Hollow Cobalt Sulfide Polyhedra-enabled Long-life, High Areal-capacity Lithium-Sulfur Batteries

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Abstract

Improving the electron and ion transport in sulfur electrodes and suppressing the lithium polysulfide shuttle have been the two major challenges with lithium-sulfur (Li-S) batteries. Here, we present a composite paper electrode consisting of hollow Co_3S_4 polyhedra, activated carbon nanofibers (ACNF), and pure sulfur powder for Li-S batteries. The hollow Co_3S_4 polyhedra with a porous shell structure provide large spaces to accommodate the polysulfides, possess ideal polar chemisorptive capability for immobilizing the polysulfide species, and have a higher conductivity than many polar metal oxides, facilitating fast reaction kinetics with the Li-S batteries. The composite electrode exhibits high sulfur utilization and maintains superior cycling stability in Li-S batteries with a high sulfur areal mass. A high capacity of 953 mAh g^{-1} at 1C rate could be achieved with a sulfur loading of 2.5 mg cm^{-2} , and the capacity remains at 610 mAh g^{-1} after 450 cycles. Even with a high sulfur loading of 13.5 mg cm^{-2} , the composite electrode delivers a high areal capacity of 13 mAh cm^{-2} at 0.3C rate.

Keywords: lithium-sulfur batteries, cobalt sulfide, polysulfide trapping, sulfur loading

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1. Introduction

Rechargeable lithium-ion batteries (LIBs) with long life and high energy density are in high demand to meet the demands of the growing portable electronics market and large-scale energy-storage systems [1]. Among the various rechargeable battery systems, lithium-sulfur batteries attract tremendous attention because of their high theoretical capacity (1675 mAh g^{-1}) and energy density (2500 Wh kg^{-1}) at an affordable cost [2, 3]. Additionally, sulfur is abundant, non-toxic, and inexpensive. These features make Li-S batteries appealing to replace the currently used LIBs based on insertion compounds [4, 5]. However, the Li-S batteries have to still overcome several obstacles before they could become commercially viable: low practical capacity, quick capacity decay, and poor Coulombic efficiency [6-9]. The insulating properties of sulfur and its discharge products $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ restrict the electrochemical utilization of sulfur. Furthermore, the generated intermediate polysulfides are prone to diffusion into the electrolyte, leading to a shuttle effect during the charge/discharge process [10]. In this regard, extensive strategies have been pursued to enhance the electron transport in sulfur electrodes and to reduce the shuttle effect [11-13].

One of the most attractive approaches is encapsulating sulfur into a porous carbon matrix [14, 15]. Carbon matrices can act as a conductive network for electron transport and are believed to trap the polysulfide intermediates within the pores [16-18]. However, the tedious complex synthesis of some of the carbon matrices could increase the cost of Li-S batteries. Furthermore, carbon is intrinsically nonpolar, and could not offer a strong binding to confine the polar polysulfides within the

cathode for long-term cycle life. Doping carbon materials with heteroatoms enhances the chemical interaction with polysulfides, but achieving a high dopant loading while maintaining high conductivity is challenging [19].

Recently, polar metal oxides with superb polysulfide absorptivity have been employed in Li-S batteries and they have shown improved cycling stability [20-25]. However, the sulfur utilization and rate capability are still not satisfying because the non-conductive metal oxides could compromise the conductivity of the sulfur cathodes. To this end, there is great interest in exploring conductive hosts. Conductive host materials such as Ti_4O_7 [26, 27], MXene phases [28], and tin-doped indium oxide [29] have proved to effectively retain polysulfides without sacrificing the conductivity of the whole electrode. However, the cycling stability of these electrodes with high sulfur loading ($> 5 \text{ mg cm}^{-2}$) has not yet been reported, which might be due to the high density of the host materials and lack of enough active sites for ion/electron transport. Therefore, exploring conductive polar host materials with adequate active sites is highly desirable for high-energy Li-S batteries, but it remains a great challenge so far.

