Manufacturing N,O-carboxymethyl chitosan-reduced graphene oxide under freeze-dying for performance improvement of Li-S battery

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Abstract

Lithium-sulfur (Li-S) batteries can provide far higher energy density than currently commercialized lithium ion batteries, but challenges remain before it they are used in practice. One of the challenges is the shuttle effect that originates from soluble intermediates, like lithium polysulfides. To address this issue, we report a novel laminar composite, N,O-carboxymethyl chitosan-reduced graphene oxide (CC-rGO), which is manufactured via the self-assembly of CC onto GO and subsequent reduction of GO under an extreme condition of 1 Pa and $-50^\circ$C. The synthesized laminar CC-rGO composite is mixed with acetylene black (AB) and coated on a commercial polypropylene (PP) membrane, resulting in a separator (CC-rGO/AB/PP) that can not only completely suppress the polysulfides penetration, but also can accelerate the lithium ion transportation, providing a Li-S battery with excellent cyclic stability and rate capability. As confirmed by theoretic simulations, this unique feature of CC-rGO is attributed to its strong repulsive interaction to polysulfide anions and its benefit for fast lithium ion transportation through the paths paved by the heteroatoms in CC.

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1. Introduction

The demands for rechargeable batteries with high energy density are increasing due to rapidly upgrading electrical devices [1–5]. Currently commercialized lithium ion batteries that provide an energy density of less than 200 Wh·kg\(^{-1}\) can not meet these demands [6–10]. Lithium-sulfur (Li-S) batteries have a theoretical energy density of 2600 Wh·kg\(^{-1}\), together with the obvious advantage of abundant and nontoxic sulfur, providing an ideal solution to the energy density limitation of lithium ion batteries, and thus have been attracting much attention [11–15]. However, challenges remain before Li-S batteries can be applied in practice [16–18]. The main issue is the soluble lithium polysulfides (LiPSs) that cause the shuttle effect due to their penetration through the separator [1, 19, 20].

To suppress the shuttle effect of LiPSs, many strategies have been proposed. The early method is to develop supports for sulfur, which can physically adsorb LiPSs, such as carbon tubes, carbon spheres, and reduced graphene oxide (rGO) [21–24], or chemically adsorb LiPSs, such as metal oxides, nitrides, and sulfides [25–28]. Recently, using modified catalysts which exhibit strong affinity with LiPSs [29–31], the acceleration of the conversion kinetics between \(S_2\) and LiS has been widely focused on [32–36]. To some extent, these efforts improve the performances of a Li-S battery, but the dissolution of LiPSs can not be completely avoided and the shuttle effect suppression is unsatisfying [20, 37–41].

Correspondingly, modifying a separator with coating materials that can block the penetration of LiPSs has been adopted to suppress the shuttle effect of LiPSs [42–46]. These efforts seem effective in blocking the penetration of LiPSs [47–49], but the introduction of other materials in the separator might also block the lithium ion transportation [50]. Therefore, it is necessary to search for the coated materials that can not only suppress LiPS penetration, but also can favor the lithium ion transportation for the Li-S battery performance improvement.

rGO has been widely used to improve the electronic conductivity of the sulfur cathode and the utilization of sulfur, and is also considered as the ideal coated material for modifying the separator of Li-S batteries [51–53], but the folded and compact multi-layer rGO sheets usually exhibit small surface area and are not beneficial for lithium ion transportation. It has been known that inserting some large molecules with heteroatoms into the interval between the two-dimension rGO sheets can unfold rGO [54, 55]. The introduced heteroatoms provide active sites not only for repelling polysulfides [56] but also for transferring lithium ions [50]. However, the syntheses of rGO from graphene oxide (GO) usually involve a hydrothermal reaction [45], calcining [57] and chemical reduction [58]. These methods are complicated and therefore simpler methods need to be developed for the application of rGO in practice.

The formation mechanism of rGO from GO reduction involves the removal of oxygen-containing groups in GO. This process can also be achieved by the reaction of oxygen-containing groups with –NH\(_2\) groups in other compounds, which is accompanied by removing \(H_2O\) molecules [59–61]. Under extreme conditions, for example, under 646.5 Pa and 0 °C, \(H_2O\) molecules can be easily removed due to its formation in a gaseous state [62, 63]. Based on this knowledge, we propose a novel formation technology of rGO from GO, and manufacture a laminar N,O-carboxymethyl chitosan-rGO composite (CC-rGO) to modify the separator of the Li-S battery. CC-rGO is manufactured via the self-assembly of CC onto GO and the subsequent reduction of GO under freeze-drying, which has been confirmed by physical characterization. The as-synthesized CC-rGO is coated on a commercial polypropylene (PP) membrane, resulting in a modified separator that can completely suppress the penetration of polysulfides and also accelerate the lithium ion transportation. Consequently, the Li-S battery using this modified separator exhibits a high initial specific capacity of 948.7 mAh·g\(^{-1}\) and maintains a specific capacity of 677.9 mAh·g\(^{-1}\) after 500 cycles at 0.5 C (0.75 mg·cm\(^{-2}\)). These excellent performances are attributed to the unique combination of CC and rGO. The introduction of CC unfolds the stacked graphene through the combination of –NH\(_2\) groups in CC with –COOH groups in GO, increasing the surface area of rGO and yielding a shield to block the penetration of polysulfides when the composite is coated on PP. The CC in CC-rGO is rich in electronegative N and O heteroatoms that are able to repel the electronegative polysulfide anions and favor lithium ion transportation [64–67]. Additionally, the intervals among rGO nanosheets formed by inserted CC molecules provide channels for lithium ion transportation. The formation of rGO does not need any other chemicals, while CC is low-cost, easily accessible and environmentally friendly [68]. Therefore, our composite provides an effective and eco solution to the shuttle effect of LiPSs and will help apply Li-S batteries in practice [69].

