Chemical Engineering Journal 332 (2018) 260–266

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Rational design of MoS_2-reduced graphene oxide sponges as free-standing anodes for sodium-ion batteries

Jinliang Li[a,b], Wei Qin[c], Junpeng Xie[a], Rui Lin[a], Zilong Wang[a], Likun Pan[b,*], Wenjie Mai[a,*]

[a] Siyuan Laboratory, Guangzhou Key Laboratory of Vacuum Coating Technologies and New Energy Materials, Department of Physics, Jinan University, Guangzhou, Guangdong 510632, China

[b] Shanghai Key Laboratory of Magnetic Resonance, School of Physics and Materials Science, East China Normal University, Shanghai 200062, China

[c] State Key Laboratory of Optoelectronic Materials and Technologies, Nanotechnology Research Center, School of Materials Science & Engineering, Sun Yat-sen University, Guangzhou, Guangdong 510275, China

ARTICLE INFO

Keywords:
MoS_2-reduced graphene oxide sponges
Sodium-ion batteries
Free-standing electrode
Anode material

ABSTRACT

Currently, the search for high capacity, low cost and free-standing electrodes for sodium-ion batteries (SIBs) is one of the major challenges in energy storage field. In this work, we rationally design MoS_2-reduced graphene oxide (MS-RGO) sponges via a simple freeze-drying of ammonium tetrathiomolybdate-graphene oxide mixed solution and a subsequent thermal treatment in N_2/H_2 atmosphere, and employ these sponges as free-standing anodes for SIBs. The MS-RGO sponges exhibit a porous conducive structure that can facilitate the charge transport and thus show an excellent electrochemical performance. The free-standing sponge electrodes display a maximal reversible specific capacity of 372.0 mAh g^{-1} (0.49 mAh cm^{-2}) at a current density of 100 mA g^{-1} after 50 cycles. Even at a high current density of 1 A g^{-1}, a capacity of 192.2 mAh g^{-1} (0.25 mAh cm^{-2}) is maintained after 345 cycles. The results show that MS-RGO sponges are promising free-standing electrode materials for rechargeable SIBs.

1. Introduction

Currently, lithium-ion batteries (LIBs) have been widely studied for energy-storage field such as portable devices due to their high energy density and long cycle life [1–5]. However, concerns for the cost and safety of lithium resources, development new rechargeable battery systems for energy storage including electric vehicles and electrical grid have been triggered [6,7]. As a promising alternative to LIBs, sodium-ion batteries (SIBs) have drawn increasing attention due to their lower cost, higher abundant storage and the similar chemical and physical properties of lithium and sodium [8–11]. However, seeking an appropriate material to store sodium ions is still a great challenge due to the radius of sodium ions (1.02 Å) is greater than that of lithium ions (0.76 Å) [12–14]. Thus it is very necessary to explore suitable anode materials for SIBs.

Due to the inability of sodium ion intercalation, the commercial graphite is recognized that it is not appropriate using as anode material for SIBs [15,16]. Thus, seeking suitable anode materials for SIBs with superior electrochemical performance (ECP) is imminently desirable. Currently, many efforts have been placed to seek appropriate metal oxides, alloys and carbonaceous materials as anode materials for SIBs. Among various anode materials, transition metal sulphides have been proven to be potential candidates due to their high specific capacities and pervasive availability [17–19]. Sodium storage performances in some representative reports are listed in Table S1. Compared with other transition metal sulphides, MoS_2 has obtained much attention due to some encouraging results from its unique property [20–22]. Recently, many studies have proved that MoS_2 exhibits a very high specific capacity and great rate capability as anode material for SIBs [23,24]. However, MoS_2 also shows a fast capacity fading due to its poor conductivity and large volume change between S-Mo-S sheets during charge-discharge processes [25–27]. To overcome this limitation, many attempts have been devoted to study MoS_2-graphene hybrid nanostructures, and it is found that such hybrid nanostructures can significantly improve the ECP of MoS_2. This is ascribed to the fact that graphene can significantly enhance the conductivity and the structure stability of the composite [28,29].

