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#### Introduction

Li–S batteries are considered as an encouraging candidate for advanced power storage technologies due to sulfur's ecofriendliness, high theoretical specific capacity (1675 mA h  $g^{-1}$ ), and substantial theoretical energy density (2600 W h kg<sup>-1</sup> and 2800 W h L<sup>-1</sup>).<sup>1–5</sup> In spite of these benefits, several challenges impede the widespread commercialization of Li–S batteries. For example, the presence of soluble polysulfide intermediates moving between electrodes during charge/discharge cycles, known as the shuttle effect of LiPSs, results in rapid capacity degradation and lowers the cycling life of Li–S batteries.<sup>6–9</sup> The origin of the shuttle effect is mainly attributed to the slow reaction of LiPSs and the sluggish redox kinetics of sulfur species.<sup>10,11</sup> Moreover, uneven Li deposition on the Li anode results in dendrite growth during cycling, creating a risk of internal short circuits.<sup>12–14</sup> To tackle the chal-

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Lithium–sulfur (Li–S) batteries are recognized as an encouraging alternative for future power storage technologies. However, their practical application is hindered by several significant challenges, including slow redox kinetics, the shuttle effect, and the formation of lithium dendrites. Here a binder-free, self-supporting multifunctional interlayer composed of lithium lanthanum titanate (LLTO) with amorphous carbon nanofiber matrices for Li–S batteries has been constructed. This multifunctional interlayer has been designed to facilitate the redox kinetics of lithium polysulfides (LiPSs), promote the nucleation of lithium sulfide (Li<sub>2</sub>S), and hinder the formation of lithium dendrites. The electrocatalytic properties of the interlayer were subjected to systematic evaluation through electrochemical testing, and the lithium deposition was assessed by examining the surface evolution of lithium metal in symmetric cells. The LLTO carbon matrix interlayer sustained a high specific capacity of 703.3 mA h g<sup>-1</sup> after 200 cycles at 0.1C, with a sulfur loading of 5.5 mg cm<sup>-2</sup>. Furthermore, it demonstrated a high capacity of 905.9 mA h g<sup>-1</sup> with a decay rate of 0.069% per cycle over 1000 cycles at a current density of 5C with a sulfur loading of 1 mg cm<sup>-2</sup>. This investigation highlights the potential of LLTO carbon composite materials as multifunctional interlayers, which could facilitate the optimization of advanced Li–S batteries.

lenges mentioned earlier, several strategies have been put forward. These strategies include creating novel frameworks for sulfur hosts, modifying separators,15,16 and developing advanced electrolytes. Various polar materials have been developed as catalysts, including metal oxides,17 nitrides,18 and sulfides.<sup>19</sup> The prevailing strategy is to combine polar material catalysts with carbonaceous materials to create electron pathways and ion diffusion channels. This combination facilitates effective LiPS capture, rapid conversion, and suppression of lithium dendrites, offering a potential path for the development of Li-S batteries.<sup>20-22</sup> It is also worth noting that these materials have been observed to demonstrate strong affinities for soluble LiPSs, which could potentially contribute to the effective reduction of their shuttling through chemical adsorption. Still, this method is inadequate for overcoming the complexities of Li-S battery reactions.

LLTO has received considerable attention due to its noteworthy ionic conductivity and thermal stability, which make it an attractive option as a solid electrolyte in Li-metal batteries.<sup>23–26</sup> Recently, LLTO has been used as a modified separator in Li–S batteries to provide a physical barrier, thereby alleviating the shuttle effect.<sup>27–30</sup> Furthermore, LLTO composite materials could trap LiPSs through sulfiphilic interactions, thereby facilitating the adsorption and catalytic conversion of LiPSs. Additionally, the lithiophilic interfaces of

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#### Paper

LLTO facilitate the migration of Li ions and regulate Li deposition.<sup>31,32</sup> Although significant progress has been made, it is imperative to gain a deeper understanding of the catalytic mechanism of LLTO-carbon composite materials as multifunctional interlayers. This understanding is crucial for optimizing their performance as effective boosters of the redox kinetics of LiPSs, promoters of Li<sub>2</sub>S nucleation, and inhibitors of lithium dendrite growth.

