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Copper sulfide microspheres wrapped with reduced graphene oxide for high-capacity lithium-ion storage



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ABSTRACT

In this study, a facile two-step approach was developed to prepare the nanocomposites (Cu_xS/rGO) of copper sulfide (Cu_xS) microspheres wrapped with reduced graphene oxide (rGO). The morphology and structure of Cu_xS/rGO materials were researched by using SEM, XRD and laser Raman spectroscopy. Asprepared Cu_xS/rGO nanocomposites, as an active anode material in LIBs, showed distinctly improved electrochemical characteristics, superior cycling stability and high rate capability. Due to the synergistic effect between the Cu_xS microspheres and the rGO nanosheets, as-prepared Cu_xS/rGO nanocomposites could effectively alleviate large volume changes, provide a 2D conductive network and trap the diffusion of polysulfides during the discharge–charge processes, therefore, the Cu_xS/rGO nanocomposites showed excellent electrochemical characteristics.

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1. Introduction

Growing market demands for portable energy storages and environmental issues have triggered significant researches on high-capacity lithium ion batteries (LIBs). The development of next-generation energy-storage devices is of primary importance to meet the challenges in the electronics and automobile industries in the near future [1–9]. In particular, there has been an increasing interest in the development of new multicomponent nanomaterials which can overcome a number of intrinsic limitations of single-component electrode materials for LIBs [10–14]. The performance of batteries depends primarily on the properties of electrode materials, therefore, it is critical to find innovative electrode materials with unique properties to meet these requirements for high-capacity battery development.

Metal sulfides were found to have exceptional electrochemical properties as an alternative material for LIBs electrodes [15,16]. As a new kind of anode electrode materials for LIBs, metal sulfides are known to be promising materials because of their high theoretical capacity [17,18]. Copper sulfides (Cu_xS), in particular, have been attracting high attention since they have such advantages as high theoretical capacity, excellent electrical conductivity and long and flat discharge voltage plateau [19,20]. However, like most other

http://dx.doi.org/10.1016/j.mseb.2016.04.004 0921-5107/© 2016 Elsevier B.V. All rights reserved. metal sulfides, the Cu_xS suffer from some major drawbacks like serious capacity fading and the loss of active material, which are caused by the pulverization of electrodes during cycling and the formation of polysulfides as Li_2S_x (2<x<8) [21–25]. The polysulfide intermediates can easily dissolve into the organic electrolytes during the electrochemical reactions and migrate to the anode side leading to the poor capacity retention of LIBs. One of usually accepted strategies to mitigate these drawbacks is to prepare nanometersized materials with designed structure [20,26]. For example, Tao et al. [27] already reported the fabrication of CuS/graphene composite by the one-pot hydrothermal method, as anode materials for LIBs, it shows a reversible capacity of $296 \text{ mA} \text{ hg}^{-1}$ after 25 cycles with a capacity retention rate of 61%. Ren et al. [28] synthesized "double-sandwich-like" CuS@reduced graphene oxide as an anode materials for LIBs, it exhibits a discharge capacity of 710.7 mA h g^{-1} after 100 cycles at a current density of 0.2C. Feng et al. [29] synthesized copper sulfide nanowires/reduced graphene oxide (CuSNWs/rGO) nanocomposites which exhibit a reversible capacity of $620 \text{ mA} \text{ hg}^{-1}$ at 0.5C after 100 cycles and $320 \text{ mA} \text{ hg}^{-1}$ at a high current rate of 4C even after 430 cycles. Our group has successfully fabricated nanorod-like CuS and Cu₂S by a hydrothermal approach without using any template and surfactant. The CuS and Cu₂S nanorod anodes for LIBs reveal that they show high reversible specific capacity, good cycling stability and outstanding rate capability [30]. However, it is still a challenge to find an easy and simple strategy to prepare large-scale nano-structural materials with designed structures and morphologies.

