

Contents lists available at ScienceDirect

Energy Storage Materials



journal homepage: www.elsevier.com/locate/ensm

Contribution of different metal nodes on stepwise electrocatalysis in lithium-sulfur batteries

Check for updates

Yu Chen^a, Yuanhong Kang^a, Huiya Yang^a, Haiming Hua^a, Jiaxiang Qin^{b,d}, Peng Liu^b, Yiyong Zhang^{c,*}, Yingjie Zhang^c, Jinbao Zhao^{a,*}

^a State Key Laboratory of Physical Chemistry of Solid Surfaces, State-Province Joint Engineering Laboratory of Power Source Technology for New Energy Vehicle, Collaborative Innovation Center of Chemistry for Energy Materials, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China ^b School of materials science and Engineering, The Key Laboratory of Low-carbon Chemistry & Energy Conservation of Guangdong Province, Sun Yat-sen University, Guangzhou 510275, PR China

^c National and Local Joint Engineering Laboratory for Lithium-ion Batteries and Materials Preparation Technology, Key Laboratory of Advanced Battery Materials of Yunnan Province, Faculty of Metallurgical and Energy Engineering, Kunning University of Science and Technology, Kunning 650093, PR China

^d State Key Laboratory of Environmental Adaptability for Industrial Products, China National Electric Apparatus Research Institute, Guangzhou 510663, PR China

ARTICLE INFO

Keywords: Metal sites Dual-chemical bonding Adsorption-catalysis mechanism Lithium-sulfur batteries

ABSTRACT

The mechanism of multifunctional sulfur-fixing materials on molecular / atomic level is important for selecting and designing effective electrocatalysts for lithium-sulfur batteries (LSBs). Therefore, metal coordination compounds (M = Co / Fe / CoFe) with unique catalytic behavior are selected as cathode additives to promote the sluggish reaction kinetics caused by multiphase conversion and focus on adsorption-catalysis mechanism. It is found that Co sites are conducive to promoting the generation of lithium sulfide that increase the specific discharge capacity, while Fe sites are beneficial for the adsorption of polysulfides that increase the capacity retention. The combination of Co and Fe sites can inhibit the polysulfides diffusion and induce the rapid and uniform deposition of lithium sulfide. Benefiting from the dual-anchoring of efficient Metal-S and Li-N bonds and special catalysis of Co sites, the CoFe PBA@S cells exhibit remarkable cyclability and capability. The cell delivers a small capacity fading rate (0.052% per cycle over 1000 cycles at 2 A g⁻¹), excellent rate capability (811.86 mAh g⁻¹ at 5 A g⁻¹) and ultrahigh capability retention (1143.7 mAh g⁻¹ after 100 cycles at 0.2 A g⁻¹). Even with a high sulfur loading of 5 mg cm⁻², it still shows reversible capacity of 789.7 mAh g⁻¹ after 100 cycles at 0.2 A g⁻¹. This work provides a rational direction to select and design effective electrocatalysts for LSBs.

1. Introduction

With the rapid development of sustainable energy and the popularization of electric vehicles, it is unable for traditional lithium-ion batteries to meet the increasing demand for high-energy-density secondary batteries. Among many new battery systems, lithium-sulfur batteries (LSBs) have attracted much attention due to their high theoretical specific capacity and high energy density [1]. High capacity means longer standby time of electronic products and longer cruising range of electric vehicles. High energy density determines smaller volume and lighter weight of products.

Although LSBs have many advantages, they also face great challenges. LSBs with solid-solid mechanism have been reported in the past [2]. However, it has a high dimensional requirement for sulfur, which is

difficult to meet. As for common sulfur with larger size, due to the poor electrical conductivity, a large portion of sulfur is not utilized if the electrons are only conducted through the solid-solid mechanism. Hence, in a sense, the dissolution of sulfur is essential since it can effectively improve the utilization of active materials. But for LSBs with solid-liquid-solid mechanism, although it increases the sulfur utilization, it also leads to the diffusion of polysulfides which will cause the loss of active substances during the charge and discharge process. Thus, the shuttle effect has become the biggest obstacle for LSBs.

In response to this problem, abundant programs have been implemented [3]. Various materials are used as host materials [4, 5], modified separators [6,7], additives [8–10], etc. Considering the polarity of polysulfides, the polar metal compound with catalytic effect is an extremely promising composite material [11–15], because it can bond with

* Corresponding authors. *E-mail addresses:* zhangyiyong2018@kust.edu.cn (Y. Zhang), jbzhao@xmu.edu.cn (J. Zhao).

https://doi.org/10.1016/j.ensm.2022.10.047

Received 7 April 2022; Received in revised form 10 October 2022; Accepted 24 October 2022 Available online 2 November 2022 2405-8297/© 2022 Elsevier B.V. All rights reserved. polysulfides through strong chemical interaction [16] and accelerate conversion. At present, most previous studies focused more on the electrochemical properties without specific mechanism explanation on molecular or atomic level. While for the rational selection and design of catalytic materials for LSBs, a basic understanding of the material properties and adsorption-catalysis mechanism is important. Consequently, metal coordination compounds of different metal centers are selected as positive electrode additives to study the specific catalytic mechanism.

In previous researches, cobalt and ferrum atoms have been confirmed to have good catalytic activity in many fields [17,18], and a large number of studies have shown that cobalt-based [19] and ferrum-based [20] compounds can effectively catalyze the conversion of polysulfides in lithium-sulfur batteries. Furthermore, bimetallic materials that combine cobalt and ferrum atoms perform better [21,22]. Herein, Prussian blue analogues (PBAs) [23–27] with cobalt and ferrum metal nodes are used as catalysts for LSBs in this work. Although similar PBAs have been utilized and exhibit stable performance in recent

research [28], the focus is mainly on structure and morphology design without in-depth mechanism research. In this work, it not only achieves better electrochemical performance with less catalyst compared with other works, but also gives further explanations for adsorption-catalysis mechanism on molecular/atomic level with various in-situ characterizations and theoretical calculation. Through research, it is found that diverse metal sites target distinct catalytic processes and improve the electrochemical performance of LSBs by different ways. For ferrum-based Prussian blue (Fe PBA), it combines with polysulfides via Li-N bonds which effectively inhibit the diffusion of polysulfides at liquid-liquid stages, improving the capacity retention rate. Whereas for cobalt-based Prussian blue analogue (Co PBA), the excessive strong Co-S bonds crack the S-S bonds in sulfur chains which accelerate liquid-solid conversion, increasing the discharge specific capacity. As for cobalt-ferrum-based Prussian blue analogue (CoFe PBA), owing to the combination of Co and Fe sites, its intrinsic electronic structure is changed in balance. Hence, it has more appropriate binding strength and lower reaction energy barrier. As a result, profiting from the adsorption



Fig. 1. Schematic diagram of (a) traditional lithium-sulfur battery and (b) the designed lithium-sulfur battery structure with catalyst; (c) Cycling performance at 0.2 A g^{-1} ; (d) Rate performance; (e, f) Discharge-charge profile of the first cycle at 0.1 A g^{-1} ; (g) The first cycle of CV curves; (h) Discharge-charge curves at different current rates of CoFe PBA@S; (i) Cycling performance of CoFe PBA@S cell at high current density; (j) Cycling performance of CoFe PBA@S cell with high sulfur loading at 0.2 A g^{-1} .

of Metal-S and Li-N bonds and specific catalysis of Co sites, the CoFe PBA exhibits the highest specific discharge capacity and the lowest capacity fading rate after cycling.

