Binary graphene-based cathode structure for high-performance lithium-sulfur batteries

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Abstract

Lithium—sulfur (Li-S) batteries are highly appealing for the next-generation energy storage because of their high energy density and low-cost features. However, the practical implementation of Li-S batteries has been hindered by fast performance degradation of the sulfur cathode, especially at a high cathode loading. Here, we propose a strategic design of binary graphene foam (BGF) as the cathode scaffold, with the incorporation of nitrogen-doped graphene and highly porous graphene. The nitrogen-doped graphene provides chemical adsorption sites for migrating polysulfides, while the highly porous graphene could increase the cathode conductivity and accelerate lithium ion transport. The freestanding foam-like cathode structure further offers a robust, interconnected, conductive framework to promote the redox reaction even at a high cathode loading. Therefore, the Li-S battery with the S/BGF electrode exhibits a high specific areal capacity over 10 mAh cm⁻² and good cycling stability over 300 cycles. This approach offers insights into multifunctional electrode structure design, with targeted functions for high-performance Li-S batteries.

1. Introduction

Development of rechargeable batteries with high energy density, long cycle life and affordable costs has been triggered by the ever-increasing demand for efficient energy storage technologies applied for consumer electronics, electric vehicles, smart grid energy storage and the penetration of renewable energy sources [1, 2]. Lithium-ion (Li-ion) batteries have revolutionized the energy supply for portable electronics since the 1990s, yet they are reaching their theoretical limit after being optimized for nearly 30 years [3, 4]. Regarding the exploration of alternatives for the next-generation energy storage, lithium-sulfur (Li-S) batteries have been considered as an appealing representative because of the high theoretical energy density of 2600 Wh kg⁻¹ [5, 6]. Moreover, sulfur is earth-abundant and low-cost, which further endow Li-S batteries with practical reliability for large-scale applications [7, 8].

Despite the advantages, Li-S batteries are facing challenges that pose barriers to their market. Unlike the intercalation-type electrode materials in Li-ion batteries, sulfur is a typical conversion-type electrode material, which undergoes a structural and compositional change during lithiation to form entirely new discharge products (Li₂S) [9]. The large volumetric expansion (80%) from S to Li₂S leads to pulverization of the electrode with isolated domains, where active materials lose electrical contact with the electrode conductive matrix and become inactive [10]. Moreover, the sulfur conversion reaction is accompanied with the formation of a series of polysulfide intermediates (Li₂Sn, n = 3~8). These intermediates are soluble in the organic electrolyte, which spontaneously diffuse to the anode and cause irreversible, active material loss and the known ‘shuttle effect’ [11].
Besides, sulfur is insulating for both lithium ions and electrons, leading to sluggish redox reaction kinetics and limited active material utilization [12]. These intrinsic issues during sulfur conversion reaction result in an undesirable battery performance, including low capacity, low coulombic efficiency and short cycle life. Rational design of composite electrode materials has proved to be an effective approach to address the above fundamental challenges. The core design principles include two mainstreams: physical confinement and chemical adsorption [13]. Physical confinement aims to minimize the migration of polysulfide intermediates by the physical adsorption effect of pore structures, or the physical blocking effect of external interception coating layers. Therefore, conductive carbon materials with abundant and tunable pore structures have received a lot of attention, as they can not only alleviate the polysulfide dissolution issue and accommodate the volumetric changes of active materials by the porous framework, but they also promote the active material utilization due to their high conductivity [14]. Various sulfur/carbon composites with micro/meso/macroporous carbons [15–18], carbon nanotubes [19, 20], graphene [21, 22], carbon fibers [23, 24] or carbon hybrids [25–27] have been developed for the promotion and stabilization of sulfur redox reactions. The chemical adsorption from the weak interactions between non-polar carbon materials and polar polysulfides arouses the concern of insufficient polysulfide-anchoring capability [28–30]. Functionalizing carbon materials such as heteroatom doping is an effective way to introduce polar surface chemistry within the cathode material, which serves to enhance the interaction with the polar polysulfides via chemical adsorption [31–33]. Besides, the metal compounds with inherent polar surfaces, such as TiN [34], TiOx [35], VN [36] and MnO2 [37], have also been used for achieving a high affinity of polysulfides in the cathode.

