Research Paper

Self-doped carbon architectures with heteroatoms containing nitrogen, oxygen and sulfur as high-performance anodes for lithium- and sodium-ion batteries

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ABSTRACT

Nitrogen, oxygen and sulfur tridoped porous carbons have been successfully synthesized from natural biomass algae-Carrageen by using a simultaneous carbonization and activation procedure. The doped carbons with sponge-like interconnected architecture, partially ordered graphitic structure, and abundant heteroatom doping perform outstanding features for electrochemical energy storage. When tested as lithium-ion battery anodes, a high reversible capacity of 839 mAh g^{-1} can be obtained at the current density of 0.1 A g^{-1} after 100 cycles, while a high capacity of 228 mAh g^{-1} can be maintained at 10 A g^{-1}. Tested against sodium, a high specific capacity of 227 can be delivered at 0.1 A g^{-1} after 100 cycles, while a high capacity of 109 mAh g^{-1} can be achieved at 10 A g^{-1}. These results turn out that the doped carbons would be potential anode materials for lithium- and sodium-ion batteries, which can be achieved by a one-step and large-scale synthesis route. Our observation indicates that heteroatom doping (especially sulfur) can significantly promote ion storage and reduce irreversible ion trapping to some extent. This work gives a general route for designing carbon nanostructures with heteroatom doping for efficient energy storage.

1. Introduction

Creating energy storage devices has fundamental significance for the improvement of electrical vehicles and renewable energy [1,2]. Over the past several decades, lithium ion batteries (LIBs) have been extensively used in energy storage systems due to their characteristics of high energy density and relatively long cycle life [3,4]. However, a continuous demand for LIBs in large-scale applications has been greatly hindered by its cost and the limited lithium resource on our earth [5,6]. Sodium is a proper alternative to lithium owing to its lower price, abundant resource and environmentally friendliness. Therefore, sodium ion batteries (SIBs) are attracting more and more attention in large-scale applications [7–10]. However, compared with lithium ion, sodium ion has a larger ionic radius, making it difficult to design a suitable electrode with a larger interlayer spacing for intercalating and accommodating sodium ions [11–14].

Nowadays, carbon material is gradually became a prevailing electrode material for energy storage systems owing to its low cost, excellent physicochemical stability, controllable pore structure, and long cycling life [15,16]. Unfortunately, because of the relatively low theoretical capacity (372 mAh g^{-1}) and poor rate performance, most common graphitic carbons do not meet the requirement for high energy and power LIBs [17–19]. Moreover, many graphitic carbons display a very limited performance or even fail when being tested as electrode materials for SIBs due to the narrow graphitic interlayer spacing, which has been greatly hindered the development of SIBs [5,20,21]. Nevertheless, the exploration of carbon electrodes with outstanding lithium and sodium storage performance remains a big challenge. Over the years, in order to promote the electrochemical performance of carbon electrodes, a variety of new approaches have been made to address these inherent problems, including manufacturing novel nanostructures to shorten the diffusion pathways [22,23], providing a high surface area for active sites to enhance charge capacity [24,25], and offering a hierarchical porosity to accelerate ion transport [26,27]. By the synergistic effect of these approaches, the electrochemical property of carbon materials as anodes for LIBs and SIBs can be greatly boosted.

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Recent results indicate that the electrochemical performance of carbon electrodes can also be effectively improved by heteroatom doping [28,29]. Noteworthy examples of heteroatom doped carbons include nitrogen-doped porous carbon (a capacity of 785 mAh g^{-1} after 1000 cycles at 5 A g^{-1} for LIBs) [30], sulfur-doped mesoporous carbon (a capacity of 579 mAh g^{-1} after 970 cycles at 0.5 A g^{-1} for LIBs) [31], nitrogen-doped graphene foams (a capacity of 605 mAh g^{-1} after 150 cycles at 0.5 A g^{-1} for SIBs) [32], and sulfur-doped carbon with enlarged interlayer distance (a capacity of 303 mAh g^{-1} after 700 cycles at 0.5 A g^{-1} for SIBs) [33]. However, most of doped carbons were prepared by post treatment with nitrogen or sulfur-containing gases or powders, and the introduced functional groups are usually unstable during cycling [34–36]. Therefore, the finding of different easy approach for the incorporation of heteroatoms is urgent.

In addition to the eminent electrochemical performance of carbon electrodes, the cost, environmental friendliness, and universality of carbon materials are all essential elements that should be considered for large-scale production [37–39]. Recent years, utilizing natural biomass to fabricate carbon electrodes has attracted extensive attention [40]. It has been proved by many successful instances that good performance can be achieved from biosources, such as peat moss [41], corn stalks [42], peanut skin [43], rice husk [44], horn [45], and garlic peel [46]. In the present work, we demonstrate that nitrogen, oxygen, and sulfur doped porous carbon with a 3D interconnected architecture, hierarchical porosity and high surface area can be derived from Carrageen through a simple carbonization and activation process. There are two main reasons for choosing algae-Carrageen as the precursor. First, algae-Carrageen is widely distributed in coastal areas [47], which can be used as an inexpensive precursor to satisfy the requirement for large-scale application. Second, Carrageen is the main algae for the production of Carrageenan, and sulfate group is present in the composition of Carrageenan, which results in the carbons being doped with sulfur. Proteins, fat and thiamine can also be present in Carrageen, which can also introduce the possible nitrogen, oxygen, and sulfur doping [48–52]. The resultant carbon anodes exhibit a high reversible capacity of 839 mAh g^{-1} and 227 mAh g^{-1} for LIBs and SIBs at 0.1 A g^{-1} after 100 cycles, indicating that they can be used as potential electrode materials for LIBs and SIBs.

