Understanding Lil-LiBr Catalyst Activity for Solid State Li₂S/S Reactions in an All-Solid-State Lithium Battery

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816.2 mAh g^{-1} at 200 mA g^{-1} and maintain 604.8 mAh g^{-1} (based on the mass of MoS₂) for 100 cycles. At a high areal capacity of 2 mAh cm⁻², the battery still delivers reversible capacity of 498 mAh g^{-1} . LiI-LiBr-carbon additive can be broadly applied for all transition-metal sulfide cathodes to enhance the cyclic and rate performance.

KEYWORDS: all-solid-state lithium battery, transition-metal sulfide, MoS2@LiI-LiBr, redox kinetic, DFT calculation

T he all-solid-state lithium-sulfur battery is promising for large-scale storage systems due to its high specific capacity and energy density.¹⁻³ However, the full utilization of sulfur is challenged due to the insulating nature, strong ionic bond of Li₂S, and large volume change of S/Li₂S during discharge/charge processes.⁴⁻⁶ Transition-metal sulfide with higher electronic conductivity and smaller volume change can partially circumvent these challenges in solid-state LillS batteries.^{7,8} However, transition-metal sulfide cathodes still suffer from decay in capacity and rate capability because partial metal sulfides will irreversibly convert into metal and S, and then S will experience a challenged S/Li₂S reaction. For example, MoS₂ experiences a two-step process during lithiation/delithiation at 0.5–3 V (*vs.* Li/Li⁺).^{9,10}

Lithiation (discharge):

$$MoS_2 + xLi^+ + xe^- \rightarrow Li_xMoS_2 \quad (\sim 1.1 \text{ V vs Li/Li}^+)$$
(1)

$$Li_{x}MoS_{2} + (4 - x)Li^{+} + (4 - x)e^{-} → Mo^{0} + 2Li_{2}S$$
(~0.6 V vs Li/Li⁺) (2)

Delithiation (charging process):

$$Mo^{0} + Li_{2}S \rightarrow MoS_{2} + Li^{+} + e^{-}$$
(3)

$$\mathrm{Li}_2 \mathrm{S} \to \mathrm{S} + 2\mathrm{Li}^+ + 2\mathrm{e}^- \tag{4}$$

After the full lithiation process, MoS₂ converts to metal Mo⁰ and Li₂S (Reactions 1 and 2). However, in the following charge process, the regeneration of MoS₂ is limited (Reaction 3), and the unreacted Li_2S will be oxidized to sulfur (Reaction 4), suggesting that, after the first cycling at 0.5-3 V (vs. Li/ Li⁺), MoS₂ will transfer to a hybrid of LillMoS₂ and LillS batteries, where the S suffers from the similar challenges of Lill S batteries, although the *in-situ* formed conductive Mo⁰@MoS₂ can improve the reversibility of sulfur.^{4,5,10-13} The accumulation of sulfur in the MoS₂ cathode during lithiation/delithiation cycles also leads to capacity decay of the LillMoS₂ all-solid-state battery at a cutoff voltage of 0.5-3.0 V. Through electrolyte/active material interface design, the interfacial resistance can be decreased, thus enhancing the electrochemical kinetics.^{14,15} Increasing the contact area between MoS₂ and the solid electrolyte through decreasing the particle size of MoS2¹⁶ or *in-situ* coating solid electrolyte on the surface of MoS₂¹⁷ can mitigate the capacity decay of the LillMoS₂ cell at a wide cutoff voltage due to the decreased interfacial resistance. However, the capacity retention of

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Figure 1. (a) XRD patterns of MoS_2 , $MoS_2@LiI-LiBr$, and $MoS_2@LiI-LiBr@C$. (b) *Ex-situ* Raman spectrum for MoS_2 in the first discharge/charge process in the solid-state cell. CV curves of (c) MoS_2 and (d) $MoS_2@LiI-LiBr$.



Figure 2. Galvanostatic discharge/charge profiles for (a) Li₂S@LiI-LiBr and (b) Li₂S. (c) Raman spectra of Li₂S, Li₂S@LiI, and Li₂S@LiI-LiBr. (d) Impedance spectra for Li₂S@LiI and Li₂S@LiI-LiBr.

