Tunnel Structure Enhanced Polysulfide Conversion for Inhibiting “Shuttle Effect” in Lithium-Sulfur Battery

Xiaotong Guo 1,2, Xu Bi 1,2, Junfeng Zhao 1, Xinxiang Yu 1,2, and Han Dai 1,2*

1 Laboratory of Advanced Light Alloy Materials and Devices, Yantai Nanshan University, Longkou 265713, China
2 Yulong Petrochemical Co., Ltd., Longkou 265700, China
* Correspondence: daihan1985@189.cn

Abstract: The Lithium sulfur (Li-S) battery has a great potential to replace lithium-ion batteries due to its high-energy density. However, the “shuttle effect” of polysulfide intermediates (Li_{2}S_{8}, Li_{2}S_{6}, Li_{2}S_{4}, etc.) from the cathode can lead to rapid capacity decay and low coulombic efficiency, thus limiting its further development. Anchoring polysulfide and inhibiting polysulfide migration in electrolytes is one of the focuses in Li-S battery. It is well known that polar metal oxides-manganese oxides (MnO_2) are normally used as an effective inhibitor for its polysulfide inhibiting properties. Considering the natural 1D tunnel structure, MnO_2 with three kinds of typical tunnel-type were screened to study the effects of the tunnel size on the adsorption capacity of polysulfide. We found that MnO_2 with larger tunnel sizes has stronger chemisorption capacity of polysulfide. It promotes the conversion of polysulfide, and corresponding cathode exhibits better cycle reliability and rate performance in the cell comparison tests. This work should point out a new strategy for the cathode design of advanced Li-S battery by controlling the tunnel size.

Keywords: lithium sulfur battery; manganese oxides; tunnel structure; cathode materials; shuttle effect

1. Introduction

With increasing demand of chemical energy storage, the lithium sulfur (Li-S) battery with a high theoretical capacity of 1675 mAh g^{-1}, is considered to be a promising candidate to replace the state-of-the-art lithium-ion batteries [1–3]. Meanwhile, sulfur is abundant, environmentally friendly and cost effective, which fully meets the requirements of secondary energy storage power [4–6]. However, the practical application of the Li-S battery is still hindered by the rapid capacity decay, low coulombic efficiency and poor rate performance, which are mostly due to the “shuttle effect” [7–11]. Recently, meso/microporous carbon [12–14], carbon nanotubes [15–17] and other porous carbon-based materials which have good conductivity and chemical stability, have been applied to suppress the shuttle of polysulfide, keep good conductivity and improve sulfur utilization. However, their ability for polysulfide adsorption is very limited due to their nonpolar nature.

As for enhancing the polysulfide adsorption ability and suppressing the “shuttle effect”, metal oxides are noticed because of their strong polar–polar chemical interaction with polysulfide [18–25]. More recently, lots of literature has reported that anchoring polysulfide by chemical reaction is much more promising and metal oxides such as SiO_2, V_2O_5, Al_2O_3, TiO_2, and MnO_2 could significantly improve cycling performance and realize high-loading sulfur in Li-S battery [26,27]. Among known metal oxides which are used as cathode materials, MnO_2 has the most potential in the Li-S battery due to its abundant resources, low cost, and nontoxicity. The previous research indicates MnO_2 has a particularly strong adsorption capacity for polysulfide compared to carbon materials and other metal oxides [28]. Moreover, MnO_2 has a large variety of crystal structures including α, β, δ, λ and so on, depending on the edge-sharing and angle-sharing MnO_6 octahedron.
Thus, 1D tunnel, 2D layer, and 3D mesh structure can be formed [29–33]. δ-MnO₂ as a layered structure can be used as an effective sulfur host material. Nazar’s group firstly reported that δ-MnO₂ can be considered as a remarkable chemical inhibitor for polysulfide based on mediating polysulfides redox [34]. For the tunnel-type MnO₂, Ni and coworkers prepared γ-MnO₂ covered with sulfur nanospheres, forming a core-shell structure to trap polysulfide through physical and chemical effects [35]. Zhang and researchers fabricated Mo-doping γ-MnO₂ to accelerate the transformation of polysulfide [36]. Wang and coworkers have synthesized highly ordered mesoporous β-MnO₂ to encapsulate sulfur and found that the thin mesoporous walls could provide short diffusion distances for Li ions [37]. These hybrid structures can physically and chemically encapsulate polysulfide and enhance the electrochemical performance of sulfur cathode. The studies above have reported synthesizing tunnel-type MnO₂ by in-situ recombination or ion doping and its application as sulfur host, but little work has focused on the effects of tunnel sizes on the polysulfide conversion abilities.

