Nickel–Cobalt Double Hydroxide as a Multifunctional Mediator for Ultrahigh-Rate and Ultralong-Life Li–S Batteries

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The performance of lithium–sulfur (Li–S) batteries is largely hindered by the shuttle effect caused by the dissolution of lithium polysulfides (LiPSs) and the sluggish reaction kinetics of LiPSs. Here, it is demonstrated that the nickel–cobalt double hydroxide (NiCo-DH) shells that encapsulate sulfur nanoparticles can play multiple roles in suppressing the shuttle effect and accelerating the redox kinetics of LiPSs by combining with graphene and carbon nanotubes to construct the conductive networks. The NiCo-DH shell that intimately contacts with sulfur physically confines the loss of sulfur and promotes the charge transfer and ion diffusion. More importantly, it can react with LiPSs to produce the surface-bound intermediates, which are able to anchor the soluble LiPSs and accelerate the redox kinetics. Such composite electrodes can load high contents of sulfur (>85 wt%) and the resulting Li–S battery exhibits a superior capacity (1348.1 mAh g\(^{-1}\) at 0.1 C), ultrahigh rate performance (697.7 mAh g\(^{-1}\) at 5 C), and ultralong cycle life (1500 cycles) with a decay rate of 0.015% per cycle.

1. Introduction

Lithium–sulfur (Li–S) batteries have gained extensive attention due to their high theoretical specific capacity (1675 mAh g\(^{-1}\)) and energy density (2600 Wh kg\(^{-1}\)), as well as the natural abundance of sulfur.\(^{[1–5]}\) The insulating nature of sulfur and its volume expansion during discharge/charge have been resolved to a large extent in the past decade;\(^{[6–9]}\) however, the dissolution of lithium polysulfides (Li\(_2\)S\(_x\), \(x \geq 4\), LiPSs) into electrolyte has been a crucial challenge that hinders the practical application, which results in the notorious “shuttle effect,” migration of LiPSs to the lithium metal anode and uncontrolled deposition.\(^{[10–12]}\) These cause the irreversible loss of active sulfur, rapid capacity decay, low coulombic efficiency, poor rate performance, and short cycle life in Li–S batteries.\(^{[7,13–15]}\) Also, the shuttle effect slows down the kinetics of polysulfide conversion along the solid (\(S_8\))–liquid (Li\(_2\)S\(_x\), \(x \geq 4\))–solid (Li\(_2\)S\(_2\) or Li\(_2\)S) route, which results in the accumulation of LiPSs in electrolyte and rapid diffusion to the lithium anode, further exacerbating the shuttle effect due to the formation of non-reusable solid Li\(_2\)S\(_2\) or Li\(_2\)S.\(^{[16,17]}\)

Many efforts have been attempted to overcome the shuttle effect in Li–S batteries, which mostly employ physical barriers or chemical adsorption for LiPSs. Typically, the physical confinement is realized by using miscellaneous carbon materials with large surface area and high conductivity to load sulfur.\(^{[18–21]}\) However, the nonpolar carbon materials can only delay rather than suppress the shuttle effect; the polar LiPSs can still easily detach from the carbon surface and re-enter into the electrolyte.\(^{[22,23]}\) The chemical adsorption can effectively suppress the dissolution of lithium polysulfides through the strong chemical bond between LiPSs and the polar materials such as heteroatom-doped carbon, transition metal oxides/sulfides/carbides/nitrides, and metal–organic framework materials.\(^{[24–28]}\) Whether physical or chemical adsorption, however, the confined LiPSs are mostly hard to be re-used, forming the so-called “dead sulfur.” Moreover, the kinetics of polysulfide conversions is difficult to be improved just through such adsorption strategies, which cannot solve the problem at the root.

It is a crucial step for overcoming the shuttle effect to simultaneously enhance the anchoring and redox kinetics of LiPSs. The electrocatalysts such as metals,\(^{[29,30]}\) metallic compounds,\(^{[30,31,32]}\) and metal-free polar materials\(^{[17,33]}\) have
been employed to accelerate the kinetics of LiPS conversions due to their high catalytic activity and revealed good results in suppressing the shuttle effect. Nevertheless, the high catalytic activity may also cause the undesired side reactions in electrolyte and impair the performance of Li–S batteries, especially in long cycling processes.[22,34] The redox mediators such as MnO2,[35,36] VO2, and CuO[37] have been used to enhance the kinetics of LiPS conversions through reacting with long-chain LiPSs to generate surface-bound intermediates. The latter subsequently can react with the newly formed long-chain LiPSs to form short-chain LiPSs and the products that can anchor the soluble LiPSs. Such positive methods can not only adsorb the soluble LiPSs but also improve the redox kinetics of LiPS conversions, exhibiting a promising potential to overcome the shuttle effect.

