Hierarchical porous carbon obtained from frozen tofu for efficient energy storage

Xuemei Sun, a Jianglin Ye, a Fei Pan, a Jin Xu, a Tao Cheng, a Xiangyang Wang, a Mujtaba Ikram b a and Yanwu Zhu a, *,d

Frozen tofu, as a carbon and nitrogen source, is converted to N (0.6–6.7 at%) and O (3.6–9.5 at%) co-doped porous carbon with a specific surface area of up to 3134 m² g⁻¹ by one-step carbonization-activation. This hierarchical carbon consists of a high volume of mesopores (1.11 cm³ g⁻¹) and micropores (0.71 cm³ g⁻¹) with a typical pore size distribution between 0.8 and 4 nm. Supercapacitors with the obtained carbon as electrodes exhibit a specific capacitance of 243 F g⁻¹ (measured at 0.1 A g⁻¹) in 1 M sulfuric acid (H₂SO₄) aqueous electrolyte with a capacitance retention of 93% after 10,000 cycles at 10 A g⁻¹. The carbon also exhibits a specific capacitance of 170 F g⁻¹ (measured at 1 A g⁻¹) with a good rate capability (135 F g⁻¹ at 20 A g⁻¹) in 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) ionic liquid electrolyte, providing an energy density of 72 W h kg⁻¹ (at an average power density of 889 W kg⁻¹). A supercapacitor fabricated from the carbon in the ionic liquid electrolyte can readily power 25 light-emitting diodes in parallel for more than 2 min after being charged for 25 s at a current density of 10 A g⁻¹. In addition, as an anode for Li-ion batteries, the porous carbon exhibits a high reversible charge capacity of 2120 mA h g⁻¹ in the first cycle (measured at 0.1 A g⁻¹) or 1035 mA h g⁻¹ after 300 cycles (measured at 1 A g⁻¹).

1. Introduction

Among various energy storage devices, electrochemical energy devices such as supercapacitors and lithium-ion batteries (LIBs) have attracted considerable attention because of their potential applications.¹,² Supercapacitors exhibit quick charge/discharge behavior and hence a good power density of more than 10 kW kg⁻¹, while LIBs exhibit a high energy density (typically 100–200 W h kg⁻¹) but need a longer charging time.³–⁵ Supercapacitors mainly store energy by two mechanisms: (i) pseudocapacitive electrodes store ions based on quick faradaic reactions at the electrode–electrolyte interface,⁶ and (ii) electrical double-layer capacitive electrodes store energy by the adsorption and desorption of ions on the large surface area of porous materials.⁷ In LIBs, lithium ions are transported between the anode and cathode, which leads to the storage or release of lithium ions via various mechanisms depending on the electrode materials.⁸ Carbon materials have been chosen as active materials for both commercial supercapacitors (e.g., activated carbon) and LIBs (e.g., graphite) because of their high electrical conductivity, tailored porosity, and chemical stability.⁹,¹⁰ It has been demonstrated that, in porous carbon materials, macropores serve as ion-buffering reservoirs in supercapacitors and mesopores provide channels for the transportation of ions to micropores, where they are eventually stored.¹¹,¹² In graphite anodes of LIBs the full intercalation of lithium ions results in an intercalated compound, LiC₆, which restricts the reversible Li-ion storage capacity to about 372 mA h g⁻¹ for graphite.¹³ Moreover, porous carbon has also been utilized as a scaffold for electrode materials or as the electrode in LIBs, as it is believed that the porous structure can shorten the path length for transportation of ions/electrons and increase the electrode-electrolyte contact areas, leading to an enhancement in the transport kinetics and hence the power density.¹⁴ The energy density of commercial supercapacitors is typically less than 6 W h kg⁻¹, which is far from the demand of future electrical devices.¹⁵ Meanwhile, the capacity and rate capability of LIB anodes also need to be further improved. For both applications, porous carbon with good electrical conductivity and a tailored three-dimensional (3D) structure is desired.