Herein, MnO₂ with three different tunnel sizes have been screened and prepared by hydrothermal reaction to investigate the effects of tunnel sizes on the polysulfide conversion. It is found that MnO₂ with a larger tunnel size has stronger chemisorption capacity of polysulfide, and therefore is more favorable to inhibiting the polysulfide shuttle. In addition, the larger tunnel size possesses faster reaction kinetics in the redox reaction in Li-S battery, hence larger-tunnel-size-MnO₂ based cathode exhibits better cycle reliability and rate performance in the cell tests. This work should provide a new perspective for the cathode design of advanced Li-S battery.

2. Materials and Methods
2.1. Synthesis of Manganese Oxides

Figure 1 illustrates the theoretical structures of the three tunnel-types of MnO₂ and how each tunnel phase is conventionally named as M × N, where M and N stand for the number of the MnO₆ octahedra constituting the height and width of the tunnel, respectively [38,39]. Depending on the number of MnO₆ units in the MnO₂, the tunnel size increases from β-MnO₂ (1 × 1 tunnel) to α-MnO₂ (2 × 2 tunnel), and to todorokite MnO₂ (3 × 3 tunnel) [40–43].

![Figure 1. Tunnel structure of MnO₂: (a) β-MnO₂ (1 × 1, 2.3 Å × 2.3 Å), (b) α-MnO₂ (2 × 2, 4.6 Å × 4.6 Å), (c) t-MnO₂ (3 × 3, 6.9 Å × 6.9 Å).](image)

The β-MnO₂ was obtained as follows: First, 1.0 g of MnSO₄·H₂O was dissolved in 60 mL of distilled deionized water, and then 0.37 g KMnO₄ was added into the solution with stirring. Then, the slurry was transferred into a Teflon-lined stainless-steel autoclave and heated at 120 °C for 12 h. The resulting product was washed and dried at 60 °C overnight.

The α-MnO₂ was prepared as follows: Firstly, 3.67 g of MnAC₂·4H₂O and 2.5 mL of CH₃COOH were dissolved in 35 mL deionized water with stirring. Then, 40 mL of
2.17 g KMnO$_4$ was added to the above mixture. Finally, the mixed solution was maintained at 100 °C for 24 h in a Teflon-lined autoclave. The resulting product was collected by centrifugation, washed with deionized water and dried at 100 °C overnight.

The todorokite MnO$_2$ (t-MnO$_2$) was synthesized as follows: First, 30 mL 6.0 M of NaOH aqueous solution was dropped into the solution (20 mL) containing 1.7 g of MnSO$_4$·H$_2$O with stirring. Then, 0.35 g of MgSO$_4$·7H$_2$O and 1.90 g of K$_2$S$_2$O$_8$ were added to the above mixture. After stirring for 3 h at room temperature and being washed with distilled water, the wet sample was dispersed in 300 mL of 1.0 M of MgCl$_2$·6H$_2$O and stirred for 24 h for ion exchange. The obtained mixture was transferred into a Teflon-lined autoclave and heated at 160 °C for 24 h. The resulting mixture was filtered and washed with distilled water. Lastly, the product was dried at 100 °C for 12 h.

2.2. Preparation of the Sulfur Composites

Sulfur and manganese oxides were mixed with a ratio of 70:30. The mixture was then transferred into a sealed stainless-steel vial and heated at 155 °C for 12 h in an oven.

2.3. Cell Assembling and Testing

The cathodes were prepared with 60 wt% active material, 30 wt% Super P carbon, and 10 wt% polyvinylidene fluoride (PVDF) binder and the slurry was casted onto Al foil current collector. The electrodes were dried at 60 °C in a vacuum for 24 h. The CR2032 coin cells with lithium metal (counter electrode) were fabricated. Sulfur cathode size is d = 12 mm, pure sulfur loading is ~1 mg cm$^{-2}$, and overall sulfur content is 42 wt%. The electrolyte was 1.0 M LiTFSI in dioxolane/dimethoxyethane solvent (DOL/DME volume ratio1:1) with 2 wt% lithium nitrate (LiNO$_3$) as an additive and PE was used as the separator.

Galvanostatic measurements were carried out between 1.8 and 2.8 V (vs. Li/Li$^+$) on a Land CT2001A system (LANHE, Wuhan, China). The cyclic voltammetry (CV) experiments were performed with a CHI600E electrochemical workstation (CH, Shanghai, China) at a scanning rate of 0.1 mV s$^{-1}$ between 1.7 and 2.8 V.

2.4. Polysulfide Adsorption Test

Typically, 5 mM Li$_2$S$_6$ solution was prepared by the reaction Li$_2$S with S in DOL and DME (v/v = 1:1). Then three samples of the same weight (5 mg) were added into three glass vials, respectively, and dispersed in 2 mL Li$_2$S$_6$ solution. Optical images were taken to compare the adsorption ability.

