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Eliminating the Detrimental Effects of Conductive Agents in Sulfide-Based Solid-State Batteries

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interface. Introducing a controllable semiconductive additive for the cathode composites in this study offers a promising design to realize the high-rate performance and overcome long-term challenges in the application of conductive additives in sulfide-based ASSLIBs.

ll solid-state lithium-ion batteries (ASSLIBs) are considered as a promising candidate for nextgeneration energy storage devices for electric vehicles.^{1,2} Compared to conventional liquid lithium-ion batteries, ASSLIBs exhibit excellent safety characteristics by utilizing nonflammable solid-state electrolytes (SSEs) and competitive energy densities by accessing the lithium metal anode and high-energy cathode materials.³ Among the developed SSEs, sulfide-based inorganic electrolytes, such as Li₁₀GeP₂S₁₂ (LGPS), Li₆PS₅Cl, Li₇P₃S₁₁, and Li₃PS₄, possess high Li⁺ conductivities ranging from 10^{-2} to 10^{-4} S cm⁻¹, which have the potential to realize high-performance ASSLIBs with stable cycling and high-rate capacities.⁴⁻⁶ However, the narrow electrochemical stable window of sulfide-based SSEs challenges the interfacial stability at the both cathode and anode, thus producing dramatically increased interfacial resistance leading to rapid capacity fading.^{7,8} In order to solve these issues, interfacial engineering approaches have been widely adopted to avoid direct exposure of the electrode materials to the SSEs and therefore prevent the occurrence of side reactions.⁹⁻¹¹ As a result, the cycling stability of ASSLIBs has been greatly improved.

realizes effective electron transfer at the cathode/SSE/carbon three-phase

On the other hand, in order to further improve the electrochemical performance of the ASSLIBs, specifically the high-rate capability, increasing the electronic conductivity in the cathode composites is of crucial importance. In conventional liquid lithium-ion batteries, carbon additives are indispensable to enhance the electronic conductivity of electrodes for high-rate capability. The application of prevailing carbon materials, such as acetylene black (AB), super P, and carbon nanotubes (CNTs), enables the homogeneous current distribution in the cathode layer.¹²⁻¹⁴ However, the application of carbon additives in the sulfide-based ASSLIBs faces tremendous obstacles. Carbon additives provide sufficient electronic percolation pathways in the cathode composites, therefore accelerating the decomposition of sulfide SSEs

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Figure 1. Structural and elemental characterizations of PEDOT modification. (a) HR-TEM image of PEDOT modification on the surface of NMC811 particles; (b-f) EDS mapping of S, Ni, Co, and Mn in PEDOT-modified NMC811 by HAADF-STEM; (g-i) EDS mapping of C and S in PEDOT-modified CNTs by HAADF-STEM. Scale bars are (a) 10 nm, (b-f) 20 nm, or (g-i) 80 nm.

during the charging process.¹⁵ As a result, even with very small amounts of carbon additives, severe decomposition of sulfide SSEs still occurs at the electrolyte/carbon interface and leads to severe side reactions and the formation of an undesirable interfacial layer between the carbon additives and SSEs.^{16–18} Therefore, the use of carbon additives hinders the electrochemical performance in ASSLIBs instead of showing a positive effect, let alone achieving high-rate capability.

To overcome the challenges of using carbon additives at cathode composites in sulfide-based ASSLIBs, in this study, we present an approach by constructing a semiconductive polymer thin film for sulfide-based ASSLIBs to realize the superior electrochemical performance with high-rate capacity. A uniform and conformal poly(3,4-ethylenedioxythiophene) (PEDOT) modification was successfully built on both carbon additives (CNTs) and Ni-rich layered cathode of Li-Ni_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) via molecular layer deposition (MLD). The underlying decomposition mechanism of sulfide SSEs (LGPS) associated with CNTs is investigated by various electrochemical tests and characterization techniques, suggesting the high electronic conductivity of CNTs accelerates the decomposition of LGPS and side reactions in the cathode composites during the electrochemical reactions, therefore leading to the fast capacity degradation especially at high current densities. Promisingly, the PEDOT modification realizes the application of semiconductive additives to modify

conductive additives in the cathode composites, therefore effectively enhancing the interfacial stability between CNTs and LGPS, resulting in the obvious improved rate capability and enhanced cycling stability. This study offers a strategy to address the long-time concern of using conductive additives in sulfide SSEs system, effectively boosting the realization of highperformance ASSLIBs.