Transition metal hydroxides (TMHs) have attracted increasing attention in application of Li–S batteries due to their favorable ability to suppress shuttle effect, as well as natural abundance and eco-friendliness.[38–46] Nevertheless, the fundamental understanding related to underlying mechanisms how TMHs suppress the shuttle effect remains elusive so far. In the reported studies, the shuttle effect has been found to be suppressed to different extents, which was usually ascribed to the strong chemical binding between TMHs and LiPSs, for instance, the formation of metal–sulfur bonds[39] or lithium–hydroxyl.[43] However, whether TMHs react with LiPSs is still unknown and lacks sufficient evidence to their possible reactions. Therefore, it is necessary to further explore the mechanism in detail.

Herein, we demonstrate that nickel–cobalt double hydroxide (NiCo-DH) can act as a multifunctional mediator and reveals the superior ability to suppress the shuttle effect and promote the kinetics of LiPS conversions. We construct a composite cathode in which sulfur nanoparticles are encapsulated within NiCo-DH shells; reduced graphene oxide (RGO) and carbon nanotubes (CNTs) are used to create interconnected conductive networks. The NiCo-DH shell not only physically confines the loss of sulfur but also promotes the charge transfer and ion diffusion. More importantly, such shell layers are able to in situ generate high oxidation state metal ions (Ni3+ and Co4+) and induce the formation of surface-bound intermediate thiosulfate groups; the latter can anchor the newly formed LiPSs and accelerate its conversion kinetics. Such a NiCo-DH mediator endows the Li–S battery with high specific capacity (1348.1 mAh g−1 at 0.1 C), ultrahigh rate capability (697.7 mAh g−1 at 5 C), and ultralong cycle life (decay rate per cycle is only 0.015% after 1500 cycles at 2 C).

2. Results and Discussion

2.1. Synthesis and Characterization

The synthesis process of S@NiCo-DH@RC composite is illustrated in Figure 1. We first prepared the sulfur particles through the reaction of sodium thiosulfate with hydrochloric acid. Subsequently, the NiCo-DH shells were coated on the as-prepared sulfur particles via reacting Ni(NO3)2 and Co(NO3)2 with urea under mild conditions. The S@NiCo-DH@RC composite was then obtained through mixing with GO/CNTs followed by moderate reduction.

The as-synthesized sulfur nanoparticles have an average diameter of ~500 nm (Figure S1, Supporting Information). After coating with NiCo-DH, their surface reveals a thin, translucent shell (Figure 2a,b). Figure 2c and Figure S2 (Supporting Information) further reveal the thickness of NiCo-DH shell is around 25 nm. It is expected that such a core–shell structure can not only avoid the loss of sulfur by physical limit but also facilitate the charge transfer and ion diffusion.[48–50] The high-resolution transmission electron microscopy (HRTEM) image (Figure 2d) shows several crystal lattice fringes with d spacings of 0.381, 0.253, 0.234, and 0.199 nm, corresponding to (006), (009), (015), and (018) planes of NiCo-DH, respectively, which are consistent with the X-ray diffraction (XRD) patterns. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image (Figure 2e) and elemental mappings (Figure 2f) exhibit the homogeneous dispersion of S, Ni, Co, and O atoms, indicating that S is well encapsulated in the NiCo-DH shell.

To enhance the conductivity of S@NiCo-DH composite, we incorporated RGO and CNTs into the S@NiCo-DH system by electrostatic adsorption in the solution mixing process (see Figure 3a,b). Figure 3c indicates that RGO/CNTs link different S@NiCo-DH nanoparticles and form conductive networks able to facilitate the charge transfer. Such mixing and reduction processes did not destroy the core–shell structure of the composite and the distribution of S, Ni, Co, and C atoms remains homogeneous spatially (Figure 3d–g). Figure 3h shows the XRD patterns of the as-prepared NiCo-DH, pure sulfur, S@NiCo-DH, and S@NiCo-DH@RC. For NiCo-DH, the characteristic diffraction peaks at 11.26°, 22.66°, 34.12°, 38.52°, 45.62°, 59.40°, and 60.64° agree with (003), (006), (009), (015), (018), (110), and (113) crystal planes of the hydrotalcite-like nickel–cobalt hydroxide, respectively; similar to α-Ni(OH)2-like phase,[51] no impurity peaks appear in the patterns. The as-prepared sulfur exists in the orthorhombic form of sulfur (JCPDS card no. 01-0478). For both S@NiCo-DH and S@NiCo-DH@RC,

