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To cite this article: Xiaoqing Zhang et al 2023 Int. J. Extrem. Manuf. 5 015501

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Int. J. Extrem. Manuf. 5 (2023) 015501 (15pp)

# Rational design and low-cost fabrication of multifunctional separators enabling high sulfur utilization in long-life lithium-sulfur batteries

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Received 23 May 2022, revised 8 June 2022 Accepted for publication 15 November 2022 Published 1 December 2022



#### Abstract

The lithium-sulfur (Li-S) battery with an ultrahigh theoretical energy density has emerged as a promising rechargeable battery system. However, the practical applications of Li-S batteries are severely plagued by the sluggish reaction kinetics of sulfur species and notorious shuttling of soluble lithium polysulfides (LiPSs) intermediates that result in low sulfur utilization. The introduction of functional layers on separators has been considered as an effective strategy to improve the sulfur utilization in Li-S batteries by achieving effective regulation of LiPSs. Herein, a promising self-assembly strategy is proposed to achieve the low-cost fabrication of hollow and hierarchically porous  $Fe_3O_4$  nanospheres (p-Fe\_3O\_4-NSs) assembled by numerous extremely-small primary nanocrystals as building blocks. The rationally-designed p-Fe<sub>3</sub>O<sub>4</sub>-NSs are utilized as a multifunctional layer on the separator with highly efficient trapping and conversion features toward LiPSs. Results demonstrate that the nanostructured p-Fe<sub>3</sub>O<sub>4</sub>-NSs provide chemical adsorption toward LiPSs and kinetically promote the mutual transformation between LiPSs and Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S during cycling, thus inhibiting the LiPSs shuttling and boosting the redox reaction kinetics via a chemisorption-catalytic conversion mechanism. The enhanced wettability of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-based separator with the electrolyte enables fast transportation of lithium ions. Benefitting from these alluring properties, the functionalized separator with p-Fe<sub>3</sub>O<sub>4</sub>-NSs endows the battery with an admirable rate performance of 877 mAh  $g^{-1}$  at 2 C, an ultra-durable cycling performance of up to 2176 cycles at 1 C, and a promising areal capacity of 4.55 mAh cm<sup>-2</sup> under high-sulfur-loading and lean-electrolyte conditions (4.29 mg cm<sup>-2</sup>, electrolyte/ratio: 8  $\mu$ l mg<sup>-1</sup>). This study will offer fresh insights on the rational design and low-cost fabrication of multifunctional separator to strengthen electrochemical reaction kinetics by regulating LiPSs conversion for developing efficient and long-life Li-S batteries.

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Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Keywords: lithium-sulfur battery, multifunctional separator, low-cost fabrication, chemisorption-catalytic conversion mechanism, hierarchically porous Fe<sub>3</sub>O<sub>4</sub> nanospheres

#### 1. Introduction

The lithium-sulfur (Li-S) battery has emerged as one of the most promising candidates for next-generation rechargeable batteries owing to its ultrahigh theoretical energy density of 2567 Wh kg<sup>-1</sup> and outstanding advantages of nontoxicity and natural abundance for sulfur active materials [1–5]. However, the sluggish reaction kinetics of active materials [6, 7] and notorious shuttling of soluble lithium polysulfides (LiPSs) intermediates [6, 8] severely hinder the practical applications of Li-S batteries, which results in low sulfur utilization, rapid capacity fading and shortened cycle life [9, 10].

Many strategies have been developed to achieve effective regulation of LiPSs by designing functional cathodes [11–14], interlayers [15, 16], and separators [16, 17] to immobilize soluble LiPSs or block their shuttling pathway, which significantly improves the electrochemical performances of Li-S batteries. Among these useful strategies, introducing functional separators into the Li-S battery has been proven a quite effective strategy for entrapping LiPSs within the cathodic region or retarding their diffusion across the separator, thus achieving effective suppression of LiPSs shuttling [17–19]. A common method is to prepare functional separators by modifying the polypropylene (PP) separators with barrier layers. In this regard, many studies have reported separators functionalized by the nanostructured carbon [20–23], polar hetero-atom doped carbon [24, 25], and metal-based compounds [26, 27] for blocking LiPSs shuttling via physical restraint or chemisorption effects. Although these functional layers on separators can effectively restrict the migration of LiPSs, the electrochemical performances of Li-S batteries are still far from satisfactory. On one hand, the soluble LiPSs are solely captured or blocked by these functional separators, which cannot be further converted into insoluble species (Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S for discharging and sulfur for charging) for reutilization, leading to a lower utilization rate of active materials. On the other hand, the functional layers on separators without rational structure design may inevitably block the transport of lithium ions, weaken the electrochemical reaction kinetics, and finally compromise the rate performance of batteries, especially at high current densities. Furthermore, the relatively complicated and costly preparation of functional layer materials using tedious multi-step procedures, expensive raw materials/precursors, or some harsh conditions inevitably bring about some drawbacks like high production cost, low output efficiency, and scalable fabrication problems, which is unsuitable for industrial production and practical applications in the battery-related fields [28]. Therefore, it remains challenging to develop cost-effective and high-performance separators with powerful regulation capability for LiPSs control and conversion, while maintaining rapid lithium-ion transfer to strengthen the sulfur redox kinetics.

To achieve high sulfur utilization and stable cycling performance in practical Li-S batteries, ideal functional layers on separators should be multifunctional to meet several critical demands: (a) strong blocking capability to suppress the shuttling of LiPSs by restraining their migration; (b) excellent affinity with the electrolyte for its efficient penetration to enhance the transport kinetics of lithium ions across the separator; (c) considerable conversion activity to boost the electrochemical reaction kinetics by facilitating the fast transformation of the trapped LiPSs to insoluble species; (d) rich natural abundance of raw material sources and facile preparation method to achieve their mass production at a low production cost.

