

Contents lists available at ScienceDirect

Chemical Engineering Journal



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

Fe₃O₄@S nanoparticles embedded/coated on the multi-wall carbon nanotubes for rechargeable lithium batteries



Guo Gao^{a,*}, Peiyan Zhai^b, Qiang Zhang^{c,*}, Cameron J. Shearer^d, Jing Zhao^d, Joseph G. Shapter^{d,*}

^a Institute of Nano Biomedicine and Engineering, Shanghai Engineering Research Center for Intelligent Diagnosis and Treatment Instrument, Department of Instrument Science and Engineering, School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China ^b Department of Chemical Engineering, Qufu Normal University, Shandong 273165, China

^c Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China ^d School of Chemical and Physical Sciences, Flinders University, Bedford Park, Adelaide 5042, Australia

G R A P H I C A L A B S T R A C T





ARTICLE INFO

Keywords: Hydrothermal Hybrid materials Lithium batteries Shuttle effects

ABSTRACT

In the present study, $Fe_3O_4@S-CNTs-1$, $Fe_3O_4@S-CNTs-2$ and $Fe_3O_4@S-CNTs-3$ were prepared via one-pot hydrothermal approach. The core–shell $Fe_3O_4@S$ structures (20–30 nm) are embedded/coated on the oxidized CNTs, inhibiting the huge volume expansion effect of active materials during the cycling process. The $Fe_3O_4@S-CNTs-2$ cathode presented an initial discharge of 986 mAhg⁻¹ (0.2 C) and gradually decreased to 503 mAhg⁻¹ after 200 cycles, exhibiting the best cycling performance among the prepared hybrid materials. Even at a high current density of 1 C, the $Fe_3O_4@S-CNTs-2$ cathode still exhibited a discharge capacity of 914 mAhg⁻¹, and maintains a high capacity (466 mAhg⁻¹) after 400 cycles. The Coulombic efficiencies of the synthesized $Fe_3O_4@S-CNTs$ hybrid materials always are 99%, indicating they could effectively diminish the shuttle effects of polysulfide Li_2S_n (2 < n < 8) intermediates in the cycling process. As for the rate performance of $Fe_3O_4@S-CNTs$ hybrid materials, the capacity still can reach up to ~400 mAhg⁻¹ a high discharge rate of 5 C. The synergy between the $Fe_3O_4@S$ nanoparticles and oxidized CNTs in the $Fe_3O_4@S-CNTs$ cathode endows the electroce with good electrical conductivity, structural stability and high charge capacity thus providing excellent electrochemical performance.

* Corresponding authors. E-mail addresses: guogao@sjtu.edu.cn (G. Gao), zhang-qiang@mails.tsinghua.edu.cn (Q. Zhang), joe.shapter@flinders.edu.au (J.G. Shapter).

