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# S-decorated Mo<sub>2</sub>C as efficient catalyst for Li–O<sub>2</sub> battery system

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Lithium–oxygen (Li–O<sub>2</sub>) batteries are considered an important candidate for the next generation of energy storage systems due to their ultra-high theoretical energy density (11 586 mA h g<sup>-1</sup>), but their slow kinetic reactions, high overpotential and cyclic instability seriously limit their practical applications. In this study, sulfur modified Mo<sub>2</sub>C (S@Mo<sub>2</sub>C) cathode materials were prepared by hydrothermal synthesis by sulfur (S) doping to optimize the electronic structure and catalytic activity of Mo<sub>2</sub>C (Mo<sub>2</sub>C). Experiments show that S@Mo<sub>2</sub>C exhibits significantly improved electrochemical performance compared to commercial Mo<sub>2</sub>C: its specific capacity is up to 3955 mA h g<sup>-1</sup> (commercial material only 508 mA h g<sup>-1</sup>), the charge and discharge overpotential is reduced to 0.26 V (53.6%), and the capacity retention rate remains 77.8% after 250 cycles. X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) analysis showed that the introduction of sulfur induced the formation of a heterostructure of MoS<sub>2</sub>/MoS<sub>3</sub> in the Mo<sub>2</sub>C lattice, which enhanced the conductivity and oxygen reduction/precipitation (ORR/OER) activity of the material. In addition, sulfur doping promotes the formation of highly conductive amorphous Li<sub>2</sub>O<sub>2</sub> and effectively inhibits the accumulation of insulating ring Li<sub>2</sub>O<sub>2</sub>, thus significantly improving the cycle stability and energy efficiency of the battery. This study provides a new structural regulation strategy for the design of high efficiency lithium oxygen battery catalysts.

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## 1 Introduction

The energy sector has undergone transformative changes aligned with modern developmental paradigms, driven by accelerated societal progress and escalating global environmental degradation. Among emerging energy storage technologies, lithium–oxygen (Li–O<sub>2</sub>) batteries have garnered substantial scientific interest due to their exceptional theoretical energy density of 11 586 mA h g<sup>-1</sup> – approximately 3–5 times greater than conventional lithium-ion systems.<sup>1,2</sup> This characteristic positions Li–O<sub>2</sub> batteries as a highly promising next-generation energy storage solution.

However, the practical implementation of this technology faces critical challenges, primarily stemming from elevated overpotentials that impede reaction kinetics and compromise cycling efficiency.<sup>3,4</sup> Current research identifies the insulating nature of lithium peroxide (Li<sub>2</sub>O<sub>2</sub>), the predominant discharge product, as a principal contributor to these high overpotentials. Although the more conductive lithium superoxide (LiO<sub>2</sub>) is also generated during the reaction process, its inherent instability prevents it from persisting as the primary discharge product.<sup>5,6</sup> This limitation underscores the necessity for advanced catalytic

materials capable of effectively decomposing Li<sub>2</sub>O<sub>2</sub>. Consequently, the development of high-performance catalysts has become a pivotal research focus, as such materials could substantially mitigate overpotential challenges and enhance battery performance through optimized reaction pathways.

Molybdenum carbide (Mo<sub>2</sub>C) is widely used as high effective catalysts. With abundant active sites, however, typical β-type Mo<sub>2</sub>C with a stable structure still does not show satisfactory performance in practice and needs more adjustment and optimization, and structural optimization is a very effective method.<sup>7–10</sup> Metal sulfides are also widely used as electrode materials.<sup>11,12</sup> The use of Mo<sub>2</sub>S as a catalyst in HER reactions has been widely investigated due to its excellent catalytic performance. Crystalline Mo<sub>2</sub>S and amorphous Mo<sub>2</sub>S<sub>x</sub> are commonly used, however, the stacking layer structure causes it to exhibit a high impedance, resulting in a decrease of its conductivity, which implies a decrease in catalytic efficiency. The catalytic efficiency of Mo<sub>2</sub>S<sub>x</sub> can be effectively improved by reconstructing the structure, which makes Mo<sub>2</sub>S<sub>x</sub> feasible as a catalyst for Li–O<sub>2</sub> batteries.<sup>13,14</sup>

While previous studies have established the catalytic potential of Mo<sub>2</sub>C- and MoS<sub>2</sub>-based cathodes in Li–O<sub>2</sub> systems,<sup>15–17</sup> critical limitations persist in addressing key electrochemical challenges. Conventional Mo<sub>2</sub>C cathodes often suffer from insufficient electrical conductivity and poor Li<sub>2</sub>O<sub>2</sub>

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decomposition kinetics, typically manifesting in high charge overpotentials ( $>0.4$  V) and rapid capacity fading ( $<50$  cycles) due to parasitic side reactions.<sup>8,18</sup> Although sulfur incorporation strategies (e.g., MoS<sub>2</sub> heterostructures) have been explored to enhance surface reactivity,<sup>19</sup> most reported systems exhibit suboptimal phase stability under deep cycling conditions, with inevitable MoS<sub>2</sub>/Mo<sub>2</sub>C phase segregation leading to active site passivation.<sup>20</sup> Furthermore, existing sulfur-doped architectures predominantly focus on single-phase modifications, neglecting the synergistic effects of multivalent Mo species (e.g., Mo<sup>3+</sup>/Mo<sup>4+</sup> redox couples) in regulating Li<sub>2</sub>O<sub>2</sub> nucleation pathways.<sup>21</sup>

In this work, the S@Mo<sub>2</sub>C structure with efficient, conductive structure and active sites were optimized successfully by using commercial Mo<sub>2</sub>C with thioacetamide, and the S element was successfully doped during calcination, and used as the cathode to explore the synergistic effect of Li–O<sub>2</sub> battery. As a result, the S-modified Mo<sub>2</sub>C structure can effectively improve the performance of the Li–O<sub>2</sub> battery system with more excellent specific capacity (3955 mA h g<sup>-1</sup>), lower overpotential (0.26 V), and improved cycling performance (over 250 cycles) compared with the conventional commercial Mo<sub>2</sub>C.