The above strategies mostly focus on battery material levels, while the practical energy density of the cell is determined by several parameters in cell-level design, such as sulfur content and cathode loading, which need to be taken into consideration to evaluate the feasibility for practical applications [7, 38]. A low cathode loading can artificially lead to high capacity and a long cycle life, but the corresponding low areal capacity will not translate to higher–energy-density cell designs. It has been estimated that an areal capacity of at least 6 mAh cm−2 is essential for Li-S batteries to compete with the state-of-the-art Li-ion batteries [5]. Nevertheless, the insulating nature of sulfur poses additional challenges in the design of a high sulfur-loaded thick cathode, as the kinetics for both lithium ions and electrons are limited in thick electrodes, leading to drastically decreased active material utilization with increased sulfur loading [39]. Therefore, challenges remain in both fundamental and practical aspects towards the development of commercially viable Li-S batteries.

Graphene, known to have many appealing properties of high conductivity, large pore volume, tunable surface functionality, and good structural stability, is among the most widely used conductive matrix for Li-S batteries [40, 41]. Herein, we report a strategic design of a graphene-based cathode structure with multifunctional features for Li-S batteries with high areal capacity and long cycle life. A binary graphene foam (BGF) comprising of both nitrogen-doped graphene and highly porous graphene was prepared via a freezing-casting method, followed by the sulfur melt-diffusion process to obtain a freestanding sulfur/graphene composite electrode. The nitrogen-doped graphene enables strong chemical adsorption of polysulfides within the cathode via strong ionic attraction between electron-rich N and terminated Li in lithium polysulfides. The highly porous graphene not only improves the conductivity of the cathode for higher sulfur utilization, but also provides abundant pore structures to allow a high sulfur content and to accommodate volumetric changes during cycling. Moreover, the freestanding foam-like cathode structure provides a robust interconnected conductive scaffold to enable efficient electron and ion transport at high sulfur loadings [26]. With these advantages, Li-S batteries with the S/BGF electrode exhibits high capacity and long cycle life at a high areal sulfur loading. This strategic design of cathode structure integrates multiple advantages to construct high-performance Li-S batteries.

2. Experimental section

2.1. Preparation of N-doped graphene

N-doped graphene was prepared through the thermal exfoliation of graphite oxide followed by an ammonia treatment. The graphite oxide was synthesized by a graphite oxidation using an improved Hummers’ method [42]. The graphite oxide was thermally exfoliated at 400 °C for 3 min in air to obtain fluffy graphene oxide powder. Then graphene oxide powder was uniformly mixed with dicyandiamide in the weight ratio of 1:1, and the mixture was subsequently transferred to the furnace and treated under a mixed gas flow of argon and ammonia (2:1) at a flow rate of 100 ml min−1. The annealing temperature was 800 °C with a heating rate of 10 °C min−1, where the temperature was constantly held for 1 h to obtain N-doped graphene.
2.2. Preparation of the freestanding graphene foams
The BGF was prepared by a freeze-casting method using N-doped graphene and highly porous graphene with a weight ratio of 1:1. Highly porous graphene was obtained according to our previous report, with a BET surface area of 771 m² g⁻¹ and a high pre volume of 3.51 cm³ g⁻¹ [22]. The N-doped graphene and highly porous graphene powder were dispersed in a 3 wt% polyvinyl pyrrolidone (molecular weight of ~10 000) aqueous solution, followed by ultrasonication for 1 h and stirring for 1 h. The obtained suspension was then frozen in the liquid nitrogen bath, followed by freeze-drying overnight to obtain a freestanding composite graphene foam. The freestanding graphene foam was further treated at 800 °C for 30 min in an argon atmosphere to obtain the BGF. The highly porous graphene and N-doped graphene foam were prepared through the same process with the use of highly porous graphene or N-doped graphene only as the precursors. The area density of the freestanding graphene foams was controlled to be around 3.5 mg cm⁻².

2.3. Preparation of the freestanding sulfur/graphene foam electrodes
The S/BGF electrode was obtained through a melt-diffusion method, where sulfur powder (99.5%, Sigma-Aldrich) was added to the surface of the BGF with a sulfur/carbon weight ratio of 7:3, followed by heat treatment at 155 °C for 12 h in a sealed stainless steel vessel. The S/HPG and S/NG electrodes were prepared through the same process with the use of highly porous graphene foam and N-doped graphene foam, respectively. The obtained freestanding sulfur/graphene foam electrodes had an areal sulfur density of around 8.2 mg cm⁻².