http://dx.doi.org/10.1016/j.cej.2017.09.156

Received 20 May 2017; Received in revised form 23 September 2017; Accepted 24 September 2017 Available online 25 September 2017 1385-8947/ © 2017 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, the rapid development of electric vehicles, hybrid electric vehicles and plug-in hybrid electric vehicles requires high energy storage devices that can not only provide high energy density, long cycling life and safety, but also need high power density and low cost [1-5]. Lithium ion batteries (LIBs) are believed to be one of the promising candidates for the energy storage because they can offer a high energy density [6,7]. However, the relatively low specific capacity of conventional LIBs can't satisfy with the increasing demands of electric vehicles. Furthermore, the energy density of traditional LIBs is nearly reaching their theoretical limits [8,9]. Lithium sulfur (Li-S) batteries have a high specific capacity (1675 $mAhg^{-1}$) and high theoretical energy density (2567 WhKg⁻¹), which are about four times than that of traditional LIBs. Li-S batteries are considered to be the ideal candidates for the next-generation high performance energy storage devices [10-12]. In addition, sulfur has a high natural abundance, low cost, long cycling life, broad operating temperature range, environmental benignity [13], and its intrinsic property which guarantees the safety of batteries [14]. As a cathode, sulfur is involved in the following electrochemical redox reaction: 16 Li (s) + S_8 (s) = 8 Li₂S (s) [15]. It is very likely that Li-S batteries should be capable of high energy storage to replace the conventional LIBs. However, the practical application of Li-S batteries is hindered by several obstacles: (1) the intrinsic poor electrical conductivity of sulfur (5 \times 10 $^{-30}\,Scm^{-1}$ at 25 °C) and lithium sulfides [16]; this is related to the insulating properties of sulfur and lithium sulfides; (2) the high solubility properties of polysulfide intermediates (Li_2S_n , 4 < n < 8) in the liquid electrolyte [17], which will lead to the continuous loss of S in the cathode and shuttle effect; (3) the huge volume expansion effect of S cathode when the repeated electrochemical reaction [18], which will lead to the low specific capacity, low Coulombic efficiency and poor cycling life. Therefore, the further development of Li-S batteries with high electrochemical performance is highly desired. It has been reported that the Fe₃O₄/S hybrid materials is more suitable for lithium batteries [19,20]. However, the huge volume variation of materials during the cycling will result in the pulverization of electrodes and often lead to the rapid degradation of cycling and rate performance [21-23]. One effective strategy to inhibit the huge volume variation of materials was encapsulated Fe₃O₄ by a thickness of S layer. In this work, we expected that the ultrafine Fe₃O₄ nanoparticles (8-10 nm) can be coated by S layer leading to the formation of smaller size Fe₃O₄@S hybrid nanoparticles (20-30 nm). We hope the Fe₃O₄@S interface may possess novel electronic and structural properties to help reduce the dissolution of Li_2S_n (2 < n < 8) intermediates. On the other hand, we expect the smaller sized Fe₃O₄@S hybrid nanoparticles can be simultaneously embedded/coated on the multi-wall carbon nanotubes (CNTs) to promote the electrical conductivity of $Fe_3O_4@S$ and reduce the huge volume expansion effect of the cathode enhancing the cycling stability and rate performance of lithium batteries. In order to confirm this idea, herein we proposed onepot hydrothermal strategy for the preparation of three kinds of Fe₃O₄@ S-CNTs hybrid composites by varying the amount of oxidized CNTs (0.5 mL, 1 mL and 1.5 mL, concentration: 0.01 g/mL), namely Fe₃O₄@ S-CNTs-1 (0.5 mL), Fe₃O₄@S-CNTs-2 (1 mL) and Fe₃O₄@S-CNTs-3 (1.5 mL) hybrid materials, respectively. When the Fe₃O₄@S-CNTs hybrid composites were evaluated as cathode materials, the discharge capacity of Fe₃O₄@S-CNTs-2 cathode is 914 mAhg⁻¹, and a high capacity of 466 mAhg⁻¹ still can be maintained after 400 cycles. The initial specific capacity and capacity retention of Fe₃O₄@S-CNTs-2 cathode are superior to those of Fe₃O₄@S-CNTs-1 cathode and Fe₃O₄@ S-CNTs-3 cathode. As for the rate performance of synthesized Fe₃O₄@S-CNTs composites, the three kinds of Fe₃O₄@S-CNTs hybrid composites all exhibit good performance at different current densities (0.1 C, 0.2 C, 0.5 C, 1 C, 2 C and 5 C).

2. Materials and methods

2.1. Synthesis of Fe₃O₄@S-CNTs hybrid materials

The chemical reagents such as FeSO₄·7H₂O, NaOH, ferric citrate and sulfur are all analytical grade (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). The oxidation of multi-wall CNTs in mixed acid was according to our reported procedure [23]. The Fe₃O₄@S-CNTs hybrid materials were synthesized using FeSO4·7H2O, ferric citrate, sulfur and the oxidized CNTs in alkaline solution. Briefly, 0.5 g FeSO4·7H₂O, different amounts (0.5 mL, 1 mL and 1.5 mL, respectively) of oxidized CNTs suspension (0.01 g/mL) and 0.1 M ferric citrate (5 mL) were poured into the solvent containing 15 mL non-ionic TX-100 and 35 mL ethylene glycol (EG). After stirring 10 min, 0.4 g sulfur was mixed with the solution, and the mixture was treated by ultra-sonication for about 15 min. After ultra-sonication, the solution was sufficiently stirred about 20 min and 0.1 g Vitamin C (Vc) was added. Then, 0.4 M NaOH solution (20 mL) was added, and the solution was continuously stirred for about 20 min. After that, the solution was heated to 220 °C for 12 h in a Teflon-lined stainless autoclave. When the autoclave is cooled to room temperature, the obtained Fe₃O₄@S-CNTs hybrid materials were washed by deionized water under ultra-sonication several times and dried via a freeze-drying apparatus.

2.2. Characterization

The as-prepared Fe₃O₄@S-CNTs hybrid materials were characterized by X-ray powder diffractometer (XRD, Rigaku, Japan) using Cu K_α radiation ($\lambda = 0.15418$ nm), scanning electron microscopy (SEM, CAMScan MX2500, Cambridge, UK) with EDS analyzer, transmission electron microscopy (TEM, JEM-2010), high-resolution transmission microscopy (HRTEM) and selected area electron diffraction (SAED). X-ray photoelectron microscopy (XPS, Leybold LHS10 spectrometer with Al and Mg anodes) analysis was used to analyze the chemical composition of Fe₃O₄@S-CNTs hybrid materials.