During the past few decades, various porous carbon materials have been developed using strategies such as activation,¹⁶ self-assembly,¹⁷ and templating.¹⁸ Compared to self-assembly and templating, which are inclined to create macropores and mesopores, activation is an efficient way to increase the surface area
of carbon by forming numerous micropores.\textsuperscript{19} Activated carbon is commercially used in supercapacitors, as it has a large specific surface area (SSA) of more than 2000 m\(^2\) g\(^{-1}\) and other features.\textsuperscript{20} Activation can also enable efficient processing of nanostructured carbon precursors for obtaining novel carbon materials. For example, upon KOH activation of microwave-exfoliated graphite oxide, graphene platelets can be completely restructured to a 3D porous carbon with a SSA of up to 3100 m\(^2\) g\(^{-1}\) and a pore size distribution of 0.6–5 nm.\textsuperscript{21} Zheng \textit{et al.} reported a porous carbon consisting of macropores (several micrometers in size) and micropores (~0.47 nm in size) by KOH activation of C\(_{70}\) microtubes.\textsuperscript{22} Proper heteroatom doping can enhance the wettability and conductivity of carbon materials.\textsuperscript{23} In addition, nitrogen atoms are electron donors and can promote the n-type conductivity in a graphite matrix.\textsuperscript{24} As the anode of LIB, N-doping carbon has been shown to benefit Li insertion due to the hybridization between the long pair electrons of nitrogen with \(\pi\) electrons of carbon.\textsuperscript{25} Recently, Tan \textit{et al.} obtained N-doped (7.5 wt\%) porous carbon by activating C\(_{60}\) with KOH in an ammonia atmosphere; the carbon demonstrated a reversible capacity of 1900 mA h g\(^{-1}\) at 0.1 A g\(^{-1}\) and a capacity of 600 mA h g\(^{-1}\) after 800 cycles at 2 A g\(^{-1}\).\textsuperscript{26}

Compared to porous carbon materials derived from coal, pitch, polymers, and other sources, those derived from biomass may be more eco-friendly.\textsuperscript{27} Researchers have shown that porous carbons for energy storage applications can be obtained from various biomass sources such as rice husk,\textsuperscript{28} rice straw,\textsuperscript{29} algae,\textsuperscript{30} and water bamboo.\textsuperscript{31} For example, Li and co-workers reported a one-step pyrolysis-activation synthesis to convert willow catkin into a cross-linked laminar porous carbon co-doped with N and sulphur (S).\textsuperscript{32} The carbon displayed an outstanding electrochemical performance with a specific capacitance of 298 F g\(^{-1}\) at 0.5 A g\(^{-1}\) in 1 M Na\(_2\)SO\(_4\) and superb cycling stability with only 2% capacitance loss after 10 000 cycles at 5 A g\(^{-1}\). Tofu, which contains moisture, proteins, carbohydrates, and trace amounts of minerals, is an abundant resource and has been regarded as a natural carbon and nitrogen resource.\textsuperscript{33} Recently, Ouyang \textit{et al.} reported the molten salt synthesis of densely N-doped porous carbon from tofu,\textsuperscript{34} in which an eutectic mixture of LiCl/KCl (45/55 by weight) was used as the solvent to dilute LiNO\(_3\), which acted as the activation agent. The as-obtained carbon (SSA: 1202 m\(^2\) g\(^{-1}\), N-content: 4.72 wt\%, density: \(\sim 0.84 \text{ g cm}^{-3}\)) exhibited a capacitance of 73.2 F g\(^{-1}\) at 0.2 A g\(^{-1}\) in a 1 M Na\(_2\)SO\(_4\) symmetric supercapacitor. Wang \textit{et al.} synthesized a N-doped porous carbon through pre-carbonization and KOH activation of tofu, achieving a SSA of 2471 m\(^2\) g\(^{-1}\) with abundant macropores/mesopores.\textsuperscript{35} The carbon exhibited a capacitance of 181 F g\(^{-1}\) at 1 A g\(^{-1}\) and 111 F g\(^{-1}\) at 20 A g\(^{-1}\) in a 1 M 1-butyl-3-methylimidazolium tetrafluoroborate/acetonitrile (BMIMBF\(_4\)/AN) soft-package symmetric supercapacitors. When the carbon was used as the anode for LIBs, it exhibited a discharge capacity of 986 mA h g\(^{-1}\) at 0.1 A g\(^{-1}\) with a coulombic efficiency (CE) of 56.7%. Clearly, tofu is a promising precursor to produce carbons for use in energy storage; however, further development is needed for enhanced comprehensive performances such as enhanced capacitance in symmetric supercapacitors and rate capability/cyclic stability in LIBs.

In this study, a N- and O co-doped porous carbon has been prepared by a one-step carbonization-activation of frozen tofu, which is popular in Asian food. Owing to the advantage of vacuum freeze-drying,\textsuperscript{26} a laminar precursor (a mixture of dried tofu and KOH) with abundant macropores can be formed by ice sublimation. The as-obtained carbon (named aTC) shows high meso- and microporous volumes of 1.11 cm\(^3\) g\(^{-1}\) and 0.71 cm\(^3\) g\(^{-1}\), respectively, and a large SSA of 3134 m\(^2\) g\(^{-1}\) with co-doped N and O (N: 0.6–6.7 at\%, O: 3.6–9.5 at\%). As an electrode in a symmetric supercapacitor, aTC exhibits capacitances of 243 F g\(^{-1}\) at 0.1 A g\(^{-1}\) and 143 F g\(^{-1}\) at 50 A g\(^{-1}\) in 1 M H\(_2\)SO\(_4\) and a capacitance retention of 93% after 10 000 cycles at 10 A g\(^{-1}\). It also shows a capacitance of 170 F g\(^{-1}\) at 1 A g\(^{-1}\) and a capacity retention of 80% at 20 A g\(^{-1}\) in BMIMBF\(_4\). With an energy density of 72 W kg\(^{-1}\) at an average power density of 889 W kg\(^{-1}\) (both normalized to the mass of the electrodes), a supercapacitor assembled using aTC in the ionic liquid can power 25 red light-emitting diodes (LEDs) in parallel. Besides, as an anode in a LIB, aTC shows a high reversible capacity of 2120 mA h g\(^{-1}\) at 0.1 A g\(^{-1}\) in the first cycle and a specific capacity of 900 mA h g\(^{-1}\) at 1 A g\(^{-1}\) or 125 mA h g\(^{-1}\) at 10 A g\(^{-1}\).