With this background, this study develops a novel separator with a rationally-designed multifunctional layer that simultaneously satisfies the above-mentioned criteria. The hierarchically porous Fe<sub>3</sub>O<sub>4</sub> nanospheres (p-Fe<sub>3</sub>O<sub>4</sub>-NSs) with a hollow nanostructure are proposed as a proof-of-concept functional layer to construct a multifunctional separator for strengthening the electrochemical reaction kinetics in Li-S batteries. A promising self-assembly strategy is proposed to prepare the as-designed p-Fe<sub>3</sub>O<sub>4</sub>-NSs that are assembled by numerous extremely-small Fe<sub>3</sub>O<sub>4</sub> nanocrystals as building blocks. The proposed p-Fe<sub>3</sub>O<sub>4</sub>-NSs layer is endowed with the following merits: (a) strong binding capability to effectively capture LiPSs and block their shuttling; (b) enhanced electrolyte wettability to ensure fast diffusion kinetics of lithium ions and accelerate the electrochemical reaction kinetics; (c) excellent catalytic conversion activity to promote the mutual transformation between LiPSs and Li<sub>2</sub>S during cycling; (d) nontoxic property and abundant raw material resources to enable largescale production at a low cost. Benefitting from these alluring properties, the use of this p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator leads to an admirable rate performance (878 mAh  $g^{-1}$  at 2 C) and a remarkable ultra-durable cyclability (over 2176 cycles at 1 C). More importantly, even under high-sulfur-loading  $(4.29 \text{ mg cm}^{-2})$  and lean-electrolyte conditions (electrolyte/ sulfur (E/S) ratio: 8  $\mu$ l mg<sup>-1</sup>), a promising areal capacity of 4.55 mAh  $cm^{-2}$  is attained for the battery. This work demonstrates a feasible strategy to construct long-life Li-S batteries through the rational design and low-cost fabrication of multifunctional separators to achieve high sulfur utilization, providing new insights on the practical development of advanced Li-S batteries.

#### 2. Experimental section

#### 2.1. Fabrication of p-Fe<sub>3</sub>O<sub>4</sub>-NSs

The p-Fe<sub>3</sub>O<sub>4</sub>-NSs were prepared via a modified solvothermal reduction reaction [29]. Specifically, 1.80 g ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O, Aladdin, 99%) and 5.04 g sodium acetate (CH<sub>3</sub>CH<sub>2</sub>OONa, Aladdin, 99%) were ultrasonically dissolved in 70 ml ethylene glycol (EG, Aladdin, 99%) for 2 h. The solution was vigorously stirred overnight and transferred to a Teflon-lined autoclave. The autoclave was heated in an oven at 200 °C for 10 h. The precipitates were repeatedly washed using ethanol and dried at 80 °C for 12 h in a vacuum atmosphere to obtain the proposed p-Fe<sub>3</sub>O<sub>4</sub>-NSs.

#### 2.2. Fabrication of functional layers on separators

The as-prepared p-Fe<sub>3</sub>O<sub>4</sub>-NSs, carbon black (CB, Shenzhen Kejing Star Technology Co., Ltd), and polyvinylidene fluoride (PVDF, Shenzhen Kejing Star Technology Co., Ltd) (mass ratio: 7:2:1) were uniformly dispersed in *N*-methyl-2-pyrrolidone (NMP, Aladdin, 98%) to form an electrode slurry. The p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator was prepared by blade-coating the above slurry on a porous PP film (Celgard 2400). The mass loading of p-Fe<sub>3</sub>O<sub>4</sub>-NSs layer was 0.41–1.0 mg cm<sup>-2</sup> by tuning the height of blade. For comparison, a CB-coated separator (denoted as CB-PP separator) with a thickness of 15  $\mu$ m was also prepared by the same process (figure S1). The mass loading of CB was 0.48 mg cm<sup>-2</sup>.

#### 2.3. Adsorption test

Li<sub>2</sub>S (Aladdin, 99.98%) and elemental sulfur (Aladdin, 99.5%) with a stoichiometric ratio of 1:5 were dissolved in 1,3-dioxolane/1,2-dimethoxy-ethane (DOL/DME, v: v = 1: 1, Aladdin, 99.5%) to make the Li<sub>2</sub>S<sub>6</sub> solution (4 mM). 40 mg CB or p-Fe<sub>3</sub>O<sub>4</sub>-NSs was separately added into 2.5 ml Li<sub>2</sub>S<sub>6</sub> solution for observation.

#### 2.4. Electrochemical measurements

CB and sulfur were uniformly mixed in a mortar, followed by a heat-melt treatment at 155 °C for 12 h to prepare the CB@S composite. A slurry containing the CB@S composite, PVDF and multi-wall carbon nanotubes (Hengqiu Tech. Inc.) (mass ratio: 7:1:2) in NMP was used to prepare the cathode. The sulfur loading at the low-sulfur-loading cathode was  $1.1-1.5 \text{ mg cm}^{-2}$ . The high-sulfur-loading cathodes were fabricated with sulfur loadings of 3.29 and 4.29 mg cm<sup>-2</sup>. The E/S ratio of 20  $\mu$ l mg<sup>-1</sup> was used for the low-sulfur-loading cathode, while much lower E/S ratios of 10 and 8  $\mu$ l mg<sup>-1</sup> were used for the cathodes with sulfur loadings of 3.29 and 4.29 mg cm<sup>-2</sup>, respectively. The Li-S battery was assembled using a porous PP film (Celgard 2400) as the separator and a lithium foil as the anode. The electrolyte (Guangdong Canrd New Energy Technology Co., Ltd) was prepared by dissolving 1 M lithium bis-(trifluromethanesulfonyl) imide in DOL/DME (v: v = 1: 1) with 1 wt% lithium nitrate. Li-S batteries were tested within a potential window of 1.7–2.6 V using the LANHE equipment (CT2001A). An AUTOLAB electrochemical workstation (PGSTAT302N) was used to measure the electrochemical impedance spectra (EIS) of Li-S batteries within a frequency window ranging from 100 000 Hz to 0.01 Hz. Cyclic voltammetry (CV) measurements of batteries were conducted on an Chenhua electrochemical workstation (CHI660E) within a potential window of 1.7–2.8 V.