In view of the reasons for the abnormally high specific capacity of our work: our analysis is composed of the following: Potential Factors Contributing to Enhanced Capacity in Lithium–Oxygen Battery Systems.

## 1.1 Material-specific reaction mechanisms

**1.1.1 Multielectron redox pathways.** The S@Mo<sub>2</sub>C composite demonstrates catalytic capabilities in facilitating multielectron transfer processes during Li<sub>2</sub>O<sub>2</sub> formation/decomposition cycles (eqn (1) and (2)). Sulfur doping enhances oxygen adsorption on the Mo<sub>2</sub>C substrate, thereby optimizing oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics through improved intermediate stabilization.

**1.1.2 Heterophasic structural synergy.** X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analyses confirm the formation of a MoS<sub>2</sub>/MoS<sub>3</sub> hybrid phase post-sulfur incorporation (Fig. 4). This composite architecture exhibits enhanced electrical conductivity compared to pristine Mo<sub>2</sub>C, with electrochemical characterization revealing a reduced reaction overpotential ( $\Delta\eta = 0.26$  V). The synergistic phase interaction consequently improves the system's reversible capacity through optimized charge transfer efficiency.

## 1.2 Nanostructural optimization effects

**1.2.1 Two-dimensional charge transport enhancement.** Transmission electron microscopy (TEM) characterization reveals the development of a 5 nm-thick nanomembrane surface layer on S@Mo<sub>2</sub>C (Fig. 3a). This ultrathin architecture facilitates rapid ion diffusion kinetics by reducing Li<sup>+</sup> and O<sub>2</sub> transport pathways while expanding the electrochemically active surface area.

**1.2.2 Crystalline defect engineering.** Sulfur doping induces structural reorganization in the Mo<sub>2</sub>C lattice (Fig. 2), as verified by XPS analysis (Fig. 4e). The modified coordination

environment generates abundant Mo<sup>3+</sup> active sites, which promote homogeneous Li<sub>2</sub>O<sub>2</sub> nucleation/decomposition processes through enhanced surface adsorption energetics.

# 2 Experimental section

## 2.1 Materials and chemicals

Commercial Mo<sub>2</sub>C (Sigma, 99.0%), deionized water, thioacetamide (Aladdin), lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, Aladdin), tetraethylene glycol dimethyl ether (TEGDME, Aladdin), polyvinylidene fluoride (PVDF, Aladdin) and *N*-methylpyrrolidone (NMP, Aladdin) are all analytical pure.

## 2.2 Preparation of S-decorated Mo<sub>2</sub>C

Commercial Mo<sub>2</sub>C (120 mg) was added to 50 ml deionized water, and thioacetamide (636.76 mg) was further added. After electromagnetic stirring for 10 min, the mixture was placed in a 100 ml teflon-lined stainless steel autoclave, and heated to 473 K and the temperature maintained for 10 h. After cooling down, the mixture precursor was obtained. After centrifugation (7800 rpm) and dry (60 °C for 12 h), the black target specimen was obtained.

## 2.3 Preparation of Li–O<sub>2</sub> cells

Commercial Mo<sub>2</sub>C (or S@Mo<sub>2</sub>C) was mixed with polyvinylidene fluoride (PVDF) and *N*-methylpyrrolidone (NMP) binder in a weight ratio of 8 : 1 : 1 to form a slurry, which was placed on carbon paper discs (14 mm diameter) and then dried in a vacuum oven at 120 °C for 12 h. The amount of mass loading is about 2 mg. The button cell used for electrochemical testing consisted of a cathode, 0.1 ml electrolyte (1 M LiTFSI in TEGDME) permeated to a glass fiber septum (Whatman GF/D microfiber filter paper, pore size 2.7 μm) and a lithium metal anode.

# 3 Results and discussion

Fig. 1a shows the process of obtaining S-decorated Mo<sub>2</sub>C by doping with sulfur for commercial Mo<sub>2</sub>C by hydrothermal method. The commercial Mo<sub>2</sub>C (Fig. 1b) was added to deionized water and thioacetamide (TAA) was added to the mixture to obtain the precursor solution, which was further heated over 200 °C to obtain S-decorated Mo<sub>2</sub>C (Fig. 1c).

