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Preparation of carbon nanosheets from petroleum asphalt via recyclable molten-salt method for superior lithium and sodium storage

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ABSTRACT

Carbon nanosheets were successfully prepared from easily available and low-cost petroleum asphalt via a facile and recyclable molten-salt method. The as-made carbon nanosheets exhibit excellent performance on energy storage both for lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs): as the anode of LIBs, they provide a high reversible specific capacity (729 mAh g^{-1} at 100 mA g^{-1}), excellent cyclability (600 mAh g^{-1} at 1 A g^{-1} after 500 cycles), and improved rate performance (280 mAh g^{-1} at 5 A g^{-1}). For SIBs, they also display a reversible capacity of 300 mAh g^{-1} at 50 mA g^{-1}, remarkable rate capability (90 mAh g^{-1} at 5 A g^{-1}) and retain as high as 95 mAh g^{-1} after 10000 cycles at 2 A g^{-1}. The superior electrochemical performance of carbon nanosheets could be attributed to their peculiar structural characteristics that integrate a variety of advantages: fast electronic and ionic conductivity, easy penetration of the electrolyte, shortened path for Li^+/Na^+ migration and structural stability. This approach paves the way for industrial scale-up due to its eco-friendliness, simplicity and versatility.

1. Introduction

Lithium-ion batteries (LIBs), first commercialized by Sony in 1991, have been most widely used in the battery market of portable electronic devices, owing to their preeminent energy and power densities, enhanced safety and long-cycle lifespan [1–3]. Of late, the continuous progress and popularity of electric vehicles and hybrid electric vehicles have placed greater requirements on next-generation LIBs as far as larger energy density, longer lifetime, lower cost and more safety [4–6]. Graphite, the current state-of-the-art anode material in commercial LIBs, can hardly meet these demands because of its limited theoretical specific capacity (372 mAh g^{-1}) and rapid capacity fading [7]. Therefore, it is urgent to develop a better substitute for traditional graphite electrode. On the other hand, in consideration of the rarity and unevenly distribution of the lithium ore around the world, the price for further development of future large-scale energy storage system would become a key issue [8]. To overcome these drawbacks, SIBs with greater abundance of sodium, much lower cost and similar working mechanism to LIBs, are regarded as one of the most promising alternatives to LIBs [9–11]. However, the progress on SIBs is relatively sluggish originating from the larger ionic radius of Na (1.06 Å) and heavier relative atomic mass (23 vs. Na) compared with those of its counterpart (0.76 Å and 6.94 vs. Li, respectively), which make them difficult to be reversibly inserted into and extracted from electrodes [12–14], for instance, the common graphite is electrochemically irreversible for SIBs [15]. In order to satisfy the surging need for electrical appliances and energy storage system, one feasible approach is to develop appropriate electrode materials with dual energy storage in both LIBs and SIBs.

Over the past few years, considerable contributions have been made in the structure design techniques of both cathode and anode materials for LIBs and SIBs [16–21]. In terms of anodes, carbonaceous materials such as carbon nanospheres, carbon nanotubes, graphene and their composites, have drawn tremendous attention on account of their natural availability, cost-effectiveness, good conductivity and nontoxicity [22–28]. Of these, two-dimensional (2D) carbon nanostructures, especially graphene and graphene-

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like nanosheets, are being ever-increasing studied for energy storage equipment [29]. They benefit from the merits of high active surface area for sufficient electrolyte wetting, fast electrical conductivity through the electrodes, shortened path for charge carrier transportation and structural stability [30–32]. To this regard, various synthetic methods including mechanical/liquid-phase exfoliation [33], chemical vapor deposition [34], and template synthesis [35], have been put forward. Nevertheless, an overwhelming majority of the aforementioned means bear such drawbacks as time-consumption, high contamination and low yield, which seriously hinder their practicality and commercialization. Thus, it is of primary significance to open up a convenient, eco-friendly and sustainable route to fabricate 2D carbon materials.

Petroleum asphalt, as a major by-product of vacuum distillation of crude oil in petrochemical industry, has been mainly applied to low level utilization such as road pavement, water conservancy and roofing material in virtue of its viscoelastic and waterproof properties, which is a great waste of resources [5]. Taking account of the high carbon yield and aromaticity content of petroleum asphalt, it is imperative to take advantage of the readily available asphalt as carbon resources to manufacture high value-added carbon products. To this end, petroleum asphalt can be a good sort of raw materials to fabricate alternative carbonaceous anodes for batteries. Wei et al. prepared graphene from asphalt with the assistance of vermiculite template. The graphene anode exhibited high reversible capacities of 692 mAh g^{-1} at 50 mA g^{-1} and ~250 mAh g^{-1} at 1 A g^{-1} for LIBs [36]. Moreover, Song et al. synthesized mesophase-pitch derived mesoporous soft carbon utilizing nano-$CaCO_3$ template. The resultant carbon anode delivered superior sodium storage capacities of 331 mAh g^{-1} at 30 mA g^{-1} and 103 mAh g^{-1} at 500 mAh g^{-1} after 3000 cycles [37]. Although the above methods achieved high performance carbon materials from asphalt, the unrecyclable templates and hazardous chemicals used during the removal of these templates still incurred inevitable environmental cost to the final product.

