Sulfur/nickel ferrite composite as cathode with high-volumetric-capacity for lithium-sulfur battery

Ze Zhang, Di-Hua Wu, Zhen Zhou, Guo-Ran Li, Sheng Liu and Xue-Ping Gao*

ABSTRACT Low volumetric energy density is a bottleneck for the application of lithium-sulfur (Li-S) battery. The low-density sulfur cooperated with the light-weight carbon substrate realizes electrochemical cycle stability, but leads to worse volumetric energy density. Here, nickel ferrite (NiFe_2O_4) nanofibers as novel substrate for sulfur not only anchor lithium polysulfides to enhance the cycle stability of sulfur cathode, but also contribute to the high volumetric capacity of the S/nickel ferrite composite. Specifically, the S/nickel ferrite composite presents an initial volumetric capacity of $1,281.7 \text{ mA h cm}^{-3}$ at 0.1 C rate, 1.9 times higher than that of S/carbon nanotubes, due to the high tap density of the S/nickel ferrite composite.

Keywords: lithium-sulfur battery, sulfur cathode, nickel ferrite nanofibers, tap density, volumetric capacity.

INTRODUCTION

As a necessity of powering electronic devices and electric vehicles, rechargeable batteries are urgently required to reach the expectation of high energy density. The inspiring development is the successful exploration of battery system with high capacity cathode, the capacity-determining electrode [1]. An alternative option is sulfur, which shows a high theoretical gravimetric capacity of $1,675 \text{ mA h g}^{-1}$ because of the light-weight characteristic and two-electron reaction with metallic Li [2]. Beyond that, the features including low price, natural abundance and non-toxicity, serve as a complement to the increasing demand of high energy density of lithium-sulfur (Li-S) battery nowadays [3,4]. However, the achievement faces several challenges: low sulfur utilization related to the poor kinetics of the dissolution/deposition processes for sulfur cathode, low cycle stability due to the dissolution and loss of soluble polysulfide intermediates, and un-

desirable volume expansion caused by the density variation between sulfur and Li_2S [5,6]. In particular, Li-S battery still suffers from the serious drawback of low volumetric energy density for the practical application due to the low density of active materials. For example, the sulfur (2.07 g cm^{-3}) is less than a half of the density of transition metal oxide cathode materials ($\sim 4.5 \text{ g cm}^{-3}$) in traditional lithium-ion batteries. Moreover, in order to improve the electrochemical performance, sulfur is forced to load onto various light-weight carbon hosts, such as porous carbon [7,8], carbon nanotubes (CNTs) [9–10] and graphene [11–13], leading to lower volumetric capacity of sulfur-based composites and undermining the volumetric energy density of Li-S battery.

To figure these issues out, various host materials are explored to accommodate sulfur volumetric expansion, improve sulfur utilization, and more importantly confine soluble lithium polysulfides (Li_2S_n , $4 \leq n \leq 8$). In this aspect, non-polar carbon materials offer weak binding ability towards polar polysulfides, since sulfur species are usually trapped in micro-/mesopores [14–17] or a designed hybrid interconnected structure [18–21] of typical sulfur/carbon composites. A new modification technology is employed to manipulate the surface chemistry of carbon hosts with dopant atoms [22–25] and functional groups [26–28]. However, such desirable polar binding sites on non-polar carbon materials are still limited for the effective adsorption to polysulfides. As a response, metal-based compounds, such as oxides [29–33], sulfides [34–37], nitrides [38–41], and carbides [42–45], are recently introduced into sulfur-based composites as polar sorbents of polysulfides. Whether used as additives or host materials, these inorganic compounds are believed to enhance electrochemical performance of sulfur cathodes owing to the strong polarity and adsorption to polysulfides than

Institute of New Energy Material Chemistry, School of Materials Science and Engineering, Nankai University, Tianjin 300350, China

* Corresponding author (xpgao@nankai.edu.cn)

that of non-polar carbon materials. Importantly, the metal-based compounds are helpful for sulfur cathodes to obtain the high volumetric capacity owing to their much higher tap density than that of carbon host materials. Specifically, among those metal-based compounds, metal oxides with identified polarity are more effective to enhance the electrochemical performance of sulfur cathodes, owing to the strong chemisorption to polysulfides [32] or the electrochemical catalysis of the polysulfide redox reaction [31,46].

Theoretically, transition metal oxides possess a high density, which are desirable host materials based on the consideration of the volumetric capacity of sulfur-based composites. Meanwhile, transition metal oxides could be designed as the one dimensional (1D) nanostructure to ensure good conductive networks and enough surface active sites, which are not only helpful to realize the electrochemical reaction of sulfur active materials with sufficient electrolyte immersion and penetration, but also beneficial for anchoring polysulfides to enhance the cycle stability. Therefore, herein, nickel ferrite nanofibers are selected as the novel host of sulfur to investigate the electrochemical performance of the sulfur-based composites with a focus on enhancing the volumetric capacity and cycle stability. The strategy is demonstrated to be feasible to other metal ferrites as the common host of sulfur for Li-S battery.

EXPERIMENTAL SECTION

Preparation of NiFe_2O_4 nanofibers and $\text{S/NiFe}_2\text{O}_4$ composite

Nickel ferrite (NiFe_2O_4) nanofibers were prepared *via* electrospinning method. Firstly, the electrospinning solution consisted of nickel acetate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 0.62 g), ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 2.0 g) and poly(vinylpyrrolidone) (PVP, $M_w \sim 58,000$, 5.0 g), which were dissolved into mixed solvent of H_2O (5.0 mL) and ethanol (5.0 mL). After rigorously stirred for 12 h, the mixed solution was deposited on the receiver at a rate of 1.2 mL h^{-1} with the static electric voltage of 30 kV. Then, the resultant precursor was calcined in air at 550°C for 2 h at the rate of 2°C min^{-1} . After the calcination, PVP core was completely removed, leading to the formation of hollow structure for NiFe_2O_4 fibers. Sulfur was introduced onto NiFe_2O_4 fibers *via* a melt-diffusion strategy by heating at 155°C for 12 h. The S/CNT composite was prepared as the control sample. In addition, other ferrites MFe_2O_4 ($\text{M} = \text{Co}$, Mg , and Zn) and $\text{S/MFe}_2\text{O}_4$ composites were also prepared to investigate the electrochemical

performances.