2. Experimental section

2.1. Materials and chemicals

The graphite powder and phosphorus pentoxide were purchased from ACROS. The concentrated sulfuric acid (95%–98%, AR), hydrochloric acid (36%–38%, AR) and potassium permanganate (99.5%, AR) were from Guangzhou Chemical Reagent Factor. The potassium persulfate (99.99%, AR) was from Aladdin. The hydrogen peroxide (30%, AR) was from Tianjin Zhiyuan Chemical Reagent Co., Ltd. The polyvinylidene fluoride (PVDF) and acetylene black (AB) were from Shenzhen Kejingzhida Technology Co., Ltd. The
CC (80%, AR) was from Shanghai Macklin Biochemical Co. Ltd. All chemicals were used without further purification.

2.2. Composite manufacturing and cell assemblies

The GO and CC aqueous solutions were prepared as described in our previous work [70]. The concentrations used in this work were 5.0 g·l−1 and 10.0 g·l−1 for GO and CC solutions, respectively. The CC-rGO composites were synthesized under freeze-drying in a lyophilizer (SCIENTZ-10N, China). Firstly, CC and GO solutions were mixed with the volume ratios of 8:1, 4:1, 1:1, 1:4, and 1:8 under stirring. Then, the mixed solutions were freeze-dried at 1 Pa and −50 °C until all the water was sublimated to obtain products labeled as CC-rGO81, CC-rGO41, CC-rGO11, CC-rGO14, and CC-rGO18, respectively.

About 60 wt% CC-rGO was mixed with 20 wt% AB and 20 wt% PVDF in N-methyl-2-pyrrolidone (NMP) under stirring in a blender (THINKYMIXER ARE-310, Japan) for 0.5 h to produce a uniform slurry. AB was used because it is an electronic conductor and is beneficial for the transformation of the deposited LiPSs on the separator. The resultant slurries were coated on one side of a commercial PP membrane and dried at 60 °C in vacuum oven for 12 h to obtain modified separators labeled as CC-rGO81/AB/PP, CC-rGO41/AB/PP, CC-rGO11/AB/PP, CC-rGO14/AB/PP, and CC-rGO18/AB/PP, respectively. The loaded mass of CC-rGO and AB were controlled to ~0.22 and ~0.073 mg·cm−2. For comparison, the AB/PP separator without CC-rGO was also prepared in the same process as CC-rGO/AB/PP separators.

About 10 wt% PVDF was dissolved in NMP to obtain a clear and transparent solution, then mixing with a content of 60 wt% S8 and 30 wt% AB under grinding for 0.5 h to prepare a homogeneous slurry that was coated on charcoal-coated Al foil and dried at 60 °C in vacuum oven for over 12 h, to prepare sulfur cathodes with sulfur and AB loading mass of ~0.75 and ~0.225 mg·cm−2, respectively. The obtained cathode was tailored to wafers that were assembled into CR2025 Li-S coin batteries together with a Li anode, an electrolyte and the above obtained separator in an Ar-filled glove box. The electrolyte was 1 M bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) and 2 wt% LiNO3 dissolved in a mixed solvent of dimethoxyethane (DME) and 1,3-dioxolane (DOL) (v/v, 1:1), and the ratio of electrolyte to sulfur was controlled at ~25 μl·mg−1.

2.3. Characterization, measurement and calculation

Electrochemical impedance spectroscopy (EIS, Zview electrochemical impedance software). The electrochemical impedance spectra (EIS) was obtained at 25 °C with the Fairbrother and Helmoltz–Smoluchowski equation with the Fairbrother and Mastin substitution [72].

A Land cell test system (Land CT2001A, China), a Solartron analytical-1470E CellTest system (AMETEK, America), and a Metrohm Autolab PGSTAT302N (AUT84217, Netherlands) were used to determine the electrochemical properties of the samples. The charge–discharge performances of the batteries were performed in a voltage range from 1.7 to 2.8 V (vs. Li/Li+) and the cyclic voltammetry (CV) curves were obtained at various scan rates between 1.7 V and 2.8 V. The electrochemical impedance spectra (EIS) was obtained at a frequency range from 0.01 to 100 000 Hz and fitted by using Zview electrochemical impedance software.

