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Improved redox reaction of lithium polysulfides on the interfacial boundary of polar CoC₂O₄ as a polysulfide catenator for a high-capacity lithium-sulfur battery

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Abstract: Herein, we report the improved performance of cobalt oxalate as an electrocatalyst in a lithium-sulfur battery (LSB) owing to the suitable adsorbent properties of sulfur. By UV-vis and surface analysis through X-ray photoelectron spectroscopy, the adsorption mechanism was elucidated. Li_2S_6 is converted to thiosulfate and polythionate by a catenation reaction on the interfacial boundary of CoC_2O_4 contacted with carbon. Following this, the active polythionate and short-chained liquid lithium polysulfides (LiPS) bound to the cobalt surface were further reduced as CoC_2O_4 reduces the overvoltage to facilitate the LiPS redox reaction, leading to high specific capacity, lower self-discharge rate, and stable long-term cycle performance.

Introduction

In today's world, it is critical to find cheap, efficient, and nonpolluting strategies for generating and storing electrical energy. At present, lithium-ion batteries (LIBs) are particularly preferred because they are used in a wide range of electronic devices such as laptops, mobile phones, and mobile sensors owing to their excellent cycle performance stability. However, as the energy consumption paradigm expands to large-scale energy-storage systems (ESSs), high-energy and long-lasting batteries are urgently required. With regard to this factor, a lithium-sulfur battery (LSB) is an excellent alternative to the current LIBs because of its four to five times higher theoretical capacity (1,672 mAh g_s^{-1}) ^[1–3].

Notwithstanding high demand in the market for an improved battery with higher capacity and longer life span than those of the conventional LIBs, the commercialization of LSB has been sluggish in progress due to the difference in the operational mechanisms between LIBs and LSB. In contrast to LIBs that are operated by an intercalation-deintercalation reaction, the primary reaction mechanism in LSBs follows a different pathway that electrochemically produces solid-phase S_8 and Li_2S species, as well as liquid-lithium polysulfide (LiPS, Li_2S_X , $6 < x \le 8$) intermediates during consecutive cycles^[4–9]. An electrocatalyst is necessary to improve the electrochemical utilization of sulfur.

Additionally, it is essential to overcome poor cycle performance stability arising from the accumulation of solid-phase S₈ and Li₂S. The central role of the electrocatalyst in the cathode is to enhance the reversibility of cells by facilitating the redox reactions of solid-phase elemental sulfur (S₈), lithium sulfide (Li₂S) and liquid-LiPSs. The electrocatalyst in LSB can improve the electrochemical utilization of sulfur by improving the retention of LiPS within the cathode structure, resulting in the enhancement of specific capacity. In addition, it is possible to mitigate the dramatic degradation in performance by uniformly distributing the final charge and discharge products, $S_{8,}$ and Li_2S within the cathode matrix. Consequently, the development of electrocatalysts for a LSB has been actively pursued in recent years.

Efficient chemical adsorption, originating from the polar surface interaction between LiPS and the electrocatalysts, is critical for the functioning of electrocatalysts. According to previous studies, oxygen-rich materials such as various metal oxides and polymer binders containing abundant oxygen functionalities have been widely used in a LSB. It is because LiPS are chemically and electrochemically bound to the hydrophilic and oxophilic surface. Cui et al. have reported that metal oxides, such as V_2O_5 and MnO_2 . exhibit superior LiPS adsorption capabilities ^[10]. This observation is consistent with the results for various other types of metal oxides such as CeO₂, Al₂O₃, La₂O₃, MgO, and CaO ^[11]. From density functional theory (DFT) calculation and surface analyses, two dominant types of interactions were evident; one is the interaction of 1) the positively charged lithium atoms in LiPS interacting with oxygen in metal oxides, and the other is between 2) the negatively charged sulfur in LiPS with the metal or oxygen atom in metal oxides [7,12]. It has been established that the use of appropriate metal oxide-based electrocatalysts results in excellent performance in terms of specific capacity and long-term cycle stability.