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Scheme 1. Synthetic sketch of the Cu_xS/rGO.

Herein, we have developed a facile two-step approach to prepare the nanocomposites (Cu_xS/rGO) of copper sulfide (Cu_xS) microspheres wrapped with reduced graphene oxide (rGO). The rGO nanosheets are porous and elastically strong, which act as a conductive agent and a substrate to produce the Cu_xS/rGO nanocomposites as anode materials. Moreover, the Cu_xS microspheres are wrapped in the interior layers of rGO. These nanocomposites could effectively alleviate large volume expansion and shrinkage, provide a 2D conducting network to enhance the electric conductivity and trap the polysulfides generated during the discharge–charge processes. As-prepared Cu_xS/rGO composites should be a promising candidate for application in high-rate LIBs due to the synergistic effect between Cu_xS microspheres and porous rGO nanosheets.

2. Materials and methods

2.1. Preparation of Cu_xS/rGO

All chemical reagents of analytic grade purity were purchased from Shanghai Chemical Co. Ltd. and used without further purification. First, bulk graphite flakes (~45 µm, 99.99%) were oxidized by a modified Hummer's method to prepared graphene oxide (GO) [31]. Then using an ultrasonicator, as-prepared GO was exfoliated and dispersed in deionized water to gain a stable GO suspension, which concentration is 4.0 mg mL⁻¹. Scheme 1 is the synthetic sketch of Cu_xS/rGO composites. To prepare Cu/rGO, at the desired ratio, copper (II) acetate was dissolved in 30 mL deionized water, then under vigorous stirring, 20 mL GO solution was added. The mass ratio of GO/Cu was 1/1. After sonicating 1 h, the mixed solution was quickly frozen by liquid nitrogen, and evaporated in vacuum at the temperatures below 0°C for 48 h using the freeze drying equipment. The dry mixed powders were transferred into a tube furnace, and heated from room temperature to 800°C at a rate of 5°C min⁻¹, and held at this temperature for 1 h under a flowing argon gas. This intermediate product was denoted as Cu/rGO. The nanocomposites (Cu_xS)/rGO were synthesized from Cu/rGO and nano-sized sulfur powders (China National Medicines Corporation Ltd.). Different mass ratios of the Cu/rGO and the sulfur powders were mixed and dispersed in N-methyl-pyrrolidone (NMP), and heated at 100 °C for 0.5 h before solvent evaporation. The synthetic Cu_xS composites are designated as Cu_xS(2:1)/rGO and Cu_xS(4:1)/rGO, respectively.

2.2. Characterization

The morphologies of as-prepared materials were characterized by using a scanning electron microscope (SEM, HITACHI S-4800) equipped with energy dispersive X-ray spectroscopy (EDX) for elemental analysis. The XRD patterns of the Cu_xS/rGO composites and Cu/rGO were recorded using a Philips X'pert Pro Super X-ray diffract meter and Cu K_α radiation. The laser Raman spectra were recorded at a resolution of 1 cm^{-1} in back scattering (180°) configuration using 532 nm excitation.

2.3. Electrochemical measurements

The slurry with composition of 80 wt% the Cu_xS/rGO active materials, 10 wt% polyvinylidene fluorides (PVDF) and 10 wt% carbon black, which were dissolved in NMP, then casted onto a copper foil to prepare the working electrodes. Afterwards, the electrodes were dried under vacuum at 60°C for overnight. The electrode loading was in $1 \sim 2 \text{ mg cm}^{-2}$. The CR2016-type coin cells were assembled using the prepared electrodes and lithium metal in an argon-filled glove box. The electrolyte was formed by adding lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 1 M) salt to the mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) at a 1:1 volume ratio. The galvanostatic charge-discharge experiments were measured at different current densities between 1.0 and 3.0V (vs. Li⁺/Li) using a CT2001A cell test instrument (XINWEI Electronic Co.). The electrochemical impedance spectroscopy (EIS) of the Cu_xS/rGO electrodes were recorded by the Autolab PGSTAT 101 cell test instrument in the frequency range of $10 \text{ mHz} \sim 100 \text{ kHz}$, using two-electrode coin cells with Li metal as the counter electrode. All of the electrochemical tests were performed at room temperature.