Theoretical calculations were carried out using a Vienna ab initio simulation package (VASP) based on density functional theory (DFT) [73, 74]. The projector augmented wave method was used to describe the influence of the core electrons, and the Perdew–Burke–Ernzerhof exchange correlation functional with the DFT-D3 correction was introduced to the generalized gradient approximation [75, 76]. An amimated rGO model was chosen to simplify CC-rGO, with only one formamide group in a 4 × 4 supercell. The thickness of the vacuum layer was set to 30 Å for all the systems. In each calculation, a 1 × 1 centered K-point mesh with a resolved value of 0.06 Å−1 was adopted to sample the Brillouin zone, and the cut-off energy for the plane wave expansion was set to 500 eV. A climbing-image nudged elastic band (CI-NEB) method was used to obtain the path with optimal energy for the lithium ion transportation [77]. In this process, three and six points were interpolated between the start and end points of the lithium ion transportation path on the surface of rGO and CC-rGO or across CC-rGO, and a fast inertial relaxation engine algorithm was used to optimize these points to obtain the energy profiles.
The peak value of the energy profiles was defined as the energy barrier for a lithium ion to overcome. The interaction of CC-rGO with Li$_2$S$_x$ was calculated based on the $4\sqrt{3} \times 4\sqrt{3}$ supercells, while that of Li$_2$S$_x$ ($x = 1, 2, 4, 6,$ and 6), and the transportation of a lithium ion on CC-rGO was obtained with the $4 \times 4$ supercells. All the relaxation calculations were finished until the maximum force was less than 0.02 Å$^{-1}$ and the total energy was converged within $2 \times 10^{-7}$ eV, while the energy convergence standard of CI-NEB calculations was $1 \times 10^{-7}$ eV. In this calculation process, the interaction energy ($E_a$) is defined as the energy difference between the system ($E_{CC-rGO+Li2Sx} (x = 1, 2, 4, 6, 8)$) and the summation of pure Li$_2$S$_x$ ($x = 1, 2, 4, 6, 8$) ($E_{Li2Sx} (x = 1, 2, 4, 6, 8)$) and the substrate ($E_{CC-rGO}$) and calculated by the equation (1):

$$E_a = E_{CC-rGO-Li2Sx} - E_{Li2Sx} - E_{CC-rGO}.$$ (1)

3. Results and discussion

3.1. Physical and chemical characteristics of CC-rGO composite

The syntheses process of laminar CC-rGO composite under freeze-drying is illustrated in figure 1(a). When the GO and CC aqueous solution were mixed, the disordered GO sheets were self-assembled with CC molecules due to the electrostatic interaction between −COOH groups in GO and −NH$_2$ groups in CC. Moreover, the acidic −COOH and alkaline −NH$_2$ groups can be partly polymerized to form amide bonds and free H$_2$O molecules. This polycondensation is too slow to proceed under room temperature, which can be accelerated via the removal of H$_2$O molecules in gaseous state under extreme conditions. Under our freeze-drying conditions (1 Pa, −50 °C), GO can be reduced to rGO due to the quick removal of H$_2$O molecules in a gaseous state and thus CC-rGO composite is successfully manufactured. The stacked GO was unfolded due to the entering of CC into the interval of the stacked GO, resulting in thin CC-rGO composite. The formation of rGO from GO due to the reaction of −COOH groups in GO with −NH$_2$ groups in CC, which forms amide bonds that is accompanied with water removal under freeze-drying conditions (1 Pa, −50 °C).

The Raman spectra of GO and CC-rGO in figure 3(b) shows the two peaks located at 1350 cm$^{-1}$ and 1581 cm$^{-1}$, which are typical D and G bands of carbon, respectively [81]. The peak intensity ratio of ($I_D/I_G$) reflects the relative content of active sites in materials [82]. The peak intensity ratio of CC-rGO$_{11}$ (1.0) is much higher than GO (0.81), suggesting that more active sites have been produced in GO after introducing CC. These active sites correspond to the N and O heteroatoms, which are helpful for repelling polysulfide anions and accelerating the lithium ion transportation [83]. Figure 3(c) shows the FTIR spectra of CC, GO, and CC-rGO$_{11}$. The absorption peak at 1602 cm$^{-1}$ corresponding to N−H stretching can be detected in both the CC-rGO$_{11}$ and CC, confirming that CC has been successfully assembled onto rGO. The peak at 1733 cm$^{-1}$ in GO can be attributed to the C=O stretching from −COOH group, while that in CC-rGO$_{11}$ can be ascribed to the C=O stretching from amide bonds formed from the reaction of the −COOH groups in GO with −NH$_2$ groups in CC. In addition, the C−H stretching peak at 2916 cm$^{-1}$ and N−H stretching peak at 3413 cm$^{-1}$ in CC can be still detected in CC-rGO$_{11}$. These results confirm that CC has been successfully assembled onto rGO via the formation of amide bonds.