2.3. Electrochemical measurements

Electrochemical evaluation of the as-prepared Fe₃O₄@S-CNTs hybrid materials was measured in 2025 coin-type cells. The cathode electrode was prepared by mixing the Fe₃O₄@S-CNTs hybrid materials (70 wt%), carbon nanotubes (20 wt%) and polyvinylidene fluoride (PVDF) (10 wt%) in the N-methyl-2-pyrrolidone solvent. After that, the active materials were coated on the aluminum foil. The surface area of working electrode materials in the experiment is 0.785 cm². The pure metallic lithium foil act as the anode electrode. The separator was Celgard 2400 polypropylene micro-porous film.

3. Results and discussion

X-ray photoelectron spectroscopy (XPS) measurements were used to analyze the chemical compositions of the synthesized Fe₃O₄@S-CNTs hybrid materials (Fe₃O₄@S-CNTs-2 was selected for XPS measurements). Fig. 1a shows the C1s XPS spectrum of the as-prepared product. The obvious characteristic peak at 284.6 eV can be attributed to the C-C bond, and the peaks at 286.3 eV, 287.6 eV and 289.1 eV correspond to C-O, C=O and O-C=O bonds, respectively [26]. The C1s XPS spectrum indicates the successful oxidation of carbon nanotubes in the mixed acid solution, and these rich-oxygen groups in the oxidized CNTs may act as the active sites for precipitation reaction of iron ions. The C1s XPS spectrum indicates the existence of oxidized CNTs in the synthesized Fe₃O₄@S-CNTs hybrid materials. Fig. 1b indicates the Fe2p XPS spectrum of the samples. Two peaks located at 707.6 eV and 720.4 eV are detected in the XPS spectrum, which can be attributed to $Fe2p_{3/2}$ and $Fe2p_{1/2}$ from ferric iron [27]. Three peaks at 711.4 eV, 713.5 eV and 724.9 eV can be observed, indicating the existence of



Fig. 1. XPS analysis of the as-prepared Fe₃O₄@S-CNTs hybrid materials. C1s region (a), Fe2p region (b), O1s region (c) and S2p (d).

Fe₃O₄ in the products. Fig. 1c showed the O1s XPS spectrum of the product. The peak at 530.4 eV matches with the oxygen in Fe₃O₄, and the two peaks at 531.8 eV and 532.1 eV originated from the oxidized CNTs [28]. The peak located at 168.8 eV can be assigned to SO_4^{2-} (FeSO₄·7H₂O was used in the reaction, and the SO_4^{2-} ions will absorb on the surface of obtained nanoparticles) on the surface of hybrid nanoparticles. The peaks at 162.4 eV and 163.8 eV can be attributed to the S2p_{3/2} and S2p_{1/2} of S [29], respectively, and a broad component at ~164.7 eV was associated with energy-loss processes [30]. XPS analysis shows that the as-prepared hybrid materials are composed of the oxidized CNTs, S and Fe₃O₄.

Fig. 2a indicates the SEM observation of the prepared $Fe_3O_4@S-CNTs-2$ hybrid materials. It is clearly observed that the oxidized CNTs are embedded/coated with plenty of small nanoparticles (~30 nm). Fig. 2b show the energy dispersive spectroscopy (EDS) elemental analysis of the as-prepared $Fe_3O_4@S-CNTs-2$ hybrid materials. The C, O, Fe and S elements in the hybrid materials are all detected while the Au element originates from the substrate. The distribution of Fe_3O_4 and S in the oxidised CNTs was also characterized by EDS elemental mapping. It is evident that the C (Fig.2c), O (Fig.2d), S (Fig.2e) and Fe (Fig.2f) elements can be observed on the Au substrate. The overlay image of Fig.2g indicates that numerous Fe, O and S elements are aggregated around the C element, suggesting the successful embedding/coated of nanoparticles of Fe_3O_4 and S on the oxidized CNTs.

Fig. 3a shows the TEM image of the synthesized $Fe_3O_4@S-CNTs-2$ hybrid materials. It is evident that the surface of oxidized CNTs was embedded/coated with lots of nanoparticles ('A' region, see the arrow). We also observed that some nanoparticles are completely filled into the oxidized CNTs ('B' region, see the arrow). The higher resolution TEM