Figure 1. Schematic illustration to fabricate S@NiCo-DH@RC composite.
only one characteristic (003) diffraction peak of NiCo-DH can be observed while for S@NiCo-DH@RC no characteristic peaks of RGO/CNTs appear in the pattern. This is possibly because the weak peaks of NiCo-DH and RGO/CNTs overlapped with those of sulfur.[41] The existence of RGO/CNTs in the composite was verified by two characteristic D- and G-band peaks (≈1350 and ≈1587 cm$^{-1}$, respectively) of graphitic carbon (Figure 3i). To determine the real contents of S, NiCo-DH, and RGO/CNTs, the S@NiCo-DH@RC composite was first treated for 12 h with hydrochloric acid solution to give the content of NiCo-DH, and then the content of sulfur was obtained with thermogravimetric analysis (TGA) (the details can be seen in the Supporting Information). Figure 3j shows the content of NiCo-DH is 7.8%, the content of RGO/CNTs is 7.0%, and the content of S is as high as 85.2%, which provides a basis to achieve high energy densities.[52]

2.2. Electrochemical Properties

Before electrochemical testing, it is important to explore whether Li$^+$ can effectively penetrate the shell and react with sulfur in such an encapsulated structure. The electron energy loss spectroscopy (EELS) was used to characterize the distribution of lithium in the cathode materials after the first discharge. As shown in Figure S3a–c (Supporting Information), both S@NiCo-DH@RC and S@Ni(OH)$_2$@RC cathodes show excellent structural stability. The insets of Figure S3b,c (Supporting Information) are the first discharge curves (0.1 C) of the S@NiCo-DH@RC and S@Ni(OH)$_2$@RC cathodes, respectively. Both of them exhibit obvious two-plateau characteristics, with high initial discharge capacities of 1437.5 and 1329.3 mAh g$^{-1}$, respectively. These superior initial electrochemical properties reflect the fact that Li$^+$ can penetrate the NiCo-DH and Ni(OH)$_2$ shells to sufficiently react with sulfur. The HAADF-STEM (Figure S3d, Supporting Information) image of the S@Ni(OH)$_2$@RC cathode (after the first discharge) exhibits a full shell structure. A region (framed by green lines) throughout the whole particle is selected to perform the EELS mapping. As displayed in Figure S3e,f (Supporting Information), the lithium is evenly dispersed in the shell structure. The Ni M$_{2,3}$-edge mapping is also detected as expected (Figure S3g,h, Supporting Information). As a result, it is concluded that the whole particle is Li$^+$-accessible.

