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2D hybrid interlayer of electrochemically exfoliated graphene and Co(OH)₂ nanosheet as a bi-functionalized polysulfide barrier for high-performance lithium–sulfur batteries

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Abstract

Lithium sulfur (Li–S) batteries have attracted much attention because of high energy density, low cost and environmental friendliness. However, developing high-energy-density Li–S batteries is seriously hindered by their short cycling life, originating from the shuttle effect of soluble polysulfides. Herein we for the first time develop a versatile and facile strategy of assembling thin and lightweight bi-functionalized hybrid interlayer constructed by two-dimensional (2D) electrochemically exfoliated graphene and Co(OH)₂ nanosheets (EG/Co(OH)₂), positioned between the cathode and commercial polypropylene (PP) separator, for high-performance Li–S batteries with remarkably enhanced capacity, rate capability and long-term cyclability. The resulting 2D EG/Co(OH)₂ hybrid interlayer features layer-stacked structure, thin thickness of 5.5 μm, high electrical conductivity of 900 S cm⁻¹, low mass loading of 0.20 mg cm⁻², and exhibits bi-functionalized roles of polysulfide physical barrier from EG nanosheets and high chemical adsorption for polysulfides by Co(OH)₂ nanosheets. As a result, the assembled Li–S batteries based on graphene-S cathode, using EG/Co(OH)₂ interlayer, showed greatly enhanced discharge capacity of 918 mAh g⁻¹ at 0.5 C, in comparison with the cells (831 mAh g⁻¹) free of EG/Co(OH)₂ interlayer. Furthermore, our Li–S batteries with EG/Co(OH)₂ interlayer displayed outstanding rate capacity of 677 mAh g⁻¹ at 5 C, and exceptional cycling stability with a high capacity of 565 mAh g⁻¹ after 300 cycles at 0.5 C, corresponding to ultralow capacity fade rate of only 0.130% per cycle. Therefore, our strategy of constructing a hybrid interlayer consisting of 2D different nanosheets will offer numerous opportunities for designing long-life and high-energy-density Li–S batteries.

1. Introduction

With the ever-increasing demand of small electronics, electric vehicles and large-scale grid applications, it is crucial to develop high-energy-density batteries with long cycling stability [1, 2]. Among them, lithium–sulfur (Li–S) batteries have drawn considerable attention owing to their high theoretical energy density of 2600 Wh kg⁻¹, and inexpensive elemental sulfur [3–5]. So far, great progresses have been achieved, however, several hurdles must be overcome before the practical commercialization of Li–S batteries. First, the electrical insulation of element sulfur and the discharge products of Li₂S/Li₂S₃ lead to low utilization of active material [6]. Second, large volumetric expansion during the cycling will cause the cracking and fracturing of the electrode structure [7]. Third, the shuttle effect related to high solubility of the polysulfides and their migration to Li anode through separator during charge/discharge process eventually induce low coulombic efficiency, poor cycling stability, and unexpected self-discharge [8, 9]. Fourth, the formation of anodic lithium dendrites could cause safety concern [10].
To address these issues, great efforts have been made for the improvement of Li–S batteries through the rational design of cathode materials that can substantially increase the sulfur utilization and physically/chemically trap the polysulfides within the sulfur supports (e.g., porous carbon [11] conducting polymers [12], metal oxides/nitriles/sulfides [13–15], and metal or covalent organic frameworks [16, 17]), development of new-type electrolytes, (e.g., solid state electrolytes [18, 19], lithium salt additives [20], ionic liquid-based electrolytes [21]), and protection of lithium anode [22]. However, these strategies are usually expensive and complex, and the rapid capacity decay induced by polysulfide shuttle effect of Li–S batteries has not been fully solved.