Structure characterization

The structure and purity of the as-prepared samples were confirmed by X-ray diffraction (XRD, Rigaku mini Flex II). Thermogravimetric analysis (TGA) was used to measure the sulfur content under Ar atmosphere. N_2 adsorption-desorption isotherms were collected by using the Brunauer-Emmett-Teller (BET) model (JW-BK112 system) to calculate the specific surface area and pore volume of the samples. The surface chemical composition was identified by X-ray photoelectron spectroscopy (XPS) in Escalab 250Xi (Thermo Fisher Scientific) with Al K (1,253.6 eV). Scanning electron microscopy (SEM, Supra 55VP) and transmission electron microscopy (TEM, FEI Tecnai F20) were employed to analyse the microstructure and morphology of the samples.

Electrochemical measurement

The cathodes consisted of $\text{S/MFe}_2\text{O}_4$ or S/CNT composites, CNTs as conductive agent and polyvinylidene fluoride (PVDF) as binder in the weight ratio of 7:2:1 on Al current collector. The identical CNTs are used as conductive agent, instead of a common carbon black (Super P), to fabricate an effectively three-dimensional conductive network for the $\text{S/NiFe}_2\text{O}_4$ electrode, thus ensuring a good sulfur utilization in parallel experiments. Sulfur loading of the cathodes was set at $1.0\text{--}1.3 \text{ mg cm}^{-2}$. The electrolyte was 1.0 mol L^{-1} lithium bis(tri-fluoromethanesulphonyl)imide (LiTFSI) in dimethyl ether (DME) and 1,3-dioxolane (DOL) (*v/v*, 1:1) with $0.2 \text{ mol L}^{-1} \text{ LiNO}_3$. The amount of electrolyte in each cell was controlled with electrolyte/sulfur (E/S) ratio of $20 \mu\text{L mg}^{-1}$. The discharge/charge tests were carried out between 1.7 and 2.8 V (*vs.* Li/Li^+) at different rates ($1 \text{ C} = 1,675 \text{ mA g}^{-1}$) using 2032-type coin cells. The specific capacity was calculated based on the composites ($\text{S/MFe}_2\text{O}_4$ or S/CNT) as the active material. Cyclic voltammogram (CV) measurements were performed on LK2005A workstation at a scan rate of 0.1 mV s^{-1} . Electrochemical impedance spectra (EIS) were measured in the frequency range of 10 mHz–100 kHz with a disturbance amplitude of 5 mV.

Polysulfide adsorption test

Li_2S_8 solution (2 mmol L^{-1}) was obtained by adding stoichiometric sulfur and Li_2S into DME/DOL (*v/v*, 1:1) mixed solvent, followed by a heat treatment at 60°C in the glove box for 24 h. All the sorbents with equal mass (10 mg), including MFe_2O_4 ($\text{M} = \text{Ni}$, Co , Mg , and Zn) and

Figure 1 Preparation and characterization of the samples: (a) the schematic diagram of the structural formation and the preparation process, (b) XRD patterns of NiFe_2O_4 nanofibers and the $\text{S/NiFe}_2\text{O}_4$ composite, and (c) TG curve of the $\text{S/NiFe}_2\text{O}_4$ composite.

CNTs, were dried before adding into the Li_2S_8 solution (10 mL). After sufficient immersion of the sorbents in Li_2S_8 solution, the liquid supernatants were taken out and used to investigate the absorbance by ultraviolet-visible (UV-vis) absorption spectrophotometry (Varian Cary 100 Conc). The standard line of absorbance-concentration was collected by altering the concentration of the blank Li_2S_8 solution (2.0, 1.67, 1.33, 1.0 and 0.67 mmol L^{-1}).

Computation method

All density functional theory (DFT) calculations were carried out with projector-augmented wave (PAW) [47] method as implemented in Vienna *Ab-initio* Simulation Package [48]. Slab model was adopted to simulate the MFe_2O_4 (111) surface structure, and 76 atoms were include in the supercell with 8 atom layers. To avoid artificial interactions between slabs, vacuum space of at least $15 \text{ \AA}$ was introduced. All the structures were optimized with generalized gradient approximation (GGA) as implemented by Perdew, Burke and Ernzerhof (PBE) [49]. $3 \times 3 \times 1$ k -points were set for Brillouin zone sampling. Spin polarization and a cut-off energy of 550 eV was adopted.

RESULTS AND DISCUSSION

NiFe_2O_4 nanofibers were prepared by the electrospinning technique with a subsequent calcination step (Fig. 1a). Here, PVP is likely to form the template with a core

structure, and inorganic salts surround PVP template by the polar interaction between carbonyl groups with metal cations. PVP-salt nanofibers are then formed during the electrospinning process. In the subsequent calcination step, PVP template is burnt out in air, and inorganic salts are decomposed to form 1D ternary metal oxides. Simultaneously, the 1D porous hollow nanofibers with the desirable specific surface area is obtained. As a result, NiFe_2O_4 nanofibers show large specific surface area of $210.5 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $0.40 \text{ cm}^3 \text{ g}^{-1}$ (Fig. S1 and Table S1). XRD patterns are collected to identify the structure and phase purity of the obtained NiFe_2O_4 . The identified peaks and relative intensity are matched well to the cubic NiFe_2O_4 (JCPDS no. 54-0964) with $Fd3m$ space group (Fig. 1b). The average grain size of the (111), (220) and (311) planes is calculated to be about 18 nm, based on the Scherrer equation. Coincidentally, other metal ferrites MFe_2O_4 ($\text{M}=\text{Co}$, Mg , and Zn) with the same $Fd3m$ cubic structure can be also obtained *via* the same process (Fig. S2). As seen in the XRD pattern of the $\text{S/NiFe}_2\text{O}_4$ composite, the peaks of the crystalline sulfur with orthorhombic structure coexist with the strong peaks of NiFe_2O_4 . The sulfur content is measured as 82.5 wt.% by TGA (Fig. 1c).