#### 2.5. Fabrication of Li<sub>2</sub>S<sub>6</sub> symmetric cells

The electrodes for the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-based symmetric cells were prepared by coating the slurry with a mixture of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs, CB, and PVDF (mass ratio: 7:2:1) in the solvent of NMP onto an Al foil. The as-prepared p-Fe<sub>3</sub>O<sub>4</sub>-NSs electrode was used to assemble the symmetric cell with 40  $\mu$ l Li<sub>2</sub>S<sub>6</sub> solution (0.25 M). For comparison, the Li<sub>2</sub>S<sub>6</sub>-free cell was also prepared using the Li<sub>2</sub>S<sub>6</sub>-free electrolyte. The CV curves of symmetric cells were collected within a potential window between -0.8 and 0.8 V. The EIS spectra of symmetric cells were collected within a frequency window ranging from 100 000 Hz to 0.01 Hz.

#### 2.6. Li<sub>2</sub>S nucleation and dissolution tests

The electrodes were prepared by loading the p-Fe<sub>3</sub>O<sub>4</sub>-NSs, PVDF and CB (mass ratio: 7:1:2) on a carbon paper (CP). The  $Li_2S_8$  solution (0.2 M) was obtained by dissolving the elemental sulfur and Li<sub>2</sub>S by a stoichiometric ratio of 7:1 in DOL/DME (v: v = 1: 1) or tetraglyme (Aladdin, 99.5%). 1 M LiTFSI and 1 wt% LiNO<sub>3</sub> were added into the above Li<sub>2</sub>S<sub>8</sub> solution. The lithium foil, porous PP film (Celgard 2400), and p-Fe<sub>3</sub>O<sub>4</sub>-NSs-CP electrode, respectively, as the counter electrode, separator, and working electrode, were used to assemble coin cells. For the test of Li2S nucleation, 20 µl Li2S8 solution (0.2 M, DOL/DME) and 20  $\mu$ l blank electrolyte without Li<sub>2</sub>S<sub>8</sub> were used as the catholyte and anolyte, respectively. The coin cells were first discharged to 2.09 V at 0.112 mA, followed by a potentiostatic discharge process at 2.08 V for Li<sub>2</sub>S nucleation. For the test of Li<sub>2</sub>S dissolution, 20 µl Li<sub>2</sub>S<sub>8</sub> solution (0.2 M, tetraglyme) and 20  $\mu$ l blank electrolyte without Li<sub>2</sub>S<sub>8</sub> were used as the catholyte and anolyte, respectively. The coin cells were first discharged to 1.7 V at 0.112 mA, followed by a potentiostatic charge process at 2.4 V for Li<sub>2</sub>S dissolution.

#### 2.7. Samples characterizations

X-ray diffractometer (XRD, X'pert 3 Power) was used to analyze the crystal structure of sample. Field emission scanning electron microscopy (FESEM, ZEISS Merlin) and field emission transmission electron microscopy (TEM, JEM-2100F) were used to characterize the microstructures and morphologies of samples. The elemental distributions of samples were analyzed using an energy dispersive x-ray spectrophotometer (EDX, Brucker). The surface chemical states of samples were characterized using an x-ray photoelectron spectrophotometer (XPS, Kratos Axis Ultra DLD). The sulfur content in the composite was analyzed using a thermogravimetry analysis (TGA)



Figure 1. Schematic illustration of LiPSs regulation in Li-S batteries with pristine PP separator and p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator.

instrument (METTLER-TOLEDO, TGA/DSC 3+) in a N<sub>2</sub> flow. Surface area and porosity analyzer instrument (Micromeritics ASAP 2460) was used to conduct the N<sub>2</sub> adsorptiondesorption test. Ultraviolet–visible (UV–vis) spectra of the as-prepared samples were collected on an UV–vis spectroscopy (TU-1901). The contact angle measurements with liquid electrolyte were conducted on a contact angle instrument (JC2000D1).

#### 3. Results and discussion

#### 3.1. Structure, morphology and composition of p-Fe<sub>3</sub>O<sub>4</sub>-NSs

Figure 1 schematically shows the working mechanisms of Li-S batteries with the pristine PP and p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separators. As shown in figure 1(left), without any modification for a pristine separator, the pristine Li-S battery suffers from severe LiPSs shuttling and lithium anode corrosion caused by the reaction between soluble LiPSs and lithium metal. In contrast, the multifunctional p-Fe<sub>3</sub>O<sub>4</sub>-NSs layer on the separator (p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator) not only significantly blocks the diffusion of LiPSs across the separator via strong chemisorption, but also kinetically propels the mutual transformation between the soluble LiPSs and insoluble Li2S2/Li2S based on a catalytic effect. Meanwhile, the p-Fe<sub>3</sub>O<sub>4</sub>-NSs with a hollow nanostructure can provide abundant pore channels and an interior cavity to facilitate efficient transportation of lithium ions to guarantee fast redox reaction kinetics under high current-density conditions. Therefore, the improved Li-S battery using the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator achieves effective regulation and fast conversion of LiPSs as well as improvement of lithium anode corrosion (figure 1(right)).