XPS was used to characterize the composition of the CC-rGO$_{11}$. The obtained results are presented in figures 3(d)−(f) and 4. Three obvious peaks of C1s at 284.9, 286.4, 287.8, and 290.7 eV can be observed, corresponding to C=C, N=C, C=O/N−C=O, and O=C, respectively (figure 3(d)). These species are from rGO, amido bonds, and the small amount of −COOH in rGO [52]. Meanwhile, two strong peaks of N1s at 399.3 and 401.3 eV, corresponding to N=C and N−H, respectively, can be identified (figure 3(e)), which are attributed to amide bonds in CC-rGO$_{11}$ [84]. Besides, the O1s spectrum was fitted with three peaks at 531.1, 532.6, and 532.7 eV, which can be ascribed to C=O from N=C=O, C=O from −COOH, respectively [85]. These results demonstrate that rGO and CC have been combined together via the formation of amide bonds from the interaction of −COOH groups in GO with −NH$_2$ groups in CC, yielding stable laminar CC-rGO with abundant N-containing and O-containing active sites for suppressing polysulfide penetration and accelerating lithium ion transportation.

Coating CC-rGO with AB on a PP membrane results in a CC-rGO/AB/PP separator. The performances of the resultant separators are compared with those of the PP and AB/PP.
The cross-section thickness of the CC-rGO$_{11}$/AB/PP separator is about 12 µm (figure 5). The PP separator has a porous structure and presents a large BET surface area (figure 6). These pores are blocked and the surface area of PP is reduced when AB or CC-rGO$_{11}$ is coated on PP. Since AB has a larger surface area than CC-rGO$_{11}$ (figure 7), AB/PP presents a larger BET surface area than CC-rGO$_{11}$/AB/PP (figure 6). Although the CC-rGO$_{11}$/AB/PP separator has a smaller surface area, it exhibits a much better wettability than PP and AB/PP separators (figure 8). Obviously, CC-rGO$_{11}$/AB/PP is more compatible to the electrolyte, which should be related to its surface with abundant N-containing and O-containing
Figure 2. FEISEM image of (a) GO and (b) CC-rGO surface under low-magnification.

Figure 3. (a) XRD patterns and (b) Raman spectra of GO and CC-rGO, and (c) IR spectra of CC, GO sheet and CC-rGO. (d)-(f) C1s, N1s and O1s XPS spectra of CC-rGO.

Figure 4. XPS spectrum of CC-rGO.
Figure 5. Cross-section FEISEM image of the CC-rGO₁₁/AB/PP separator.

Figure 6. Nitrogen adsorption and desorption isotherms and pore size distribution curve of (a), (b) PP, (c), (d) AB/PP, and (e), (f) CC-rGO₁₁/AB/PP separators.
Figure 7. Nitrogen adsorption and desorption isotherms, and pore size distribution curves of (a), (b) AB and (c), (d) CC-rGO$_{11}$.

Figure 8. Contact angles of (a)–(c) PP, (d)–(f) AB/PP, and (g)–(i) CC-rGO$_{11}$/AB/PP separators at different times after dropping electrolyte.
which manifests the significance for the application of CC-rGO and 10 mg mass is increased to 3.41 mg coating CC-rGO to some extent by coating AB and significantly improved by isons suggest that the PP separator is poor in the suppression efficiency of 89.6% and 99.3%, respectively. These comparisons using PP and AB/PP separators deliver an initial capacity of only 142.4 and 378.6 mAh·g⁻¹ and specific capacities of 99.9% after 500 cycles. Comparatively, the Li-S battery using the CC-rGO composite manufactured with a volume ratio 1:1 of CC to GO solutions was considered for further investigations.

3.2. Improved performances of CC-rGO modified separator

Figure 10(a) compares the cyclic stability of Li-S batteries based on a sulfur loading mass of 0.75 mg·cm⁻² and using different separators at 0.5 C, with their selected charge/discharge curves presented in figure 11. As shown in figures 11(c)–(e), the voltage plateaus at 2.3 V and 2.1 V in the discharge curves are ascribed to the transformation of S₈ into LiPSs (Li₂S₈, 4 ≤ n ≤ 8) and then to Li₂S₂/Li₂S, respectively. The Li-S battery using the CC-rGO₁₁/AB/PP separator exhibits an initial specific capacity of 948.7 mAh·g⁻¹, retaining a capacity of 677.9 mAh·g⁻¹ with an average coulombic efficiency of 99.9% after 500 cycles. Comparatively, the Li-S batteries using PP and AB/PP separators deliver an initial capacity of only 749.2 and 799.3 mAh·g⁻¹, and retain a capacity of only 142.4 and 378.6 mAh·g⁻¹ with an average coulombic efficiency of 89.6% and 99.3%, respectively. These comparisons suggest that the PP separator is poor in the suppression of the shuttle effect of LiPSs, which can be improved to some extent by coating AB and significantly improved by coating CC-rGO₁₁/AB. Particularly, when the sulfur loading mass is increased to 3.41 mg·cm⁻² (figures 12(a) and (b)) and 10 mg·cm⁻² (figures 12(c) and (d)), the Li-S battery using CC-rGO₁₁/AB/PP separator still run well (figure 12), which manifests the significance for the application of the CC-rGO₁₁/AB/PP separator in practice.