In this research, we developed amorphous carbon nanofiber matrices containing LLTO through an electrospinning method, followed by thermal treatment. These matrices were utilized as binder-free, self-supporting interlayers in Li-S batteries to facilitate enhanced sulfur redox reactions and overall performance. The synergistic effect of LLTO and the continuous structure of the amorphous carbon nanofiber matrices results in the effective immobilization of LiPSs, preventing their shuttling, and facilitating the redox interactions during charging and discharging. A comprehensive investigation was conducted into the underlying chemical anchoring mechanisms of LiPSs by the LLTO/C composite, the polysulfide conversion pathways, and the precipitation behavior of lithium sulfide (Li2S). The LLTO/C composite also exhibits a homogeneous electric field and uniform distribution of LLTO as lithiophilic sites within a three-dimensional structure, which facilitates the diffusion of Li ions and expands the uniformity of the Li-ion flux.33 This enhances the battery's long-term cycling stability. Consequently, the LLTO/C interlayer exhibits high capacity, outstanding rate performance, and extended cycling life at elevated current densities, marking a significant enhancement in Li-S battery performance.

#### **Results and discussion**

The schematic diagram (Fig. 1) illustrates the synthesis procedure of a free-standing LLTO nanofiber interlayer created through an electrospinning method. The procedure began with preparing a solution of polyvinylpyrrolidone (PVP) by dissolving PVP in a mixture of acetic acid and N,N-dimethylformamide (DMF), and stirring vigorously for a uniform solution. Lithium nitrate, lanthanum nitrate, and titanium isopropoxide were then added and stirred overnight for complete mixing. Next, the prepared spinning liquid was electro-spun into nanofibers. The scanning electron microscopy (SEM) images of the as-electro-spun fiber presented a loose structure, smooth surface, and an average diameter of 680 nm, as shown in Fig. 2(a-c). Subsequently, these fibers were annealed to obtain LLTO/C nanofibers. As shown in Fig. 2(d-g), the SEM and transmission electron microscopy (TEM) images of the fibers show a reduced diameter of about 276 nanometers and a slightly roughened surface. High-resolution TEM (HRTEM) images reveal that the spacing of the parallel fringes aligns with the (110) lattice plane distances of LLTO (Fig. 2(h and i)), which was inconsistent with the X-ray diffraction (XRD) result. Elemental mapping was carried out with TEM. As illustrated in Fig. 2(j), signals from C, O, Ti, and La were evenly dispersed

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Fig. 1 Schematic representation of the synthesis procedure for LLTO/C.

throughout the LLTO/C nanofiber. Moreover, the obtained LLTO with carbon 3D matrices *via* electro-spinning was anticipated to enhance the LLTO composite's conductivity, thus facilitating rapid electron and lithium ion transport, uniform lithium deposition, buffer against volume change, and a barrier to LiPS diffusion.

The XRD pattern of the sample (Fig. 2k) shows that the distinct diffraction peaks align well with the crystalline phase of  $La_{0.55}Li_{0.35}TiO_3$  (JCPDS no. 46-465). Additionally, the peak at 23.32° indicates that amorphous carbon is found in the nanofibers. The surface area and porosity of the LLTO/C composite were determined using N<sub>2</sub> adsorption/desorption as depicted in Fig. 2l and m, revealing a surface area of 25.2 m<sup>2</sup> g<sup>-1</sup>. The available evidence indicates that the LLTO/C composite contains both micropores and mesopores. The micropores serve to impede the movement of lithium polysulfides, while the mesopores facilitate the diffusion of lithium ions.

Coin-type cells were fabricated using the LLTO/C interlayer and MWCNT modified separators (labeled as LLTO/C and MWCNT cells), together with a standard Li–S battery electrolyte and a lithium foil anode. Fig. 3a illustrates the galvanostatic charge/discharge (GCD) profiles of both LLTO/C and MWCNT cells, which exhibit two distinct discharge plateaus and a single charge plateau. The LLTO/C cell exhibits a lower polarization potential (140 mV) than the MWCNT cell (145 mV). In addition, as shown in Fig. 3b, during the oxidation of Li<sub>2</sub>S and the reduction of LiPS to Li<sub>2</sub>S, the LLTO/C cell exhibits a lower overpotential (16 mV for oxidation and 20 mV for reduction).



**Fig. 2** SEM image of (a) electrospinning nanofiber, (b) corresponding diameter distribution from (a), and (c) local magnified SEM image of (a). (d) SEM image of LLTO/C, (e) corresponding diameter distribution from (d), and (f) local magnified SEM image of (d). (g) TEM and (h and i) HRTEM images of LLTO/C. (j) TEM image of an LLTO/C nanofiber with associated elemental mapping. (k) XRD pattern of LLTO/C. (l) Isotherms of N<sub>2</sub> adsorption/desorption and (m) pore size distribution of LLTO/C.