2. Results and Discussion

The synthesis method of the metal-based PBA (M PBA) is the same as we reported before [29]. As cathode additives, different PBAs are mixed with sulfur in a ratio of 1:9 by ball milling to form the composite cathode materials (M PBA@S). All fabricated materials are tested by XRD. **Fig. S1** shows the result patterns. Owing to the high sulfur content, the composites display almost sulfur peaks (PDF#08-0247) with weak peaks of M PBA. The morphologies of M PBA and M PBA@S (M=Co/Fe/CoFe) are measured by SEM. As shown in **Fig. S2**, all the M PBAs are cubic in shape. The Co/Fe, C and N elements on the material surfaces are uniform. The SAED pattern (**Fig. S3**a) shows that it is a high-quality crystal. HRTEM image (**Fig. S3**c) reveals the lattice fringe spacing of 0.51 nm, which can be assigned to (200) planes. In **Fig. S4**, the EDS indicates the homogeneous distribution of sulfur in M PBA@S.

The impact on the electrochemical performance of Co/Fe sites on the PBAs are investigated. Fig. 1a and b are the internal schematic diagrams of the tested cells. Due to the disparate adsorption abilities of different sites, the amount of active material retained on the positive electrode side is inequality. To compare the true catalysis of different metal sites through the specific capacity, carbon-coated membrane is used as the barrier layer. As shown in Fig. 1c and d, the cycling performances and rate capacities of all samples are analyzed. At the beginning of the cycle, Co PBA@S has higher specific capacity than Fe PBA@S, implying the better conversion of polysulfides by Co sites. With cycles continuing, the specific capacity of Co PBA@S starts to be lower than that of Fe PBA@S, which shows that the Co sites are not as capable of adsorbing polysulfides as the Fe sites. The better adsorption ability of Fe sites relieves polysulfides diffusion, resulting in higher capacity retention rate. For CoFe PBA@S, it exhibits greater improvement in electrochemical performance because of synergistic activity from Co and Fe centers. After 100 cycles at 0.2 A g^{-1} , the capacity retention rates of Co PBA@S and Fe PBA@S cells are 56.2% and 65.4%, respectively. Compared with them, CoFe PBA@S cell exhibits better cycle stability with a capacity retention rate of 77.3% and superior rate performance. The discharge-charge profile of the first cycle at 0.1 A g^{-1} and its enlarged view are shown in Fig. 1e and f. The specific discharge capacities of the first cycle of Co PBA@S, CoFe PBA@S, Fe PBA@S and S are 1474.9, 1428.0, 1255.6 and 925.2 mAh g^{-1} , respectively. The materials contain Co sites have higher specific capacity. What is more, the discharge curve of Co PBA@S shows peculiar characteristics, which also corresponding to the CV curve in Fig. 1g. It may indicate that the Co sites can promote the transformation of Li₂S₂ to Li₂S [30]. However, it may be the characteristics of Fe sites cover that of Co sites, so it is not reflected in the discharge curve of CoFe PBA@S. In addition, from the analysis of the oxidation peak of CV curves, it is found that the combination of Co and Fe sites is also beneficial to reduce the energy barrier of conversion from Li₂S to S. Based on these electrochemical performances, it is reasonable to speculate that the Fe sites are beneficial for the adsorption of polysulfides to improve the capacity retention rate of the long-term cycles, while the Co sites conduce to promote the liquid-solid conversion so that increase the discharge specific capacity. Hence, the electrochemical performances of CoFe PBA@S are greatly improved due to the synergistic effect of Co and Fe sites within one structure. Fig. 1h displays the discharge-charge curves at different current densities of CoFe PBA@S. Even at a high current density of 5 A g⁻¹, it still has a high specific capacity. Long-term cycle performance is tested at 2 A g^{-1} (Fig. 1i), the CoFe PBA@S electrode delivers an excellent initial capacity of 985.5 mAh g^{-1} , and after 1000 cycles, the capacity decay rate is only 0.052%, demonstrating the CoFe PBA@S has remarkable cycle stability. When increase the sulfur loading amount, the specific capacity of CoFe PBA@S will be reduced, but it still shows good performance (Fig. 1j). There is an activation

process of the electrode material with the specific capacity rising when the sulfur loading is about 5 mg cm⁻². And after 100 cycles, it still maintains 789.7 mAh g⁻¹. Besides, compared with many materials previously reported [31], the CoFe PBA@S cathode represents better electrochemical performance (**Table S1**).

In order to explore the mechanism of Co/Fe sites affecting on the electrochemical performance, a series of tests are used. The experimental research is based on the adsorption-diffusion model (Fig. 2a) [32]. At first, the static adsorption tests are executed to analyze the chemical interactions between samples and polysulfides. In Fig. 2b, acetylene black hardly changes the color of the solution, suggesting that it has no interaction with polysulfides. The color of the Li₂S₆ solutions added Fe PBA and CoFe PBA powders become almost transparent after 24 h, while the solution added Co PBA powders become darker [33,34]. These phenomena indicate that the Fe sites have a stronger adsorption effect on polysulfides, while the Co sites will dissociate the sulfur bond which is conducive to the conversion of polysulfides to Li₂S. The polysulfides adsorption capacity of the PBAs also affect the transmission speed of lithium ions in the electrolyte. The more suitable the adsorption capacity, the lower the concentration of polysulfides in the electrolyte, and the lower the viscosity of the electrolyte, which is beneficial to the diffusion of lithium ions. The results of rate-dependent CV (Fig. S5) demonstrate that Fe sites can promote better Li ion diffusion performance. The reaction pathway for LSBs without/with PBA catalysts can be illustrated with Fig. 2c. With PBAs, they can adsorb polysulfides to accelerate liquid-liquid transformation and further promote liquid-solid transformation [35]. But different metal-based PBA focus on selectively conversion phase. In Fig. 2d, there are two pairs of redox peaks related to the reaction of Li₂S₆. Peak I and peak III represent the reversible transformation between Li₂S₆ and S₈, while peak II and peak IV represent the reversible transformation from Li₂S₆ to Li₂S [36-38]. The CV curves of symmetric cells [39,40] reveal that the Fe PBA accelerates the conversion to soluble polysulfides through suitable adsorption, the Co PBA promotes the conversion of polysulfides to lithium sulfide via catalysis, and the CoFe PBA facilitates the both stages at the same time [41]. In order to analyze the liquid-solid (Li₂S_n to Li₂S₂/Li₂S) conversion process more specifically, the nucleation experiment [42,43] of lithium sulfide is carried out. In Fig. 2e, under the same voltage, the inflection point of current rise of Co PBA is earlier than that of Fe PBA, and the peak current and the integration area of Co PBA are also bigger than Fe PBA, which demonstrate that the lithium sulfide nucleation of Co PBA is faster than Fe PBA, and the Co PBA can contribute more capacity in lithium sulfide deposition. It may be attributed to the greater role of Co sites in the solid-state nucleation process [44]. After combining Co and Fe sites, the synergistic effect of CoFe PBA makes lithium sulfide easier to nucleate and grow by balanced adsorption and catalysis. In the process of liquid-solid transition, although Co sites can promote the transition to solid state, they cannot induce uniform deposition of solid substances. While the Fe sites can lead homogeneous deposition of products through adsorption. Therefore, the electrode surface of the battery with CoFe PBA catalysts is more uniform after cycling (Fig. S6). And the impedance of CoFe PBA@S cell after 100 cycles is smaller (Fig. 2f).

