Selective Catalysis Remedies Polysulfide Shuttling in Lithium-Sulfur Batteries

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The shutting of soluble lithium polysulfides between the electrodes leads to serious capacity fading and excess use of electrolyte, which severely bottlenecks practical use of Li-S batteries. Here, selective catalysis is proposed as a fundamental remedy for the consecutive solid-liquid-solid sulfur redox reactions. The proof-of-concept Indium (In)-based catalyst targetedly decelerates the solid-liquid conversion, dissolution of elemental sulfur to polysulfides, while accelerates the liquid-solid conversion, deposition of polysulfides into insoluble Li$_2$S, which basically reduces accumulation of polysulfides in electrolyte, finally inhibiting the shuttle effect. The selective catalysis is revealed, experimentally and theoretically, by changes of activation energies and kinetic currents, modified reaction pathway together with the probed dynamically changing catalyst (LiInS$_2$ catalyst), and gradual deactivation of the In-based catalyst. The In-based battery works steadily over 1000 cycles at 4.0 C and yields an initial areal capacity up to 9.4 mAh cm$^{-2}$ with a sulfur loading of $\approx$9.0 mg cm$^{-2}$.

1. Introduction

Lithium-sulfur (Li-S) batteries show great promise among future battery techniques due to their theoretically high energy density ($\approx$2600 Wh kg$^{-1}$), low cost, and environmental benign.$[1,2]$ However, their real use in large scale is still plagued with challenges, such as the poor electrical conductivity of sulfur and solid-state discharge products (Li$_2$S/Li$_2$S$_2$), and the large volume change ($\approx$80%) of the sulfur cathode during cycling.$[3]$ The operation of Li-S batteries involves solid-liquid-solid consecutive reactions both for the discharge and charge process and creates a series of polysulfide ions (LiPSs, also denoted Li$_2$S$_n$, 4 $\leq$ n $\leq$ 8) that are soluble in the organic electrolytes. Thus, a more serious problem for practical Li-S batteries is the shuttling of the soluble Li$_2$S$_n$ from the cathode to anode side to form non-reusable solid Li$_2$S$_2$/Li$_2$S, which causes the so-called “shuttle effect”. This bottlenecks the real applications with rapid capacity fade (short cycling life) and excess use of electrolyte (far lower energy density than the theoretical value).$[3-6]$ Physical confinement (Scheme 1a) mostly with porous carbons and chemical anchoring (Scheme 1b) by polar substrates are commonly used to inhibit the shuttle effect.$[7-13]$ However, both strategies are intrinsically passive solutions, where Li$_2$S$_n$ are “confined” and “blocked” among the cathode system. The shuttle effect is basically driven by the concentration gradient of the soluble Li$_2$S$_n$, and thus a root solution is required that...
accelerates the conversion of Li$_2$S$_n$ in the sulfur reduction reaction (SRR, corresponding to discharge process) and sulfur evolution reaction (SER, corresponding to charge process) to reduce the opportunities of the Li$_2$S$_n$ shuffling and finally suppressing the shuttle effect.

Catalysis has recently been introduced into Li-S batteries as a proactive strategy for accelerating the conversion of Li$_2$S$_n$ and thereby tackling the shuttle effect.\[14–16\] and sulfides, nitrides, phosphides, and their heterostructures were widely used as the catalysts.\[17–27\] Most recently, Peng et al. have presented a fundamental look at the catalysis in Li-S batteries.\[28\]

Specially, they directly profile the electron-transfer numbers to characterize the electrocatalytic sulfur reduction and confirm catalysis as a promising pathway to tackle the fundamental challenges for Li-S batteries. However, what is the “right” catalyst for Li-S batteries toward practical application remains unclear.\[29\]

The root cause of the shuttle effect is the accumulation of soluble Li$_2$S$_n$ in the consecutive solid-liquid-solid reactions, and therefore, as shown in Scheme 1c, we propose that an ideal catalyst for the discharge process is expected not only to accelerates the liquid-solid reaction, deposition of Li$_2$S$_n$ into insoluble Li$_2$S as reported widely,\[15\] but also to decelerate the previous step of solid-liquid reaction, dissolution of elemental sulfur to Li$_2$S$_n$; the composition of “accelerating” and “decelerating” basically reduces the accumulation of polysulfides in the electrolyte, providing a fundamental scheme for inhibiting the shuttle effect.

In this work, we use nanoparticulated indium oxides (In$_2$O$_3$ NP) as a proof-of-concept catalyst (In-based catalyst) to demonstrate the selective catalysis for the consecutive solid-liquid-solid reaction, which is not only confirmed by the changes of kinetic currents and activation energies of different steps of sulfur redox reaction, but also in situ monitoring of the modified reaction pathway together with the probed dynamically changing catalyst, LiInS$_2$, as well as the featured catalyst deactivation. The SRR process (discharge) of the assembled battery well characterizes the selective catalysis, where the In-based catalyst, with strong adsorption toward elemental sulfur, decelerates the dissolution of elemental sulfur to soluble Li$_2$S$_n$, while accelerates the Li$_2$S$_n$ disposition to insoluble Li$_2$S due to the strong catalytic ability with LiInS$_2$ catalyst. For the SER process (charge), the catalysis with the probed LiInS$_2$ catalyst greatly reduces the energy barrier of Li$_2$S being oxidized to Li$_2$S$_n$ and eventually converted to elemental sulfur, which, however, is hardly accomplished in the In-free cell under the same charge voltage. Benefiting from the catalysis, the Li-S battery shows a good cycling stability and works steadily with negligible capacity decay over 1000 cycles at an ultrahigh rate of 4.0 C; moreover, the battery displays a high initial areal capacity up to 9.4 mAh cm$^{-2}$ at a current density of 0.9 mA cm$^{-2}$ even with a high sulfur loading ($≈9.0$ mg cm$^{-2}$). This work featured with selective catalysis rightly indicates a rational design principle for the catalysts toward a practical Li-S battery with suppressed shuttle effect.