The  $Q_{\rm H}$  designation represents the discharge capacity of the high-voltage plateaus, while the  $Q_{\rm L}$  designation represents the discharge capacity of the low-voltage plateaus. The ratio of  $Q_{\rm H}$ to  $Q_{\rm L}$  is a quantitative measure of the electrocatalytic efficiency associated with the conversion of LiPSs. As depicted in Fig. 3c, the LLTO/C cell exhibits higher  $Q_{\rm H}$ ,  $Q_{\rm L}$ , and a more favorable  $Q_{\rm L}/Q_{\rm H}$  ratio in comparison to the MWCNT cell, confirming its superior electrocatalytic capability. Additionally, the rate performance of the LLTO/C cell and the MWCNT cell was evaluated, as illustrated in Fig. 3d and S1.<sup>†</sup> The GCD profiles indicate that the LLTO/C cell maintains two distinct discharge plateaus up to a high rate of 7C. Conversely, the MWCNT cell shows an increased overpotential and diminished capacity, with distinct plateaus disappearing at a lower rate of 2C, which can be attributed to high surface energy barriers. Fig. 3e presents the rate performance of the LLTO/C cell across various C rates, ranging from 0.1 to 7C. The LLTO/C cell demonstrates high specific capacities, achieving 1431.0, 1256.2, 1157.0, 1077.7, 990.2, 944.0, 912.9, 899.6, 879.4, and 837.1 mA h g<sup>-1</sup> at rates of 0.1 to 7C, respectively. Remarkably, when the rate reverted to 0.1C, the specific capacity was sustained at 1254.5 mA h  $g^{-1}$ . In contrast, the MWCNT cell exhibits specific capacities of 975.9, 807.6, 655.9, 629.1, and 208.6 mA h  $g^{-1}$  at



**Fig. 3** (a) GCD profiles of both LLTO/C and MWCNT cells with 0.1C current density. (b) A detailed view of a specific charge–discharge curve from (a). (c) The metrics  $Q_{\rm H}$ ,  $Q_{\rm L}$ , and their ratio  $Q_{\rm L}/Q_{\rm H}$ . (d) GCD profiles and (e) rate performances of both LLTO/C and MWCNT cells across various current rates. Cycling performance of both LLTO/C and MWCNT cells at (f) 0.1C and (g) 1C. (h) Cycling performance of an LLTO/C cell under sulfur loadings of 4.1 mg cm<sup>-2</sup> and 5.5 mg cm<sup>-2</sup>. (i) Cycling performance of an LLTO/C cell at 5C.

rates of 0.1 to 2C. Moreover, as shown in Fig. S2,† a comparative analysis of the polarization potentials based on the rate performance indicates that the LLTO/C cell shows a lower polarization potential, thereby evidencing its superior electrochemical performance.

To assess the cycling performance, both the LLTO/C and the MWCNT cells at a rate of 0.1C were tested by galvanostatic cycling, as shown in Fig. 3f. The LLTO/C cell shows an initial capacity of 1428.0 mA h  $g^{-1}$  and maintains a capacity of 1223.1 mA h g<sup>-1</sup> after 100 cycles, outperforming the MWCNT cell, which shows an initial capacity of 1232.0 mA h  $g^{-1}$  and deteriorates to 835.8 mA h  $g^{-1}$  over the same number of cycles. As shown in Fig. S3,† it is noteworthy that the charge-discharge curves of the LLTO/C cell from the first to the 300th cycle at 0.1C show an excellent overlap with no significant polarization. Furthermore, the cycling stability of both the LLTO/C and MWCNT cells was assessed at a rate of 1C. As illustrated in Fig. 3g, the LLTO/C cell demonstrates an initial discharge capacity of 1228.3 mA h g<sup>-1</sup>. The capacity decay rate is 0.058% per cycle within 500 cycles. In comparison, the MWCNT cell exhibits an initial capacity of 868.7 mA h  $g^{-1}$  that is reduced to 431.8 mA h  $g^{-1}$  after 500 cycles, equating to a decay rate of 0.10% per cycle. The electrochemical performance of the LLTO/C interlayer significantly exceeds the majority

of previously reported results, as shown in Fig. S4.<sup>†</sup> When compared to other approaches,<sup>40–43</sup> the LLTO/C interlayer offers a superior cycling life with minimal capacity decay. The cell with the LLTO/C interlayer not only exhibits a considerably elevated capacity but also demonstrates a reduced capacity decay rate, indicating superior long-term cycling stability. The enhanced electrocatalytic activity of the LLTO/C interlayer resulted in improved performance.