image in Fig. 3b illustrated that these embedded/coated nanoparticles possessed core-shell structures with a diameter of 20-30 nm, and the core size is 8-10 nm in diameter. The HRTEM images of Fig. 3c and Fig. 3d show the fringe spacing of the core is 0.481 nm which was consistent with the (1 1 1) crystal facet of cubic Fe₃O₄ whereas the shell appeared to be amorphous. As for the reaction, the precursors of ultrafine Fe₃O₄ nanoparticles were used as seeds to induce the growth of S in the hydrothermal system. According to the TEM and HRTEM results, it appears that the Fe₃O₄ nanoparticles were coated by amorphous S, and the produced Fe₃O₄@S hybrid structures which are also simultaneously embedded in the oxidised CNTs. The decomposition products of ferric citrate are Fe₃O₄, CO₂ and H₂O. Therefore, formation of carbon layer on the surface of Fe₃O₄ is impossible. The as-prepared Fe₃O₄@S-CNTs-2 hybrid materials were further characterized by XRD, as shown in Fig. 3e. The sharp peak at $2\theta = 26.2^{\circ}$ was consistent with the (0 0 2) plane in CNTs, and the characteristic peak in the region of 40-45 °confirms the multi-wall nature of CNTs. The HRTEM images of Fig. 3c and d clearly reveals the high crystallinity of Fe₃O₄ in the hybrid materials whereas no diffraction peaks arising from cubic Fe₃O₄ are observed, confirming the Fe₃O₄ nanoparticles are coated by amorphous S. Fig. 3f and g indicate the TEM observation and HRTEM images of the as-prepared Fe₃O₄@S-CNTs-1 hybrid materials, respectively. It is evident that the oxidized CNTs was embedded/coated by a lot of nanoparticles. The successful embedding/coated of Fe₃O₄@S hybrid nanoparticles in the oxidised CNTs could inhibit the huge volume expansion effect of electrode materials during repeated cycling process. Fig. 3h and i provide the TEM and HRTEM images of Fe₃O₄@S-CNTs-3 hybrid materials. It clearly found that the shape of Fe₃O₄@S-CNTs-3 hybrid materials is similar to the Fe₃O₄@S-CNTs-1 hybrid materials and



Fig. 2. SEM image (a), EDS (b) of the as-prepared Fe₃O₄@S-CNTs-2 hybrid materials and EDS elemental mapping analysis: C (c), O (d), S (e), Fe (f) and overlay of all elements (g).

 $Fe_3O_4@S\text{-}CNTs\text{-}2$ hybrid materials. It shows that the $Fe_3O_4@S$ hybrid nanoparticles present relatively regular size distribution and well-dispersed property in the matrix of oxidized CNTs. It is known that the

oxidized CNTs network could not only act as an effective matrix to inhibit the agglomeration of nanomaterials, but also provide an improvement in the conductivity of the hybrid materials [19]. It is clear



Fig. 3. TEM images (a-b), HRTEM images (c-d) and XRD patterns (e) of the as-prepared Fe₃O₄@S-CNTs-2 hybrid materials, TEM image (f) and HRTEM image (g) of the Fe₃O₄@S-CNTs-1 hybrid materials, TEM image (h) and HRTEM image (i) of the Fe₃O₄@S-CNTs-3 hybrid materials.

that the increase in the amount of oxidized CNTs (0.5 mL, 1 mL and 1.5 mL) in hydrothermal system does not significantly influence the morphology evolution of Fe₃O₄@S-CNTs hybrid materials. As for the synthesized Fe₃O₄@S-CNTs-1 (0.5 mL), Fe₃O₄@S-CNTs-2 (1 mL) and Fe₃O₄@S-CNTs-3 (1.5 mL) hybrid materials, we expect that the introduction of oxidised CNTs could promote the formation of a good conductive network between the Fe₃O₄@S hybrid nanoparticles and the oxidized CNTs, which will be helpful for the fast movement of Li⁺ and electrons during the cycling process which will strengthen the cycling and rate capability.

Fig. 4a indicates the cycling tests of the prepared Fe₃O₄@S-CNTs hybrid materials (Fe₃O₄@S-CNTs-1, Fe₃O₄@S-CNTs-2 and Fe₃O₄@S-CNTs-3) at 0.2 C (1 C = 926 mA g^{-1}) after 200 cycles. Compared with pure CNTs, the cycling performance of the synthesized Fe₃O₄@S-CNTs hybrid materials has been significantly improved. As for the synthesized Fe₃O₄@S-CNTs hybrid materials (Table 1), the Fe₃O₄@S-CNTs-2 cathode exhibits the best cycling performance among the synthesized Fe₃O₄@S-CNTs hybrid materials. It can be seen from Fig. 4a that both the initial specific capacity and capacity retention of Fe₃O₄@S-CNTs-2 cathode are much superior to those of Fe₃O₄@S-CNTs-1 cathode and Fe₃O₄@S-CNTs-3 cathode. The Fe₃O₄@S-CNTs-2 cathode presented a capacity of 986 mAhg⁻¹, and the capacity reduced to 678 mAhg⁻¹ after 20 cycles and fades gradually to 503 mAhg⁻¹ after 200 cycles. The discharge capacity of the Fe₃O₄@S-CNTs hybrid materials during the initial 20 cycles can be attributed to the solid electrolyte interface (SEI) film, decomposition of electrolyte and the irreversible reaction between Li, S and the oxidized CNTs [22,24]. For comparison, the discharge capacity of Fe₃O₄@S-CNTs-1 cathode and Fe₃O₄@S-CNTs-3 cathode exhibited relatively low capacities of 463 mAhg⁻¹ and 402 mAhg⁻¹