 CoC_2O_4 is structurally similar to metal oxides with the advantage of a facile and, straightforward synthesis by precipitation without any additional heat treatment. Interestingly, metal oxalates generally develop to form one-dimensional layered structures. Therefore, numerous studies have focused on the

applications of metal oxalates as precursors for producing metal oxide nanowires or nanorods *via* thermal decomposition ^[13–15]. In particular, various types of metal oxalates such as FeC₂O₄, CuC₂O₄, NiC₂O₄, and MnC₂O₄, have been confirmed as suitable anode materials for LIBs. However, the use of metal oxalates as electrode materials has been limited because of their poor cycle durability originating from the irreversible reactions under 1 V such as unnecessary solid-electrolyte interface (SEI) and lithium oxide formation ^[16–20].

In this study, we explore the electrocatalytic behavior of a novel electrocatalyst, CoC_2O_4 , for the LiPS redox reaction in the cathode of a LSB. Although CoC_2O_4 has rarely been studied as an electrocatalyst, we have observed in our previous studies that the synthesized CoC_2O_4 shows superior electrocatalytic activity for oxygen evolution and reduction reactions in an aqueous alkaline electrolyte ^[21,22]. These properties are attributed to the strong interaction between the surface of CoC_2O_4 and the OH⁻ ions. Considering its electrochemical behavior, we hypothesized that the polar CoC_2O_4 would exhibit similar electrocatalytic behavior for the LiPS redox reaction as well. It would, in turn, increase both the specific capacity and cycle durability of an LSB.

Results and Discussion

Following our previous reports, a highly active CoC_2O_4 electrocatalyst was synthesized *via* a one-pot precipitation reaction ^[21,22]. The molecular structure of CoC_2O_4 has a high molecular polar surface area (PSA), the definition of which is the sum of all polar atom surface areas in a molecule and is useful for predicting absorption. It has been successfully used for the prediction of intestinal absorption and drug transport in biochemistry and pharmaceuticals ^[23]. According to a molecular PSA release from the open-source, CoC_2O_4 is calculated to have a PSA of 80.3 Å², which is higher than that of Co_3O_4 (4 Å²), MnO₂ (34.1 Å²) and V₂O₅ (77.5 Å²)^[24]. It connotes that CoC_2O_4 has a suitable molecular structure for the absorption of polar species.

To elucidate the electrochemical activity of CoC2O4 for the LiPS redox reaction, cyclic voltammetry for the electrodes with different CoC₂O₄ ratios, was measured by assembling the symmetric cell, as shown in Figure 1(a). In the presence of the catholyte with 0.2 M Li₂S₆, these symmetric electrodes with different contents of CoC₂O₄ showed different CV peak current patterns. Although the symmetric redox peak current seems to be flat at higher contents of CoC_2O_4 (50%), the redox peak currents were inversely proportional to the decrease of weight ratio of CoC2O4 and conductive carbon (W_{CoC2O4} / W_{carbon}). It implies that a lower value of the weight ratio of CoC₂O₄ to conductive carbon enhances the LiPS redox reaction by increasing the active interfacial boundary. Because CoC₂O₄ is non-conductive material, CoC₂O₄ cannot participate in the electrochemical reduction reaction alone. Thus, the peak current is increase by increasing carbon ratio leading to increase of active sites contacting with carbon and CoC2O4. Interestingly, an additional redox peak at 0.05 V was observed in the cathodic scan (- 0.05 V in the anodic scan) for the electrodes with CoC₂O₄. For the electrodes with both 15 and 30% CoC₂O₄, conventional two redox peak patterns were observed. The two redox peaks observed at - 0.1 V and - 0.35 V in the cathodic scan (0.1 V and 0.35 V in the anodic scan) corresponded to the reduction reaction of a longer-chain (Li₂S_x, $4 \le x \le 8$) and a shorter-chain (Li₂S_x, $2 \le x \le 4$) LiPS, respectively^[25-27]. Notably, Manuscrip