The electrochemical performances of the S@NiCo-DH@RC, S@Ni(OH)$_2$@RC, and pure sulfur cathodes in Li–S batteries were systematically investigated. Figure S4 (Supporting Information) shows the typical cyclic voltammetry (CV) curves of S@NiCo-DH@RC electrode at scan rate of 0.2 mV s$^{-1}$ with the voltage range of 1.7–2.8 V for the first five cycles. In the first cycle, two cathodic peaks at 2.25 and 2.0 V are associated with the reduction of sulfur (S$_8$) to long-chain soluble lithium polysulfides (Li$_x$S$_{8-x}$, $x \geq 4$) and the subsequent reduction to short-chain insoluble lithium polysulfides (Li$_2$S$_y$, $y < 3$), respectively. The anodic peak at 2.45 V is ascribed to the oxidation of Li$_2$S$_y$ to S$_8$. Compared with the first cycle, the second to fifth CV curves maintain the similar shape with only slight shifts, suggesting the superior cycling stability of S@NiCo-DH@RC cathode.[54] Figure 4a exhibits the rate capabilities of S@NiCo-DH@RC, S@Ni(OH)$_2$@RC, and pure S cathodes at the current densities
ranging from 0.1 to 5 C and then returning to 0.5 and 0.2 C (1 C = 1675 mA g\(^{-1}\)). The pure S cathode delivers 1013.2 mAh g\(^{-1}\) at first cycle of 0.1 C, but its capacity dramatically decreases with the increase of cycle numbers and current density, until approaching no capacity (=2 mAh g\(^{-1}\)) at 5 C, which signifies the severe loss of sulfur due to the dissolution of LiPSs at the early cycles.\[^5^5\] By comparison, the S@NiCo-DH@RC cathode exhibits the highest reversible capacity (1373.1 mAh g\(^{-1}\)) with excellent coulombic efficiency (99.0%) at first cycle of 0.1 C. At 0.1, 0.2, 0.5, 1, and 2 C, it shows stabilized average specific capacities of 1348.1, 1148.2, 989.2, 909.2, and 814.3 mAh g\(^{-1}\), respectively. Even when the current density increases to 5 C, it still retains a competitive capacity of 697.7 mAh g\(^{-1}\), indicating the ultrahigh rate performance of S@NiCo-DH@RC, as opposed to the previous reports listed in Table S1 (Supporting Information). When the current density returns to 0.5 and 0.2 C, the capacities of 956.8 and 1006.3 mAh g\(^{-1}\) are recovered, indicating the remarkable structure stability of S@NiCo-DH@RC cathode during the high-rate cycling. In contrast, the S@Ni(OH)\(_2\)@RC cathode also reveals a decent capacity (1348.4 mAh g\(^{-1}\)) with a coulombic efficiency of 96.4% at the first cycle of 0.1 C, but its capacity decreases rapidly, compared with that of S@NiCo-DH@RC, with the average specific capacities of 1231.4, 956.2, 809.7, 701.6, 569.5, and 443.9 mAh g\(^{-1}\) at 0.1, 0.2, 0.5, 1, 2, and 5 C, respectively, indicating the advantage of NiCo-DH encapsulation. For S@NiCo-DH@RC, its discharge/charge curves at different rates are displayed in Figure 4b. Two reductive plateaus from the cathode and one oxidic plateau from the anode are observed, which are consistent with the results of CV curves. These characters are still held even at 5 C, reflecting the excellent electrochemical reaction kinetics of S@NiCo-DH@RC.\[^3^1\] The CV and discharge/charge curves of S@Ni(OH)\(_2\)@RC are presented in Figure S5a,b (Supporting Information), and further comparison between S@NiCo-DH@RC and S@Ni(OH)\(_2\)@RC will be discussed later (see Figure 7c–f).

Figure 4c shows the cycling performance of S@NiCo-DH@RC and S@Ni(OH)\(_2\)@RC cathodes measured at 0.2 C. The S@NiCo-DH@RC cathode exhibits a prominent reversible capacity of 1132.3 mAh g\(^{-1}\) with a coulombic efficiency of 99.8% at the first discharge and even after 250 cycles it still remained at

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**Figure 3.** a–c) FESEM images of the S@NiCo-DH@RC composite at different magnifications. d–g) The elemental mapping analysis of S, Ni, Co, and C in the S@NiCo-DH@RC composite. h) XRD patterns of the pure NiCo-DH, pure sulfur, S@NiCo-DH, and S@NiCo-DH@RC composites. i) Raman spectrum and j) thermogravimetric analysis of the S@NiCo-DH@RC composite.
971.9 mAh g\(^{-1}\) (85.8%) with a coulombic efficiency of over 99% (99.8%), indicating that the dissolution of lithium polysulfides into electrolyte and the shuttle effect are well inhibited in the S@NiCo-DH@RC composite.\(^{[56]}\) In contrast, the S@Ni(OH)\(_2\)@RC cathode exhibits a lower capacity (955.7 mAh g\(^{-1}\)) with a coulombic efficiency of 98.3% at the first discharge and the capacity rapidly decreases with increasing cycle numbers, only 55.2% of retention with the coulombic efficiency less than 97% after 250 cycles. This implies the occurrence of limited sulfur utilization due to the continuous dissolution of lithium polysulfides occurred in the S@Ni(OH)\(_2\)@RC electrode. To further elucidate this, we compared their electrochemical impedance spectra (EIS) before and after 250 cycles at 0.2 C. As shown in Figure 4d, the charge transfer resistances (R\(_{ct}\), corresponding to the diameter of the depressed semicircle at high frequency) of S@NiCo-DH@RC and S@Ni(OH)\(_2\)@RC cathodes are close to each other, around 59.5 and 64.7 \(\Omega\), respectively. However, after 250 cycles at 0.2 C, R\(_{ct}\) of S@NiCo-DH@RC only increases to 78.2 \(\Omega\), far smaller than that of S@Ni(OH)\(_2\)@RC (131.7 \(\Omega\)). This implies less deposition of poorly conductive Li\(_2\)S or Li\(_2\)S\(_2\) on the lithium anode, that is, better to suppress the shuttle effect and better structure stability for the S@NiCo-DH@RC cathode. The comparison of separators for these two cathodes (Figure S6, Supporting Information) and the corresponding field emission scanning electron microscopy (FESEM) images after cycles (Figure S7, Supporting Information) also confirm this conclusion.