The *in-situ* impedance (Fig. 3a–d) of cells after cycling is used to study the multi-step reaction kinetics with solid-liquid-solid phase transition [45–47]. Such measurements are performed at different depths of charge and discharge. Taking the discharge process as an example, from the overall trend, due to the dissolution of solid sulfur, the impedance decreases rapidly with the subtraction of poor conductive sulfur at first (2.4 V-2.35 V). Then, as the voltage drops from 2.35 V to 2.25 V, the impedance gradually increases. This is because of the solution and conversion of long-chain polysulfides, which enlarges the viscosity of the electrolyte and hinders the transport of lithium ions. But from 2.25 V to 2.1 V, the impedance decreases little by little. It may be that the effect of the impedance reduction caused by the conversion of the remaining sulfur which makes the electrode surface loose and porous



Fig. 2. (a) Schematic diagram of the research model; (b) Visual adsorption test of Li₂S₆ solutions; (c) Schematic illustration of the reaction pathway for lithium-sulfur battery; (d) CV curves of symmetric cells; (e) Potentiostatic discharge curves of a Li₂S₈/tetraglyme solution; (f) Electrochemical impedance spectra after cycling.

is greater than the impedance increase caused by the raising of the viscosity of electrolyte. Subsequently, in the second discharge platform, soluble long-chain polysulfides slowly transformed into short-chain and solid Li₂S₂/Li₂S. The deposition of insulating Li₂S₂/Li₂S on the electrode surface will cause a sharp increase in impedance. In general, when the active material is in a liquid state, the charge transfer resistance is small, which is mainly controlled by diffusion of lithium ions in electrolyte. At 2.1 V during discharge process (Fig. 3e), the active substances are present in the form of soluble polysulfides. The impedances of Fe PBA@S and CoFe PBA@S are obviously smaller than Co PBA@S and S cells. It can be attributed to the Fe sites with beneficial polysulfides adsorption which reduce the viscosity of the electrolyte and increase the ion transmission rate. When the active material is in a solid state, the charge transfer is dominant. As the discharge drops to 2.05 V (Fig. 3f), the liquid active substances begin to transform into solid states. Since there are more primary insulating Li₂S₂/Li₂S on the surface of the CoFe PBA@S electrode, the impedance is bigger. This shows that combination of Co and Fe sites can best promote the liquid-solid transition. Based on the previous CV results for symmetrical cells, lithium sulfide nucleation tests and the impedance data, it reveals that Co sites can promote the generation of solid products, but they weakly capture the active substances in the liquid. While Fe sites can strongly anchor polysulfides and accelerate their transition, but without in-depth degree. Therefore, strong adsorption capacity and catalysis ability are both essential in the liquid-solid reaction process. After binding the Co and Fe sites, the adsorbed polysulfides can be quickly converted into Li2S2/Li2S. Similarly, during the charging process, combining Co and Fe sites can accelerate the dissolution of Li2S2/Li2S (Fig. 3g). From the in-situ impedance results, the CoFe PBA@S is more conducive to the deposition and dissolution of solid substances to improve electrochemical performance owing to synergistic effect of Co and Fe nodes.

To further understand the specific mechanisms of different sites, XPS measurements on M PBA before and after adsorption tests are carried

out to confirm the chemical interaction between M PBA and polysulfides. Fig. 4a is the schematic diagram of PBA and its mechanism of polysulfides adsorption inferred from XPS results. The electron cloud density of the metal center and its ligand changes with different metal atoms, which causes the various ways the M PBA materials absorb polysulfides [48]. In analysis, the carbon peak at 484.8 eV in C 1s spectrum is used for correction. For the Co 2p spectrum (Fig. 4b) [49, 50], there are two spin-orbit peaks (2p1/2 and 2p3/2), which can be divided into Co²⁺ (798.01 and 782.63 eV of Co PBA, 800.74 and 785.52 eV of CoFe PBA) and Co³⁺ (796.85 and 781.76 eV of Co PBA, 797.64 and 782.27 eV of CoFe PBA). After adsorbing Li_2S_6 solution, the binding energies of Co²⁺ (797.80 and 782.42 eV of Co PBA-Li₂S₆, 800.64 and 785.42 eV of CoFe PBA-Li₂S₆) and Co³⁺ (794.48 and 779.39 eV of Co PBA-Li₂S₆, 797.61 and 782.24 eV of CoFe PBA-Li₂S₆) are all diminished. For Fe 2p spectrum (Fig. 4c) [34,51], there are also two spin-orbit peaks which can be divided into four peaks. The four peaks of Fe PBA and CoFe PBA are at 723.84, 721.89, 710.45, 708.98 eV and 723.77, 721.42, 709.75, 708.55 eV, respectively. After Li₂S₆ adsorption, the peaks shift to 724.92, 722.97, 711.53, 710.06 eV and 723.71, 721.49, 709.69, 708.62 eV, respectively. Fig. 4d displays the Li 1s spectrum of PBAs after adsorption. There is only a small peak for Co PBA, but there are two peaks for Fe PBA and CoFe PBA. The 56.97 and 55.26 eV belong to Li-N and Li-S bonds [52-54,53] of Fe PBA. And for CoFe PBA, the two peaks are at 55.94 and 54.78 eV. Fig. 4e is the S 2p spectrum [53], which shows different sulfur bonds (sulfate, sulfide, S_T and S_B [55–57]). For Co PBA, the adsorption capacity of Co atoms for polysulfides by Co-S bonds which can easily lead to the rupture of S-S bonds. Therefore, the binding energy of Co reduced, the peak of sulfide appears in the S 2p spectrum and there is only a small peak of Li-S bond reflected in Li 1s spectrum. The sulfide generated by S-S bonds break can dissolve in the electrolyte causing the deeper color, which explains the result of the adsorption test. While for Fe PBA, the principle of adsorption is completely different. After the adsorption of polysulfides, the binding energy of Fe



Fig. 3. In-situ EIS of (a) CoFe PBA@S cell, (b) Co PBA@S cell, (c) Fe PBA@S cell and (d) pure S cell, (e-g) EIS at 2.1 V, 2.05 V during discharge process and 2.2 V during charge process.

increases, and Li-N bonds will appear, indicating that polysulfides are mainly combined through Li and N sites. In contrast, CoFe PBA combines Co and Fe sites to balance the electron cloud density and show different characteristics. The Co^{2+} and Co^{3+} peaks all shift to lower binding energies. The same as the Fe³⁺. While the Fe²⁺ shift to higher binding energies. The combination of Li and N is stronger, and the combination of metal and S is also enhanced, demonstrating the CoFe PBA has better dual-anchoring capability to lithium polysulfides [58]. The appropriate adsorption capacities through both Li-N and M-S bonds hinder the diffusion of polysulfides, so that CoFe PBA@S cells have remarkable capacity retention rates. Furthermore, the bonding methods are further verified in subsequent theoretical calculations.