Recently, modifying separator with an interlayer between sulfur cathode and separator has been proven to significantly enhance the cyclability of Li–S batteries. For instance, non-polar conducting nanocarbon interlayers, such as carbon black [23], carbon nanofiber [24], porous carbon [25], carbon nanotubes [26], and reduced graphene oxide (rGO) [27] have been reported as a physical barrier to block polysulfides during cycling and as an extra conductive current collector to further improve the sulfur utilization. However, the weak interaction between non-polar carbons and polar polysulfides cannot fully suppress the diffusion of polysulfides in the organic electrolyte to lithium anode. The polar interlayers composed of such as oxides [28, 29], sulfides [30, 31], nitriles [32], polymer [33], hydroxide [34, 35], and heteroatom-doped carbons [36, 37], can greatly strengthen their interfacial interactions between polysulfides and interlayer, resulting in the enhancement of cyclabilities. However, high mass density loading of the polar materials would decrease energy densities of Li–S batteries. Recently, two-dimensional (2D) nanosheets (e.g. graphene [38], MXene [39], MoS2 [40], boron nitride [41]) with ultra-thinness, large surface area, mechanical flexibility, tunable chemistry, have been developed as one novel class of the interlayers to unprecedentedly boost the cyclability of Li–S batteries [42, 43]. To this end, we consider that the rational construction of 2D hybrid interlayer that combines 2D polar nanosheets with electrically conducting graphene could become an efficient protocol of polysulfides entrapment for improving Li–S batteries.

Here we for the first time demonstrate the rational construction of thin and lightweight bi-functionalized hybrid interlayer composed of 2D electrochemically exfoliated graphene (EG) and Co(OH)₂ nanosheets (denoted as EG/Co(OH)₂), coated on one side of commercial PP separator, for high-performance Li–S batteries with remarkably enhanced capacity, rate capability and cyclability. The resulting 2D EG/Co(OH)₂ interlayer showed layer-stacked structure, thin thickness of 5.5 μm, excellent electrical conductivity of 900 S cm⁻¹, low mass loading of 0.20 mg cm⁻². Importantly, the EG sheets in hybrid interlayer can serve as a polysulfide physical barrier and electrical conductive network to increase the reuse of polysulfide trapped while the polar Co(OH)₂ nanosheets can fulfill the role of chemical adsorption of polysulfides. As a consequence, high-capacity Li–S batteries with 918 mAh g⁻¹ at 0.5 C, accompanied with exceptional rate capability (677 mAh g⁻¹ at 5 C) and stable cycle capacity (565 mAh g⁻¹ after 300 cycles at 0.5 C), are achieved.

2. Experimental section

2.1. Synthesis of Co(OH)₂ nanosheets

The Co(OH)₂ nanosheets were prepared by self-assembled lamellar soft template method [44]. Typically, cobalt acetate tetrahydrate (10 mmol) was dissolved in deionized water (50 ml) under magnetic stirring. After stirring for 15 min, sodium carboxymethylcellulose (CMC) solution (100 ml, 1 mg ml⁻¹) was added, and the mixture was continuously stirred for 30 min. Then, 1 ml diluted ammonia solution (ammonia/water = 1:9) was added into the above solution. Subsequently, the solution was transferred to a 250 ml autoclave, sealed and heated at 80 °C for 12 h. Finally, the precipitate was collected by centrifuging, washed several times with distilled water and ethanol, and dried in air.

2.2. Preparation of EG/Co(OH)₂ hybrid interlayer

EG nanosheets were prepared by electrochemical exfoliation of graphite in aqueous solution according to the reported procedure previously [45]. To prepare the interlayer, EG and Co(OH)₂ nanosheets with a mass ratio of 3:1 were uniformly dispersed in the absolute ethyl alcohol by ultrasonication for 2 h. Then, the mixture was vacuum-filtered onto one side of a PP membrane. The resulting EG and Co(OH)₂ hybrid interlayer coated on PP separator was dried at 60 °C for 12 h, and cut into the standard circular disks for test.