 $Li_7P_3S_{11}$ solid electrolyte coated MoS_2 was 75%,¹⁷ and the initial reversible capacity of the MoS_2 nanosheet is 439 mAh g^{-1} due to the incomplete solid-state reaction.¹⁶ Narrowing the cutoff voltage to 1.0–3.0 V can suppress the generation of the Li_2S/S redox couple with low reaction kinetics, however, the reversible reaction between MoS_2 and Li_xMoS_2 significantly reduced the capacity. To achieve both high capacity and long cycle life, the reversibility and reaction kinetics of LillS chemistry need to be improved.

Inspired by the significant enhancement of ionic conductivity of solid sulfide electrolyte $(Li_2S-P_2S_5)$ by replacing S with halogen (Cl, Br, and I),¹⁸ we introduced LiI-LiBr into MoS₂ to facilitate the oxidation and enhance the ionic conductivity of Li₂S because LiI-LiBr can reduce the interaction between Li⁺ and S²⁻, leading to a decreased overpotential for the Li₂S delithiation process. To further enhance the reaction kinetics, we also added carbon black into the MoS₂@LiI-LiBr composite by ball-milling the mixture to decrease the particle size of MoS₂ and ensure a sufficient electronic conduction pathway in the cathode. Under charge/discharge protocol of 0.5–3.0 V cutoff voltage in the first cycle and 1.0–2.8 V in the following cycles, the MoS₂@LiI-LiBr@Cll Li all-solid-state battery provided a reversible capacity of 437.8 mAh g⁻¹ (mass of MoS₂@LiI-LiBr) at a current density of 200 mA g⁻¹ for 100 cycles.

Figure 1a shows the X-ray powder diffraction (XRD) pattern of MoS₂, MoS₂@LiI-LiBr, and MoS₂@LiI-LiBr@C composites. The main diffraction peaks at $2\theta = 14.1^{\circ}$, 32.9° , 39.5° , and 58.7° are assigned to MoS₂.¹⁷ The diffraction peak at $2\theta = 26.0^{\circ}$ in the MoS₂@LiI-LiBr@C composite derives from carbon black.¹⁹ No diffraction peaks assigned to LiI and LiBr were observed due to the low amount or amorphous property of the LiI-LiBr compound after ball-milling. We first investigated the lithium storage mechanism of the MoS₂

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Figure 3. DFT calculations of the Li_2S -I-Br system. (a) Defect formation energies in Li_2S . (b) Crystal orbital Hamilton population (COHP) of the Li-S bond in Li_2S bulk and around complex defects. (c) Defect formation energies in LiI. (d) Defect formation energies in Li_4I_3Br .

cathode in the solid-state cell using ex-situ Raman tests. As shown in Figure 1b, for the pristine MoS₂ electrode, the Raman shifts at 376 and 401 cm⁻¹ are assigned to vibrational modes of 2H-MoS₂.²⁰ When MoS₂ was discharged to 0.5 V, the Raman peaks for MoS₂ disappeared. After it was charged back to 1.7 V, and no Raman peaks for MoS₂ can be observed. Only when the MoS_2 was further charged to 2.1 and 3.0 V, the peaks for MoS₂ and S appear, demonstrating that the LillMoS₂ cell has transferred to a hybrid of LillMoS₂ and LillS cells after the first cycle at a cutoff voltage of 0.5-3.0 V. In the following cycles, the battery was discharged and charged at a cutoff voltage of 1.0-2.8 V to suppress the accumulation of sulfur. The enhancement of reaction kinetics for the MoS₂ cathode by LiI-LiBr was confirmed in cyclic voltammetry (CV) curves (Figure 1c,d), where the LiI-LiBr compound acts as a catalyzer to promote the S/Li₂S redox reaction in the MoS₂@LiI-LiBr cathode (Figure 1d) compared with that in the MoS_2 cathode (Figure 1c). In the first cycle of the MoS₂@LiI-LiBr cathode (Figure 1d), the reduction peaks at 1.7 and 1.1 V in the second curve derive from the reduction of S to Li_2S and lithiation of MoS₂ to Li_xMoS₂, respectively. In the second anodic scan, oxidation peaks at 1.9 and 2.3 V are ascribed to the delithiation of Li_xMoS₂ to MoS₂ and Li₂S to S, respectively.⁹ Obviously, the peak intensity for the S/Li₂S redox couple is much higher than that of MoS_2/Li_xMoS_2 , implying the S/Li₂S is the dominant redox couple after the first cycle.