Figure 2(a) schematically shows the preparation process of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs with a hollow nanostructure. The formation of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs is based on a facile self-assembly strategy. In the alkaline condition (CH<sub>3</sub>CH<sub>2</sub>OONa as an alkali source), EG serving as both the solvent and reductant can easily react with Fe<sup>3+</sup> to form abundant extremely-small Fe<sub>3</sub>O<sub>4</sub> nanocrystals during the solvothermal reduction reaction at 200 °C [29, 30]. As the reaction proceeds, these extremelysmall Fe<sub>3</sub>O<sub>4</sub> nanocrystals continue to self-assemble into the p-Fe<sub>3</sub>O<sub>4</sub>-NSs as building blocks. The microstructure and morphology of the as-prepared p-Fe<sub>3</sub>O<sub>4</sub>-NSs are characterized using FESEM and TEM. It is observed that the obtained p-Fe<sub>3</sub>O<sub>4</sub>-NSs exhibit a rough and porous spherical morphology (figure 2(b)). The high-magnification FESEM image shows that the p-Fe<sub>3</sub>O<sub>4</sub>-NSs consist of numerous extremelysmall primary nanocrystals with a grain size of 10-15 nm (figure 2(c)). The porous spherical morphology and primary nanocrystals of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs can be also clearly identified by TEM images (figures 2(d) and (e)) and verified by the scan transmission electron microscopy image (figure 2(g)). In addition, a well-defined lattice fringe of 0.294 nm that corresponds to the (220) plane of  $Fe_3O_4$  is identified in figure 2(f), corroborating the formation of p-Fe<sub>3</sub>O<sub>4</sub>-NSs. The XRD pattern in figure S2 also confirms the crystal structure of p-Fe<sub>3</sub>O<sub>4</sub>-NSs, which exhibits many characteristic diffraction peaks matching with the crystal phase of Fe<sub>3</sub>O<sub>4</sub> (PDF#19-0629) [31, 32]. Furthermore, the EDX elemental mappings shown in figures 2(h)-(k) illustrate the homogeneous elemental distribution of iron and oxygen throughout the nanosphere.

The hierarchically porous features of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs are revealed by the N<sub>2</sub> adsorption–desorption test (figure 3(a)). It is observed that the p-Fe<sub>3</sub>O<sub>4</sub>-NSs sample displays a type-IV



**Figure 2.** Fabrication and characterizations of  $p-Fe_3O_4$ -NSs. (a) Schematic fabrication procedure. (b), (c) FESEM images, (d), (e) TEM images, (f) high-resolution TEM image, (g) STEM image, and (h)–(k) EDX elemental mappings of  $p-Fe_3O_4$ -NSs.

isotherm [33, 34], indicating the porous nature of this sample. The p-Fe<sub>3</sub>O<sub>4</sub>-NSs sample exhibits a specific surface area of 23.63 m<sup>2</sup> g<sup>-1</sup>. Figure 3(b) shows the pore size distribution curve of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs sample. It is observed that there are many pores in the range of 1–5 nm, proving that the p-Fe<sub>3</sub>O<sub>4</sub>-NSs include some micropores and abundant mesopores. These results illustrate the formation of p-Fe<sub>3</sub>O<sub>4</sub>-NSs with a porerich structure through the self-assembly of abundant Fe<sub>3</sub>O<sub>4</sub> nanocrystals. In this hierarchically porous structure, the combination of micropores and mesopores can facilitate effective permeation of the electrolyte to enable fast lithium-ion transfer [4, 20, 35], while the mesopores are beneficial to entrapping

LiPSs via a physical restraint so as to suppress their shuttling [36, 37]. Furthermore, the hierarchically porous structure of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs can synergistically afford rich active sites for effective anchoring and fast conversion of LiPSs, thereby improving the cycling stability of Li-S batteries.

The surface chemical composition of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs was investigated using XPS. Figure 3(c) displays the XPS spectrum of C 1 s for the as-prepared p-Fe<sub>3</sub>O<sub>4</sub>-NSs. Two fitted characteristic peaks located at 284.6 and 285.3 eV, respectively, are associated with C–C and C–O bonds [38–40]. Two broad peaks are observed in the XPS spectrum of Fe 2p (figure 3(d)), indicating the typical characteristic resonances of Fe  $2p_{1/2}$ 



**Figure 3.** (a)  $N_2$  adsorption-desorption isotherm, (b) pore size distribution curve of p-Fe<sub>3</sub>O<sub>4</sub>-NSs, (c) XPS spectra of (c) C 1 s and (d) Fe 2p for p-Fe<sub>3</sub>O<sub>4</sub>-NSs.

and Fe 2p<sub>3/2</sub>, respectively. Two characteristic peaks located at 711.5 and 710.4 eV are fitted for the broad Fe  $2p_{3/2}$  peak, relating to Fe<sup>3+</sup>  $2p_{3/2}$  and Fe<sup>2+</sup>  $2p_{3/2}$  [41, 42], respectively. Furthermore, the peak area ratio of Fe<sup>3+</sup> to Fe<sup>2+</sup> is calculated to be 1.9:1, which is near the ratio of 2:1 for stoichiometric Fe<sub>3</sub>O<sub>4</sub>. Overall, the morphology, structure and composition characterizations illustrate the successful fabrication of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs with a pore-rich structure in this study.

#### 3.2. Characterization of p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator

The as-prepared p-Fe<sub>3</sub>O<sub>4</sub>-NSs were used to prepare the multifunctional p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator (figures 4(a) and (b)). It is shown that the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator could be bent and folded without cracking, demonstrating its excellent mechanical properties with good flexibility and strong adhesion (figure 4(c)). Morphology characterization in figure 4(d) indicates that the p-Fe<sub>3</sub>O<sub>4</sub>-NSs are uniformly distributed on the separator without obvious aggregation, while the EDX elemental mappings confirm the homogenous depth distribution of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs (figures 4(g)–(j)). The cross-sectional FESEM image of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator in figure S3 displays that the thickness of this functional layer is about 6.6  $\mu$ m. The electrolyte wetting behavior is an important factor for the modified separator, which has a significant impact on the infiltration of electrolyte and diffusion kinetics of lithium ions across a separator [43]. As shown in figure 4(f), the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator exhibits a low contact angle of 13.1° with the electrolyte in contrast with the pristine PP separator (31.2°, figure 4(e)). In addition, the electrolyte permeates into the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator quickly so that the contact angle turns almost zero within 10 s (figure S4). In contract, the contact angle of PP separator with the electrolyte decreases to 22.0° after 60 s. This verifies the excellent electrolyte wettability of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator owing to the hierarchical porous and hollow nanostructure of p-Fe<sub>3</sub>O<sub>4</sub>-NSs, which is conductive to promoting fast transport kinetics of lithium ions during the electrochemical processes [44].