2. Results and Discussion

2.1. Selective Catalysis in the Consecutive Redox Reaction

To evaluate the In-based catalyst for the Li-S batteries, the In$_2$O$_3$ NPs were hybridized with a porous carbon support composed of reduced graphene oxides (G) and carbon nanotubes (CNT), which yielded a In$_2$O$_3$-G-CNT/S denoted In-based cathode (an optimized 2.8 wt% In$_2$O$_3$ accommodating $≈70$ wt% sulfur (see the preparation details in Figures S1–S3 and Note S1 in the Supporting Information). For reference, the In-free sample (G-CNT/S) was prepared with the same procedure except for the absence of In$_2$O$_3$.\[30\]

Cyclic voltammetry (CV) curves for the In-based and In-free cells were compared in Figure 1a that were respectively assembled by coupling In-based and In-free cathodes with the referenced Li foil anodes. For the discharge, the two cathodic (reduction) peaks (P$_C_1$, P$_C_2$ correspond to the reduction of elemental sulfur to Li$_2$S$_n$ and then to Li$_2$S, respectively. For the charge, two distinguishable anodic (oxidation) peaks (P$_A_1$, P$_A_2$)
are observed, which are respectively attributed to the conversions from Li$_2$S to Li$_2$S$_n$, and finally to elemental sulfur.[31] When compared to that of In-free case, the CV curve of the In-based cell shows a definite positive shift of the cathodic peak and negative shift of the anodic peak (Figure S9 and Table S1, Supporting Information), indicating the catalytic activity of In-based catalyst.[14,15] Specially, the In-based cell shows a slightly lower kinetic current than the In-free cell for the dissolution from S$_8$ to Li$_2$S$_n$ as observed by the Pc$_1$ peak in Figure 1a. By comparison, the Li$_2$S$_n$-to-Li$_2$S conversion is greatly enhanced due to the presence of catalyst, which is evidenced by the apparently larger current density of Pc$_2$. The different changes (reduced or enhanced) of the kinetic currents for various reaction steps concisely prove the selective catalysis during the discharge process.

The selective catalysis is further confirmed by the comparison of Tafel plots for In-based and In-free cells (Figure 1b,c). The reduction and oxidation overpotentials of Li$_2$S$_n$ have been significantly decreased due to the introduction of the In-based catalyst (Figure 1c; Figure S10, Supporting Information). Exchange current densities were calculated from the Tafel plots, which reflect the intrinsic electron transfer rate between electrode and electrolyte (Table S1, Supporting Information). The In-based cell shows larger exchange current densities in both discharge and charge process, which are 6.02 and 0.20 mA cm$^{-2}$ respectively, compared to those of In-free case (3.29 and 0.16 mA cm$^{-2}$). The increase of exchange current densities indicates faster charge transfer induced by the In-based catalyst. The Tafel slope, which is an indicator for the kinetics of sulfur redox reactions, was further compared between In-based and In-free cells. Very interestingly, the In-based cell shows the higher Tafel slope of 121 mV dec$^{-1}$ for the S$_8$-to-Li$_2$S conversion than the In-free case (111 mV dec$^{-1}$), while the lower Tafel slope of 67 mV dec$^{-1}$ for the Li$_2$S$_n$-to-Li$_2$S conversion compared with the In-free case (75 mV dec$^{-1}$), indicating the decreased solid-to-liquid conversion rate while accelerated liquid-to-solid conversion. The difference in activation energy ($E_a$) can be calculated from the exchange current densities[32] (see details in Note S2 in the Supporting Information). As shown in Figure 1d, the $E_a$ value for the reduction for S$_8$ to Li$_2$S$_n$ is increased by 10 kJ mol$^{-1}$ for the In-based cell as compared to that for the In-free case, also indicating that the formation rate of Li$_2$S$_n$ slows down. In the following reaction step, the $E_a$ value for the reduction of Li$_2$S$_n$ to Li$_2$S is greatly decreased by 19 kJ mol$^{-1}$ with the In-based cell as compared to the In-free case, increasing their conversion rate. The increase of the activation energy for the formation of Li$_2$S$_n$ and the obvious decrease in the activation energy for the following reduction to Li$_2$S strongly support the proposed selective catalysis, where the dissolution of S$_8$ to Li$_2$S$_n$ becomes more sluggish but the conversion from Li$_2$S$_n$ to Li$_2$S goes faster by using the In-based catalyst. For the charge, the $E_a$ value for the oxidation of Li$_2$S to Li$_2$S$_n$ is greatly decreased by 19 kJ mol$^{-1}$ with the In-based cell compared to that of the In-free case, indicating accelerated conversion of the deposited Li$_2$S (Note S2 and Figure S11, Supporting Information). Besides, the In-based cell shows the lower charge-transfer resistance ($R_{ct}$) as identified by the electrochemical impedance spectroscopy (EIS) data.
(Figure S12, Supporting Information), suggesting an enhanced interfacial affinity toward Li$_2$S$_n$ with the In-based catalyst.\[33\]