2.5. Structure Characterization

The morphology was examined by using scanning electron microscopy (SEM, JSM-2100F, JEOL, Tokyo, Japan). XRD patterns were collected using a D/max-TTR III (Rigaku Corporation, Shibuya-ku, Japan) with Cu Ka radiation, 40 kV, 200 mA). Nitrogen adsorption/desorption isotherms were performed on a Quantachrome Autosorb-IQ system (Quantachrome Instruments, Boynton Beach, FL, USA). The nanostructures of manganese oxides were characterized by high-resolution transmission electron microscopy (HRTEM, JEOL, Tokyo, Japan, 2010). For XPS, the samples were sealed in a vial before being quickly transferred to the chamber of an ultra-high vacuum Imaging XPS Microprobe system for analysis (Thermo Scientific ESCALAB 250Xi, Waltham, MA, USA).

3. Results

As illustrated in Figure 2, the morphology of prepared three tunnel-type MnO$_2$ was carefully characterized. In the Figure 2a,c, the SEM images clearly showed the nanofiber morphology of the β-MnO$_2$ and α-MnO$_2$, with a length ranging from tens of nanometers to hundreds of nanometers. No extra phase was found on the surface of nanofiber. Because of the different reaction mechanism, the synthesized t-MnO$_2$ is nano-flake and with some long nanoribbons (Figure 2e). HTEM was used to measure the tunnel sizes of β-MnO$_2$, α-MnO$_2$ and t-MnO$_2$. In the Figure 2b, the HRTEM image shows the interlayer distance is
0.31 nm, which agrees with the (110) plane in the crystal structure of $\beta$-MnO$_2$, and hence the existence of $1 \times 1$ tunnel is confirmed. The clear lattice fringes in Figure 2d show that the crystal plane spacing of $\alpha$-MnO$_2$ is 0.70 nm, which corresponds to the (110) plane. For the t-MnO$_2$ structure, the crystallinity can be observed from the distinct lattice fringes in HRTEM image (Figure 2f). The interlayer distance of 0.97 nm corresponds to the (100) plane at an angle of 9.2°, thereby confirming the existence of $3 \times 3$ tunnel.

**Figure 2.** Morphological characterization: (a,c,e) SEM images of $\beta$-MnO$_2$, $\alpha$-MnO$_2$ and t-MnO$_2$, respectively; (b,d,f) TEM images of $\beta$-MnO$_2$, $\alpha$-MnO$_2$ and t-MnO$_2$, respectively (Insert: HRTEM images).
X-ray diffraction (XRD) measurement was used to confirm the crystal structure of synthetic tunnel-type MnO$_2$ (Figure 3). As shown in Figure 3a, the diffraction pattern for the $\beta$-MnO$_2$ has five sharp peaks at 28.7°, 37.3°, 42.8°, 56.6° and 59.3°, corresponding to (110), (101), (111), (211), and (220) of pyrolusite (JCPDS: 24-735), respectively. For the synthesized $\alpha$-MnO$_2$, peaks appearing in the Figure 3b can be well indexed to the pure tetragonal cryptomelane structures of $\alpha$-MnO$_2$ (JCPDS card 29-1020). In addition, as for the XRD pattern of t-MnO$_2$ (Figure 3c), peaks at 9.1°, 18.5°, 36.5°, 37.6° and 38.4°, also well coincide with the standard crystallographic tables JCPDS card 13-0164, showing the todorokite-type with the monoclinic phase. Thus, the MnO$_2$ of three different tunnel sizes were successfully synthesized through simple hydrothermal reaction without impurities.

Figure 3d presents the N$_2$ adsorption/desorption analysis of the MnO$_2$ samples. The BET (Brunauer-Emmett-Teller) surface area and total pore volume of $\beta$-MnO$_2$, $\alpha$-MnO$_2$ and t-MnO$_2$ presented in Figure S1 are 9.27 m$^2$/g and 0.018 cm$^3$/g, 103.82 m$^2$/g and 0.38 cm$^3$/g, 35.47 m$^2$/g and 0.074 cm$^3$/g, respectively. As a result, few micropores are formed on these three types of MnO$_2$. The reason why $\alpha$-MnO$_2$ has the largest BET surface area should be attributed to the smaller nanofiber morphology.

To compare the polysulfide adsorption capacity of three tunnel-type MnO$_2$, polysulfide adsorption test was performed. Typically, three samples of the same weight (5 mg) were added into three glass vials, respectively, and dispersed in 2 mL Li$_2$S$_6$ solution. After 1 h adsorption, the solution changed from dark-yellow to light yellow (Figure 4d). Obviously, the solution containing t-MnO$_2$ was noticeably lighter in color than other solutions, which
indicates t-MnO$_2$ has greater ability to adsorb polysulfide faster. It is usually believed that larger surface area means stronger adsorption capacity, but the BET surface area of t-MnO$_2$ is 35.47 m$^2$g$^{-1}$, smaller than half of that of α-MnO$_2$ (103.82 m$^2$g$^{-1}$). As a result, adsorption capacity of these atomic tunnels of MnO$_2$ were not well reflected by normal surface area tests. Similar adsorption independent of specific surface area by MnO$_2$ on methylene blue has also been reported by ref. [44], which apparently exhibits the special adsorption properties. Therefore, the stronger adsorption of t-MnO$_2$ of polysulfide mentioned above should be partially attributed to the special adsorption properties of the larger tunnel size of the polysulfide.

