A review of metal catalysts for lithium-sulfur battery applications

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Abstract. When compared to ordinary lithium batteries now on the market, lithium-sulfur batteries stand out as the future research direction for energy storage systems owing to their higher volumetric energy density, theoretical specific energy, and gravimetric energy density. However, Li-S batteries' drawbacks have significantly impeded their use and commercialization. A series of problems such as shuttle effects and volume expansion can remarkably reduce the service lifespan of Li-S batteries. By adding metal catalysts to the positive electrode of Li-S batteries, it is possible to improve the reaction kinetics of these batteries and efficiently address issues like the shuttle effect. During the paper, metal catalysts are separated into three groups based on the many ways they express themselves: metal single-atom catalysts, metal nanocatalysts, and metal compound catalysts. Metal single atom catalysts have catalytic active sites that are shaped like a single metal atom. Metal nanocatalysts are catalysts composed of metal particles with a size of 1-100 nm. Metal compound catalysts refer to catalysts composed of compounds formed by metals and other elements (such as oxygen, nitrogen, sulfur, etc.), including metal oxides, metal nitrides, metal sulfides, etc. It also lists and summarises the research progress of previous generations for the reference of related personnel.

1 Introduction

In this day and age, the continued consumption of fossil energy sources and the environmental problems they bring have led to a growing focus on new and clean energy sources. High-performance energy storage systems are becoming more and more in demand, and the battery field is attracting much attention and developing rapidly. Among them, lithium-ion batteries are widely used commercially by virtue of their unique advantages. However, the existing commercial lithium-ion batteries' energy density (200–300 Wh kg^{-1}) is still inadequate, and the high production cost (> $300 kW-1h-1) has failed to meet current demand within the market, significantly restricting their promotion. Therefore, the development of the elevated energy density batteries as a new generation of energy storage systems has become an urgent task. Lithium-sulfur batteries are gradually gaining focus because of their high gravimetric energy density (2600 Wh kg^{-1}), elevated theoretical specific capacity (1675 mA h g^{-1}) and high volumetric energy density (2800 Wh L^{-1} ,assuming a

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2.15V average voltage). Nevertheless, the commercialisation of lithium-sulfur batteries has not yet occurred, mainly due to problems with electron/ion insulation, shuttle effects as well as volume growth of the cathode material of monomeric sulfur and its product sulfide. Li2S, the discharge product, and sulphur are both electrical insulators, so the reaction must be facilitated by the introduction of a conductive substrate to promote a smooth reaction. Secondly, the conversion reaction of sulphur is multistep and results in the development of a variety of soluble polysulphide intermediates (Li2Sx,4 $\leqslant$ x $\leqslant$ 8), which have the opportunity to traverse the separator to the exterior of the lithium metal anode as a soluble substance and react with lithium on the lithium metal anode's surface to be reduced to a solid deposit, leading to a self-discharge. In addition, the lithium precipitates will return to the cathode surface to undergo oxidation again, causing the active sulphur and lithium metal to be lost.. Since Li_2S_2 and Li_2S occur in solid form, the interconversion of the two is very slow, resulting in slow overall kinetics. It has been found that the efficient conversion of polysulfides can be effectively promoted by introducing various catalytic substances at different parts of the Li-S battery. Among them, boosting the reaction kinetics of Li-S batteries by introducing metal catalysts at the anode is a major research hotspot. The introduction of metal catalysts can impede the lithium polysulphide shuttle, improve the sulfur utilisation as much as possible by speeding up the sulfur redox process in addition to enhance the lithium-sulfur batteries' overall performance.

This paper classifies and describes the metal catalysts used in lithium-sulfur batteries. Additionally, prior research advancements in this area are presented for the benefit of researchers in related domains.

