Microporous carbon derived from Apricot shell as cathode material for lithium–sulfur battery

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ABSTRACT

Unique activated carbon (AAC) is prepared by pyrolysis of natural waste Apricot shell following with KOH activation. The facile and cost-effective bio-inspired method possesses a high product yield of 40.7 wt%. The AAC sample has a high BET surface area of 2269 $m^2 g^{-1}$ and large pore volume of 1.05 $cm^3 g^{-1}$, which is beneficial to effectively hold the sulfur and restrain the diffusion of polysulfides during the galvanostatic charge/discharge processes using as the cathode matrix for the rechargeable Li–S battery. The pore size distribution of the AAC sample is ranging from 0.6 to 2.0 nm, which leads to the nonconductive sulfur being loaded into the micropores of the carbon matrix in highly dispersed state, having and/or losing electrons easily at the same time. The optimized AAC/S composite material shows an excellent cycle performance and a good rate capability when using as the cathode in Li–S battery. The initial discharge capacity of 1277 mAh g^{-1} can be obtained at 0.1 C. A stable discharge capacity of about 710 mAh g^{-1} at a current density of 0.2 C and the discharge capacity of 613 mAh g^{-1} at a high current density of 1 C may be achieved after 200 charge/discharge cycles.

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1. Introduction

Lithium-ion batteries (LIBs) have become necessary in our daily life since commercialized by the Sony Company in the early 1990s. But the poor energy density of current commercial LIBs hinders the application in the field of emerging technologies such as electric vehicles, smart grids and so on [1–3]. Li–S batteries are the prospective choice for next generation rechargeable batteries based on their high theoretical energy density of 2600 Wh kg^{-1}, which is 3–5 times greater than that of the LIBs [4–6]. Furthermore, the Li–S batteries have the advantages of low-cost and environmentally benign characteristics since the sulfur element is abundant, nontoxic and cheap. Despite those significant strengths, there are still some challenges such as significant capacity fading, poor rate performance and low Coulombic efficiency hindering the development and utilization of the Li–S batteries. The poor sulfur electronic/ionic conductivities, the volume expansion and shrinkage of sulfur during the galvanostatic charge and discharge processes, and the solubility of polysulfides in organic electrolyte during cycling processes are the three main factors for drawbacks of Li–S batteries [7–10].

During the last decades, the structures and preparation methods of nanoporous material such as zeolites [11], activated carbon [12,13], metal–organic frameworks (MOFs) [14] and zeolitic imidazolate frameworks (ZIFs) [15] have been explored extensively. Because of plenty of micropores (pore diameter < 2 nm), mesopores (2–50 nm) and macropores (>50 nm) may exist in the structures, the nanoporous materials have a wide variety of applications including gas separation, adsorption, catalysis and electronics [16–20], for example, Wu et al. [19] prepared a flexible MOF material, $[Zn_2(bpdc)_2(bpee)]\cdot 2DMF$ (bpdc = 4,4′-biphenyl dicarboxylate; and bpee = 1,2-bis(4-pyridyl)ethylene), exhibiting remarkably high adsorption selectivity of CO_2 over other small gases with a separation ratio of 294, 190, 257 and 441 (v/v) for CO_2/N_2, CO_2/H_2, CO_2/CH_4 and CO_2/CO, respectively. Recently, Korenblit et al. [20] used ordered mesoporous silicon carbide-derived carbon (CDC) as the electrodes of double layer capacitors. The produced CDC exhibits a specific surface area up to 2430 $m^2 g^{-1}$ and a high specific capacitance of 170 F g^{-1} when tested in 1 M tetraethylammonium tetrafluoroborate acetonitrile solution. To overcome the problems of Li–S batteries, the carbon-based nanoporous materials *e.g.*, template carbon [21–23], carbon nanofiber [24,25], graphene [26,27], graphene oxide [28] *etc.* with high electronic/ionic conductivity and structural stability, high specific surface area and large pore volume, have been used as the cathode matrix in Li–S batteries. They have been proved to be able to effectively improve the sulfur

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utilization and constrain the soluble polysulfides. Nevertheless, most of the conductive carbon matrixes require sophisticated, costly and/or toxic preparation processes that may offset the advantage of Li–S batteries in some extent.

Bio-inspired activated carbons derived from biomass have been extensively used in LIBs, demonstrating good electrochemical properties. Biomass as diverse as sucrose [29], dead leaf [30], husk rice [31], coconut shell [32], pistachio nutshell [33], peat moss [34], hazelnut shell [35], cherry stone [36] etc. have been used as the precursors of activated carbons. The common preparation method [37,38] includes two steps: carbonization of the precursors at a high temperature under an inert environment, and then physical or chemical activation of the carbonized precursors to enhance the surface area and adjust the pore size distribution of the activated carbons. As to the chemical activation, reactive chemicals such as NaOH, KOH, $ZnCl_2$ and H_3PO_4 were often chosen to intermix with the carbonized products, and the mixtures were heated in an inert atmosphere at a temperature that typically ranged from 450 to 900 °C. Notably, the activated carbons obtained after the chemical activation usually possess abundant interconnected micropore textures in the structure which can effectively confine the size of the encapsulated sulfur, ensuring good electrical contacts between the sulfur and conductive carbon framework.