![Figure 4](image)

**Figure 4.** (a) S2p XPS spectra of β-MnO$_2$-Li$_2$S$_6$; (b) S2p XPS spectra of α-MnO$_2$-Li$_2$S$_6$; (c) S2p XPS spectra of t-MnO$_2$-Li$_2$S$_6$; (d) Polysulfides adsorption test.

X-ray photoelectron spectroscopy (XPS) analysis was used to find out the absorption type between polysulfide and tunnel-type MnO$_2$. By examining the specimens taken out from the Li$_2$S$_6$ solution after the adsorption test, it is found that all the S2p XPS spectra of β-MnO$_2$, α-MnO$_2$ and t-MnO$_2$ with polysulfides reveal four types of sulfur environment, as shown in Figure 4a–c. In the lower-binding-energy region from 163 eV to 165 eV, two pairs of S2p peaks refer to the same terminal (ST) and bridging sulfur (SB) peak, coming from the sulfides and polysulfides. The peaks in the higher-binding-energy region between 171 and 166 eV correspond with the binding energy of thiosulfate and polythionate species, which arise from the redox reaction between Li$_2$S$_6$ and MnO$_2$ [34]. Therefore, the chemisorption process occurs in such a way: the tunnel-type MnO$_2$ reacts with polysulfide and converts polysulfide to thiosulfate and polythionate, thereby anchoring polysulfide on the surface of MnO$_2$. 
Considering the excellent inhibiting effects on the “shuttle effect” by the tunnels of MnO₂, then, electrochemical experiments with the cathodes of tunnel-type MnO₂ were performed. Cyclic voltammograms (CV) of cells in the first cycle were shown in Figure 5a. Two typical cathodic peaks of the three cathodes were all observed at ~2.3 V and ~2.0 V, which could be ascribed to the reduction process of sulfur. These two peaks are, respectively, assigned to the transformation of S₈ to the long-chain polysulfide and then the reduction of long-chain sulfide species to solid products (Li₂S₂/Li₂S). When sweeping back, two sharp peaks of t-MnO₂/S cathode were found at 2.35 V and 2.4 V, which is mainly due to the oxidation of short-chain sulfide to polysulfide and S₈. Similarly, the β-MnO₂/S cathode exhibits two peaks located at 2.44 V and 2.5 V. However, for the α-MnO₂/S cathode, only one peak was observed at 2.4 V, indicating the complete conversion of Li₂S and polysulfides into element sulfur. A large number of studies reported that it was a common phenomenon in the first CV scan of Li-S battery [45,46]. Notably, the peak current of t-MnO₂/S electrode is greater than that of the α-MnO₂/S and β-MnO₂/S electrodes, which represents higher kinetics and reversibility of redox reaction. It makes sense that ions diffuse more easily in larger channels or more open structures. Moreover, the larger the cavity of tunnel-type MnO₂, the higher the ionic conductivity [47]. Relevant studies on kinetics of MnO₂ have already been widely reported [37,48]. Thus, the t-MnO₂ with 3 × 3 tunnel could provide wider pathways and more spacious cavities for the incorporation of Li⁺ ions into the material bulk than other smaller tunnel sizes.

Figure 5. Electrochemical performance of Li-S battery: (a) CV profiles; (b) the first charge-discharge curves; (c) long cycle performance; and (d) rate performance.

Figure 5b shows the typical galvanostatic discharge/charge profiles of the Li-S battery at 1 C rate. For the initial cycle, the t-MnO₂/S based cell delivers an excellent discharge
capacity of 1431.9 mAh g\(^{-1}\) at 1 C, which is significantly larger than the 935.9 mAh g\(^{-1}\) of \(\beta\)-MnO\(_2\)/S and 956.7 mAh g\(^{-1}\) of \(\alpha\)-MnO\(_2\)/S cathodes. The maximum discharge capacity reflects the utilization degree of sulfur when the battery carries on galvanostatic discharge. In order to enhance sulfur utilization, the sulfur in the electrode needs to be fully exposed to lithium ions and electrons, so as to effectively reduce to the lithium polysulfide species. The high initial discharge of t-MnO\(_2\)/S cathode is due to the larger tunnel structure, which enhances sulfur utilization. In addition, the first discharge curves exhibited two plateaus at \(\sim 2.0\) V and \(\sim 2.3\) V, which coincides with the CV results. Upon charge process, the platform voltage is also consistent with the corresponding CV results.