One of the obstacles to commercializing Li-S batteries is the requirement for a substantial sulfur load to realize their application in actual devices. As shown in Fig. 3h, the cells with sulfur loadings of 4.1 mg  $cm^{-2}$  and 5.5 mg  $cm^{-2}$  on the cathode, incorporating an LLTO/C interlayer, have been fabricated. The cycling performances of these cells indicate that both configurations achieve high discharge capacities of 1029.9 and 808.2 mA h g<sup>-1</sup>, respectively, at a current density of 0.1C, alongside notable cycling stability. These results suggest that the LLTO/C interlayer holds promise for the practical application of Li-S batteries. Furthermore, the capacity retention at high current densities was evaluated, with results presented in Fig. 3i. The battery demonstrates an initial capacity of 905.9 mA h  $g^{-1}$  and exhibits a capacity decay rate of 0.069% per cycle following 1000 cycles at a current density of 5C. The GCD profile (Fig. S5<sup>†</sup>) demonstrates that the battery with an LLTO/C interlayer maintains its discharge plateaus even after 1000 cycles at a current density of 5C, indicating durable longterm performance.

The adsorption test of LLTO/C and MWCNT was conducted (Fig. 4a). The  $\text{Li}_2\text{S}_6$  solution mixed with LLTO/C was colorless after 12 h. In contrast, the  $\text{Li}_2\text{S}_6$  solution exhibits minimal change following the addition of MWCNTs, demonstrating that LLTO/C exhibits a markedly superior chemisorptive capacity for LiPSs in comparison to MWCNTs. To gain further insight into the chemical interactions between LLTO/C and

Fig. 4 (a) Adsorption tests of  $Li_2S_6$ . (b) XPS survey spectrum for LLTO/C. (c) High-resolution XPS spectra of Ti 2p and (d) the calculated percentages of characteristic chemical bonds derived from Ti 2p analysis.

LiPS, X-ray photoelectron spectroscopy (XPS) analyses were conducted.

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The obtained XPS survey spectrum as shown in Fig. 4b demonstrates the presence of four elements La, Li, Ti, and O, along with C that corresponded to the expected chemical composition.<sup>24</sup> The high-resolution XPS spectrum of LLTO/C before contact with L<sub>2</sub>S<sub>6</sub> (Fig. 4c) reveals the presence of Ti 2p peaks at 458.4 and 464.1 eV, which are assigned to  $Ti^{4+} 2p_{1/2}$ and Ti<sup>4+</sup> 2p<sub>3/2</sub>, respectively.<sup>27</sup> Additionally, all the other peaks observed within the 457.1, 462.9, 455.8, and 461.3 eV ranges are attributed to Ti<sup>3+</sup> 2p and Ti<sup>2+</sup> 2p, respectively.<sup>34</sup> The presence of lower oxidation state species associated with oxygen vacancies can significantly improve the conductivity, thus enhancing its catalytic performance in the conversion of LiPSs. In comparison to the pristine LLTO/C, the Ti 2p peaks exhibit a shift towards a lower binding energy. Simultaneously, the concentration of Ti<sup>4+</sup> and Ti<sup>3+</sup> ions decreases (Fig. 4d), while Ti<sup>2+</sup> increases, suggesting a strong correlation between Ti and S. It can be observed that the La 3d spectrum for LLTO/ C (Fig. S6<sup> $\dagger$ </sup>) indicates the presence of two bonds of  $3d_{3/2}$  and 3d<sub>5/2</sub>, positioned at 851.3 and 834.7 eV, which appear to be associated with La<sup>3+</sup> valence. The La 3d peaks exhibit a shift towards lower binding energies when compared with pristine LLTO/C. This indicates that electrons are transferred from Li<sub>2</sub>S<sub>6</sub> to the surface of LLTO/C. Furthermore, LLTO/C may function as an electrocatalyst, facilitating the conversion of Li<sub>2</sub>S<sub>6</sub>. In the pristine LLTO/C nanofiber, the O 1s spectrum (Fig. S7<sup>†</sup>) exhibits two peaks at 529.5 and 531.5 eV, which are attributed to O-Ti and Ti-OH, respectively.<sup>27</sup> Following the absorption of  $Li_2S_6$ , a proportional increase was observed in the content of oxygen-hydrogen bonds. Potential explanations for this observation include the existence of the oxygen-hydrogen bond in oxygen-containing acid sulfate salts of sulfur.

Further investigation was conducted into the electrocatalytic conversion of LLTO/C to polysulfides using symmetrical cells containing  $\text{Li}_2\text{S}_6$  electrolyte. The cyclic voltammetry (CV) profiles (Fig. 5a) reveal that the redox current response for the LLTO/C is stronger compared to that for the MWCNT symmetrical cell. All potentials in this work are measured relative to the Li<sup>+</sup>/Li reference electrode. This suggests that the LLTO/C may exhibit strong catalytic capabilities for the conversion of LiPSs, resulting in accelerated kinetics of the polysulfide reaction. The enhanced electrocatalytic capability of LLTO towards LiPSs and the enhanced electric conductivity resulting from the continuous carbon structure are the main factors contributing to the superior performance of LLTO/C.