2.3. Materials characterizations

Materials characterization was conducted by scanning electron microscopy (SEM) (JEOL JSM-7800F), transmission electron microscopy (TEM) (JEM-2100), x-ray diffraction (XRD) (Xpert Pro), x-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250Xi equipped with monochromatic Al Kα source of 1486.5 eV), Raman spectrometer (LabRAM HR 800 Raman spectrometer, 532 nm), four-point probe system.
2.4. Electrochemical measurement

The S cathodes were prepared by grinding spray-drying rGO nanosheets with commercial sulfur powder at a S: graphene mass ratio of 3:1 (9:1 for high mass loading) and subsequently heated at 155 °C for 12 h in a sealed container within Ar atmosphere. Note that the mass loading of sulfur was about 75% (90% for high mass loading). The cathode was made of 70% graphene-S hybrid, 20% ketjen black, and 10% polyvinylidene fluoride (PVDF) in N-methylpyrrolidone, spread onto aluminum foil by a doctor blade, and then dried 12 h at 60 °C under vacuum. The foil was punched into round disks (12 mm), and the areal mass loading of sulfur on the disk was 0.5–1.8 mg cm⁻². For comparison, carbon black-S cathode was prepared via the same method of graphene-S cathode, only replacing rGO with carbon black. Li–S batteries were assembled using CR 2016 coin cells with lithium foil as the counter and reference electrode, and graphene-S electrode as working electrode. The electrolyte contains 1 M bis(trifluoromethane)sulfonamide lithium salt (LiTFSI) and 1.0 wt% LiNO₃ dissolved in a mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 v/v). The galvanostatic charge and discharge (GCD) profiles were obtained using a LAND CT2001A battery tester between 1.7 and 2.8 V, and specific capacity was calculated by per gram of sulfur loaded in the electrode. The CHI600E electrochemical measurement system was used for cyclic voltammetry (CV) and electrochemical impedance spectrometry (EIS) measurements. CV was conducted at a scan rate of 0.1 mV s⁻¹ in the potential window from 1.7–2.8 V versus Li⁺/Li. The EIS were recorded in the frequency range between 0.01 Hz–100 kHz.

3. Results and discussion

The fabrication of 2D EG/Co(OH)₂ hybrid interlayer is schematically illustrated in figure 1(a). To assemble this interlayer, we first chose two different 2D nanosheets.

One is non-polar high-conducting graphene nanosheets (1000 S cm⁻¹), derived from electrochemical exfoliation of graphite [46]. Raman spectrum of EG nanosheet showed a low intensity ratio 0.113 of I_D/I_G, and TEM images displayed 2D flat and transparent nanosheets with ≤3 layers, indicative of high-quality graphene. High-resolution TEM (HRTEM) image of bilayer graphene represented an interlayer distance of 0.34 nm (figures 1(b)–(e)) [47]. Another is the polar Co(OH)₂ nanosheets, prepared by self-assembled lamellar soft
template approach employing long-chain CMC with rich functional side groups, such as carboxyl and hydroxyl groups, which are critical to combine with inorganic salts through electrostatic forces for the formation of layered Co(OH)$_2$ nanosheets under hydrothermal condition. XRD pattern confirmed the successful preparation of Co(OH)$_2$ (JCPDS card no. 30-0443) nanosheets (figure 1(f)). SEM and TEM images revealed high homogeneity of ultrathin thickness, and freestanding 2D nanosheet-like morphology (figures 1(g) and (h)), and HRTEM image validated high-order crystalline structure of Co(OH)$_2$ with an interlayer spacing of 0.466 nm, corresponding to the (001) crystal plane (figure 1(i)). Then, the EG/Co(OH)$_2$ hybrid interlayer, with a typical mass loading of 0.2 mg cm$^{-2}$, was assembled by vacuum-filtration of the solution of EG and Co(OH)$_2$ nanosheets on the commercial PP separator.