The density functional theory (DFT) calculations are carried out to explore the adsorption mechanism of catalysts. After calculating the

adsorption configurations and energies of Li₂S₆ with different orientations on Fe PBA (**Fig. S7**), Co PBA (**Fig. S8**) and CoFe PBA (**Fig. S9**). The most stable adsorption structures are shown in Fig. 5a–c. The binding energies of Fe PBA- Li₂S₆, Co PBA- Li₂S₆ and CoFe PBA- Li₂S₆ are -4.005 Ev, -2.584 eV and -3.363 eV, respectively, indicating the adsorption capacity Fe PBA > CoFe PBA > Co PBA, which matches the results of the visual adsorption test. And it is evident that there is almost no chemical bond between Fe and S ion in Fe PBA-Li₂S₆ (bond length of Fe-S is 3.56Å and bond order is almost zero), while Li ions are tightly bound to N atoms (shortest Li-N bond length is 2.04 Å). Besides, the frame structure of cyano-group is visibly deformed. On the contrary, Co and S atoms form strong chemical bonds in Co PBA-Li₂S₆ (bond length of Co²⁺-S and Co³⁺-S are 2.34Å and 2.31Å, respectively, bond orders are 0.501 and 0.924, respectively), while Li ions bond weakly with N atoms (shortest



Fig. 4. (a) Schematic diagram of M PBA and its mechanism of polysulfides adsorption, High-resolution XPS spectra of (b) Co 2p, (c) Fe 2p, (d) Li 1s, (e) S 2p.

Li-N bond length is 2.10 Å). Moreover, the basic framework of catalyst surface almost unchanged. For CoFe PBA-Li₂S₆, it is more complicated. The bonding situation can also be verified in the differential charge density map (Fig. 5d-f), more electrons are concentrated between Li and N atoms in Fe PBA-Li₂S₆ while more electrons are concentrated between Co and S atoms in Co PBA-Li₂S₆. For CoFe PBA-Li₂S₆, the electrons are concentrated both between Co, S atoms and Li, N atoms. It is obvious that the chemical interaction of Li₂S₆ species on Fe PBA, Co PBA and CoFe PBA are via Li-N, Co-S, and Li-N/Co-S bonds, respectively. In order to investigate why the adsorption orientation of Li₂S₆ is significantly different on these catalysts with similar structure, an analysis focus on the bonding and electron distribution of the catalysts were performed. The spin density of catalysts and d-orbital distributions of Fe^{3+} , Co^{2+} and Fe²⁺ with unpaired electron are analyzed (Fig. 5g–i). In Fe PBA, the magnetic moments of Fe atoms are 4.3 emu (5 unpaired electron) and 0.0 emu (0 unpaired electron), respectively. While in Co PBA, the magnetic moments of Co atoms are 0.93 emu (1 unpaired electron) and 0.0 emu (0 unpaired electron), respectively. Therefore, it is speculated that the unit structures are Fe^{II}-C-N-Fe^{III} in Fe PBA and Co^{III}-C-N-Co^{II} in Co PBA. For CoFe PBA, its unstable structure will decompose into the above two and the stable structure is dominated by Co^{III}-C-N-Fe^{II}. It can be seen that the distribution of unpaired electron of Fe^{3+}/Fe^{2+} and Co^{2+} ions are spherical and spindle plus ring shape, respectively. According to the Crystal-Field theory, the arrangements of d-electron are obtained. For Fe³⁺/Fe²⁺, all five d orbitals are occupied, while for Co²⁺, the $d_{x^2-y^2}$ orbital is not occupied, which means that Co²⁺ had a prominent Jahn-Teller effect, resulting in weaker repulsion force in x/y-axis directions than $Fe^{3+}/Fe^{2+}.$ So Co^{2+} has stronger bonds with N atoms in the same layer, which is proved by bond orders shown in Fig. 5i–l. The bind orders of Co-N (0.580, 0.700, 0.612, 0.700) in Co PBA are significantly higher than Fe-N (0.383, 0.548, 0.416, 0.548) in Fe PBA. Hence, the Fe-N bond is easier to deform and break while absorbing Li₂S₆, facilitating the formation of Li-N ionic bonds. The strong combination of Li and N greatly limits the spatial orientation of Li₂S₆, leading to weak bonding of Fe and S atoms. In contrast, Co-N bonding is more stable and the Li-N bonding is weak, so it is easier for Co atoms to connect with S atoms in Co PBA-Li₂S₆, causing the S-S bond more liable to fracture. For CoFe PBA-Li₂S₆, it combines the above two bonding methods. It is found that for catalysts with similar crystal structures, the catalytic ability depends not only on the central atom itself but also on the surface structural stability determined by the bond strength of the ligands and central atoms. which provides a new insight for catalyst design. In conclusion, the Fe PBA adsorbs polysulfides through Li-N bonds, while Co PBA adsorbs polysulfides mainly through Co-S bonds. For CoFe PBA, it adsorbs polysulfides through both Li-N and Co-S bonds. In addition, the binding energies with various polysulfides (Fig. S10a) are also presented and the relative energies (Fig. S10b) are calculated based on them. For the step from S₈ to Li₂S₈, Fe PBA has smaller reaction energy barrier than Co PBA, while from Li_2S_4 to Li_2S_2 , the energy barrier of Co PBA is lower than Fe PBA, which demonstrate the Fe PBA is beneficial to accelerate the conversion of long-chain polysulfides, and Co PBA contributes to the conversion of short-chain polysulfides. It is consistent with the previous CV conclusion of symmetrical cells. The results show that the adsorption energies are closely related to the reaction energy barriers. Therefore, when designing catalysts, it is necessary to balance adsorption and catalysis.