The surface chemical state of the as-prepared samples is evaluated by XPS in Fig. 2. Both the Ni 2p and Fe 2p core levels present $2p_{1/2}$ and $2p_{3/2}$ doublet peaks with two

Figure 2 XPS spectra: (a) Ni 2p, (b) Fe 2p and (c) O 1s of NiFe_2O_4 nanofibers; (d) O 1s and (e) S 2p of the $\text{S}/\text{NiFe}_2\text{O}_4$ composite; (f) S 2p of the S/CNT composite.

shakeup satellites, indicating the existence of Ni^{2+} and Fe^{3+} . Further, the fitted results of Ni 2p and Fe 2p core levels suggest a partially inverse structure of NiFe_2O_4 with cations (Ni^{2+} and Fe^{3+}) located in both tetrahedral sites (A sites) and octahedral sites (B sites) [50,51]. Commonly, the inverse spinel structure is endowed with good conductivity owing to the electron hopping between different valence states of cations in B sites [52–54], as well as the partially inverse spinel NiFe_2O_4 here. Compared with the O 1s core level (Fig. 2c, d), the area ratio of adsorbed hydroxyl oxygen (O_H , 530.9 eV) is increased from 28.5% in NiFe_2O_4 to 43.6% in the $\text{S}/\text{NiFe}_2\text{O}_4$ composite, which is helpful to confine sulfur species. As shown in S 2p core level (Fig. 2e), sulfur exists dominantly as S_8 ($2p_{3/2}$, 163.6 eV; and $2p_{1/2}$, 164.7 eV). While, a trace of sulfide (162.4 eV), SO_3^{2-} (168.3 eV) and SO_4^{2-} (169.4 eV) is also detected in the $\text{S}/\text{NiFe}_2\text{O}_4$ composite, further confirming the existence of chemical interaction between NiFe_2O_4 host surface and sulfur. In particular, a slight increase of binding energy of Ni 2p is observed, while there are no any changes in Fe 2p core level after the infusion of sulfur (Fig. S3). It means that the interaction between Ni and S is weak. It seems that the formation of such sulfide, SO_3^{2-}

and SO_4^{2-} depends on the high catalytic action of nickel (II) in NiFe_2O_4 . Correspondingly, the increase of the surface adsorbed O_H after the infusion of sulfur (Fig. 2d) is attributed to the increased oxygen vacancy on the surface of NiFe_2O_4 by the formation of S–O bonds. However, in the case of S/CNT composite, only S_8 ($2p_{3/2}$, 163.6 eV; and $2p_{1/2}$, 164.7 eV) can be assigned without the formation of any sulfides and sulfates. It means that sulfur can be partially confined on the surface of NiFe_2O_4 nanofibers, and such strong chemical interaction with sulfur is also found in other metal ferrites (Fig. S4).

TEM is employed to reveal the morphology of the as-prepared NiFe_2O_4 and $\text{S}/\text{NiFe}_2\text{O}_4$ composite. Firstly, the lattice fringe with the distance of 0.48 nm is observed clearly (Fig. 3c), corresponding to the (111) plane of cubic NiFe_2O_4 . The obtained NiFe_2O_4 exists as nanocrystals with the average size of ~20 nm (inset of Fig. 3b), almost identical to the calculated value from XRD pattern. These NiFe_2O_4 nanocrystals are assembled together to form 1D porous hollow nanofibers with diameter of 80–160 nm (Fig. 3a, b). Thus, with a simple polymer-assisted electrospinning method, 1D porous hollow NiFe_2O_4 nanofibers can be obtained effectively, as well as other metal

Figure 3 Morphology features of the NiFe_2O_4 nanofibers and $\text{S/NiFe}_2\text{O}_4$ composite: TEM images of (a–c) NiFe_2O_4 nanofibers and (d) $\text{S/NiFe}_2\text{O}_4$ composite; (e) the TEM image recorded by the high angle annular dark field (HAADF) detector, and (f–i) the corresponding elemental mappings in the selected region of the $\text{S/NiFe}_2\text{O}_4$ composite.

ferrites (Figs S5 and S6). After loading sulfur on NiFe_2O_4 nanofibers by the melt-diffusion method, the 1D parent nanofiber morphology is still retained (Fig. S7). In the meanwhile, the sulfur distribution is uniform along the nanofiber, coexisting with Ni, Fe and O elements as demonstrated by the elemental mapping (Fig. 3f–i). The difference in TEM images is that the hollow space in NiFe_2O_4 nanofibers is loaded uniformly with sulfur. The change can be further confirmed by the drop of both the specific surface area ($41.8 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.07 \text{ cm}^3 \text{ g}^{-1}$) in the $\text{S/NiFe}_2\text{O}_4$ composite (Table S1). However, such change in the surface area and pore volume is not enough to accommodate the large content of sulfur inside the hollow space of NiFe_2O_4 nanofibers. It means that the surface of NiFe_2O_4 nanofibers is also covered by sulfur in the crystalline state as detected by XRD pattern.

