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Editorial

Recent Progress of Lithium-Sulfur Batteries

Meijuan Xiao [1] and Zhenyu Xing [1,2,3,*]

[1] School of Chemistry, South China Normal University, Guangzhou 510006, China
[2] Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, South China Normal University, Guangzhou 510006, China
[3] Department of Electrical Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong 999077, China
* Correspondence: xingzhenyu@m.scnu.edu.cn

1. Introduction

Compared with lithium-ion batteries, lithium sulfur batteries possess a much lower cost and much higher theoretical energy density, and they are, therefore, becoming a research hotspot [1–5]. However, their inherent problems, including poor rate performance due to low electric conductivity and fast capacity fading from polysulfide dissolution and the shuttle effect, greatly impede their commercialization. Great exploration has been performed to solve the above problems. To date, porous carbon materials have been intensively investigated due to their effective physical confinement to restrain polysulfide dissolution [6–10]. Compared with the nonpolar interaction of the carbon host, the polar substrate provides stronger chemical adsorption to anchor polysulfide, including metal organic frameworks, transition metals and their compounds [11–15]. Recently, the concept of electrocatalysis has been introduced into lithium sulfur batteries, aiming at reducing the detention time of polysulfide by accelerating the electrochemical redox kinetics.

In this context, more and more attention has been paid to cathode structure design and separator modification during the past few years. Therefore, this mini review aims to introduce recent progress focusing on cathode materials, separator modification and other components published in Batteries. Topics of interest for publication include, but are not limited to:

- Novel cathode materials;
- Proxy sulfur cathodes;
- Carbon host;
- Separator modification;
- Metal organic frameworks;
- Electrocatalytic conversion;
- Proton exchange membranes;
- Polysulfide shuttle effect.

2. Recent Progress

The capacity fading and low utilization of an active material, caused by polysulfide dissolution, seriously hinders its practical application. To solve this problem, lots of work has been done. As summarized by M. Suzanowicz et al., it is imperative to develop a highly conductive carbon host with rich porosity [16]. The first example they discussed is MoS_3 without polysulfide dissolution, which is being considered as a potential cathode material to replace sulfur. To further improve the electrical conductivity, MoS_3 was embedded into porous reduced graphene oxide. As a result, this composite delivered a much higher capacity. In addition, the authors also introduced their C/MnO_2, $C/g\text{-}C_3N_4$ and C/AlF_3 double hollow shells as the sulfur host. Taking C/AlF_3 as an example, C/AlF_3 infiltrated with sulfur delivers a capacity of 702 mAh/g even after 500 cycles at 1 C, with a capacity fading rate of only 0.052% per cycle.

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After realizing the importance of porosity, researchers have become eager to know how to prepare carbon–sulfur composites of better interface contact, which directly determine the electrode uniformity and subsequent battery performance. Despite mechanical milling, gas mixing, and melting–diffusion having been investigated, these methods still fall short of current energy-density requirements. Therefore, Laverde et al. investigated the effect of fusion–diffusion time and sulfur content on the electrode structure [17]. They found that a six-hour melting–diffusion time and 10 wt% sulfur content gives rise to the most uniform sulfur distribution, which not only adsorbs polysulfide more effectively but also enhances the overall conductivity of the electrode.

Compared with pure carbon, a carbon–transition metal compound as a cathode host shows better electrochemical performance due to its strong chemical adsorption and accelerated reaction kinetics. Among various materials, a carbon–transition metal compound derived from metal organic frameworks attracted special attention because abundant channels and open active sites can be well preserved after pyrolysis. Wang et al. prepared carbon–cobalt by pyrolyzing ZIF-67 with a uniform and smooth dodecahedral shape as the template under 700 °C for 3 h [18]. The as-derived three-dimensional spider network not only increased sulfur accommodation, but also buffered the volume change during cycling. Meanwhile, nanosized cobalt particles catalyzed the polysulfide conversion with accelerated reaction kinetics. In the electrochemical test, the initial specific discharge capacity was 1425.2 mAh/g at 0.1 C. After 1000 cycles at 1 C, the decay rate is only 0.028%.