The long-term cycling stability of S@NiCo-DH@RC at high current density of 2 C is displayed in Figure 4e. After three cycles of activation at 0.1 C, the S@NiCo-DH@RC cathode delivers the first discharge capacity of 871.5 mAh g\(^{-1}\) with a coulombic efficiency of \(\approx\)100%, and still retains 675.6 mAh g\(^{-1}\) (77.5%) with a coulombic efficiency of 99.4% after 1500 cycles.
superior to most of the reported cathodes for Li–S batteries (see Table S1 in the Supporting Information). Only 0.015% of capacity decay per cycle is the important evidence that NiCo-DH can effectively block the dissolution of lithium polysulfides and suppress the shuttle effect. The EIS before and after cycles, the separator, and FESEM image with corresponding elemental mapping after cycles (Figure S8, Supporting Information) also point to this advantage. Figure S9 (Supporting Information) shows the superior rate performance of S@NiCo-DH@RC cathode after long cycles, further indicating a remarkable structure stability and capability to suppress the shuttle effect.

2.3. Mechanism of Suppressing Shuttle Effect

To elucidate the mechanism how transition metal hydroxides limit the shuttle effect, we first employed X-ray photoelectron spectroscopy (XPS) to investigate the elemental composition and chemical state of the S@NiCo-DH@RC and S@Ni(OH)2@RC composites. In general, it is mainly the divalent chemical state for nickel and cobalt (Ni2+ and Co2+) in the pure nickel–cobalt hydroxide.[57,58] The high-resolution Ni 2p3/2 spectrum in Figure 5a shows a peak at 856.5 eV, attributed to the high oxidation state of nickel (Ni3+) appearing abnormally, besides Ni2+ (at 855.1 eV) and a shake-up satellite (Sat., at 861.4 eV). Similarly, one peak at 782.0 eV (assigned to Co3+) also appears in the Co 2p3/2 spectrum (Figure 5b). This phenomenon of variation in chemical valence of metal ions would arise from the binding interaction between S and NiCo-DH.[45] In the S 2p spectrum (Figure 5c), the fitting peaks at 164.0 and 165.3 eV originate from S 2p3/2 and S 2p1/2 of sulfur, respectively, while the obvious broad peak at 169.2 eV would stem from the chemical binding between sulfur and metals (nickel and cobalt).[59] This proves the existence of strong binding interactions between S and NiCo-DH in the composite; the latter can anchor sulfur during discharge/charge process. The C 1s spectrum can be deconvolved into three peaks at 284.8, 286.2, and 288.6 eV, as shown in Figure 5d, which are ascribed to the contributions of sp2-hybridized carbon (C–C), epoxy/alkoxy carbon (C–O), and carbonyl carbon (C=O), respectively. Likewise, the XPS data of S@Ni(OH)2@RC reveals similar results (Figure S10, Supporting Information).

To further confirm the mechanism of the polysulfide adsorption via transition metal hydroxides and why the performance of NiCo-DH is better than that of Ni(OH)2, the adsorption experiment was carried out and subsequently the obtained supernatant was detected using UV–vis followed by XPS analysis for the solid collected from the solution. Before testing, we obtained the NiCo-DH and Ni(OH)2 from S@NiCo-DH and S@Ni(OH)2 composites, respectively, by removal of sulfur. Figure S11 (Supporting Information) shows the obtained NiCo-DH shell structure containing no sulfur, though some shells were broken. As shown in the inset of Figure 6a and Figure S12 (Supporting Information), both the obtained NiCo-DH and Ni(OH)2 show a good adsorption capability for Li2S6 (as a representative of soluble polysulfides, Li2Sx, 4 ≤ x ≤ 8), but the NiCo-DH/Li2S6 solution is closer to colorless. The concentration change of Li2S6 in the supernatant was further detected by UV–vis (Figure 6a). The intensity of Li2S6 absorption peak in the supernatant of NiCo-DH/Li2S6 solution is smaller than that of Ni(OH)2/Li2S6 solution, which confirms again that compared with Ni(OH)2, NiCo-DH has a stronger capability to anchor
lithium polysulfides and suppress the shuttle effect during discharge/charge. The XPS data can further unveil the mechanism related to the interaction of polysulfides with transition metal hydroxides. Figure 6b shows that in Ni 2p3/2 spectrum of the NiCo-DH shell the appearance of Ni3+ is caused by the above-mentioned chemical binding with sulfur. After contact with Li2S6, the variation of valence, as observed in Figure 6c, indicates that Ni3+ on the surface was reduced to Ni2+ and a similar phenomenon is also shown in the Co 2p3/2 spectrum (Figure 6d,e). This suggests a redox reaction between NiCo-DH and Li2S6 occurred on the surface of NiCo-DH. Actually, the variation of Ni3+ reduced to Ni2+ can also be observed in the XPS data of Ni(OH)2 and Ni(OH)2/Li2S6 (Figure S13, Supporting Information).