To investigate the electrochemical performance, the obtained cathodes are dried overnight and coin cells (2032-type) are assembled in the glove box filled with argon atmosphere. CV profiles of $\text{S/NiFe}_2\text{O}_4$ and S/CNT composites are collected, and both the profiles present two pairs of cathodic and anodic peaks, in accord with the typical multistep electrochemical redox reaction of sulfur (Fig. 4a, b). In particular, the curve shape, current density and peak potential are almost identical for both electro-

des, indicating the good redox reversibility in the $\text{S/NiFe}_2\text{O}_4$ composite as compared to the S/CNT composite. In spite of the inferior intrinsic conductivity of NiFe_2O_4 , the lower polarization and better capability of $\text{S/NiFe}_2\text{O}_4$ composite from CV profiles are realized by the strong chemical confinement of sulfur species on NiFe_2O_4 nanofibers, since the desirable electrochemical redox of sulfur depends on both good electron transport and favorable affinity between host material and sulfur, as reported previously [32]. In the meantime, the low surface charge transfer resistance is also obtained for the $\text{S/NiFe}_2\text{O}_4$ composite in the following impedance section, demonstrating that the electrochemical activity of the $\text{S/NiFe}_2\text{O}_4$ composite can be improved based on good electrocatalytic activity of Ni-based transition metal oxides for the redox among sulfur/polysulfides/sulfide. In addition, two typical potential plateaus are observed nearly at 2.3 V and 2.1 V in the discharge process (Fig. 4c, d), and the overlapped long potential plateau is shown in the subsequent charge process, corresponding to the coupled peaks in CVs. The potential polarization between the charge and discharge processes is similar for both electrodes. It means that NiFe_2O_4 nanofibers can be used as substrate as good as CNTs for fabricating sulfur cathode with good reversibility and low potential polarization at low rate, which is helpful for the high utilization

Figure 4 CVs of the (a) S/NiFe₂O₄ composite and (b) S/CNT composite with the potential range from 1.7 to 2.8 V (vs. Li/Li⁺) at the scan rate of 0.1 mV s⁻¹; Comparison of the initial discharge/charge curve based on (c) gravimetric calculation and (d) volumetric calculation of the S/NiFe₂O₄ composite and S/CNT composite.

of sulfur active materials in NiFe₂O₄ nanofibers. Here, the capacity contribution of NiFe₂O₄ nanofibers is negligible in the potential range of 1.7–2.8 V (Fig. S8). When the composite is considered as active material, the S/NiFe₂O₄ composite presents an initial discharge capacity of 963.6 mA h g⁻¹_{-composite} at 0.1 C rate, slightly lower than that (1,044.3 mA h g⁻¹_{-composite}) of the S/CNT composite based on the mass calculation. Correspondingly, when calculated by the weight of sulfur, the initial discharge capacity is 1,168 mA h g⁻¹_{-sulfur}, implying an acceptable sulfur utilization. Importantly, a dramatic reversal is observed when the capacity is reassessed in terms of the volume calculation. Once the initial gravimetric capacity is converted (Fig. 4d), the volumetric capacity of 1,281.7 mA h cm⁻³_{-composite} is obtained for the S/NiFe₂O₄ composite, 1.9 times higher than that (668.4 mA h cm⁻³_{-composite}) of S/CNT composite. It comes

as no surprise that the tap density (1.33 g cm⁻³) of the S/NiFe₂O₄ composite is obviously larger as compared to that (0.64 g cm⁻³) of the S/CNT composite. Such sulfur-based composites with both the high gravimetric/volumetric capacity are indispensable for fabricating Li-S battery with high gravimetric/volumetric energy density. Although the fabricated electrode is not compacted when assembling the battery, the volumetric capacity of the fabricated cathode is the key factor for volumetric energy density in battery design, depending on the tap density of the composite powders with heavy metal ferrites as matrix.

Usually, the good capacity retention of S-based composites at 0.1 C is a challenge, which is a time-consuming process as compared with cycling at the high rate of above 1 C. Here, the S/NiFe₂O₄ composite provides better cycle stability and higher Coulombic efficiency during cycling

Figure 5 The cycle stability in terms of (a) gravimetric capacity and (b) volumetric capacity at 0.1 C rate of S/NiFe₂O₄ and S/CNT composite.

at 0.1 C (Fig. 5a). In particular, the S/NiFe₂O₄ composite delivers the low capacity fading rate of 0.15% per cycle within 200 cycles at 0.1 C rate, a half of that (0.31% per cycle) of the S/CNT composite. Meanwhile, the Coulombic efficiency during long-term cycling is relatively stable for the S/NiFe₂O₄ composite, due to the strong interaction of intermediate polysulfides with NiFe₂O₄ nanofibers. When the capacity is expressed as the volumetric capacity, the superiority of the S/NiFe₂O₄ composite is apparent. The huge gap of the volumetric capacity between S/NiFe₂O₄ and S/CNT composites is stably maintained within 200 cycles at 0.1 C rate (Fig. 5b).

Undoubtedly, CNTs are desirable substrate of sulfur for achieving good high-rate capability [10,21], because of the unique conductive network and good penetration of electrolyte through the network. When NiFe₂O₄ nanofibers are used as substrate to replace CNTs, the high-rate capability of the composite is not undermined. Specifically, the S/NiFe₂O₄ composite delivers the gravimetric discharge capacity of 962.1, 823.3, 724.5, 625.9 and 507.2 mA h g⁻¹ at 0.1, 0.2, 0.5, 1 and 2 C rates, respectively (Fig. 6a). Moreover, as shown in charge-discharge curves (Fig. 6b), the potential polarization is lower at various C-rates and the shrinkage of the second discharge plateau is moderate for the S/NiFe₂O₄ composite. More importantly, after 80 cycles at varied discharge/charge rates, the capacity recovery of the S/NiFe₂O₄ composite at the low rate (0.1 C) is much superior to the

S/CNT composite (Fig. S9). Therefore, the S/NiFe₂O₄ composite can retain the good stability upon cycling at various rates.