after 200 cycles, respectively. It should be noted that the cycling performance decreases with increasing amounts of oxidized CNTs from 1 mL (Fe₃O₄@S-CNTs-2) to 1.5 mL (Fe₃O₄@S-CNTs-3). The excellent electrochemical performance of Fe₃O₄@S-CNTs-2 cathode can be assigned to the good synergy between S and oxidized CNTs in the hybrid materials, which endows the Fe₃O₄@S-CNTs-2 cathode with good electrical conductivity, structural stability and high charge capacity. Fig. 4b shows the cycling tests of the prepared Fe₃O₄@S-CNTs hybrid materials at a high current density of 1 C. It can be seen that even at 1 C, the Fe₃O₄@S-CNTs-2 cathode still exhibits the best cycling property (Table 2). The discharge capacity of Fe₃O₄@S-CNTs-2 cathode is 914 mAhg⁻¹, while the capacity reduced to 649 mAhg⁻¹ after the 20th cycle. Even after 400 cycles, a high capacity of 466 mAhg⁻¹ still could be maintained, indicating that the Fe₃O₄@S-CNTs-2 cathode has excellent cycling performance. As for Fe₃O₄@S-CNTs-1 cathode and $Fe_3O_4@S-CNTs-3$ cathode, high capacities of 420 mAhg^{-1} and 429 mAhg⁻¹ after 400 cycles can be observed. The cycling performance of the synthesized Fe₃O₄@S-CNTs hybrid materials at both low current density (0.2 C) and high current density (1 C) showed that the capacity retentions are low, the polarization characteristics are not evident and the Coulombic efficiencies are always 99%, demonstrating that the synthesized Fe₃O₄@S-CNTs hybrid materials could effectively diminish the shuttle effects of polysulfide Li_2S_n (2 < n < 8) intermediates. The enhanced performance can be attributed to the special structure of ultra-fine Fe₃O₄@S nanoparticles embedded/coated in oxidized CNTs could effectively confine $\mathrm{Li}_2 S_n$ intermediates into the nanopores and inhibit them from the dissolution/solving into the electrolyte.

Fig. 5a indicates the charge (lithium extraction) and discharge (lithium insertion) tests of the $Fe_3O_4@S-CNTs-1$ cathode at 1 C, which



Fig. 4. Cycling tests of the obtained Fe₃O₄@S-CNTs-1, Fe₃O₄@S-CNTs-2 and Fe₃O₄@S-CNTs-3 hybrid materials at a low current density of 0.2 C (a), and high current density of 1 C (b).

exhibits discharge capacities of 742, 706, 687 and 667 mAhg⁻¹ and charge capacities of 761, 722, 698 and 678 mAhg⁻¹ at the 2nd, 20th, 50th and 100th cycle, respectively. As for Fe₃O₄@S-CNTs-2 cathode (Fig. 5b), it represents the discharge capacities of 753, 716, 688 and 648 mAhg^{-1} and charge capacities of 756, 737, 703 and 662 mAhg^{-1} at the 2nd, 20th, 50th and 100th cycle, respectively. As for Fe₃O₄@S-CNTs-3 cathode (Fig. 5c), it shows the discharge capacities of 675, 652, 623 and 590 mAhg^{-1} and charge capacities of 695, 671, 637 and 603 mAhg⁻¹ at the 2nd, 20th, 50th and 100th cycle, respectively. It is clearly seen that the discharge capacities of Fe₃O₄@S-CNTs-2 cathode at 2nd cycle (753 mAhg⁻¹) and 100th cycle (648 mAhg⁻¹) is higher than those of Fe₃O₄@S-CNTs-1 cathode (742 mAhg⁻¹ at 2nd cycle, 667 mAhg⁻¹ at 100th cycle) and Fe₃O₄@S-CNTs-3 cathode $(675 \text{ mAhg}^{-1} \text{ at 2nd cycle}, 590 \text{ mAhg}^{-1} \text{ at 100th cycle})$. As for the charge/discharge curves of the synthesized Fe₃O₄@S-CNTs hybrid materials, the discharge plateau is near 2.4 V, corresponding the formation of Li₂S [25]. The capacity of oxidized CNTs can be neglected because the Li⁺ intercalation-extraction potential of carbon is less than 0.5 V. The results illustrate that the synthesized Fe₃O₄@S-CNTs-2 cathode has better electrochemical property than Fe₃O₄@S-CNTs-1 cathode and Fe₃O₄@S-CNTs-3 cathode when the cycling process. Rate performance is also important for the application of high power battery. Fig. 5d shows the rate capability of the synthesized Fe₃O₄@S-CNTs