2. Experimental

2.1 Preparation of aTC samples

Frozen tofu was obtained from a local supermarket and all frozen tofu samples were purchased from the same batch to ensure the similar source. Typically, tofu is manufactured by grinding soy bean to soy milk and boiling it with bittern under slow stirring. The precipitates formed as a result of the colloidal coagulation are then shaped using a pressing mold. A typical pressed tofu consists of 80 wt% water, 7.8 wt% protein, 4.2 wt% lipid, and 2 mg g\(^{-1}\) of calcium.\textsuperscript{33} Frozen tofu is the product of tofu after being frozen in a freezer. Potassium hydroxide (KOH, Sinopharm Chemical Reagent Co., Ltd, China, AR) was used as received.

To prepare aTC, the frozen Tofu was washed with deionized water to remove dust and desiccated by freeze-drying. In a typical preparation, \(\sim 12\) g of dried tofu was mixed with KOH in weight ratios (KOH to tofu) of 0.2, 0.4, 0.6, and 0.8 in 150 mL of deionized water and sonicated for 1 h to obtain homogeneous mixtures. Then the mixtures were frozen in a freezer (\(\sim 18^\circ\)C) for 12 h, and were vacuum freeze-dried for 5 days in a lyophilizer. The carbonization of the freeze-dried tofu/KOH was performed under an argon (Ar) gas flow of 100 sccm at 800 °C for 2 h at a heating rate of 5 °C min\(^{-1}\). After grinding, the powders were washed with 2 M hydrochloric acid (HCl) under stirring for 12 h and flushed with deionized water. The samples were then dried at 60 °C in an oven for 24 h and named aTC-x (x: the mass ratio of KOH/tofu, e.g., aTC-0.2). Besides, a control sample was prepared by the direct carbonization of the frozen tofu under a 100 sccm Ar gas flow at 800 °C for 2 h without KOH, which is represented as TC.
2.2 Characterization

The morphologies of the samples were characterized by scanning electron microscopy (SEM, JSM-6700F) and transmission electron microscopy (TEM, JEOL 2100F). The structural features were characterized by X-ray diffraction (XRD, D/max-TTR III) with Cu Kα radiation (V = 40 kV, I = 200 mA) at a scan rate of 5° min⁻¹ from 10° to 80° (2θ) and Raman spectroscopy (Renishaw inVia Raman Microscope, 532 nm laser, 5 mW). The chemical composition was examined by Fourier transform infrared spectroscopy (FT-IR, NICOLET 8700) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250). The SSA and pore size distribution were analyzed by N₂ adsorption/desorption (Quantachrome, Autosorb-iQ) measurements using the Brunauer–Emmett–Teller (BET) method (calculated in the linear relative pressure range of 0.005–0.05) and the quenched solid density functional theory (QSDFT) model, respectively.

2.3 Electrochemical evaluations

2.3.1 Supercapacitors. A mixture of 95 wt% aTC and 5 wt% polytetrafluoroethylene (5 wt% dispersion in water) was mixed using a mortar and pestle, rolled into a membrane and then punched into electrodes. The as-fabricated electrodes were dried at 110 °C for 48 h in an oven before measurements. Two identical (by weight and size, see Table S1, ESI†) electrodes were assembled in a cell for supercapacitor evaluation. Celgard® 3501 was used as the separator. Electrolytes such as 1 M sulfuric acid (H₂SO₄), 6 M potassium hydroxide (KOH), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) dissolved in acetonitrile (AN) in a weight ratio of 1 : 1, and 1 M tetraethylammonium tetrafluoroborate (TEABF₄) dissolved in AN were obtained from Sigma Aldrich. Platinum and carbon-coated aluminium foils (Exopack™ 0.5 mil, 2-side coating) were used as the current collectors in the aqueous and ionic liquid electrolytes, respectively. The assembly of the cells in the ionic liquids was performed in an Ar-filled glove box (OMNI-LAB, VAC, USA). The specific capacitance C, energy density E, and power density P of the electrodes were calculated using galvanostatic charge–discharge (GCD) curves according to the following formulae:

\[ C = \frac{4I_{\text{cons}}/(mdV_{\text{max}}/dt)}{\text{ms}} \]