Figures 2(a)–(c) showed the typical photographs of the different hybrid interlayers of pure Co(OH)$_2$, pure EG, and EG/Co(OH)$_2$ films, respectively. It can be seen that the pure Co(OH)$_2$ interlayer was hard to stably adhere to the PP separator, but the interlayer consisting of large-size EG nanosheets exhibited good adhesion (figures 2(a)–(c)), indicative of the great importance of EG for the formation of EG/Co(OH)$_2$ interlayer. The SEM image of EG/Co(OH)$_2$ interlayer represented the formation of a densely stacked film with a thickness about 5.5 μm (figure 2(d)), relatedly uniform incorporation of Co(OH)$_2$ nanosheets into the EG nanosheets (figure S1 is available online at stacks.iop.org/JENERGY/1/015002/mmedia), and strong adhesion to the PP membrane without any structural delamination of the interlayer from PP membrane when it was bent in a large bending state (figure 2(e)). Benefitting from the intimate interactions between the EG/Co(OH)$_2$ interlayer and PP membrane, the hybrid separator showed outstanding flexibility, excellent electrical conductivity.
interlayer nanosheets (figure 2(g)). In a sharp contrast, commercial PP separator displayed porous polymer-like structure (figure 2(f)), which can act as a short-circuit barrier but not substantially prevent the shuttle effect of polysulfides through the separator (figure 2(h)) [48].

To highlight the importance of 2D hybrid interlayer, we first assembled the Li–S batteries based on based on the EG/Co(OH)2 interlayer/PP separator sandwiched between grapheme–S cathode (figure S3) and Li foil anode, using 1 M LiTFSI and 1.0 wt% LiNO3 dissolved in DOL and DME (1:1 v/v), as depicted in figure 2(g). For comparison, we also assembled the Li–S cell with only commercial PP separator, while other steps kept unchanged (figure 2(h)). The CV curves with and without EG/Co(OH)2 interlayer on PP separators were carried out ranging from 1.7 to 2.8 V (versus Li+/Li) at a scan rate of 0.1 mV s⁻¹. As show in figures 3(a) and (b), both of them presented two cathodic peaks appear at around 2.30 and 2.04 V, ascribe to the phase transitions from solid S8 to liquid high-order Li2S6 (4 ≤ x ≤ 8) and phase transitions from soluble polysulfides to solid Li2S/Li2S2, respectively [48]. From the second cycle, Li–S batteries with the 2D EG/Co(OH)2 interlayer have negligible current changes or potential shifts in these CV peaks with repeated scans, and the shapes of CV curves are almost overlapped, but the cells with only commercial PP separator represented obvious evolution of both current and potential. This result indicated the presence of interlayer could greatly enhance the electrochemical reversibility of Li–S batteries (figures 3(a) and (b)). The GCD profiles are carried out at current density of 0.2 C (1 C = 1675 mAh g⁻¹) to further illustrate the superior of EG/Co(OH)2 interlayer/PP separator over the individual PP separator, as shown in figure 3(c). Apparently, the Li–S battery using 2D EG/Co(OH)2 interlayer delivered higher specific capacity of 1089 mAh g⁻¹ (2nd cycle) in comparison with the battery with individual PP separator (816 mAh g⁻¹ at 2nd cycle). Further, the plateaus of Li–S battery using the EG/Co(OH)2 interlayer are more flat and stable with a low polarization of 156 mV, while in the case of commercial PP separator, a higher voltage hysteresis of 196 mV was attained. The role of EG/Co(OH)2 interlayer in Li–S batteries was further probed by EIS (figure 3(d)). Both the EIS of Li–S batteries with and without EG/Co(OH)2 interlayer presented two typical semicircles, corresponding to the ion transportation resistance in high-frequency (Rt) and charge transfer resistance in the medium-frequency (Rct). From this comparison, it is obvious that the cell with EG/Co(OH)2 interlayer displayed two smaller semicircles, corresponding to lower Rt of ~17.6 Ω and Rct of ~8.6 Ω than the cell without interlayer (Rt = 24.5 Ω, Rct = 13.3 Ω). Moreover, it is calculated that EG/Co(OH)2 interlayer exhibited higher Li ion diffusion coefficient of 1.49 × 10⁻⁹ cm² s⁻¹, which is nearly three times that of the PP separator (4.51 × 10⁻¹⁰ cm² s⁻¹), indicative of improved lithium ion conductivity of EG/Co(OH)2 interlayer/PP (figure S4) [49]. Therefore, it is evidenced that the EG/Co(OH)2 interlayer can not only efficiently suppress the polysulfides shuttling, but also significantly enhance the interfacial charge transfer for increasing rate capability. As expected, our Li–S batteries with EG/Co(OH)2 interlayer exhibited excellent rate capability, measured at varying current densities from 0.2 to 5 C (figures 3(e), (f)). With increasing current density from 0.2, 0.5, 1, 3 to 5 C, high reversible capacities were achieved from 1090 (2nd cycle), 945 (6th cycle), 876 (11th cycle), 795 (16th cycle), 740 (21st cycle), to 677 mAh g⁻¹ (26th cycle). Importantly, after abruptly switching the current density back to 0.5 C, a large capacity of 908 mAh g⁻¹ (31th cycle) was still restored. In contrast, the Li–S batteries with only PP separator delivered only lower reversible capacities from 817 (2nd cycle), 679 (6th cycle), 613 (11th cycle), 558 (16th cycle), 523 (21th cycle), to 466 mAh g⁻¹ (26th cycle), respectively, at the corresponding current densities from 0.2, 0.5, 1, 3 to 5 C. It is noted that the capacity contribution of the sulfur-free cathode and EG/Co(OH)2 interlayer, tested 1.7–2.8 V versus Li/Li⁺ at 1 C, is less than ~1.6% of the total discharge capacity of Li–S batteries based on graphene-sulfur cathode and EG/Co(OH)2 interlayer (figure S5).