2.4. Materials characterization
Scanning electron microscope (SEM) observations were carried out using a FEI Nova NanoSEM 450 (10 kV) instrument. Transmission electron microscope (TEM) observations were performed using Tecnai F20. High angle annular dark-field scanning transmission electron microscopy (STEM) imaging and element mapping were carried out using FEI Titan G2 80–200 TEM/STEM with ChemiSTEM Technology operating at 200 kV. XPS (Thermal Escalab 250) was conducted with an Al Kα source. Raman spectra were performed using a Jobin Yvon Lab RAM HR800 instrument, using a 632.8 nm He–Ne laser. Nitrogen adsorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 instrument. The sample powders were degassed at 200 °C before the measurements, until a pressure of 2 mm Hg was reached. The DFT model was used for pore size analysis of adsorption isotherms, which is automatically performed by the Micromeritics ASAP 2020 instrument. TGA was obtained with a NETZSCH STA 449 C thermo-balance in argon atmosphere from room temperature to 600 °C with a heating rate of 10 °C min⁻¹. XRD patterns were recorded on a Rigaku diffractometer using Cu Kα radiation.

2.5. Electrochemical measurements
2025-type coin cells were assembled inside an Ar-filled glove box for electrochemical measurements. The S/BGF, S/HPG and S/NG electrodes were cut into square pieces with an area of 1 cm² for the working electrodes, with lithium metal foil as the anode and Celgard 2400 as the separator. The electrolyte was 1 M lithium bis-trifluoromethanesulphonylimide (LiTFSI, Sigma-Aldrich) in 1, 2-dimethoxyethane (DOL, 99.5%, Sigma-Aldrich) and 1, 3-dioxolane (DOL, 99.5%, Sigma-Aldrich) with 1:1 volume ratio, with 0.2 M lithium nitrate (LiNO₃, 99.9%, Sigma-Aldrich) as the additive. The electrolyte amount added to each cell was 60 μl. LAND galvanostatic charge/discharge instruments were used to perform electrochemical measurements. The charge/discharge voltage window was 1.8–2.8 V. The cyclic voltammetric (CV) test and the electrochemical impedance spectroscopy (EIS) measurements were carried out with a Biologic VSP-300 multichannel workstation. The frequency range of the EIS measurements was 100 KHz to 10 mHz with an AC voltage amplitude of 10 mV at an open-circuit potential.

3. Results and discussion
The N-doped graphene was obtained via ammonia treatment of graphene oxide at 800 °C, which leads to both reduction of the graphite oxide and nitrogen heteroatom doping on the graphene sheets. The SEM and TEM images of the N-doped graphene are shown in figures 1(a) and (b), which exhibit a corrugated laminar structure with a typically wrinkled morphology. An x-ray photoelectron spectroscopy (XPS) survey was carried out to investigate the detailed chemical state of doped nitrogen heteroatoms in graphene, as shown in the high-resolution N1s XPS spectrum in figure 1(c). The nitrogen doping content was 3.8 wt%. Four different types of doped nitrogen were detected, including pyridinic, pyrrolic, quaternary, and pyridine oxide with binding energies centred at 398.0, 399.3, 401.1, and 403.3 eV, respectively [32]. Notably, pyridinic N and pyrrolic N are the dominant doping species, which are considered as strong polysulfide adsorption sites because they can serve as electron-rich donors to bond with lithium ions owing to the existence of lone pair electrons in their atomic.
structures [43, 44]. Raman spectrum of the N-doped graphene was shown in figure 1(d), where characteristic D band at 1320 cm$^{-1}$ and G band at 1580 cm$^{-1}$ can be observed. Basically, the D band represents the disordered non-sp$^2$ stretching mode, which is mainly derived from disorders and defects; while the G band represents ordered graphitic sp$^2$ stretching mode [45]. Heteroatom doping often results in less ordered sp$^2$ domains on the graphene laminar structure, leading to increased D band to G band intensity ratio (ID/IG) [46]. Raman spectrum of higher porous graphene prepared according to our previous report is also exhibited in figure 1(d) for comparison, and the N-doped graphene has a higher ID/IG (1.15) compared to that of highly porous graphene (1.10). This reveals that the N-doped graphene has less ordered graphitic structure, which often leads to decreased electronic conductivity. Nitrogen adsorption-desorption isotherms were implemented to investigate the pore structures of the N-doped graphene, as shown in figure 1(e). The Brunauer–Emmett–Teller (BET) surface area was calculated to be 418 m$^2$ g$^{-1}$ with a pore volume of 1.82 cm$^3$ g$^{-1}$. The corresponding pore size distributions were analysed via the Density Functional Theory (DFT) method, as shown in figure 1(f). The N-doped graphene has a broad pore size distribution ranging from 0.6 to 63 nm, which is beneficial for electrolyte penetration and lithium ion transport.