Apricot shell as a kind of usual natural waste mainly consists of cellulose, hemicellulose and lignin (about 920 g kg^{-1}) [39] which may form carbon after roasted at the high temperature. Herein, a kind of unique activated carbon (AAC) derived from Apricot shell by carbonization and activation with KOH has been applied to construct the AAC/S composite material. Compared to the typical synthesis routes to obtain the porous carbons, such as carbonization of organic/polymeric precursors [40,41], chemical vapor deposition [42,43], CDC method [44,45], template synthesis method, etc. [46,47], this bio-inspired method is facile, cost-effective, safe, possessing of high product yield (40.7 wt%) and easy for mass production. The AAC matrix has suitable conductivity, high specific surface area, large pore volume and narrow pore size distribution in micropore range [48–61]. The AAC/S composite sample exhibits good specific capacity with excellent cycling stability using as the cathode material in the rechargeable Li–S battery.

2. Experimental

2.1. Preparation of the AAC and S-infiltrated AAC (AAC/S) composite samples

The fresh Apricot shell was washed under ultrasound with distilled water for 3–5 times and dried at room temperature before use. 20 g of Apricot shell was pretreated at 300 °C for 2 h and then pyrolyzed at 750 °C for 1 h with a heating rate of 3 °C min^{-1} under a flowing Ar atmosphere in a tubular furnace. The carbonized intermedia mixed with KOH in the weight ratio of 1:3 was grinded and mixed well in an agate mortar and was heated at 750 °C for 1 h with a heating rate of 3 °C min^{-1} under Ar flow. The resultant AAC sample was washed with HF solution to dissolve the impurity such as silica and then with distilled water for several times and dried at room temperature. Sublimed sulfur and the AAC sample was mixed well with the sulfur/carbon weight ratio of 3.5:1 in a ball milling quartz mortar for 0.5 h. The mixture was heated to and maintained at 155 °C for 15 h in order to lead to the chain-like sulfur molecules entering the nanopores by capillary action since the sulfur has the lowest viscosity at 155 °C. The mixture was further heated to and maintained at 300 °C for 0.5 h under Ar flow for removing the excess sulfur through the sublimation process. The obtained AAC and AAC/S composite samples were characterized in detail.

2.2. Characterization

X-ray diffraction (XRD) patterns were determined by the X-ray diffractometry (Labx XRD-6000, Shimadzu, Japan) with Cu Kα radiation (wavelengths λ = 0.15418 nm) in the range of $10° \leqslant 2\theta \leqslant 80°$ (scan speed 5° min^{-1} and scan step 0.02°) at room temperature. Raman spectroscopy analysis was examined on a confocal microprobe Ramon system (LabRAM HR800) with the laser wavelength of 514 nm. Morphologies and microstructures of the samples were observed and analyzed by using the scanning electron microscope (SEM, Quanta-250 FEG, Holland, operating at 10 kV) and transmission electron microscopy (TEM, JEOL JEM2100-F, operating at 200 kV). The compositions of the AAC/S sample were analyzed by the energy dispersive X-ray spectroscopy (EDS, JSM-7500F). The sulfur content was detected by using the thermogravimetric/differential thermal analyzer (TG/DTA) measurement (NETZSCH STA 449F3) under air atmosphere, and the temperature range was from room temperature to 700 °C with a heating rate of 10 °C min^{-1}. Nitrogen sorption isotherms at 77 K were measured on the Micromeritics ASAP 2020 system. The specific surface area (S_{BET}) was calculated by the Brunauer–Emmett–Teller (BET) method using a surface area and porosimetry analyzer (Micromeritics ASAP 2020). The pore size distributions were evaluated by using the density functional theory (DFT) method applied to the nitrogen adsorption data, assuming slit-shaped geometry and low regularization.

2.3. Electrochemical measurements

To estimate the electrochemical performance of the AAC/S composite material, 2025-type coin cells were assembled in an argon-filled glovebox. The cathode slurry was prepared by mixing the AAC/S (80 wt%), acetylene black (10 wt%) and poly(vinylidene fluoride) (PVDF) (10 wt%) in N-methylpyrrolidone (NMP) solvent dispersant. The positive electrodes were prepared by coating the slurry onto aluminum foil and drying at 60 °C for 12 h in vacuum. The active material loading density was about 0.8–1.0 mg cm^{-2}. The cells were assembled by using lithium metal as the counter electrode and porous membrane (Celgard 2400) as the separator. The electrolyte was 1 M lithium bis-trifluoromethane sulfonylimide in 1,3-dioxolane (DOL) and dimethoxymethane (DME) with a volume ratio of 1:1 containing LiNO$_3$ (1 wt%). The charge–discharge curves were tested by using LAND-CT2001A battery test system in a voltage range of 1.6–3.0 V. The specific capacities at different current densities were calculated based on the mass of sulfur alone. Cyclic voltammetry (CV) curves were tested in a voltage range of 1.6–3.0 V at a scan rate of 0.2 mV s^{-1}. The electrochemical impedance spectra (EIS) were acquired in the frequency range of 0.1 Hz-1 MHz at alternating current of 5 mV. The CV and EIS measurements were applied on the CHI660D electrochemical workstation.

3. Results and discussion

SEM and TEM of the AAC sample were taken with the images shown in Fig. 1. The AAC sample has irregular morphologies with widely distributed particle sizes from several to a dozen of micrometers from the SEM images (Fig. 1a and b). Multilayer structures could be found for the AAC sample from the TEM image (Fig. 1c). Further enlarged TEM image (Fig. 1d) indicates that the partially graphitized domains exist in the AAC structure, which is beneficial for the electron transmission, indicating a good electric conductivity characteristic as the cathode matrix of the rechargeable Li–S battery. N$_2$ sorption isotherms of the AAC and AAC/S samples are shown in Fig. 2. The adsorption curve of the AAC sample is