In this study, PEDOT thin film is synthesized via MLD as an interfacial material for both NMC811 and CNTs. To investigate the thickness effect, 2, 5, and 10 nm of PEDOT are deposited on the surface of NMC811 and CNTs, respectively, by controlling the MLD reaction cycles. Figures 1 and S1 illustrate the morphology and fine structure of the PEDOT-modified NMC811 and CNTs as confirmed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images. The particle size of the commercial NMC811 secondary spheres is around 10 μ m (Figure S1a). After 10 cycles of MLD, an amorphous and conformal interfacial layer of PEDOT with the thickness around 5 nm can be observed at the surface of NMC811 as shown in Figure 1a. The energy-dispersive X-ray spectroscopic (EDX) mappings detected by the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and SEM are shown in Figures 1b-f and S2, respectively, demonstrating the uniform distribution of S element with Ni, Co, and Mn among the NMC811 particles, explicitly



Figure 2. Investigation of the stability between CNTs and LGPS during electrochemical reactions. (a) Schematic illustration of the designed model cells, (b and c) CV profiles at 0.1 mV s⁻¹ during the first cycle, (d) EIS spectra at various constant voltages, and (e-g) S 2p XPS spectra after CV test in the different cathode composites.

confirming the successful modification of PEDOT on the surface of NMC811. Meanwhile, C 1s and S 2p X-ray photoelectron spectroscopy (XPS) spectra for the PEDOTmodified NMC811 are shown in Figure S3. Typical C 1s XPS spectrum of PEDOT is demonstrated in Figure S3a, including the aromatic C=C bond at 284.2 eV and the C=S bond at 288.1 eV. In the S 2p XPS spectrum shown in Figure S3b, the band between 162.9 and 168.5 eV with doublet peaks is attributed to the sulfur atoms of PEDOT.^{19,20} The EDX mappings of PEDOT-modified CNTs are demonstrated in Figures 1g-i and S4, also confirming the uniform modification of PEDOT on the surface of CNTs. Furthermore, X-ray diffraction (XRD) analysis is conducted to evaluate the crystal and chemical structure of the bare and PEDOT-modified NMC811 and CNTs. As shown in Figures S5-7, XRD patterns of the bare and PEDOT-modified NMC811 and CNTs show good retention of the crystallinity without the introduction of a noticeable impurity phase, indicating that the material properties are well-maintained throughout the MLD process.

In order to investigate the effect of PEDOT modification on the stability between carbon additives and sulfide SSEs and, five different model cells are designed as shown in Figures 2a and S11a. Indium foil and LGPS are employed as the anode and electrolyte layer, respectively. For the cathode layer, (i) the pristine LGPS, (ii) bare CNTs mixed with LGPS, (iii) PEDOT-modified CNTs mixed with LGPS, (iv) bare CNTs, and (v) PEDOT-modified CNTs (denoted as LGPS, bare

CNTs-LGPS, PEDOT@CNTs-LGPS, bare CNTs, and PEDOT@CNTs, respectively) are employed for the following characterizations. The chemical stability between CNTs and LGPS is first studied by electrochemical impedance spectroscopy (EIS) as shown in Figure S8. After several hours' rest (no electrochemical operation), the EIS plots of both (ii) bare CNTs-LGPS and (iii) PEDOT@CNTs-LGPS cells remain almost the same, indicating the high chemical stability between CNTs and LGPS. The electrochemical stability between CNTs and LGPS is then investigated as follows. A linear sweep voltammetry (LSV) test is first conducted to investigate the thickness effect of PEDOT coating. The onset potential shown in Figure S9 is delayed with the increased thickness of PEDOT coating, indicating the thicker PEDOT coating is more effective to alleviate the decomposition of LGPS. From the cyclic voltammogram (CV) profiles of the first cycle shown in Figure 2b,c, there is no appreciable peak in the (i) LGPS cell, indicating the good electrochemical stability during the voltage range of 1.0-3.8 V vs Li⁺/Li-In (1.6-4.4 V vs Li⁺/Li). However, the obvious onset potential of 1.97 V can be observed in the (ii) bare CNTs-LGPS cell, which is much lower than the onset potential of 2.17 V in the (iii) PEDOT@ CNTs-LGPS cell. Meanwhile, the intense anodic peaks can be detected in the (ii) bare CNTs-LGPS cell with the peak current of 5.63 mA g⁻¹, which is 3.3 times higher than that of the (iii) PEDOT@CNTs-LGPS cell. Although the anodic peaks decrease significantly during the following CV cycles as shown in Figure S10, the intensities of the peak current in the



