Biomass-derived mesopore-dominant porous carbons with large specific surface area and high defect density as high performance electrode materials for Li-ion batteries and supercapacitors

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ABSTRACT

Porous carbons with high specific surface area and high defect density have been prepared through direct carbonization of cattle bones without any additional activators and templates. Benefiting from self-activation induced by hydroxyapatites within the cattle bones, the high-defect porous carbons obtained at 1100 °C (PC-1100) possess the high specific surface area (2096 m² g⁻¹), largest mesopore volume (1.829 cm³ g⁻¹), a narrow mesopore size distribution centered at approximately 4.0 nm and good electrical conductivity (5141 S m⁻¹). Due to the synergistic effect of the defects and pores, PC-1100 as the anode for Li-ion battery exhibits a high reversible capacity of 1488 mA h g⁻¹ after 250 cycles at 1 A g⁻¹ and 661 mA h g⁻¹ after 1500 cycles at 10 A g⁻¹. Even at 30 A g⁻¹, PC-1100 can still deliver a high reversible capacity of 281 mA h g⁻¹, showing superior lithium storage capability. Moreover, the symmetric supercapacitor based on the PC-1100 in neat EMIM-BF₃ electrolyte delivers a high energy density of 109.9 W h kg⁻¹ at a power density of 4.4 kW kg⁻¹, and maintains an energy density of 65.0 W h kg⁻¹ even at an ultrahigh power density of 81.5 kW kg⁻¹, as well as a superior cycling performance (96.4% of the capacitance retention after 5000 cycles).

1. Introduction

Driven by the increased concern about energy and environment issues, high-performance energy-storage devices are needed for renewable energy [1,2], and the application of electric vehicles requires devices that are low-cost and highly safe with high energy density and power density [3]. Supercapacitors (SCs) and lithium-ion batteries (LIBs) are two typical energy-storage devices that have been widely studied in the past few decades [1,4]. However, SCs and LIBs still possess multiple disadvantages (i.e., the former have high power density but low energy density [5,6], and the cathode and anode electrode materials of the latter still need to be improved on rate capability and long cycling performance [7–9]). Carbon-based materials are promising electrode materials for SCs and LIBs due to their low costs, high safety and good electrical conductivities [10]. However, as the commercial anode materials for LIBs, graphitic carbons possess a low theoretical capacity (372 mA h g⁻¹) as well as a poor lithium (Li) diffusion kinetics [11]. Commercially available activated carbons are used as the main electrode materials for SCs but still show low specific capacitance especially at a high current load [12]. Therefore, new carbonaceous materials with integrated high capacities and good rate capabilities must be designed and prepared for LIBs and SCs, and the principles should be based on the components of the capacity for LIBs and SCs. The total storage of electrode materials for LIBs is composed of three parts: (i) the faradaic contribution from the Li ions insertion process, (ii) the faradaic contribution from the charge-transfer process with surface atoms (pseudocapacitance), and (iii) the nonfaradaic contribution from the double layer effect (double layer capacitance) [13,14]. The storage of electrode materials for SCs is composed of the latter two [6].

Defect engineering is a powerful approach for improving the capabilities of electrode materials for LIBs and SCs [15,16]. The defects on the carbon layers (e.g., vacancies and edges) can adsorb more Li ions to increase the capacity from the faradaic contribution, and change the surface structure to increase the double layer capacitance [16–18]. Moreover, some heteroatoms that are doped on the surface carbon layers contribute to the reversible energy storage through combining with Li ions or electrolyte ions to increase the pseudocapacitance [19–23]. Apart from the defects, creating pores to increase surface area, and tailoring the pore size and pore size distribution (PSD) are also efficient strategies to obtain high double layer capacitance and good rate performance [6,24]. Generally, the high surface area of porous carbon
is an essential requirement to obtain high double-layer capacitance. If the pore size matches the size of bare/desolvated electrolyte ions (mostly less than 2 nm), the porous carbons can provide maximum surface area normalized double-layer capacitance [25,26]. However, micropores tend to increase the equivalent series resistance (ESR), especially in organic and ionic liquid electrolytes that can supply high operating voltage windows, resulting in a substantial power decrease [27,28]. Additionally, the small micropore volume is easily to be saturated by electrolyte species, which limits the maximum operating voltage and the energy storage [29]. Mesopores can store more ions than micropores, and the ESR caused by the desolvation process and high viscosity of electrolyte might be cancelled out in mesopores, resulting in a good rate capability [30]. However, too large mesopores will decrease the specific surface area (SSA) of porous carbon, lowering the specific double-layer capacitance. Besides, narrowing the PSD of porous carbon is also an effective way to increase the reversible capacity and enhances the rate capability since the narrow PSD can significantly reduce ion scattering and improve electrode kinetics [31].