Herein, we present hollow Co_3S_4 polyhedra as an efficient sulfur host for high-energy-density Li-S batteries. The conductive, polar Co_3S_4 host can not only chemically bind the polar polysulfides and effectively reduce the shuttle effect, but can also endow fast electron transfer and guarantee high sulfur utilization. Furthermore, the hollow interior could serve as an ideal cavity for polysulfide storage and offer a large amount of active sites. These advantages could facilitate the use of

commercial sulfur powder as an active material. When activated carbon nanofiber (ACNF), hollow Co_3S_4 host, and sulfur powder are vacuum-filtrated into a dry cake, the composite electrode exhibits a high-rate capacity of 752 mAh g^{-1} at 2C rate and excellent cycle stability over 450 cycles. In addition, the sulfur loading could be easily increased by enhancing the thickness of the composite electrode. For an electrode with a thickness of $300 \text{ }\mu\text{m}$, a sulfur loading as high as 13.5 mg cm^{-2} could be achieved; the cell with this ultrahigh sulfur loading delivers a high areal capacity of 13 mAh cm^{-2} at 0.3C rate.

2. Experimental

Fabrication of ACNF/ Co_3S_4 /S paper electrode: The ACNF and hollow Co_3S_4 were synthesized as reported previously [30, 31]. Commercial sulfur powder was used as a sulfur source. The composite paper was prepared as follows: 8 mg of ACNF, 12 mg of hollow Co_3S_4 , and 25 mg of sulfur powder were suspended in a mixture of water and isopropanol, followed by probe ultrasonication for 25 min. The uniform suspension was then vacuum-filtered on a flexible filter, detached from the filter paper, and dried at $60 \text{ }^\circ\text{C}$ overnight. The collected composite paper was then punched into circular disks with a sulfur loading of $\sim 2.5 \text{ mg cm}^{-2}$ and a sulfur content $\sim 50 - 55 \text{ wt.}\%$. High sulfur loadings of 7.5 and even 13.5 mg cm^{-2} could also be achieved by simply increasing the thickness of the composite paper. The ACNF/S paper without Co_3S_4 was also prepared as a control following a similar procedure described above.

Materials Characterization: Morphology, microstructure, and elemental analysis were performed with scanning electron microscopy (SEM, FEI Quanta 650) and transmission electron microscopy (TEM, JEOL 2010F). XRD patterns were collected on a Rigaku MiniFlex 600 instrument. The cycled electrodes were retrieved inside a glove-box, washed with 1, 3-dioxolane (DOL), sealed with a Kapton film for XRD testing, and transferred into an argon-protected vessel for XPS measurement. XPS measurements were carried out on a Kratos spectrometer at room temperature. TGA was conducted to determine the sulfur content on a TGA 4000 Thermogravimetric analyzer (Perkin Elmer) in N₂ flow. Brunauer–Emmett–Teller (BET) analysis was realized on an AutoSorb iQ2 (Quantachrome Instruments) at 77 K.

Electrochemical measurements: 2032 type coin cells were assembled in an Ar-filled glove box with the composite ACNF/Co₃S₄/S paper as cathode, lithium metal as anode, and Celgard 2500 as a separator. The electrolyte comprised 1.0 M LiCF₃SO₃ salt and 0.2 M LiNO₃ in 1, 2-dimethoxyethane (DME) and 1, 3-dioxolane (DOL) (1 : 1 by volume). The as-assembled cells were charged and discharged with an Arbin battery test station at 1.8 – 2.8 V (*versus* Li/Li). All the capacities were calculated based on the sulfur mass in the cathode. Cyclic voltammetry (CV) curves were collected on an electrochemical work station (VoltaLab PGZ 402) at a scan rate of 0.1 mV s⁻¹.

3. Results and Discussion

Hollow Co₃S₄ was fabricated by a facile self-sacrificing template method involving an *in-situ* transformation of Co-based metal-organic frameworks (MOFs) in

thioacetamide solution and post heat-treatment in N₂ atmosphere [32]. The Co-based MOFs (ZIF-67) template was synthesized *via* a co-precipitation reaction between Co(NO₃)₂ and 2-methylimidazole in methanol solution [33, 34].