\[ E = CV_{\text{max}}^2/8 \]

and \[ P = E/t \]

where \( I_{\text{cons}} \) is the charge/discharge current, m is the total mass of the two electrodes, \( t \) is the discharge time, and \( V_{\text{max}} \) is the initial voltage before discharge. The effective series resistance (ESR), \( R_{\text{ESR}} \), was estimated by substituting the voltage drop at the beginning of the discharge, \( V_{\text{drop}}/(2I_{\text{cons}}) \), into the formula \( R_{\text{ESR}} = V_{\text{drop}}/(2I_{\text{cons}}) \). Cyclic voltammetry (CV), Galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) were performed in the frequency range of 100 kHz–0.01 Hz on an electrochemical station (PARSTAT 4000, Princeton Applied Research).

2.3.2 Li-ion batteries. The performance of aTC as an anode for LIBs was evaluated at room temperature using coin cells (CR2032) on LAND CT2001A in the voltage range of 0–3.0 V vs. Li+/Li (lithium foil brought from Shenzhen Bijuian Electronic, Inc.). To prepare the working electrodes, the as-prepared aTC samples were mixed with Ketjen black and poly(vinylidene fluoride) (PVDF) in a weight ratio of 70 : 10 : 20 to form a slurry, which was then coated on copper foil, followed by drying in a vacuum oven at 50 °C for 12 h. Typically, the electrodes have a loading of around 0.4 mg cm⁻². The cells were assembled in an Ar-filled glove box with a 1 M lithium hexafluorophosphate (LiPF₆) solution in ethylene carbonate (EC) and diethyl carbonate (DEC) at 1 : 1 (v/v) as the electrolyte.

3. Results and discussion

Fig. 1 illustrates the preparation of the N and O co-doped hierarchical porous carbon (aTC) from frozen tofu by one-step carbonization-activation. After the frozen tofu (Fig. 1a) was freeze-dried, the dried tofu had a loose and crumbly texture (Fig. 1b). Upon mixing the dried tofu with the KOH solution, a milk-like suspension (Fig. 1c) was formed due to the denaturation or hydrolysis reaction of proteins and carbohydrates. Then, the mixed suspension was frozen at −18 °C and vacuum freeze-dried to obtain a yellow precursor with a soft laminar framework (Fig. 1d). Energy dispersive spectroscopy (EDS) mapping indicates that the C, O, and K signals are homogeneously distributed on the surface of the precursor as shown in Fig. S1 a–d (ESI†). Compared to the typical KOH activation of pre-carbonized materials, our procedure is beneficial for a uniform mixture of KOH with the precursor and the subsequent activation. After grinding and washing the carbonized product, a black powder was obtained as shown in Fig. 1e. Based on previous studies on the activation of carbon using KOH, aromatization and development of the graphitic structure may occur in the tofu/KOH mixtures at temperatures below 700 °C; the KOH activation could start above 700 °C. Then the reconstruction of the carbon species in the latter process results in the porosity and high SSA of aTC.

As shown in Fig. S1e (ESI†), TC derived from the frozen tofu without KOH activation possesses a bulk morphology with...
particle sizes from 1 to 10 μm and macropores. With the introduction of KOH, aTC-0.2 shows an irregular morphology (Fig. S1f, ESI†) with some mesopores, which can be further seen in the TEM image (Fig. S1j, ESI†). When the KOH/tofu ratio is increased, aTC-0.4 shows a sponge-like structure (Fig S1g, ESI†) and a hierarchical porous carbon with a large quantity of macropores and mesopores around the skeleton is observed by TEM (Fig S1k, ESI†). Remarkably, when the KOH/tofu ratio is further increased to 0.6, aTC-0.6 seems to be etched more significantly, and the macropores in the sponge-like structure are destroyed, forming small fragments (Fig. 2a). These small fragments possess more edges (Fig. 2b), which may facilitate the adsorption of the oxygen and nitrogen species and so on.10

The TEM image in Fig. 2c reveals a high fraction of mesopores in the fragments; the high-resolution TEM image (Fig. 2d) shows an amorphous morphology with wrinkled carbon walls. From the diffraction pattern of aTC-0.6 (the inset of Fig. 1d), a subtle concentric annulus can be seen, indicating a partially graphitic structure with an interlayer distance of approximately 0.417 nm. As predicted, when the amount of KOH is further increased, the structure of aTC-0.8 is severely etched into smaller fragments (Fig. S1h, ESI†), and the TEM image shows a flake-like framework (Fig. S1i, ESI†).