hybrid materials at various rates of 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C and 5 C, respectively. It can be seen that the Fe₃O₄@S-CNTs hybrid materials exhibits a good performance at different rates. As for the Fe₃O₄@S-CNTs-1 cathode, the electrode represents a high capacity of 937 (0.1 C), 828 (0.2 C), 717 (0.5 C), 654 (1 C), 606 (2 C) and 419 mAhg⁻¹ (5 C). As for the Fe₃O₄@S-CNTs-2 cathode, the capacity can reach 901 (0.1 C), 805 (0.2 C), 719 (0.5 C), 665 (1 C), 614 (2 C) and 391 mAhg⁻¹ (5 C). When the current density of Fe₃O₄@S-CNTs-1 electrode and Fe₃O₄@S-CNTs-2 electrode were returned to 0.2 C, a high reversible capacity of 752 and 754 mAhg⁻¹ can still be reversed, respectively, indicating the excellent electrochemical performance of Fe₃O₄@S-CNTs hybrid materials. Chen et al. reported the CNTs-RGO/S cathode composite for high performance lithium/sulphur batteries [31]. As for the synthesized CNTs-RGO/S cathode composite, it exhibited a 613 mAhg⁻¹ at 1 C. Such good electrochemical performance can be attributed to the unique coaxial structure of CNTs-RGO/S composite. Jin et al. reported that sulphur/carbon nanotube composite as flexible cathode for LIBs [32]. The porous and film-like composites can improve the electrical conductivity of S and promote the diffusion of Li⁺. It showed that a reversible capacity of 520 mAhg^{-1} can be obtained at 2 C. As for our synthesized Fe₃O₄@S-CNTs-2 cathode composite, the capacity can reach up to 665 mAhg^{-1} (1 C) and 614 mAhg^{-1} (2 C), respectively, which is higher than that of reported work. The results

Table 1

ycling	tests of the	obtained	Fe ₃ O ₄ @S-	CNTs hybrid	materials at	a current	density	of 0.	2 C.
--------	--------------	----------	------------------------------------	-------------	--------------	-----------	---------	-------	------

Current density (0.2 C)	Initial discharge capacity (mAhg ⁻¹)	Discharge capacity after 20 cycles $(mAhg^{-1})$	Discharge capacity after 200 cycles $(mAhg^{-1})$	Coulombic efficiency (%)
Fe ₃ O ₄ @S-CNTs-1	882	656	463	~ 99
Fe ₃ O ₄ @S-CNTs-2	986	678	503	~ 99
Fe ₃ O ₄ @S-CNTs-3	859	598	402	~ 99

Table 2

Cycling tests of the obtained $Fe_3O_4@S$ -CNTs hybrid materials at a current density of 1 C.

Current density (1 C)	Initial discharge capacity (mAhg ⁻¹)	Discharge capacity after 20 cycles $(mAhg^{-1})$	Discharge capacity after 400 cycles $(mAhg^{-1})$	Coulombic efficiency (%)
Fe ₃ O ₄ @S-CNTs-1	895	637	420	~ 99
Fe ₃ O ₄ @S-CNTs-2	914	649	466	~ 99
Fe ₃ O ₄ @S-CNTs-3	710	598	429	~ 99

indicated that the synthesized Fe₃O₄@S-CNTs-2 materials have good rate performance. As for the Fe₃O₄@S-CNTs-3 cathode, the capacity is slightly lower than that of Fe₃O₄@S-CNTs-1 cathode and Fe₃O₄@S-CNTs-2 cathode at relatively low current densities from 0.1 C to 2 C. However, the Fe₃O₄@S-CNTs-3 cathode exhibits a higher capacity (480 mAhg⁻¹) than that of Fe₃O₄@S-CNTs-1 cathode (419 mAhg⁻¹) and Fe₃O₄@S-CNTs-2 cathode (391 mAhg⁻¹) at the high current density of 5 C. One of the primary reasons is that the higher amount of oxidized CNTs in the Fe₃O₄@S-CNTs-3 hybrid material may be helping

to maintain the structural integrity of electrode at a high current density (5 C).