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Figure 1. CV curves for a symmetric coin cell (electrode // catholyte // electrode) of (a) electrodes with different contents of (i) 50% (black), (ii) 30% (blue) and (iii) 15% (red) CoC₂O₄ in the use of 0.2 M Li₂S₆ contained catholyte, and (b) 15% CoC₂O₄ contained electrodes with the catholyte in different concentration of (i) 0, (ii) 0.05, (iii) 0.1, (iv) 0.2 M of Li₂S₆ (All CV curves measured at the scan rate of 3 mV s⁻¹ were compared, and specific current were calculated by the weight of CoC₂O₄)

an additional peak over 0 V has rarely been reported in the CV studies of symmetric cells with liquid Li_2S_6 . Only the three redox peak patterns observed in CV studies have been reported in the literature, emphasizing the superior ability of LiPS adsorption on the surface of the redox mediators^[28,29]. Based on this finding, we conclude that a spontaneous and strong adsorption reaction, requiring a lower overpotential occurs on the surface of the CoC₂O₄ prior to the electrochemical redox reaction.

In addition to the CV studies of the electrodes comprising various contents of CoC_2O_4 , we have also performed the CV in the electrolyte with different concentrations of Li_2S_6 . The peak current value showed a directly proportional relationship with the concentration of Li_2S_6 (from 0 to 0.2 M) in the catholyte, as shown in **Figure 1(b)**. In the case of the reference electrolytes without any Li_2S_6 (0 M Li_2S_6), there were no significant redox peaks. These peak patterns and the effect of CoC_2O_4 also appeared in the CV curves with different scan rates, as shown in **Figure S5**. This indicates that CoC_2O_4 does not solely participate in undesirable reactions such as lithiation/delithiation, and there occurs formation of an SEI layer on the CoC_2O_4 surface in the

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Figure 2. Cyclic voltammogram of asymmetric cells (Li // electrolyte // cathode) with (a) CoC_2O_4 cathode (15% of CoC_2O_4 : 75% of SuperP : 10% of PVDF) with 1 M LiTFSI in DME/DOL electrolytes containing (i) 0 mM (black) and (ii) 0.5 mM Li₂S₆ (red); and (b) cathode containing 50% of sulfur (i) without and (ii) with CoC_2O_4 (15%) and 1 M LiTFSI in DME/DOL. All the tests were performed under a scan rate of 0.1 mV/s and all the curves correspond to the 5th cycle.

working range of the LSB's voltage. On increasing the concentration of Li_2S_6 in the catholyte, the three LiPS redox peaks appeared in all the cells including Li_2S_6 , unlike in the case of the reference cell. Therefore, we confirmed that CoC_2O_4 surrounded by a conductive carbon exhibits electrochemical redox ability for the soluble LiPS species, such as Li_2S_6 .

To verify the capability of CoC_2O_4 for the redox reaction of LiPS in the symmetric coin cell, we have also performed CV tests using an asymmetric coin cell test, as shown in **Figure 2(a)**. Li metal was used as an anode and a CoC_2O_4 -based electrode without sulfur was used as a cathode. In the presence of conventional electrolytes, the cell with the CoC_2O_4 -based cathode did not show any electrochemical redox activity during multiple cycles. In contrast, the CoC_2O_4 -based cathode showed several redox peaks even after the 5th cycle when electrolytes containing 0.5 mM Li₂S₆ species were employed. The multiple reduction peaks may be resulted from the successive reduction reaction of multiple Li₂S_x (1 ≤ X ≤ 8) species^[2,30]. The CV results from both symmetric and asymmetric cell tests support two factors. First, CoC_2O_4 is stable within the LSB operational voltage range (1.5 – 3.0 V) against



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Figure 3. Voltage profiles of sulfur cathodes in the presence of (a) CoC_2O_4 during galvanostatic discharge and the charge steps at 1st (black), 2nd (red) and 50th (blue) cycles, (b) initial peak charge voltage value (dashed shadow area in (a)) of (i) the reference cell and (ii) the cell with CoC_2O_4 , and (c) its long-term cycle performance of (i) the reference cell and (ii) the cell with CoC_2O_4 , and (c) all electrochemical tests were operated under 0.2 C (=334 mA/g_s).

irreversible reactions such as lithium oxide formation and unnecessary SEI formation, which have been frequently encountered in other studies of LIB electrodes. In other words, there is no capacity contribution by the additional lithiationdelithiation reaction of CoC₂O₄. Second, the interface of Li₂S₆absorbed CoC₂O₄ surrounded with conductive carbon facilitates the LiPS redox reaction. This positive effect on the CoC₂O₄ electrocatalytic activity was also evident in the CV curves of the sulfur cathode with CoC₂O₄, as depicted in Figure 2(b). In the presence of CoC₂O₄, the two reduction peaks and one oxidation peak were narrow and more intense than those for the cathode without CoC₂O₄. The reduction potential peak shifted to a higher potential by 59 mV, and the oxidation peak shifted to a lower potential by 49 mV in the case of the sulfur cathode with CoC₂O₄. These results imply that CoC₂O₄ helps improve the kinetics of the electrochemical redox reaction of LiPS during the charge and discharge processes in LSBs.

