENCF underwent an obvious volume shrinkage compared with the preetched MS precursor but still inherited the rough surface morphology.

Figure 2d depicts the transmission electron microscopy (TEM) image of ENCF, in which representative carbon fibers with rough surfaces can be observed. The composition of ENCF was investigated by X-ray photoelectron spectroscopy (XPS). The survey XPS image (Figure S1a) clearly revealed that the product contains C, N, O, and Mn elements. On the basis of a previous report, the peak binding-energy separation between Mn 2p3/2 and Mn 2p1/2 of approximately 11.8 eV is characteristic of MnO₂. A careful examination by thermogravimetric (TG) analysis in air revealed that the weight percentage of MnO₂ was estimated to be approximately less than 10% (Figure S2). The essence of this strategy lies in the transformation of residual KMnO₄ into MnO₂ at high temperatures, which triggers the enhanced graphitization of the carbon fiber. As verified by high-resolution TEM (HRTEM) images (Figures 2e and S3), MnO₂ nanoparticles were embedded in the graphitized carbon matrix. Interestingly, TEM observation reveals the homogeneous distribution of
mesopores with diameter in the range of 10−20 nm (Figure 2f); furthermore, Brunauer−Emmett−Teller (BET) measurements (Figure S4a) verify the mesoporous nature. Significantly, the specific surface area of ENCF increased by more than one order of magnitude from 5.3 to 61.2 m² g⁻¹ compared to that of untreated NCF (Figure S4b). The elemental mappings of a single-carbon fiber reveal a uniform distribution of carbon, nitrogen, oxygen, and manganese in the ENCF fiber (Figure 2g,h).

An important advantage of this smart etching process is the dramatically increased number of effective active sites (surface area accessible to the electrolyte ions) in ENCF. To prove the enhancement in the accessible surface area, the dye-adsorption method was used to investigate the ENCF and untreated NCF samples (Figure 3a). The ENCF and untreated NCF samples were immersed in a 2 mg L⁻¹ aqueous methylene blue (MB) solution for 2 h in the dark, which is the most commonly used solid absorber for determining the ion-accessible surface area.²⁹,³⁰ Clearly, the absorption peaks of MB with ENCF almost disappear, whereas those for the untreated NCF sample are greatly changed but still exist. Digital photographs of the adsorption tests vividly demonstrate the enhanced adsorption properties. In these photos, the final color of the MB solution with the ENCF and untreated NCF samples was transparent and light blue, respectively. This shows that MB molecules were absorbed more easily by the ENCF sample than by the untreated NCF sample, indicating a distinct enhancement in the ion-accessible surface area upon chemical etching.

Moreover, analysis of Raman spectra (Figure S5) confirms that more graphitized carbon was produced during high-temperature processes with the MnO₂ catalyst. The G peak in the spectrum of ENCF associated with crystalline carbon (located at approximately 1600 cm⁻¹) is significantly enhanced compared to that of untreated NCF, producing an obvious increase in the ratio of G mode to D mode (associated with carbon defects) (I⁰/G/I⁰/D) from 0.801 to 0.967.³² The increased I⁰/G/I⁰/D ratio indicates that the calcining process with MnO₂ nanoparticles can promote an increase in the carbonization degree, with partial structural transformation from defective carbon to crystallized carbon. As a consequence, superior
electrical conductivity of the ENCF samples can be obtained by this catalytic thermal treatment process.\textsuperscript{22} The electrical conductivity was calculated from the $I-V$ curves presented in Figure S6. Taking various NCF samples as examples, the electrical conductivity of the untreated NCF samples was enhanced by increased temperature and ranged from 0.46 to 3.8 S cm$^{-2}$ (Figure 3b). However, the high graphitization of carbon tends to collapse or distort under compression because of the relatively poor compressibility and springiness limit. Therefore, the samples of NCF-800 and NCF-900 could not maintain their original morphology after several continuous compressions.\textsuperscript{14} Significantly, the highly graphitized ENCF achieved a high electrical conductivity of 6.4 S cm$^{-2}$, higher than that of the untreated NCF-900 sample, while still maintaining its outstanding mechanical properties.