Figure 1a and **b** show that uniform ZIF-67 of 500 nm were generated after the room-temperature precipitation reaction. X-ray diffraction (XRD) patterns (Figure S1) with strong peaks confirm that these polyhedra have a pure-phase ZIF-67 structure, matching well with the previous results [35]. Upon subsequent solvothermal sulfidation and thermal annealing, the resulting particles inherit the polyhedral morphology of the parent Co-MOFs precursor (Figure 1c). Close observation of a single cracked particle (Figure 1d) confirms the formation of a hollow interior, which can serve as a polysulfide reservoir. Transmission electron microscopy (TEM) images (Figure 1e and f) further reveal that the hollow polyhedral wall was constructed by fine nanoparticles and their interstitial pores. This cavity and porous shell provides a high Brunauer–Emmett–Teller (BET) specific surface area of 91 m² g⁻¹ (Figure S2a). The fine particles have a size of around 10 nm (Figure S2b) and can be indexed as cubic Co₃S₄ based on the XRD pattern (**Figure 2e**). Energy dispersive spectroscopy (EDS) (Figure S2c) detects only Co, S and C elements.

An ACNF/Co₃S₄/S film electrode was fabricated through a facile vacuum filtration of ACNF, Co₃S₄, and sulfur powder [36, 37]. The obtained film **with a sulfur loading of ~ 2.5 mg cm⁻²** shows good flexibility without cracking under bent condition (Figure 2a). Figure 2b shows the top-view image of the composite paper. We can see that large sulfur-rich areas with sizes of 2 – 10 μm are entangled by

ACNF. These large sulfur particles along with small Co_3S_4 nanoparticles (Figure 2c) could effectively prevent the compact stacking of ACNF. Therefore, the composite paper with a thickness of $\sim 60\ \mu\text{m}$ (Figure 2d) still preserves a porous structure that effectively facilitates the penetration of the electrolyte. Meanwhile, ACNF provides highly conductive paths for sulfur, securing efficient sulfur utilization. XRD characterization of the ACNF/ Co_3S_4 /S paper shows that the strong diffraction peaks mainly come from the crystalline sulfur; ACNF and Co_3S_4 display relatively weak peaks. EDS spectrum (Figure 2f) indicates the existence of C, Co, and S elements, and the strong sulfur peak implies a large amount of sulfur in the composite paper electrode. As measured by thermogravimetric analysis (TGA), the sulfur content is around 53% (Figure 2g). TEM elemental mapping images (Figure S3) show a uniform distribution of Co and S in the carbon matrix.

Benefiting from the hollow Co_3S_4 polyhedra that store polysulfides and the ACNF providing electronic pathways, the as-prepared ACNF/ Co_3S_4 /S composite paper could be directly employed as a cathode in Li-S cells. **Figure 3a** depicts the cyclic voltammograms (CV) of the composite electrode for the initial five cycles, showing the typical redox peaks of sulfur. The two cathodic peaks located at around 2.0 and 2.3 V are assigned to the conversion of sulfur to soluble high-order polysulfides and subsequent production of solid short-chain $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ [38-40]. The curves are stable in both shape and size after the first scan, which suggests that the active material is well-confined and efficiently trapped during cycling. Figure 3b presents the charge/discharge voltage profiles of the composite ACNF/ Co_3S_4 /S

electrode under various current densities from 0.2C to 2C rate. All the curves display well-defined voltage plateau for the charge and discharge processes, which indicates a good electrochemically reversible conversion between sulfur and polysulfides. Additionally, these plateaus show small polarization at all current densities. For example, the voltage gap between oxidation and reduction is 0.16 V at 0.2C rate and maintains 0.4 V even at a high rate of 2C. These values are lower than most reported results, indicating fast electrochemical kinetics enabled by the conductive Co₃S₄ and ACNF.