The Li-S battery using a CC-rGO₁₁/AB/PP separator also exhibits excellent rate capacity (figures 10(b) and 11(b), (d), (f)), delivering stable specific capacities of 1158.5, 921.1, 804.9, 708.6, and 648.1 mAh·g⁻¹ at 0.2, 0.5, 1, 2, and 3 C, respectively. On the contrary, both the Li-S batteries using PP and AB/PP separators present a sharp reduction in specific capacity with the increase of current rates. When the current rate is increased to 3 C, the specific capacity of the Li-S batteries using PP and AB/PP separators are only 190.9 and 158.4 mAh·g⁻¹, respectively. Especially, the discharge voltage plateaus disappear for the Li-S batteries using PP and AB/PP separators at the current rates higher than 1 C, but remain for that using a CC-rGO₁₁/AB/PP separator (figure 11). Obviously, the separator modified CC-rGO₁₁ significantly improved not only cycling stability but also the rate capability of Li-S battery, indicating that the CC-rGO plays an important role for the utilization of sulfur and the suppression of the shuttle effect of LiPSs [87, 88]. Compared with the polymer-coated separators reported in literatures (table 1), our CC-rGO₁₁/AB/PP separator provides an Li-S battery with comparable electrochemical performances, featuring a facile syntheses process without using toxic organic solvents.

The improved cycling stability and rate capability of Li-S battery CC-rGO₁₁/AB/PP separator using can be confirmed by the CV curves in figures 10(c)–(e) and 13. It can be found from these CV curves that there appear two couples of oxidation and reduction peaks. The reduction peaks located at around 2.30 V and 2.02 V are ascribed to the transformation of S₈ into LiPSs (Li₂S₈, 4 ≤ n ≤ 8), and then into Li₂S₂/Li₂S, corresponding to two discharge voltage plateaus in figure 11, respectively [98]. Compared with the Li-S batteries using PP and AB/PP separators, the Li-S battery using a CC-rGO₁₁/AB/PP separator exhibits the largest peak currents and less current change during initial five cycles, indicating the excellent cyclic stability and rate capability of the battery using CC-rGO₁₁/AB/PP separator. On the other hand, the oxidation peak current for the transformation of LiPSs (Li₂S₈, 4 ≤ n ≤ 8) is significantly higher than that for the transformation of Li₂S₂/Li₂S, suggesting that more soluble LiPSs (Li₂S₈, 4 ≤ n ≤ 8) has been
Figure 10. (a) Cycling stability of Li-S batteries using PP, AB/PP, and CC-rGO/AB/PP separators at 0.5 C (0.75 mg cm\(^{-2}\) areal sulfur loading). (b) Rate capacity of Li-S batteries using PP, AB/PP, and CC-rGO/AB/PP separators. CV curves of the batteries using (c) PP, (d) AB/PP, and (e) CC-rGO/AB/PP separators at 0.05 mV s\(^{-1}\).

transformed into \(S_8\) and that polysulfide anions are blocked by the separator, rather than migrating to Li anode.

CV is often used to understand electrochemical processes of sulfur cathode, which involves the lithium ion diffusion in solution and follows the Randles–Sevcik equation that describes the current-scan rate relationship for a freely-diffusing species in solution [19]. Figure 13 presents the CV curves of Li-S batteries using different separators at various scan rates (figures 13(a), (c) and (e)) and the corresponding relations of peak currents with the square root of scan rates (figures 13(b), (d) and (f)). The peak currents, A1/C2 for the transformations between \(S_8\) and LiPSs and A2/C1 for those between LiPSs and \(Li_2S_2/Li_2S\), were extracted by subtracting the background current, which follows the Randles–Sevcik equation. The larger absolute slope in the plot of the peak current (\(I_p\)) to the square root of the scan rate (\(v^{1/2}\)) represents fast lithium ion diffusion speed [99]. As shown in figures 13(b), (d) and (f), the cathode using a
Figure 11. Charge/discharge curves of the Li-S batteries using (a), (b) PP, (c), (d) AB/PP, and (e), (f) CC-rGO$_{11}$/AB/PP separators at 0.5 C for selected cycles (a), (c), (e) and at various rates (b), (d), (f).

Figure 12. Cycling stability of Li-S batteries with a high areal sulfur loading of (a), (b) 3.41 mg·cm$^{-2}$ and (c), (d) 10 mg·cm$^{-2}$ using CC-rGO$_{11}$/AB/PP separators at 0.1 C.
CC-rGO11/AB/PP separator exhibits much faster lithium ion diffusion speed than these using PP and AB/PP separators, confirming that the CC-rGO11/AB/PP separator is beneficial for lithium ion transportation for an Li-S battery. This benefit can be ascribed to the improved Li$^{+}$ transference number ($t_{i_{Li}^{+}}$) of the CC-rGO11/AB/PP separator. The $t_{i_{Li}^{+}}$ of the CC-rGO11/AB/PP separator is 0.51, which is much higher than that of PP (0.26) and AB/PP (0.36) separators (figure 14 and table 2). Consequently, the CC-rGO11/AB/PP separator shows much higher ionic conductivity (0.33 mS cm$^{-1}$) than the PP (0.18 mS cm$^{-1}$) and AB/PP (0.26 mS cm$^{-1}$) separators (figure 15 and table 3). In addition, the Li-S battery using CC-rGO11/AB/PP separator presents a A2 peak current obviously higher than its A1 peak current, illustrating the remarkable oxidation conversion from Li$_2$S$_2$ into long-chain Li$_3$S$_2$/Li$_2$S$_8$ and the effective suppression of LiPSs penetration.