N-doped graphene and highly porous graphene are integrated into a foam-like architecture via a freeze-casting process [47, 48], which is considered an effective approach to construct electrode architectures with interconnected conductive network. According to our previous report [22], the highly porous graphene has high pore volume to accommodate volumetric changes of sulfur, and high conductivity to facilitate fast electron transport. Therefore, the BGF enables the combination of chemical adsorption capability, high conductivity and high pore volume, which is beneficial for stabilization of sulfur redox reactions at a high sulfur loading. Sulfur was incorporated into the BGF through a typical melt-diffusion process, the as-obtained freestanding S/BGF electrode is shown in figure 2(a). SEM images of the S/BGF electrode at different magnifications are shown in figures 2(b)–(d). The foam electrode exhibits a porous surface with graphene flakes interconnected with each other. These micro-sized graphene flakes are self-assembled from graphene nanosheets during the freeze-casting process, which contribute to a dense electrode structure with improved volumetric energy density. Moreover, no obvious bulk sulfur agglomerates can be observed on the S/BGF electrode surface, indicating uniform sulfur impregnation in the graphene scaffold.

In order to further elucidate the distribution of sulfur in the S/BGF electrode, TEM high angle annular dark-field STEM imaging and element mapping were carried out. Figure 3(a) shows the TEM image of the S/BGF, where ultrathin graphene sheets interweave together with no obvious sulfur particles. The STEM image in figure 3(b) and corresponding elemental maps of carbon, sulfur, and nitrogen in figures 3(c)–(e) further indicate homogeneous sulfur distribution on the graphene sheets. This ensures essential electrical contact between the insulating sulfur and the conductive graphene matrix and thus contributes to improved charge transfer kinetics during the redox reactions.

Figure 1. Morphological and structural characterizations of N-doped graphene: (a) SEM image, (b) TEM image, (c) N1s XPS spectrum, (d) Raman spectra, (e) nitrogen adsorption-desorption isotherms and (f) corresponding pore size distributions.
The sulfur content in the S-BGF electrode was examined by thermogravimetric analysis (TGA), as shown in figure 4(a). Although the addition of NG in BGF unavoidably leads to slightly lower surface area and porosity than those of HPG, the BGF still enables a high sulfur content of 70 wt%, and the corresponding areal sulfur loading is 8.2 mg cm$^{-2}$. The evacuation temperature of sulfur in the S-BGF is obviously higher than that of pristine sulfur, and this is often an indicator of strong confinement effect of sulfur in the graphene matrix. Figure 4(b) displays the XRD patterns of both the S/BGF electrode and pristine sulfur. The sulfur in the S/BGF electrode exhibits the same characteristic diffraction peaks as pristine sulfur, which can be indexed to the typical crystal structure of orthorhombic sulfur.

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Coin cells were assembled to investigate the electrochemical properties of the S/BGF electrode, with lithium metal as both the counter and reference electrode. To clearly elucidate the merits of the strategic design of using binary graphene in the BGF, S/HPG and S/NG foam electrodes, with the use of highly porous graphene or N-doped graphene only, were also prepared for comparison. Figure 5(a) shows the comparison of the first charge/discharge curves of the three electrodes at 0.1 C rate with marked bounds for the first and second discharge plateaus. (b) Upper plateau discharge capacities and lower plateau discharge capacities of three electrodes during the first discharge. (c) Cycling performance and coulombic efficiencies of three electrodes at 0.1 C. (d) Charge/discharge curves of the S/BGF electrode at different cycles.

Figure 4. Comparison of (a) TGA curves and (b) XRD patterns of the S/BGF electrode and pristine.