To further verify this, EELS has been employed to test the valence change of Ni and Co in the NiCo-DH and NiCo-DH/Li2S6. As shown in the EELS spectra of Co L2,3 edges (Figure S14a, Supporting Information), the L3/L2 intensity ratio of NiCo-DH is about 1.3. After contacting with Li2S6, the L3/L2 intensity ratio increases to 2.3, suggesting a decreased Co valence state. A similar phenomenon is also observed in the Ni L2,3 edge spectrum (Figure S14b, Supporting Information, from 1.5 to 2.8), suggesting a decreased Ni valence state. These results indicate a consistent change trend in valence state with the XPS results. To extract the information of the valence states for Ni and Co after NiCo-DH adsorption with polysulfides, Ni and Co K-edge X-ray absorption spectroscopy (XAS) characterizations were carried out. As shown in Figure S15a (Supporting Information), the Co K-edge X-ray absorption near-edge structure (XANES) shows that the absorption edge is sensitive to the oxidation state of Co, which shifts to higher energy from valence of 2+ to 2.67+ (average valence state). The main peak of Co in NiCo-DH/Li2S6 is located between that of 2+ and 2.67+, indicating the valence of Co is a mixture of 2+ and 3+, which is consistent with the XPS data. In combination with the XPS and EELS results, it can be confirmed that a part of Co3+ was indeed reduced to Co2+ after polysulfide adsorption. As shown in the Ni K-edge XANES (Figure S15b, Supporting Information),
the valence of Ni is close to but larger than 2+, revealing a similar phenomenon. These results in EELS and XAS spectra well support the XPS results.

In the S 2p spectrum (Figure 6f) of NiCo-DH/Li2S6, the fitting peaks at 162.3 and 163.6 eV are ascribed to “terminal” (S1) and “bridging” sulfur (S2) from polysulfides, respectively. Those more intense peaks between 166 and 172 eV can be fitted with two sulfur species. The fitting peaks at 167.4 and 168.1 eV are assigned to the surface-bound thiosulfate, which is caused by the oxidation of sulfur species from polysulfides. The peaks at 168.9 and 169.7 eV are in accord with the polythionate complex, which is formed by the reaction between the anchored thiosulfate and polysulfides following the equation:

\[
\text{O-S-S}^\text{2-} + \text{Li}_2\text{S}_x \rightarrow \text{O-S-} \left( \text{S}^\text{x}_{y} \right) \text{O}^\text{2-} + \text{Li}_2\text{S}_y (x \geq 4, y < 3)
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Therefore, the polythionate complex would be formed through catenating polysulfides to thiosulfate via insertion in the S–S bond. The soluble polysulfides (Li2Sx, x ≥ 4) are converted to a less soluble mediator polythionate complex and short-chain polysulfides (Li2Sy, y < 3), which not only exhibits effective entrapment of polysulfides, but also promotes the kinetics of a series of polysulfide conversions and finally leads to significant suppression of the shuttle effect. As shown in Figure 6g, two peaks at 170.5 and 171.7 eV, attributed to the highest oxidation state of sulfur species from sulfates, appear in the S 2p spectrum of Ni(OH)2/Li2S6, besides the peaks from S8, S6, thiosulfate, and polythionate complex. Sulfates are electrochemically inert, which accumulate and block the surface of the electrode during discharge/charge process, leading to poor cycling performance, as observed in our electrochemical results. As for Li 1s spectra of NiCo-DH/Li2S6 and Ni(OH)2/Li2S6 (Figure S16, Supporting Information), the fitting peak at 54.9 eV is ascribed to Li–S bond from polysulfides. The other weak peak at 55.8 eV may be assigned to Li–O bond due to the interaction between Li+ and OH−, while its amounts are too little to affect the redox reaction of polysulfides and NiCo-DH (or Ni(OH)3).