The diffusion characteristics of lithium ions can be evaluated by conducting CV tests according to the Randles–Sevcik equation [45, 46].

$$I_{\rm p} = (2.69 \times 10^5) n^{1.5} A D_{\rm Li^+}^{0.5} C_{\rm Li^+} \nu^{0.5}$$

where  $I_p$ , A, n,  $D_{Li^+}$ ,  $C_{Li^+}$  and  $\nu$  represent the peak current, area of electrode, number of electron transfer in the reaction, diffusion coefficient of lithium ions, concentration of lithium ions, and scan rate of CV test, respectively. It can be deduced



**Figure 4.** Structure and properties of p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator. Digital photos of (a) front and (b) back sides of p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator. (c) Digital photos of p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator for bending and folding tests. (d) FESEM image of p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator. Contact angles of (e) pristine PP separator and (f) p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator with electrolyte. (g)–(j) Electron image and corresponding elemental mappings of cross-section of p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator.

that the square root of  $D_{\text{Li}^+}$  is proportional to the slope for the fitting line of  $I_p - \nu^{0.5}$ , since  $n \ (n = 2)$ ,  $A \ (A = 1.13 \text{ cm}^{-2})$ and  $C_{\text{Li}^+} \ (C_{\text{Li}^+} = 0.001 \text{ mol cm}^{-3})$  are constant in this battery system.

As shown in figures 5(a)-(c), the shifts of cathodic and anodic peaks are observed as the scan rate increases, indicating the electrochemical polarization at a high scan rate. Figures 5(d)–(f) show the linear plots of  $I_p - \nu^{0.5}$ . The slope values and diffusion coefficients of lithium ions are listed in tables S1 and S2, respectively. The largest slope values and diffusion coefficients of lithium ions of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator among three kinds of separators highlight the fastest transportation of lithium ions during the redox reactions [47]. This can be attributed to the fact that the unique hollow and hierarchically porous nanostructure of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs can facilitate efficient lithium ions transfer [20, 35]. Therefore, the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator is believed to endow Li-S batteries with the enhanced electrochemical reaction kinetics, which will be verified by a series of electrochemical tests in the following section.

## 3.3. Electrochemical performance of p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator

To evaluate the important role of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator in improving sulfur utilization in a Li-S battery, batteries based on the pristine PP separator and CB-PP separator were also prepared for comparison. A CB@S composite with a sulfur content of  $\sim$ 69.4 wt% was used to prepare the cathode, as measured by TGA (figure S5). Figure 6(a) displays the CV curves of Li-S batteries based on different separators. The battery based on the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator exhibits two cathodic peaks and two anodic peaks. Two cathodic peaks located at 2.30 and 2.03 V correspond to the reduction of sulfur to soluble LiPSs and the further transformation of LiPSs to insoluble Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S [44, 47], respectively. Two anodic peaks located at 2.32 and 2.38 V are associated with the reversible oxidation of Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S to LiPSs and then to sulfur [48], respectively. It should be noted that the battery with the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator exhibits distinctly positive shift for two cathodic peaks (peaks A and B) and negative shift for the anodic peak



**Figure 5.** CV curves of Li-S batteries based on different separators at various scan rates: (a) pristine PP separator, (b) CB-PP separator and (c) p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator. Linear fitting lines of  $I_p - \nu^{0.5}$  for (d) peak A, (e) peak B, and (f) peak C.

(peak C) in comparison with the counterparts based on the pristine PP and CB-PP separators (figure S6). This difference indicates the boosted redox reaction kinetics in the presence of the multifunctional p-Fe<sub>3</sub>O<sub>4</sub>-NSs layer on the separator [49], which is further confirmed by the EIS test (figure 6(b)). All the batteries exhibit a depressed semicircle in the high-middle frequency region and an inclined line in the low-frequency region, corresponding to the charge transfer resistance  $(R_{ct})$ and Warburg diffusion impedance  $(W_d)$  [50], respectively. An equivalent circuit model (the inset of figure 6(b)) was proposed to fit the Nyquist plots and the fitting results are listed in table S3. A lower  $R_{ct}$  (34.2  $\Omega$ ) is identified for the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator in comparison with those values for the PP separator (74.0  $\Omega$ ) and CB-PP separator (40.2  $\Omega$ ), which is indicative of fast charge transfer as well as rapid electrochemical reaction kinetics in the case of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator [48]. In addition, the steeper inclined line for the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator illustrates more efficient diffusion kinetics of lithium ions [51], which agrees well with the fast infiltration of electrolyte into the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator. Moreover, the almost overlapped CV curves for the first five scans without obvious peak shift manifest excellent electrochemical reversibility of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-based Li-S battery (figure S7) [52].