Fig. 5. Adsorption configurations and energies of Li₂S₆ on (a) Fe PBA, (b) Co PBA and (c) CoFe PBA, Differential charge density of (d) Fe PBA-Li₂S₆, (e) Co PBA-Li₂S₆ and (f) CoFe PBA-Li₂S₆, Distribution of spin density and orbital of (g) Fe PBA, (h) Co PBA and (i) CoFe PBA, The bond order and length parameters of (j) Fe PBA, Fe PBA-Li₂S₆, (k) Co PBA, Co PBA-Li₂S₆ and (l) CoFe PBA, CoFe PBA-Li₂S₆.

The in-situ Raman spectroscopy [59] is employed to monitor the changes of active materials during discharge-charge process. As shown in Fig. 6a, CR2016 coin cell with a drilled hole is placed in a sealed device with a quartz window for measurement. There are 12 and 3 positions which are selected for data analysis on discharge and charge curves marked as F1-F12 and C1-C3, respectively. During the charging process (Fig. 6b-e), the sulfur signals with different intensity are detected in all cells, thus we pay little attention to the charging process. In contrast, the discharge process is significantly different (Fig. 6f-i). At the open-circuit voltage (OCV) for all cells, the detected peaks at 152, 219 and 473 cm⁻¹ belong to elemental sulfur (S₈) [60,61]. After the discharge begins, the voltage gradually drops, the new peaks located at 200, 400 and 451 cm^{-1} appear, because the solid sulfur is dissolved in the electrolyte and transformed into polysulfides (Li_2S_n) [62]. The other new peak near 500 cm⁻¹ at the second plateau is attributed to the formation of Li₂S₂ [63]. Of interest, after the sulfur peak disappeared completely, there gradually began to detect a special peak around 282 cm⁻¹ for Co PBA@S and CoFe PBA@S cells, which is considered as the dynamically changing catalyst. But S and Fe PBA @S cells do not have this peak. And it is the same of peak at 345 cm^{-1} which may be assigned to conversion to Li₂S. At the end of discharge (F12), the S and Fe PBA@S

cells still have strong peaks of Li₂S_n, indicating the sluggish liquid-solid conversion. By contrast, the Co PBA@S and CoFe PBA@S cells have better conversion from Li₂S_n to Li₂S₂/Li₂S with weaker Li₂S_n peaks and stronger Li₂S₂/Li₂S peaks, which is contributed by the intermediate catalyst [64]. From a comprehensive comparison, the addition of positive electrode additives is beneficial to the transition from solid sulfur to liquid Li₂S_n. But when the liquid polysulfides are converted to solid Li₂S₂/Li₂S, Co PBA@S and CoFe PBA@S cells show better characteristics. Therefore, they have higher capacities.

3. Conclusion

In conclusion, metal-based PBAs are used as cathode additives to adsorb polysulfides and catalyze their conversion. In this work, the mechanism of different metal sites is studied. The results show that Fe sites change the electron cloud density of the surrounding ligands so that polysulfides can form stronger adsorption through Li-N bonds, which can relieve the polysulfides shuttling and reduce the loss of active substances. The strong adsorption ability can assist the liquid phase reaction to improve capacity retention rate. While Co sites can absorb polysulfides through Co-S bonds and catalyze the lithium sulfide deposition



Fig. 6. (a) Schematic diagram of the test points location on the discharge-charge curves and device of *in-situ* Raman cell. Raman spectra of (b) S (c) Co PBA@S (d) Fe PBA@S (e) CoFe PBA@S cell during charge process. Raman spectra of (f) S (g) Co PBA@S (h) Fe PBA@S (i) CoFe PBA@S cell during discharge process.

with dynamic intermediate catalyst to enhance the specific discharge capacity. What is more, CoFe PBA possess two catalytic sites in tandem within one structure, which promote reactions of both stages through Li-N and Metal-S bonds. Benefiting from the synergy of Co and Fe nodes, the CoFe PBA@S cathode represents the best electrochemical performance. Therefore, we can control the bonding method and strength of adsorption by choosing various metal centers with different catalytic activities to synergistically balance the relationship between adsorption and catalysis to obtain the helpful electrocatalyst for effectively performance improvement. This research provides a new view on the design of catalyst additives for LSBs.

CRediT authorship contribution statement

Yu Chen: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft. Yuanhong Kang: Data curation, Formal analysis, Visualization, Writing – review & editing. Huiya Yang: Data curation, Writing – review & editing. Haiming Hua: Methodology, Visualization, Writing – review & editing. Jiaxiang Qin: Software, Validation. Peng Liu: Software, Validation. Yiyong Zhang: Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing. Yingjie Zhang: Resources, Supervision. Jinbao Zhao: Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge the National Natural Science Foundation of China (21875198), the Key Project of Science and Technology of Xiamen (3502Z20201013), the Applied Basic Research Plan of Yunnan Province (202001AU070079, 202101BE070001-018, 202101AT070214) and the Key Research and Development Program of Yunnan Province (202103AA080019).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ensm.2022.10.047.