To confirm the contribution of CC-rGO to the suppression of polysulfide anions and the acceleration of lithium ion transportation, more physical and electrochemical characterizations combining with theoretical calculations were performed. The surface zeta potentials of the CC-rGO11 and CC-rGO11/AB/PP separators were measured and the obtained results are presented in figures 16 and 17. The CC-rGO11 carries negative charges, which has not been changed after it is coated on PP (figure 17) in the solutions with pH less 3. Compared with the AB/PP separator (IEP$_{AB/PP}$ = 3.53 mV), the CC-rGO11/AB/PP separator exhibits stronger electronegativity (IEP$_{CC-rGO11/AB/PP}$ = 2.95 mV), suggesting that the CC-rGO11/AB/PP separator tends to combine species with a positive charge and to repel species with a negative charge, which are responsible for the suppression of polysulfide anions penetration and the acceleration of lithium ion transportation.

To further confirm the suppression of polysulfide anions by CC-rGO11/AB/PP separator, the Li anodes and separators taken from the cycled Li-S batteries using different separators were performed with FEISEM, FEITEM and XPS characterizations. As revealed in figure 18, the Li anodes matched with PP (figures 18(a) and (b)) and AB/PP (figures 18(c) and (d)) separators are completely covered with flocculent substance, while the Li anode matched with CC-rGO11/AB/PP separator still maintains a clear and smooth surface (figures 18(e) and (f)), suggesting that deposits are formed on the anodes when the batteries with PP and AB/PP separators, which can be avoided by applying a CC-rGO11/AB/PP separator.

Correspondingly, the surface of fresh PP (figure 19(a) and AB/PP (figure 19(d)) separators remain clear after cycling (figures 19(b), (c) and (e), (f)), while the surface of CC-rGO11/AB/PP (figure 19(g)) shows a large quantity of sediments (figures 19(h) and (i)), suggesting that the soluble LiPSs blocked by the CC-rGO can be transformed to the insoluble species. FEISEM elemental mapping images of the CC-rGO11/AB/PP separator surface after cycling (figure 20) shows the existence of N (discharge 8%, charge 12%), O (discharge 47%, charge 51%), and S (discharge 44%, charge 37%), confirming the contribution of CC-rGO.

The HR FEITEM image of CC-rGO11 at the fully discharged state after 25 cycles at 0.5 C presents marked lattice fringe spacing of about 0.32 nm (figures 21(a)–(c)), which corresponds to the (111) facet of standard cubic Li$_2$S (PDF card no. 77-2145). However, this lattice fringe spacing cannot be

| Separators with the polymer coating on PP | Organic solvent used in materials synthesizing | Areal sulfur loading (mg·cm$^{-2}$) | Sulfur content (%) | Initial specific capacity (mAH·g$^{-1}$) | Cycle rate (C) | Cycle number | Reserved specific capacity (mAH·g$^{-1}$) | Coulombic efficiency of the final cycle (%) | References |
|----------------------------------------|-----------------------------------------------|----------------------------------|-----------------|---------------------------------|---------------|-------------|---------------------------------|----------------------------------------|-----------|
| P0.4NG-1000/PP                         | Water                                         | 2.7                              | 75              | 0.5                            | ≈460          | 300         | 591.2                          | None                                  | [89]      |
| PEDOT: PSS/PP                          | Water                                         | 3.9                              | 66              | 0.5                            | 1096          | 500         | 911.0                          | 97                                    | [90]      |
| GNP/s/PP                               | Poly(ethylene oxide)                          | 1.8                              | 63.8            | 0.3                            | ≈580          | 160         | 620                             | ≈93                                   | [91]      |
| PIN/PP                                 | Tetrafluoroterephthalonitrile,                | 4.0                              | 70              | 0.2                            | 988           | 200         | 780                             | ≈99                                   | [92]      |
|                                        | tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane |                    |                 |                                |               |             |                                 |                                        |           |
| AB-SO$_3$$^-$/PP                       | (CH$_2$CO)$_2$O                               | 3                                | 70              | 0.1                            | 1262          | 100         | 955                             | None                                  | [93]      |
| PEO/SL/PP                              | Water                                         | 1.12                             | 60              | 0.1                            | 740           | 100         | 450                             | None                                  | [94]      |
| IPA/Ac/PP                              | Isopropyl alcohol                             | 3.17                             | 49              | 0.2                            | 1656          | 100         | 830                             | None                                  | [95]      |
| PP/FC/PP                               | Methanol                                      | 1.5                              | 63              | 1.0                            | 724           | 400         | 638                             | ≈99                                   | [96]      |
| APP/CB@PP@LAGP                         | Ethanol, PVDF, DMSO                           | 1.0–1.2                         | 56              | 0.5                            | 1153.8        | 100         | 945.2                          | ≈99                                   | [97]      |
| CC-rGO$_{11}$/AB/PP                    | Water                                         | 0.75                             | 60              | 0.5                            | 948.7         | 500         | 677.9                          | ≈99.9                                 | This work |