Aside from the cathode host design, separator modification has also effectively depressed the polysulfide shuttle. As reported by Liao et al., adjusting the number of separators greatly inhibits the shuttle during cycling [19]. By increasing the separator number, cycling performance improves significantly. However, the separator number increase also hindered lithium-ion diffusion, impairing the rate capability as a side effect. Recently, a Nafion separator has been studied to replace the traditional polypropylene separator. Comparing with the polypropylene separator, Yaroslavtsev et al. found that a Nafion separator greatly reduced the polysulfide shuttle and improved the battery cycling performance [20]. After ten cycles, capacity decreased by 78% for the cell using the polypropylene separator. In contrast, the capacity only decreased by 19% for the cell using the Nafion separator.

3. Conclusions

This mini review focuses on original research articles and editorials about Li-S batteries published in Batteries. The articles reviewed here were committed to the most relevant topics correlated with lithium-sulfur batteries This mini review will generate academic resonance and a collision of ideas, helping Batteries to harvest more research results and promoting Li-S batteries towards a more promising future.

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References

1. Wang, D.W.; Zeng, Q.; Zhou, G.; Yin, L.; Li, F.; Cheng, H.M.; Gentle, I.R.; Lu, G.Q.M. Carbon-sulfur composites for Li-S batteries: Status and prospects. *J. Mater. Chem. A* **2013**, *1*, 9382–9394. [CrossRef]
2. Pang, P.; Wang, Z.; Deng, Y.; Nan, J.; Xing, Z.; Li, H. Delayed Phase Transition and Improved Cycling/Thermal Stability by Spinel $LiNi_{0.5}Mn_{1.5}O_4$ Modification for $LiCoO_2$ Cathode at High Voltages. *ACS Appl. Mater. Interfaces* **2020**, *12*, 27339–27349. [CrossRef] [PubMed]