References

- S.H. Chung, C.H. Chang, A. Manthiram, Progress on the critical parameters for lithium-sulfur batteries to be practically viable, Adv. Funct. Mater. 28 (2018), 1801188, https://doi.org/10.1002/adfm.201801188.
- [2] Z. Li, L. Yuan, Z. Yi, Y. Sun, Y. Liu, Y. Jiang, Y. Shen, Y. Xin, Z. Zhang, Y. Huang, Insight into the electrode mechanism in lithium-sulfur batteries with ordered microporous carbon confined sulfur as the cathode, Adv. Energy Mater. 4 (2014), 1301473, https://doi.org/10.1002/aenm.201301473.
- [3] C. Deng, Z. Wang, S. Wang, J. Yu, Inhibition of polysulfide diffusion in lithiumsulfur batteries: mechanism and improvement strategies, J. Mater. Chem. A 7 (2019) 12381–12413, https://doi.org/10.1039/C9TA00535H.
- [4] S. Chen, J. Luo, N. Li, X. Han, J. Wang, Q. Deng, Z. Zeng, S. Deng, Multifunctional LDH/Co₉S₈ heterostructure nanocages as high-performance lithium-sulfur battery cathodes with ultralong lifespan, Energy Storage Mater. 30 (2020) 187–195, https://doi.org/10.1016/j.ensm.2020.05.002.
- [5] L. Luo, J. Li, H. Yaghoobnejad Asl, A. Manthiram, *In-situ* assembled VS₄ as a polysulfide mediator for high-loading lithium-sulfur batteries, ACS Energy Lett. 5 (2020) 1177–1185, https://doi.org/10.1021/acsenergylett.0c00292.
- [6] J. Lin, K. Zhang, Z. Zhu, R. Zhang, N. Li, C. Zhao, CoP/C nanocubes-modified separator suppressing polysulfide dissolution for high-rate and stable lithium-sulfur batteries, ACS Appl. Mater. Interfaces 12 (2020) 2497–2504, https://doi.org/ 10.1021/acsami.9b18723.
- [7] S. Hu, M. Yi, H. Wu, T. Wang, X. Ma, X. Liu, J. Zhang, Ionic-liquid-assisted synthesis of N, F, and B Co-Doped CoFe₂O_{4-X} on multiwalled carbon nanotubes with enriched oxygen vacancies for Li-S batteries, Adv. Funct. Mater. 32 (2022), 2111084, https://doi.org/10.1002/adfm.202111084.
- [8] Z. Han, S. Zhao, J. Xiao, X. Zhong, J. Sheng, W. Lv, Q. Zhang, G. Zhou, H.M. Cheng, Engineering d-p orbital hybridization in single-atom metal-embedded threedimensional electrodes for Li-S batteries, Adv. Mater. 33 (2021), 2105947, https:// doi.org/10.1002/adma.202105947.
- [9] H. Ye, J.Y. Lee, Solid additives for improving the performance of sulfur cathodes in lithium-sulfur batteries – adsorbents, mediators, and catalysts, Small Methods 4 (2020), 1900864, https://doi.org/10.1002/smtd.201900864.
- [10] G. Xia, J. Ye, Z. Zheng, X. Li, C. Chen, C. Hu, Catalytic FeP decorated carbon black as a multifunctional conducting additive for high-performance lithium-sulfur batteries, Carbon 172 (2021) 96–105, https://doi.org/10.1016/j. carbon.2020.09.094.
- [11] P. Zeng, C. Liu, X. Zhao, C. Yuan, Y. Chen, H. Lin, L. Zhang, Enhanced catalytic conversion of polysulfides using bimetallic Co₇Fe₃ for high-performance lithiumsulfur batteries, ACS Nano 14 (2020) 11558–11569, https://doi.org/10.1021/ acsnano.0c04054.
- [12] F. Ma, Y. Wan, X. Wang, X. Wang, J. Liang, Z. Miao, T. Wang, C. Ma, G. Lu, J. Han, Y. Huang, Q. Li, Bifunctional atomically dispersed Mo-N₂/C nanosheets boost lithium sulfide deposition/decomposition for stable lithium-sulfur batteries, ACS Nano 14 (2020) 10115–10126, https://doi.org/10.1021/acsnano.0c03325.
- [13] M. Wang, L. Fan, X. Sun, B. Guan, B. Jiang, X. Wu, D. Tian, K. Sun, Y. Qiu, X. Yin, Y. Zhang, N. Zhang, Nitrogen-doped CoSe₂ as a bifunctional catalyst for high areal capacity and lean electrolyte of Li-S battery, ACS Energy Lett. 5 (2020) 3041–3050, https://doi.org/10.1021/acsenergylett.0c01564.
- [14] H.M. Kim, J.Y. Hwang, S. Bang, H. Kim, M.H. Alfaruqi, J. Kim, C.S. Yoon, Y.K. Sun, Tungsten oxide/zirconia as a functional polysulfide mediator for high-performance lithium-sulfur batteries, ACS Energy Lett. 5 (2020) 3168–3175, https://doi.org/ 10.1021/acsenergylett.0c01511.
- [15] Z. Shi, Z. Sun, J. Cai, Z. Fan, J. Jin, M. Wang, J. Sun, Boosting dual-directional polysulfide electrocatalysis via bimetallic alloying for printable Li-S batteries, Adv. Funct. Mater. 31 (2021), 2006798, https://doi.org/10.1002/adfm.202006798.
- [16] L. Zhou, D.L. Danilov, R.A. Eichel, P.H.L. Notten, Host materials anchoring polysulfides in Li-S batteries reviewed, Adv. Energy Mater. 11 (2021), 2001304, https://doi.org/10.1002/aenm.202001304.
- [17] C. X. Zhao, B.Q. Li, J.N. Liu, Q. Zhang, Intrinsic electrocatalytic activity regulation of M-N-C single-atom catalysts for the oxygen reduction reaction, Angew. Chem. Int. Ed. 60 (2021) 4448–4463, https://doi.org/10.1002/anie.202003917.
- [18] I.H. Kim, J. Lim, S.O. Kim, Discovery of single-atom catalyst: Customized heteroelement dopants on graphene, Acc. Mater. Res. 2 (2021) 394–406, https:// doi.org/10.1021/accountsmr.1c00016.