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Figure 4. UV-vis absorbance spectra of DME / DOL containing 0.5 mM Li_2S_6 (a) without, and (b) with CoC_2O_4 powder (inset of digital photos were taken 10 min after addition of CoC_2O_4 powder).

To confirm the electrocatalytic effect of CoC2O4 on the specific capacity and cycle stability in LSBs, we have conducted a galvanostatic charge and discharge cycle, as shown in Figure 3. Figure 3(a) shows the potential profiles of sulfur cathode cells containing CoC₂O₄. The profiles indicate that the CoC₂O₄ enhances the electrochemical utilization rate of non-conductive sulfur by 22.44 % at the initial cycle and by 60.19 % at the 50th cycle as compared to that of the reference cell (Figure S3). A comparison of the peak overvoltage at the initial charge step, marked as the shadowed area in Figure 3(a) are shown in Figures 3(b). A higher peak charge voltage value implies that a higher overvoltage is required to dissociate the solid-phase Li₂S. This increases the irreversible capacity and cell performance degradation rate. As shown in Figure 3(b), the CoC2O4containing cathode reduces the peak charge voltage by 41 mV (from 2.263 V to 2.222 V), while the sulfur cathode with 0 % CoC₂O₄ maintained the initial overvoltage level (a decrease of 3 mV was observed, from 2.250 V to 2.247 V) on increasing the cycle number. From the decrease in the overvoltage at the initial charge step, it can be deduced that CoC₂O₄ could contribute to the electrochemical dissociation of not only the liquid-phase LiPS intermediates but also the solid-phase Li2S2 and Li2S. The electrocatalytic effect of CoC2O4 was well demonstrated by the long-term cycle stability, as shown in Figure 3(c). The CoC₂O₄ based cathode exhibited a superior specific capacity and a lower cell performance degradation rate of 0.12% per cycle, as compared to the 0.35 % per cycle observed for the reference cell without CoC₂O₄. The cell performance degradation rate was calculated from the 10th cycle and final capacity values after stabilizing the electrode surface.

LiPS adsorption tests were carried out on the surface of CoC_2O_4 Li₂S₆ (0.5 mM) in a solvent mixture of DOL/DME to be prepared to investigate the reaction on the interfacial boundary. Subsequently, CoC_2O_4 powder was added for the adsorption of LiPS. As shown in the inset of **Figure 4**, the initial 0.5 mM Li₂S₆ solution was bright yellow, and the color rapidly dissipated, resulting in a transparent solution within 10 min of the addition of CoC_2O_4 powder. Furthermore, the color of the surface of the CoC_2O_4 precipitates changed from pink to dark brown. These changes indicate that Li₂S₆ is chemically adsorbed onto the



Figure 5. XPS spectra of (a) Co2p, and (b) S2p on the surface of (i) pristine CoC_2O_4 and (ii) CoC_2O_4 precipitates after the adsorption of Li_2S_6 .(Filled curves : $S2p_{3/2}$, dashed curves : $S2p_{1/2}$)

surface of the CoC₂O₄ powder. For quantitative observation, a certain amount of the supernatant was carefully extracted to minimize the interference by powder redispersion, and UV-Vis analysis was performed on the liquid. The UV-Vis spectra profiles shown in **Figure 4** help determine the relative adsorption capabilities of different LiPS species in the supernatant solution in comparison with the pristine Li₂S₆ solution. The bands at 320 and 420 nm are ascribed to S₄²·species. On the other hand, the bands at 350 and 264 nm are assigned to S₆² and the dissolved S₈ species, respectively, as per previous studies ^[31–33]. Considering the bands mentioned above, distinctly strong