Figure 6(c) shows the cycling performances of Li-S batteries based on different separators at 0.2 C (1 C = 1675 mA g<sup>-1</sup>). The p-Fe<sub>3</sub>O<sub>4</sub>-NSs-based Li-S battery produces a high specific capacity (1266 mAh g<sup>-1</sup>), which is much higher than the one based on the PP separator (1072 mAh g<sup>-1</sup>) or CB-PP separator (1187 mAh g<sup>-1</sup>). This difference indicates the significantly enhanced sulfur utilization with the aid of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator. In addition, the new separator can maintain a high specific capacity of 901 mAh  $g^{-1}$  after 100 cycles, which prominently outperforms the PP separator (622 mAh  $g^{-1}$ ) and CB-PP separator (705 mAh  $g^{-1}$ ). This strongly verifies the outstanding superiority of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator to improve the sulfur utilization. To exclude the capacity contribution from the p-Fe<sub>3</sub>O<sub>4</sub>-NSs, the electrochemical performance of the bare p-Fe<sub>3</sub>O<sub>4</sub>-NSs electrode without sulfur was tested. As shown in figure S8, the p-Fe<sub>3</sub>O<sub>4</sub>-NSs electrode yields a low specific capacity at 0.2 C for 200 cycles, demonstrating the negligible contribution of the bare p-Fe<sub>3</sub>O<sub>4</sub>-NSs to the total capacity of the battery. The mass loading of p-Fe<sub>3</sub>O<sub>4</sub>-NSs layer on the separator was also optimized to achieve excellent cycling stability for Li-S batteries (figure S9). The p- $Fe_3O_4\text{-}NSs\text{-}PP$  separator with a mass loading of  $0.52\ \text{mg}\ \text{cm}^{-2}$ endows the battery with the best electrochemical performance because neither low or high mass loading of p-Fe<sub>3</sub>O<sub>4</sub>-NSs can achieve high sulfur utilization as well as cycling stability. Therefore, the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator with an optimal mass loading is chosen for further test.

The multifunctional p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator also enables the Li-S battery to produce an enhanced rate performance (figure 6(d)). The Li-S battery based on the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator exhibits the best rate capability among the three types of batteries. The p-Fe<sub>3</sub>O<sub>4</sub>-NSs-based battery delivers high discharge capacities of 1332, 1023 and 989 mAh g<sup>-1</sup> at 0.2, 0.5 and 1 C, respectively. In addition, the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-based battery can yield a promising discharge capacity



**Figure 6.** Electrochemical performances of Li-S batteries based on different separators. (a) CV curves, (b) EIS spectra, (c) cycling tests, and (d) rate performances of Li-S batteries based on different separators. (e) Charge–discharge profiles of battery integrating p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator at various current densities. (f) Rate performance comparison of p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator with other advanced separators. (g) Long-term cycling test of battery integrating p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator at 1 C. (h) Cycling stability of Li-S battery using p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator under high-sulfur-loading and lean-electrolyte conditions.

of 878 mAh  $g^{-1}$  at a higher current rate of 2 C. When the current rate returns to 0.2 C, the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-based battery retrieves a high capacity of 1134 mAh  $g^{-1}$ , showing its outstanding reversibility. Such an admirable rate performance is impressive in comparison with other previously reported separators (figure 6(f)) [49, 53-62]. In contrast, those Li-S batteries based on the PP separator and CB-based separator deliver much lower discharge capacities at various current rates, especially in the case of high-current operation. The significant enhancement of rate performance in the case of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator confirms the rapid redox kinetics of LiPSs in the Li-S battery [47]. Figure 6(e) displays chargedischarge profiles of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-based battery under various current rates. It is observed that the battery using the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator displays two well-defined discharge plateaus. Impressively, the battery based on the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator still exhibits obvious chargedischarge plateaus with a small polarization even at 2 C,

illustrating the significantly improved conversion kinetics of LiPSs [63]. However, the battery based on the CB-PP separator shows a much larger polarization at 2 C, while the second discharge plateau even disappears in the case of using a PP separator owing to severe polarization at 2 C (figure S10). These results clearly demonstrate that the multifunctional p-Fe<sub>3</sub>O<sub>4</sub>-NSs layer on the separator helps achieve high sulfur utilization by expediting the electrochemical reaction kinetics of sulfur species during discharging–charging.

Figure 6(g) displays the long-term cycling test of the battery integrating the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator. The battery with the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator has an ultra-long cycle life of over 2176 cycles at 1 C accompanied with an ultralow capacity decay rate of 0.035% per cycle, which proves the important role of the newly-designed p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator in endowing the battery with an ultra-durable cyclability. However, the Li-S batteries based on the pristine PP and CB-PP separators deliver a poor cycling performance in contrast with the one based on the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator (figure S11). In addition, obvious capacity fluctuations can be identified for the batteries based on the pristine PP and CB-PP separators owing to the shuttling of soluble LiPSs in a high current rate of 1 C. It is observed that the battery using the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator even retains a high Coulombic efficiency approaching 98% after such an ultra-long cycling process. The ultra-long cycle life with a high Coulombic efficiency indicates that the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator can effectively entrap the soluble LiPSs species within the cathode region to suppress their shuttling. Furthermore, the Li-S battery based on the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator yields a superior electrochemical performance to the representative Fe<sub>3</sub>O<sub>4</sub>-based or other functional separators reported in the recent literatures (table S4). It is worth noting that the preparation of the proposed p-Fe<sub>3</sub>O<sub>4</sub>-NSs is facile and scalable without any posttreatments like high-temperature annealing process [64, 65] or compositing with other components [54, 55, 57] as reported in other researches, highlighting the advantage of using the newly-designed p-Fe<sub>3</sub>O<sub>4</sub>-NSs to prepare multifunctional separators at a low fabrication cost in this work. Since the use of conductive carbon materials like carbon nanotubes, carbon coating/layer and nano-carbon network can effectively improve the properties of electrode materials by facilitating fast electron transfer during cycling [66-71], a significant enhancement of electrochemical performance is expected for Li-S batteries with the incorporation of carbon materials with the proposed p-Fe<sub>3</sub>O<sub>4</sub>-NSs.