Another crucial parameter for evaluating the electrocatalytic performance of cathode materials in Li–S batteries is  $\text{Li}_2\text{S}$  precipitation. Consequently, potentiostatic discharge/charge profiles were obtained utilizing  $\text{Li}_2\text{S}_8$  as the electrolyte. As illustrated in Fig. 5b–d, LLTO/C symmetric cells exhibit the minimal nucleation time and the maximal capacity for  $\text{Li}_2\text{S}$ precipitation in comparison to MWCNT symmetric cells, indicating that the presence of LLTO/C markedly diminishes the surface energy barrier for  $\text{Li}_2\text{S}$  nucleation and considerably accelerates the reduction kinetics for  $\text{Li}_2\text{S}$ . The findings reveal





Fig. 5 (a) CV curves of symmetric cells. (b–d) Potentiostatic discharge profiles of  $Li_2S_6$  solution at 2.05 V.

that the LLTO/C composite effectively anchors LiPSs through robust physical and chemical adsorption and efficiently accelerates the conversion reactions of LiPSs.

To verify the catalytic activities within Li–S batteries, CV tests were carried out with coin cells including S cathodes, Li anodes, and interlayer/separators. Fig. 6a illustrates the oxi-



**Fig. 6** (a) CV curves of LLTO/C and MWCNT cells at 0.1 mV s<sup>-1</sup>. (b and c) Tafel plots for S<sub>8</sub> reduction to Li<sub>2</sub>Sn and further to Li<sub>2</sub>S. (d) Relative activation energy of LLTO/C and MWCNT. (e) LLTO/C CV curves across various scan rates. (f)  $D_{\rm Li^+}$  comparison between LLTO/C and MWCNT cells.

dative and reductive behavior. The presence of two distinct reduction peaks can be attributed to the sequential conversion of S<sub>8</sub> to Li<sub>2</sub>S<sub>n</sub> ( $4 \le n \le 8$ ) and subsequently to Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S, respectively.<sup>35</sup> The sustained oxidation peak indicates the reversal of the Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S conversion to LiPSs and then S<sub>8</sub>, in alignment with the GCD profiles. The reduction/oxidation peaks of the LLTO/C cell shift towards high/low potential compared to peaks of the MWCNT cell. These findings suggest a significant reduction in electrochemical polarization, highlighting the LLTO/C composite's strong catalytic influence on the conversion of LiPSs and the acceleration of their redox kinetics. This observation aligns with the GCD curves.

To better understand the electrocatalytic properties of the LLTO/C interlayer, Tafel plots of the reduction (R1, R2) and oxidation (O1) peaks were obtained (Fig. 6b, c and S8<sup>†</sup>). The Tafel slopes for reduction (R1, R2) and oxidation (O1) peaks for LLTO/C are notably lower, indicating enhanced kinetics for the reduction reactions involving sulfur and the expedited oxidation of Li<sub>2</sub>S. Furthermore, Tafel slope analysis has been utilized to determine the activation energies for these reduction and oxidation processes. As depicted in Fig. 6d and S9,† the LLTO/C catalyst significantly reduces the reaction energy barrier by 67.67 kJ mol<sup>-1</sup> compared to the MWCNT interlayer during the reduction of S<sub>8</sub> to Li<sub>2</sub>S<sub>4</sub>. Moreover, the LLTO/C catalyst decreases the activation energy to 91.07 kJ mol<sup>-1</sup> during the conversion of long-chain Li<sub>2</sub>S<sub>4</sub> to short-chain Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S. Additionally, for the oxidation process, which involves the rapid oxidation of deposited Li<sub>2</sub>S, the LLTO/C catalyst lowers the activation energy by 80.06 kJ mol<sup>-1</sup>, further demonstrating its effectiveness in enhancing redox reactions.36

The assessment of lithium-ion diffusion rates is of value in evaluating the kinetics of redox reactions. The CV tests (Fig. 6e and S10<sup>†</sup>), conducted at scan rates ranging from 0.1 to 0.4 mV s<sup>-1</sup>, enabled this evaluation through the Randles–Sevcik equation.<sup>37</sup> The diffusion coefficients of  $D_{\text{Li}^+}$  for both LLTO/C and MWCNT cells were derived from the slope of the linear relationship between  $I_p$  and the square root of the scan rate (Fig. S11<sup>†</sup>).