2 Metal monoatomic catalysts

While an increase in the bulk metal-based materials' weight ratio can improve the utilisation of sulphur in lithium-sulfur batteries, the introduction of inactive components reduces the sulphur loading rate, thus decreasing polysulphide conversion and battery energy density. Single-atom catalysts (SACs), which comprise uniformly scattered metal sites with excellent catalytic performance and close to 100% atom utilization, can effectively alleviate this problem. The introduction of single atom catalysts does not sacrifice the cathode's sulphur ratio, thus increasing the energy density of lithium-sulfur batteries. The unsaturated coordination environment and distinct electronic structure of single-atom catalysts endow them with obvious catalytic advantages, which make them more competitive than traditional catalysts. Since single atoms have high free energy, in order to preserve structural stability, they are typically coordinated with other atoms (such as N and O). By anchoring atomically dispersed metal atoms on various carbon substrates, the redox reaction of sulfur can be catalyzed efficiently. SACs were first reported in 2011, and scientists have developed and designed a number of different high-quality SACs through many different synthesis methods. Currently, a number of SACs have been synthesized that can exhibit electrocatalytic activities better than those of metal nanoparticles. Their use in Li-S batteries is currently in the investigation stage, though[1]. Currently, the mainstream metal monatomic catalysts for lithium-sulfur batteries include Fe, Co, and other monatomic metals such as Ni, Zn, Mo, V, W, and Ru.

Because of their exceptional cost-effectiveness and environmental friendliness, atomic iron electrocatalysts with Fe-Nx activity centres have garnered a lot of interest. Wang prepared FeN4 /CN-SAC consisting of nitrogen-doped Fe-N4 active sites. Despite the comparatively low iron loading (1.14 wt %), FeN4 /CN-SAC exhibited low overpotentials at different scanning speeds were able to exhibit lower overpotentials, suggesting an enhancement of the kinetics of the polysulfide conversion reaction [2].

Density Functional Theory (DFT) calculations have shown that single-atom sites can lower the energy barrier for polysulfide conversion and enhance the cell multiplicity performance [3]. The coordinating environment has a major impact on the catalytic activity of individual atoms. The tetra-coordinated structure of M-N4 (M stands for metal) has great stability and is often used as the active site for sulfur reduction reactions. Even though the structure is stable, the tetra-coordinated configuration may not exhibit the best catalytic performance, and thus it is an effective strategy to enhance solitary atoms' catalytic activity by modulating the atmosphere of coordination. For example, the adsorption capacity of Fe-N5-C is significantly superior to that of Fe-N4-C, and the migration energy barrier of lithium ions on the surface of Fe-N5-C is significantly reduced thanks to the increase of N coordination number.

Wang uniformly embedded single iron atoms (SAFe) on a porous nitrogen-rich carbon matrix (NC) and subsequently placed it at the anode of a Li-S battery, and a series of electrochemical analyses and theoretical simulations and spectroscopic analyses showed that the uniformly distributed single iron atoms (SAFe) could create a lithium-sulfur battery with low activation voltage without sacrificing the current rate due to their sufficiently high catalytic activity. At the same time, they also created ultra-high-speed lithium-sulfur batteries by using single-atom catalytic cathodes, which were tested to be excellent in terms of long cycle life at 5 C and excellent rate performance at 12 C. The results showed that the long cycle life lithium-sulfur batteries at 5 C and excellent rate performance at 12 C were very good. The aforementioned evidence clearly demonstrated that single-atom catalysts are capable of efficiently accelerating the kinetics of high-performance batteries' ultrafast conversion reactions [2].

Chen et al. integrated Co complexes into conjugated microporous polymers (CMP-CoN_2) as monatomic metal catalysts for Li-S batteries. Due to the enhancement of hybridisation between the 3d orbitals of the cobalt atoms and the 3p orbitals of the sulfur atoms in the polysulphides, the monatomic catalysts possessed superior catalytic activity in facilitating polysulphide conversion in Li-S batteries when in contrast to the saturated analogues, and the experimental The obtained experimental data show that the single-atom catalyst has a great multiplicative capacity of 673.2 mA h g-1 at 6 C and a high specific capacity of 1393 mA h g-1 at 0.1 C. At 2 C after 1000 cycles, it likewise exhibits a very low capacity decay rate of 0.045. [4].