Fig. 2a presents the X-ray diffraction (XRD) patterns of commercial Mo<sub>2</sub>C and S@Mo<sub>2</sub>C. Significant strong peaks are observed at 34.5, 38.0, 39.6, 52.3, 61.9, 69.8, and 75.0°, corresponding to the (100), (002), (101), (102), (110), (103), and (112) planes of the typical β-Mo<sub>2</sub>C crystal structure, respectively. Further analysis indicates that the original crystal structure is preserved after sulfur modification. Compared with the Mo<sub>2</sub>C sample before sulfidation, the diffraction peak intensities on the (002), (101), (102), (110), (103), and (112) planes have increased to varying degrees, and the peak widths have narrowed, suggesting an increase in grain size. This phenomenon can be attributed to the sulfur atom radius (0.104 nm) being larger than that of carbon (0.077 nm) during the sulfidation



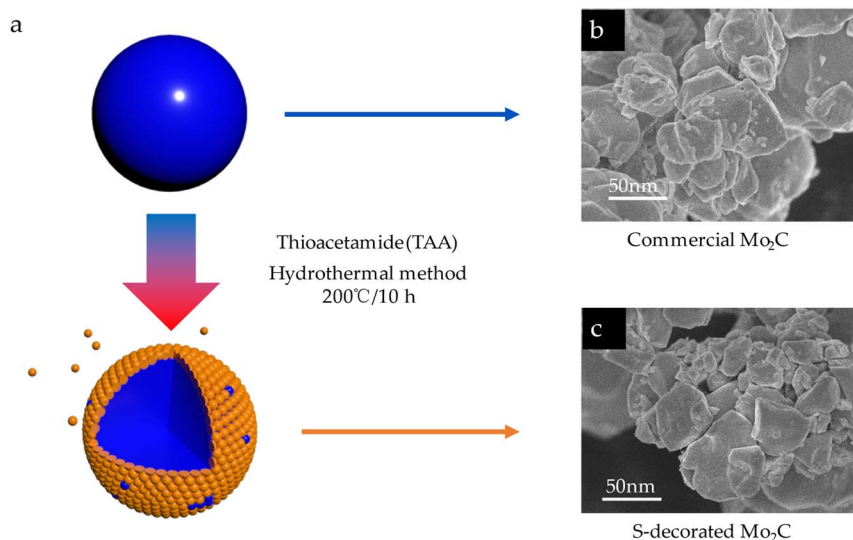


Fig. 1 (a) Schematic synthesis process of S-decorated Mo<sub>2</sub>C; (b) the SEM image of commercial Mo<sub>2</sub>C; (c) the SEM image of S@Mo<sub>2</sub>C.

process, leading to lattice expansion and reconstruction of the crystal structure, thereby causing changes in the crystal diffraction characteristics. On the other hand, the decrease in the intensity of the (100) peak of Mo<sub>2</sub>C may be due to sulfur replacing carbon atoms on the (100) plane, forming MoS<sub>2</sub> with a 2H structure, which reduces the number of Mo<sub>2</sub>C structures on the (100) plane (see Fig. 2b). The enhanced intensity of the (002) plane is attributed to sulfur doping optimizing the inter-layer stacking of Mo<sub>2</sub>C, promoting the preferential growth of the S@Mo<sub>2</sub>C (002) plane.

To deeply explore the microstructural characteristics of S-modified Mo<sub>2</sub>C, this study employed transmission electron microscopy (TEM) techniques for detailed observation and analysis. The high-resolution TEM image of S-modified Mo<sub>2</sub>C (Fig. 3a) reveals the uniform distribution of the S-modified Mo<sub>2</sub>C structure. The TEM image clearly shows a thin nanometer-thick film layer with a thickness of about 5 nanometers on the outer layer of Mo<sub>2</sub>C. By magnified scanning

transmission electron microscopy (STEM) images, significant changes in the Mo<sub>2</sub>C lattice spacing can be observed, where the complete Mo<sub>2</sub>C lattice spacing distorts from 0.26 nanometers (corresponding to Mo<sub>2</sub>C (100), PDF#35-0787) to 0.21 nanometers (corresponding to MoS<sub>2</sub> (006), PDF#73-1508). In the X-ray photoelectron spectroscopy (XPS) S 2p spectrum, the double peaks at 162.02 eV and 163.32 eV correspond to the 2p<sup>3/2</sup> and 2p<sup>1/2</sup> orbitals of s<sup>2-</sup>, confirming the presence of sulfur in the form of s<sup>2-</sup> (Fig. 4c). Additionally, in the Mo 3d spectrum of XPS, the peaks at 228.85 eV and 231.8 eV shift, indicating the formation of Mo–S bonds. This result further verifies that the change in layer spacing is caused by the formation of MoS<sub>2</sub> structures due to sulfur doping in the Mo<sub>2</sub>C lattice, consistent with the analysis results of the X-ray diffraction (XRD) spectrum. Fig. 3b shows the scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) surface scanning image of S-doped Mo<sub>2</sub>C, and Fig. 3c–f display the content and distribution of Mo, S, C, and O elements, respectively. Mo, S, C, and O

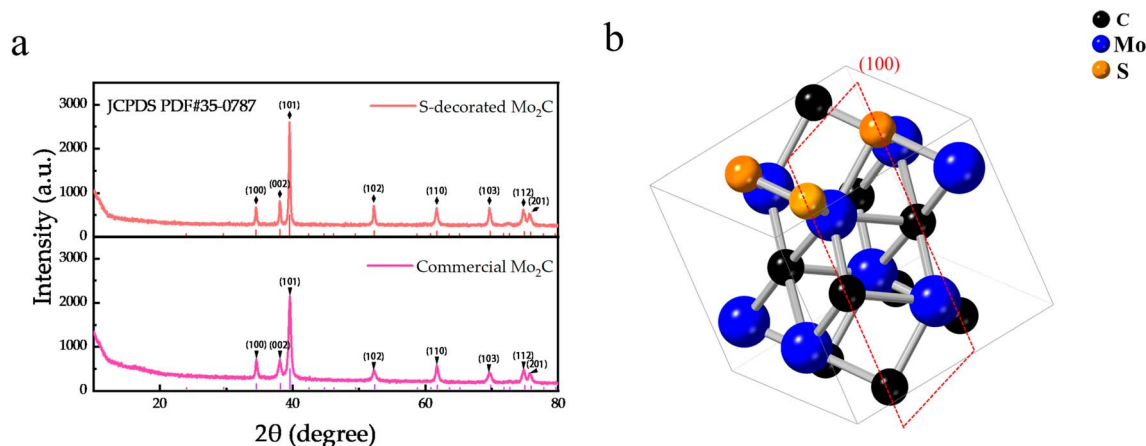


Fig. 2 (a) XRD patterns of commercial Mo<sub>2</sub>C and S-decorated Mo<sub>2</sub>C; (b) crystal structure of S-decorated Mo<sub>2</sub>C.