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Surface on the CoC2O4 electrocatalysts

Figure 6. Schematic illustration of LiPS redox reaction on the surface of CoC_2O_4 placed on the interfacial boundary contacted with a conductive carbon, CoC_2O_4 and LiPS reactor (blue : cobalt, red : oxygen, grey : carbon, yellow : sulfur, and purple : lithium atom).

absorbances of the polysulfide species, mainly S_4^{2-} (73.4 % adsorbed at 420 nm and 83.4 % adsorbed at 320 nm) and S_6^{2-} (87.5 % adsorbed at 350 nm), are evident. Among the various LiPSs, trapping the Li₂S₆ and Li₂S₄ species within the cathode matrix is crucial because the long-chain Li₂S₆ has the highest solubility among the various LiPSs, and the short-chain Li₂S₄ contributes to higher specific capacity during a cycle ^[34-36].

To further prove the presence of chemical interactions between the LiPS and cobalt oxalates, X-ray photoelectron spectroscopy (XPS) was performed on the surface of cobalt oxalate precipitates following the LiPS adsorption tests. Figure 5 and S4 depict the spectra of pristine cobalt oxalate reacted with Li₂S₆. As shown in the survey spectra (Figure S4(a)), the characteristic signals of Co2p, O1s, and C1s (atomic ratio = 12.1: 47.1: 40.8, respectively) appeared for the as-synthesized cobalt oxalate powder, whereby the additional peak from S2p confirmed the adsorption of Li₂S₆ onto the surface of cobalt oxalates after the precipitation. In the deconvoluted O1s spectra of pristine cobalt oxalates as shown in Figure S4(b), two dominant peaks were present, one for the oxalate anions (O-C=O) at 532.34 eV, and the other for the O2species in Co-O bonds at 531.63 eV. Interestingly, the two dominant peaks did not change in terms of binding energy and peak intensities after the Li₂S₆ adsorption test. It implies that the oxalate anions are chemically stable against the effect of sulfur species [37]. However, the adsorption effect of sulfur in LiPS was revealed in the Co2p and S2p spectra as observed in Figure 5(a) and (b). In contrast to the Co2p spectrum of pristine cobalt oxalate, wherein the dominant Co2+ peak is located at 781.6 eV, new peaks appear at 778.3 eV for Co2p_{3/2} and 793.2 eV for Co2p_{1/2}. The additional peak observed at lower binding energy than that of the Co2+ peak correlates with the results from the previous XPS studies of cobalt sulfides, cobalt phosphide, CoOOH, and sulfurdoped cobalt compounds, indicating strong Co-S interaction [38-42]. Chemical bonds between the cobalt and sulfur can be identified in the S2p spectra. Upon contact with Li₂S₆, four distinct S2p_{3/2} peaks were observed, for the terminal sulfur (S_T^{-1}) at 161.7 eV, bridged sulfur (S_B^0) at 163.7 eV, thiosulfate at 166.1 eV and polythionate at 168.7 eV, as shown in Figure 5(b).

Additionally, the S2p_{1/2} spectra showed higher binding energy of 1.16 eV with a peak intensity ratio of 0.51 as compared to each of the peaks of S2p_{3/2}. The S2p spectra in **Figure 5(b)** can be categorized into two binding energy regions, one from S_T^{-1} at

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Figure 7. Long-term cycle performance and Coulombic efficiency of 15% CoC_2O_4 -containing carbon layer on a sulfur cathode with CoC_2O_4 under various current densities (0.2 C, 0.3 C, 0.5 C and 1 C) after 3 cycles of activation steps under 0.05 C. (Operating voltage range: (a) 2.2 - 2.5 V at 0.05 C activation step, 1.8-2.6 V at (b) 0.2 C and (c) 0.3 C, 1.5-2.8 V at (d) 0.5 C and (e) 1 C; arrow marked pause period for (i) 24 h, and (ii) 72 h, here, 1 C = 1,672 mA/gs).