In order to directly demonstrate the effects of strong chemisorption on polysulfide by tunnel-type MnO\(_2\), we further studied the cycle performance and rate capacity of Li-S cells assembled with \(\beta\)-MnO\(_2\)/S, \(\alpha\)-MnO\(_2\)/S and t-MnO\(_2\)/S as cathodes. As shown in the Figure 5c, the long-term cycle stability of Li-S battery in terms of discharge capacity and coulombic efficiency was also studied at 1 C. The cycle performance of the three electrodes was compared, and the cell with t-MnO\(_2\)/S was found to have the best cycle stability in the long cycle. The residual capacity maintains in 583.7 mAh g\(^{-1}\) even over 500 cycles, which is still superior to 408 mAh g\(^{-1}\) of \(\alpha\)-MnO\(_2\)/S and 345 mAh g\(^{-1}\) of \(\beta\)-MnO\(_2\)/S. Moreover, impressively, the coulombic efficiency of the t-MnO\(_2\)/S based battery remain over 99% during the long-term cycling, which indicates its excellent intrinsic reversibility. In addition, SEM images of the discharged MnO\(_2\)/S cathode after 100 cycles under 1 C, which further proves the stable structure of t-MnO\(_2\)/S cathode to buffer the volume changes during repeated lithiation processes. Therefore, the enhanced chemisorption of t-MnO\(_2\) to polysulfide effectively promotes anchoring polysulfide and inhibiting the shuttle of polysulfide, and thus greatly improving the cyclic stability and coulomb efficiency of the Li-S battery.

The rate performance of the cell was obtained in Figure 5d. It is noteworthy that the cell with t-MnO\(_2\)/S shows a superior rate capability of 447 mAh g\(^{-1}\) at 2 C, which is 82 mAh g\(^{-1}\) higher than the specific discharge capacity of \(\alpha\)-MnO\(_2\)/S cathodes and 291 mAh g\(^{-1}\) higher than that of \(\beta\)-MnO\(_2\)/S cathodes. In addition, t-MnO\(_2\)/S cathode shows 1371, 676, 581, 498 mAh g\(^{-1}\) at 0.1, 0.2, 0.5 and 1 C, respectively. The preferable rate capability of t-MnO\(_2\)/S based cell should mainly be attributed to the larger 3 \(\times\) 3 tunnel structure, which accelerates the conversion of polysulfide and improves the reaction kinetics at higher current density.

4. Conclusions

In summary, MnO\(_2\) with three different types of tunnel sizes were designed to investigate their chemisorption capacity for polysulfide. MnO\(_2\) with larger tunnel size shows stronger chemisorption capacity through the redox reaction. The larger tunnel size of t-MnO\(_2\) not only anchors and accelerates the conversion of polysulfide but also possesses faster reaction kinetics in Li-S battery. Thus, the t-MnO\(_2\) based battery, with an ultrahigh initial capacity of 1431.9 mAh g\(^{-1}\) and a capacity of 583.7 mAh g\(^{-1}\) after 500 cycles, shows better cell performance and higher coulombic efficiency than the other two electrodes. Apparently, this work will bring some new concepts and strategies to the material selection and structure design for advanced Li-S battery.

**Supplementary Materials:** The following supporting information can be downloaded at: [https://www.mdpi.com/article/10.3390/nano12162752/s1](https://www.mdpi.com/article/10.3390/nano12162752/s1). Figure S1: Pore–size distribution obtained using the Barrett–Joyner–Halenda (BJH) method; Figure S2: EX situ SEM images of the discharged MnO\(_2\)/S cathodes after 100 cycles under 1 C. (a,b) t-MnO\(_2\)/S cathode; (c,d) \(\alpha\)-MnO\(_2\)/S cathode; and (e,f) \(\beta\)-MnO\(_2\)/S cathode. Reference [49] is cited in Supplementary Materials.
Author Contributions: Conceptualization, X.G. and X.B.; methodology, X.G.; software, J.Z.; validation, H.D.; formal analysis, X.Y.; investigation, X.G.; resources, X.G.; data curation, X.G.; writing—original draft preparation, X.G. and H.D.; writing—review and editing, H.D.; visualization, H.D.; supervision, H.D.; project administration, H.D.; funding acquisition, H.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Yantai Double Hundred Talent Plan 2019, Shandong Provincial Youth Innovation Science and Technology Project of Colleges and Universities (Grant Nos. 2021K[089], Shandong Provincial Natural Science Foundation, (Grant Nos. ZR2020ME005), Yantai science and technology innovation development plan, (Grant Nos. 2022YT06810644), Doctoral Fund of Yantai Nanshan University, (Grant Nos. B202002, B202003, B202006, B202007, Q202020) and The APC was funded by Yantai Double Hundred Talent Plan 2019.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available in a publicly accessible repository.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Liang, X.; Nazar, L.F. In Situ Reactive Assembly of Scalable Core–Shell Sulfur–MnO2 Composite Cathodes. ACS Nano 2016, 10, 4192–4198. [CrossRef] [PubMed]

2. Wang, S.; Huang, F.; Zhang, Z.; Cai, W.; Jie, Y.; Wang, S.; Yan, P.; Jiao, S.; Cao, R. Conductive metal-organic frameworks promoting polysulfides transformation in lithium-sulfur batteries. J. Energy Chem. 2021, 63, 336–343. [CrossRef]