The ACNF/Co₃S₄/S electrode also exhibits excellent rate capability. As shown in Figure 3c, high capacities of 1012, 946, 859, and 752 mAh g⁻¹ are obtained at, respectively, 0.2C, 0.5C, 1C, and 2C rates. Furthermore, the capacity can recover to 925 mAh g⁻¹ when the current density returns from 2C to 0.5C rate. In contrast, the capacity of ACNF/S without Co₃S₄ fades quickly, and only retains 430 mAh g⁻¹ after 2C rate. The obvious improvement in the electrochemical performance can be attributed to the suppressed polysulfide shuttle by Co₃S₄, which was also confirmed by the visual observation in Figure S4). To further demonstrate the advantages of Co₃S₄ in trapping polysulfides, long-term cycling of the ACNF/Co₃S₄/S electrode was evaluated at 1C rate in the voltage window of 1.8 – 2.8 V. As shown in Figure 3d, the cell delivers a stabilized capacity of 953 mAh g⁻¹ at 1C rate, corresponding to a volumetric capacity of 397 mAh cm⁻³ at 4.2 mA cm⁻². After 450 cycles, the capacity still remains at 610 mAh g⁻¹, implying a slow capacity fade of 0.079% per cycle. In addition, the Coulombic efficiency is maintained at 98.5% for the long-term cycling.

Both the slow decay in capacity and the high Coulombic efficiency indicate a successful immobilization of polysulfides in the cathode.

Figure 4a shows the XRD pattern of the ACNF/Co₃S₄/S electrode after the 1st discharge. Compared to the strong peaks of crystalline sulfur in the original ACNF/Co₃S₄/S electrode, weak and inconspicuous peaks belonging to Li₂S come out after the 1st discharge in the composite electrode. A high-resolution S 2p X-ray photoelectron spectroscopy (XPS) (Figure 4b) of the discharged electrode also reveals the generation of short-chain Li₂S. Both the XRD and XPS results confirm that the sulfur powder was completely converted into Li₂S after the first discharge process. SEM images and the corresponding elemental mapping further verify this conclusion. As shown in Figure 4c, there is no visual observation of sulfur particles or sulfur-rich spots across the whole ACNF paper in the discharged electrode. The corresponding elemental mapping images also reveal that sulfur is distributed homogeneously in the ACNF paper.

With a vacuum-filtration method, the sulfur loading could be further increased simply by enhancing the thickness of the filtered cake-like composite. In this way, we can obtain composite electrodes with high sulfur loadings of approximately 7.5 and 13.5 mg cm⁻², respectively, when the thickness of the dried cake is increased to 160 and 300 μm, (**Figure 5a, b**). It's worth noting that the interior of the thick paper still maintains a porous structure even at a thickness of 300 μm (Figure 5c); the porous structure could facilitate well the accessibility of electrolyte throughout the whole electrode. Figure 5d presents the galvanostatic voltage profiles of the thick electrode

with sulfur loadings of 7.5 and 13.5 mg cm⁻² at 0.5C rate. The two thick electrodes still exhibit typical multi-stage plateaus with low overpotentials of 0.27 V for 7.5 mg cm⁻² and 0.37 V for 13.5 mg cm⁻². Additionally, the thick electrode with a high sulfur loading delivers high sulfur utilization and good capacity retention. As demonstrated in Figure 5e, the cell with a sulfur loading of 7.5 mg cm⁻² delivers a high capacity of 950 mAh g⁻¹, corresponding to an areal capacity of 7.1 mAh cm⁻², and maintains a reversible capacity of 701 mAh g⁻¹ (5.25 mAh cm⁻²) after 100 cycles. As for the thicker electrode with a sulfur loading of 13.5 mg cm⁻², the initial capacity reaches a high value of 957 mAh g⁻¹ (13 mAh cm⁻²), indicating a high sulfur utilization enabled by efficient electrolyte penetration and electron transport. After 100 cycles, the capacity remains at 550 mAh g⁻¹ with a retention of 70% in the stabilized third cycle. These values are comparable to or better than the previously reported results with high sulfur loadings [16, 41-46].