161.7 eV to S_B^0 at 163.7 eV, and the other corresponding to the thiosulfate and polythionate region. Pristine Li₂S₆ should show a value close to 1/2 of S_T^{-1} / S_B^0 because of the dominant bridged sulfur atom in Li₂S₆. In contrast, for Li₂S₆ interacting with CoC₂O₄, a much higher value of the ST-1/SB0 ratio was obtained, implying that the intensity of S_T -1 that is assigned to both Li-S and Co-S chemical bonds may overlap. A higher ST-1 ratio in S2p is in agreement with the appearance of the new peak at 778.3 eV for the Co-S bond of Co2p_{3/2}. The existence of thiosulfate and polythionate is vital evidence to prove the chemical interaction between CoC₂O₄ and LiPS and the electrochemical redox activity of LiPS on the surface [10,43-48]. According to Nazar's studies, a moderate affinity of the host material to LiPS is crucial. On such surfaces, the soluble LiPS are chemically converted to polythionate, and lower molecular weight LiPS species via the disproportionation reaction, except for the production of inactive sulfate species (SO₃²⁻ and SO₄²⁻), occurring over 170 eV ^[43,44]. The reaction mechanism conforms with other recently published reports, wherein an electrocatalytic redox activity was strongly emphasized for the LiPS redox reaction^[49-55].

Summarizing the CV, UV-vis and XPS results, we speculate that the strongly nucleophilic thiosulfate formed on CoC2O4 initiates the catenation reaction. The thiosulfate on CoC2O4 attacks the bridged S-S bond (S_B⁰) in the longer-chain LiPS molecules that are generated by opening the octa-ring of sulfur as soon as a reduction current is applied. Following this, the formation of polythionate and short-chained LiPS is triggered by an internal disproportionation reaction. Additionally, Co²⁺ may be bound to a fraction of the LiPS. Then, the ions get partially reduced to Co⁺ after the adsorption of the edged sulfur atom in LiPS, as illustrated in Figure 6. An additional redox peak near 0.05 V in the cathodic scan (-0.05 V in the anodic scan) reflects the catenation processes, as shown in Figure 1, although this peak has not yet been reported in the CV analysis. We also confirmed the stability of CoC2O4 by analyzing the surface of cathode containing CoC2O4 after several galvanostatic charge and discharge cycles, as shown in Figure S7.

To improve the positive effect on the performance of LSBs, a cell with a dual-layer structure was tested for long-term cycle performance with various current densities. The dual-layer cathode structure has already demonstrated outstanding advantages in our previous studies ^[56,57]. Briefly, the carbon layer, a crucial component, is placed directly on the conventional sulfur

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cathode. The carbon interlayer plays dual roles; as a filter to physically trap the diffused LiPS, and as an additional electrode in which the retained LiPS undergoes further electrochemical reaction. Thus, the specific capacity was effectively improved by the enhancement of the sulfur utilization rate and long-term cycle stability. Here, we fabricated and tested an LSB cell using a carbon interlayer with 15 % CoC_2O_4 placed between the separator and the cathode containing CoC_2O_4 , as shown in **Figure 7**. First, the specific capacity did not dramatically decrease, increasing the charge/discharge rates from a low value of 0.2 C to high current of 1 C. This indicates that the kinetics of the LiPS redox reaction was relatively rapid. Notably, the specific capacity at 0.5 C increased because the operating voltage range also increased from $1.8 \sim 2.6$ V to $1.5 \sim 2.8$ V to allow adequate charge and discharge time.

Interestingly, the cell performance was maintained against two intermittent pause states, lasting one day and three days, respectively. This finding indicates that in this study, the dual-layer cathode with CoC_2O_4 effectively confined the LiPS within the conductive matrix in an open circuit state. It also minimized the self-discharge reaction on the Li anode surface arising from LiPS cross-over throughout the entire cell. From the electrocatalytic behavior of CoC_2O_4 , we verified that the high specific capacity and long-term cycle performance were attained with a minimal performance degradation rate of 0.0594 % per cycle (from 794.26 mAh g_s^{-1} to 699.94 mAh g_s^{-1}), even under a high C-rate of 1 C.