- [19] D. Fang, Y. Wang, C. Qian, X. Liu, X. Wang, S. Chen, S. Zhang, Synergistic regulation of polysulfides conversion and deposition by MOF-derived hierarchically ordered carbonaceous composite for high-energy lithium-sulfur batteries, Adv. Funct. Mater. 29 (2019), 1900875, https://doi.org/10.1002/ adfm.201900875.
- [20] J. Wang, W. Qiu, G. Li, J. Liu, D. Luo, Y. Zhang, Y. Zhao, G. Zhou, L. Shui, X. Wang, Z. Chen, Coordinatively deficient single-atom Fe-N-C electrocatalyst with optimized electronic structure for high-performance lithium-sulfur batteries, Energy Storage Mater. 46 (2022) 269–277, https://doi.org/10.1016/j. ensm.2021.12.040.
- [21] N. Gao, Y. Zhang, C. Chen, B. Li, W. Li, H. Lu, L. Yu, S. Zheng, B. Wang, Lowtemperature Li-S battery enabled by CoFe bimetallic catalysts, J. Mater. Chem. A 10 (2022) 8378–8389, https://doi.org/10.1039/D2TA00406B.
- [22] Y. Wang, L. Zhu, J. Wang, Z. Zhang, J. Yu, Z. Yang, Enhanced chemisorption and catalytic conversion of polysulfides via CoFe@NC nanocubes modified separator for superior Li-S batteries, Chem. Eng. J. 433 (2022), 133792, https://doi.org/ 10.1016/j.cej.2021.133792.
- [23] J. Chen, L. Wei, A. Mahmood, Z. Pei, Z. Zhou, X. Chen, Y. Chen, Prussian blue, its analogues and their derived materials for electrochemical energy storage and conversion, Energy Storage Mater. 25 (2020) 585–612, https://doi.org/10.1016/j. ensm.2019.09.024.
- [24] K. Hurlbutt, S. Wheeler, I. Capone, M. Pasta, Prussian blue analogs as battery materials, Joule 2 (2018) 1950–1960, https://doi.org/10.1016/j. joule.2018.07.017.
- [25] Y. Peng, B. Li, Y. Wang, X. He, J. Huang, J. Zhao, Prussian blue: a potential material to improve the electrochemical performance of lithium-sulfur batteries, ACS Appl. Mater. Interfaces 9 (2017) 4397–4403, https://doi.org/10.1021/ acsami.6b06890.
- [26] X. Song, S. Song, D. Wang, H. Zhang, Prussian blue analogs and their derived nanomaterials for electrochemical energy storage and electrocatalysis, Small Methods 5 (2021), 2001000, https://doi.org/10.1002/smtd.202001000.
- [27] M. Du, X. Wang, P. Geng, Q. Li, Y. Gu, Y. An, H. Pang, Polypyrrole-enveloped Prussian blue nanocubes with multi-metal synergistic adsorption toward lithium polysulfides: high-performance lithium-sulfur batteries, Chem. Eng. J. 420 (2021), https://doi.org/10.1016/j.cej.2021.130518.
- [28] H. Jo, Y. Cho, T. Yoo, Y. Jeon, H. Hong, Y. Piao, Polyaniline-encapsulated hollow Co-Fe Prussian blue analogue nanocubes modified on a polypropylene separator to improve the performance of lithium-sulfur batteries, ACS Appl. Mater. Interfaces 13 (2021) 47593–47602, https://doi.org/10.1021/acsami.lc12855.
- [29] Y. Chen, J. Li, X. Kong, Y. Zhang, Y. Zhang, J. Zhao, Enhancing catalytic conversion of polysulfides by hollow bimetallic oxide-based heterostructure nanocages for lithium-sulfur batteries, ACS Sustain. Chem. Eng. 9 (2021) 10392–10402, https:// doi.org/10.1021/acssuschemeng.1c04036.
- [30] H. Lin, S. Zhang, T. Zhang, S. Cao, H. Ye, Q. Yao, G.W. Zheng, J.Y. Lee, A Cathodeintegrated sulfur-deficient Co₉S₈ catalytic interlayer for the reutilization of "lost" polysulfides in lithium-sulfur batteries, ACS Nano 13 (2019) 7073–7082, https:// doi.org/10.1021/acsnano.9b02374.
- [31] S.H. Chung, A. Manthiram, Lithium-sulfur batteries with the lowest self-discharge and the longest shelf life, ACS Energy Lett. 2 (2017) 1056–1061, https://doi.org/ 10.1021/acsenergylett.7b00245.
- [32] X. Tao, J. Wang, C. Liu, H. Wang, H. Yao, G. Zheng, Z.W. Seh, Q. Cai, W. Li, G. Zhou, C. Zu, Y. Cui, Balancing surface adsorption and diffusion of lithiumpolysulfides on nonconductive oxides for lithium-sulfur battery design, Nat. Commun. 7 (2016) 11203, https://doi.org/10.1038/ncomms11203.
- [33] S. Feng, H. Zhong, J. Song, C. Zhu, P. Dong, Q. Shi, D. Liu, J. Li, Y..C. Chang, S. P. Beckman, M.k. Song, D. Du, Y. Lin, Catalytic activity of Co-X (X = S, P, O) and its dependency on nanostructure/chemical composition in lithium-sulfur batteries, ACS Appl. Energy Mater. 1 (2018) 7014–7021, https://doi.org/10.1021/acsaem.8b01434.
- [34] Z. Qiao, Y. Zhang, Z. Meng, Q. Xie, L. Lin, H. Zheng, B. Sa, J. Lin, L. Wang, D. L. Peng, Anchoring polysulfides and accelerating redox reaction enabled by Febased compounds in lithium-sulfur batteries, Adv. Funct. Mater. 31 (2021), 2100970, https://doi.org/10.1002/adfm.202100970.
- [35] H. Yuan, H.J. Peng, B.Q. Li, J. Xie, L. Kong, M. Zhao, X. Chen, J.Q. Huang, Q. Zhang, Conductive and catalytic triple-phase interfaces enabling uniform nucleation in high-rate lithium-sulfur batteries, Adv. Energy Mater. 9 (2019), 1802768, https://doi.org/10.1002/aenm.201802768.
- [36] Y. Li, J. Wu, B. Zhang, W. Wang, G. Zhang, Z.W. Seh, N. Zhang, J. Sun, L. Huang, J. Jiang, J. Zhou, Y. Sun, Fast conversion and controlled deposition of lithium (poly)sulfides in lithium-sulfur batteries using high-loading cobalt single atoms, Energy Storage Mater. 30 (2020) 250–259, https://doi.org/10.1016/j. ensm.2020.05.022.
- [37] H. Lin, L. Yang, X. Jiang, G. Li, T. Zhang, Q. Yao, G.W. Zheng, J.Y. Lee, Electrocatalysis of polysulfide conversion by sulfur-deficient MoS₂ nanoflakes for lithium-sulfur batteries, Energy Environ. Sci. 10 (2017) 1476–1486, https://doi. org/10.1039/C7EE01047H.
- [38] H. Lin, S. Zhang, T. Zhang, H. Ye, Q. Yao, G.W. Zheng, J.Y. Lee, Simultaneous cobalt and phosphorous doping of MoS₂ for improved catalytic performance on polysulfide conversion in lithium-sulfur batteries, Adv. Energy Mater. 9 (2019), 1902096, https://doi.org/10.1002/aenm.201902096.
- [39] J. Zhou, X. Liu, L. Zhu, J. Zhou, Y. Guan, L. Chen, S. Niu, J. Cai, D. Sun, Y. Zhu, J. Du, G. Wang, Y. Qian, Deciphering the modulation essence of p bands in Cobased compounds on Li-S chemistry, Joule 2 (2018) 2681–2693, https://doi.org/ 10.1016/j.joule.2018.08.010.
- [40] Z. Yuan, H.J. Peng, T.Z. Hou, J.Q. Huang, C.M. Chen, D.W. Wang, X.B. Cheng, F. Wei, Q. Zhang, Powering lithium-sulfur battery performance by propelling

polysulfide redox at sulfiphilic hosts, Nano Lett. 16 (2016) 519–527, https://doi.org/10.1021/acs.nanolett.5b04166.