CV tests were further carried out for the symmetric dummy cells that were assembled by coupling two same In-based electrodes with Li$_2$S$_6$ electrolyte (Figure 1e). As expected, the In-based cell shows a much higher current density than the In-free case even at a fast scan rate of 20 mV s$^{-1}$, indicating the ultrafast conversion of Li$_2$S$_n$.\[33,34\] Potentiostatically Li$_2$S precipitation test is specially used for evaluating the Li$_2$S$_n$-to-Li$_2$S conversion with the In-based catalyst. The coin cells for the tests were assembled using In-based or In-free carbon fiber paper (CP) as the cathodes, Li foil as the anode, and a Li$_2$S$_6$/tetraglyme solution as the catholyte. As shown in Figure 1f, potentiostatic discharge profiles at 2.05 V were collected. The results show that the In-based cell accelerates the Li$_2$S nucleation ($\approx$2500 s) compared with that free of catalyst. In addition, the Li$_2$S precipitate for the In-based cell, which was evaluated based on the quantity of electric charge according to Faraday’s law, shows a much higher capacity with a shorter nucleation time than those for the In-free cell (Figure S13, Supporting Information). Thus, Li$_2$S precipitation test gives a direct proof for the enhanced Li$_2$S$_n$-to-Li$_2$S conversion with the In-based catalyst.\[33–36\]

2.2. Battery Performance

An In-based battery was evaluated for rate and cycling performances in comparison to the In-free battery also with an optimized 2.8 wt% In$_2$O$_3$ in the cathode, where the battery gave the highest capacity at various rates (Figure S3a, Supporting Information). The rate performances of the Li-S batteries assembled by coupling In-based or In-free cathodes with a Li foil anode are shown in Figure 2a. With the In-based catalyst, the battery achieves a high discharge capacity of 1427, 876, 773, 692, and 502 mAh g$^{-1}$ at a rate of 0.2 C, 0.5 C, 1.0 C, 2.0 C, and 4.0 C, respectively, all of which are much higher than those for the In-free batteries. When abruptly switching the rate from 4.0 C back to the initial rate of 0.2 C, the original capacity is largely

Figure 2. Electrochemical performance of In-based Li-S battery in comparison to the In-free battery. a) rate performance with a sulfur loading of 1.0 mg cm$^{-2}$ (1C = 1675 mA g$^{-1}$); b) galvanostatic discharge-charge profiles at 0.2 C; c) galvanostatic charge-discharge profiles of the In-based battery at various current rates; d) cycling stability at 0.5 C with a sulfur loading of 1.0 mg cm$^{-2}$; e) cycling performance with a high sulfur mass loading of 5.9 mg cm$^{-2}$ at 0.5 C and 0.2 C; f) a comparison with other sulfur cathodes with E/S $\leq$ 8 $\mu$L mg$^{-1}$ (SRef: Supporting Information References).
recovered, indicating the excellent reversible capacity of the In-based battery at various rates.[37] The In-based battery shows a lower voltage difference (ΔE = 131 mV) which was calculated based on the charge plateau and discharge plateau in the third cycle, as compared to the ΔE value of 141 mV for the In-free case (Figure 2b).[38] Besides, the In-based battery exhibits much lower potential barrier in the charging process, indicating the activation energy (Ea) of the Li2S-to-Li2S2 conversion is greatly reduced (Figure S14, Supporting Information), consistent with that obtained from Tafel plots. The charge-discharge curves of the batteries at various current rates (0.2–4.0 C) are illustrated in Figure 2c and Figure S15 (Supporting Information). Note that the typical two discharge plateaus of the In-based battery are clearly seen even at a very high rate of 4.0 C, while the second plateau of the In-free battery, corresponding to the conversion of Li2Sn to Li2S2/Li2S, disappears when cycled at this current.

The cycling performances were further compared at a 0.5 C as shown in Figure 2d. The In-based battery exhibits superior capacity retention with stable coulombic efficiency. Specifically, it maintains a high capacity of 721 mAh g−1 after 500 cycles with a small capacity degradation of 0.04% per cycle. In a sharp contrast, for the In-free battery, the capacity quickly decays to 511 mAh g−1 with 0.17% decay per cycle over 250 cycles. The Coulombic efficiency of the In-based battery is 96.1%, higher than that of the In-free battery (95.2%) after 250 cycles (Figure S16, Supporting Information). The excellent cycling performance and Coulombic efficiency of the In-based cell indicate the great suppression of the shuttling effect.[38,39] The SEM images (Figure S17a–d, Supporting Information) show that for the In-based cell, the discharge products are homogeneously distributed at the surface after cycling at 0.5 C, while, for the In-free case, the cracked and exposed filaments are seen.