To investigate the catalytic effect of the LiI-LiBr compound on the reaction of the S/Li₂S redox couple, Li₂S and Li₂S@LiI-LiBr composite (Figure S1) were prepared by the same ballmilling procedure, and then the performances of the two cathodes were compared in all-solid-state battery. As shown in Figure 2, the Li₂S/S redox overpotential in the Li₂S@LiI-LiBr (Figure 2a) cathode was obviously decreased after the first cycle, and the capacity is also much larger than that of the Li₂S cathode without LiI-LiBr compound (Figure 2b). The charge transfer resistance of the cycled Li₂S@LiI-LiBr cathode is also lower than that of Li₂S (Figure S2) due to the enhanced Li₂S/S redox kinetics in the Li₂S@LiI-LiBr composite. Raman spectra of Li₂S, Li₂S@LiI, and Li₂S@LiI-LiBr in Figure 2c shows that adding the LiI-LiBr compound into Li₂S induced a red-shift for the Li–S bond due to the reduced interaction between Li⁺ and S^{2-,21} which can facilitate the delithiation of Li₂S. Moreover, the ionic conductivity of Li₂S was also improved by incorporation of the LiI-LiBr compound (Figure 2d). It is reported that Li₂S has a low ionic conductivity of 10⁻¹³ S cm⁻¹;²² after introducing LiI, the ionic conductivity was improved to 6.4 × 10⁻⁸ S cm⁻¹ for the Li₂S@LiI composite. Further introducing the LiI-LiBr compound, the obtained Li₂S@LiI-LiBr composite exhibits a 7 orders of magnitude increase in ionic conductivity (1.08 × 10⁻⁶ S cm⁻¹) compared with Li₂S.

The catalytic effect of LiI-LiBr on the conversion reaction of Li₂S/S was also confirmed by the DFT calculation. Figure 3a shows that the Li vacancies (V_{Li}) are the main intrinsic defects in Li₂S. With incorporating LiBr in Li₂S, Li vacancies along with Br-on-S substitution (complex defect) will be formed. The formation energy of this complex defect is even lower than that of intrinsic Li vacancies. For the LiI incorporation, the complex defect of Li vacancies along with I-on-S substitution is also one of the most possible states. These complex defects are mainly due to valence inconsistencies between Br/I and S. Therefore, a small amount of Br and I doped into Li₂S will generate complex defects in Li₂S, increasing the Li-ion conductivity. The impact of the complex defects on the Li-S bond strength was also evaluated using crystal orbital Hamilton population (COHP) analysis. As shown in Figure 3b, the bonding state of the Li-S bond around complex defects decreases and reduces the integral COHP value. Therefore, Br/I incorporation can effectively improve the decomposition of Li₂S, implying Br/I incorporation can promote the Li₂S/S reaction. Besides, Li₄I₃Br shows lower intrinsic Li vacancy formation energy than that of LiI (Figure 3c,d), implying Br incorporation can also improve the Li-ion conductivity of LiI, thus improving the ionic conductivity of the Li₂S@LiI-LiBr composite.

The characterizations and calculation demonstrated that the enhanced redox reaction of Li₂S/S by LiI-LiBr introduction is attributed to the increased ionic conduction and decreased Li–



Figure 4. Galvanostatic discharge/charge profiles for (a) MoS_{22} (b) MoS_{22} @LiI-LiBr, and (c) MoS_{22} @LiI-LiBr@C. (d) Cyclic performances of MoS_{22} , MoS_{22} @LiI-LiBr, and MoS_{22} @LiI-LiBr@C at a current density of 200 mA g⁻¹. SEM images of (e) MoS_{22} (f) MoS_{22} @LiI-LiBr, and (g) MoS_{22} @LiI-LiBr@C.