Renewable biomass can be used as the precursor for preparing high-defect and low-cost porous carbon materials [32]. In a general way, the defects, such as vacancies, edges and heteroatoms can be generated during the pyrolysis process, and the porous structure can also be obtained by activation or templating methods [33,34]. However, the activation method that often needs to be carried out under harsh conditions might generate numerous ion-inaccessible and tortuous micropores as well as a wide mesopore size distribution [35]. Although the ordered mesoporous carbons that are prepared by templating method possess a relatively narrow PSD, their SSA is not high enough to obtain the desirable capacity when they are used as electrode materials for LIBs and SCs [36]. Moreover, the templating method still suffers from multiple disadvantages, including expensive and complicated template preparation process, poor dispersion of templates within carbon precursors and harsh conditions for removal of templates after carbonization [5].

As one of the low-cost precursors for the preparation of carbon materials, animal bone is primarily composed of hydroxyapatite (HA, Ca10(PO4,CO3)6(OH)) and collagen. HA is a plate-shaped crystal with an approximate thickness, width and length of 4×25×50 nm. Collagen is cylindrically shaped and composed of three polypeptide chains in a triple helix [37]. In our previous studies, the pig bone-based hierarchical porous carbons obtained by using KOH activation exhibited good performance as electrode materials for SCs and LIBs [38,39]. Herein, we present a facile, low-cost and environmental friendly method to prepare porous carbons (PCs) with high defect density via direct carbonization of cattle bone without any additional activators or templates. Due to the in-situ HA-induced self-activation, the PCs obtained at 1100 °C (PC-1100) possessed a mesopore-dominated hierarchical porous structure with a large specific surface area (2096 m² g⁻¹), a narrow small-mesopore size distribution centered at approximately 4.0 nm and a high electrical conductivity, and showed outstanding rate capability and superior cycling performance as electrode materials for LIBs and SCs.

2. Experimental section

2.1. Sample preparation

Cattle bone powder was directly carbonized in an Ar atmosphere to T °C (T=600, 850, 900, 1000, 1100, 1200) at a heating rate of 2.5 °C min⁻¹, and held for 1 h. The products were then washed by 1 M HCl and deionized water, and dried at 80 °C for 12 h.

2.2. Material Characterization

The obtained samples were characterized with scanning electron microscopy (SEM, JEOL, JSM-6701F), high resolution transmission electron microscopy (HRTEM, JEOL TEM 2010 microscope), thermogravimetric analysis/differential scanning calorimetry (TGA/DSC, STA449 Jupiter, NETZSCH from room temperature to 1200 °C at a heating rate of 10 °C min⁻¹ in air and Ar atmospheres), Fourier transform infrared spectroscopy (FTIR, PerkinElmer, Spectrum 100), X-ray diffraction (XRD, Rigaku RINT 2200 VPC at a scan rate of 5° min⁻¹), X-ray photoelectron spectroscopy (XPS, ESCALAB 250 with monochromatic Al K X-ray sources with a pass energy of 30 eV in 0.5 eV step over an area of 650 µm ×650 µm) and Raman scattering (LabRam HR800). The nitrogen absorption isotherm was measured on a Quantachrome AUTOSORB-1. The TGA/FTIR measurements were carried out on a METTLER TOLEDO TGA/DSC1 thermogravimetric coupled with a Nicolet 6700 FTIR spectrophotometer (from room temperature to 800 °C at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere). The electrical conductivity was measured with a Nanometrics HL5550 cryostat based on the standard four-probe technique developed by Van der Pauw at a load pressure of 10 MPa. The Ca and P concentrations of the collected solution were measured using an inductively coupled plasma mass spectrometry (ICP-MS, 7700, Agilent Technologies Inc., USA).