Figure 3. Effects of PEDOT modification on the electrochemical performance. (a) Charge-discharge curves of the first cycle at 0.05*C*, (b) rate and cyclic stability, (c) Coulombic efficiency, (d) average discharge voltage and energy density of cathodes, (e) EIS spectra after 100 cycles, (f) CV profiles at the first cycle, (g) GITT curve during the charge process, and (h) the corresponding polarization plots.

(ii) bare CNTs-LGPS cell are still much higher than that of the (iii) PEDOT@CNTs-LGPS cell. The above results indicate that the decomposition of LGPS in the (ii) bare CNTs-LGPS cell is more severe than in the (iii) PEDOT@CNTs-LGPS cell.

The above CV results indicate the decomposition of LGPS may arise in the cathode composites (the interface between CNTs and LGPS particles) and/or the interface between the cathode layer and electrolyte layer. In order to investigate the extent of the electrochemical reactions at these two interfaces, both the (iv) bare CNTs and (v) PEDOT@CNTs model cells are designed and shown in Figure S11a. Because there are only CNTs in the cathode layer, it means that the possible electrochemical reactions can be detected only at the interface between cathode layer and electrolyte layer. As shown in Figure S11b,c, the obviously reduced intensity of anodic peaks in the first CV cycle can be observed in both (iv) bare CNTs and (v) PEDOT@CNTs cells. The peak current is only 0.054 mA g^{-1} in the (iv) bare CNTs cells. Comparing with the peak current in the (ii) bare CNTs-LGPS and (iv) bare CNTs cells, the decomposition of sulfide SSEs mainly occur in the cathode composites with the direct contact between CNTs and LGPS particles rather than at the interface between the cathode layer and electrolyte layer.

EIS plots of the (i) pristine LGPS, (ii) bare CNTs-LGPS, and (iii) PEDOT@CNTs-LGPS cells tested at various constant voltages are shown in Figures 2d and S12. The cells are held at the certain voltage for 2 h and then tested by the EIS. The obviously increased resistance can be observed in the (ii) bare CNTs-LGPS cell with the increase of the voltages. In contrast, the resistance growth can be effectively suppressed by the PEDOT modification. To further evaluate the effect of PEDOT on the interfacial stability between carbon additives and sulfide SSEs, the CV tested cathode samples were characterized by XPS. From the S 2p XPS spectra as shown in Figures 2e and S13, there is no distinctive peak in the (i) pristine LGPS cell after CV testing. However, the peaks, corresponding to the decomposition products of LGPS, can be detected in the (ii) bare CNTs-LGPS cathode (Figure 2f) with the formation of Li₂S, -S-S-, and germanium sulfides or polysulfide species (peak A),^{8,21} indicating the bare CNTs accelerate the decomposition of LGPS during the electrochemical process. In contrast, the decomposition of sulfide electrolyte in the (iii) PEDOT@CNTs-LGPS cathode can be effectively alleviated as shown in Figure 2g, demonstrating PEDOT modification is able to retard the electrochemical reactions between CNTs and LGPS.