- [41] H. Ye, J. Sun, S. Zhang, H. Lin, T. Zhang, Q. Yao, J.Y. Lee, Stepwise electrocatalysis as a strategy against polysulfide shuttling in Li-S batteries, ACS Nano 13 (2019) 14208–14216, https://doi.org/10.1021/acsnano.9b07121.
- [42] F.Y. Fan, W.C. Carter, Y.M. Chiang, Mechanism and kinetics of Li₂S precipitation in lithium-sulfur batteries, Adv. Mater. 27 (2015) 5203–5209, https://doi.org/ 10.1002/adma.201501559.
- [43] Y.X. Ren, T.S. Zhao, M. Liu, P. Tan, Y.K. Zeng, Modeling of lithium-sulfur batteries incorporating the effect of Li₂S precipitation, J. Power Sources 336 (2016) 115–125, https://doi.org/10.1016/j.jpowsour.2016.10.063.
- [44] R. Meng, Q. Du, N. Zhong, X. Zhou, S. Liu, S. Yin, X. Liang, A tandem electrocatalysis of sulfur reduction by bimetal 2D MOFs, Adv. Energy Mater. 11 (2021), 2102819, https://doi.org/10.1002/aenm.202102819.
- [45] N.A. Cañas, K. Hirose, B. Pascucci, N. Wagner, K.A. Friedrich, R. Hiesgen, Investigations of lithium-sulfur batteries using electrochemical impedance spectroscopy, Electrochim. Acta 97 (2013) 42–51, https://doi.org/10.1016/j. electacta.2013.02.101.
- [46] J. Conder, C. Villevieille, S. Trabesinger, P. Novák, L. Gubler, R. Bouchet, Electrochemical impedance spectroscopy of a Li-S battery: Part 1. Influence of the electrode and electrolyte compositions on the impedance of symmetric cells, Electrochim. Acta 244 (2017) 61–68, https://doi.org/10.1016/j. electacta.2013.02.101.
- [47] Y.W. Song, Y.Q. Peng, M. Zhao, Y. Lu, J.N. Liu, B.Q. Li, Q. Zhang, Understanding the impedance response of lithium polysulfide symmetric cells, Small Sci. 1 (2021), 2100042, https://doi.org/10.1002/smsc.202100042.
- [48] X. Chen, H.J. Peng, R. Zhang, T.Z. Hou, J.Q. Huang, B. Li, Q. Zhang, An analogous periodic law for strong anchoring of polysulfides on polar hosts in lithium sulfur batteries: S- or Li-binding on first-row transition-metal sulfides? ACS Energy Lett. 2 (2017) 795–801, https://doi.org/10.1021/acsenergylett.7b00164.
- [49] L. Kang, H. Ren, Z. Xing, Y. Zhao, Z. Ju, Hierarchical porous Co_xFe_{3-x}O₄ nanocubes obtained by calcining Prussian blue analogues as anodes for lithium-ion batteries, New J. Chem. 44 (2020) 12546–12555, https://doi.org/10.1039/D0NJ01027H.
- [50] W. Wang, J. Li, Q. Jin, Y. Liu, Y. Zhang, Y. Zhao, X. Wang, A. Nurpeissova, Z. Bakenov, Rational construction of sulfur-deficient NiCo₂S_{4-x} hollow microspheres as an effective polysulfide immobilizer toward high-performance lithium/sulfur batteries, ACS Appl. Energy Mater. 4 (2021) 1687–1695, https:// doi.org/10.1021/acsaem.0c02839.
- [51] X. Chen, S. Zeng, H. Muheiyati, Y. Zhai, C. Li, X. Ding, L. Wang, D. Wang, L. Xu, Y. He, Y. Qian, Double-shelled Ni-Fe-P/N-doped carbon nanobox derived from a Prussian blue analogue as an electrode material for K-ion batteries and Li-S batteries, ACS Energy Lett. 4 (2019) 1496–1504, https://doi.org/10.1021/ acsenergylett.9b00573.
- [52] J.H. Park, K.M. Choi, D.K. Lee, B.C. Moon, S.R. Shin, M.K. Song, J.K. Kang, Encapsulation of redox polysulphides via chemical interaction with nitrogen atoms

in the organic linkers of metal-organic framework nanocrystals, Sci. Rep. 6 (2016) 25555, https://doi.org/10.1038/srep25555.

- [53] G. Li, F. Lu, X. Dou, X. Wang, D. Luo, H. Sun, A. Yu, Z. Chen, Polysulfide regulation by the zwitterionic barrier toward durable lithium-sulfur batteries, J. Am. Chem. Soc. 142 (2020) 3583–3592, https://doi.org/10.1021/jacs.9b13303.
- [54] Z.W. Seh, H. Wang, P.C. Hsu, Q. Zhang, W. Li, G. Zheng, H. Yao, Y. Cui, Facile synthesis of Li₂S-polypyrrole composite structures for high-performance Li₂S cathodes, Energy Environ. Sci. 7 (2014) 672–676, https://doi.org/10.1039/ C3EE43395A.
- [55] X. Liang, C. Hart, Q. Pang, A. Garsuch, T. Weiss, L.F. Nazar, A highly efficient polysulfide mediator for lithium-sulfur batteries, Nat. Commun. 6 (2015) 5682, https://doi.org/10.1038/ncomms6682.
- [56] I.J. Kartio, C.I. Basilio, R.H. Yoon, An XPS study of sphalerite activation by copper, Langmuir 14 (1998) 5274–5278, https://doi.org/10.1021/la970440c.
- [57] Q. Pang, D. Kundu, M. Cuisinier, L.F. Nazar, Surface-enhanced redox chemistry of polysulphides on a metallic and polar host for lithium-sulphur batteries, Nat. Commun. 5 (2014) 4759, https://doi.org/10.1038/ncomms5759.
- [58] X. Song, D. Tian, Y. Qiu, X. Sun, B. Jiang, C. Zhao, Y. Zhang, X. Xu, L. Fan, N. Zhang, Efficient polysulfide trapping and conversion on N-doped CoTe₂ via enhanced dual-anchoring effect, Small 17 (2021), 2102962, https://doi.org/ 10.1002/smll.202102962.
- [59] W. Zhu, A. Paolella, C.S. Kim, D. Liu, Z. Feng, C. Gagnon, J. Trottier, A. Vijh, A. Guerfi, A. Mauger, C.M. Julien, M. Armand, K. Zaghib, Investigation of the reaction mechanism of lithium sulfur batteries in different electrolyte systems by *in situ* Raman spectroscopy and *in situ* X-ray diffraction, Sustain. Energy Fuels 1 (2017) 737–747, https://doi.org/10.1039/C6SE00104A.
- [60] M. Hagen, P. Schiffels, M. Hammer, S. Dörfler, J. Tübke, M.J. Hoffmann, H. Althues, S. Kaskel, *In-situ* Raman investigation of polysulfide formation in Li-S cells, J. Electrochem. Soc. 160 (2013) A1205–A1214, https://doi.org/10.1149/ 2.045308jes.
- [61] J.T. Yeon, J.Y. Jang, J.G. Han, J. Cho, K.T. Lee, N.S. Choi, Raman spectroscopic and X-ray diffraction studies of sulfur composite electrodes during discharge and charge, J. Electrochem. Soc. 159 (2012) A1308–A1314, https://doi.org/10.1149/ 2.080208jes.
- [62] N. Li, L. Yu, J. Yang, B. Zheng, X. Qiu, J. Xi, Identifying the active sites and multifunctional effects in nitrogen-doped carbon microtube interlayer for confining-trapping-catalyzing polysulfides, Nano Energy 79 (2021), 105466, https://doi.org/10.1016/j.nanoen.2020.105466.
- [63] J.J. Chen, R.M. Yuan, J.M. Feng, Q. Zhang, J.X. Huang, G. Fu, M.S. Zheng, B. Ren, Q.F. Dong, Conductive lewis base matrix to recover the missing link of Li₂S₈ during the sulfur redox cycle in Li-S battery, Chem. Mater. 27 (2015) 2048–2055, https:// doi.org/10.1021/cm5044667.
- [64] W. Hua, H. Li, C. Pei, J. Xia, Y. Sun, C. Zhang, W. Lv, Y. Tao, Y. Jiao, B. Zhang, S. Z. Qiao, Y. Wan, Q.H. Yang, Selective catalysis remedies polysulfide shuttling in lithium-sulfur batteries, Adv. Mater. 33 (2021), 2101006, https://doi.org/10.1002/adma.202101006.