2.3. Electrochemical measurements

For the LIB tests, the electrochemical measurements were performed using a CR2032 corn-type cell. For preparing working electrodes, polyvinylidene difluoride (PVDF) (15 wt%), acetylene black (15 wt %) and active material (70 wt%) were coated on Cu foil current collector followed by drying at 80 °C for 4 h. Then the Cu foil was compacted using a tablet machine at 5 MPa and dried at 120 °C for 12 h. The loading weight of the active material was controlled within 0.8–1 mg cm⁻². A 1 M LiPF₆ solution with a mixture of ethylene carbonate and diethyl carbonate (1:1 in vol%) was used as the electrolyte, a polyethylene was used as the separator, and a Li foil was used as the counter electrode. After assembly, the cells were charged and discharged using a Land CT2001A battery test at various current densities in a voltage range from 0.01 to 3 V. Cyclic voltammetry (CV) and electrochemical impedance spectral (EIS) measurement were carried out on a CHI600E working station. For the CV measurements, the sweep rates were 0.1, 0.5, 1, 2, 5 and 10 mV s⁻¹, and the potential ranged from 0.01 to 3 V. For the EIS measurements, the frequency range was from 100 kHz to 10 mHz.

For the SC tests, the electrochemical experiments were carried out using two-electrode system in a CR2032 corn-type cell. For preparing working electrodes, PVDF (10 wt%), acetylene black (10 wt%) and the active material (80 wt%) were coated on nickel foam disk followed by drying at 80 °C for 4 h. Then the nickel foam disk was compacted using a tablet machine at 5 MPa and dried at 120 °C for 12 h. The loading weight of the active material was approximately 2 mg cm⁻². A glass-fiber membrane was used as the separator and the neat EMIM-BF₄ was used as the electrolyte. After assembly, galvanostatic charge/discharge (GCD), CV and EIS measurements were carried out on a CHI660E working station. For the GCD measurements, the current densities were 5, 10, 20, 30, 50, 70, 100 A g⁻¹, and the potential ranged from 0 to 3.5 V. For the CV measurements, the sweep rates were 50, 100, 200, 300, 400 and 500 mV s⁻¹, and the potential ranged from 0 to 3.5 V. For the EIS measurements, the frequency range was from 100 kHz to 10 mHz. The specific capacitance C (F g⁻¹) based on the GCD was calculated based on the following equations [12,28]:

\[
C = \frac{2I\Delta t}{m\Delta V}
\]

where \( m \) (g) is the effective mass loaded on a single working electrode, \( I \) (A) is the discharge current, \( \Delta t \) (s) is the discharge time, and \( \Delta V \) (V) is the potential change excluding the voltage drop within \( \Delta t \), respectively. The energy density \( E \) (W h kg⁻¹) and power density \( P \) (W kg⁻¹) were calculated based on the following equations [12,28]:
\[ E = \frac{1}{2} \times 4 \times 3.6 \times C \Delta V^2 \]  
(2)

\[ P = \frac{3600E}{\Delta t} \]  
(3)

The complex form of capacitance \( C(\omega) \) is dependent on real part the cell capacitance \( C'(\omega) \), the imaginary part \( C''(\omega) \) related to the losses of energy dissipation and frequency, which is defined as follows [40]:

\[ C(\omega) = C'(\omega) - jC''(\omega) \]  
(4)

\[ C'(\omega) = \frac{-Z'(\omega)}{\omega |Z(\omega)|^2} \]  
(5)

\[ C''(\omega) = \frac{Z''(\omega)}{\omega |Z(\omega)|^2} \]  
(6)

where \( Z'(\omega) \) and \( -Z'(\omega) \) are the real and imaginary parts of the complex impedance \( Z(\omega) \), respectively. \( \omega \) is the angular frequency which is given by \( \omega = 2\pi f \).

