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The Optimization of a Carbon Paper/MnO\textsubscript{2} Composite Current Collector for Manufacturing a High-Performance Li–S Battery Cathode

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Abstract: High theoretical energy density endows lithium–sulfur batteries to be a promising candidate of the secondary batteries. Numerous studies have been implemented relying on exploring efficient host materials or separator modifying layers to solve the problematic shuttling and insufficient conversion of soluble polysulfides, whereas few studies have focused on the modification of the cathode collector. Herein, a high-performance sulfur cathode is manufactured with carbon paper/MnO\textsubscript{2} as the cathode collector and liquid lithium polysulfides as the electrode material. The interface of carbon paper/MnO\textsubscript{2} is proposed to afford fast electronic transport, strong chemical adsorption, and effective electrocatalysis to confine the diffusion of lithium polysulfides and facilitate their conversion during the charge/discharge process. More importantly, with no conductive additives and binders assisting, the gravimetric energy density of the sulfur cathode could be largely improved. Specifically, lithium–sulfur batteries using carbon paper/MnO\textsubscript{2} as a cathode collector could stably circulate for 200 cycles at 0.2 C with a capacity of 664 mAh g\textsuperscript{-1}, which is higher than that of carbon paper as a cathode collector (486 mAh g\textsuperscript{-1}). This work may provide a new perspective to enhance the electrochemical performance of lithium–sulfur batteries by optimizing the cathode collector.

Keywords: Li–S battery; carbon paper; MnO\textsubscript{2}; hybrid collector; optimization

1. Introduction

Commercial lithium-ion batteries have brought revolutionary changes to society in the past decades [1,2], but they are involved in a dilemma of achieving the expected high-energy density by employing active materials with a limited capacity [3,4]. High-theoretical-energy-density lithium–sulfur (Li–S) batteries (2600 Wh kg\textsuperscript{-1}) show the competitive potential by using economical, eco-friendly, and high-capacity sulfur as a cathode [5,6]. However, some complex problems, such as the insulative property of S and Li\textsubscript{2}S, the volumetric fluctuation during the reaction process, and the unrestrained lithium polysulfides (LiPS) [7,8], have impeded the electrochemical performance of Li–S batteries.

To solve the above issues, researchers have concentrated on optimizing the sulfur cathode to improve the electrochemical properties of lithium–sulfur batteries. The applicable hosts are vital to guarantee a fast electrochemical reaction [9,10]. Carbon materials, including graphene, carbon nanotubes, carbon fibers and porous carbon, are the common candidates due to their inherently benign conductivity [11,12]. However, the
intrinsically weak interaction of carbon matrixes with LiPS is seemingly insufficient to alleviate the adverse results caused by the shuttle effect, except for the exquisite structural design and heteroatomic doping [13,14]. Polar compounds, such as metal oxides [15,16], metal nitrides [17,18], metal sulfides, and carbides [19,20], have been extensively studied and have been demonstrated to effectively confine the LiPS by chemical adsorption and even accelerate their conversion by catalysis [21,22]. However, metal compounds always possess an inferior conductivity in contrast with carbon, which may induce large cell resistance and limit electrochemical availability and stability [23,24]. Constructing the sulfur composites with the hybrid hosts involving conductive carbon and polar metal compounds could be a wise strategy for improving the electrochemical performance of the sulfur cathode [25,26]. However, to exert the electrochemical performance of sulfur cathodes with these traditional composite sulfur cathode materials, the common conductive additives, binders, and cathode collector are necessary to provide the required functions [27,28], which would increase the proportion of the electrochemical inactive materials and compromise the enhancement of energy density to some extent [29,30]. Therefore, a multifunctional hybrid cathode collector equipped with the characteristics of a cathode collector and host material is ideal. On one hand, the multifunctional cathode collector dispensing with the extra accessory components could be an effective solution to balance the electrochemical capacity and energy density of Li–S batteries [31–34]. On the other hand, the relevant optimization could provide fast electron transfer, and facilitate the electrochemical reaction near the triple-phase interface. Carbon paper has shown a certain competitive advantage in fabricating the high-loading and flexible electrode with an excellent conductive framework [35,36], but its weak anchoring ability on soluble LiPS may lead to obvious capacity decay. MnO₂ has been proven to act as the chemical adsorbent and electrocatalysis for LiPS to improve the electrochemical performance of Li–S batteries, by forming the active mediators (thiosulfate and polythionate) [37–39], as well as the valid chemical restriction. Thus, the hybrid cathode collector based on carbon paper and MnO₂ could simultaneously combine the conductivity and chemical interaction during the electrochemical process of the Li–S batteries without the extra conductive additives and binders, which could be conductive to fabricate high-performance Li–S batteries.