Electrochemical characterizations of the ASSLIBs, in which the cathode layer is composed of the as-prepared NMC811/ CNTs/LGPS composites combining with LGPS and indium foil as electrolyte layer and anode, respectively, are illustrated in Figure 3 to investigate the effect of PEDOT modification on performance. Both NMC811 and CNTs are coated by PEDOT with the thickness of 2, 5, and 10 nm. The first charge– discharge profiles of the bare and PEDOT-modified cathodes at 0.05C are shown in Figure 3a. Compared to the bare cathode, the 5 nm PEDOT-modified cathode shows the maximum discharge capacity with an obviously reduced polarization. Interestingly, the rate and cycling performances of the four cathodes show considerable differences (Figure 3b). The rate capacities of the bare cathode dramatically decay with



Figure 4. Understanding the interfacial chemical evolution during electrochemical reaction. S 2p XPS spectra of the (a) cycled bare electrode (C-bare) and (b) cycled PEDOT-modified electrode (C-PEDOT); (c) S K-edge XANES spectra of the C-bare and C-PEDOT electrodes with the pristine LGPS as reference; (d-f) Mn, Co, and Ni K-edge XANES spectra of the bare, PEDOT, C-bare, and C-PEDOT electrodes: (d) Mn K-edge, (e) Co K-edge, and (f) Ni K-edge.

the increase in current density. The discharge capacities drop to less than 10 mAh g⁻¹ when the current density increases to 1C. In contrast, the PEDOT-modified cathodes demonstrate much improved rate capacities at each current density. Even at 1C, 5 nm PEDOT-modified cathode still delivers a discharge capacity of over 100 mAh g⁻¹, which is over 10 times that of the bare cathode. The 5 nm PEDOT-modified cathode also demonstrates much improved cycling stability during the following cycles with the capacity retention of 51.1% after cycling when the current density returns to 0.1C. However, the capacity retention of the bare cathode is only 13.6%, illustrating its poor cycling performance. The chargedischarge profiles of the bare and PEDOT-modified cathodes at the 100th cycle also demonstrate the reduced polarization by PEDOT modification (Figure S14). The corresponding Coulombic efficiencies of the bare and PEDOT-modified cathodes are shown in Figure 3c. Interestingly, the initial Coulombic efficiencies at each current density show the obvious differences in the four cathodes. Especially at 1C, the bare cathode demonstrates the lowest initial Coulombic efficiencies of 67.7%. However, the initial Coulombic efficiencies in 5 and 10 nm PEDOT-modified cathodes are much improved and demonstrate 87.3% and 89.0%, respectively. Furthermore, the PEDOT-modified cathodes also show improved average discharge voltages, thus obtaining an energy density greater than that of the bare cathode (Figure 3d). As shown in Figure 3e and Table S1, the 5 nm PEDOTmodified cathode shows the smallest internal resistance after 100 cycles among all the cells, demonstrating that the PEDOT

modification effectively suppress the side reactions at the threephase interface in the cathode composites. Meanwhile, optimizing the thickness of the PEDOT layer is also very important to get the best electrochemical performance. The thicker PEDOT layer enables less side reactions but limits the capacity because of the lower conductivity.

CV profiles of the four cathodes are observed in Figure 3f. Interestingly, PEDOT-modified cathodes demonstrate reduced redox potential gaps and higher peak intensities compared to the bare cathode with increasing thickness in the PEDOT interfacial layer, indicating the enhanced electrochemical reaction activity of batteries with lower resistance by PEDOT modification. PEDOT-modified cathodes also demonstrate lower currents at the cutoff voltage (3.8 V vs Li⁺/Li-In), which indicates a smaller potential polarization at high operating voltage. Furthermore, the galvanostatic intermittent titration technique (GITT) curves of the bare and PEDOTmodified cathodes during the charge process are given in Figure 3g along with the corresponding polarization plots in Figure 3h. Obviously, the 5 nm PEDOT-modified cathode presents the smallest polarization potential with the highest capacity during the whole charging process, indicating effective stabilization of the cathodic interface throughout the charging process by PEDOT modification. The CV and GITT results indicate that PEDOT modification effectively reduce the interfacial resistance at the cathode/SSE/carbon interface in cathode composites during the electrochemical reactions. The effect of various coating strategies is also investigated in this study. The rate and cycling stability of different interfacial



Figure 5. Schematic illustration of the role of PEDOT modification.

materials on the NMC811 cathode and CNTs are shown in Figure S15. The results indicate the PEDOT modification on the both NMC811 and CNTs demonstrates the best rate and cycling capacities.