3. Kang, B.; Ceder, G. Battery materials for ultrafast charging and discharging. Nature 2009, 458, 190–193. [CrossRef] [PubMed]

4. Evers, S.; Nazar, L.F. New Approaches for High Energy Density Lithium–Sulfur Battery Cathodes. Acc. Chem. Res. 2013, 46, 1135–1143. [CrossRef]

5. Wang, G.; Lai, Y.; Zhang, Z.; Li, J.; Zhang, Z. Enhanced rate capability and cycle stability of lithium–sulfur batteries with a bifunctional MCNT@PEG-modified separator. J. Mater. Chem. A 2015, 3, 7139–7144. [CrossRef]

6. Zhang, S.; Ueno, K.; Dokko, K.; Watanabe, M. Recent Advances in Electrolytes for Lithium–Sulfur Batteries. Adv. Energy Mater. 2015, 5, 1500117. [CrossRef]

7. Huang, Y.; Lin, L.; Zhang, C.; Liu, L.; Li, Y.; Qiao, Z.; Lin, J.; Wei, Q.; Wang, L.; Xie, Q.; et al. Recent Advances and Strategies toward Polysulfides Shuttle Inhibition for High-Performance Li–S Batteries. Adv. Sci. 2022, 9, 2106004. [CrossRef]

8. Li, Z.; Zhang, J.; Lou, X.W. Hollow Carbon Nanofibers Filled with MnO2 Nanosheets as Efficient Sulfur Hosts for Lithium–Sulfur Batteries. Angew. Chem. Int. Ed. 2015, 54, 12886–12890. [CrossRef]

9. Guo, J.; Zhang, X.; Du, X.; Zhang, F. A Mn3O4 nano-wall array based binder-free cathode for high performance lithium–sulfur batteries. J. Mater. Chem. A 2017, 5, 6447–6454. [CrossRef]

10. Cao, R.; Xu, W.; Lv, D.; Xiao, J.; Zhang, J.-G. Anodes for Rechargeable Lithium–Sulfur Batteries. Adv. Energy Mater. 2015, 5, 1402273. [CrossRef]

11. Yang, L.; Li, Q.; Wang, Y.; Chen, Y.; Guo, X.; Wu, Z.; Chen, G.; Zhong, B.; Xiang, W.; Zhong, Y. A review of cathode materials in lithium-sulfur batteries. Ionics 2020, 26, 5299–5318. [CrossRef]

12. Li, Z.; Jiang, Y.; Yuan, L.; Yi, Z.; Wu, C.; Liu, Y.; Strasser, P.; Huang, Y. A Highly Ordered Mesoporous Carbon Nanofibers Filled with MnO2 Nanosheets as Efficient Sulfur Hosts for Lithium–Sulfur Batteries. ACS Nano 2014, 8, 9295–9303. [CrossRef]

13. Ji, X.; Lee, K.T.; Nazar, L.F. A highly ordered nanostructured carbon–sulphur cathode for lithium–sulphur batteries. Nat. Mater. 2009, 8, 500–506. [CrossRef]

14. Knoop, J.E.; Ahn, S. Recent advances in nanomaterials for high-performance Li–S batteries. J. Energy Chem. 2020, 47, 86–106. [CrossRef]

15. Sahore, R.; Levin, B.D.A.; Pan, M.; Muller, D.A.; DiSalvo, F.J.; Giannelis, E.P. Design Principles for Optimum Performance of Porous Carbons in Lithium–Sulfur Batteries. Adv. Energy Mater. 2016, 6, 1600134. [CrossRef]

16. Guo, J.; Xu, Y.; Wang, C. Sulfur-Impregnated Disordered Carbon Nanotubes Cathode for Lithium–Sulfur Batteries. Nano Lett. 2011, 11, 4288–4294. [CrossRef]

17. Yuan, L.; Yuan, H.; Qiu, X.; Chen, L.; Zhu, W. Improvement of cycle property of sulfur-coated multi-walled carbon nanotubes composite cathode for lithium/sulfur batteries. J. Power Sources 2009, 189, 1141–1146. [CrossRef]

18. Tao, X.; Wang, J.; Ying, Z.; Cai, Q.; Zheng, G.; Gan, Y.; Huang, H.; Xia, Y.; Liang, C.; Zhang, W.; et al. Strong Sulfur Binding with Conducting Magnéli-Phase TiO2n-1 Nanomaterials for Improving Lithium–Sulfur Batteries. Nano Lett. 2014, 14, 5288–5294. [CrossRef]