Herein, the carbon paper/MnO₂ cathode collector is prepared by a one-step hydrothermal method and assembled into Li–S batteries without any auxiliary modification. Liquid LiPS are employed as the active sulfur sources. Carbon paper could provide the benign electron pathway and sufficient space for the electrochemical conversion, as well as the growth sites for MnO₂. The in situ formed MnO₂ could restrict the LiPS by chemical adsorption, accelerate their conversion by forming active thiosulfate and polythionate, and further enhance the electrochemical performance of Li–S batteries. Moreover, the simple cathode without certain traditional components (such as conductive additives, and binders) may contribute to the battery fabrication and energy density. The obtained Li–S batteries deliver the reversible capacity of 664 mAh g⁻¹ at 0.2 C after 200 cycles and show a good rate of performance.

2. Materials and Methods
2.1. Synthesis of Carbon Paper/MnO₂
Carbon paper was purchased from Toray (Tokyo, Japan, TGP-H-060). MnO₂ particles were decorated on carbon paper (marked as CP) through the hydrothermal reaction, and the corresponding content was adjusted by adding H₂SO₄ with different usages, as shown in Figure 1 [40]. Typically, KMnO₄ (0.0015 mol) was dissolved in a solution containing H₂SO₄ (0.1, 0.3, and 0.5 mL) and water (15 mL) with continuous stirring for 30 min. A piece of carbon paper (2 × 3 cm²) and the reaction solution were placed in the hydrothermal reactor (25 mL), followed by heating treatment at 120 °C for 3 h. The fetched carbon paper/MnO₂ hosts were washed with water and ethanol several times, dried at 60 °C
overnight, and cut into discs (Φ = 10 mm), which were marked as MC-1, MC-3, and MC-5, according to the usage of H$_2$SO$_4$.

Figure 1. Schematic illustration of preparing the composite cathode collector and Li–S batteries.

2.2. Synthesis of Li$_2$S$_6$ Catholyte

Li$_2$S$_6$ catholyte (0.5 mol L$^{-1}$) was synthesized through a reaction between Li$_2$S (114.88 mg) and sulfur (400.81 mg) in 1,3-dioxolane (DOL)/dimethoxyethane (DME) solution (v/v = 1/1, 5 mL) at 50 °C for 24 h, followed by the continual stirring for 12 h after adding 1M lithium bis(trifluoromethylsulfonyl) imide (LiTFSI, Sigma-Aldrich, Darmstadt) and 2 wt% LiNO$_3$[41]. The prepared Li$_2$S$_6$ catholyte could be employed as the active materials’ resources to replace the common elemental sulfur.

2.3. Assembly of Lithium–Sulfur Battery

The test Li–S cells (CR2032) were assembled in an argon-filled glove box by adding Li$_2$S$_6$ catholyte (0.5 M, 10 uL) in the cathode collectors, and using lithium foils (Φ = 14 mm) as reference electrodes, and microporous polypropylene film (Celgard 2400, Φ = 16 mm) as a separator with a moderate amount of electrolyte. The sulfur loading of the cathode was approximately 1.2 mg cm$^{-2}$. The electrolyte was composed of 1 M LiTFSI and 2 wt% LiNO$_3$ in DOL/DME (1:1 by volume).

2.4. Structural Characterization

Field emission scanning electron microscopy (FESEM, SU8010, Hitachi Company, Tokyo, Japan) was employed to obtain the morphology information and elemental distribution. X-ray diffraction (XRD, X’pert PRO, PANalytical B.V., Almelo, The Netherlands) with an angle resolution of ±0.0001, Raman spectroscopy (HORIBA EVOLUTION, Kyoto, Japan), and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific, Massachusetts) were utilized to acquire the structural information. Thermogravimetry (TG) was adopted to confirm the actual content of MnO$_2$ from the ambient temperature to 900 °C in air.