S bond, which will enhance the electrochemical performances of MoS₂ since Li₂S will be formed during charge/discharge cycles at a wide voltage window of 0.5-3.0 V. The electrochemical performances of MoS₂, MoS₂@LiI-LiBr, and MoS2@LiI-LiBr@C cathodes were evaluated in all-solid-state lithium batteries. All the batteries are cycled at a cutoff voltage of 0.5-3 V (vs. Li/Li⁺) in the first cycle and then tested at a cutoff voltage of 1.0-2.8 V (vs. Li/Li⁺) in the following cycles at a current density of 200 mA g^{-1} . As shown in Figure 4a-c, the overpotential for the MoS2@LiI-LiBr cathode is smaller than that of MoS₂. Besides, the resistance of the MoS₂@LiI-LiBrllLi cell was much smaller than that of the MoS₂llLi cell after 100 cycles (Figure S3). After introducing carbon, the overpotential further decreased for MoS2@LiI-LiBr@C, and the highest reversible capacity of 437.8 mAh g^{-1} (based on the mass of MoS₂@LiI-LiBr) was maintained for the MoS₂@LiI-LiBr@CllLi cell after 100 cycles. In contrast, pure MoS₂ only delivers reversible capacity of 110.7 mAh g^{-1} (Figure 4d). The best electrochemical performance for the MoS₂@LiI-LiBr@Cll Li cell is attributed to the catalytic effect of LiI-LiBr on MoS₂ and the increased contact between MoS2@LiI-LiBr and electronic conductive carbon black due to the reduced particle size of MoS₂ in MoS₂@LiI-LiBr@C as demonstrated in Figure 4g. For both MoS₂ (Figure 4e) and MoS₂@LiI-LiBr (Figure 4f), a micrometer sized sheet with thickness of several nanometers was observed in scanning electron microscopy (SEM) images. After carbon black was introduced during ballmilling, the particle size of obtained MoS₂@LiI-LiBr@C was significantly reduced from the microscale to the nanoscale (Figure 4g), which is beneficial to enhance interfacial contact between MoS₂ and carbon black, thus further improving the electrochemical performance of the all-solid-state lithium battery. $^{\rm 23}$

The electrochemical performance of the MoS₂||Li battery was also affected by the mole ratio of LiI to LiBr. As shown in Figures S4 and S5, the reversible capacities of the MoS₂@LiI-LiBr@C composite with the LiI:LiBr mole ratios of 100:0 (Figure S4) and 50:50 (Figure S5) are lower than that of the MoS₂@LiI-LiBr@C composite with the optimized LiI:LiBr mole ratio of 75:25. The ratio of LiI-LiBr to Li₂S also affects the catalytic activity. We prepared Li₂S@LiI-LiBr and MoS₂@ LiI-LiBr cathodes at the same molar ratio of LiI-LiBr to S, where the mole ratio of MoS₂ to LiI-LiBr was 2:1 and that of Li₂S to LiI-LiBr was 4:1. Since only partial MoS₂ was converted into Li₂S, the ratio of LiI-LiBr to Li₂S in MoS₂@ LiI-LiBr is high. As shown in Figure S6, after the initial activation process, the capacity retention for Li₂S@LiI-LiBr was only 79.7%, while for MoS2@LiI-LiBr, the capacity retention was 94.7% after 30 cycles. Besides, the charge transfer resistance of the MoS2@LiI-LiBrllLi cell was much lower than that of the Li₂S@LiI-LiBrllLi cell after cycling (Figure S7). In addition, when the battery was cycled at 0.5– 3.0 V in all discharge/charge processes to increase the Li₂S amount, the capacity of the MoS2@LiI-LiBr@C||Li cell decreased rapidly after 30 cycles (Figure S8). All these results imply that increasing the amount of LiI-LiBr can enhance the cycling stability and reaction kinetics. However, it also reduces the total capacity, so the molar ratio of LiI-LiBr to MoS₂ is controlled at 1:2.

The reaction kinetic enhancement of MoS_2 cathodes by LiI-LiBr was also evaluated by CV. Figure 5a,b shows the CV curves of MoS_2 with and without LiI-LiBr@C addition at scan rates from 0.2 to 1.0 mV s⁻¹. For the CV curves in the



Figure 5. CV curves of (a) MoS₂@LiI-LiBr@C and (b) MoS₂ at different scan rates from 0.2 mV s⁻¹ to 1.0 mV s⁻¹. Plots of log(ν) vs log(*i*) for (c) MoS₂@LiI-LiBr@C and (d) MoS₂. (e) Fitting *b* values for MoS₂@LiI-LiBr@C and MoS₂. (f) Galvanostatic discharge/charge profiles and (g) cyclic performance of the MoS₂@LiI-LiBr@C electrode at different cathode loadings (the specific capacity was based on the mass of MoS₂).