The structural features were investigated by XRD and nitrogen adsorption–desorption measurements. Fig. 3a shows the powder XRD patterns, in which the (100) reflections at around 43° indicate the presence of honeycomb structures formed by the sp²-hybridized carbons during the interlayer condensation.11

The (002) reflections between 20° and 25° indicate the small domains of the coherent and parallel stacking of the graphitic layers.42 The (100) and (002) reflections of the aTC samples have a lower intensity and a broader shape compared to those of TC, suggesting the disordered porous structure. As observed from the isotherm curves shown in Fig. 3b, all the samples show a typical I feature (according to IUPAC) with significant adsorption at low relative pressures and the adsorption branch levels off at high relative pressures, indicating the existence of a hierarchical structure.43 The H4-type hysteresis loop (the inset of Fig. 3b) in the desorption curve of aTC-0.6 reveals the formation of plate-like meso- and micropores.44 As confirmed by QSDFT (Fig. 3c), aTC-0.2, aTC-0.4, and aTC-0.6 possess numerous micropores (~0.8 nm and ~1.2 nm) and small mesopores (~2.4 nm). The pores could provide accessible pathways to the electrolyte ions, such as hydrated H⁺ (0.28 nm) and HSO₄⁻ (0.37 nm), and BMIM⁺ (0.402 nm), BF₄⁻ (0.48 nm), and TEA⁺ (0.67 nm).45,46

More detailed characteristics of all the samples are listed in Table 1. From the table, we can see that aTC-0.6 has a SSA of 3134 m² g⁻¹, in contrast to 633 m² g⁻¹ of TC. In total SSA, which calculated from pores with size >2 nm, has shown 10 time increase from 102 m² g⁻¹ for TC to 1061 m² g⁻¹ for aTC-0.6. However, when the KOH amount was increased further, the SSA of aTC-0.8 decreased to 2439 m² g⁻¹ due to the collapsed pore structure.

The Raman spectra of TC and aTC-0.6 (Fig. 3d) show characteristic D and G peaks at 1350 cm⁻¹ and 1575 cm⁻¹, respectively.47 The relative intensity ratio of D to G bands (I_D/I_G), as calculated from the peak height, could be used as an indication of the defects degree of the carbon materials.16

TC has an I_D/I_G value of 0.994, while aTC-0.6 shows a slightly larger I_D/I_G value of 1.004. The blue shift of the D band and the red shift of the G band could be attributed to the decreased nitrogen content in aTC-0.6.47

XPS analysis was conducted to evaluate the surface chemistry and the elemental composition of all the carbon samples (Table 2). As we can see, the C content gradually increases with an increased KOH/tofu ratio, but the opposite tendency is observed for the doping of the heteroatoms (N and O). The N and O contents in aTC-0.6 are ~0.82 at% and ~4.18 at%, respectively, indicating that most of the N and O functional groups were removed by the chemical activation. The deconvolution (Fig. 3e) of the N 1s spectrum of aTC-0.6 shows the existence of pyridinic N (398.2 eV), pyrrolic N (400.2 eV), graphitic N (400.8 eV), and amino N (401.5 eV), in which graphitic N is predominant.48 The C 1s spectrum of aTC-0.6 (Fig. 3f) could also be deconvoluted into five peaks: sp² C (284.7 eV), sp³ C (285.1 eV), C–N (285.9 eV), ...

Fig. 3 (a) XRD of the TC and aTC samples prepared from frozen tofu under different activation conditions. (b) Nitrogen adsorption–desorption isotherms of the TC and aTC samples. The inset shows the isotherm of aTC-0.6 in the relative pressure range of 0.2 to 1. (c) Pore size distribution of the TC and aTC samples calculated using DFT and nitrogen adsorption isotherms. (d) Raman spectra of aTC-0.6 and TC. (e) XPS N 1s and (f) XPS C 1s spectra of aTC-0.6.
Table 1 Structural properties of the samples derived from frozen tofu

<table>
<thead>
<tr>
<th>Samples</th>
<th>S_{BET} (m^2 g(^{-1}))</th>
<th>V_{total} (cm^3 g(^{-1}))</th>
<th>S_{micro} (m^2 g(^{-1}))</th>
<th>S_{meso} (m^2 g(^{-1}))</th>
<th>V_{micro} (cm^3 g(^{-1}))</th>
<th>V_{meso} (cm^3 g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC</td>
<td>633</td>
<td>0.42</td>
<td>531</td>
<td>102</td>
<td>0.2</td>
<td>0.22</td>
</tr>
<tr>
<td>aTC-0.2</td>
<td>2325</td>
<td>1.18</td>
<td>1530</td>
<td>640</td>
<td>0.64</td>
<td>0.54</td>
</tr>
<tr>
<td>aTC-0.4</td>
<td>2724</td>
<td>1.29</td>
<td>1570</td>
<td>721</td>
<td>0.69</td>
<td>0.6</td>
</tr>
<tr>
<td>aTC-0.6</td>
<td>3134</td>
<td>1.82</td>
<td>1406</td>
<td>1061</td>
<td>0.71</td>
<td>1.11</td>
</tr>
<tr>
<td>aTC-0.8</td>
<td>2439</td>
<td>1.69</td>
<td>1282</td>
<td>1009</td>
<td>0.66</td>
<td>1.03</td>
</tr>
</tbody>
</table>

\(^{a}\) BET (Brunauer–Emmett–Teller) surface area. \(^{b}\) Total pore volume, measured at P/P_0 = 0.995. \(^{c}\) Micropore surface area, calculated from the nitrogen sorption isotherm with the t-plot method. \(^{d}\) Mesopore surface area, calculated from the nitrogen sorption isotherm with the t-plot method. \(^{e}\) Micropore volume, based on density functional theory (DFT). \(^{f}\) Mesopore volume, based on density functional theory (DFT).