3. Results and discussion

3.1. Structure characterization

Cattle bone powder was directly carbonized in an Ar atmosphere at T °C (T=600, 850, 900, 1000, 1100, 1200). The as-prepared products were formed in a fiber bundle-like shape derived from the mineralized collagen fibril bundle within cattle bone (Fig. S1a), and were denoted as CP-T, where CP represented the carbonized product, and T represented the carbonization temperature. HRTEM images of CPs indicated that hydroxyapatite (HA) shrunken from acicular to irregular with the temperature increasing (Fig. S2), especially above 900 °C. In addition, porous carbon appeared along the edge of the granular HA. After the HA were removed by diluted hydrochloric acid, two kinds of carbons appeared depending on the temperature condition (non-porous carbon (NPC-T), porous carbon (PC-T)). The SEM images (Fig. S1b) show the specific structures of the carbons. For the carbons that were obtained at 600 °C, carbon layers were stacked in a disorder structure, and no obvious pores were observed (NPC-600). As the temperature increased to 850 °C, some micropores were generated (PC-850). Despite an increase of only 50 °C, elliptic mesopores with a size of approximately 4 nm appeared in the sample obtained at 900 °C (PC-900). At the temperature continued to increase (1000 °C), the number of mesopores increased (PC-1000). As shown in the HRTEM images of samples that were obtained at 1100 and 1200 °C, the mesopores were closely connected with the ultrathin pore wall and some pores even coalesced (PC-1100 and PC-1200).

\( \text{N}_2 \) adsorption-desorption curves of the sample obtained at 600 °C showed a type II adsorption-desorption isotherm (Fig. S3a), indicating that almost no pores were present in NPC-600. In contrast, the other carbons showed combined type I/IV adsorption-desorption isotherms with strong adsorption at low pressure and hysteresis loops at a relative pressure of more than 0.4, indicating the presence of micropores and mesopores. Moreover, the hysteresis loops of PC-900, PC-1000, PC-1100 and PC-1200 were much larger than that of PC-850 (Fig. 1b, inset), indicating that the mesopores were primarily generated above 900 °C. The pore size of PC-850 ranged from 1 to 4 nm. For PC-900, the pore size increased and the PSD centered at 4 nm were observed. The specific surface area (SSA) of mesopores substantially increased but the SSA of micropores decreased (Fig. 1c). Notably, the PSD centered at 4 nm remained as the temperature increased from 900 to 1200 °C. The SSA of micropores and the SSA of mesopores reached minimum and maximum value of 210.7 m² g⁻¹ and 1884.9 m² g⁻¹ at 1100 °C, respectively. The mesopore volume of PC-1100 also reached maximum value of 1.829 cm³ g⁻¹ (accounted for 95.6% of the total), showing an extremely high mesoporosity. At 1200 °C, the SSA of mesopore decreased, and the variation trend of pore volume was consistent with that of SSA (Fig. 1d). By comparing with the previously reported studies in recent years (we highlighted some data of those studies in Table S1), it is important to note that the pore parameters of PC-1100 were quite different from those of previously reported porous carbons prepared by alkaline activation or templating methods. Moreover, the unique synthesis method proposed in this study is obviously superior over those reported in term of both operability and reproducibility.