The long-term cycling stabilities of Li–S batteries with EG/Co(OH)2 hybrid interlayer/PP and individual PP separator were further examined for 300 times at 0.5 C. Apparently, it is demonstrated that, with the EG/Co(OH)2 interlayer, the Li–S battery showed discharge capacities of 918 (5th cycle) and 565 mAh g⁻¹ (300th cycle) (figure 3(a)), much higher than the cells without interlayer, e.g. 831 (5th cycle) and 384 mAh g⁻¹ (300th cycle) (figure 4(b)). Furthermore, the former showed a slow capacity fade rate of 0.130% per cycle, while the latter without interlayer revealed a larger capacity fade rate of 0.222% per cycle (figure 4(c)). In addition, the Li–S batteries with EG/Co(OH)2 interlayer also exhibited excellent long-term cycling performance over 300 cycles at 1 C (figure S8) and 500 cycles at 2 C (figure S9), with capacity fade rate of as low as 0.116% and 0.062% per cycle. From the performance comparison of Li–S batteries employed EG/Co(OH)2 hybrid interlayer and other functional interlayers summarized in table S1, it is concluded that the battery with EG/Co(OH)2 interlayer presented enhanced capacity and cycling stability. Impressively, when a high mass loading of sulfur (~1.7 mg cm⁻²) in cathode was used to evaluate the cycling stability, the Li–S batteries still delivered exceptionally high capacity of 994 mAh g⁻¹ at 0.2 C and maintained a large capacity of 762 mAh g⁻¹ after 70 cycles (figure S10), demonstrative of the wide applicability of EG/Co(OH)2 interlayer. This result suggested that EG/Co(OH)2 interlayer played a
key role in suppressing the migration of polysulfides and thus alleviated the loss of active material during cycling process.

To highlight the superiority of EG/Co(OH)₂ hybrid interlayer over individual EG interlayer, we also fabricated and compared the Li–S batteries based on individual EG interlayer, while other steps kept unchanged (figure S11). Obviously, it can be seen that the Li–S batteries with pure EG interlayer presented stable cyclability but lower capacity than the cell with hybrid interlayer, suggestive of the nature of physical blocking of polysulfide by graphene. In this case, both the diffusion of lithium ions, to some extent, and permeability of polysulfide were physically blocked through the EG interlayer on separator, but the catalytic re-utilization of polysulfides chemically absorbed on interlayer were not efficiently implemented. Moreover, the performances of Li–S batteries based on 2D nanosheet hybrid interlayer are well comparable to those based on other individual 2D
nаносветлые интерлийеры, как было ранее отмечено (таблица S2), дающие предположение о синергетическом эффекте EG и Co(OH)2nanosheets. В дополнение, процесс обогащения и оптимизации массы EG и Co(OH)2nanosheets в интерляйерах (фигуры S6, S7) является важным для максимизации лучших емкости и циклической стабильности Li–S аккумуляторов.