The cathodes with high sulfur loadings were fabricated to evaluate the potential for practical applications.[40] The In-based battery with a high sulfur areal loading up to 5.9 mg cm−2 delivers a higher initial capacity of 906 mAh g−1 and a reversible capacity is maintained at 665 mAh g−1 with the retention of 73.4% over 200 cycles at 0.5 C; the initial capacity and its retention capability are much superior to those of the In-free battery even at a current density of 0.2 C (Figure 2e). What’s worse, the In-free battery displayed faster capacity fading and lower retention of Coulombic efficiency, which is attributed to the accumulation of Li2Sn and severe shuttle effect in such a high sulfur mass loading. When the areal sulfur loading increases to 9.0 mg cm−2, the In-based battery displays a high initial areal capacity up to 9.4 mAh cm−2 (1046 mAh g−1) at a current density of 0.06 C even with a electrolyte/sulfur (E/S) ratio (8 μL mg−1); with an increased current density up to 0.12 C, the battery can be steadily cycled over 100 cycles with a reversible areal capacity of 5.3 mAh cm−2, much higher than that of the commercial Li-ion batteries (~4.0 mAh cm−2) (Figure S18, Supporting Information).[41] The corresponding discharge plateaus are clearly seen even at such a high sulfur mass loading as shown in Figure S19 in the Supporting Information. In short, the areal capacities with high sulfur loadings are remarkable when compared to those for the reported sulfur hosts (Figure 2f; Table S2, Supporting Information). Limited Li usage and lean electrolyte conditions are required to maximize the system-level specific energy of Li-S batteries.[4,41] As shown in Figure S20 in the Supporting Information, the In-based battery presents a high initial capacity of 1284 mAh g−1 at 0.05 C, and maintains stable cycling at 0.1 C. It should be noted that the performance is achieved with a low capacity ratio of negative to positive electrode (N/P = 4.7) and a limited E/S ratio (4.6 μL mg−1). The initial energy density based on cathode, anode and electrolyte is estimated to be ~362 Wh kg−1 (Table S3, Supporting Information). In a sharp contrast, the In-free battery only shows a much lower initial capacity of ~158 mAh g−1, leading to a much lower energy density (~45 Wh kg−1) and unsatisfactory cycling performance. This excellent stability with high sulfur loadings strongly implies that the In-based catalyst effectively prevent the accumulation of Li2S in the electrolyte and decrease the need of electrolyte to some extent.[42]

2.3. Reaction Pathway In Situ Monitored by Raman Spectroscopy

The Raman spectroscopy with 532 nm laser was employed to in situ monitor the charge-discharge process of Li-S batteries with or without In-based catalyst.[43] As shown in Figure 3a,b, for the discharge, the peaks located at 156, 223 and 476 cm−1 for elemental sulfur (S8) and 134 and 310 cm−1 for In2O3 are detected at the open-circuit voltage (OCV) for the In-based cell.[44,45] Raman spectra at the OCV in different regions were collected in order to clearly identify the signal of In2O3 as shown in Figure S21 in the Supporting Information. Three characteristic peaks of S8 remain until 2.04 V, indicative of strong adsorption of elemental sulfur on the In-based catalyst and sluggish conversion to Li2S. Upon the second plateau at 2.08 V a new peak at 398 cm−1 appears, attributed to the formation of Li2S2. When the voltage decreases to the end of the second plateau (=1.95 V), new peaks located at 448, 203, and 514 cm−1 are detected, implying the change from S82− to S62−, then S42− and Li2S2.[46,47] Note that the Li2S peak at 378 cm−1 is not detected even the Li-S cell was discharged to 1.7 V, which may be attributed to the sluggishness of solid state diffusion of Li ions and the signal is hard to be captured in the in situ measurement.[48] Of interests, the peaks of In2O3 disappear before discharging to 1.95 V (Figure 3a), and a new peak at 288 cm−1 is then detected, which is due to a combination of stretching and torsion of S-In bonds and Li atom translational movements, probing the dynamically changing catalyst, LiInS2 catalyst, involved in the catalytic process.[49] Raman spectra in different regions at 1.7 V were collected on the sulfur cathode to prove the formation of the LiInS2 catalyst (Figure S22, Supporting Information). Comparatively, in the In-free cell, Raman results (Figure 3e) indicate much faster conversion from S8 to soluble Li2S by demonstrating that the three characteristic peaks of elemental S were weakened at 2.20 V and totally disappeared at 2.08 V. However, it is hard to identify the solid discharge products even at 1.95 V for the In-free battery; instead, the peaks for Li2Sn are still maintained indicative of high concentrations of Li2Sn in the electrolyte and a sluggish reduction to Li2S. The sharp comparison for In-based and In-free cells well coincide with the above activation energy calculations obtained with the Tafel plots, which indicate, for the In-based cell, the selective
catalysis is well demonstrated in the discharge process decelerating the \(S_8\)-to-\(Li_2S\) conversion with a higher energy barrier while accelerating the \(Li_2S\)-to-\(Li_2S\) conversion with a reduced energy barrier.

For the charge process (Figure 3b), the probed LiInS2 catalyst facilitates the \(Li_2S\) fast and full conversion to soluble \(Li_2S\), and eventually back to \(S_8\) as the battery is charged to 2.7 V, completing a reaction cycle for sulfur redox reaction (Figure 3c,d), which indicates that the LiInS2 catalyst catalyze both directions of a process (\(Li_2S\)-to-\(Li_2S\) and \(Li_2S\)-to-\(Li_2S\)); in a sharp contrast, this is hardly accomplished in In-free cell under the same charge voltage and no \(S\) peaks are detected at 2.70 V (Figure 3f).