The volume of ENCF after compression can expand to recover its original volume without any discernible variation because of its outstanding elasticity and robust carbon fiber network (Figure 3c). Figure S7a,b shows the stress–strain measurements of the NCF samples under different compressive degrees with 20, 40, 60, and 80% strain. During the unloading process, the compressive stress always remains above zero and almost returns to the original value, indicating that the reduction of stress is accompanied by the immediate recovery of ENCF and no plastic deformation.\textsuperscript{14} The cyclic compression curves of ENCF for 1000 loading–unloading cycles at a strain rate of 50% for 15 s with a maximum strain of 50% are presented in Figure S7c. Although the first compression curve is different from that of the subsequent cycles because of its higher Young’s modulus, maximum stress, and high energy-loss coefficient,\textsuperscript{35} the representational stress–strain curves of the 500th and 1000th cycles perfectly overlap, which highlights the high recovery rate and the fact that the mechanical properties can be maintained by ENCF upon long-term deformation. Moreover, changes in the relative height of multicycle compression testing for ENCF are shown in Figure 3d. It is evident from the figure that the relative height of NCF after 1000 cyclic compressions remained almost the same without any observable height deformation.

The advantage of its unique structure, which allows for large and long-term deformations combined with increased ion-accessible active sites and superior electrical conductivity, makes ENCF suitable to be used directly as a high-performance and compressible electrode for SCs. We first tested the electrochemical performance in a three-electrode electrochemical cell. $C-V$ curves of freestanding ENCF as the working electrode directly in 5 M LiCl electrolyte show a typical electrochemical double-layer capacitive behavior.\textsuperscript{36} The ENCF electrodes (Figure S8) display an enhanced specific capacitance of 473 mF cm$^{-2}$ at a scan rate of 1 mV s$^{-1}$ and a superior rate capability (196 mF cm$^{-3}$ for ENCF at 1 V s$^{-1}$) compared to those of the NCF electrode.\textsuperscript{14} The rate capability during ultrastart charging/discharging is critical for high-performance electrode materials. In general, large distortions in the shape of $C-V$ curves under ultrastart scan rates result in an unsuppressing rate capability.\textsuperscript{35} The rectangular $C-V$ curves of the ENCF electrode are retained even at ultrahigh scan rates (e.g., up to 20 V s$^{-1}$), and the linear dependence of the discharge current on the scan rate was observed at scan rates of up to 10 V s$^{-1}$, showing that our ENCF electrode has excellent rate capability. The enhanced electrochemical performance of the ENCF electrode compared to that of the untreated NCF electrode suggests that a large specific surface area and a good electrical conductivity of the electrode are crucial to boost the specific capacitance and rate capabilities.

Having determined that the chemically etched and highly graphitized ENCF electrode exhibits enhanced capacitive behavior as well as fascinating ability to withstand various compression deformations, we sought to test its practical application as a two-electrode SSC. In this study, a simple all-solid-state SSC device with two ENCF electrodes and 5 M LiCl/PVA (polyvinyl alcohol) as the gel electrolyte was assembled (Figure S9). The electrochemical properties of the as-fabricated SSC device were evaluated by $C-V$ and galvanostatic charge–discharge (GCD) testing. The $C-V$ and GCD curves of the SSC device present nearly rectangular (Figure 4a,b) and symmetric triangular traces (Figure S10a,b), respectively, which are indicative of ideal capacitive behavior and fast charge–discharge properties. In particular, the SSC device is robust and capable of charging/discharging at scan rates as high as 100 V s$^{-1}$ and can complete one charge/dischARGE cycle within 3 s at a current density of 20 mA cm$^{-2}$. It is important to note that data on the excellent rate capability of SCs reported in the literature are often provided over a different scan rate range. In this case, certain capacitances at scan rates of 10 mV s$^{-1}$ and 1 V s$^{-1}$ were chosen for a better comparison. Specifically, a remarkable capacitance retention rate of 56% was achieved, which is noticeably higher than the rate capability of the untreated NCF electrode and even comparable to the best rate capability reported previously in the literature obtained under the aforementioned scan rate range.\textsuperscript{19,36,37} The volumetric capacitance of the SSC device was calculated from the $C-V$ curves at various scan rates (Figure 4d). Because the mass of all-solid-state (active material or entire device) SCs is observed to vary in the literature, volumetric capacitance is a fair parameter for a better comparison. At the low scan rate of 10 mV s$^{-1}$, the volumetric capacitance is 56 mF cm$^{-3}$, which is among the superior values of all-solid-state compressible SCs (Table S1). These findings indicate that chemical etching promotes the formation of more efficient EDLC active sites and that high graphitization is beneficial to rapid ion transport within the electrodes.