The use of a high-loading cathode is helpful to construct the high-energy-density Li-S battery toward practical application. The p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator enables the renewed battery to generate a high capacity of 1181 mAh  $g^{-1}$  at 0.1 C in the first cycle with a high mass loading of  $3.29 \text{ mg cm}^{-2}$  as well as a low E/S ratio of 10  $\mu$ l mg<sup>-1</sup> (figure S12). The battery integrating the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator can maintain a high capacity of 701 mAh  $g^{-1}$  after 130 cycles. In addition to high sulfur utilization, two distinct discharge plateaus are evidenced with a small potential polarization (figure S13). Furthermore, when the mass loading of sulfur increases to 4.29 mg  $cm^{-2}$ and E/S ratio decreases to 8  $\mu$ l mg<sup>-1</sup>, the battery using the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator can produce a promising areal capacity of 4.55 mAh  $cm^{-2}$  at 0.1 C and attain a high retention rate of 76.2% after 40 cycles (figure 6(h)), illuminating potential application of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator in the future.

To show the effectiveness of using the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator to restrain LiPSs diffusion, the battery samples after cycling were disassembled to evaluate the anode corrosion caused by LiPSs. In comparison with the smooth surface morphology of a fresh lithium anode (figure S14(a)), the lithium anode with the pristine PP separator exhibits a rough surface morphology with severe corrosion (figure S14(b)) due to the uncontrollable shuttling of LiPSs across the PP separator is adopted, the lithium anode shows an improved surface morphology as shown in figure S14(c). Furthermore, a much smoother surface morphology is identified for the battery sample with the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator (figure S14(d)),

indicating that the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator can significantly alleviate LiPSs shuttling owing to the synergistic mechanism of chemisorption and catalytic conversion activity of the p-Fe<sub>3</sub>O<sub>4</sub>-NS toward LiPSs. This mechanism will be further discussed in the following section.

### 3.4. Chemisorption and catalytic conversion mechanism on p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator

For the sake of exploring the adsorption capability of the as-prepared p-Fe<sub>3</sub>O<sub>4</sub>-NSs toward LiPSs, the p-Fe<sub>3</sub>O<sub>4</sub>-NSs and CB with an equivalent mass were separately added into the as-prepared Li<sub>2</sub>S<sub>6</sub> solution for observation. As shown in figure 7(a), the initial dark brown  $Li_2S_6$  solution turns slightly light yellow in the presence of p-Fe<sub>3</sub>O<sub>4</sub>-NSs after the adsorption test for 24 h, while the Li<sub>2</sub>S<sub>6</sub> solution remains almost unchanged when using CB as an adsorbent. These results suggest that most of the Li<sub>2</sub>S<sub>6</sub> species were captured by the adsorptive p-Fe<sub>3</sub>O<sub>4</sub>-NSs, which is confirmed by the UV-vis spectra of the supernatants after the test (figure 7(b)). It is observed that the UV-vis spectra of Li<sub>2</sub>S<sub>6</sub> solution with and without CB display similar adsorption bands in the range of 340-450 nm, which are consistent with some previous literatures [72–74]. Impressively, a significant reduction of the absorbance intensity in the range of 340-450 nm is identified for the solution with the rationally-designed p-Fe<sub>3</sub>O<sub>4</sub>-NSs. This further verifies the strong adsorption capability of the asprepared p-Fe<sub>3</sub>O<sub>4</sub>-NSs toward LiPSs, which is conductive to mitigating and even suppressing the notorious shuttle effect of LiPSs. The chemical affinity of the as-designed p-Fe<sub>3</sub>O<sub>4</sub>-NSs with LiPSs is revealed by XPS. As shown in figure 7(c), a new characteristic peak located at 708.3 eV is observed for p-Fe<sub>3</sub>O<sub>4</sub>-NSs sample after the adsorption test, which can be ascribed to the Fe–S bond [75, 76]. This proves the chemical interaction between p-Fe<sub>3</sub>O<sub>4</sub>-NSs and Li<sub>2</sub>S<sub>6</sub> species. In addition, the obvious down shift of binding energy after adsorption indicates the electron transfer between the p-Fe<sub>3</sub>O<sub>4</sub>-NSs and  $Li_2S_6$  species [77, 78] (figure S15). The chemical interaction between the p-Fe<sub>3</sub>O<sub>4</sub>-NSs and LiPSs can be also confirmed by the characteristic peak assigned to the Fe-S bond at 161.3 eV [79] (figure S16), attesting the chemical affinity of  $p-Fe_3O_4$ -NSs with Li<sub>2</sub>S<sub>6</sub>.

In addition to the strong chemisorption for LiPSs, the proposed p-Fe<sub>3</sub>O<sub>4</sub>-NSs exhibit an excellent catalytic conversion activity to promote fast transformation of soluble LiPSs, which helps restrain the LiPSs shuttling in Li-S batteries. The catalytic activity of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs toward LiPSs transformation can be evaluated by assembling symmetric cells using the p-Fe<sub>3</sub>O<sub>4</sub>-NSs electrode as the identical counter and working electrodes with a Li<sub>2</sub>S<sub>6</sub> electrolyte. The Li<sub>2</sub>S<sub>6</sub>-free symmetric cell was also prepared to evaluate the capacitive contribution, which shows a negligible contribution to the redox current value. As shown in figure 7(d), the p-Fe<sub>3</sub>O<sub>4</sub>-NSs electrode displays two strong symmetric redox peaks with a high redox current, in stark contrast to the weak redox current without obvious redox peak in the case of the CB-based electrode. This suggests that the use of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs can significantly facilitate the redox kinetics of LiPSs [47, 80]. Particularly,