In the other words, without the catalyst, the battery cannot have a complete sulfur redox cycle upon charging to 2.70 V (Figure 3g,h). More informatively, for In-based battery, the disappearance of the LiInS2 catalyst, together with the re-detection of \(In_2O_3\) peaks upon charging to 2.42 V, indicates that catalysts may be \(In_2O_3\) and LiInS2. Besides, some secondary reactions may be involved due to the involvement of LiInS2 catalyst in this complex battery system, which synergistically facilitates the conversion of \(Li_2S\) to the discharge/charge products in accompany with a fully cycled sulfur redox reaction.

We further combined the computational simulation to gain a better understanding on the formation of the LiInS2 catalyst and the interaction between \(Li_2S\) and \(In_2O_3\) in comparison to the clean graphene. To construct an accurate model of \(In_2O_3\) catalyst, we have captured the annular dark-field scanning transmission electron microscopy (ADF-STEM) image as displayed in Figure 4a. It shows a lattice fringe with spacings of 1.79 and 2.92 Å, corresponding to the (44) and (222) plane of \(In_2O_3\); in sharp contrast, this is hardly accomplished in In-free cell under the same charge voltage and no \(S\) peaks are detected at 2.70 V (Figure 3f). More informatively, for In-based battery, the disappearance of the LiInS2 catalyst, together with the re-detection of \(In_2O_3\) peaks upon charging to 2.42 V, indicates that catalysts may be \(In_2O_3\) and LiInS2. Besides, some secondary reactions may be involved due to the involvement of LiInS2 catalyst in this complex battery system, which synergistically facilitates the conversion of \(Li_2S\) to the discharge/charge products in accompanies with a fully cycled sulfur redox reaction.

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charge transfer state, we constructed a 2D charge maps of In, S, and O atoms in Figure 4e, where the yellow and blue regions suggest the negative and positive charges, respectively. There are obviously accumulated positive charges around the In atom, indicating that In atom tends to dissolve from the In$_2$O$_3$ lattice. Figure 4f shows the projected density of the state (PDOS) of the surface In 3d and S 2p. Obvious orbit overlapping of In 3d and S 2p is observed at the electron state around −2 eV below Fermi level, further confirming the interaction between In and S as well as the easy formation of LiInS$_2$ catalyst. Then, we provided all the optimized structures of Li$_2$S$_4$, Li$_2$S$_8$, Li$_2$S$_{8*}$, Li$_2$S$_{8*}$, Li$_2$S$_{8*}$ and S$_8$ on In$_2$O$_3$ surface (Table S4, Supporting Information), which further confirms Li$_2$S$_n$ binds with In$_2$O$_3$ through In−S bond. S$_8$ on In$_2$O$_3$ is extracted from the optimized results to investigate the binding energies. As shown in Figure 4g, there is a much higher binding energy of −3.07 eV between In$_2$O$_3$ and S$_8$, compared to that of −0.74 eV of clean graphene substrate. Hence, S$_8$ is hard to be desorbed from the In$_2$O$_3$ surface, and this decelerates the conversion from S$_8$ to Li$_2$S$_8$; h) the reaction pathway from Li$_2$S$_{8*}$, Li$_2$S$_{8*}$, Li$_2$S$_{8*}$ to Li$_2$S$_{8*}$ intermediates on the In$_2$O$_3$ and graphene substrates.

Figure 4. Computational simulation for the reaction pathway and LiInS$_2$ catalyst. a) ADF-STEM image of the G-In$_2$O$_3$ hybrids; b) the superimposed FFTs of In$_2$O$_3$; c) the optimized structure of Li$_2$S$_4$ on In$_2$O$_3$ surface; The In−S bond length are 2.42 and 2.61 Å, which are very close to the standard In−S bond length in LiInS$_2$ (2.49 Å); d) 3D charge difference of Li$_2$S$_4$ on In$_2$O$_3$; e) 2D charge maps between In, O, and S; f) the projected DOS of In 3d and S 2p; g) there is a much high binding energy of −3.07 eV between In$_2$O$_3$ and S$_8$, compared to that of −0.74 eV of clean graphene substrate. Hence, S$_8$ is hard to be desorbed from the In$_2$O$_3$ surface, and this decelerates the conversion from S$_8$ to Li$_2$S$_8$; h) the reaction pathway from Li$_2$S$_{8*}$, Li$_2$S$_{8*}$, Li$_2$S$_{8*}$ to Li$_2$S$_{8*}$ intermediates on the In$_2$O$_3$ and graphene substrates.
surface due to the higher binding energy resulting from the strong In–S bonds, which decelerates the conversion from \( \text{S}_8 \) to \( \text{Li}_2\text{S}_8 \) to some extent. Finally, we build the reaction pathways by considering the \( \text{Li}_2\text{S}_8^* \), \( \text{Li}_2\text{S}_6^* \), \( \text{Li}_2\text{S}_4^* \), and \( \text{Li}_2\text{S}_2^* \) polysulfide intermediates (Figure 4h). As expected, the energy barrier for polysulfide conversion is greatly reduced with the catalyst. For example, there is an obvious energy barrier of 0.47 eV for the conversion from \( \text{Li}_2\text{S}_6^* \) to \( \text{Li}_2\text{S}_4^* \) on the clean graphene substrate. In contrast, this conversion on the In\(_2\)O\(_3\) catalyst is only 0.13 eV, confirming that the catalyst accelerates the redox conversions from the long-chain to short-chain polysulfides.