Another fascinating feature of this ENCF electrode is its natural ability to act as a compressible SC. To study the compression stability of the ENCF–SSC device, the as-prepared ENCF–SSC device was examined by $C-V$ and GCD measurements under different compression conditions, as shown in Figure 4e. When the as-prepared ENCF–SSC device was compressed from its normal state by 20, 40, and 60% (based on the whole height of the device, including substrates and separator), it almost maintains its curvilinear shape. Moreover, the long-term stability of the ENCF–SSC device under various compression states was further tested, and the corresponding data are given in Figures 4f and S11. Our ENCF–SSC device shows excellent long-term stability (less than 4% decrease in capacitance at each compression state). This suggests that the ENCF electrodes are highly stable and durable under compression. In general, the voltage window of a single SC device is too low (less than 1 V for SSC and less than 2 V for ASC) to power electronic equipment in practical applications. Therefore, several SC units were arranged in series to enhance the output voltage to necessary levels. In this case, a smart design of a PET/Au current collector was developed to assemble the ENCF–SSC device in series on one chip to produce high working voltages. As shown in Figure 4g, three ENCF–SSC units could be assembled on two PET collectors.
with patterned Au films to form “one” integrated device. The working-voltage output of the integrated device can be readily increased to 3.0 V (Figure 4h). Our integrated device design not only removed redundant interconnects between device units but also readily increased the voltage by increasing the unit numbers.

■ CONCLUSIONS

In summary, NCF electrodes were developed via a smart etching and catalytic process to fabricate highly compressible all-solid-state SCs. The as-prepared SC device based on treated carbon foam electrodes reveals enhanced specific capacitance and marked high-rate capability that are much higher than those presented in previous reports. Moreover, the excellent electrochemical performances are well maintained under a high compressive strain of 60% and after compression over 4000 cycles. The enhanced mechanical and electrochemical properties of the compressible ENCF electrodes are particularly promising for their application as next-generation flexible and elastic electronics.

■ METHODS

Preparation of ENCF. MS was purchased from Outlook Company (Chengdu). Through surface etching of MS fibers, ENCF precursor was obtained. Specifically, MS (5 × 3 × 2.5 cm³) was immersed in 50 mL of 10 mM KMnO₄ solution for 48 h at room temperature. The resulting etched MS was continuously washed in deionized water and ethanol until the final cleansing solution became clear. The obtained etched MS was vacuum-dried in an oven at 60 °C for 48 h. Then, the ENCF precursor was annealed in a tubular furnace at 700 °C under an argon atmosphere for 2 h (heating rate, 5 °C min⁻¹). For comparison, the NCF was annealed by the same steps, but without KMnO₄.

Fabrication of Solid-State SSCs. The LiCl/PVA gel electrolyte was prepared as previously reported.²⁵ PVA powder (2 g) and LiCl (4.24 g) were mixed in 20 mL of deionized water, and the mixture was heated at 85 °C under vigorous stirring for 2 h. The NCF—SSCs were assembled by two pieces of NCF and PET/Au film substrates with one piece of separator sandwiched between; the LiCl/PVA gel electrolyte was spread onto the electrode and the separator until the NCF was spread onto the electrode and the separator until the NCF was sandwiched between; the LiCl/PVA gel electrolyte (4.24 g) were mixed in 20 mL of deionized water, and the mixture was heated at 60 °C for 2 h. The ENCF—SSCs were annealed in a tubular furnace at 700 °C under an argon atmosphere for 2 h (heating rate, 5 °C min⁻¹). For comparison, the NCF was annealed by the same steps, but without KMnO₄.

Additional XPS patterns, TG curve, HRTEM image, pore-size distribution curve, Raman spectrum, stress-strain curves, electrochemical characterization of ENCF electrode, and I−V curves of ENCF and NCF (PDF)

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