TGA/DSC was performed to determine the formation process of PCs. In an Ar atmosphere (Fig. 2a), two exothermic peaks were observed at 380 and 460 °C, which were due to the thermolysis of collagen and primary carbonization, respectively. A small exothermic peak was observed at approximately 750 °C. In contrast to the first two peaks, this peak did not shift even in an air atmosphere (Fig. S4a), which indicated that the change in bone at approximately 750 °C was not related to carbon but HA. TG-IR was performed to further study this phenomenon. As shown in Fig. 2b, the characteristic band of H2O at 3400–4000 cm⁻¹ was enhanced when the temperature increased from 730 to 770 °C [41]. This result indicated that exothermic peak at 750 °C in DSC curve was due to the production of H2O from the thermal decomposition of HA [42]. Moreover, the characteristic bands of CO at 2030–2240 cm⁻¹ increased in intensity [43]. The increase in the CO content could be due to a possible steam-activation process according to Eq. (7). Fig. 2c shows the XRD patterns of CPs without acid treatment. The characteristic peaks of HA became intense and narrow as temperature increased due to the crystallinity increased due to the regrowth of HA [44], which was in agreement with the morphology change observed in the HRTEM images. In addition, a peak at 37.4° was observed in the pattern for PC-1200. This peak is the characteristic of CaO, which is a further decomposition product of HA. The XRD patterns of the cattle bones heat-treated in an air atmosphere indicated that CaO was generated practically at 900 °C (Fig. S4b). The weak peak corresponding to CaO was obscured due to the existence of carbon. Furthermore, this peak became more intense at 1200 °C, indicating that more CaO and H2O were generated with further decomposition of HA at 1200 °C than at other temperatures [42]. Fig. 2d shows the FT-IR patterns of the cattle bones carbonized in an Ar atmosphere. The bands at 1418 and 1456 cm⁻¹ correspond to B-type carbonate groups [45], indicating the presence of numerous carbonate groups in the HA of cattle bone. The ICP-MS results indicated that the Ca/P ratio was 2.01. Therefore, the molecular formula of HA was Ca10(PO4)6(CO3)(OH). When the temperature increased to 900 °C, these two bands disappeared, indicating that CO2 was generated with CaO [44,45]. CO2 can also be used as an activating agent according to Eq. (8) [46]. The use of a CO2-steam mixture produced high specific surface area and large pore size due to the combine effect [47].

\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \]  
(7)

\[ \text{C} + \text{CO}_2 \rightarrow 2\text{CO} \]  
(8)

Base on the above analysis, we deduced that HA was decomposed and generated H2O at ~750 °C, and the sizes of pores were less than 4 nm after steam-activation at 850 °C. Then, the further decomposition of HA generated CO2 at 900 °C, and the micropore size increased due to the steam-CO2 activation. As the pore size reached the thickness of HA (~4 nm), the HA crystal pulled away from carbon-encapsulated structure and regrew. The remaining porous carbon maintained its porosity due to the formation of HA-induced activation. Therefore, the PSD was centered at ~4 nm even though the temperature continued to increase. The micropores were gradually enlarged to mesopores, resulting in the decreased SSA of micropore. Some pores with 5–
Fig. 1. (a) Transformation process of NPC into PC illustrated by TEM images. (b) Nitrogen adsorption-desorption isotherms (inset) and pore size distributions of PCs. (c) SSA and (d) pore volume of PCs.