Conclusion

LSBs face critical technical barriers as a replacement for LIBs owing to the inadequate electrochemical utilization of insulating sulfur, and cell performance degradation resulting from "shuttle phenomena." Thus, a novel concept to utilize an electrocatalyst is necessary for the successful development of cathode. We have investigated the electrocatalytic behavior of a new electrocatalyst, CoC_2O_4 , for the LiPS redox reaction in LSBs. It has been observed that CoC_2O_4 shows outstanding electrocatalytic reaction and long-term stability owing to its adsorption capability on the interfacial boundary of the LiPS complex and electrocatalyst. These phenomena can be demonstrated as follows:

1) Surface analysis

CoC₂O₄ produced using a straightforward synthetic process, exhibited excellent LiPS adsorption ability, which is proved by the UV-Vis results. Among the many LiPS species, S₄²⁻ and S₆²⁻ species that have the highest solubility in DOL/DME electrolytes, were adsorbed onto the polar surface of CoC₂O₄. We confirmed that a CoC₂O₄ electrocatalyst could effectively suppress the diffusion of the highly soluble S₄²⁻ and S₆²⁻ species. The results of the XPS analysis revealed that the polar LiPS is absorbed on the CoC₂O₄'s interfacial boundary with carbon. Here, the active polythionate species and shorter-chained LiPS are produced by successive disproportionation reactions, as catenation reactions, as well as positively charged Co²⁺ sites resulting in the partial reduction to Co⁺ after binding S_T⁻¹ in LiPS.

2) Electrochemical results

Because of the moderate affinity of CoC_2O_4 toward polar LiPS, the CV analysis under a range of electrolyte and cathode conditions were performed to demonstrate the electrocatalytic behavior of CoC₂O₄. In the case of electrolytes containing 0.1 M LiPS solution, the CoC₂O₄ electrode with no sulfur resulted in LiPS redox curves during multiple cycles. In the CV curves of the sulfur-containing CoC₂O₄ cathode, the potential gap between the LiPS reduction and oxidation peaks continually decreased. It implies that CoC₂O₄ facilitated the LiPS redox reaction, and the rate of the irreversible cell reaction decreased. Based on the fundamental electrochemical analysis, the enhancement of the LSB performance was demonstrated by an increase in the sulfur utilization rate, a decrease in the initial charge overvoltage, and a decrease in the cell performance degradation rate. Additionally, the long-term cycle performance of LSB with a CoC₂O₄ cathode was verified by the low degradation rate of 0.059 % per cycle under 1 C. In conclusion, we have elucidated from the electrocatalytic behavior of CoC2O4 that it can be used in batteries and that CoC₂O₄ synthesized herein can be employed as an efficient electrocatalyst in LSBs.

Experimental Section

Preparation of CoC₂O₄ electrocatalyst

The CoC₂O₄ electrocatalyst was prepared using a direct precipitation method. $H_2C_2O_4 \cdot 2H_2O$ (0.1 M) (Sigma Aldrich) was added to 0.1 M CoCl₂ (Sigma Aldrich) in deionized water. After completely dissolving the precursors, the CoC₂O₄ $\cdot 2H_2O$ precipitate was formed after 30 mins, and it was allowed to settle. Subsequently, the precipitate was collected by filtration and was washed several times with deionized water and ethanol to remove impurities. Finally, the gram-scale CoC₂O₄ powder was obtained after drying at 80°C for over 24 h under vacuum, as shown in **Figure S1(a)**.