Table 2 XPS elemental composition of the samples derived from frozen tofu

<table>
<thead>
<tr>
<th>Elements</th>
<th>TC (%)</th>
<th>aTC-0.2 (%)</th>
<th>aTC-0.4 (%)</th>
<th>aTC-0.6 (%)</th>
<th>aTC-0.8 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>83.8</td>
<td>89.5</td>
<td>95</td>
<td>95</td>
<td>95.6</td>
</tr>
<tr>
<td>N</td>
<td>6.7</td>
<td>1.24</td>
<td>0.76</td>
<td>0.82</td>
<td>0.6</td>
</tr>
<tr>
<td>O</td>
<td>9.5</td>
<td>8.75</td>
<td>4.11</td>
<td>4.18</td>
<td>3.6</td>
</tr>
</tbody>
</table>

C–O (286.7 eV), and C==O (287.8 eV), revealing the presence of a hybridized carbon system. \(^{48}\)

3.1 Supercapacitors

The electrochemical performances of the carbon samples as supercapacitor electrodes were characterized by CV, GCD and EIS in 1 M H_2SO_4 at room temperature. The GCD curves (Fig. 4a) of TC and aTC obtained at a current density of 1 A g\(^{-1}\) show a nearly symmetrical triangular profile. As calculated from the discharge curves, TC, aTC-0.2, aTC-0.4, aTC-0.6, and aTC-0.8 show specific capacitances of 35 F g\(^{-1}\), 149 F g\(^{-1}\), 173 F g\(^{-1}\), 208 F g\(^{-1}\), and 181 F g\(^{-1}\), respectively. Clearly, the activation has dramatically enhanced the electrochemical performance. From Fig. 4b we can see that all the samples exhibit rectangular CV curves in the voltage range of 0.0–1.0 V at a sweeping rate of 100 mV s\(^{-1}\), indicating a typical electrical double-layer behavior. The barely-observed pseudopotential behaviour could be ascribed to the low extent of N/O doping and the configuration of symmetric supercapacitors. \(^{49}\) In the Nyquist plots shown in Fig. 4c and the inset, a semicircle associated with the bulk and charge-transfer resistance in the high-frequency region and a straight line representing the electrolyte diffusion in the porous electrode in the low-frequency region are observed. \(^{50}\) The higher bulk and charge-transfer resistance of aTC-0.6 and aTC-0.8 may be caused by the lower heteroatom content and the vast boundary of the small flake-like structure, respectively. The straight line with an angle of 45° corresponds to the Warburg resistance, which is the result of ion diffusion across the electrolyte-electrode interface. \(^{51}\) All the aTC samples show almost vertical lines parallel to the imaginary axis, which shall be attributed to their high SSA values and interconnected hierarchical porous structure. From the GCD curves of aTC-0.6 at different current densities in Fig. 4d, the specific capacitance was calculated to be 243 F g\(^{-1}\) at 0.1 A g\(^{-1}\), 209 F g\(^{-1}\) at 0.5 A g\(^{-1}\), 156 F g\(^{-1}\) at 0.1 A g\(^{-1}\) and 143 F g\(^{-1}\) at 0.5 A g\(^{-1}\), indicating an excellent rate performance. Correspondingly, aTC-0.6 maintains a roughly rectangular curve even at a fast sweeping rate of 1 V s\(^{-1}\) (Fig. 4e), implying efficient charge transfer and electrolyte diffusion. As shown in Fig. 4f, after 10 000 cycles of measurements at 10 A g\(^{-1}\) in 1 M H_2SO_4, the capacitance of aTC-0.6 decayed to about 93.7%. Considering the more spindle-shaped CV curve (Fig. S2a, ESI†) and the increased slope at low-frequency in the EIS plot (Fig. S2b, ESI†) after cycling, the capacitance fading of aTC-0.6 in 1 M H_2SO_4 could be attributed to the increased resistance of the electrodes. Besides, the supercapacitors based on aTC were also tested in 6 M KOH (Fig. S4, ESI†); the results are similar to those obtained in 1 M H_2SO_4, with aTC-0.6 showing the highest capacitance (180 F g\(^{-1}\)) at 1 A g\(^{-1}\).