Certainly, the strong polarity and chemical adsorption of NiFe₂O₄ nanofibers to soluble polysulfides play a vital role in improving the electrochemical performance of the S/NiFe₂O₄ composite. Thus, both the adsorption experiment and DFT calculation are performed to verify the adsorption of both NiFe₂O₄ nanofibers and CNTs to polysulfides. Firstly, the adsorption test to polysulfides (Li₂S₈) is carried out by immersing NiFe₂O₄ nanofibers and CNTs into Li₂S₈ solution (2.0 mmol L⁻¹), respectively. As shown in Fig. 7a, the color of the Li₂S₈ solution containing NiFe₂O₄ nanofibers is much lighter, and the absorbance in UV-vis spectra of the solution is much lower, demonstrating the strong adsorption ability of polar NiFe₂O₄ nanofibers to polysulfides, as compared with non-polar CNTs. The preliminary quantitative analysis is carried out based on the linear correlation between the solution concentration and the absorbance at 415 nm (Fig. S10). The specific polysulfide-adsorption quantity is calculated as 7.1 μmol m⁻² on NiFe₂O₄ nanofibers, much higher than that (1.4 μmol m⁻²) on CNTs (Fig. 7c). Furthermore, a good comprehension of the adsorption mechanism is revealed by the DFT calculation (Fig. 7b), where Li₂S₈ is accordingly chosen to confirm the adsorption energy and sites. In general, Li₂S₈ undergoes the structure reformation upon adsorption on the substrate

Figure 6 (a) The rate capability and (b) the initial discharge/charge curves of S/NiFe₂O₄ composite at various rates from 0.1 C to 2 C rate.

surface, especially the NiFe₂O₄ with strong polarity. On polar NiFe₂O₄, the most stable Li₂S₈ exists as Li atom in the bridge site of two O atoms, and the interaction between Li and O atoms plays an important role in adsorption on the basis of the optimized adsorption geometry [32]. The adsorption energy of Li₂S₈ on NiFe₂O₄ nanofibers is 1.23 eV (Fig. 7d), higher than that (0.13 eV) on CNTs. Therefore, NiFe₂O₄ nanofibers present the strong adsorption to Li₂S₈, which is beneficial to the cycle stability of the S/NiFe₂O₄ composite. The similar experimental phenomenon and reaction mechanism on adsorption and cycle stability can be also shown in heteroatom (N/O)-doped carbon materials with more chemical binding sites for polysulfides [21,55].

To further probe the contribution of the NiFe₂O₄ nanofibers, EIS profiles are measured as shown in Fig. 8, and the fitted data are presented in Table S2. Before cycling, the electrochemical reaction is simple with a semicircle and a sloped line for both the S/NiFe₂O₄ and S/CNT composites, corresponding to the interfacial charge-transfer process and the semi-infinite Warburg diffusion process, respectively. Both the interfacial charge-transfer resistance (R_{ct}) and Warburg impedance (W_o) are slightly large for the S/NiFe₂O₄ composite (Table

S2), resulting in the relatively low initial discharge capacity. Upon cycling, two depressed semicircles appear gradually in the high-frequency region, accompanied with a sloped line in the low-frequency region. It means that the additional process is induced, which is assigned to the deposition of the insoluble Li₂S₂/Li₂S layer within the discharge/charge cycles for both the composites. More clearly, for the S/NiFe₂O₄ composite, R_{ct} is decreased sharply from 97.8 Ω before cycling to the lowest value (13.6 Ω) in the 10th cycle, revealing that the surface activation process is initiated upon cycling. Subsequently, R_{ct} is increased slowly to 22.8 Ω in the 200th cycle, accompanied simultaneously with the slight increase of the resistance of the insoluble Li₂S₂/Li₂S layer. On the other hand, the Warburg impedance is gradually increased from the 1st cycle to the 200th cycle for the S/NiFe₂O₄ composite, however, which is lower than that of the S/CNT composite. It means that the surface passivation happens gradually during long-term cycling by the irreversible deposition and aggregation of Li₂S₂/Li₂S layer on the surface of the composite. Consequently, the activities on the surface and ion diffusion through Li₂S₂/Li₂S layer are reduced. In comparison with the S/CNT composite, the S/NiFe₂O₄ composite possesses the good electro-

Figure 7 Anchoring effect of polysulfide on spinel NiFe_2O_4 and CNTs: (a) UV-vis absorption spectra of 2 mmol L^{-1} Li_2S_8 solution (the inset shows the photos of sealed vials containing Li_2S_8 solutions before and after fully contacting with NiFe_2O_4 and CNTs); (b) the stable adsorption geometries of Li_2S_8 on both spinel NiFe_2O_4 and CNTs, and the atoms are marked in different colors: Li (pink), S (yellow), O (red), Ni (green), Fe (purple), C (grey); (c) the experimental quantities of Li_2S_8 adsorption; (d) the adsorption energy of Li_2S_8 on spinel NiFe_2O_4 and CNTs.

chemical activity and low diffusion impedance during long-term cycling without serious loss of sulfur active material and bad surface passivation by the thick $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ layer, leading to the good cycle stability and high-rate capability. In other words, the high electrocatalytic activity of NiFe_2O_4 nanofibers is beneficial to facilitate the reversible reverse transformation of $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ passivation layer to sulfur during cycling, which was demonstrated in N-doping Lewis base matrix of sulfur [56]. Therefore, the electrocatalytic activity, polarity and adsorption of NiFe_2O_4 nanofibers act synergistically to enhance the electrochemical performance of the S/ NiFe_2O_4 composite.

Similar to NiFe_2O_4 nanofibers, the other metal ferrites MFe_2O_4 ($\text{M}=\text{Co}$, Mg , and Zn) have the same spinel structure and strong adsorption to polysulfides. After loading sulfur on MFe_2O_4 nanofibers, these S/ MFe_2O_4

composites show the similar electrochemical performance, including the discharge capacity, cycle stability and high-rate capability (Fig. 9 and Fig. S8). It implies that the metal ferrites as substrate of sulfur have the common structural and physicochemical features for improving the electrochemical performance. Of course, among all the metal ferrites investigated here, nickel ferrite is the best substrate of sulfur based on the optimization of the electrochemical performance, which is further confirmed by UV-vis absorption and DFT calculation (Figs S10 and S11). In the adsorption test, the adsorption amount of Li_2S_8 on MFe_2O_4 is expressed as $7.1 \mu\text{mol m}^{-2}$ for NiFe_2O_4 , $6.5 \mu\text{mol m}^{-2}$ for ZnFe_2O_4 , $3.4 \mu\text{mol m}^{-2}$ for CoFe_2O_4 , and $3.2 \mu\text{mol m}^{-2}$ for MgFe_2O_4 (Figs. S10c and S11), which is responsible for the different adsorption ability of polysulfides. The different adsorption ability of polysulfides is mainly attributed to the

Figure 8 EIS plots of the (a) S/NiFe₂O₄ and (b) S/CNT composites at full charged state at 0.1 C after different cycles. (c) EIS plots of the S/NiFe₂O₄ and S/CNT composites at the open circuit voltage and the used equivalent circuit to fit the experimental data.