2.5. Electrochemical Characterization

A cyclic voltammetry (CV) measurement on an electrochemical workstation (CHI660D, Shanghai Chenhua Instruments Ltd., Shanghai) was conducted among 1.7–2.8 V (vs. Li/Li$^+$) at an ambient temperature with a scanning rate of 0.1 mV s$^{-1}$. Capacity tests on LAND systems (CT-2001A, Wuhan LAND Electronic Co. Ltd., Wuhan) were carried out within the potential window of 1.7–2.8 V (vs. Li/Li$^+$) at an ambient temperature and various current densities (1 C = 1675 mAh g$^{-1}$). The specific capacity was related to the elemental sulfur.
3. Results and Discussion

3.1. Structure and Morphology

The fabrication process of the 3D binder-free cathode collector is depicted in Figure 2a. Flexible CP could serve as the conductive framework and growing substrates of MnO₂ during the hydrothermal reactions with the typical fiber-jointed structure (Figure 2b). The aggregation state and microstructures of the formed MnO₂ on the CP could be regulated by adjusting the usage of H₂SO₄. After hydrothermal treatment in the aqueous solution containing H₂SO₄ and KMnO₄, the grey CP is partly decorated with the black MnO₂. The optical images show the obvious reduction of MnO₂ on the CP with the increase of H₂SO₄. The MC-1 sample is black with a nearly full coverage of MnO₂ (Figure 2c). Fibrous carbon could be hardly observed, and the MnO₂ clusters are assembled by the nanoplates. The sea urchin-like MnO₂ with close packing is loaded on CP in MC-3 (Figure 2d). The MC-5 sample also possesses the urchin-like MnO₂ with low content and uniform distribution (Figure 2e). By continually increasing the amount of H₂SO₄, the matrix could be obtained containing CP and MnO₂ but its flexibility drops sharply corresponding to the fragile structure during the battery assembly, which may impair the electrochemical performance of Li–S batteries. Thus, adding different amounts of H₂SO₄ significantly affects the generated MnO₂ on CP.

Figure 2. Schematic illustration of the fabrication of carbon paper/MnO₂ (a), optical (in the green outline), and SEM images of CP (b), MC-1 (c), MC-3 (d), and MC-5 (e).
The XRD patterns in Figure 3a show that the pristine CP possesses a high graphitization with the typical characteristic peaks of graphite (PDF#41-1487), which may signify the benign electric conductivity and facilitate the electrochemical conversion [42]. The diffraction peaks of graphite are negligible in MC-1 with the appearance of α-MnO₂ (PDF#44-0141) [43,44], mainly owing to the excessive coverage of MnO₂ on CP. Then, the graphite peak at 26.4° could be detected in MC-3, demonstrating that the increasing H₂SO₄ avails to reduce the immoderate loading of MnO₂ on the conductive skeleton. The MC-5 sample displays the more obvious peaks of graphite and MnO₂, which may simultaneously endow the electric conductivity and chemical interaction in Li–S batteries. Meanwhile, the particle sizes of MnO₂ in thickness direction could be calculated according to the Scherrer formula. The values for MC-1, MC-3 and MC-5 are 25.0 nm, 23.0 nm and 56.1 nm, respectively, based on the lattice plane of (110) in MC-1, (211) in MC-3 and MC-5. The actual content of MnO₂ in the prepared samples is confirmed by thermogravimetry. As shown in Figure 3b, some impurities exist in the pristine CP with a mass ratio of 3.26%. The residual of MC-1, MC-3, and MC-5 after full combustion includes the impurities and oxidation products of MnO₂ at a high temperature [45]. The detailed content of MnO₂ in MC-1, MC-3, and MC-5 could be 14.06%, 8.81%, and 3.44%, respectively, manifesting the reduction of MnO₂ along with the increase of H₂SO₄, which is consistent with the results of SEM and XRD.

Raman spectrum is adopted to further explore the effect of the loaded MnO₂ on CP. The pristine CP has the typical D peak, G peak, and 2D peak (Figure 3c), which are located at 1355 cm⁻¹, 1598 cm⁻¹, and 2689 cm⁻¹, respectively. The corresponding ratio of ID/IG is calculated to be 1.17, which signifies some existing defects in the CP [46]. In contrast, MC-5 possesses the D peak, G peak, and 2D peak at 1349 cm⁻¹, 1582 cm⁻¹, and 2717 cm⁻¹, respectively, with an ID/IG ratio of 0.25. The significant decrease of ID/IG by decorating...
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MnO₂ on CP indicates the enhanced graphitization with fewer defects, which may contribute to the electron transfer and the electrochemical reaction [47]. Furthermore, a small characteristic peak of Mn-O bond occurs at ~327.5 cm⁻¹ in the inset figure [48]. The XPS spectrum in Figure 3d confirms the loaded MnO₂ on CP with the characteristic peak of Mn⁴⁺ at 642.6 eV and the related three satellite peaks at 643.8 eV, 644.8 eV and 645.4 eV [37], while some Mn⁵⁺ at 641.6 eV exist in the prepared MnO₂, which may be the intermediate reaction products on the MnO₂ surface [49].