However, the question is why sulfate groups can form in the reaction of Ni(OH)3 with polysulfides but not in the reaction of NiCo-DH with polysulfides. In this regard, it is important to recognize that polysulfides can be oxidized to sulfate and polythionate complex when the redox potential (vs Li+/Li) is greater than 3.4 V, polysulfides will be oxidized to higher oxidation states (sulfate). For NiCo-DH and Ni(OH)2, their redox potentials (vs Li+/Li) were determined to be 2.74 and 3.43 V via CV tests, respectively (Figure 6h,i), the data were derived from the intersection of the first reduction peak with the x-axis. As for the reason why NiCo-DH possesses smaller redox potential, it is reasonable to conclude that it is due to the existence of electron transfer and strong coupling effect between Ni and Co ions in NiCo-DH.

The formation of short-chain polysulfides in the reversible redox reaction of thiosulfate with LiPSs means that NiCo-DH does not just passively adsorb with LiPSs, but actively participates in and promotes a series of redox reactions of polysulfides, actually playing a “catalytic” role. To evaluate this “catalytic effect,” we observed the redox behavior of Li2S6 in symmetrical cells using NiCo-DH or Ni(OH)2 as electrode with 0.5 m Li2S6 in electrolyte, by means of the CV tests performed at 10 mV s−1 within a voltage window of −1.0 to 1.0 V. As a control, the symmetrical cell of NiCo-DH without Li2S6 was also assembled. As shown in Figure 7a, the Li2S6-free cell reveals small contribution of capacitive current; the redox current of Li2S6 in NiCo-DH cell is much larger than that in Ni(OH)2 cell. Furthermore, the redox curve of Li2S6 in NiCo-DH cell shows an excellent reversibility. These substantiate that NiCo-DH plays an active role in the redox reactions of lithium polysulfides. The CV curves of NiCo-DH cell at different scan rates are displayed in Figure 7b. All redox curves reveal a similar shape and retain good reversibility, even at scan rate as high as 100 mV s−1, which indicates that NiCo-DH greatly facilitates the kinetics of a series of polysulfide conversions. In contrast, the redox curves of Li2S6 in Ni(OH)2 cell (Figure S17, Supporting Information) show severe polarization, implying that the redox behavior of Li2S6 is not completely reversible due to the formation of electrochemically inert sulfate groups. In addition, this “catalytic effect” is reflected in the discharge/charge and CV profiles of S@NiCo-DH@RC and S@Ni(OH)2@RC cathodes in Li–S batteries. Figure 7c shows that the S@NiCo-DH@RC cathode has smaller potential polarization (ΔE), that is, a faster redox reaction kinetics. Similarly, according to the CV curves (Figure 7d), the cathodic peak voltages (1 and 2) of S@Ni(OH)2@RC electrode are higher but along with a lower anodic peak voltage (3), compared with those of S@Ni(OH)2@RC electrode (Figure 7e). The corresponding variation of onset voltages is also similar to that of peak voltages (Figure 7f), which proves again the enhanced redox kinetics of LiPSs owing to the “catalytic effect” of NiCo-DH for the redox reaction of polysulfides.

Based on the above analysis, we propose a mechanism to elucidate how NiCo-DH suppresses shuttle effect of polysulfides in the S@NiCo-DH@RC cell. First, the high oxidation state metal ions (Ni4+ and Co3+) are formed in S@NiCo-DH@RC composite through the strong binding interaction between S and NiCo-DH. Second, the soluble lithium polysulfides initially formed during discharge process are oxidized on the NiCo-DH surface by Ni4+ and Co3+, generating the thiosulfates. Then, the newly formed polysulfides are confined by the anchored thiosulfates through catenating them to form the intermediates polythionate complex, and meanwhile, the short chain polysulfides are also produced. The reaction is highly reversible and thus guarantees the superb adsorption of polysulfides and the enhanced kinetics of a series of polysulfide conversions, as illustrated in Figure 8. Owing to the highly efficient synergy of multiple functionalities, NiCo-DH-based Li–S batteries exhibit superior rate performance and ultralong cycle life.

3. Conclusions

We demonstrate a novel nickel–cobalt double hydroxide–based composite, S@NiCo-DH@RGO/CNTs, as the cathode in Li–S batteries. The S@NiCo-DH@RGO/CNT cathode with 85.2 wt% sulfur achieves simultaneously the remarkable capacity of 1348.1 mAh g−1 at 0.1 C, ultrahigh rate performance...
Figure 7. a) CV profiles of symmetric cells using NiCo-DH and Ni(OH)₂ as electrodes with or without 0.5 \text{mM} Li₂S₆ in electrolyte at 10 \text{mV s}⁻¹ within a voltage window of −1.0 to 1.0 V. b) CV curves of symmetric NiCo-DH cell at scan rates ranging from 10 to 100 \text{mV s}⁻¹. c) Galvanostatic discharge–charge curves of S@NiCo-DH@RC and S@Ni(OH)₂@RC cathodes at 0.1 C in Li–S batteries. d) CV curves of S@NiCo-DH@RC and S@Ni(OH)₂@RC cathodes at 0.2 \text{mV s}⁻¹ in Li–S batteries. e) The peak voltages and f) onset voltages of S@NiCo-DH@RC and S@Ni(OH)₂@RC cathodes from the CV data in (d).