19. Zhang, Y.; Zhao, Y.; Yermukhambetova, A.; Bakenov, Z.; Chen, P. Ternary sulfur/polyacrylonitrile/Mg0.6Ni0.4O composite cathodes for high performance lithium/sulfur batteries. J. Mater. Chem. A 2013, 1, 295–301. [CrossRef]
20. Sun, F.; Wang, J.; Long, D.; Qiao, W.; Ling, L.; Lv, C.; Cai, R. A high-rate lithium–sulfur battery assisted by nitrogen-enriched mesoporous carbons decorated with ultrathin La2O3 nanoparticles. *J. Mater. Chem. A* **2013**, *1*, 13283–13289. [CrossRef]

21. Liu, J.; Yuan, L.; Yuan, K.; Li, Z.; Hao, Z.; Xiang, J.; Huang, Y. SnO2 as a high-efficiency polysulfide trap in lithium–sulfur batteries. *Nanoscale* **2016**, *8*, 13638–13645. [CrossRef]

22. Li, B.; Sun, Z.; Zhao, Y.; Zhang, Z. Facile synthesis of three-dimensional carbon nanotube/Fe3O4 microspheres as sulfur host for high performance lithium-sulfur batteries. *Mater. Lett.* **2019**, *255*, 126529. [CrossRef]

23. Lin, H.; Zhang, S.; Zhang, T.; Ye, H.; Yao, Q.; Zheng, G.W.; Lee, J.Y. Simultaneous Cobalt and Phosphorous Doping of MoS2 for Improved Catalytic Performance on Polysulfide Conversion in Lithium–Sulfur Batteries. *Adv. Energy Mater.* **2019**, *9*, 1902096. [CrossRef]

24. Chen, Y.; Ji, X. Bamboo-like Co3O4 nanofiber as host materials for enhanced lithium-sulfur battery performance. *J. Alloys Compd.* **2019**, *777*, 688–692. [CrossRef]

25. Tao, X.; Wang, J.; Liu, C.; Wang, H.; Yao, H.; Zheng, G.; Seh, Z.W.; Cai, Q.; Li, W.; Zhou, G.; et al. Balancing surface adsorption and diffusion of lithium-polysulfides on nonconductive oxides for lithium–sulfur battery design. *Nat. Commun.* **2016**, *7*, 11203. [CrossRef]

26. Huang, Y.-C.; Hsiang, H.-I.; Chung, S.-H. Investigation and Design of High-Loading Sulfur Cathodes with a High-Performance Polysulfide Adsorbent for Electrochemically Stable Lithium–Sulfur Batteries. *ACS Sustain. Chem. Eng.* **2022**, *10*, 9254–9264. [CrossRef]

27. Chen, Z.; Hu, Y.; Liu, W.; Yu, F.; Yu, X.; Mei, T.; Yu, L.; Wang, X. Three-Dimensional Engineering of Sulfur/MnO2 Composites for High-Rate Lithium–Sulfur Batteries. *ACS Appl. Mater. Interfaces* **2021**, *13*, 38394–38404. [CrossRef]

28. Wu, D.S.; Shi, F.; Zhou, G.; Zu, C.; Liu, C.; Liu, K.; Liu, Y.; Wang, J.; Peng, Y.; Cui, Y. Quantitative investigation of polysulfide adsorption capability of candidate materials for Li-S batteries. *Energy Storage Mater.* **2018**, *13*, 241–246. [CrossRef]

29. Wang, X.; Li, Y. Synthesis and Formation Mechanism of Manganese Dioxide Nanowires/Nanorods. *Chem. A Eur. J.* **2003**, *9*, 300–306. [CrossRef]

30. Ding, Y.S.; Shen, X.F.; Gomez, S.; Luo, H.; Aindow, M.; Suib, S.L. Hydrothermal Growth of Manganese Dioxide into Three-Dimensional Hierarchical Nanoarchitectures. *Adv. Funct. Mater.* **2006**, *16*, 549–555. [CrossRef]

31. Suib, S.L. Porous Manganese Oxide Octahedral Molecular Sieves and Octahedral Layered Materials. *Acc. Chem. Res.* **2008**, *41*, 479–487. [CrossRef] [PubMed]

32. Li, Y.-F.; Zhu, S.-C.; Liu, Z.-P. Reaction Network of Layer-to-Tunnel Transition of MnO2. *J. Am. Chem. Soc.* **2016**, *138*, 5371–5379. [CrossRef] [PubMed]

33. Shen, X.F.; Ding, Y.S.; Liu, J.; Cai, J.; Laubernds, K.; Zerger, R.P.; Vasiliev, A.; Aindow, M.; Suib, S.L. Control of Nanometer-Scale Tunnel Sizes of Porous Manganese Oxide Octahedral Molecular Sieve Nanomaterials. *Adv. Mater.* **2005**, *17*, 805–809. [CrossRef]

34. Liang, X.; Hart, C.; Pang, Q.; Garsuch, A.; Weiss, T.; Nazar, L.F. A highly efficient polysulfide mediator for lithium–sulfur batteries. *Nat. Commun.* **2015**, *6*, 5682. [CrossRef]