3.2. Electrochemical Performance

Controlling the usage of H₂SO₄ could regulate the microstructure of the prepared cathode, and the corresponding impact on the cycle performance of the Li–S batteries is shown in Figure 4a. The battery using MC-5 possesses the superior electrochemical performance at 0.2 C in contrast to the batteries with MC-1 and MC-3. The capacity could stabilize at 704 mAh g⁻¹ after 50 cycles, which is higher than those of the MC-1/S (442 mAh g⁻¹) and MC-3/S (506.5 mAh g⁻¹). The corresponding coulombic efficiency could stabilize at about 100%, showing the benign reversible redox conversion. Therefore, increasing the content of H₂SO₄ is inclined to fabricate the satisfying collector with moderate MnO₂ loading, which may be derived from the balance of conductivity and chemical interaction [18,50]. Nanoplate-like MnO₂ with excessive coverage on carbon paper may possess limited active sites and impede the charge transfer during the redox processes, while the sea urchin-like MnO₂ with good crystallinity and modest coverage could guarantee the sufficient contact with LiPS, and the unhindered charge transport. The emphasis is then focused on the comparison between MC-5 and CP in Li–S batteries.

![Figure 4. (a) Cycle performance of the Li–S batteries using MC-1, MC-3, and MC-5. (b) Cyclic voltammograms of the Li–S batteries with CP and MC-5 as collectors.](image)

The cyclic voltammograms curves in Figure 4b show the typical redox pairs of the Li–S batteries [51], except for the weak reduction peaks at ~2.3 V (vs. Li/Li⁺) in the initial cycle, owing to the usage of liquid LiPS as sulfur resources. Meanwhile, the second reduction peaks of the CP/S during the CV tests are smaller than those of the MC-5/S, indicating the unsatisfactory anchoring of LiPS and the insufficient redox conversion from LiPS to Li₂S/LiS [52]. Decorating MnO₂ on CP could inhibit the shuttle of LiPS and promote their transformation.

The cycle performance of Li–S batteries at 0.2 C (Figure 5a) further demonstrates the advantage of MC-5. The Li–S battery with MC-5 possesses a higher capacity and better cyclic stability in contrast with the battery using CP. The capacity of MC-5/S could reach 606 mAh g⁻¹ (vs. 411 mAh g⁻¹) in the first cycle and be maintained at 664 mAh g⁻¹ (vs. 486 mAh g⁻¹) after 200 cycles with a stable coulombic efficiency near 100%. The corresponding charge/discharge curves (Figure 5b) show two reduction plateaus after the first cycle in consistence with the results of the CV tests, which are associated with the electrochemical conversion from solid sulfur to soluble LiPS and solid Li₂S/LiS. The shorter voltage platforms in the CP/S battery with smaller capacities indicate the limited LiPS restriction and inadequate electrochemical reaction compared to MC-5/S. The pristine CP with good
conductivity endows the Li–S battery inferior capacity, while the composite collector with decorated MnO₂ on CP could improve the electrochemical conversion in the Li–S battery. Thus, the prepared cathode collector could balance the conductivity and chemical interaction and further enhance the reliability of the Li–S battery [50].

Figure 5. Cycle performance (a) and rate property (c) of the CP and MC-5 as collectors in Li–S batteries with the corresponding charge/discharge profiles (b,d).

The rate property of the Li–S batteries in Figure 5c provides more evidence of promoting the electrochemical performance by adopting the hybrid collector. MC-5 endows the Li–S battery with high capacity and stability at relatively small current densities, such as 0.1 C, 0.2 C, and 0.5 C. The capacity at 1.0 C is fairly close and stabilizes at ~200 mAh g⁻¹, which may be ascribed to the inherently sluggish reaction kinetics of LiPS, especially at large currents [53]. As the current switches back to 0.1 C, the capacity of the Li–S battery with MC-5 could reach 933 mAh g⁻¹, which is higher than that of the Li–S battery using CP (~400 mAh g⁻¹), indicating the enhanced rate of performance by employing MC-5 as a cathode collector. The coulombic efficiency in different C-rates maintains a high level, indicating the highly reversible electrochemical reactions. The related charge–discharge curves in Figure 5d also show the advantage of MC-5 in facilitating the electrochemical transformation at different C-rates, with the long voltage platforms. Carbon paper has been reported to directly load with sulfur as the cathode of Li–S batteries [54]. The corresponding initial capacity is 480 mAh g⁻¹ and maintains only 150 mAh g⁻¹ after 100 cycles. MnO₂/acetylene black composites have been reported as the efficient host in Li/dissolved polysulfide batteries by Sivakumar and co-workers [55]. The related Li–S battery delivers a high initial capacity of 1540 mAh g⁻¹ at 0.1 C but fast capacity decay occurs (649 mAh g⁻¹ after 50 cycles). In this work, MnO₂ was loaded on carbon paper to serve as the current collector for Li–S batteries. The electrochemical results demonstrate that the fabricated MC-5 collector could cycle for 200 cycles with considerable capacity and improve the performance of the Li–S battery.
3.3. Mechanism Analysis