electrochemical redox process, the relationship between peak current (i) and scan rate (v) follows the equation log(i) = b $\log(v) + \log(a)$ (Figure 5c,d). When the *b* value equals 0.5, the electrochemical reaction is an ideally diffusion-controlled process, whereas b = 1.0 indicates a surface-controlled process, and when the b value lies between 0.5 and 1.0, the electrochemical reactions involve both processes.²⁴ The fitted *b* values for reduction and oxidation peaks R1 (S \rightarrow Li₂S), O2 $(Li_xMoS_2 \rightarrow MoS_2)$, and O1 $(Li_2S \rightarrow S)$ in the MoS₂@LiI-LiBr@C cathode are 0.8073, 0.8011, and 0.7877 (Figure 5e), respectively, which is much higher than that of the MoS₂ cathode (R1 = 0.5292, O2 = 0.5734, and O1 = 0.5173), implying the surface-controlled process dominates in the MoS₂@LiI-LiBr@C cathode due to the reduced particle size. Besides, the *b* value of O1 is low in both MoS_2 and MoS_2 @LiI-LiBr@C cathodes, implying reaction O1, where Li₂S was oxidized to S, is the rate-determining step in the electrochemical reactions.²⁵ The significantly improved b value for reaction O1 in the MoS2@LiI-LiBr@C cathode further proved the catalytic effect of LiI-LiBr on the Li₂S/S redox reaction.

The electrochemical performance of the MoS₂@LiI-LiBr@C electrode at different cathode loadings was also tested. As shown in Figure 5f, at low current density of 100 mA g^{-1} , the MoS₂@LiI-LiBr@C electrode shows a reversible capacity of 819.6 mAh g^{-1} (based on the mass of MoS₂) after 20 cycles at an areal capacity of 0.87 mAh cm^{-2} (active material: 0.922 mg cm^{-2}). When increasing the current density to 200 mA g^{-1} , a high reversible capacity of 711.3 mAh g⁻¹ was still maintained after 20 cycles. Further increasing the cathode loading, MoS₂@ LiI-LiBr@C||Li cells deliver high initial reversible specific capacities of 626.3 and 498 mAh g^{-1} (based on the mass of MoS_2) at areal capacities of 1.15 mAh cm⁻² (1.844 mg cm⁻²) and 2.02 mAh cm⁻² (4.058 mg cm⁻²), respectively. Besides, after 20 cycles, high reversible capacities of 546.6 and 255.9 mAh g⁻¹ were still maintained for the batteries at active materials loading of 1.844 and 4.058 mg cm⁻², respectively (Figure 5g). Compared with the reported conversion reactiontype transition-metal sulfide $(MoS_2, TiS_2, and FeS_2)$ based allsolid-state lithium battery, the MoS2@LiI-LiBr@C||Li cell exhibits an extraordinary electrochemical performance (Table

S1), which is derived from the *in-situ* formation of electronic conductive S@Mo@MoS₂ composite and the catalytic effect of the LiI-LiBr compound on the redox reaction of Li₂S/S. Such a universal design principle can also be employed in the FeS₂@ S@LiI-LiBr composite, where LiI-LiBr acts as a catalyzer to promote the S/Li₂S redox kinetics. As shown in Figure S9, a reversible discharge capacity of 795.0 mAh g⁻¹ was maintained after 10 cycles at a current density of 150 mA g⁻¹, which is higher than the capacity of FeS₂@S that was reported in our previous work.²⁶

In summary, we demonstrated that the redox kinetics of Li_2S in solid-state batteries can be significantly enhanced by LiI-LiBr due to its high catalytic activity and improved ionic conductivity to Li_2S . After ball-milling carbon black and $MoS_2@LiI-LiBr$, the reduction of the particle size of $MoS_2@$ LiI-LiBr and the enhancement of electronic conductivity further enhance the MoS_2 reversibility and kinetics. The $MoS_2@LiI-LiBr@ClILi$ all-solid-state lithium battery shows excellent electrochemical performance with reversible capacities of 816.2, 626.3, and 498 mAh g⁻¹ at areal capacities of 0.87 mAh cm⁻², 1.15 mAh cm⁻², and 2.02 mAh cm⁻², respectively. This facile strategy can also be employed to improve the electrochemical performance of other conversion reaction-type transition-metal sulfide based all-solid-state lithium batteries.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c03415.

Detailed experimental section, XRD patterns of Li₂S with and without LiI-LiBr additive, impedance and electrochemical performance of Li₂S and MoS₂ cathode with and without LiI-LiBr additive, cyclic performance profile of MoS₂@LiI-LiBr@C cathode at different cutoff voltages, performance comparison of conversion reaction-type transition metal sulfide, and electrochemical performance of the FeS₂@S@LiI-LiBr composite (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Author Contributions

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Notes

The authors declare no competing financial interest.

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