Table 1. Comparison in electrochemical performances of Li-S cell using CC-rGO$_{11}$/AB/PP separator with those using other polymer-coated PP separators reported in literatures.
Figure 13. CV curves of Li-S batteries using PP, AB/PP, and CC-rGO$_{11}$/AB/PP separators at various scan rates from 0.1–0.6 mV·s$^{-1}$ and the corresponding relations of peak currents with square root scan rates.
identified in the CC-rGO_{11} at the charged state (figure 21(d)), confirming that the polysulfides blocked by CC-rGO_{11} can be transformed into Li_{2}S reversibly, which ensures the high capacity retention of the sulfur cathode.

The contribution of CC-rGO_{11} coating can be further verified by XPS spectra and Raman spectra of the CC-rGO_{11}/AB/PP separator after 25 cycles at 0.5 C. Figure 22 presents the XPS results. The relative magnitude and shape of the C1s, N1s and O1s peaks for the cycled CC-rGO_{11}/AB/PP separator are different from those for the fresh CC-rGO_{11}, confirming that the chemical interaction existing between CC-rGO_{11} composite and LiPSs happens after cycling. On the other hand, the peak locations of C1s (C=C, N=C), N1s and O1s keep unchanged after cycling, except for the C1s (–C=O/N–C=O, O–C) that are related to deposition of LiPSs, confirming that the structure of CC-rGO_{11} keeps stable. The obtained Raman results are presented in figure 23(a). The $I_d/I_G$ value (0.90) of CC-rGO_{11} at the fully discharged state

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### Table 2. Li$^+$ transference numbers in PP, AB/PP, and CC-rGO_{11}/AB/PP separators.

| Separator          | $I_{initial}$ (mA) | $I_{steady}$ (mA) | $R_{initial}$ (Ω) | $R_{steady}$ (Ω) | $t_{Li^+}$ |
|-------------------|--------------------|-------------------|-------------------|------------------|------------|
| PP                | 0.0479             | 0.0196            | 103.03            | 96.58            | 0.256      |
| AB/PP             | 0.0512             | 0.0255            | 77.65             | 68.29            | 0.362      |
| CC-rGO_{11}/AB/PP | 0.0826             | 0.0756            | 102.63            | 96.21            | 0.511      |

The Li$^+$ transference number $t_{Li^+}$ is obtained by Vincent–Bruce equation [100]:

$$t_{Li^+} = \frac{I_{steady} \times (V - I_{initial} \times R_{initial})}{I_{initial} \times (V - I_{steady} \times R_{steady})}$$

where, $I_{initial}$ and $I_{steady}$ represent initial and steady current recorded during potentiostatic polarization, $R_{initial}$ and $R_{steady}$ represent the cell resistances before and after polarization, respectively. The cell resistance is the sum of $R_{ct}$, $R_f$ and $R_b$ representing charge transfer, film and Ohmic resistances, respectively.
Figure 15. Electrochemical impedance spectra of SS/SS batteries using PP, AB/PP, and CC-rGO₁/AB/PP separators.

Table 3. Ionic conductivity calculated from the Ohmic resistance ($R_b$) obtained by electrochemical impedance spectroscopy.

| Separator             | $d$ (µm) | $R_b$ (Ω) | $\delta$ (mS cm$^{-1}$) |
|-----------------------|----------|-----------|-------------------------|
| PP                    | 22       | 4.7       | 0.18                    |
| AB/PP                 | 38       | 5.8       | 0.26                    |
| CC-rGO₁/AB/PP         | 40       | 4.8       | 0.33                    |

Figure 16. Zeta potential of CC-rGO₁.

...is smaller than that (0.99) at the fully charged state, suggesting that partial active sites of CC-rGO₁ have been occupied by LiPSs during discharging and can be recovered during charging. Similarly, the S2p XPS spectra in figure 23(b) shows that the CC-rGO₁/AB/PP separator at the fully discharged state presents much stronger peaks than that at the fully charged state, especially the Li-S peak, signifying the reversible transformation between LiPSs and Li$_2$S.

The interactions between CC-rGO and LiPSs can be further confirmed by DFT calculation. The calculated interaction energy between Li$_2$S$_x$ ($x = 1, 2, 4, 6, 8$) and CC-rGO ($E_x = E_{Li_2S_x-CC-rGO} - E_{CC-rGO} - E_{Li_2S_x}$) are $-1.99$, $-0.88$, $-0.8$, $-1.04$, and $-1.26$ eV, respectively (figures 23(c)–(g)), which is more negative than that between Li$_2$S$_x$ and rGO ($-0.63$, $-0.71$, $-0.76$, $-0.95$, and $-1.18$ eV) (figure 24), suggesting that CC-rGO exhibits the ability to accelerate Li$^+$ transportation, which should be ascribed to the affinity of CC-rGO for Li$^+$ ions. As shown in figure 25, the colors of the Li$_2$S$_6$-free electrolyte in the batteries using PP (figures 25(a)–(c)) and AB/PP (figures 25(d)–(f)) separators become yellower and yellower as the time elapses, suggesting that the Li$_2$S$_6$ can penetrate through the separator from...
Figure 17. Zeta potentials of AB/PP and CC-rGO11/AB/PP separators. The isoelectric point (IEP) of the separator is the pH values of the solution for the separator surface with zero charge.