Fig. 2. (a) TGA/DSC curves and (b) TG-IR patterns of cattle bone tested in an Ar atmosphere. (c) XRD patterns and (d) FT-IR patterns of samples carbonized at different temperatures in an Ar atmosphere.
The defects on the carbon layers and the structural change of carbons were investigated using Raman spectroscopy and XRD. The Raman spectra were fitted by five Gaussian peaks as follows: G (located at ~1580 cm$^{-1}$, attributable to the E$_{2g}$ vibration mode present in sp$^2$-boned graphitic carbons), D (located at ~1350 cm$^{-1}$, attributable to the A$_{1g}$ vibration mode that is characteristics of sp$^3$ defects), I (located at ~1220 cm$^{-1}$, attributable to impurities or heteroatoms, such as N, on the graphitic plane), and D$'$ and D$''$ (located at ~1620 cm$^{-1}$ and ~1290 cm$^{-1}$, respectively, corresponding to defects in graphene layer stacking) [48–50]. The contents of these peaks for carbons were calculated according to the fitted result in Fig. 3a. As shown in Fig. 3b, the content of D was much higher than that of G and increased with the temperature increasing. This result indicated that more defects were generated on carbon layers due to the activation process. In addition, the (D$'$+D$''$) content reached maximum value at 850 °C but decreased as the temperature increased, indicating that the stacked structure was formed and grew by steam-activation at 850 °C, and then etched away by enhanced CO$_2$-steam activation above 900 °C. The structural change was also confirmed by XRD analysis. Fig. 3c shows the XRD patterns of all the carbons. For NPC-600, a broad peak was observed at approximately 26°, corresponding to the (002) reflection of a graphitic-type lattice [51]. For PC-600, the (002) peak became broad and weak as temperature increased, and nearly disappeared in the patterns of PC-1000, PC-1100 and PC-1200. The disappeared (002) peak of carbon was a very interesting phenomenon that only reported in few works [52], which might be due to the structural change from the turbostratic stacking layers to ultrathin and spherical layers, corresponding to the porosity change from nonporous structure to porous structure. The I peak also became weak when temperature increased due to N atoms being removed, which was observed in the XPS spectra shown in Fig. 3d. The element contents and percentages of total N1s (Table S2) showed that N-6 (398.4 eV) and N-5 (399.9 eV) were removed, and only N-Q (401.0 eV) remained as the temperature above 900 °C [53]. It has been reported that N-Q plays a very important role in improving electron transfer [6]. The high-resolution C1s spectra for all the carbons were deconvoluted into four individual component peaks as follows: C$\equiv$C (284.6 eV), C-C (285.2 eV), C-O or C-N (286.7), and C=O (288.5 eV) [54]. The content of C=O reached minimum value at 850 °C and then increased with the temperature increasing. The content of G peak also followed the same trend, resulting in a reduction of the resistivity (Fig. 3e). Although PC-850 possesses the most defects, numerous oxygen-containing functional groups that were not beneficial for electron transport were removed at 850 °C. Therefore, its electroconductivity was higher than that of NPC-600. The resistivity of PC-1200 was higher than that of PC-1100 because the structural integrity of PC-1200 was partly broken by the enhanced activation [55]. Despite the numerous defects, PC-1100 possessed the best electrical conductivity of 5141 S m$^{-1}$ due to the relatively high content of sp$^2$-boned graphitic carbons, low O content and integrated fiber bundle-like structure. The electrical conductivity of PC-1100 was much higher than those of the previously reported porous carbons (Table S1). High defect density, large SSA, narrow mesopore distribution, and good electrical conductivity made PC-1100 as high performance electrodes for LIBs and SCs.

Fig. 3. (a) Fitting of the Raman spectra of all the carbons using five Gaussian peaks. (b) Contents of integrated peaks of all the carbons. (c) XRD patterns, (d) XPS spectra and (e) resistivities and electrical conductivities of all the carbons.

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3.2. Electrochemical performances of PC-1100 as LIB anodes