Figure 8. Schematic illustration of the mechanism to elucidate how NiCo-DH suppresses the shuttle effect of polysulfides.
Synthesis of S@NiCo-DH Composite: The S@NiCo-DH composite was synthesized through a coprecipitation method. First, 0.2 mmol Ni(NO$_3$)$_2$·6H$_2$O, 0.2 mmol Co(NO$_3$)$_2$·6H$_2$O, and 4 mmol urea were successively dissolved in 50 mL deionized water. After stirring for 2 h, the solution was mixed with the as-synthesized sulfur nanoparticles with stirring for 2 h, and the obtained mixture solution was transferred to a 250 mL flask and refluxed at 95 °C for 2 h. Then, the slurry was uniformly coated onto an Al foil and then dried at 90 °C, and the mass loading was 1.5 mg cm$^{-2}$. The CV responses were measured on a CHI 660E electrochemical workstation with an amplitude of 5 mV, and the electrolyte was 1 M LiTFSI and 0.1 M LiNO$_3$ in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (1:1 by volume) solution. Galvanostatic discharge/charge tests were conducted on a battery testing instrument (Land CT2001A, Wuhan, China) in the voltage range of 1.7–2.8 V (vs Li$^+$/Li). CV curves were recorded with an amplitude of 5 mV, and from 100 kHz to 0.1 Hz at open-circuit potential.

NiCo-DH/Li Metal Cell Assembly and Electrochemical Measurements: For the NiCo-DH/Li metal cell, the preparation procedure was similar to the assembly of S–Li cells. The active materials were pure NiCo-DH or Ni(OH)$_2$, the electrolyte was 1 M LiTFSI in DOL/DME (1:1 by volume) solution as electrolyte. CV curves were measured at 0.1 mV s$^{-1}$ with a potential window of 1.7–3.8 V. The Ni(OH)$_2$/Li cell was assembled with the similar method.

Symmetric Electrochemical Cell Assembly and Electrochemical Measurements: For the symmetric electrochemical cell, the active materials were pure NiCo-DH or Ni(OH)$_2$, the electrolyte was 1 M LiTFSI in DOL/DME (1:1 by volume) solution with (or without) 0.5 mL Li$_2$S$_6$, and the anode was the coated Al foil instead of a Li foil. CV curves were measured at different scanning rates of 10–100 mV s$^{-1}$ in a potential window of −1.0 to 1.0 V.

Synthesis of Lithium Polysulfide (Li$_2$S$_6$): To synthesis 0.5 mL of Li$_2$S$_6$ solution, 115 mg of Li$_2$S and 400 mg of S were added to 5 mL of DOL/DME solution (1:1 by volume). Then the suspension was heated at 80 °C for 20 h with stirring to obtain the Li$_2$S$_6$ solution. It should be noted that the experiment was conducted under the protection of argon gas.

Lithium Polysulfide Adsorption Test: Under the protection of argon gas, 4 mL of as-prepared Li$_2$S$_6$ solution (0.5 mL) was added into 2 mL of DOL/DME solution (1:1 by volume), and then 10 mg of active samples (NiCo-DH or Ni(OH)$_2$) were added with stirring for 0.5 h. After standing for 20 h, the adsorption effect can be preliminarily judged according to the change of the color of the solution.

Supporting Information

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

The authors are grateful for the financial support by the 973 project (2011CB605702), the National Science Foundation of China (51173027), and Shanghai Key Basic Research Project (14JC140600). The authors appreciate Dr. Du Yonghua in SSLS, Singapore for the XANES and extended X-ray absorption fine structure (EXAFS) measurements. The authors appreciate the XAS measurements from SSLS, SUV (Soft X-Ray—Ultraviolet) beamline.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

accelerating kinetics, chemical adsorption, lithium–sulfur batteries, multifunctional mediator, nickel–cobalt double hydroxide

Received: August 6, 2018
Revised: September 27, 2018
Published online: