



Full paper

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-BF₄ 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 safeties 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

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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, $\text{Ca}_x(\text{PO}_4)_y(\text{OH})_z$) and collagen. HA is a plate-shaped crystal with an approximate thickness, width and length of $4 \times 25 \times 50$ 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-dominant hierarchical porous structure with a large specific surface area ($2096 \text{ m}^2 \text{ g}^{-1}$), 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 $2.5 \text{ }^\circ\text{C min}^{-1}$, 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 $10 \text{ }^\circ\text{C min}^{-1}$ in air and Ar atmospheres), Fourier transform infrared spectroscopy (FTIR, PerkinElmer, Spectrum 100), X-ray diffraction (XRD, Rigaku RINT 2200 V/PC 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 $650 \mu\text{m} \times 650 \mu\text{m}$) 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 thermogravimeter coupled with a Nicolet 6700 FTIR spectrophotometer (from room temperature to 800 °C at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ 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 coin-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 $0.8\text{--}1 \text{ mg cm}^{-2}$. A 1 M LiPF_6 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 coin-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- BF_4 was used as the electrolyte. After assembly, galvanostatic charge/discharge (GCD), CV and EIS measurements were carried out on a CHI600E 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]:

$$C = \frac{2I\Delta t}{m\Delta V} \quad (1)$$

where m (g) is the effective mass loaded on a single working electrode, I (A) is the discharge current, Δt (s) is the discharge time, and ΔV (V) is the potential change excluding the voltage drop within Δt , respectively. The energy density E (Wh kg^{-1}) and power density P (W kg^{-1}) were calculated based on the following equations [12,28]:

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