Фигура 5(a) показала SEM изображение EG/Co(OH)2интерлийера после 100 циклов (на заряженном уровне 2.8 В), показывая стабильную и плотно упакованную структуру 2D наносветлой интерлийера. И соответствующие элементарные карты в фигурах 5(c)–(f) показывают равномерное распределение сильного сигнала серы в EG/Co(OH)2интерлийере, демонстрируя, что мигрирующие полисульфиды безусловно застревают в EG/Co(OH)2интерлийере и трудно управлять из тонкого покрытия, обдувывая эффективное повторное использование активного материала серы. Для подтверждения существования форм полисульфидов в EG/Co(OH)2интерлийере, был анализирован S 2p XPS спектр EG/Co(OH)2интерлийера после 100 циклов (фигура 5(b)). Можно видеть два основных характеристических серных компонента, один из S2–/S22– при 161.5/162.2 eV от заряженных продуктов Li2S/Li2S2 [50, 51], другой из SOx–2–, возникающий из химически адсорбированных серных компонентов, таких как сульфон/сульфат при 166.8/168.6 eV [48]. Это подчеркивается отсутствием наблюдения за Co–S пик (~1685 eV [52]). Дополнительно, XRD паттерны (фигура S12) не показывали появления новых фаз после зарядки и разрядки, и оба CV и GCD кривые (фигура S13) также не показывали никаких очевидных восстановительных пиков. Следовательно, можно предположить, что Co(OH)2 может не химически реагировать с серой.

Для просмотра этого процесса, мы установили визуализированную ячейку, чтобы проверить роль EG/Co(OH)2интерлийера в предотвращении диффузии полисульфидов ионов. Специфически, H-типа стеклянная ячейка была использована для хранения 0,1 M Li2S6тетраэфиролуран (THF) раствора и чистого THF были отделены EG/Co(OH)2гибридным интерляйером/PP разделяемым и чистым PP разделяемым, соответственно. При отсутствии света, желтовато-белый цвет был четко виден в случае индивидуальных PP разделяемого только после 6 часов из-за быстрого Li2S6разлива из Li2S6содержащего THF раствора (правая сторона) к чистому THF (левая сторона) (фигура 5(g) нижняя). В отличии от этого, только малые количества Li2S6 прошли через EG/Co(OH)2гибридный интерляйер/PP разделяемый после 24 часов (фигура 5(g) верхняя). Этот результат подтверждается дополнительно по UV– видимым поглощающим спектрам чистого THF сторон разделенных EG/Co(OH)2интерляйером/PP разделяемым, показывающим...
lower absorption intensity, indicative of the limited permeability of polysulfides using EG/Co(OH)₂ hybrid interlayer in comparison with pure PP separator (figure 5(h)). The superior performance of EG/Co(OH)₂ hybrid interlayer/PP separator over pure PP separator was assigned to the bi-functionalized synergistic barriers of EG and Co(OH)₂ nanosheets to prevent the permeation of polysulfides through porous PP separator.

4. Conclusion

In summary, we demonstrated a general approach of creating 2D hybrid interlayer consisting of physically-blocked high-conducting graphene and chemically-adsorbed Co(OH)₂ nanosheet as an efficient bi-functionalized polysulfide barrier for boosting high-performance Li–S batteries. The assembled Li–S batteries based on thin, conductive, and lightweight EG/Co(OH)₂ interlayer validated high specific capacity, outstanding rate capability, and excellent long-life cycle stability. The diffusion of polysulfide was efficiently prohibited by the combination of physical blocking of 2D graphene and chemical adsorption of Co(OH)₂ nanosheets. Considering high performance achieved and a large pool of 2D materials, we believe that our proposed strategy of constructing a hybrid interlayer derived from 2D different nanosheets will open new possibilities for developing long-life and high-energy-density Li–S batteries.
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