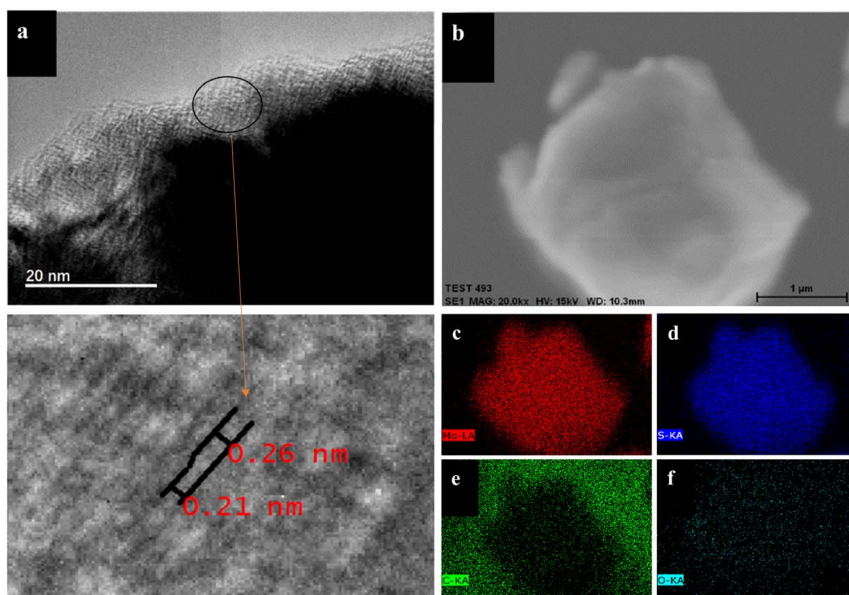


Fig. 3 (a) The TEM and magnified STEM images of S-decorated Mo<sub>2</sub>C; (b–f) elemental mapping analysis of S-decorated Mo<sub>2</sub>C.

elements are uniformly distributed throughout the sample, further confirming the formation of S@Mo<sub>2</sub>C. Notably, throughout the sample, especially in Fig. 3f, the distribution of O elements can be clearly observed, which may be due to the oxidation reaction of the sample with oxygen in the air under exposure conditions, leading to the formation of some MoO<sub>x</sub>. However, the MoO<sub>x</sub> signal in the XPS analysis is weak, so the

impact of MoO<sub>x</sub> contamination on the experimental results can be ignored. Moreover, a trace amount of MoO<sub>x</sub> may act as a protective layer to inhibit the decomposition of the electrolyte.

To further analyze the composition of the chemical states on the surface of S@Mo<sub>2</sub>C, X-ray photoelectron spectroscopy (XPS) was used. The XPS spectrum (Fig. 4) shows that S@Mo<sub>2</sub>C is comprised of Mo, C, O and S elements. From Fig. 4a, Mo 3d