Despite the low content, the effect of N and O co-doping was investigated by annealing aTC-0.6 in H_2 (leading to a sample named aTC-0.6-anneal-H_2); the elemental composition and porosity of aTC-0.6-anneal-H_2 are presented in Table S1 and Fig. S3 (ESI†). After annealing, the N and O contents further reduced to 0.46 at% and 2.79 at%; the SSA and pore volume reduced to 2441 m^2 g\(^{-1}\) and 1.56 cm^3 g\(^{-1}\), respectively. As shown in Fig. S3c (ESI†), aTC-0.6-anneal-H_2 undergoes charging longer than discharging in 1 M H_2SO_4 and the discharging capacitance of 179 F g\(^{-1}\) at 1 A g\(^{-1}\) is lower than 208 F g\(^{-1}\) at 1 A g\(^{-1}\) for aTC-0.6, but close to aTC-0.8 (181 F g\(^{-1}\)). The Nyquist plot of aTC-0.6-anneal-H_2 (Fig. S3d, ESI†) shows higher bulk and charge transfer resistances compared to the other two, even though aTC-0.8 has a similar pore structure. The results suggest that the SSA and porosity have more significant effects than heteroatom doping on the capacitance in our work. The longer charging of aTC-0.6-anneal-H_2 could be related to the
lower surface wettability of the electrolyte due to the lower N/O contents.

The supercapacitor performance of aTC was also evaluated using ionic liquids, such as BMIMBF4/AN and TEABF4/AN, as the electrolytes. As shown in Fig. 5a, aTCs especially aTC-0.6 exhibits rectangular CV curves in BMIMBF4/AN. Based on the discharge curves at 1 A g\(^{-1}\) (Fig. 5b), aTC-0.2, aTC-0.4, aTC-0.6, and aTC-0.8 show specific capacitances of 113 F g\(^{-1}\), 145 F g\(^{-1}\), 170 F g\(^{-1}\), and 152 F g\(^{-1}\), respectively. Meanwhile, the Nyquist plots (Fig. 5c) show a gradually decreasing semicircle diameter with increasing KOH ratio, revealing the decreased charge transfer resistance in the aTC samples due to the increased number of mesopores. The semicircles have larger radii in the ionic liquid electrolyte than in the aqueous electrolyte, indicating the higher charge-transfer resistance in the former owing to the larger ion size and the higher electrolyte viscosity. Fig. 5d and e show the CV and GCD curves of aTC-0.6 at different sweeping rates and current densities, respectively. We can see that aTC-0.6 shows nearly rectangular shaped curves without polarization even at 500 mV s\(^{-1}\) and a high capacitance of 135 F g\(^{-1}\) with a small voltage drop of 0.302 V at 20 A g\(^{-1}\). As calculated from the GCD curves, aTC-0.6 exhibits an energy density of 72 W h kg\(^{-1}\) at a power density of 889 W kg\(^{-1}\) and an energy density of 38 W h kg\(^{-1}\) at a high power density of 53.4 kW kg\(^{-1}\). The Ragone plots shown in Fig. 5f indicate that the supercapacitor performance of aTC-0.6 is superior or comparable to those of other biomass-derived carbon materials.\(^{30,30,51-56}\) In addition, the as-prepared symmetric supercapacitor based on aTC-0.6 could readily power 25 red LEDs in parallel (the inset of Fig. 5f) for more than 2 min after being charged for 25 s at a current density of 10 A g\(^{-1}\) (Video S1, ESI†). The cycling measurement of aTC-0.6 (Fig. S5a, ESI†) shows that 83% of capacitance remains after 4000 cycles performed at a current density of 5 A g\(^{-1}\). As shown in Fig. S5b (ESI†), the CV curve of aTC-0.6 after cycling has an obvious polar potential; the Nyquist plots of aTC-0.6 after cycling show high bulk and charge transfer resistances and ion diffusion resistance compared to those obtained in the initial cycle (Fig. S5d, ESI†). Therefore, the capacitance fading in the organic electrolyte could be attributed to the side reaction and the electrode change at high potentials. In addition, aTC-0.6 also shows good compatibility to a commercial 1 M TEABF\(_4\) electrolyte up to 2.7 V (Fig. S6, ESI†) with good rate capability (130 F g\(^{-1}\) at 1 A g\(^{-1}\) and 100 F g\(^{-1}\) at 50 A g\(^{-1}\)). To obtain a hint about the mechanism of the improved supercapacitor performances of the aTC samples, the capacitance was normalized to SSA and also separated based on the fraction of SSA from micropores or mesopores, as a function of current density in 1 M H\(_2\)SO\(_4\) and 1 M BMIMBF\(_4\)/AN electrolytes, as shown in Fig. S7 (ESI†). The surface-area-normalized capacitance of aTC-0.8 is higher than those of other carbon materials, indicating the beneficial effects of the surface area and pores. Although the aTC samples exhibit a similar capacitance contributed by the micropores, the contribution from the mesopores shows a more significant effect on the capacity, which were largely developed upon KOH activation.

