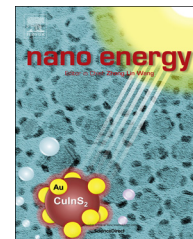




Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy



RAPID COMMUNICATION

Sulfur covalently bonded graphene with large capacity and high rate for high-performance sodium-ion batteries anodes



Xiaolei Wang^a, Ge Li^a, Fathy M. Hassan^a, Jingde Li^a, Xingye Fan^a, Rasim Batmaz^a, Xingcheng Xiao^b, Zhongwei Chen^{a,*}

^aDepartment of Chemical Engineering, University of Waterloo, 200 University Avenue West, Waterloo, ON, Canada, N2L3G1

^bChemical Sciences and Materials Systems, General Motors Global Research and Development Center, 30500 Mound Road, Warren, MI 48090, United States

Received 20 March 2015; received in revised form 28 May 2015; accepted 31 May 2015
Available online 7 June 2015

KEYWORDS

Sodium-ion battery;
Sulfur-doped graphene;
Covalent bonding;
Nanoporous;
Long stability;
High rate

Abstract

Na-ion battery is playing an important role as a low-cost alternative power source to Li-ion battery. Developing novel carbonaceous anode materials is highly demanded for high performance and environmental benignity. We report, for the first time, the graphene sheets covalently bonded with sulfur atoms as Na-ion battery anode material with a large reversible capacity of 291 mA h g^{-1} and an outstanding rate capability with 127 and 83 mA h g^{-1} at 2.0 and 5.0 A g^{-1} (charging/discharging in 3.8 and 1 min, respectively), and a long cycling stability as well. Both experiment and density functional theory calculation proves that the superior performance is mainly attributed to the unique nanoporous structure stemmed from the chemically S doping. This material holds great promise in future application of low cost, high-performance Na-ion batteries.

© 2015 Elsevier Ltd. All rights reserved.

Introduction

There is an ever-increasing demand for the rechargeable lithium-ion batteries (LIBs) in the upcoming era of portable

electronics, electric transportation and smart grids, owing to their high energy and mature fabrication technologies [1–3]. The further development and large-scale application of LIBs, however, has brought growing concern from both academia and industry in recent years regarding the increasing cost and an uneven geological distribution of lithium source [4]. By comparison, sodium (Na) is environmentally benign and is the sixth abundant element in the

*Corresponding author.

E-mail address: zhwchen@uwaterloo.ca (Z. Chen).

Earth's crust, while the sodium salts used to prepare battery materials are plentiful [5]. Furthermore, the standard electrode potential of Na/Na⁺ at 2.71 V and of Li/Li⁺ at 3.02 V are very close to each other, and the non-aqueous electrolytes containing sodium salts usually show similar electrochemical windows, comparable ionic conductivities and stabilities to lithium-ion counterparts [6,7]. In this context, sodium-ion based rechargeable batteries hold great promise as low-cost alternative power sources to LIBs for future energy storage technologies.

Compared to LIBs technology, the energy and power performance of SIBs cannot meet the current needs due to the limited capacity and slow kinetics of the SIBs electrodes [8]. It is well recognized that reversible and rapid sodium ions insertion and extraction is more complicated and difficult than Li⁺ in host materials, due to the larger ion radius (1.02 Å of Na⁺ vs. 0.76 Å of Li⁺) [9]. Therefore, the key factor is to develop suitable electrode materials with sufficient interstitial space for sodium ions storage and transportation [10]. Recent research shows that many transition metal oxides [11,12], fluorophosphates [13–15], fluorosulphate [16], and ferricyanide [17–19] can serve as cathode materials with a certain capacity [20]. However, these non-carbon based inorganic materials can hardly be dominant due to the environmental benignity and cost considerations.

Although graphite, which is the dominant anode material in current LIBs technology, is not suitable for SIBs anode since no staged intercalation compounds can form [21], other carbonaceous materials still attract considerable research attention. For example, hollow carbon nanowires deliver a high reversible capacity of 251 mA h g⁻¹ [22], while hollow carbon nanospheres exhibit excellent rate capability (75 mA h g⁻¹ at 5.0 A g⁻¹) [23]. Many other carbon materials such as petroleum cokes [24–26], carbon black [27], template carbon [28], and hard carbon [29] have also been reported, however, the capacity and rate capability of SIBs anode are still hardly comparable to that of LIBs. It is widely accepted that the sodium insertion mechanism strongly depends on the size, the graphitization degree, the structure or textural disorder, and the porosity [30]. In this context, developing novel carbon-based anode materials with high reversible capacity and rate capability is still challenging and urgently needed.