3 Metal nanocatalysts

Pt was the first metal to be used in metal nanoresearch, and as the field has grown, Co, Fe, and nano-alloys have been widely developed. Co is the most widely studied metal, and its synergistic interaction with carbon-doped materials can quicken the reaction of sulphur reduction, raise the quantity of active sites and enhance interactions with polysulfides, and boost the rate of the reaction. Fe nanometals have likewise attracted attention, and Ye have reported a highly graphitised Fe-enriched and N-site-rich carbon tubes for catalysing the electrochemical reaction of lithium-sulphur batteries [5], while Ru nanometal has been shown to quicken Li2S2's transformation into Li2S. In order to integrate the advantages of single metals, the combination of nano-alloys is highly valued, specifically such as CoFe, FeNi, ZnPd alloys and high-entropy alloys, which are all supported by carbon substrates with a view to enhancing the catalytic effect.

Chen synthesised and used Co-Fe mixed phosphide nanotubes as lithium-sulfur cathode electrodes, which have a network of interconnected, very porous pores, together with excellent metal conductivity, and which can significantly enhance the Li-S batteries' redox reaction kinetics. Chen found that Co-Fe-P nanotubes have a strong influence on polysulfide by using UV-visible absorption spectroscopy.

LiPS with strong chemisorption ability, and also Co-Fe-P nanotubes with strong chemotrapping ability for LiPS as shown by DFT studies, and the conversion reaction's kinetics were increased by these interactions between LiPS and cathode materials. The battery's capacity was 678 mAh g-1 following 500 cycles of continuous cycling, with a 0.043% cycle-average capacity decrease [6].

Yang studied basic problems such as the in-situ conversion process of monometallic catalysts in Li-S batteries and the chemical state of the resulting catalytically active centers in addition to examining the reaction kinetics of lithium polysulphide in Li-S batteries. In order to convey sulfur, they uniformly loaded nickel nanoparticles into a flexible material made of a carbon-based bacterial cellulose framework (CBC/Ni). They then used in situ XRD and in situ Raman experiments to investigate the precise chemical processes taking place in this material. They confirmed that during battery operation, the nanoscale nickel catalyst in the S@CBC/Ni electrodes changes into NiS2 through interactions with lithium ions, serving as the new active center to aid in the conversion of lithium ions. After 500 cycles, the average capacity decay rate is only 0.064%, and the lithium-sulfur battery with the nickel nanocatalyst exhibits a high multiplicative capacity of 798.7 mAh g^{-1} at 2C., which can be considered an excellent performance. The experimental data are satisfactory[7].

4 Metal compound catalysts

After a comparative study of the abundance and price of each element in the periodic table, compared to the previous two, there are numerous benefits to employing metal oxides in Li-S batteries as cathode catalysts. Thus, the application of metal compounds—more especially, metal carbides, metal nitrides, metal phosphides, metal sulfides, metal selenides, and metal oxides—as sulfur redox catalysts is a significant area of scientific interest. The catalysts of different metal compounds have different electronic structures and surface properties, so their catalytic activities are also very different. There is a wide variety of metal oxides, which have a better catalytic effect than non-polar carbon and can react with polysulphides to form thiosulphates and polysulphates to enhance sulfur utilisation. The polar bonding between the metal cation and oxygen anion in metal oxides provides sufficient active sites to anchor the polysulfides. Nevertheless, the lack of electrical conductivity of metal oxides remains a drawback. As a result, future designs ought to concentrate on enhancing Li-S batteries' performance by boosting their conductivity through the addition of carbon or conductive polymers. Metal sulfides are well anchored to polysulphides due to their better conductivity and strong sulphophilicity. Selenides are similar to metal sulfides but exhibit better catalytic activity due to the high conductivity of selenium. Because of their high conductivity, metal nitrides have garnered a lot of interest, but are expensive to prepare and optimising their cost has become an important research direction. Metal phosphides are more mild and economical to prepare, and possess high electrical conductivity and excellent catalytic effect, but are easily oxidized at room temperature, and there is an urgent need to explore the one-step synthesis of metal phosphides with excellent performance.As shown in fig 1, by introducing modification strategies such as internal and surface defects, micromorphology, and elemental doping, more active sites can be generated to improve the catalyst activity and achieve rapid conversion of polysulfides.