Figure 9 Cycle performance of S/MFe₂O₄ (M=Co, Mg, and Zn) composites at 0.1 C rate.

function of M (II) components in MFe₂O₄, which might offer different electrocatalytic activity for the conversion of polysulfides. Consistently, the difference in adsorption ability of those MFe₂O₄ is reflected on the capacity recovery after cycling at various rates (Fig. S9a).

The dissolution of polysulfides is unavoidable in the dissolution-deposition processes of sulfur cathode, which achieves the good utilization of sulfur, as well as the high reversible capacity. The key issue is to confine dissolution

and loss of polysulfides as much as possible. As the desirable substrate of sulfur, metal ferrites with large polarity show strong adsorption to polysulfides to control the undesirable shuttling effect of the sulfur cathode, resulting in an enhanced electrochemical performance. In the case of the S/NiFe₂O₄ composite, the soluble polysulfides can be mainly trapped on the cathode side of the Li-S cell. Consequently, the corrosion with S-rich by-products on the Li anode is weakened, and the smooth

surface is well maintained during long-term cycles (Fig. S12), which in turn contributes to the excellent performance of the sulfur cathode. Therefore, the effective trapping of polar lithium polysulfides here is highly related to the intrinsic polarity of metal ferrites. Further, the Li–O interaction plays an important role in polysulfide adsorption as indicated in the stable adsorption geometry of Li_2S_8 on NiFe_2O_4 (Fig. 7b). Besides, the chemical confinement of sulfur on the surface of metal ferrites reveals a trace of sulfur species, including sulfide, sulfurous and sulfate by XPS analysis (Fig. 2e and Fig. S4), suggesting the chemical bonds between sulfur and metal ferrites. Apart from the strong anchoring effect to polysulfides, more importantly, the metal ferrites endow the sulfur-based composites with high tap density to achieve high-volumetric-capacity.

CONCLUSIONS

In summary, NiFe_2O_4 nanofibers are designed and prepared by electrospinning method as the novel substrate of sulfur for Li–S battery. The as-prepared NiFe_2O_4 nanofibers show excellent anchoring effect to soluble polysulfides and moderate shuttling effect due to the strong polarity and adsorption to polysulfides, resulting in an enhanced cycle stability of the S/ NiFe_2O_4 composite. More importantly, owing to the high tap density of the S/ NiFe_2O_4 composite, the initial volumetric capacity of the S/ NiFe_2O_4 composite ($1,281.7 \text{ mA h cm}^{-3}_{\text{-composite}}$) is obtained as much higher than that ($668.4 \text{ mA h cm}^{-3}_{\text{-composite}}$) of the S/CNT composite. After 200 cycles, the discharge capacity of $873.2 \text{ mA h cm}^{-3}_{\text{-composite}}$ retains for the S/ NiFe_2O_4 composite, nearly 3.3 times higher than that of the S/CNT composite. Therefore, the superiority of metal ferrites as the substrate to achieve the stable sulfur cathode with high volumetric capacity is evidently verified, which is of great significance for practical Li–S battery with high volumetric energy density in future.