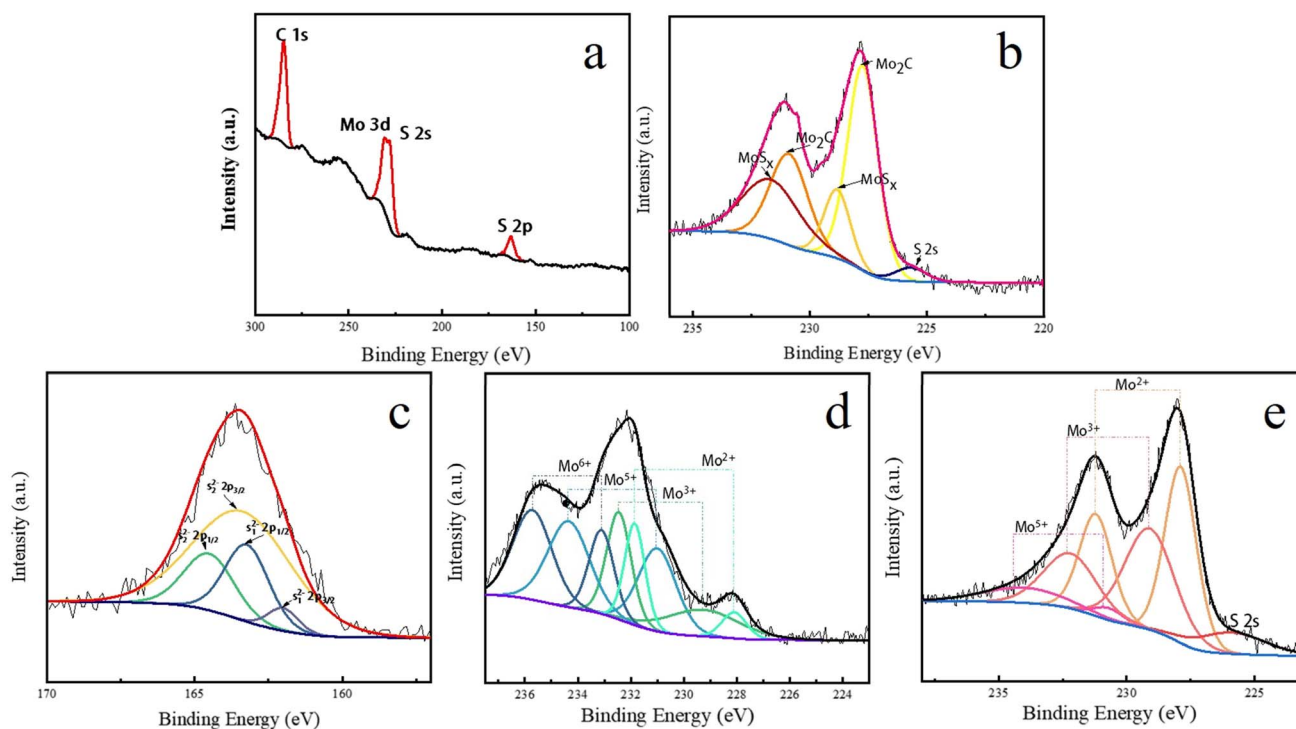


Fig. 4 (a and b) XPS images of S@Mo<sub>2</sub>C sample; (c) XPS spectra of S element of S@Mo<sub>2</sub>C; (d and e) XPS images of different ion valences of Mo element in commercial Mo<sub>2</sub>C and S@Mo<sub>2</sub>C.





Table 1 The atomic percent and mass percent of S@Mo<sub>2</sub>C

	C 1s	Mo 3d	S 2p
At%	79.89%	9.77%	10.34%
Wt%	43.05%	42.09%	14.86%

peaks and S 2s, S 2p peaks can be clearly observed, indicating that S element is present in large quantities of the S@Mo<sub>2</sub>C sample, with a mass fraction of 14.86% corresponding to Table 1, which is highly close to previous research.<sup>22</sup> Strong peaks were observed at 227.75 eV (3d<sup>5/2</sup>) and 230.9 eV (3d<sup>3/2</sup>), and the binding energy characteristics were consistent with β-Mo<sub>2</sub>C. Compared with the typical Mo 3d peak (~229 eV) of 2H-MoS<sub>2</sub>, the Mo 3d peak in S@Mo<sub>2</sub>C shifts 0.15 eV towards the high binding energy, which corresponds to the lattice expansion caused by the incorporation of S in the XRD pattern ( $\Delta d = 1.36\%$ ). It is indicated that Mo and S may form a complex coordination structure of crystalline MoS<sub>2</sub> and amorphous MoS<sub>3</sub>, MoS<sub>x</sub>.

Fig. 4b shows the high-resolution spectrum of the binding energy in the range of 220–237.5 eV, where the presence of Mo<sub>2</sub>C and Mo<sub>2</sub>S<sub>x</sub> with different valence Mo elements can be clearly observed. The peak of S 2s is located at around 225.7 eV. Mo 3d exhibits strong peaks at 227.75 and 230.9 eV, respectively, showing a doublet with β-Mo<sub>2</sub>C characteristics.<sup>23</sup> The Mo 3d peaks at 228.85 and 231.8 eV has shifted ~0.15 eV compared with the normal value of 2H-MoS<sub>2</sub> (229 eV), which can be certified by the characteristic double peaks of the Mo element of MoS<sub>x</sub> in the Mo<sup>4+</sup> state.<sup>24</sup> As shown in the high-resolution S 2p spectrum (Fig. 4c), the peaks of S<sub>1</sub><sup>2-</sup> and S<sub>2</sub><sup>2-</sup> ligands at 162.02 and 163.32 eV corresponding to S<sub>1</sub><sup>2-</sup> 2p<sup>3/2</sup> and S<sub>1</sub><sup>2-</sup> 2p<sup>1/2</sup>, respectively, can be observed. The ~1.2 eV energy separation between S<sub>1</sub><sup>2-</sup> and S<sub>2</sub><sup>2-</sup> is the characteristic of S<sup>2-</sup> in MoS<sub>2</sub>. Moreover, the peaks at 163.52 and 164.62 eV corresponding to S<sub>2</sub><sup>2-</sup> 2p<sup>3/2</sup> and S<sub>2</sub><sup>2-</sup> 2p<sup>1/2</sup> are also observed, respectively. The energy separation of doublet is close to 1.2 eV, which is characteristic of S<sup>2-</sup> in MoS<sub>3</sub> species.<sup>25</sup> Thus, the poorly crystalline “MoS<sub>x</sub>” in S@Mo<sub>2</sub>C is identified as a mixture of crystalline MoS<sub>2</sub> and non-crystalline MoS<sub>3</sub>. The XPS spectra of Mo elements show the presence of different chemical valence states on the Mo