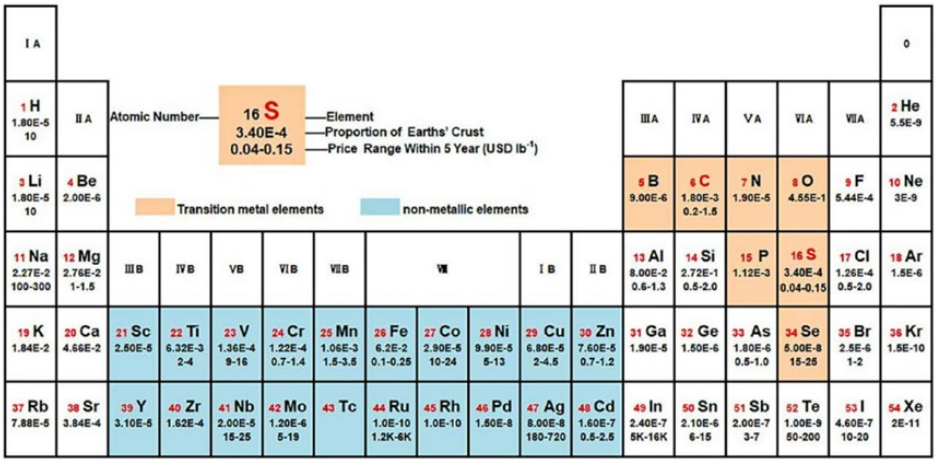

Fig. 1. Prices and abundance of elements related to lithium battery catalysts [1].

Iron oxide was studied as a catalyst for use in the cathode region of Li-S batteries beginning as soon as 2014, marking the beginning of research on metal oxides. Zhao prepared porous iron oxide by wet chemistry, and then the prepared porous iron oxide was embedded in the cathode section of Li-S batteries, where sulphur from the cathode portion was combined with it. The shuttle effect was lessened by using the porous iron oxide as a reservoir for polysulfides. The experimental results show that the lithium-sulfur battery containing 5% iron oxide has improved cycling performance and greater battery stability, having a 574 mAh g-1 charging capacity that remains usable after 50 cycles at 0.5°C ambient temperature. [8]

Taking metal sulphides as an example, metal sulphide catalysts have been improved through continuous research and exploration to obtain catalysts with better catalytic effects.Lin introduced MoS2 as an efficient electrocatalyst in lithium-sulphur batteries. The CV result plots of the symmetric cell containing MoS2-x showed that the narrow inter-peak distance and sharp peaks of the MoS2−x electrode indicate excellent electrode electrochemical reversibility, which suggests that the LiPs conversion reaction is easy to carry out. This improves the use of sulphur by significantly and successfully reducing the buildup of discharge products on the cathode surface. A little amount of MoS2 combined with sulfur may cycle 1600 times at 5 C rate with a capacity degradation of 0.083% per cycle thanks to this kinetic effect, which is already an exceptional cycle life performance. [9]

The immobilisation of polysulfides in hollow conducting carbon is a major research direction to limit the shuttle reaction, and a variety of carbon materials including graphene, carbon nanotubes, graphene oxide, and microcarbon/medium carbon have been extensively explored and investigated by the previous researchers with a view to turn them into cathodic sulphur hosts to capture polysulfides to inhibit the shuttle reaction. Iron carbide (Fe_3C) stands out due to its excellent magnetic and catalytic activity. Its excellent ability to capture sulfides and catalytic activity for lithium-sulphur battery cathodes is worth exploring in research. Gao et al. proposed to prepare ACT@Fe/Fe_3 C/graphene sulphur hosts by embedding Fe/Fe_3C into graphene shells and placing them on flexible activated cotton-twisted (ACT) fibres, which were put into lithium-sulfur battery cathodes to be used as catalysts. They discovered that this catalyst's superior magnetic field-enhanced trapping mechanism allows it to efficiently prevent the diffusion and dissolution of polysulfides, opening up a new avenue to lessen the polysulphide shuttle effect. In contrast to the 100-cycle cycle life that pure ACT/S can accomplish, the cycle life with ACT@Fe/Fe3 C/S can be greatly enhanced to 600 cycles, which is about six times more than that without iron carbide, and it has a 764 mAh g^{-1} initial discharge capacity [10].