**Figure 7.** Chemisorption and catalytic conversion mechanism: (a) Visual  $Li_2S_6$  adsorption test. (b) UV–vis spectra of various supernatants after the adsorption test. (c) XPS spectrum of Fe 2p for p-Fe<sub>3</sub>O<sub>4</sub>-NSs-Li<sub>2</sub>S<sub>6</sub> composite after adsorption. (d) CV curves and (e) EIS spectra of symmetric cells based on CB and p-Fe<sub>3</sub>O<sub>4</sub>-NSs electrodes. (f) First three CV curves of symmetric cell using p-Fe<sub>3</sub>O<sub>4</sub>-NSs electrode. (g)–(i) Potentiostatic discharge profiles of Li<sub>2</sub>S nucleation at 2.08 V and (j)–(l) potentiostatic charge profiles of Li<sub>2</sub>S dissolution at 2.40 V on CP, CP-CB, and CP-p-Fe<sub>3</sub>O<sub>4</sub>-NSs electrodes, respectively.

the p-Fe<sub>3</sub>O<sub>4</sub>-NSs electrode displays the almost overlapped CV curves in the first three scans at 1 mV s<sup>-1</sup>, reflecting the highly stable catalytic behavior of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs toward LiPSs redox (figure 7(f)) [48, 52]. In addition, the EIS spectra in figure 7(e) show that the symmetric cell based on the p-Fe<sub>3</sub>O<sub>4</sub>-NSs electrode harvests a smaller semicircle than the CB counterpart, indicating more efficient charge transfer at the

interface of  $p-Fe_3O_4-NSs/Li_2S_6$  [81]. All these results confirm the accelerated redox kinetics of LiPSs conversion enabled by the  $p-Fe_3O_4-NSs$  [60, 82].

The reaction kinetics toward the liquid–solid mutual transformation can be also strengthened by the p-Fe<sub>3</sub>O<sub>4</sub>-NSs, as illustrated by the Li<sub>2</sub>S nucleation and dissolution experiments. Figures 7(g)–(i) show the potentiostatic discharge profiles of batteries using different electrodes (e.g. CP, CP-CB, and CP-p-Fe<sub>3</sub>O<sub>4</sub>-NSs). Evidently, the CP-p-Fe<sub>3</sub>O<sub>4</sub>-NSs electrode yields the highest Li<sub>2</sub>S precipitation capacity and the earliest response of Li<sub>2</sub>S nucleation among the three samples, showing the promoted redox kinetics of Li2S nucleation on the catalytic p-Fe<sub>3</sub>O<sub>4</sub>-NSs [52, 83]. The potentiostatic charge profiles of batteries using different electrodes reveal the enhanced redox kinetics of Li<sub>2</sub>S dissolution on the p-Fe<sub>3</sub>O<sub>4</sub>-NSs (figure 7(1)). The CP-p-Fe<sub>3</sub>O<sub>4</sub>-NSs electrode delivers a higher dissolution capacity in contrast with the CP and CP-CB electrodes. These results display the superior capability of the p-Fe<sub>3</sub>O<sub>4</sub>-NS in facilitating Li<sub>2</sub>S dissolution during the solid-liquid conversion process [84]. In a word, the above results manifest the excellent chemisorption and catalytic activity of the well-designed p-Fe<sub>3</sub>O<sub>4</sub>-NSs toward LiPSs, thus disclosing an effective chemisorption-catalytic mechanism for expediting the reaction kinetics of LiPSs conversion. This is of great significance to the structural and performance improvement for Li-S batteries.

To summarize, the above-discussed results demonstrate that the proposed p-Fe<sub>3</sub>O<sub>4</sub>-NSs endow the renewed separator with strong chemisorption and conversion capability for effective regulation of LiPSs in the Li-S battery owing to their unique structure and multifunction: (a) the hollow and hierarchically porous nanostructure is conductive to offering abundant anchoring sites to confine LiPSs and facilitating fast diffusion kinetics of lithium ions to improve the rate performance; (b) the strong chemical adsorption capability of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs effectively immobilizes LiPSs to retard their shuttling; (c) the highly efficient conversion activity of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs accelerates the redox kinetics of the immobilized LiPS and promotes nucleation/decomposition of Li2S. Combining these merits, the newly-designed p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator endows the Li-S battery with an excellent electrochemical performance.

#### 4. Conclusions

In summary, this study proposes a feasible scheme to construct advanced Li-S batteries through rational design and low-cost fabrication of the p-Fe<sub>3</sub>O<sub>4</sub>-NSs used as a multifunctional layer on the separator for effective regulation of LiPSs. The hollow p-Fe<sub>3</sub>O<sub>4</sub>-NSs composed of plenty of extremelysmall nanocrystals integrate the merits of strong chemisorption, enhanced ions diffusion and excellent catalytic conversion activity, providing a promising chemisorption-catalytic conversion mechanism for efficient trapping and transformation of LiPSs, as well as promoting rapid ions transport to boost the electrochemical reaction kinetics. Consequently, the p-Fe<sub>3</sub>O<sub>4</sub>-NSs-PP separator enables the Li-S battery to harvest admirable electrochemical performances with a high capacity of 1266 mAh  $g^{-1}$  at 0.2 C, a favorable rate performance of 865 mAh g<sup>-1</sup> at 2 C as well as an ultra-durable cyclability of up to 2176 cycles at 1 C. In addition, the renewed battery produces a promising areal capacity of 4.55 mAh  $cm^{-2}$ with a stable cyclability under high-sulfur-loading and leanelectrolyte conditions (4.29 mg cm<sup>-2</sup>, 8  $\mu$ l mg<sup>-1</sup>). It is believed that the present work sheds light on the rational design and low-cost fabrication of an efficient multifunctional layer to construct an integrated separator for the advanced Li-S battery, which is expected to facilitate practical development of high-performance Li-S batteries.

#### Acknowledgments

This work was financially supported by National Natural Science Foundation of China (Nos. U22A20193 and 51975218), Fundamental Research Funds for the Central Universities (No. 2022ZYGXZR101), Natural Science Foundation of Guangdong Province (No. 2021A1515010642), Guangdong-Hong Kong Joint Innovation Project of Guangdong Province (No. 2021A0505110002), Guangdong-Foshan Joint Foundation (No. 2021B1515120031), and Innovation Group Project of Foshan (No. 2120001010816).

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