3. Results and discussion

The morphology and microstructure of the GO, Cu/rGO and Cu_xS/rGO are shown in Fig. 1a-f, respectively. The SEM image in Fig. 1a shows that the GO with dozens of layers forms a 2D structured network with numerous wrinkles. After reduction, the Cu spheres with diameter of several hundred nanometers coated by the rGO nanosheets are obtained, as shown in Fig. 1b. The SEM images in Fig. 1c and e reveal that as-prepared Cu_xS microspheres are embedded in the rGO nanosheets as expected. Fig. 1d and f further reveals that nano-sized holes are formed on the surface of rGO nanosheets in this process. XRD patterns of samples in Fig. 2a also confirm their structural and compositional differences. $Cu_x S(2:1)/rGO$ can be readily indexed to the hexagonal phase of CuS (JCPDS 001-1281) and there are no metallic copper peaks observed significantly. The XRD pattern of $Cu_x S(4:1)$ shows that it is a mixing phase: one set of the peaks (32.8° and 46.2°) are indexed to Cu_2S (JCPDS 003-1071), the others (43.3°, 50.5° and 74.1°) belong to the unreacted copper powders, and the peak at 48.1° and the broad peaks at about 32.0° and 59.2° indicate the presence of certain amount of CuS.

After chemical oxidation, as-prepared GO shows a strong and sharp peak at 11.6° , indicating that the original sp²-C bonds of graphite are broken during oxidization [32]. The characteristic peak of GO disappears for the Cu/rGO composites (Fig. 2a), this is due to the considerable reduction capability at high temperature. However, because of its low amount and low diffraction intensity, the characteristic stacking peak of the rGO nanosheets at around 26° cannot be identified from the XRD pattern of the Cu/rGO nanocomposites [27].

The reduction of GO was also analyzed by laser Raman spectroscopy. Fig. 2b shows the Raman spectra of the GO and Cu/rGO. For both spectra, there are two major characteristic peaks at ~1350 cm⁻¹ and ~1600 cm⁻¹, respectively. The G band at ~1600 cm⁻¹ attributes to the vibration of sp2 carbon atoms in a 2D hexagonal lattice and the D band at ~1350 cm⁻¹ corresponds to



Fig. 1. SEM images: (a) GO, (b) Cu/rGO, (c and d) Cu_xS(4:1)/rGO and (e and f) Cu_xS(2:1)/rGO at different magnifications.

the disorder and defects in the hexagonal graphitic layers [32–34]. It is found that the ratio of ID/IG for Cu/rGO nanocomposites is 1.01, which is higher than that of GO (0.92). The increased I_D/I_G gives evidence that the GO is successfully reduced to graphene [35]. The laser Raman spectroscopic analysis agrees well with the XRD data.

The electrochemical properties of the Cu_xS/rGO nanocomposites were investigated by galvanostatic measurements. As shown in Fig. 3a and b, both materials show similar electrochemical behaviors. In the first discharge, each of the materials shows two voltage plateaus at around 2.0 V and 1.7 V. As cycling continued, the 2.0 V discharge plateaus for all materials keep shrinking while the 1.7 V plateaus keep increasing. Similar changes occur during the charge process. They all exhibit a small plateau around 1.85 V and a large plateau at 2.3 V in the first charging step. The 2.3 V plateau keeps shrinking while 1.85 V plateau keeps increasing, and eventually the 2.3 V plateau is barely observable. The 2.3 V charge plateau and 2.0 V discharge plateau of the Cu_xS(4:1)/rGO disappear faster than those of the Cu_xS(2:1)/rGO as cycling continued.