Figure 18. FEISEM images of cycled Li anodes taken from Li-S batteries using (a), (b) PP, (c), (d) AB/PP, and (e), (f) CC-rGO11/AB/PP separators at fully discharged and charged states after 25 cycles at 0.5 C.
one side to the other side of the battery. In contrast, the battery using CC-rGO₁₁/AB/PP (figures 25(g)–(i)) separator keeps its electrolyte color unchanged, demonstrating that CC-rGO₁₁/AB/PP separator can completely suppress the polysulfide penetration.

To understand the mechanism for the CC-rGO/AB/PP separator to accelerate lithium ion transportation, the energy profiles for lithium ion transporting on and across the CC-rGO were calculated with VASP. The obtained results are presented in figures 26 and 27, where simplified models for calculation are included. It can be found that the energy barrier for lithium ion to cross CC-rGO (7.04 eV) is much higher than those for rGO (0.30 eV) and CC-rGO (0.29 eV) surface, suggesting that it is easier for lithium ion to transport through the surface of the laminar CC-rGO, which should be ascribed to the active sites of the heteratoms on the CC-rGO surface [101]. The CC not only functions as a binder to connect rGO sheets in two dimensions, forming a shield to block the polysulfide penetration, but also provides abundant active sites with its negative heteratoms’ lone pair electrons for repelling negative polysulfides and accelerating lithium ion transportation, leading to the excellent cycling stability and rate capability of a Li-S battery.

It should be mentioned that the application of our CC-rGO₁₁/AB/PP separator is accomplished with a high sulfur loading and a thin layer of polysulfides barrier (12 μm). The former is higher and the latter is thinner than the commercial viability of polysulfide-retaining barriers, in which sulfur
Figure 21. HR FEITEM images of CC-rGO\(_{11}\) taken from CC-rGO\(_{11}\)/AB/PP separator of the Li-S batteries at fully (a) discharged and (d) charged states after 25 cycles at 0.5 C. The lattice of (b) Li\(_2\)S at fully discharged, (c) Fourier transform image of Li\(_2\)S (111).

Figure 22. The C1s, N1s and O1s XPS spectra of CC-rGO\(_{11}\)/AB/PP separator taken from Li-S cell at (a)–(c) fully discharged and (d)–(f) charged states after 25 cycles at 0.5 C.
Figure 23. (a) Raman spectra of CC-rGO, and (b) S2p XPS spectra of CC-rGO/AB/PP separator taken from Li-S cell at fully discharged and charged states after 25 cycles at 0.5 C. (c)–(g) The front view of simulated Li$_2$S$_x$ ($x = 1, 2, 4, 6,$ and $8$) interaction on the CC-rGO as well as corresponding interaction energies.

Figure 24. The front view of simulated Li$_2$S$_x$ ($x = 1, 2, 4, 6,$ and $8$) interaction on the rGO as well as corresponding interaction energies.
Figure 25. Photos of separator-isolated batteries with Li$_2$S$_6$-containing and free electrolyte in two sides, respectively, for (a)–(c) PP, (d)–(f) AB/PP, and (g)–(i) CC-rGO$_{11}$/AB/PP separators.

Figure 26. (a) Energy profiles of Li$^+$ transportation on the surface of rGO and the CC-rGO and (b), (c) the models for the energy calculation.

Figure 27. (a) Energy profile of Li$^+$ transportation across CC-rGO and (b) the model for the energy calculation.
loading and polysulfides-barrier thickness are recommended to be 2–3 mg·cm⁻² and 40–60 μm, respectively [69].

4. Conclusions

In summary, we have successfully manufactured a laminar polymer-rGO composite that can efficiently suppress the shuttle effect of LiPSs resulting in a performance improvement of a Li-S battery. CC is self-assembled on GO, which is accompanied by the formation of rGO from GO reduction under an extreme condition of 1 Pa and −50 °C, resulting in the laminar CC-rGO composite. When a conventional PP membrane is coated with CC-rGO and used as a separator, the Li-S battery provides excellent cycling stability and rate capability. This feature is attributed to different contributions from CC and rGO. Firstly, the CC functions as a binder to connect rGO nanosheets in two dimensions, forming a shield to block the polysulfide penetration. Secondly, the CC provides abundant active sites by its heteroatoms with lone pair electrons for repelling polysulfides and accelerating lithium ion transportation. The formation process of rGO is environmentally friendly and therefore the manufactured laminar CC-rGO composite is promising to be applied at large scale for high-performance Li-S batteries.

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