The excellent electrochemical performances of the composite ACNF/Co₃S₄/S electrode could be attributed to the synergistic effects of the hollow Co₃S₄ particles and the ACNF electronic network, both of which enable the successful adoption of commercial sulfur as active material. Specifically, the hollow Co₃S₄ polyhedra provide an ideal cavity to accommodate and chemically adsorb the polar polysulfides, effectively suppressing the shuttle effect. Further, Co₃S₄ possesses a relatively high conductivity compared to many metal oxides, which facilitates fast electron transport within the composite electrode [47-49]. Additionally, ACNF effectively entangles the hollow Co₃S₄ and sulfur particles, builds electron network for electron transport, and

provides a large interstitial space for electrolyte penetration. This integrally-designed paper electrode effectively boosts the electrochemical reaction kinetics, holding great promise for excellent cycling stability and high capacity with the Li-S cells even when using commercial sulfur powder as cathode at loadings as high as 13.5 mg cm^{-2} .

4. Conclusion

In summary, we have presented a conductive hollow Co_3S_4 polysulfide-adsorbent, which boosts the reaction kinetics and suppresses the polysulfide shuttle effect for realizing high-performance Li-S batteries. Thick electrodes, built with hollow Co_3S_4 , pure sulfur powder, and ACNF were prepared *via* a facile vacuum-filtration approach. Benefiting from this advanced electrode design, sulfur cathodes with high sulfur loadings of 2 to 13.5 mg cm^{-2} exhibit remarkably stable cycling performance with high capacity and excellent rate capability. The synergistic effect of conductive hollow Co_3S_4 and the ACNF electron network enables the use of commercial sulfur as an active material. Meanwhile, the vacuum-filtration approach facilitates a uniform distribution of high-loading sulfur throughout the whole cathode, bringing the use of pure sulfur one step closer for commercial Li-S batteries.

Appendix A: Supplementary material

Supplementary data associated with this article can be found in the online version.

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Figure Captions:

Figure 1. (a, b) SEM images of the ZIF-67 template. (c, d) SEM images, (e, f) TEM images, and (g) the corresponding elemental mapping of the hollow Co_3S_4 polyhedra.

Figure 2. (a) A digital image of the filtered ACNF/ Co_3S_4 /S composite paper, showing its flexibility under bent condition. (b-d) SEM images of the ACNF/ Co_3S_4 /S film. (e) XRD patterns of ACNF, hollow Co_3S_4 polyhedra, and ACNF/ Co_3S_4 /S film. (f) EDS spectrum and (g) TGA curve of the composite ACNF/ Co_3S_4 /S paper.

Figure 3. Electrochemical performance of the Li-S cells with the ACNF/ Co_3S_4 /S paper as the cathode: (a) CV curves at a scan rate of 0.1 mV s^{-1} , (b) charge/discharge curves at various scan rates from 0.2C to 2C rate, (c) comparison of the rate performances of ACNF/ Co_3S_4 /S and ACNF/S electrodes, and (d) cycling performance at 1C rate. Here, the volumetric capacities were calculated based on the volume of the composite paper.

Figure 4. (a) XRD pattern, (b) high-resolution S 2p XPS spectrum, and (c) SEM and elemental mapping of the composite ACNF/ Co_3S_4 /S electrode after the first discharge.

Figure 5. SEM images of the filtered ACNF/ Co_3S_4 /S paper electrodes with a thickness of (a) $160 \mu\text{m}$ and (b) $300 \mu\text{m}$. (c) SEM image showing the interior structure of the thick paper. (d) Charge/discharge curves in the stabilized third cycle and (e)

cycling performances of cells with a sulfur mass of 7.5 and 13.5 mg cm⁻² at 0.3C rate.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Vitae

Henghui Xu is currently a postdoctoral research fellow at the Texas Materials Institute of the University of Texas at Austin. He received his Ph.D. in Materials Science in 2015 at Huazhong University of Science and Technology. His research interests are mainly on the design, synthesis, and applications of composite materials for lithium-sulfur batteries, lithium-ion batteries, and supercapacitors.

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