surface, as shown in Fig. 4 (d, commercial Mo<sub>2</sub>C) and (e, S@Mo<sub>2</sub>C). The Mo–C bond in Mo<sub>2</sub>C contributes to the Mo<sup>2+</sup> state and the partially low oxidation state of Mo<sup>3+</sup>, while other reports have shown that the Mo–O bond can also be assigned to Mo<sup>3+</sup> and Mo<sup>5+</sup> in MoO<sub>2</sub>, as well as Mo<sup>6+</sup> in MoO<sub>3</sub> due to air contamination.<sup>26</sup> In Fig. 4d, Mo 3d<sup>5/2</sup> peaked at 229.0 eV, and Mo 3d<sub>3</sub> peaked at 232.1 eV, corresponding to Mo<sup>3+</sup> (mainly MO–C bond). A weak peak at 235.5 eV was attributed to Mo<sup>6+</sup> (MoO<sub>3</sub>) formed by surface oxidation. In Figure e, the Mo 3d<sup>5/2</sup> peak migrates towards the low binding energy to 227.75 eV and the Mo 3d<sup>3/2</sup> peak is located at 230.9 eV, indicating a reduction in the oxidation state of Mo (Mo<sup>3+</sup>, Mo<sup>2+</sup>). The peak strength of Mo<sup>6+</sup> decreased significantly (peak weakening at 235.5 eV), indicating that S doping inhibited surface oxidation and induced partial reduction of high-priced Mo (Mo<sup>6+</sup>, Mo<sup>5+</sup>) to low-priced Mo (Mo<sup>3+</sup>, Mo<sup>2+</sup>). The phenomena of lower valence states of eMo in Fig. 4c and d are both due to the incorporation of S, and the electronegativity of S is higher than that of C, resulting in S atoms attracting electrons from Mo and reducing the electron density of D orbital of Mo (increasing binding energy). Moreover, the introduction of S simultaneously provides electronic compensation by forming Mo–S bonds. It can be observed that the peaks of Mo<sup>6+</sup> disappear, the intensity of Mo<sup>5+</sup> peaks decreases, and the intensity of Mo<sup>3+</sup> and Mo<sup>2+</sup> peaks increases, indicating that Mo<sup>6+</sup> and part of Mo<sup>5+</sup> are reduced to lower Mo<sup>3+</sup> and Mo<sup>2+</sup> due to S doping. The appearance of a slight amount of S 2s peaks may be due to the oxidation of a slight amount of S<sup>2-</sup> to SO<sub>4</sub><sup>2-</sup> during the preparation process.<sup>27</sup>

The plateau fraction of carbon (79.89%) was mainly derived from the carbon paper substrate used in electrode preparation (Fig. 3c SEM-EDX surface scan shows uniform distribution of carbon). Sulfur doping (10.34 at%) leads to a decrease in molybdenum content (9.77 at%) due to the partial substitution of sulfur atoms for carbon atoms in the Mo<sub>2</sub>C lattice to form the Mo<sub>2</sub>C<sub>1-x</sub>S<sub>x</sub> hybrid structure. The reduction of Mo–C bond strength in the XPS analysis (Fig. 4) further supports this substitution mechanism.

To verify the properties of kinetics reaction of S@Mo<sub>2</sub>C, a coin-type Li–O<sub>2</sub> battery consisting of a lithium metal anode was used for the electrochemical test. The galvanostatic full

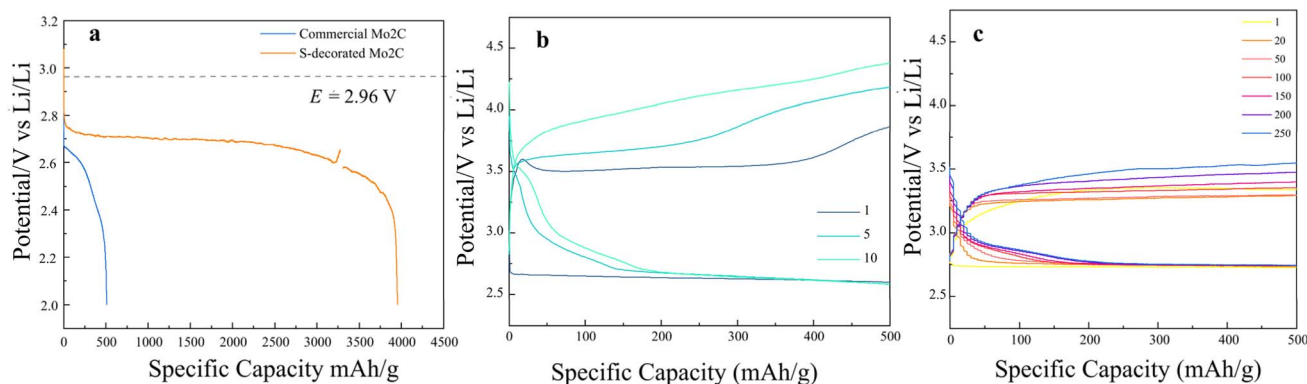


Fig. 5 (a) Voltage profile of the full discharge for commercial Mo<sub>2</sub>C and S@Mo<sub>2</sub>C in Li–O<sub>2</sub> batteries; (b) charge and discharge curves of commercial Mo<sub>2</sub>C at a current density of 100 mA g<sup>-1</sup>; (c) charge and discharge curves of S@Mo<sub>2</sub>C at a current density of 100 mA g<sup>-1</sup>.