4. Conclusions

In summary, a facile one-pot hydrothermal approach has been successfully developed for embedding/coating $Fe_3O_4@S$ nanoparticles on the oxidized CNTs to prevent the huge volume expansion effect of electrode materials during repeated cycling processes. The Fe_3O_4



Fig. 5. Cycling curves of the obtained Fe₃O₄@S-CNTs-1 (a), Fe₃O₄@S-CNTs-2 (b) and Fe₃O₄@S-CNTs-3 (c) hybrid materials at a current density of 1 C, and rate capability (d).

nanoparticles (8-10 nm) with high crystallinity are encapsulated by amorphous S layer, presenting a core-shell Fe₃O₄@S structure (20-30 nm) which are embedded/coated in the oxidized CNTs yielding a Fe₃O₄@S-CNTs hybrid composites. The results confirm that the application of the precursors of ultrafine Fe₃O₄ nanoparticles as seeds can induce the growth of S in the hydrothermal system, and reduce the problems associated with larger S particles. When the synthesized Fe₃O₄@S-CNTs hybrid materials were evaluated as cathode for LIBs, the discharge capacity of Fe₃O₄@S-CNTs-2 cathode presented a high capacity of 914 mAhg⁻¹, and a high capacity of 466 mAhg⁻¹ still can be maintained after 400 cycles. The initial specific capacity and capacity retention of Fe₃O₄@S-CNTs-2 cathode are superior to the cathodes made using the other hybrids prepared. As for the rate performance of Fe₃O₄@S-CNTs hybrid materials, the capacity still can reach up to \sim 400 mAhg⁻¹ at a high rate of 5 C. The Coulombic efficiencies are always are 99%, suggesting the Fe₃O₄@S-CNTs hybrid materials can effectively diminish the shuttle effects of polysulfide Li2Sn (2 < n < 8) intermediates. The excellent electrochemical performance of Fe₃O₄@S-CNTs hybrid materials is attributed to the rational design and the good synergic between Fe₃O₄@S and oxidized CNTs in the Fe₃O₄@S-CNTs hybrid composites.

Acknowledgements

We thank the National Natural Science Foundation of China (Nos. 91634108, 21422604 and 81671737). We acknowledge the use of South Australian nodes of the Australian Microscopy & Microanalysis Research Facility (AMMRF) and the Australian National Fabrication Facility (ANFF) at Flinders University.

Author contributions

G.G., Q.Z. and J.G.S. conceived and designed the research project. P.Z., C.J.S. and J.Z. performed the experiments, data acquisition and characterization. All the authors contributed to the data analysis and the writing of this manuscript, and all authors reviewed the manuscript, and given approval to the final version of the manuscript.

Competing interest

The authors declare to no competing financial interests.

References

- C.Y. Wang, et al., Lithium-ion battery structure that self-heats at low temperatures, Nature 529 (2016) 515–518.
- [2] J.-M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, Nature 414 (2001) 359–367.
- [3] L.M. Pazos-Outón, et al., Photo recycling in lead iodide perovskite solar cells, Science 351 (2016) 1430–1433.
- [4] G. Zhou, et al., A graphene-pure-sulfur sandwich structure for ultrafast, long-life lithium-sulfur batteries, Adv. Mater. 26 (2014) 625–631.
- [5] M.Q. Zhao, et al., Hierarchical vine-tree-like carbon nanotube architectures: in-situ CVD self-assembly and their use as robust scaffolds for lithium-sulfur batteries, Adv. Mater. 26 (2014) 7051–7058.
- [6] G. Zhou, F. Cheng, H.M. Li, Progress in flexible lithium batteries and future prospects, Energy Environ. Sci. 7 (2014) 1307–1338.