In order to further improve the power density for SIBs, free-standing electrodes were proposed, in which all the electrode materials can contribute to the charge storage [30]. Such free-standing electrodes can not only predigest the cell packing, but also reduce the total mass (including current collectors and binders) and improve overall

* Corresponding authors.
E-mail addresses: jinliang.li@qq.com (J. Li), qinw6@mail.sysu.edu.cn (W. Qin), 737500461@qq.com (J. Xie), 1098463950@qq.com (R. Lin), zilong@email.jnu.edu.cn (Z. Wang), lkpan@phy.ecnu.edu.cn (L. Pan), wenjiemai@gmail.com (W. Mai).

http://dx.doi.org/10.1016/j.cej.2017.09.088
Received 25 July 2017; Received in revised form 10 September 2017; Accepted 13 September 2017
Available online 14 September 2017
1385-8947/

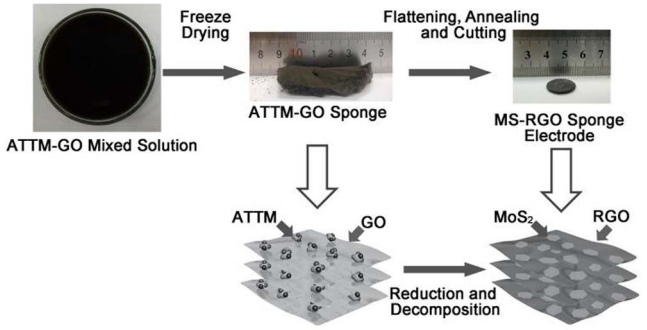

Fig. 1. Schematic of the synthesis process of MS-RGO sponges.

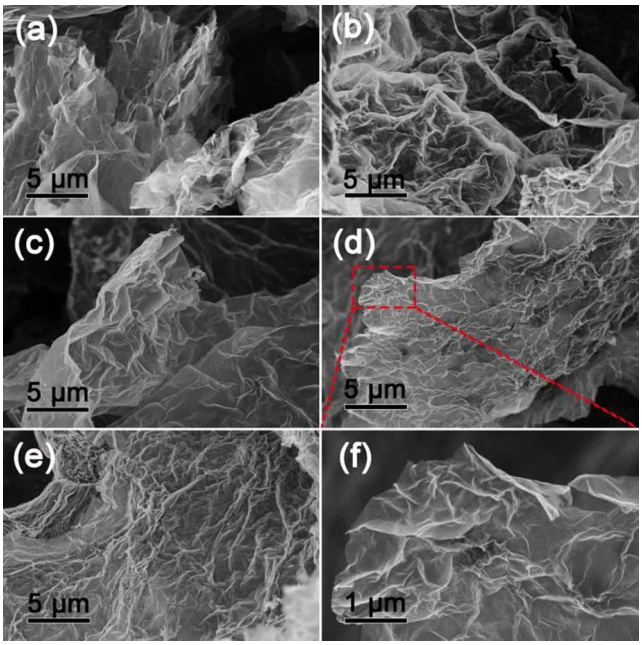

Fig. 2. FESEM images of (a) RGO, (b) MR-1, (c) MR-2, (d) MR-3, (e) MR-4 and (f) enlarged image of MR-3.

performance of the device [31,32]. Therefore, some studies have been focused on the free-standing MoS_2 composite electrodes for SIBs. David et al. [33] synthesized MoS_2-graphene paper via vacuum filtration of acid-treated MoS_2 flakes and graphene oxide (GO) homogeneous dispersions and found that the composite as a flexible free-standing electrode exhibited a specific capacity of 218 mAh g^{-1} at a current density of 25 mA g^{-1} after 20 cycles for SIBs. Xiong et al. [34] synthesized flexible membranes of MoS_2-carbon nanofibers by electrospinning and found that the composite as a free-standing electrode showed a specific capacity of 283.9 mAh g^{-1} at a current density of 100 mA g^{-1} after 600 cycles. Xie et al. [35] prepared MoS_2-carbon paper by hydrothermal method and the result showed that the composite as a free-standing electrode exhibited a capacity of 286 mA h g^{-1} at a current density of 80 mA g^{-1} after 100 cycles. In spite of these progresses to date, the low specific capacities of these free-standing electrodes make them far away from practical applications. Therefore, further investigation should be needed to explore free-standing MoS_2-carbon composite anodes with superior performance for SIBs.