He and colleagues looked on the use of nickel metal boride (NiB) in Li-S batteries as a catalyst. According to the theoretical study, it can be concluded that NiB can effectively enhance the charge transfer and accelerate the sulfur redox kinetics, thus enhancing battery performance considerably. Lithium-sulfur battery's discharge capacity with NiB catalyst under cycling conditions at a sulfur loading of 5 mg cm^{-2}, 0.5 C, is 1239 mAh g^{-1}, which is retained by 83.2% after 150 cycles, indicating that the theory is highly accurate based on the analysis of the experimental results. Additionally, it maintains a 590 mAh g^{-1} capacity with a 14.89 mA cm-2 current density with a degradation rate of just 0.07%. This study has significant research value and significance since it demonstrates how metal boride catalysts can enhance lithium-sulfur batteries' performance [11].

The excellent electron orbital assignment ability of phosphorus can enhance the activity of phosphide catalysts, and Huang proposed the use of iron phosphide nanocrystals as catalysts uniformly embedded in 3D porous graphene-carbon nanotubes scaffolds (FeP/rGO/CNTs) for Li-S batteries. According to the DFT theory, FeP has the ability to efficiently adsorb LiPSs and encourage their conversion, preventing their dissolution and diffusion, thus alleviating the shuttle effect, enhancing the redox kinetics, and boosting the battery performance. On the basis of this study, the research on FeP catalysts has never stopped; Ma constructed hollow sea urchin FeP by phosphorylating self-assembled sea urchin FeOOH precursors in a solvothermal procedure in order to provide enough active surfaces for LiPSs; Xia et al. used gradient porous conductive carbon skeletons as FeP catalysts in order to maximize the active Li-poly(II) sulfide binding sites and catalytic sites to ensure high sulfur utilisation and catalytic efficiency; and Xia et al. used gradient porous conductive carbon skeletons as FeP catalysts in order to maximize the active Li-poly(II) sulfide binding sites and catalytic sites. In order to maximise the active lithium polysulphide binding sites and catalytic sites to ensure high sulfur utilisation and catalytic efficiency, Xia et al. used a gradient-conducting carbon skeleton as a carrier for FeP nanoparticles to fabricate a lithium-sulfur battery cathode body, PCM/FeP [12].

5 Conclusion

Because of their great theoretical capacity, Li-S batteries are very competitive and have garnered a lot of interest in current energy storage device development. However, there are still a number of issues with Li-S batteries that need to be resolved, including the shuttle effect, volume expansion, and the low conductivity of polysulfides. Solving these problems is a must to promote the commercialisation of Li-S batteries. The aforementioned issues can be successfully improved and resolved by adding metal catalysts to the Li-S battery's cathode.

Currently, the research on metal catalysts for lithium-sulfur batteries is primarily separated into three groups, namely metal single atom, metal nano and metal compounds, each with its own advantages and disadvantages. All things considered, metal catalysts can significantly enhance lithium-sulfur batteries' performance by lowering the polysulphide shuttling phenomenon and increasing the electrode reaction kinetics. However, there is a certain impact on the sulphur loading when metal catalysts are introduced. The research on metal catalysts for Li-S batteries is still going on steadily. Maintaining the sulfur loading in order to attain a high sulphur loading while enhancing the Li-S batteries' performance through the introduction of metal catalysts may become a major research direction to promote the realisation of metal catalysts in practical applications.

The criteria for evaluating the performance of metal catalysts should be multidimensional, primarily in lithium-sulfur batteries' electrochemical performance, including their specific capacity, multiplicity, and cycling stability, among other aspects. However, the potential mechanism of action of the catalysts still needs to be studied in depth. A deeper understanding

of catalysts through the development of advanced characterisation methods can greatly facilitate the advancements in research and practical applications of lithium-sulphur batteries.

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