- [7] A. Manthiram, S.H. Chung, C. Zu, Lithium-sulfur batteries: progress and prospects, Adv. Mater. 27 (2015) 1980–2006.
- [8] A. Manthiram, Materials challenges and opportunities of lithium ion batteries, J. Phys. Chem. Lett. 2 (2011) 176–184.
- [9] H.D. Yoo, E. Markevich, G. Salitra, D. Sharon, D. Aurbach, On the challenge of developing advanced technologies for electrochemical energy storage, Mater. Today 17 (2014) 110–121.
- [10] J. Wang, X. Meng, X. Fan, W. Zhang, H. Zhang, C. Wang, Scalable synthesis of defect abundant Si nanorods for high-performance Li-ion battery anodes, ACS Nano 9 (2015) 6576–6586.
- [11] Z. Xiao, Z. Yang, H. Nie, Y. Lu, K. Yang, S. Huang, Porous carbon nanotubes etched by water steam for high-rate large-capacity lithium-sulfur batteries, J. Mater. Chem. A 2 (2014) 8683–8689.
- [12] L. Ma, et al., Enhanced Li-S batteries using amine-functionalized carbon nanotubes in the cathode, ACS Nano 10 (2016) 1050–1059.
- [13] L. Zhang, et al., Sulfur synchronously electrodeposited onto exfoliated grapheme sheets as a cathode material for advanced lithium-sulfur batteries, J. Mater. Chem. A 3 (2015) 16513–16519.
- [14] J. Hassoun, B. Scrosati, Moving to a solid-state configuration: a valid approach to making lithium-sulfur batteries viable for practical applications, Adv. Mater. 22 (2010) 5198–5201.
- [15] X. Ji, K.T. Lee, L.F. Nazar, A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries, Nat. Mater. 8 (2009) 500–506.
- [16] N. Jayaprakash, J. Shen, S.S. Moganty, A. Corona, L.A. Archer, Porous hollow carbon@sulfur composites for high-power lithium-sulfur batteries, Angew. Chem. Int. Ed. 50 (2011) 5904–5908.
- [17] C. Barchasz, F. Molton, C. Duboc, J.C. Leprêtre, S. Patoux, F. Alloin, Lithium/sulfur cell discharge mechanism: an original approach for intermediate species identification, Anal. Chem. 84 (2012) 3973–3980.
- [18] G. He, S. Evers, X. Liang, M. Cuisinier, A. Garsuch, L.F. Nazar, Tailoring porosity in carbon nanospheres for lithium-sulfur battery cathodes, ACS Nano 7 (2013) 10920–10930.
- [19] L. Wang, J. Wu, Y. Chen, X. Wang, R. Zhou, S. Chen, Q. Guo, H. Hou, Y. Song, Hollow nitrogen-doped Fe₃O₄/Carbon nanocages with hierarchical porosities as anode materials for lithium-ion batteries. Electrochim. Acta 186 (2015) 50–57.
- [20] Y. Chen, L. Zheng, Y. Fu, R. Zhou, Y. Song, S. Chen, MOF-derived Fe₃O₄/carbon octahedral nanostructures with enhanced performance as anode materials for lithium-ion batteries. RSC Adv. 6 (2016) 85917–85923.
- [21] F. Han, W.C. Li, D. Li, A.H. Lu, Ammonia-treatment assisted fully encapsulation of Fe₂O₃ nanoparticles in mesoporous carbons as stable anodes for lithium ion batteries, J. Energy Chem. 22 (2013) 329–335.
- [22] Y. Zuo, et al., Hybridization of graphene nanosheets and carbon-coated hollow Fe₃O₄ nanoparticles as a high-performance anode materials for lithium-ion batteries, J. Mater. Chem. A 4 (2016) 2453–2460.
- [23] G. Gao, et al., Ultrafine ferroferric oxide nanoparticles embedded into mesoporous carbon nanotubes for lithium ion batteries, Sci. Rep. 5 (2015) 17553.
- [24] S.M. Yuan, J.X. Li, L.T. Yang, L.W. Su, L. Liu, Z. Zhou, Preparation and lithium storage performances of mesoporous Fe₃O₄@C microcapsules, ACS Appl. Mater. Interfaces 3 (2011) 705–709.
- [25] L. Liu, Z. Yuan, C. Qiu, J. Liu, A novel FeS₂/CNT micro-spherical cathode material with enhanced electrochemical characteristics for lithium-ion batteries, Solid State Ionics 241 (2013) 25–29.
- [26] D. Briggs, G. Beamson, High Resolution XPS of Organic Polymers: The Scienta ESCA 300 Database, John Wiley and Sons, New York, 1992.
- [27] J. Xia, et al., Facile synthesis of FeS₂ nanocrystals and their magnetic and electrochemical properties, RSC Adv. 3 (2013) 6132–6140.
- [28] T. Fujii, F.M.F. de Groot, G.A. Sawatzky, F.C. Voogt, T. Hibma, K. Okada, In situ XPS analysis of various iron oxide films grown by NO₂-assisted molecular-beam epitaxy, Phys. Rev. B 59 (1999) 3195–3202.
- [29] B. Li, S. Li, J. Liu, B. Wang, S. Yang, Vertically aligned sulfur-graphene nanowalls on substrates for ultrafast lithium-sulfur batteries, Nano Lett. 15 (2015) 3073–3079.
- [30] H.W. Nesbitt, M. Scaini, H. Höchst, G.M. Bancroft, A.G. Schaufuss, R. Szargan, Synchrotron XPS evidence for Fe2+-S and Fe3+-S surface species on pyrite fracture-surfaces, and their 3D electronic states, Am. Mineral. 85 (2000) 850–857.
- [31] Y. Chen, S. Lu, X. Wu, J. Liu, Flexible carbon nanotube-graphene/sulphur composite film: free-standing cathode for high-performance lithium/sulphur batteries, J. Phys. Chem. C 119 (2015) 10288–10294.
- [32] K. Jin, X. Zhou, L. Zhang, X. Xin, G. Wang, Z. Liu, Sulfur/carbon nanotube composite film as a flexible cathode for lithium-sulfur batteries, J. Phys. Chem. C 117 (2013) 21112–21119.