The adsorption experiments in Figure 5a reveal that the anchoring capability of MC-5 on LiPS is more prominent compared to CP, with fast and obvious color fading. According to the UV–Vis spectra in Figure 6a, the characteristic absorption peak of Li$_2$S$_6$ at 350 nm [56] is significantly weakened by using MC-5, while the related peak of the Li$_2$S$_6$ solution containing CP is almost unchanged. This indicates that the MC-5 could interact with the lithium polysulfide in the solution and reduce the content of Li$_2$S$_6$ in the solution. The tested XPS spectrum of Mn after adsorption implies the interaction between MC-5 and Li$_2$S$_6$ (Figure 6b). The binding shift of Mn$^{4+}$ from 642.6 eV to 641.9 eV proves the specific chemical interaction [57], while the emerging peaks of Mn$^{2+}$ at 641.0 eV and Mn$^{3+}$ at 640.5 eV and 639.8 eV illustrate the catalysis of MnO$_2$ on LiPS by forming thiosulfate and polythionate as active mediators to accelerate the electrochemical processes [37,58]. Meanwhile, the obtained SEM images of the cathode and anode after 200 cycles provide more information (Figure 6c–f). The cycled cathode with CP becomes dense (Figure 6c), and the fibrous structure vanishes due to the repeated dissolution/deposition of S and Li$_2$S, which may be detrimental to the electrochemical stability. The corresponding Li surface is covered with swellings and gullies (Figure 6d), showing the uneven deposition behavior and excessive side-reaction with LiPS. Instead, the cycled cathode with MC-5 (Figure 6e) still possesses the porous structure, and the Li anode has a flat morphology (Figure 6f). These phenomena show that loading moderate MnO$_2$ on carbon paper could inhibit LiPS shuttle and guarantee the electrochemical and structural stability of the Li–S battery.

Figure 6. (a) Adsorption experiments of CP and MC-5 in Li$_2$S$_6$ solution including the digital photos and UV–Vis spectra, and (b) Mn 2p$^{3/2}$ spectra of MC-5 after the adsorption experiment. SEM images of the cycled sulfur cathodes (c,e) and lithium anodes (d,f) from the Li–S batteries by using CP (c,d) and (e,f) MC-5 as collectors.
The published literatures have demonstrated that MnO$_2$ loaded on graphene [37], CNTs [59], carbon fibers [60], and designed carbon with an exquisite structure [61] could significantly enhance the electrochemical performance of Li–S batteries, along with loading elemental sulfur into the hosts and employing conductive additives and polymer binders. Developing a high-performance current collector without other accessories (binders, conductive additives, metal collectors) could increase the proportion of the active materials to fabricate high-energy-density Li–S batteries. Meanwhile, different kinds of active materials, such as solid elemental sulfur, lithium sulfides, and liquid LiPS, are all appropriate for the 3D current collector and even could match the Li-free anode to enhance the safety of Li–S batteries.

4. Conclusions

In summary, the hybrid cathode collector containing carbon paper and MnO$_2$ is fabricated by a simple hydrothermal method. The loaded MnO$_2$ could be flexibly regulated by altering the usage of H$_2$SO$_4$. Increasing H$_2$SO$_4$ is inclined to generate urchin-like MnO$_2$ with low content and uniform distribution. The composite collector is proven to alleviate the shuttling of soluble LiPS and improve the electrochemical performance of the Li–S battery by virtue of the moderate chemical adsorption and catalysis. The corresponding Li–S battery could deliver 664 mAh g$^{-1}$ at 0.2 C after 200 cycles with good stability. This strategy of designing a multifunctional cathode collector for Li–S batteries without the auxiliary components (conductive additives, binders, and metal collector) is a feasible way to manufacture high-performance Li–S batteries.

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