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- Bruce PG, Freunberger SA, Hardwick LJ, *et al.* Li–O₂ and Li–S batteries with high energy storage. *Nat Mater*, 2012, 11: 19–29
- Gao XP, Yang HX. Multi-electron reaction materials for high energy density batteries. *Energy Environ Sci*, 2010, 3: 174–189
- Gao J, Abruña HD. Key parameters governing the energy density of rechargeable Li/S batteries. *J Phys Chem Lett*, 2014, 5: 882–885
- Pang Q, Liang X, Kwok CY, *et al.* Advances in lithium–sulfur batteries based on multifunctional cathodes and electrolytes. *Nat Energy*, 2016, 1: 16132
- Manthiram A, Fu Y, Chung SH, *et al.* Rechargeable lithium–sulfur batteries. *Chem Rev*, 2014, 114: 11751–11787
- Fang X, Peng H. A revolution in electrodes: recent progress in rechargeable lithium–sulfur batteries. *Small*, 2015, 11: 1488–1511
- Lai C, Gao XP, Zhang B, *et al.* Synthesis and electrochemical performance of sulfur/highly porous carbon composites. *J Phys Chem C*, 2009, 113: 4712–4716
- Xu T, Song J, Gordin ML, *et al.* Mesoporous carbon–carbon nanotube–sulfur composite microspheres for high-area-capacity lithium–sulfur battery cathodes. *ACS Appl Mater Interfaces*, 2013, 5: 11355–11362
- Cheng XB, Huang JQ, Zhang Q, *et al.* Aligned carbon nanotube/sulfur composite cathodes with high sulfur content for lithium–sulfur batteries. *Nano Energy*, 2014, 4: 65–72
- Zhang Z, Jing HK, Liu S, *et al.* Encapsulating sulfur into a hybrid porous carbon/CNT substrate as a cathode for lithium–sulfur batteries. *J Mater Chem A*, 2015, 3: 6827–6834
- Babu G, Reddy Arava LM. Graphene-decorated graphite–sulfur composite as a high-tap-density electrode for Li–S batteries. *RSC Adv*, 2015, 5: 47621–47627
- Zhang Y, Li K, Huang J, *et al.* Preparation of monodispersed sulfur nanoparticles–partly reduced graphene oxide–polydopamine composite for superior performance lithium–sulfur battery. *Carbon*, 2017, 114: 8–14
- Zhang Y, Li K, Li H, *et al.* High sulfur loading lithium–sulfur batteries based on a upper current collector electrode with lithium-ion conductive polymers. *J Mater Chem A*, 2017, 5: 97–101
- Ji X, Lee KT, Nazar LF. A highly ordered nanostructured carbon–sulfur cathode for lithium–sulfur batteries. *Nat Mater*, 2009, 8: 500–506
- Zhang B, Qin X, Li GR, *et al.* Enhancement of long stability of sulfur cathode by encapsulating sulfur into micropores of carbon spheres. *Energy Environ Sci*, 2010, 3: 1531–1537
- Li GC, Hu JJ, Li GR, *et al.* Sulfur/activated-conductive carbon black composites as cathode materials for lithium/sulfur battery. *J Power Sources*, 2013, 240: 598–605
- Li Z, Yuan L, Yi Z, *et al.* Insight into the electrode mechanism in lithium–sulfur batteries with ordered microporous carbon confined sulfur as the cathode. *Adv Energy Mater*, 2014, 4: 1301473
- Li GC, Li GR, Ye SH, *et al.* A polyaniline-coated sulfur/carbon composite with an enhanced high-rate capability as a cathode material for lithium/sulfur batteries. *Adv Energy Mater*, 2012, 2: 1238–1245
- Xie J, Yang J, Zhou X, *et al.* Preparation of three-dimensional hybrid nanostructure-encapsulated sulfur cathode for high-rate lithium sulfur batteries. *J Power Sources*, 2014, 253: 55–63
- Li G, Sun J, Hou W, *et al.* Three-dimensional porous carbon composites containing high sulfur nanoparticle content for high-performance lithium–sulfur batteries. *Nat Commun*, 2016, 7: 10601
- Zhang Z, Kong LL, Liu S, *et al.* A high-efficiency sulfur/carbon composite based on 3D graphene nanosheet@carbon nanotube matrix as cathode for lithium–sulfur battery. *Adv Energy Mater*, 2017, 7: 1602543
- Yang CP, Yin YX, Ye H, *et al.* Insight into the effect of boron doping on sulfur/carbon cathode in lithium–sulfur batteries. *ACS Appl Mater Interfaces*, 2014, 6: 8789–8795
- Qiu Y, Li W, Zhao W, *et al.* High-rate, ultralong cycle-life lithium/sulfur batteries enabled by nitrogen-doped graphene. *Nano Lett*, 2014, 14: 4821–4827
- Zhou W, Wang C, Zhang Q, *et al.* Tailoring pore size of nitrogen-