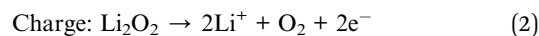
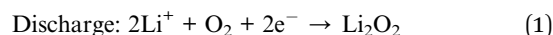


discharge curves of Mo<sub>2</sub>C and S@Mo<sub>2</sub>C at a 100 mA g<sup>-1</sup> current density with 0.1 mV s<sup>-1</sup> scan rate from 2.0 to 4.5 V (vs. Li/Li<sup>+</sup>) were obtained in Fig. 5a. Obviously, the coexistence of S and Mo<sub>2</sub>C as a cathode for Li–O<sub>2</sub> battery presents the largest capacity (3955 mA h g<sup>-1</sup>), which shows a much higher specific capacity compared to commercial Mo<sub>2</sub>C cathode (508 mA h g<sup>-1</sup>). Moreover, the discharge overpotential is significantly decreases from 560 mV to 260 mV for the S@Mo<sub>2</sub>C cathode, indicating that the more completely ORR (oxidation–reduction reaction) have occurred at the positive electrode and the discharge products have grown more fully on the S@Mo<sub>2</sub>C cathode than commercial Mo<sub>2</sub>C. S@Mo<sub>2</sub>C with better electrical conductivity and ORR performance can be attributed to lower overpotential and more fully grown discharge products.<sup>28</sup>

The discharge and charge curves of Mo<sub>2</sub>C and S@Mo<sub>2</sub>C cathodes with a cut off capacity of 500 mA h g<sup>-1</sup> at a current density of 100 mA g<sup>-1</sup> were investigated in Fig. 5b and c. It can be observed clearly that commercial Mo<sub>2</sub>C cathode presents a good OER (oxygen evolution reaction) kinetics in Fig. 5b. As the charge/discharge proceeds, the overpotential continues to increase after 5 and 10 cycles rapidly (~1.5 V overpotential, ~630 mV increased after 10 cycles), while the round-trip efficiency degrades from 75.1% down to 63.2%. Compared with

commercial Mo<sub>2</sub>C, S@Mo<sub>2</sub>C cathode presents a better, stable and reversible charge/discharge characteristic in Fig. 5c. The charge/discharge curves from the 1st to even 250th cycle of S@Mo<sub>2</sub>C presents a great overpotential difference (~0.8 V overpotential, ~250 mV increased after 250 cycles) and a smooth charge/discharge plateau with little overpotential difference (3.7% degradation of round-trip efficiency, 77.8% remained after 250 cycles). Lower overpotential allows the discharge products Li<sub>2</sub>O<sub>2</sub> decomposing effectively, OER occurring more fully at the cathode and avoiding the generation of by-products effectively.<sup>29,30</sup> Besides, charging plateaus below 3.5 V is very beneficial to the cycling performance for the Li–O<sub>2</sub> battery, as carbon materials decompose above 3.8 V.<sup>31</sup> In order to better reveal the mechanism, the charge/discharge characteristics of S@Mo<sub>2</sub>C cathode will be analyzed next. A direct comparison with the previous material properties is tabulated as shown in Table 2 below.

In lithium–oxygen batteries, S@Mo<sub>2</sub>C is used as the cathode material, and its charge–discharge process is monitored using a scanning electron microscope (SEM), corresponding to the different states shown in Fig. 6a (Fig. 6b–d). The charge–discharge reactions of the battery follow the following chemical eqn (1) and (2):<sup>32</sup>



The initial state of S@Mo<sub>2</sub>C presents a flat and undamaged surface, as shown in Fig. 6b. As the discharge process progresses, a small-sized, high-crystallinity annular film forms on the cathode surface, a phenomenon clearly visible in Fig. 6c. This annular film is considered the typical discharge product Li<sub>2</sub>O<sub>2</sub>. Under normal circumstances, the annular Li<sub>2</sub>O<sub>2</sub> is the

Table 2 Material performance comparison

Catalyst	Specific capacity (mA h g <sup>-1</sup> )	Overpotential (V)	Cycle stability
S@Mo <sub>2</sub> C	3955	0.26	250 cycles
Mo <sub>2</sub> C	508	0.56	<50 cycles
Co <sub>3</sub> O <sub>4</sub> HPNT	4146	0.099	40
Mo <sub>2</sub> C/MoO <sub>2</sub> @RGO	2365	0.56	
Mo <sub>2</sub> C/C	7500	1.2	100 cycles
MoN	7400	0.19	

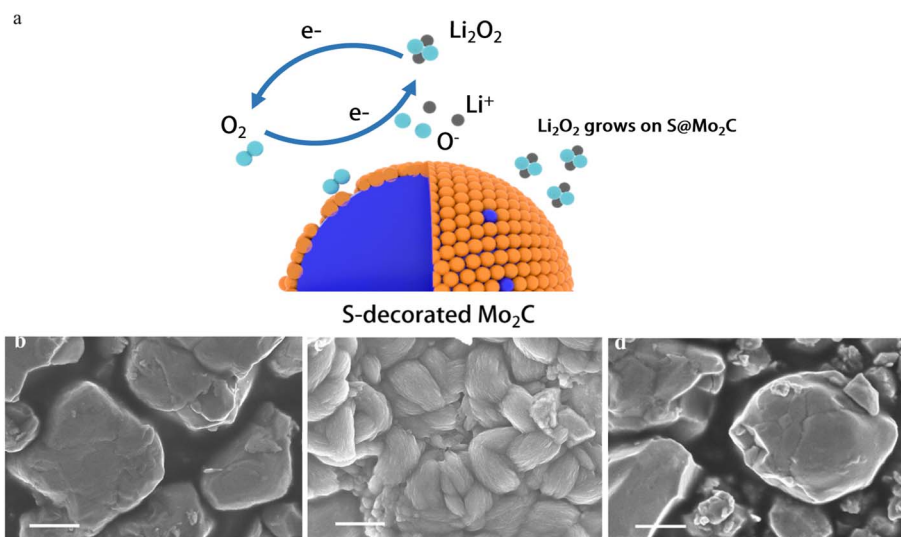


Fig. 6 (a) The schematic diagram of S@Mo<sub>2</sub>C electrode Li–O<sub>2</sub> battery; (b) pristine S@Mo<sub>2</sub>C cathode with uniform nanoparticles. (c) post-discharge: toroidal Li<sub>2</sub>O<sub>2</sub> and amorphous Li<sub>2</sub>O<sub>2</sub> deposited on the surface. (d) Post-recharge: complete decomposition of Li<sub>2</sub>O<sub>2</sub>, restoring the cathode morphology. The (c) and (d) two figures are TEM images after 250 cycles.