This is due to the presence of Cu_2S in the $Cu_xS(4:1)/rGO$ composite material. After the several cycles, there is only one voltage



Fig. 2. (a) XRD patterns of the Cu/rGO, Cu_xS(4:1)/rGO, Cu_xS(2:1)/rGO and (b) laser Raman spectra of the GO and Cu/rGO.

plateau at 1.7 V. This is due to the copper ions in all the copper sulfides are monovalent, and more appropriate formulae would be $(Cu^+)_3(S^{2-})(S_2)^-$ for CuS and $(Cu^+)_2(S^{2-})$ for Cu₂S. When an excess of copper, copper sulfides in which copper ions are considered as $(Cu^+)_2$ and sulfur ions as (S^{2-}) , react electrochemically as Cu₂S. The mechanism for Cu_xS underlithiation and delithiation process as following:

$$CuS + 2Li^{+} + 2e^{-} \leftrightarrow Li_{2}S + Cu$$
(1)

$$Cu_2S + 2Li^+ + 2e^- \leftrightarrow Li_2S + 2Cu$$
⁽²⁾

The specific electrochemical reaction mechanism can be obtained from our previous research work [36].

The galvanostatic cycle performances of these Cu_xS/rGO electrodes at the current density of 200 mA g⁻¹ are shown in Fig. 4. It is observed that the initial discharge capacity is higher, which is due to the insertion of Li⁺ into rGO. After a few cycles, the Cu_xS/rGO electrode shows a stable discharge capacity. After 100 cycles, the capacity of the Cu_xS(4:1)/rGO electrode maintains at 250 mA h g⁻¹, and the capacity keeps at 320 mA h g⁻¹ for the Cu_xS(2:1)/rGO electrode. Compared to various CuS as electrode material for LIBs have been studied, for example, Lai et al. [37] prepared copper sulfide nanowire array cathodes with a capacity of 230 mA h g⁻¹ after 100 cycles (2C, 0.05–3.0V), however, its capacity is lower and capacity retention rate of only 50% after 100 cycles. Compared to Wang et al. [38] synthesized CuS cathode, we can see that it

holds a reversible capacity around 390 mA h g⁻¹ after 100 cycles (1C, 1.2–3.0 V). Although its capacity is high, but it is calculated in accordance with the weight of the CuS. It is obvious that the composites have high capacity and cycle stability. This may attribute to the unique structure of the Cu_xS/rGO composites, the Cu_xS microspheres are embedded in the rGO nanosheets and evenly distributed in the sheets, at the same time, nano-sized holes are formed on the surface of rGO nanosheets. Therefore, the Cu_xS/rGO composites can efficiently trap the polysulfides and suppress the outward diffusion of polysulfides, which restricts the diffusion of polysulfides to some extent, as well as, the Cu_xS/rGO nanocomposites could effectively alleviate large volume expansion and shrinkage, provide a 2D conducting network.

Besides having high capacity and cycle stability, both the $Cu_xS(4:1)/rGO$ and $Cu_xS(2:1)/rGO$ also have excellent rate capability. Following the electrochemical studies and long-term cycle capability of the $Cu_xS(4:1)/rGO$ and $Cu_xS(2:1)/rGO$, we next investigated their rate capabilities as shown in Fig. 5. At the maximum discharge rates of $7 A g^{-1}$, particularly, the $Cu_xS(4:1)/rGO$ and $Cu_xS(2:1)/rGO$ deliver average capacities of $140 \text{ mA h } g^{-1}$ and $205 \text{ mA h } g^{-1}$, respectively.

According to the former reports [39–41], it is the synergistic effect between Cu_xS nanospheres and rGO nanosheets that leads to the superior electrochemical performance of the Cu_xS/rGO . On the one hand, the excellent electrochemical performance derives from the novel structure for which the uniform distribution of



Fig. 3. Electrochemical performance of Li/(Cu_xS/rGO) cells. Discharge-charge profiles: (a) $Cu_xS(4:1)/rGO$ and (b) $Cu_xS(2:1)/rGO$. Discharge-charge profiles were obtained between 1.0 and 3.0 V vs. Li⁺/Li at a current density of 200 mA g⁻¹.