### 2.4. Reversible Redox Reaction with the LiInS\(_2\) Catalyst

The crystalline LiInS\(_2\) was synthesized (see Experimental section) to further demonstrate how the dynamically changing catalyst works in the \( \text{Li}_2\text{S}_n \) conversion, and the XRD pattern (Figure 5a) confirms the orthorhombic LiInS\(_2\) structure with a space group of \( \text{Pna2}_1 \) (the standard PDF #36-1352). A LiInS\(_2\)-based battery was then assembled with the LiInS\(_2\) loaded carbon paper (CP) coupled with a Li anode and Li\(_2\)S\(_8\) catholyte. A LiInS\(_2\)-free battery for reference was assembled in the same way. Upon discharged to 2.1 V, two new peaks at 288 and 303 cm\(^{-1}\) due to the stretching and torsional movement of S-In bonds in LiInS\(_2\) are detected by Raman spectroscopy except for the original characteristic peaks (Figure 5b). These newly appearing peaks have similar positions to that of LiInS\(_2\) detected in in situ Raman measurement for In-based battery as shown in Figure 3a. As expected, it is hard to probe \( \text{Li}_2\text{S}_n \) in the Raman spectrum for the LiInS\(_2\)-based battery, indicating the greatly accelerated \( \text{Li}_2\text{S}_n \) conversion with the LiInS\(_2\). It is reasonable that no LiInS\(_2\) peaks are observed for the LiInS\(_2\)-free battery from 260 to 310 cm\(^{-1}\), and the peaks corresponding to...
the Li$_2$S$_n$ at 398, 448, and 533 cm$^{-1}$ are detected, indicating the sluggish conversion. The above results confirm the critical role of LiInS$_2$ catalyst in the fast conversion of Li$_2$S$_n$.

The evolution of the LiInS$_2$ catalyst can be also demonstrated by the X-ray photoelectron spectra (XPS) spectra at the fully discharged state of the In-based cathode. The In 3d core-level XPS spectrum for the fresh cathode shows typical doublets at 445.0 and 452.6 eV for In$_2$O$_3$. After complete discharge, two additional signals at 445.2 and 452.8 eV are detected, which are possibly attributed to the binding of In$-S$ in LiInS$_2$ when compared to the XPS spectrum for pure LiInS$_2$ (Figure 5c). In addition, the doublets for the S 2p core bands of the discharged In-based cathode can be deconvoluted into four phases; the signals at 169.0, 170.0 eV and 167.1, 168.1 eV fitted can be assigned to sulfate and thiosulfate, which may arise from a surface redox reaction between Li$_2$S$_n$ and the oxides in In$_2$O$_3$, and the over-oxidation of Li$_2$S$_n$ by LiTFSI$^{[5]}$ and the relatively weak peaks can be attributed to Li$_2$S and the LiInS$_2$ catalyst, respectively.

The ADF-STEM images with line scan elemental maps were used to characterize the In-based cell before and after charging. The comparison of the cases for the fresh (Figure 5f) and the fully charged (Figure 5g) In-based cells show that sulfur is enriched at the In$_2$O$_3$ surface for the fully charged case, which coincide well with the in situ Raman results suggesting that sulfur is completely converted back to crystalline S. In addition, according to the XPS results (Figure 5d), the disappearance of Li$_2$S peak (160.0 and 161.0 eV) together with the appearance of S peak (164.2 and 165.2 eV) at the fully charged state confirm high reversibility of the sulfur species during the discharge-charge cycle. In a sharp contrast, Li$_2$S peaks were detected both in the discharged and charged states from the In-free cell (Figure 5e) suggesting poor reversibility of the insoluble discharge products.$^{[14]}$ In short, the In-based catalyst together with the LiInS$_2$ catalyst plays a crucial role in accelerating Li$_2$S$_n$ conversion and specially in the charge process, converts them into elemental sulfur.

2.5. Understanding of Deactivation of the In-Based Catalysts

To gain insight on the stability of the In-based catalyst, a critical operation condition was carried out that is a long run battery test at an ultrahigh rate of 4.0 C. As shown in Figure 6a and Figure S24 (Supporting Information), the In-based battery demonstrates outstanding stability with negligible capacity decay up to 1000 cycles. The selective catalysis enabled by the In-based catalyst reduces the accumulation of Li$_2$S$_n$ in the electrolyte and the shuttle effect of Li$_2$S$_n$ from cathode to Li anode is therefore restrained (Figures S25 and S26, Supporting Information), resulting in an improved cyclic stability. In addition, soluble indium ions are dissolved in the electrolyte during cycling for the In-based batteries. This is evidenced by the Inductively Coupled Plasma Mass Spectrometry (ICP-MS), XPS, Raman spectra, and elemental mapping of the cycled Li anode (Figures S26–S28, Supporting Information). The results indicate the formation of LiInS$_2$ protective layer on the Li anode. Symmetrical cells were then assembled using fresh Li anode and LiInS$_2$-protected Li anode and long-time galvanostatic
cycling was conducted (Figure S29, Supporting Information). The LiInS2-protected Li anode is stable with smooth voltage output and presents invisible changes during cycling. By contrast, the Li anode free of LiInS2 protective layer is unstable as observed by the obvious voltage fluctuating. After cycling, the LiInS2 protected Li anode shows smooth surface as seen from SEM images (Figure S30a,b, Supporting Information) while the Li anode free of LiInS2 layer presents obvious cracks (Figure S30c,d, Supporting Information). These comparisons clearly demonstrate the excellent anode stability protected by LiInS2 protective layer.[32] Therefore, the LiInS2 layer protects Li anode, and together with the catalysis-induced supression of shuttle effect, contributes to the improved cyclic stability.