main factor causing the high overpotential of lithium–oxygen batteries.<sup>33</sup> However, during the recharging process, the decomposition of  $\text{Li}_2\text{O}_2$  is observed, and  $\text{S@Mo}_2\text{C}$  returns to its original flat and undamaged state, which is very similar to Fig. 6b, indicating that  $\text{S@Mo}_2\text{C}$  can return to its initial form after charging. After 250 cycles of electrochemical stability testing, the capacity retention rate reaches 77.8%, and the overpotential only increases by 250 mV. The low overpotential (0.8 V) indicates a high reversibility of  $\text{Li}_2\text{O}_2$  decomposition, reducing structural stress, thus indicating that the nanosheets did not undergo structural collapse or peeling during the charge–discharge cycles, showing good crystal structure stability. This suggests that not only is annular  $\text{Li}_2\text{O}_2$  formed, but also amorphous  $\text{Li}_2\text{O}_2$  with higher conductivity. Under high current density conditions, the formation of small annular  $\text{Li}_2\text{O}_2$  is more easily observed.<sup>34</sup> Typically, amorphous  $\text{Li}_2\text{O}_2$  promotes rapid electron tunneling during the charging process, resulting in rapid and efficient decomposition of  $\text{Li}_2\text{O}_2$ .<sup>35,36</sup> Interestingly, although S doping may adversely affect the number of active sites on the  $\text{Mo}_2\text{C}$  cathode, leading to an increase in cathode impedance, S doping also improves the quality of the effective active sites, significantly enhancing the conductivity of  $\text{S@Mo}_2\text{C}$ .<sup>37</sup> High-quality active sites may also more effectively break the O–O bond, thereby significantly reducing the activation energy required for the reaction. While experimental evidence including XPS analysis of  $\text{Mo}^{4+}/\text{Mo}^{6+}$  ratios strongly supports the proposed mechanism of Mo valence tuning and O–O bond activation, future density-functional theory (DFT) calculations will contribute to a comprehensive understanding of the mechanism. Such computational studies can quantitatively verify synergistic effects between Co/Mo sites, accurately map reaction pathways (e.g., O–O cleavage energies), and reveal electronic structure modifications at the atomic level. Nevertheless, the consistency between our structural characterization (XRD, XPS, TEM) and the excellent electrochemical properties (low overpotential, high stability) provides a reliable empirical validation of the material's design strategy.<sup>38–40</sup>

## 4 Conclusions

In this study, we successfully modified commercial  $\text{Mo}_2\text{C}$  ( $\text{S@Mo}_2\text{C}$ ) cathode material by sulfur doping strategy, and prepared sulfur modified  $\text{Mo}_2\text{C}$  ( $\text{S@Mo}_2\text{C}$ ) cathode material. The system characterization indicated that the introduction of sulfur not only optimized the crystal structure of  $\text{Mo}_2\text{C}$  and formed a heterogeneous interface of  $\text{MoS}_2/\text{MoS}_3$ , but also significantly increased the conductivity and catalytic activity of the material. Electrochemical tests show that the  $\text{S@Mo}_2\text{C}$ -based lithium–oxygen battery achieves a high specific capacity of  $3955 \text{ mA h g}^{-1}$  at a current density of  $100 \text{ mA g}^{-1}$ , reduces the charge and discharge overpotential to 0.26 V, and exhibits excellent cycle stability (capacity retention rate of 77.8% after 250 cycles). The mechanism study shows that sulfur doping can improve battery performance in the following ways: (1) enhance electron transport capacity and promote ORR/OER reaction kinetics; (2) induce the formation of highly conductive

amorphous  $\text{Li}_2\text{O}_2$  and inhibit the irreversible accumulation of insulating ring  $\text{Li}_2\text{O}_2$ ; (3) optimize the distribution of active sites and reduce the reaction energy barrier. In addition, the  $\text{S@Mo}_2\text{C}$  stable charge and discharge platform (<3.5 V) effectively avoids the decomposition of carbon-based materials, further extending the battery life. This study provides an important theoretical and experimental basis for the development of efficient and long-lived lithium–oxygen battery catalysts. Subsequent studies can be extended to explore the generalizability of the sulfur doping strategy in other transition metal carbide systems and large-scale preparation techniques, while incorporating density-functional theory (DFT) modeling in order to establish a clear conformational relationship and guide the further optimization of the bimetallic catalysts.

## Author contributions

Yanhong Ding was responsible for the experimental design and writing the first draft of the paper, Zhichao Gao was responsible for writing or revising the chapters, Rongpeng Lin was responsible for the experimental part, Yong Cao assisted in completing the experiments, Haoyang Liu assisted in completing the experiments or data analysis, Yulin Zhou assisted in completing the data analysis, Haifeng Xu was responsible for finding the related papers on Li–O<sub>2</sub>, Jiayi Liu was involved in the XRD part of the revisions, Fangqi Ren was involved in the XPS part of the revisions, Yirong Zhu was responsible for the paper submission, response to review comments and communication with journals.

## Data availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

## Conflicts of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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