### 3.2 Li-ion batteries

Owing to their large surface areas, hierarchical porous structures, and heteroatom doping, the aTC samples are also considered as promising anode materials for LIBs. Fig. 6a shows the CV profiles of aTC-0.6 for the first, second, and third cycles at a scan rate of 0.1 mV s\(^{-1}\). A pronounced cathodic peak at around 0.7 V is observed during the first cycle, which could be attributed to the electrolyte decomposition and the formation of a solid electrolyte interphase (SEI) layer on the surface of the electrode material.\(^{13}\) The intensity of this peak remarkably decreased in the following cycles, indicating the occurrence of irreversible reactions in the first cycle such as the formation of lithium organic compounds. Fig. 6b shows the discharge/charge profiles for aTC-0.6 for the first three cycles at 0.1 A g\(^{-1}\) between 0 and 3.0 V. The plateau observed at ~0.9 V in the first cycle also corresponds to the formation of the

**Fig. 5** (a) CV curves of aTCs at a sweeping rate of 100 mV s\(^{-1}\) in BMIMBF\(_4\)/AN. (b) GCD curves of aTCs at 1 A g\(^{-1}\). (c) Nyquist plots of aTCs. (d) CV curves of aTC-0.6 at different sweeping rates. (e) GCD curves of aTC-0.6 at different current densities. (f) Comparison of the Ragone plots of aTC-0.6 in BMIMBF\(_4\)/AN with those of biomass-derived carbon materials.\(^{30,30,51-56}\) The inset shows a module of 25 red LEDs (2.2 V) being powered by a single supercapacitor device made up of aTC-0.6.

**Fig. 6** (a) CV curves at 0.1 mV s\(^{-1}\) and (b) GCD profiles at 0.1 A g\(^{-1}\) for aTC-0.6 in a half-cell with 1 M LiPF\(_6\) in EC/DMC as the electrolyte. (c) Rate capability of TC, aTC-0.2, aTC-0.4, aTC-0.6, and aTC-0.8 tested at various current densities ranging from 0.1 to 20 A g\(^{-1}\). (d) Comparative cycling performance of different samples at 1 A g\(^{-1}\) and the related CE of aTC-0.6.
theoretical capacity of graphite (372 mA h g\(^{-1}\)). Although the initial CE is 56.5%, it is still much higher than those of mesoporous carbon nanosheets (<30%),\(^{57}\) nitrogen-doped carbon nanosheets (49.2%),\(^{58}\) and nitrogen-doped carbon nanofibers (48.4%).\(^{59}\)

After the second cycle, a reversible specific capacity of 2013 mA h g\(^{-1}\) was obtained with a CE of almost 100%. The rate performance shown in Fig. 6c indicates that aTC-0.6 exhibits the highest capacity at higher currents, coinciding with the supercapacitor evaluation results. As shown in Fig. S8 (ESI\(^{\ddagger}\)), the large radii of the semicircles, compared to the reported results, indicate large contact and SEI resistances which severely weaken the transport and insertion of Li\(^+\) at high current density and thus may result in an unsatisfactory rate capability (290 mA h g\(^{-1}\) at 5 A g\(^{-1}\) and 125 mA h g\(^{-1}\) at 10 A g\(^{-1}\)).\(^{10,58}\) In addition, TC-0.6 also outperforms the other samples in terms of cycling performance with a capacity of 1035 mA h g\(^{-1}\) at 1 A g\(^{-1}\) after 300 cycles (Fig. 6d).

**Conclusions**

In summary, a N-doped hierarchical porous carbon has been successfully derived from a low-cost, eco-friendly, and scalable biomaterial precursor, frozen tofu, via one-step carbonization-activation. Upon optimizing the activation conditions aTC-0.6 exhibited a high SSA of 3134 m\(^2\) g\(^{-1}\) and a large pore volume of 1.82 m\(^3\) g\(^{-1}\), superior to those of conventional biomass-derived activated carbon materials. The aTC-0.6-based supercapacitors showed a high specific capacitance of 243 F g\(^{-1}\) in 1 M H\(_2\)SO\(_4\) and a remarkable energy density of 72 W h kg\(^{-1}\) at an average power density of 889 W kg\(^{-1}\) in BMIMBF\(_4\)/AN. aTC-0.6 also showed excellent performance as a LIB electrode with a capacity of 2120 mA h g\(^{-1}\) at 0.1 A g\(^{-1}\) or 1035 mA h g\(^{-1}\) at 1 A g\(^{-1}\) with negligible capacity decay after 300 cycles at 1 A g\(^{-1}\). Our method provides a potentially useful strategy to design carbon electrode materials from abundant sustainable resources with superior performance for supercapacitors and LIBs.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

This work was supported by the China Government 1000 Plan Talent Program; the China MOE NCET Program and the National Natural Science Foundation of China (Grant No. 51322204, 51772282).

**Notes and references**