Unfortunately, the battery is then presented capacity decay (Figure S31, Supporting Information), which implies the deactivation of In-based catalyst due to the surface “poising”. Figure 6b shows the S 2p XPS spectra of In-based cathode after the first cycle of discharge. As expected, the S 2p core level bands for the discharge product Li2S and the LiInS2 catalyst (In–S bond) are obviously detected on the catalyst surface, indicative of a fast conversion of Li2S, in presence of LiInS2. In a sharp contrast, the S 2p core level bands for Li2S and LiInS2 (In–S bond) are undetected in the cathode over 1000 cycles of discharge. Instead, the signals at 163.5 and 164.5 eV corresponding to the S 2p core level bands for accumulated Li2S were detected (Figure 6c), suggesting that most of Li2S are not converted into Li2S. Furthermore, the sulfate contents of In-based sulfur cathode increases from 31.6% (1st cycle) to 64.7% (1000th cycle) in the fully-discharged state (Figure S32, Supporting Information). Additionally, sulfates are also identified for the In-free sulfur cathode, covering on the carbon host (Figure S33, Supporting Information). The high coverage of In-based catalyst with the irreversible sulfate (excess oxidation product, see Figure S17e,f, Supporting Information) is the possible reason to inhibit the formation of LiInS2 catalyst, thereby resulting in deactivation of the catalyst and the slow conversion from Li2S to Li2S. In fact, the high coverage of strong adsorbate on the surface is a general reason for deactivation of a solid catalyst in a S-containing reaction,[53] which indicates, in spite of accelerated conversion of Li2S to Li2S, the catalyst poising is still an important issue to overcome for the design of high-performance catalyst for Li-S batteries.

4. Experimental Section

Material Synthesis: The carbon nanotube/sulfur composites (CNT/S) were prepared by a simple melt-diffusion method. In a typical procedure, the CNTs and sulfur (99.999% pure metal basis, Aladdin) were mixed in the desired ratio. Then the powder was ground and heated under ambient atmosphere at 155 °C for 12 h. Graphite oxide (GO) was synthesized from natural graphite by a modified Hummers method as reported previously.[54] In2O3 supernatant was prepared through liquid phase stripping, in which 200 mg commercial In2O3 and 50 mL water were mixed together then ultrasonicated for 2 h. After aged 6 h, The In2O3 supernatant was collected. The sediment was dried in a vacuum oven at 80 °C for 24 h and then weighed to deduce the amount of In2O3 in the supernatant. The In2O3 supernatant and a graphene oxide suspension (6.5 mg mL−1) with the precalculated target compositions were dispersed in the water ethanol mixtures and a homogenized GO-In2O3 (GO, 2.0 mg mL−1) liquid was formed by sonication for 2 h.

Synthesis of In2O3-G-CNT/S, G-CNT/S, and G-In2O3 Composites: The homogenized GO-In2O3 suspension was added to the CNT/S composites under continuous ultrasonication and then a certain amount of L-ascorbic acid sodium salt as the reducing agent was added to the solution. The mixture was transferred to a sealed glass bottle, which was heated to 70 °C for 24 h. The prepared sample was rinsed with deionized water several times and a stiff rod-like In2O3-G-CNT/S composite was formed after drying. C-CNT/S and G-In2O3 composites were synthesized using a similar process to that for the In2O3-G-CNT/S composite without adding In2O3 or a CNT/S composite.

Assembly of Symmetric Dummy Cells: Li2S and S in amounts corresponding to the nominal stoichiometry of Li2S2 were added to a 1:1 (v/v) DOL/DME mixture and stirred overnight at 50 °C. The concentration of the Li2S2 solution prepared was 0.2 mol L−1. The CP was punched into small disks with a diameter of 10.0 mm. 0.3 mg cm−2 G-In2O3 and graphene powders was loaded onto CP disks and were denoted as In-based and In-free electrodes, respectively. The typical loading procedure involved a sequence of ultrasonic dispersing G-In2O3 powders in NMP, dropwise adding the suspension onto CP disks, and then drying the electrodes at 55 °C for 12.0 h. Two identical electrodes were assembled into a standard 2032 coin cell, and 20.0 μL Li2S electrolyte was added.

Cell Assembly and Electrochemical Measurements: The In-based cathodes were prepared by mixing In2O3-G-CNT/S powder (95 wt%) and poly(vinylidene fluoride) (5 wt%) as a binder dissolved in N-methyl-2-pyrrolidone (NMP) to form a slurry, which was then coated onto an Al foil and vacuum-dried at 55 °C for 12 h. For reference, In-free cathodes were also fabricated with G-CNT/S powder. The foil was then cut into a circle of diameter 10 mm for use as the cathode. CR2032 coin cells were assembled using the coated Al foil as the current collector for cathode, a lithium metal foil anode, Celgard 2400 as the separator, and
1.0 M lithium bis-trifluoromethanesulphonimide (LiTFSI) dissolved in 1, 3-dioxolane and 1, 2-dimethoxyethane (DOL: DME, 1:1 vol) with 1.0 wt% LiNO₃ additive as the electrolyte. The E/J ratios were about 20, 10, and 8 µL mg⁻¹ for the electrodes with sulfur loadings of 1.0, 5.9, and 9.0 mg cm⁻², respectively. The thickness of lithium metal anode was 200 µm, and the ratios of N/P were 27.6, 4.7, and 3.1 with sulfur loading of 1.0, 5.9, and 9.0 mg cm⁻², respectively.