The superior  $D_{\text{Li}^+}$  values for the LLTO/C cell, compared to those of the MWCNT cell (Fig. 6f), indicate enhanced Li<sup>+</sup> diffusion and sulfur redox reaction facilitation, thus improving Li–S batteries' rate capability.

A Li||Li symmetric cell test was conducted to evaluate the polarization effect. The results are presented in Fig. 7a. The Li symmetric cell with an MWCNT separator demonstrates a high overpotential of 62 mV. In contrast, the Li symmetric cell with the LLTO/C interlayer exhibits a lower overpotential of 26 mV. The rate performance of symmetric cells was also evaluated to investigate the overpotential across current densities ranging from 0.5 to 3 mA cm<sup>-2</sup>, as illustrated in Fig. 7b. As the current density increases, the symmetric cell with an LLTO/C interlayer consistently demonstrates a low overpotential. As illustrated in Fig. 7c and d, the symmetric cell with an MWCNT separator exhibits a notable rise in polarization voltage, potentially attributable to the proliferation of Li dendrites and the consumption of electrolytes.<sup>12</sup> Conversely, the symmetric cell with



**Fig. 7** (a) Li plating/stripping efficacy in symmetric cells using an MWCNT separator and LLTO/C interlayer across variable current densities, maintaining a 1 mA h cm<sup>-2</sup> areal capacity, and (b) detailed voltage profiles for 0.5–3 mA cm<sup>-2</sup> current densities. (c) Cycles in the periods of 450–500 h and (d) 1450–1500 h. (e) Li plating/stripping in symmetric cells with MWCNT separators and LLTO/C interlayers at 1 mA cm<sup>-2</sup> current density. (f) Schematic representations of Li deposition pathways in electrodes with MWCNTs and LLTO/C. SEM images detailing Li anode conditions with (g and h) MWCNT separator and (i and j) LLTO interlayer.

an LLTO/C interlayer exhibits a consistent level of polarization voltage. This phenomenon is also observed at a current density of 1 mA cm<sup>-2</sup>, as shown in Fig. 7e. These findings indicate that the LLTO/C interlayer facilitates uniform Li stripping and plating. As illustrated in Fig. 7f, the LLTO/C interlayer ensures homogeneous Li-ion flux and prevents the growth of Li dendrites.<sup>38,39</sup> After cycling, SEM analysis of the lithium anode surface reveals that lithium deposition on the anode for the MWCNT separator was scattered and irregularly distributed (Fig. 7g and h). In contrast, uniform deposition of Li metal was observed on the anode surface for the LLTO/C interlayer (Fig. 7i and j). This indicates that the LLTO/C interlayer can effectively redistribute lithium ions, regulating lithium deposition and ensuring that the Li-S battery has long cycling performance. The inherent high Li<sup>+</sup> conductivity of LLTO ensures rapid migration of Li<sup>+</sup> ions along the nanofiber surface. Meanwhile, the 3D structure serves as an accelerated Li<sup>+</sup> transport medium. Consequently, this improvement in Li-ion transport and suppression of dendrite formation significantly enhances the cycling performance and stability of the Li-metal anode in the presence of the LLTO/C interlayer.

#### Conclusions

In summary, a multifunctional interlayer for Li-S batteries has been developed. This interlayer is composed of LLTO with amorphous carbon nanofiber matrices. The configuration utilizes the synergistic effects of LLTO and the continuous structure of the carbon nanofiber matrices to effectively immobilize LiPSs, thereby mitigating their shuttling and enhancing redox reactions throughout the charge/discharge cycles. Moreover, it enables uniform lithium deposition. The LLTO carbon matrix interlayer demonstrated a sustained high specific capacity of 703.3 mA h  $g^{-1}$  following 200 cycles at 0.1C, with a sulfur loading of 5.5 mg cm<sup>-2</sup>. Furthermore, it demonstrated a high capacity of 905.9 mA h  $g^{-1}$  with a minimal decay rate of 0.069% per cycle across 1000 cycles at a current density of 5C, with a sulfur loading of 1 mg cm<sup>-2</sup>. This research emphasizes the promising capabilities of LLTO carbon composite materials as effective multifunctional interlayers, with the capacity to significantly improve the performance of advanced Li-S batteries.

#### Data availability

All data generated or analyzed during this study are included in this published article and its ESI.†

### Conflicts of interest

The authors declare that they have no conflict of interest.