Fig. 4. Cycling performances at constant current of 200 mAg^{-1} : (a) Cu_xS(4:1)/rGO and (b) Cu_xS(2:1)/rGO.



Fig. 5. Rate capability and Coulombic efficiency of the $Cu_xS(4:1)/rGO$ and $Cu_xS(2:1)/rGO$ from 1.00 to 3.00 V.

 Cu_xS microspheres on the rGO nanosheets prevents the restacking of the rGO nanosheets as well as the aggregation of the Cu_xS nanospheres [42]. This kind of structure can make the composites effectively contact with the electrolyte, which facilitate the diffusion of Li ion. On the other hand, the electronic transport is largely accelerated and the interface resistance among particles is reduced because of the outstanding conductivity of rGO nanosheets [43]. In addition, the rapid capacity fading caused by the dissolution of Li₂S_x into the electrolyte is well weaken by the conductive graphene.

To further interpret the superior electrochemical performance of the Cu_xS/rGO nanocomposites electrode, the electrochemical impedance spectroscopy was also measure (Fig. 6). The Nyquist plots show a sloping line in the low-frequency region and a compressed semicircle which consists of two partly overlapped semicircles in the high-to-medium frequency region. An equivalent circuit was adapted to fit the plots (inset of Fig. 6) [28,44]. As is shown, the high-frequency region semicircle to be equivalent to SEI layer dielectric relaxation capacitance and resistance (CPE1 and R_f), and the semicircle in medium-frequency region to be equivalent to the CPE2 and charge-transfer resistance R_{ct} of electrode/electrolyte interface. The sloping line is referred to the lithium-diffusion process. The values of R_f of Cu_xS(4:1)/rGO and Cu_xS(2:1)/rGO composites are 23.52 and 13.89 Ω , the values of R_{ct} of $Cu_x S(4:1)/rGO$ and $Cu_x S(2:1)/rGO$ composites are 65.72 and 82.51 Ω . The result confirms that the Cu_xS/rGO nanocomposites electrode possesses the high conductivity and remarkably enhances rapid electron transfer as well during the charge and discharge. Therefore, the Cu_xS/rGO



Fig. 6. Electrochemical impedance spectroscopy of the $Cu_xS(4:1)/rGO$ and $Cu_xS(2:1)/rGO$ electrodes and corresponding equivalent circuit model of the studied system (inset).

nanocomposite electrode shows excellent electrochemical performance, namely superior cycling stability and high rate capability.

4. Conclusions

In summary, we have developed a facile two-step approach to prepare the Cu_xS/rGO nanocomposite of Cu_xS microspheres wrapped with rGO. The composites show excellent electrochemical performance, namely superior cycling stability and high rate capability. Both the Cu_xS(4:1)/rGO and Cu_xS(2:1)/rGO nanocomposites show significantly high capacities of 250 mA hg⁻¹ and $320 \text{ mA} \text{ hg}^{-1}$, respectively, at 200 mAg^{-1} after 100 cycles. Even at a high current density of 7 Ag^{-1} , the discharge capacities of Cu_xS(4:1)/rGO and Cu_xS(2:1)/rGO nanocomposite electrodes keep stable still and remain at $140 \text{ mA} \text{ hg}^{-1}$ and $205 \text{ mA} \text{ hg}^{-1}$, respectively. The excellent electrochemical performance of the Cu_xS/rGO composites is mainly due to the Cu_xS/rGO nanocomposites can effectively alleviate large volume expansion and shrinkage, provide a 2D conducting network to enhance the electric conductivity and trap the polysulfides generated during the discharge-charge processes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mseb.2016.04. 004.

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