Considering the low initial efficiency for porous carbon materials, all the NPC and PC samples were prelithiated prior to the electrochemical tests in a half-cell configuration versus Li metal. Fig. S7a shows the cyclic voltammetry curves of carbons. The cathodic and anodic peaks above 0.5 V are attributed to the Li ion adsorption and desorption on the defects [56,57], or Li ion combination and separation with heteroatoms on carbon layers [19,58,59]. As aforementioned, NPC-600 and PC-850 possessed more defects (including defects from graphene stacking and impurities) and heteroatoms than other carbons. However, these two samples possessed a lower current density above 0.5 V than other carbons with mesopore-dominant porosity. This result indicates that numerous defects and heteroatoms in non-porous NPC-600 and microporous PC-850 could not efficiently store Li ions due to the high SEI resistances ($R_s$) and charge-transfer resistances ($R_{ct}$) during the ion and electron transport process (Fig. S8 and Table S3). The poor kinetic of electrochemical process might be attributable
to the turbostratic graphene stacking and low electrical conductivity that hindered the fast transport of ions and electrons. On the contrary, the highly interconnected mesopore structure was beneficial to the kinetic of the electrochemical process. The $R_r$ and $R_c$ of PC-1100 and PC-1200 were much smaller than those of other carbons, and the defects and heteroatoms in them could sufficiently store Li ions, resulting in high current densities as the voltage was above 0.5 V in CV curves. The cathodic peaks below 0.5 V are associated with the lithium metal deposition [18,60], and the mesopore-dominant PCs possessed higher capacities than NPC-600 and microporous PC-850 under low potentials. The GCD test at 0.1 A g$^{-1}$ also confirmed the different capabilities among non-porous, microporous and mesopore-dominant carbons (Fig. S7b). Interestingly, the charge and discharge capacities of carbons were positively correlated with the pore volume. This phenomenon is due to the capacity arising from Li metal plating under low potentials, which depends not only on the defects but also on the storage space in carbon materials [17,18]. It is evident that the large mesopore volume also plays an important role in Li storage.

Due to its numerous defect sites and unique pore structure, PC-1100 exhibited good capability both at low and high current densities. The reversible capacities of PC-1100 were 1230, 951, 682, 491 and 343 mA h g$^{-1}$ at 1, 2, 5, 10, 20 A g$^{-1}$, respectively (Fig. 4a, b). Even at a high current density of 30 A g$^{-1}$, a reversible capacity of 281 mA h g$^{-1}$ still retained. Furthermore, PC-1100 showed superior long cycling performance. As shown in Fig. 4c, d, PC-1100 exhibited a high reversible capacity of 1488 mA h g$^{-1}$ after 250 cycles at 1 A g$^{-1}$, and 661 mA h g$^{-1}$ after 1500 cycles at 10 A g$^{-1}$. The mesopore-dominant structure and good electrical conductivity of PC-1100 could supply abundant pathways for rapid transport of both ions and electrons, resulting in a high columbic efficiency and good cycling performance [61]. Moreover, the long cycling life was also attributed to the fiber bundle-like structure, which leaded to a relatively good mechanical stability of PC-1100 [61].

To further confirm the contribution of the defects and pore structure to rate capability of the electrode, the discharge capacity of the PC-1100 at scan rate of 10 mV s$^{-1}$ (calculated based on the CV curves at scan rates from 0.5 to 10 mV s$^{-1}$, Fig. 5a and Fig. S10) was.

Fig. 4. Electrochemical performance of half-cell using PC-1100 as the electrode and Li metal as the counter electrode in 1 M LiPF$_6$ electrolyte. (a) Rate capacity and (b) charge-discharge processes of PC-1100 electrode at various current densities from 1 to 30 A g$^{-1}$. Cycling performance of PC-1100 electrode at current densities of (c) 1 A g$^{-1}$ and (d) 10 A g$^{-1}$. 

divided into two parts, corresponding to capacitance and diffusion-controlled process, respectively [14,62]. As shown in Fig. 5b, the capacity contributed from the capacitance effect accounted for 49.0% of the total due to the unique pore structure, and numerous defect sides can still efficiently storage Li ions under a high scan rate, resulting in a superior rate performance of PC-1100. We reviewed the typical results from the literatures for the electrochemical performance of biomass-based carbon [59,63–66] and other carbon electrodes [11,67–75] for LIBs (Fig. 5c, d, all the electrochemical performance was evaluated in half-cell configurations versus Li metal). Based on above analysis, it can be concluded that the PC-1100 anode exhibited superior capability and long cycling performance, which could be used as high performance anode for Li ion storage devices.