Preparation of the CoC₂O₄ based electrode and sulfur cathode

To test the electrocatalytic behavior of CoC2O4, we fabricated CoC₂O₄ based electrodes using a slurry coating method. A certain amount of the synthesized CoC₂O₄ powder, and conductive SuperP (Timcal, US) were mixed well with 10% PVDF (Kynar, Japan) binder in the N-methyl-2pyrrolidone (NMP) solvent. After vigorous stirring, the slurry was coated on an Al foil, and the solvent was utterly evaporated at 70°C in a vacuum for over a day. The ratio of CoC₂O₄ and carbon was modulated at each step to verify the electrochemical behavior of CoC2O4 under various conditions. The detailed contents of each material used in this study have been described in the main text. To demonstrate the effect of CoC_2O_4 on the LSB performance, sulfur cathodes were prepared as the reference cathode by homogenizing the sulfur and carbon (S-C) composites as the active material, SuperP, and poly(vinylidene difluoride) (PVDF) binder in a weight ratio of 70:20:10, respectively, in NMP. The slurry for the CoC₂O₄containing cathode consisted of CoC2O4 instead of 10 % SuperP. Here, we employed a melt-diffusion synthesis to prepare the S-C composite. In brief, sulfur powder and activated carbon (Ketjen Black, EC600JD, Lion Specialty Chemicals) were mixed with a hand-mill in an S⁻C ratio of 4.1. After transferring the mixture to an alumina boat, a two-step heat treatment was conducted at 155°C over 20 h, and then at 250°C for 1 h, under an argon atmosphere. Sulfur content of 80 % in the S-C composite was confirmed by measuring the weight loss after the heat treatment at 700 °C for 1h in argon atmosphere. The well-mixed slurries were coated on aluminium foil using a doctor blade to produce a loading amount of 1.5 - $2.0 \text{ mg}_{s} \text{ cm}^{-2}$. For testing the long-term cycle performance, a cathode with a dual-layer was used. It consisted of a carbon interlayer with CoC2O4 composed of 75 % carbon, 15 % CoC₂O₄ powder, and 10 % PVDF, coated on a Celgard 2320 separator resulting in a coating layer thickness of 10 μm.

Electrochemical analysis and other characterizations

For the electrochemical analysis, a 2032-coin cell was assembled both by stacking a separator sandwiched between two electrodes containing CoC₂O₄ for a symmetric coin cell. The asymmetric coin cell was composed of stacking Li metal, a pristine separator (or interlayer) and a sulfur cathode with a certain amount of electrolyte. The electrolyte was composed of 1 M lithium bis-trifluoromethanesulfonimide (LiTESI) in 1, 3dioxolane (DOL)/1, 2-dimethyl ethane (DME) (1:1 vol %). All the coin cells were assembled in an Ar-filled glovebox (< 0.5 ppm H₂O) and a 12 µl mg ¹s electrolyte amount was used. To observe the electrochemical redox reaction for CoC2O4, cyclic voltammetry (CV) was conducted using a symmetric cell configuration. The CV studies were performed on a Biologic potentiostat with 0.1 mV s⁻¹, and the galvanostatic charge and discharge tests were performed using a WBSC3000 cycler (Won-A Tech, Republic of Korea). To investigate the LiPS adsorption and electrochemical redox reactions of CoC_2O_4 , Li₂S₆ solution was prepared by dissolving the stoichiometric weight ratio of elemental sulfur and Li2S in a DOL/DME mixture at 70 °C for two hours. To observe the degree of Li₂S₆ adsorption, we placed 0.1 g of CoC₂O₄ powder in 0.5 mM Li₂S₆ solution, and then analyzed the diluted supernatant by measuring UV-Vis absorption (UV-1800, Shimadzu). CoC_2O_4 formed a one-dimensional rod of 20 - 30 nm thickness, as observed by transmission electron microscopy (TEM) as shown in Figure S1(b) and Figure S6. The crystallographic structures of CoC₂O₄ showed two C₂O₄²⁻ ligands to be coordinated to the central Co metal ion, and both $C_2O_4^{2-}$ ligands were seen to reside in approximately the same plane, with two water molecules arranged trans to each other, as illustrated in Figure S1(c) [17,58]. The crystal structure of the synthesized CoC₂O₄ powder and the prepared cathode was analyzed by X-ray diffraction (XRD) (Miniflex II, Rigaku) as shown in Figure S2. Following the adsorption of Li_2S_6 , the resultant precipitates were sufficiently dried in a vacuum chamber and subjected to surface analysis by X-ray photoelectron spectroscopy (XPS) at the KBSI Busan Center.

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Keywords: Lithium-sulfur batteries • Cobalt oxalates • Interfacial boundary · Electrocatalyst · Polysulfides redox

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A new finding of a polar CoC_2O_4 electrocatalyst: Cobalt oxalate (CoC_2O_4) effectively adsorbed lithium polysulfides (LiPS) and acted as a catenator to facilitate the formation of polythionate. Subsequently, CoC_2O_4 acts as an electrocatalyst to further improve the electrochemical redox reaction of LiPS on the interfacial boundary, resulting in improving long-term stability with a low decay rate of 0.059% per a cycle.