In order to investigate the interfacial chemical evolution as well as the protective role of the PEDOT modification, XPS and X-ray absorption near edge structure (XANES) measurements are performed. Panels a and b of Figure 4 show the S 2p XPS spectra of the LGPS electrolytes collected from the cycled bare electrode (denoted as C-bare) and cycled PEDOTmodified electrode (denoted as C-PEDOT). The decomposition products of LGPS are observed at 160.1 and 162.9 eV corresponding to the Li₂S and -S-S-, respectively.²² While the side reactions between NMC811 and LGPS induce the further oxidation of LGPS and the formation of SO_3^{2-} and SO₄²⁻ species at 166.8 and 168.8 eV, respectively.^{23,24} The Cbare electrode shows higher relative content of Li₂S and -S-S- decomposition products than the C-PEDOT electrode, indicating different degrees of electrolyte decomposition caused by the bare CNTs and PEDOT-modified CNTs. Meanwhile, the high relative peak intensities of SO_3^{2-} and SO₄²⁻ in C-bare electrode suggest the presence of severe side reactions between the unprotected NMC811 and LGPS.^{25,26} Impressively, both the SO_3^{2-} and SO_4^{2-} signals are suppressed when using the C-PEDOT electrode, proving the effective suppression of side reactions by the PEDOT modification. The S and P K-edge XANES spectra of the C-bare and C-PEDOT electrodes are compared in Figures 4c and S16 and are in agreement with the XPS results. In the S K-edge XANES, the peak intensity of the C-bare electrode at 2481.9 eV increases noticeably more than that of the C-PEDOT electrode, indicating the formation of SO_x from the severe side reactions

between NMC811 and LGPS during cycling.²⁷ However, the C-PEDOT electrode demonstrates the alleviated side reactions with sulfide SSEs, therefore effectively suppressing the formation of SO_{x^*}

The K-edge XANES spectra of transition metals (TMs, including Co, Mn, and Ni) are presented in Figure 4d-f to understand the structural evolution of the layered NMC811 during cycling. Generally, the local structural environment of the TMs and surrounding oxide corresponds to the shape of the K-edge XANES peaks, while the threshold energy position is indicative of the TM oxidation state.²⁸⁻³⁰ Before cycling, there is no obvious difference in both the edge energy and the shape of the peaks in the K-edge XANES spectra between the bare and PEDOT-modified electrodes, suggesting the PEDOT modification did not change the chemical environments of the TMs. However, both Mn and Co K-edge XANES spectra of the C-bare electrode show spectral shape variations after cycling, indicating the changes of local environment of Mn and Co atoms. In contrast, the shape changes of the spectra for the C-PEDOT are less prominent. Meanwhile, the obvious entire rigid edge shift toward higher energy for the Ni K-edge can be observed in the spectra for the C-bare electrode, indicating the oxidation of Ni even though the XANES spectrum was tested after being fully discharged to 2.1 V vs Li⁺/Li–In. In contrast, the C-PEDOT electrode shows less change in the Ni K-edge energy position after cycling. The oxidation of Ni after cycling suggests that a portion of the lithium ions were unable to intercalate back into the layered structure of the NMC811 cathodes even at full discharge, because of the formation of cathode electrolyte interface (CEI) through severe side reactions with the sulfide electrolyte. This is further demonstrated in the XRD patterns as shown in Figure S17.

The (110) peak in the C-bare electrode shifts to higher scattering after cycling in comparison to the C-PEDOT electrode, meaning that the incomplete lithiation after cycling leads to a decrease in the interplanar spacing in the C-bare electrode. Therefore, the obvious shape variations of Mn, Co K-edge XANES spectra and energy shift of Ni K-edge XANES spectra after cycling combining with the XRD results demonstrate that severe side reactions between NMC811 and LGPS lead to the surficial structure evolution of cathode for the C-bare electrode, which can be effectively alleviated by the PEDOT modification. As a result, the cracks on the surface of NMC811 are also suppressed by the PEDOT protection as shown in Figures S18 and S19.