Recently, Liu et al. demonstrated an interesting approach converting glucose to graphene through tuning carbonization conditions in a liquid molten-salt (MS) medium [38], which shed light on the possibility of assembling aromatic hydrocarbon into few-layer graphene sheets. Since petroleum asphalt contains a large amount of organic aromatic molecules, herein, petroleum asphalt was used as the raw material to prepare carbon nanosheets through a simple molten-salt method. A eutectic salt mixture of NaCl/KCl with a melting point of 657 °C was selected as the liquid media. The obtained carbon nanosheets were used as anode material both for LIBs and SIBs, their electrochemical performances and application possibilities were investigated.

2. Experimental

2.1. Samples synthesis

Petroleum asphalt (PA) obtained from Sinopec Group (7.1 wt% of saturates, 24.9 wt% of aromatics, 46.1 wt% of resins and 18.0 wt% of asphaltenes) was selected as the carbon precursor. All other chemicals were of analytical reagent grade and directly used without any further purification process. Typically, 0.5 g PA was dissolved in 20 ml toluene under sonication for 20 min. Then, 10 g eutectic composition of NaCl/KCl (4.5:5.5 by weight) were grounded in an agate mortar for 20 min and then added to the obtained solution. The above mixture was dried at 90 °C in an oil bath under mild magnetic stirring (160 rpm) to form a homogeneous mixture and reclaimed the toluene. The obtained dark-brown powder was thereafter transferred to a ceramic boat and put in the center of a tube furnace. Subsequently, the sample was heated to 800 °C at a ramp rate of 5 °C min^{-1} and dwelled for 2 h under a continuous nitrogen flow. After naturally cooled down to room temperature, the as-prepared sample was washed with sufficient deionized water to remove salts and collected by vacuum filtration, finally dried at 60 °C for 24 h to obtain the final sample nominated as MSC. For comparison, bare PA was treated by the same procedure without the addition of the eutectic salts and denoted as PAC.

For salt recycling test, after the sample was washed with deionized water, the resulting solution was collected by filtration, then heated at 90 °C to evaporate the water to obtain white crystals and finally dried at 100 °C overnight. The recovered salts were used to prepare the subsequent sample (denoted as RMSC) under the same condition.

2.2. Materials characterization

The morphologies of the as-prepared products were observed using field emission scanning electron microscopy (SEM, Hitachi S-4800). Transmission electron microscopy (TEM), selected area electron diffraction (SAED), and energy dispersive spectroscopy (EDS) were carried out on JEM-2010 system at 220 kV. X-ray diffraction (XRD, X'Pert PRO MPD) operated at 40 kV and 40 mA (Cu Kα radiation, $\lambda = 1.5406$ Å) and Raman spectroscopy (Renishaw RM2000) were used to examine the graphitization degree of the obtained samples. The interlayer spacing was calculated by Bragg equation ($2d\sin\theta = n\lambda$). The elemental composition and chemical bonding were studied by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250XI) with Mg Kα radiation and Fourier transform infrared spectra (FT-IR, Nicolet 6700 Spectrometer). Thermogravimetric analysis (TGA) was recorded on Shimadzu TA-60Ws Thermal Analyzer at a heating rate of 10 °C min^{-1}, from room temperature to 1000 °C in nitrogen. The pore property was tested by nitrogen adsorption-desorption isotherms on ASAP 2000 Micromeritics instrument.

2.3. Electrochemical measurements

The electrochemical performance was conducted with CR2032-type coin cells assembled in an argon-filled glove box (H_2O < 0.1 ppm, O_2 < 0.1 ppm). The working electrode was prepared by mixing 80 wt% as-prepared samples, 10 wt% carbon black, and 10 wt% poly(vinylidene fluoride) (PVDF) in *N*-methyl-2-pyrrolidinone (NMP) solvent to form a homogeneous slurry. Then the resulting slurry was pasted onto Cu foil, and dried in a vacuum oven at 80 °C for 12 h. The areal loading amount of the electrodes was about 0.8 mg cm^{-2}. LIBs were assembled with lithium metal foil as the counter electrode, 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 v/v) as the electrolyte, and polypropylene film as separators. For the assembly of SIBs, sodium metal foil served as the counter electrode, 1 M $NaClO_4$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 v/v) was used as the electrolyte while the separator was made of glass fibers. The typical adding amount of the electrolyte in each cell was 80 μL for LIBs and 100 μL for SIBs. The galvanostatic charge-discharge tests were investigated by a Land CT2001A battery test system at a potential window of 0.01–3 V (vs. Li^+/Li) and 0.01–2.8 V (vs. Na^+/Na). Cyclic voltammetry (CV) at a scan rate of 0.1 mV s^{-1} and electrochemical impedance spectroscopy (EIS) at a frequency range of 100 kHz to 10 mHz with AC amplitude of 5 mV were both performed on CHI760D electrochemical workstation. All the electrochemical measurements were carried out at room temperature.

3. Results and discussion

The preparation procedures for MSC nanosheets are illustrated