35. Ni, L.; Wu, Z.; Zhao, G.; Sun, C.; Zhou, C.; Gong, X.; Diao, G. Core–Shell Structure and Interaction Mechanism of γ-MnO2 Coated Sulfur for Improved Lithium-Sulfur Batteries. *Small* **2017**, *13*, 1603466. [CrossRef]

36. Zhang, L.; Liu, Q.; Wang, Y.; Xu, C.; Bi, J.; Mu, D.; Wu, B.; Wu, F. Modifying γ-MnO2 to enhance the electrochemical performance of lithium-sulfur batteries. *Chem. Eng. J.* **2011**, *170*, 306–311. [CrossRef]

37. Wang, S.; Yang, Z.; Zhang, H.; Tan, H.; Yu, J.; Wu, J. Mesoporous β-MnO2/sulfur composite as cathode material for Li-S batteries. *Electrochem. Acta* **2013**, *106*, 307–311. [CrossRef]

38. Yuan, Y.; Liu, C.; Byles, B.W.; Yao, W.; Song, B.; Cheng, M.; Huang, Z.; Amine, K.; Pomerantseva, E.; Shahbazian-Yassar, R.; et al. Ordering Heterogeneity of [MnOx] Octahedra in Tunnel-Structured MnO2 and Its Influence on Ion Storage. *Joule* **2019**, *3*, 471–484. [CrossRef]

39. Turner, S.; Buseck, P.R. Manganese Oxide Tunnel Structures and Their Intergrowths. *Science* **1979**, *203*, 456–458. [CrossRef]

40. Lee, S.-Y.; Wu, L.; Poyraz, A.S.; Huang, J.; Marschik, A.C.; Takeuchi, K.J.; Takeuchi, E.S.; Kim, M.; Zhu, Y. Lithiation Mechanism of Tunnel-Structured MnO2 Electrode Investigated by In Situ Transmission Electron Microscopy. *Adv. Mater.* **2017**, *29*, 1703186. [CrossRef]

41. Byles, B.W.; West, P.; Cullen, D.A.; More, K.L.; Pomerantseva, E. Todorkite-type manganese oxide nanowires as an intercalation cathode for Li-ion and Na-ion batteries. *RSC Adv.* **2015**, *5*, 106265–106271. [CrossRef]

42. Islam, S.; Alfaruqui, M.H.; Mathew, V.; Song, J.; Kim, S.; Kim, S.; Jo, J.; Baboo, J.P.; Pham, D.T.; Putro, D.Y.; et al. Facile synthesis and the exploration of the zinc storage mechanism of β-MnO2 nanorods with exposed (101) planes as a novel cathode material for high performance eco-friendly zinc-ion batteries. *J. Mater. Chem. A* **2017**, *5*, 23299–23309. [CrossRef]

43. Koutani, M.; Hayashi, E.; Kamata, K.; Hara, M. Synthesis and Aerobic Oxidation Catalysis of Mesoporous Todorkite-Type Manganese Oxide Nanoparticles by Crystallization of Precursors. *J. Am. Chem. Soc.* **2022**, *144*, 14090–14100. [CrossRef]

44. Jiang, S.; Yu, T.; Xia, R.; Wang, X.; Gao, M. Realization of super high adsorption capability of 2D δ-MnO2 /GO through intra-particle diffusion. *Mater. Chem. Phys.* **2019**, *232*, 374–381. [CrossRef]

45. Guo, Y.; Zhao, G.; Wu, N.; Zhang, Y.; Xiang, M.; Wang, B.; Liu, H.; Wu, H. Efficient Synthesis of Graphene Nanoscrolls for Fabricating Sulfur-Loaded Cathode and Flexible Hybrid Interlayer toward High-Performance Li-S Batteries. *ACS Appl. Mater. Interfaces* **2016**, *8*, 34185–34193. [CrossRef]
46. Ji, L.; Rao, M.; Zheng, H.; Zhang, L.; Li, Y.; Duan, W.; Guo, J.; Cairns, E.J.; Zhang, Y. Graphene Oxide as a Sulfur Immobilizer in High Performance Lithium/Sulfur Cells. *J. Am. Chem. Soc.* **2011**, *133*, 18522–18525. [CrossRef]

47. Ghodbane, O.; Pascal, J.-L.; Favier, F. Microstructural Effects on Charge-Storage Properties in MnO₂-Based Electrochemical Supercapacitors. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1130–1139. [CrossRef]

48. Nie, J.; Liu, H. Efficient aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran on manganese oxide catalysts. *J. Catal.* **2014**, *316*, 57–66. [CrossRef]

49. He, B.; Rao, Z.; Cheng, Z.; Liu, D.; He, D.; Chen, J.; Miao, Z.; Yuan, L.; Li, Z.; Huang, Y. Rationally Design a Sulfur Cathode with Solid-Phase Conversion Mechanism for High Cycle-Stable Li-S Batteries. *Adv. Energy Mater.* **2021**, *11*, 2003690. [CrossRef]