In our work, a simple freeze-drying of ammonium tetrathiomolybdate (ATTM) with GO mixed solution and subsequent thermal treatment in N_2/H_2 atmosphere was used to synthesize the MoS_2-reduced graphene oxide (MS-RGO) sponges. The as-prepared MS-RGO sponges were investigated as free-standing electrodes for SIBs and they show excellent sodium-ion storage performance.

2. Experimental

2.1. Synthesis

GO was synthesized by a modified Hummers method [36,37]. For the preparation of RGO and MS-RGO sponges, in a typical process, different amount of ATTM (Apollo Scientific Ltd) was added into 50 mL 2 mg L^{-1} GO solution to form a uniformly-dispersed solution under magnetic stirring and then transferred to culture dishes in a refrigerator. After freezing the mixed solution, the culture dish was transferred to a freeze-dryer (~53 °C, pressure < 15 Pa) for 48 h to obtain ATTM-GO sponges. Then the ATTM-GO sponges were calcined at 800 °C for 2 h in N_2/H_2 (95:5, v/v) atmosphere to obtain the MS-RGO sponges. The MS-RGO sponge samples synthesized using 100, 200, 300 and 400 mg ATTM in precursor solution were named as MR-1, MR-2, MR-3 and MR-4, respectively. RGO sponge was also prepared for the similar procedure except the use of ATTM.

2.2. Characterization

The morphologies of the RGO and MS-RGO sponges were characterized by scanning electron microscopy (Hitachi S-4800, SEM) and transmission electron microscopy (JEOL-2010, TEM). The structures were measured by X-ray diffraction (Panalytical PRO PW3040/60, XRD) with Cu Ka radiation and Raman spectra (Horiba T64000) with a wavelength of 532 nm, respectively. Thermogravimetric analysis (NETZSCH, TGA) was measured from 30 to 700 °C in air. X-ray photoelectron spectroscopy (XPS) was recorded by an Image Photoelectron Spectrometer (Kratos Analytical Ltd.) with Al Ka X-ray source.

2.3. Electrochemical measurement

The RGO and MS-RGO sponges were used as free-standing electrode for SIBs to assess their ECP. Generally, the samples were cut to 14 mm diameter of the composite sponges and used as working electrodes. CR2032 coin type cells were packaged in MBRAUN glove box (MB-10-compact), where sodium foil was used as the counter electrode and the Whatman glass fiber was utilized as separator. The electrolyte is 1 M $NaClO_4$ solution in propylene carbonate and ethylene carbonate (1:1, w/w) with 5% fluoroethylene carbonate. The galvanostatic charge-discharge measurement was recorded by battery test system (LAND2001A) in a voltage of 0.005–3.0 V at a current density of 100 mA g^{-1} except as otherwise noted. Cyclic voltammetry (CV) was performed by an electrochemical workstation (AUTOLAB, EW) at a scan rate of 0.2 mV s^{-1} in a voltage range of 0.005–3.0 V. The electrochemical impedance spectroscopy (EIS) was recorded by the same EW with a frequency range of 0.1 Hz–10 kHz after 50 charge-discharge cycles.

3. Results and discussion

Fig. 1 illustrates the process to synthesize MS-RGO sponges. As shown, GO was first mixed with ATTM to obtain ATTM-GO mixed solution. Due to the large number of functional groups on GO, after freeze-drying, ATTM-GO sponge frame was obtained, and ATTM was attached firmly on the surface of GO sheet. The close contact was helpful to mitigate the aggregation of GO nanosheets to awaken its superior physical and chemical properties. Subsequently, ATTM-GO sponge was flattened and annealed at 800 °C under the atmosphere of N_2/H_2 flow. At this time, the GO was reduced to RGO and ATTM decomposed to MoS_2, resulting in the formation of MS-RGO sponge.

The MoS_2 mass percentages are 53.7%, 66.8%, 73.5% and 77.8% for MR-1, MR-2, MR-3 and MR-4, respectively, which are derived from TGA measurement (Fig. S1 in Supporting Information). Fig. 2 shows the morphologies and structures of RGO and MS-RGO sponges. From Fig. 2(a), the RGO sponge exhibits a 3D interconnected porous structure