The galvanostatic discharge/charge measurements were conducted using a Neware battery test system. The cathode specific capacities were normalized only by the mass of sulfur, as per common practice. The charge-discharge voltage range was 1.7–2.7 V (versus Li⁺/Li). CV curves were obtained using an Autolab workstation at a scan rate of 0.1 mV s⁻¹ with a potential range of 1.7–2.7 V (versus Li⁺/Li) and EIS was conducted using an Autolab workstation with a frequency range of 0.01–10³ Hz.

Measurement of the Nucleation of Lithium Sulfide (Li₂S): A Li₂S₈ solution (0.2 mol L⁻¹) was used as the electrolyte and was prepared by combining stoichiometric amounts of lithium sulfide and sulfur powder in tetracylme under vigorous magnetic stirring. The CP was punched into circular disks with diameters of 10 mm and used as the current collector to load 0.3 mg G or G-In₂O₃ powders for cell assembly and then a lithium foil was used as the anode. 20 µL LiS₂₈ electrolyte was first distributed in the cathode and then 20 µL of the electrolyte without Li₂S₈ was dropped onto the lithium anode compartment. The assembled cells were first discharged galvanostatically at 0.112 mA to 2.06 V and then discharged potentiostatically at 2.05 V for Li₂S nucleation and growth. The potentiostatic discharge was terminated when the current fell below 10⁻¹ A.[2]

Synthesis of the Crystalline LiInS₂: The commercial LiF (98%, Alfa) and In₃S₅ (99.99% metal basis, Aladdin) were mixed with a molar ratio of 2:1. Then the powder was ground and heated under vacuum atmosphere at 750 °C for 5 h and cooled at room temperature to obtain the crystalline LiInS₂. CP-LiInS₂ Cell Assembly: The CP was punched into circular disks with diameters of 10 mm and used as the current collector to load 1.0 mg LiInS₂ powders for cell assembly and a lithium foil was used as the anode. 20 µL LiS₂₈ electrolyte was first distributed in the cathode and then 20 µL of the electrolyte without Li₂S₈ was dropped onto the lithium anode compartment. The assembled cells were assembled as the same procedure using the CP as the current collector without LiInS₂ powders.

Assembly of Li//Li Symmetrical Cells with LiInS₂ Protective Layers: The In-based Li-S batteries were disassembled after 5 cycles. The LiInS₂ layer forms on the Li anode surface. Two peaces of anodes were assembled for symmetrical cells. Cells without LiInS₂ layer were assembled for comparison.

In Situ Raman Spectroscopy: Li-S coin cells with a quartz window and a hole on the stainless steel (Figure S34, Supporting Information) were used for the in situ Raman spectroscopy analysis at 332 nm Laser. Each spectrum was acquired for 20 s with the frequency of 5%. The sulfur cathodes were prepared by mixing In-based/in-free powder (95 wt%) and poly tetra fluoroethylene (5 wt%) dissolved in ethanol as a binder to form a self-supporting electrode and vacuum-dried at 55 °C for 12 h. The cells (sulfur loading: 1.0 mg cm⁻²) were tested at a rate of 0.05 C.

Computational Section: All calculations in this work were carried out using density functional theory (DFT) method as implemented in the VASP code. The electronic exchange-correlation energy was modeled using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA). The projector augmented wave (PAW) method was used to describe the ionic cores. For the plane-wave expansion, a 450 eV kinetic energy cut-off was used after testing a series of different cut-off energies. A Monkhorst-Pack 3 x 3 x 1 k-point grid was used to sample the Brillouin zone. The convergence criterion for the electronic structure iteration was set to be 10⁻⁶ eV, and that for geometry optimizations was set to be 0.01 eV Å⁻¹ on force. A Gaussian smearing of 0.1 eV was applied during the geometry optimization and for the total energy calculations. For the density of states (DOS) computations, a tetrahedron method with Bloch correction was employed. Denser k-points (5 x 5 x 1) were used to improve the quality of DOS computations. The projected DOS patterns were extracted from the total DOS results.

Structural Characterization: SEM was performed on a Hitachi S4800 (Hitachi Japan) instrument. ADF-STEM measurements were conducted on a Hitachi HF5000 coupled with an energy dispersive spectrometer (EDS). The Raman spectra were recorded on a MicroRaman system (LabRAM HR spectrometer, Horiba) with an Olympus BX microscope and an argon ion laser (532 nm). XRD patterns were collected on a Bruker D-8 diffractometer (Cu Kα radiation, λ = 0.154 nm) at room temperature. TG (Rigaku, Japan) was performed in air from room temperature to 500 °C at a heating rate of 10 °C per minute to calculate the amount of sulfur in the hybrids. Nitrogen adsorption measurement was conducted at 77 K using a BEL-mini instrument (BEL Inc., Japan). The specific surface area was obtained by Brunauer–Emmett–Teller (BET) analysis of the adsorption isotherm. XPS data were recorded by an ESCALAB 250Xi (Thermo Fisher) with a monochromatic Al Kα source to analyze the surface species and their chemical states.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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