Considering the electrochemical testing and characterization results, the role of PEDOT modification is demonstrated in Figure 5. Electrons act as the charge carrier in the CNTs as a metallic conductor, while PEDOT is a p-type semiconductor, meaning the charge carriers are holes.^{31–33} PEDOT thin film is deposited on the surface of CNTs by MLD, forming a metal/ p-type semiconductor contact interface. As shown in Figure 5, the Fermi energy $(E_{\rm F})$ of CNTs is higher than that of the PEDOT because the work function $(Ø_M)$ of CNTs is lower than that of the PEDOT (\emptyset_s) .^{34–38} In order to maintain the equilibrium of $E_{\rm F}$ after contact, electrons have to flow from CNTs into PEDOT until the Fermi energies are finally equalized. As a result, the holes in the PEDOT are filled by the electrons, causing decreased PEDOT thin-film conductivity. Therefore, the conductivity of the modified CNTs is also decreased. Through this process, the semiconductive additives are achieved from the conductive additives of CNTs by PEDOT modification. The conductivity of the semiconductive additives is manipulated by the different thicknesses of the PEDOT layer. During the charge-discharge process, the bare CNTs with excellent electronic conductivity accelerate the decomposition of sulfide SSEs, leading to the severe side reactions between cathode particles and sulfide SSEs in the cathode composites, therefore damaging the performance of ASSLIBs especially the high-rate capability. In contrast, the PEDOT modification with the optimized thickness provides a strategy by adopting semiconductive additive in the cathode composites, which effectively alleviates the decomposition of sulfide SSEs and the side reactions with cathode particles.

In conclusion, we present a strategy to significantly improve the electrochemical performance of sulfide-based ASSLIBs by building a controllable polymer PEDOT thin film as a semiconductive additive in the cathode composites. This interfacial engineering approach breaks through the limitations of conductive agents applied in the sulfide-based ASSLIBs. The PEDOT modification not only effectively alleviates the decomposition of sulfide SSEs induced by carbon additives in the cathode but also significantly suppresses the side reactions between cathode materials and sulfide SSEs during the charge-discharge process. As a result, the developed ASSLIBs demonstrate notably improved electrochemical performance, including higher initial discharge capacity, enhanced cycling stability, improved average discharge potential, as well as reduced voltage polarization. More importantly, the successful application of semiconductive additives in the cathode composites bolsters the rate capability significantly with a capacity of over 100 mAh g^{-1} at 1C, 10 times that of the bare electrode. As confirmed by XPS and synchrotron XANES analyses, the decomposition of sulfide SSEs and severe interfacial side reactions in the cathode

composites are effectively suppressed by the PEDOT modification. The above results demonstrate that PEDOT modification realizes the use of semiconductive additives which enhance the interfacial stability. This work provides an effective approach to modify conductive additives by semiconductive additives in sulfide-based ASSLIBs and will attract more efforts regarding the development of fast-charged cathodes in the ASSLIBs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.0c00256.

Detailed experimental procedures; SEM images, SEM-EDX mappings, and XRD patterns of PEDOT-modified cathode composites; additional electrochemical characterizations; XPS spectrum of pristine LGPS; XANES spectra and XRD patterns of cycled bare and PEDOTmodified electrodes (PDF)

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Author Contributions

Sixu Deng and Yipeng Sun contributed equally to this work. Xueliang Sun supervised the overall project. Sixu Deng conceived this idea, synthesized the electrodes, characterized the samples, tested the electrochemical performances, and wrote the manuscript. Yipeng Sun performed the MLD process. Xia Li carried out SEM characterization and electrochemical analysis. Zhouhong Ren and Jun Luo performed the TEM characterization in Tianjin University of Technology. Jianwen Liang carried out XRD characterization. Kieran Doyle-Davis improved the language. Weihan Li, Mohammad Norouzi Banis, and Yongfeng Hu carried out the synchrotron radiation characterization in CLS. Jianneng Liang and Qian Sun performed fundamental analysis. Ruying Li carried out SEM characterization and purchased all the chemicals.

Notes

The authors declare no competing financial interest.

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