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#### Notes and references

- 1 M. Zhao, H. J. Peng, B. Q. Li and J. Q. Huang, Acc. Chem. Res., 2024, 57, 545-557.
- 2 J. Y. Li, L. Gao, F. Y. Pan, C. Gong, L. M. Sun, H. Gao,
   J. Q. Zhang, Y. F. Zhao, G. X. Wang and H. Liu, *Nano-Micro Lett.*, 2024, 16, 12.
- 3 C. C. Li, W. N. Ge, S. Y. Qi, L. Zhu, R. Z. Huang, M. W. Zhao, Y. T. Qian and L. Q. Xu, *Adv. Energy Mater.*, 2022, **12**, 2103915.
- 4 L. Wang, W. X. Hua, X. Wan, Z. Feng, Z. H. Hu, H. Li, J. T. Niu, L. X. Wang, A. S. Wang and J. Y. Liu, *Adv. Mater.*, 2022, **34**, 2110279.

- 5 Z. Y. Han, R. H. Gao, Y. Y. Jia, M. T. Zhang, Z. J. Lao, B. Chen, Q. Zhang, C. Li, W. Lv and G. Zhou, *Mater. Today*, 2022, 57, 84–120.
- 6 X. H. Liu, L. R. Zhang, X. Z. Ma, H. Q. Lu, L. Li, X. T. Zhang and L. L. Wu, *Chem. Eng. J.*, 2023, **454**, 140460.
- 7 C. Zhang, L. R. Zhang, Z. G. Zhang, X. T. Zhang and L. L. Wu, J. Colloid Interface Sci., 2024, 661, 472–481.
- 8 Y. Lei, Z. Y. Zhang, Z. Lin, S. Bhattacharjee and C. Chen, *Dalton Trans.*, 2024, **53**, 3985–3989.
- 9 Y. F. Zhao, L. Wu, Y. Yu, Y. Q. Dai, B. Liao and H. Pang, *Dalton Trans.*, 2022, **51**, 11665–11674.
- 10 X. H. Liu, Z. Z. Zhang, X. T. Zhang and L. L. Wu, *Electrochim. Acta*, 2024, 477, 143793.
- 11 F. F. Han, Z. L. Wang, Q. Jin, L. W. Fan, K. H. Tao, L. Li, L. Shi, H. Q. Lu, Z. G. Zhang, J. J. Li, X. Zhang and L. L. Wu, ACS Nano, 2024, 18, 15167–15176.
- 12 R. Razaq, M. M. U. Din, D. R. Småbråten, V. Eyupoglu, S. Janakiram, T. O. Sunde, N. Allahgoli, D. Rettenwander and L. Deng, *Adv. Energy Mater.*, 2024, 14, 2302897.
- 13 Q. Jin, K. X. Zhao, L. L. Wu, L. Li, L. Kong and X. T. Zhang, J. Energy Chem., 2023, 84, 22–29.
- 14 Q. Jin, M. L. Zhao, K. X. Zhao, J. P. Xiao, J. Yao, L. Li, L. L. Wu and X. T. Zhang, *Chem. Eng. J.*, 2024, 153227.
- 15 W. C. Zhang, K. X. Zhao, Q. Jin, J. P. Xiao, H. Q. Lu, X. T. Zhang and L. L. Wu, *Electrochim. Acta*, 2022, 430, 141104.
- 16 G. F. Tang, X. M. Song, X. L. Qiu, J. L. Wang, X. X. Sun, F. S. Chen, Z. Y. Cao and S. S. Gao, *J. Alloys Compd.*, 2024, 971, 172698.
- 17 X. Liu, J. Q. Huang, Q. Zhang and L. Q. Mai, *Adv. Mater.*, 2017, **29**, 1601759.
- 18 H. Liu, X. J. Yang, B. Jin, M. Y. Cui, Y. Y. Li, Q. C. Li, L. Li, Q. D. Sheng and X. Y. Lang, *Small*, 2023, **19**, 2300950.
- 19 M. Y. Chen, T. Zeng, L. Luo, L. H. Wu, S. H. Fu, J. Shen and B. Jin, *J. Alloys Compd.*, 2024, **984**, 173969.
- 20 X. T. Zuo, L. F. Wang, M. M. Zhen, T. T. You, D. P. Liu and Y. Zhang, *Angew. Chem., Int. Ed.*, 2024, **63**, e202408026.
- 21 X. L. Wei, Y. H. Luo, X. H. Du, L. L. Wu, G. H. Liu and J. D. Li, *Chem. Eng. J.*, 2023, **454**, 140152.
- 22 W. Q. Yao, J. Xu, L. B. Ma, X. M. Lu, D. Luo, J. Qian, L. Zhan, I. Manke, C. Yang and P. Adelhelm, *Adv. Mater.*, 2023, 35, 2212116.
- 23 W. J. Kwon, H. Kim, K. N. Jung, W. Cho, S. H. Kim, J. W. Lee and M. S. Park, *J. Mater. Chem. A*, 2017, 5, 6257– 6262.
- 24 S. Ulusoy, S. Gulen, G. Aygun, L. Ozyuzer and M. Ozdemir, *Solid State Ionics*, 2018, **324**, 226–232.
- 25 L. Zhu, P. H. Zhu, Q. X. Fang, M. X. Jing, X. Q. Shen and L. Z. Yang, *Electrochim. Acta*, 2018, **292**, 718–726.