3.3. Electrochemical behavior of PC-1100 for SCs

SC experiments were conducted in a symmetric supercapacitor with two-electrode configuration. To increase the energy density of SCs, ionic liquid (neat EMIM-BF₄) was used as the electrolyte in the symmetrical SCs. EMIM-BF₄ possesses low flammability, negligible vapor pressure, good thermal stability and high operating windows (3–4 V) [76–78]. However, due to the high viscosity, low ionic diffusivity and large ion size of EMIM-BF₄, the conventional microporous carbons show poor rate performances at high current loads in EMIM-BF₄ electrolyte [28,59]. Different from the microporosity in conventional activated carbons, the highly interconnected mesoporous structure in PC-1100 could act as an ion highway for facilitating the fast transport of electrolyte ions into electrodes. Moreover, the large SSA and numerous defects of the PC-1100 were beneficial for the enhanced specific capacitance, consequently ensuring the simultaneous realization of high energy density and power density.

CV curves of the PC-1100 exhibited ideal rectangular-shape even at the scan rate of 500 mV (Fig. 6a), and the GCD curves of PC-1100 showed highly linear and symmetrical even at the current density of 100 A g⁻¹ (Fig. 6b), suggesting an ideal capacitive behavior and outstanding rate capability. Additionally, the PC-1100 exhibited very small IR drop even at high current densities, indicating that the mesoporous structure of PC-1100 was beneficial for fast ion transport [79,80]. Conversely, the micropore-dominant PC-850 exhibited obvious IR drop at high current densities (Fig. S11b), indicating that the excessively micropores did increase the resistance during the charge-discharge process. These results were also evidenced by EIS analysis in Fig. S12. The ESR and Rₚ of PC-1100 were 2.5 and 0.3 Ω, respectively, which were much lower than those of PC-850 (3.2 and 6.0 Ω, respectively). Furthermore, the characteristic relaxation time constant τ₀ of PC-1100 was only 2.6 s, much smaller than that of PC-850 (14.7 s), further confirming the excellent rate capabilities of PC-1100 [40,81]. Due to the mesopore-dominant structure of PC-1100, the large surface and numerous defects efficiently contributed to a high capacitance. The PC-1100 electrode exhibited a high reversible specific capacitance of 258 F g⁻¹ at a current density of 5 A g⁻¹, and a high reversible capacitance of 176 F g⁻¹ was maintained even at a high current density of 100 A g⁻¹ (Fig. 6c). On the contrary, the reversible capacitance of PC-850 was only 58 F g⁻¹ at 100 A g⁻¹ (Fig. S11c). The symmetrical SC based on the PC-1100 electrode delivered a high energy density of 109.9 Wh kg⁻¹ at a power density of 4.4 kW kg⁻¹, and retained a remarkable energy density of 65.0 Wh kg⁻¹ even at a high power density of 81.5 kW kg⁻¹. Due to the high energy and power property, the assembled symmetrical SC based on PC-1100 electrode could easily power 33 red LEDs in parallel (Fig. 6d). It is worth noting that the energy and power densities of the symmetrical SC based on PC-1100 electrode are comparable to or even better than those of the symmetrical SCs based on other carbonaceous electrodes (all the electrochemical performance was evaluated in symmetric supercapacitors).
Electrochemical performance of assembling two-electrode symmetric SC using PC-1100 as the electrode in a neat EMIM-BF$_4$ electrolyte. (a) CV curves at different scan rates. (b) GCD curves at different current densities. (c) Specific capacitances of PC-1100 electrode at different current densities. (d) Photograph of 33 red LEDs powered by one symmetrical SC based on PC-1100 electrode. (e) Ragone plot and performance comparison with those of other carbon materials. (f) Cycling performance of PC-1100 at 10 A g$^{-1}$ for 5000 cycles.

4. Conclusions

We have developed an environmental friendly and facile method for the preparation of high-defect carbons with a narrow mesopore size distribution using low-cost cattle bones as precursors through hydroxyapatite-induced self-activation. Due to the synergistic effect of the defects and pores, porous carbons exhibited high specific capacity, superior rate capability and long cycling life, which can be expected as promising electrode materials for LIBs and SCs with integrated high energy and power densities.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2017.04.042.

References