2. Experimental

2.1. Material synthesis

The employed Carrageen precursor in this article was purchased from Rizhao, China. In a typical preparation process, the as-received Carrageen was washed by ethanol and distilled water to remove impurities, and then dried in an oven at 80 °C for 6 h. After that, 3.0 g of dried Carrageen was immersed in 50 mL KOH solution (1 M, 2 M, and 3 M) for 24 h. After adsorbing enough solution, the Carrageen was directly collected from the solution and dried at 80 °C in an oven. The simultaneous carbonization and activation were carried out in a tubular furnace at 700 °C with a ramping rate of 3 °C min^{-1} for 1 h under a nitrogen atmosphere. Finally, the activated samples were washed by 2 M HCl and distilled water. The resultant carbon samples were dried at 60 °C for 12 h. The finally Nitrogen, Oxygen, and Sulfur Doped Carbon Architecture was labeled as NOSDCA-*n*, where *n* indicates the used concentration of KOH solution (mol L^{-1}). The mass ratio of KOH to Carrageen for NOSDCA-1, NOSDCA-2, and NOSDCA-3 is about 1:10, 2:10, and 3:10. For comparison, 3.0 g of dried Carrageen was also heated at 700 °C with a heating rate of 3 °C min^{-1} for 1 h under nitrogen flow without the immersion with KOH solution, and the obtained carbon sample was labeled as NOSDCA-0.

2.2. Material characterization

X-ray diffraction (XRD) patterns from 10° to 80° were recorded with a BrukerD8 Advance powder diffractometer using Cu Kα radiation. Scanning electron microscopy (SEM) image was performed using the Hitachi-4800 scanning electron microscope. Transmission electron microscopy (TEM) image was conducted with a JEOL 2010 microscope at 200 kV. Nitrogen adsorption and desorption isotherms were performed on a Micromeritics 3 Flex^{TM} surface characterization analyzer at 77 K. Raman spectroscopy analysis was performed with a Laser Confocal Micro-Raman Spectroscopy (LabRAM HR800). Furthermore, in order to analyze the chemical composition of the samples, X-ray photoelectron spectroscopy (XPS) was measured by using Axis Ultra Spectrometer.

2.3. Electrochemical evaluation

A slurry was prepared by mixing active material with poly (vinylidenedifluoride) and super P at a weight ratio of 8:1:1 in *N*-methyl-2-pyrrolidone solvent. The slurry was coated on the copper foil to obtain the electrode. The mass loading of active materials was about 1 mg cm^{-2}. After drying at 120 °C under vacuum, the coin cells were assembled in the Ar-filled glovebox by using the above prepared carbon electrode as working electrode, lithium metal foil or sodium metal foil as the counter electrode, and polyethene as the separator. 1 M Lithium hexafluorophosphate (LiPF$_6$) or sodium perchlorate (NaClO$_4$) in ethylenecarbonate (EC) and dimethylcarbonate (DEC) with a volume ratio of 1:1 was used as the electrolyte. A Land battery measurement system (CT2001A) was used to measure the galvanostatic charge-discharge profiles in the voltage range between 0.01 and 3.0 V (vs. Li$^+$/Li or Na$^+$/Na). A CHI 660 workstation was introduced to record the cyclic voltammograms (CV) at a scan rate of 0.1 mV s^{-1} in a voltage window of 0.01-3.0 V. A Gamry Interface 1000 workstation was carried out to measure the electrochemical impedance spectroscopy (EIS) in the frequency range of 1 MHz to 10 mHz with an AC signal amplitude of 10 mV.

3. Results and discussion

3.1. Physicochemical characterization

As Fig. 1 illustrated, the dried dendritic Carrageen can adsorb the KOH solution during the impregnation process. The adsorption effect of Carrageen can allow efficient enrichment of KOH inside the cells, which can be converted into KOH/Carrageen composite after drying. Then, a simultaneous carbonization and activation process is performed at 700 °C in a nitrogen atmosphere to produce NOSDCAs. During the activation step, the carbon can react with KOH to generate micro/mesoporosity in the final products. The activation process of Carrageen with KOH is followed by 6KOH + 2C ↔ 2K + 3H$_2$ + 2K$_2$CO$_3$, then decomposition of K$_2$CO$_3$ and/or reaction of K/K$_2$CO$_3$/CO$_2$ with carbon [53]. The morphology and structure evolution of NOSDCAs can be evaluated by SEM and TEM analysis. Fig. 2 and Fig. S1 shows the SEM images of NOSDCAs, revealing that NOSDCAs have the sponge-like morphology constituted by interconnected carbon walls. With the increase of KOH loading, the thickness of carbon wall becomes thinner. Owing to the KOH etching, lots of macropores (~0.2–1 μm) can be found on the NOSDCAs. For comparison, the macropores couldn't be observed in NOSDCA-0 specimen prepared without the addition of KOH. Fig. 3 shows the TEM micrographs for NOSDCA samples, illustrating that the sponge-like structure is composed of carbon nanosheets. Lots of randomly distributed micro/mesopores can be seen on the surface of carbon nanosheets. It can be concluded that