- 26 S. Yan, C. H. Yim, V. Pankov, M. Bauer, E. Baranova, A. Weck, A. Merati and Y. Abu-Lebdeh, *Batteries*, 2021, 7, 75.
- 27 M. Y. Wang, S. H. Han, C. Q. Niu, Z. S. Chao, W. B. Luo, H. G. Jin, W. J. Yi, Z. Q. Fan and J. C. Fan, ACS Sustainable Chem. Eng., 2020, 8, 16477–16492.
- 28 H. Wang, B. Li, Y. L. Shen, Z. Y. Zhang, Y. Z. Sun, W. T. Zhou, S. T. Liang, W. T. Li and J. X. He, ACS Appl. Mater. Interfaces, 2024, 16, 12500–12508.
- 29 S. S. Liang, S. Chauque, M. Ricci and R. P. Zaccaria, *Mater. Today Energy*, 2024, 40, 101497.
- 30 L. Wang, X. Yin, B. Li and G. W. Zheng, *Nano Lett.*, 2021, 22, 433–440.
- 31 X. J. Zhang, Y. F. Chen, F. Ma, X. Chen, B. Wang, Q. Wu, Z. H. Zhang, D. W. Liu, W. L. Zhang and J. R. He, *Chem. Eng. J.*, 2022, **436**, 134945.
- 32 S. Abdul Ahad, S. Bhattacharya, S. Kilian, M. Ottaviani, K. M. Ryan, T. Kennedy, D. Thompson and H. Geaney, *Small*, 2023, **19**, 2205142.
- 33 Q. Jin, L. R. Zhang, M. L. Zhao, L. Li, X. B. Yu, J. P. Xiao, L. Kong and X. T. Zhang, *Adv. Funct. Mater.*, 2024, 34, 2309624.
- 34 K. Y. Yang, K. Z. Fung and M. C. Wang, J. Appl. Phys., 2006, 100, 056102.
- 35 Y. Chen, W. X. Zhang, D. Zhou, H. J. Tian, D. W. Su, C. Y. Wang, D. Stockdale, F. Kang, B. Li and G. Wang, *ACS Nano*, 2019, **13**, 4731–4741.
- 36 W. H. Hua, H. Li, C. Pei, J. Y. Xia, Y. F. Sun, C. Zhang, W. Lv, Y. Tao, Y. Jiao and B. S. Zhang, *Adv. Mater.*, 2021, 33, 2101006.
- 37 M. J. Shi, Z. Liu, S. Zhang, S. C. Liang, Y. T. Jiang, H. Bai, Z. M. Jiang, J. Chang, J. Feng and W. S. Chen, *Adv. Energy Mater.*, 2022, **12**, 2103657.
- 38 Y. J. Li, T. T. Gao, D. Y. Ni, Y. Zhou, M. Yousaf, Z. Guo, J. H. Zhou, P. Zhou, Q. Wang and S. J. Guo, *Adv. Mater.*, 2022, 34, 2107638.
- 39 F. Ma, X. J. Zhang, K. Sriniva, D. W. Liu, Z. H. Zhang, X. Chen, W. L. Zhang, Q. Wu and Y. F. Chen, *J. Mater. Chem.*, 2022, **10**, 8578–8590.
- 40 J. Xia, W. Hua, L. Wang, Y. Sun, C. Geng, C. Zhang,
   W. Wang, Y. Wan and Q. Yang, *Adv. Funct. Mater.*, 2021, 31, 2101980.
- 41 Y. Lei, Z. Zhang, Z. Lin, S. Bhattacharjee and C. Chen, *Dalton Trans.*, 2024, **53**, 3985–3989.
- 42 J. Lee, C. Choi, J. B. Park, S. Yu, J. Ha, H. Lee, G. Jang, Y. S. Park, J. Yun and H. Im, *J. Energy Chem.*, 2023, 83, 496– 508.
- 43 J. Xie, B. Q. Li, H. J. Peng, Y. W. Song, M. Zhao, X. Chen, Q. Zhang and J. Q. Huang, *Adv. Mater.*, 2019, **31**, 1903813.