- doped hollow carbon nanospheres for confining sulfur in lithium-sulfur batteries. *Adv Energy Mater*, 2015, 5: 1401752
- 25 Zhou G, Paek E, Hwang GS, *et al.* Long-life Li/polysulphide batteries with high sulphur loading enabled by lightweight three-dimensional nitrogen/sulphur-codoped graphene sponge. *Nat Commun*, 2015, 6: 7760–7770
 - 26 Wang L, Dong Z, Wang D, *et al.* Covalent bond glued sulfur nanosheet-based cathode integration for long-cycle-life Li-S batteries. *Nano Lett*, 2013, 13: 6244–6250
 - 27 Zu C, Manthiram A. Hydroxylated graphene-sulfur nanocomposites for high-rate lithium-sulfur batteries. *Adv Energy Mater*, 2013, 3: 1008–1012
 - 28 Wang Z, Dong Y, Li H, *et al.* Enhancing lithium-sulphur battery performance by strongly binding the discharge products on amino-functionalized reduced graphene oxide. *Nat Commun*, 2014, 5: 5002–5009
 - 29 Wei Seh Z, Li W, Cha JJ, *et al.* Sulphur-TiO₂ yolk-shell nanoarchitecture with internal void space for long-cycle lithium-sulphur batteries. *Nat Commun*, 2013, 4: 1331–1336
 - 30 Pang Q, Kundu D, Cuisinier M, *et al.* Surface-enhanced redox chemistry of polysulphides on a metallic and polar host for lithium-sulphur batteries. *Nat Commun*, 2014, 5: 4759–4766
 - 31 Liang X, Kwok CY, Lodi-Marzano F, *et al.* Tuning transition metal oxide-sulfur interactions for long life lithium sulfur batteries: the “goldilocks” principle. *Adv Energy Mater*, 2016, 6: 1501636
 - 32 Tao X, Wang J, Liu C, *et al.* Balancing surface adsorption and diffusion of lithium-polysulfides on nonconductive oxides for lithium-sulfur battery design. *Nat Commun*, 2016, 7: 11203–11211
 - 33 Fan Q, Liu W, Weng Z, *et al.* Ternary hybrid material for high-performance lithium-sulfur battery. *J Am Chem Soc*, 2015, 137: 12946–12953
 - 34 Yuan Z, Peng HJ, Hou TZ, *et al.* Powering lithium-sulfur battery performance by propelling polysulfide redox at sulfiphilic hosts. *Nano Lett*, 2016, 16: 519–527
 - 35 Li X, Liang J, Lu Y, *et al.* Bi₂S₃ *in-situ* formed in molten S environment stabilized sulfur cathodes for high-performance lithium-sulfur batteries. *J Power Sources*, 2016, 329: 379–386
 - 36 Lei T, Chen W, Huang J, *et al.* Multi-functional layered WS₂ nanosheets for enhancing the performance of lithium-sulfur batteries. *Adv Energy Mater*, 2017, 7: 1601843
 - 37 Babu G, Masurkar N, Al Salem H, *et al.* Transition metal dichalcogenide atomic layers for lithium polysulfides electrocatalysis. *J Am Chem Soc*, 2017, 139: 171–178
 - 38 Cui Z, Zu C, Zhou W, *et al.* Mesoporous titanium nitride-enabled highly stable lithium-sulfur batteries. *Adv Mater*, 2016, 28: 6926–6931
 - 39 Deng DR, An TH, Li YJ, *et al.* Hollow porous titanium nitride tubes as a cathode electrode for extremely stable Li-S batteries. *J Mater Chem A*, 2016, 4: 16184–16190
 - 40 Hao Z, Yuan L, Chen C, *et al.* TiN as a simple and efficient polysulfide immobilizer for lithium-sulfur batteries. *J Mater Chem A*, 2016, 4: 17711–17717
 - 41 Sun Z, Zhang J, Yin L, *et al.* Conductive porous vanadium nitride/graphene composite as chemical anchor of polysulfides for lithium-sulfur batteries. *Nat Commun*, 2017, 8: 14627
 - 42 Zhao X, Liu M, Chen Y, *et al.* Fabrication of layered Ti₃C₂ with an accordion-like structure as a potential cathode material for high performance lithium-sulfur batteries. *J Mater Chem A*, 2015, 3: 7870–7876
 - 43 Bao W, Su D, Zhang W, *et al.* 3D metal carbide@mesoporous carbon hybrid architecture as a new polysulfide reservoir for lithium-sulfur batteries. *Adv Funct Mater*, 2016, 26: 8746–8756
 - 44 Liang X, Rangom Y, Kwok CY, *et al.* Interwoven MXene nanosheet/carbon-nanotube composites as Li-S cathode hosts. *Adv Mater*, 2017, 29: 1603040
 - 45 Peng HJ, Zhang G, Chen X, *et al.* Enhanced electrochemical kinetics on conductive polar mediators for lithium-sulfur batteries. *Angew Chem*, 2016, 128: 13184–13189
 - 46 Liang X, Hart C, Pang Q, *et al.* A highly efficient polysulfide mediator for lithium-sulfur batteries. *Nat Commun*, 2015, 6: 5682–5689
 - 47 Blöchl PE. Projector augmented-wave method. *Phys Rev B*, 1994, 50: 17953–17979
 - 48 Kresse G, Joubert D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys Rev B*, 1999, 59: 1758–1775
 - 49 Perdew JP, Chevary JA, Vosko SH, *et al.* Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys Rev B*, 1992, 46: 6671–6687
 - 50 Chinnasamy CN, Narayanasamy A, Ponpandian N, *et al.* Mixed spinel structure in nanocrystalline NiFe₂O₄. *Phys Rev B*, 2001, 63: 184108–184113
 - 51 Carta D, Casula MF, Falqui A, *et al.* A structural and magnetic investigation of the inversion degree in ferrite nanocrystals MFe₂O₄ (M=Mn, Co, Ni). *J Phys Chem C*, 2009, 113: 8606–8615
 - 52 Rios E, Gautier JL, Poillat G, *et al.* Mixed valency spinel oxides of transition metals and electrocatalysis: case of the Mn_xCo_{3-x}O₄ system. *Electrochim Acta*, 1998, 44: 1491–1497
 - 53 Ponpandian N, Balaya P, Narayanasamy A. Electrical conductivity and dielectric behaviour of nanocrystalline NiFe₂O₄ spinel. *J Phys-Condens Matter*, 2002, 14: 3221–3237
 - 54 Zhao X, Fu Y, Wang J, *et al.* Ni-doped CoFe₂O₄ hollow nanospheres as efficient bi-functional catalysts. *Electrochim Acta*, 2016, 201: 172–178
 - 55 Zhang YZ, Zhang Z, Liu S, *et al.* Free-standing porous carbon nanofiber/carbon nanotube film as sulfur immobilizer with high areal capacity for lithium-sulfur battery. *ACS Appl Mater Interfaces*, 2018, 10: 8749–8757
 - 56 Cao Y, Li X, Zheng M, *et al.* Ultra-high rates and reversible capacity of Li-S battery with a nitrogen-doping conductive lewis base matrix. *Electrochim Acta*, 2016, 192: 467–474
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Ze Zhang is a Lecturer in the School of Chemistry, Nanchang University. He received his BS degree in 2012 from the College of Chemistry, and PhD degree in 2017 from the School of Materials Science and Engineering, Nankai University of China. His general research interest is in the area of advanced functional materials for rechargeable batteries with a focus on the exploration of high-energy Li-S battery.

Xue-Ping Gao is a Professor in the Institute of New Energy Material Chemistry, Nankai University, China. He received his doctorate at the Department of Chemistry from Nankai University in 1995. He used to work as a visiting research fellow at Kogakuin University in Japan from 1997 to 1999. Currently, his main research focuses on energy storage materials for power sources, including Li-ion batteries, Li-S battery and solar rechargeable battery.

锂-硫电池用高体积比容量硫/铁酸镍复合正极材料

张泽, 吴迪华, 周震, 李国然, 刘胜, 高学平*

摘要 锂-硫电池因其较高的理论质量能量密度而广为人知. 然而, 与以重质过渡金属氧化物作为正极材料的传统锂离子电池相比, 锂-硫较低的体积能量密度是其实际应用的瓶颈. 此外, 硫单质通常与轻质导电碳基底材料复合, 以实现其电化学循环稳定性. 这使得锂-硫电池实际体积能量密度更低. 本文通过静电纺丝方法制备了铁酸镍纳米纤维, 并将其用作新型载体材料. 铁酸镍不仅可以化学固定多硫化锂, 提高硫电极的循环稳定性, 而且有利于硫/铁酸镍的高体积比容量. 测试结果显示, 相比于硫/碳纳米管复合材料, 硫/铁酸镍复合材料具有更高的振实密度; 在0.1 C倍率充放电时, 以复合材料为活性物质计算, 该复合材料的初始体积比容量为 $1281.7 \text{ mA h cm}^{-3}$, 是硫/碳纳米管复合材料容量的1.9倍. 本工作提出以高振实密度的金属铁氧体材料来实现硫正极的高稳定性和高体积比容量, 这一新策略有助于实现锂-硫电池的高体积能量密度.