Herein, we report for the first time the utilization of chemically sulfur-doped graphene (SG) as anode material for high-performance sodium-ion based energy storage. Recently, graphene has been attracting tremendous interest due to its unique two-dimensional, single atomic layer structure. Different from graphite with well ordered layers which is not favorable for Na⁺ insertion, graphene with a few layers stack shows improved sodium storage property [31,32]. In this work, benefiting from the sulfur atoms covalently bonded to the graphene sheets, the obtained SG material exhibits a high reversible capacity of 291 mA h g⁻¹, a long stability over 200 cycles, and a superior rate capability (83 mA h g⁻¹ at 5.0 A) as well, which is mainly attributed to the electronic structure changes in graphene sheets.

Results and discussion

The SG was prepared starting from graphene oxide (GO) using phenyl disulfide (PDS) as the sulfur precursor through a

high-temperature flash heat treatment, where the sulfur atoms and graphene sheets covalently bond together. The morphology and microstructure of the chemically S-doped graphene were characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM). Figure 1A shows the representative SEM image of the as-prepared SG material. Similar to pure graphene materials, a two-dimensional sheet-like structure with wrinkled and folded features was obtained. Figure 1B shows the representative TEM image of the as-prepared SG material. Transparent and crumpled silk veil-like structures with single or a few graphene layers can be clearly observed. In order to confirm the presence of element sulfur in SG, the elemental composition analysis from EDX pattern was applied, showing ~2.52% S exists in atomic ratio (Figure 1C). The distribution of S atoms is further verified by EDS element mapping. As shown in Figure 1D, the S atoms are uniformly dispersed in the graphene sheets, indicating the successful formation of chemically S-doped graphene. The electron energy loss spectroscopy (EELS) was also performed, confirming the existence of element C and S in SG. Based on the EELS analysis, the S content in the SG is 2.29% in atomic ratio (Figure S1).

In order to investigate how sulfur atoms are covalently bonded to graphene sheets, X-ray photoelectron spectroscopy (XPS) measurements were carried out (Figure S2). Figure 2A shows the XPS core-level spectrum of S 2p, where two major peaks locating at 163.74 and 164.92 eV can be observed, indicating a significant amount of S (3.33%). The doublet possesses an area ratio of 2:1 with a splitting of 1.18 eV, which well matches the standard value [33]. The lower energy shift (164.00 eV for standard S 2p_{3/2}) of S 2p_{3/2} and 2p_{1/2} doublet is associated with lower valence states, suggesting the covalent bonding of S atoms to carbon atoms in a heterocyclic configuration. Four minor peaks can also be found at higher energy, which can be attributed to a small amount of carbon bonded SO_x species [34]. Obviously, in the corresponding structural scheme of SG material shown in Figure 2B, the C-S-C species exist in the thiophene form residing on the edge plane and defect sites of SG, which is the dominant S dopants in SG materials (~79%, Table S1). The existence of minor peaks of C 1s at higher energy from the core-level spectrum also implies the successful doping of S atoms with C (Figure S3). Figure 2C shows the representative X-ray diffraction pattern of SG material, with the characteristic (002) peak of graphite observed at 25.6°. The interlayer distance of SGs was calculated to be 0.348 nm, which was larger than that of graphite crystal structure with 0.335 nm. No obvious peaks from pure sulfur can be observed, further confirming the absence of element S. The porous structure of SG is characterized by the nitrogen adsorption-desorption isotherms. As shown in Figure 2D, the SG material exhibits a type IV isotherm with a Brunauer-Emmett-Teller (BET) surface area of 280 m² g⁻¹. Besides, the SG material possesses both micropores below 2 nm and mesopores generated from SG crumpling and piling (Figure 2D, inset).

The Na⁺ insertion/extraction behavior in SG was first investigated by cyclic voltammetry using 2032-type coin-cells with sodium foil as the counter electrode. The mass loading of active materials in each electrode was controlled to be 1.2 mg cm⁻². Figure 3A shows the cyclic

Download English Version:

<https://daneshyari.com/en/article/1557425>

Download Persian Version:

<https://daneshyari.com/article/1557425>

[Daneshyari.com](https://daneshyari.com)