3. Li, D.; Han, F.; Wang, S.; Cheng, F.; Sun, Q.; Li, W.-C. High Sulfur Loading Cathodes Fabricated Using Peapodlike, Large Pore Volume Mesoporous Carbon for Lithium-Sulfur Battery. *ACS Appl. Mater. Interfaces* **2013**, *5*, 2208–2213. [CrossRef] [PubMed]
4. Pang, P.; Wang, Z.; Tan, X.; Deng, Y.; Nan, J.; Xing, Z.; Li, H. $LiCoO_2$@$LiNi_{0.45}Al_{0.05}Mn_{0.5}O_2$ as high-voltage lithium-ion battery cathode materials with improved cycling performance and thermal stability. *Electrochim. Acta* **2019**, *327*, 135018. [CrossRef]
5. Li, G.; Wang, S.; Zhang, Y.; Li, M.; Chen, Z.; Lu, J. Revisiting the Role of Polysulfides in Lithium-Sulfur Batteries. *Adv. Mater.* **2018**, *30*, 1705590. [CrossRef] [PubMed]
6. Zhang, K.; Hu, Z.; Chen, J. Functional porous carbon-based composite electrode materials for lithium secondary batteries. *J. Energy Chem.* **2013**, *22*, 214–225. [CrossRef]
7. Cheng, L.; Ma, C.; Lu, W.; Wang, X.; Yue, H.; Zhang, D.; Xing, Z. A graphitized hierarchical porous carbon as an advanced cathode host for alkali metal-selenium batteries. *Chem. Eng. J.* **2022**, *433*, 133527. [CrossRef]
8. Yang, D.; Xiong, X.; Zhu, Y.; Chen, Y.; Fu, L.; Zhang, Y.; Wu, Y. Modifications of Separators for Li-S Batteries with Improved Electrochemical Performance. *Russ. J. Electrochem.* **2020**, *56*, 365–377. [CrossRef]
9. Zhang, S.; Zheng, M.; Cao, J.; Pang, H. Porous Carbon/Sulfur Composite Cathode Materials for Lithium-Sulfur Batteries. *Prog. Chem.* **2016**, *28*, 1148–1155.
10. Fu, A.; Wang, C.; Pei, F.; Cui, J.; Fang, X.; Zheng, N. Recent Advances in Hollow Porous Carbon Materials for Lithium-Sulfur Batteries. *Small* **2019**, *15*, 1804786. [CrossRef] [PubMed]
11. Gao, N.; Li, B.; Zhang, Y.; Li, W.; Li, X.; Zhao, J.; Yue, W.; Xing, Z.; Wang, B. CoFe Alloy-Decorated Interlayer with a Synergistic Catalytic Effect Improves the Electrochemical Kinetics of Polysulfide Conversion. *ACS Appl. Mater. Interfaces* **2021**, *13*, 57193–57203. [CrossRef] [PubMed]
12. Xing, Z.; Tan, G.; Yuan, Y.; Wang, B.; Ma, L.; Xie, J.; Li, Z.; Wu, T.; Ren, Y.; Shahbazian-Yassar, R.; et al. Consolidating Lithiothermic-Ready Transition Metals for Li_2S-Based Cathodes. *Adv. Mater.* **2020**, *32*, 2002403. [CrossRef] [PubMed]
13. Tao, X.; Yang, Z.; Yan, R.; Cheng, M.; Ma, T.; Cao, S.; Bai, M.; Ran, F.; Cheng, C.; Yang, W. Engineering MOFs-Derived Nanoarchitectures with Efficient Polysulfides Catalytic Sites for Advanced Li-S Batteries. *Adv Mater Technol.* **2022**, 2200238. [CrossRef]
14. Gao, N.; Zhang, Y.; Chen, C.; Li, B.; Li, W.; Lu, H.; Yu, L.; Zheng, S.; Wang, B. Low-temperature Li-S battery enabled by CoFe bimetallic catalysts. *J. Mater. Chem. A* **2022**, *10*, 8378–8389. [CrossRef]
15. Wu, J.; Ye, T.; Wang, Y.; Yang, P.; Wang, Q.; Kuang, W.; Chen, X.; Duan, G.; Yu, L.; Jin, Z.; et al. Understanding the Catalytic Kinetics of Polysulfide Redox Reactions on Transition Metal Compounds in Li-S Batteries. *ACS Nano* **2022**, *16*, 15734–15759. [CrossRef] [PubMed]
16. Suzanowicz, A.M.; Mei, C.W.; Mandal, B.K. Approaches to Combat the Polysulfide Shuttle Phenomenon in Li-S Battery Technology. *Batteries* **2022**, *8*, 45. [CrossRef]
17. Laverde, J.; Rosero-Navarro, N.C.; Miura, A.; Buitrago-Sierra, R.; Tadanaga, K.; Lopez, D. Impact of Sulfur Infiltration Time and Its Content in an N-doped Mesoporous Carbon for Application in Li-S Batteries. *Batteries* **2022**, *8*, 58. [CrossRef]
18. Wang, H.; Jamil, S.; Tang, W.; Zhao, J.; Liu, H.; Bao, S.; Liu, Y.; Xu, M. Melamine-Sacrificed Pyrolytic Synthesis of Spiderweb-like Nanocages Encapsulated with Catalytic Co Atoms as Cathode for Advanced Li-S Batteries. *Batteries* **2022**, *8*, 161. [CrossRef]
19. Liao, J.; Ye, Z. Nontrivial Effects of Trivial Parameters on the Performance of Lithium-Sulfur Batteries. *Batteries* **2018**, *4*, 22. [CrossRef]
20. Yaroslavtsev, A.B.; Novikova, S.A.; Voropaeva, D.Y.; Li, S.A.; Kulova, T.L. Perfluorosulfonic Acid Membrane for Lithium-Sulfur Batteries with S/C Cathodes. *Batteries* **2022**, *8*, 162. [CrossRef]