Figure 5. (a) Comparison of the first charge/discharge curves of the S/BGF, S/HPG and S/NG foam electrodes at 0.1 C with marked bounds for the first and second discharge plateaus. (b) Upper plateau discharge capacities and lower plateau discharge capacities of three electrodes during the first discharge. (c) Cycling performance and coulombic efficiencies of three electrodes at 0.1 C. (d) Charge/discharge curves of the S/BGF electrode at different cycles.
of the S/BGF and S/HPG foam electrodes. This can be ascribed to the lower conductivity of the N-doped graphene, which impedes the charge transfer kinetics during the redox process. Figure 5(b) shows the detailed analysis of the corresponding upper (first) plateau discharge capacities and lower (second) plateau discharge capacities. The ratios of capacities delivered by the second plateau and first plateau are 2.29, 1.68, and 1.82 for of the S/BGF, S/HPG and S/NG foam electrodes, respectively. Although the S/HPG foam electrode shows a comparable discharge capacity as the S/BGF electrode during the upper discharge plateau, the discharge capacity delivered at the lower discharge plateau is obviously lower. Basically, the upper discharge plateau is assigned to the reduction of elemental sulfur to soluble long chain polysulfides, and high conductivity is essential to achieve a higher utilization rate of sulfur to polysulfides; while the lower discharge plateau corresponds to the reduction of soluble polysulfides to solid lithium sulfides, and the utilization rate is significantly determined by the polysulfide-anchoring effect of the cathode [32]. For the S/HPG foam electrode, despite its high conductivity to realize high utilization of sulfur during the upper discharge plateau, the lack of polysulfide immobilization sites lead to uncontrolled polysulfide diffusion, which thus results in decreased utilization rate of polysulfides in the lower discharge plateau. Therefore, the combination of high conductivity and good chemical adsorption capability in the S/BGF electrode benefits high active material utilization throughout the sulfur conversion reaction, contributing to high capacity and low voltage polarizations. The cycling performance and coulombic efficiencies of the three electrodes are shown in figure 5(c). The S/HPG foam electrode shows obvious capacity decay over 80 cycles due to insufficient polysulfide immobilization capability. For the S/NG foam electrode, despite the good cycling stability, the capacity is much lower due to low electronic conductivity. The S/BGF electrode demonstrates both high capacity and good cycling stability compared to the S/BGF and S/HPG foam electrodes. Figure 5(d) shows the charge/discharge curves of the S/BGF electrode at different cycles, and the voltage plateaus and capacities can be well-retained.

The electrochemical impedance spectra (EIS) of the S/BGF electrode before cycling and after five cycles are shown in figure 6(a), where a single depressed semicircle in the high frequency region representing the charge transfer resistance (Rct). After cycling, the Rct of the S/BGF electrode shows an obvious decrease, indicating kinetically favored charge transfer kinetics at the electrode/electrolyte interface [24]. Figure 6(d) shows the cyclic
voltammetry (CV) profiles of the S/BGF electrode in the initial five cycles. The two cathodic peaks can be
ascribed to the stepwise reduction of sulfur to polysulfides and lithium sulfides, corresponding to the two
discharge plateaus in figure 5(d). Both the cathodic and anodic peaks remain stable during the examined cycles,
indicating high reversibility and stability of the sulfur conversion reaction in the binary graphene scaffold. Long
term stability of the S/BGF electrode is shown in figure 6(c). The capacity increased slightly during the initial 60
cycles, which is a common phenomenon for high sulfur-loaded electrodes at a relatively high current density,
and indicates gradually increased sulfur participation in the redox reactions during continuous cycles. The cell
shows good stability over 300 cycles with an average coulombic efficiency of 99% and a low capacity decay rate of
0.089%. An areal capacity of 6.6 mAh cm$^{-2}$ can be retained after 300 cycles, higher than the state-of-the-art Li-
ion batteries (4 mAh cm$^{-2}$), which demonstrates the practical significance for real full cell design.

4. Conclusion

In summary, we have proposed a strategic design of a BGF cathode scaffold, integrating the merits of nitrogen-
doped graphene and highly porous graphene for Li-S batteries with high areal capacity and a long cycle life. The
BGF affords both chemical adsorption capability and high conductivity for effective polysulfide immobilization
and fast redox reaction kinetics. The robust and interconnected graphene conductive framework further enables
the realization of a high sulfur loading without sacrificing the active material utilization. Consequently, the Li-S
battery with the S/BGF electrode exhibits a high specific areal capacity over 10 mAh cm$^{-2}$ and good cycling
stability with an ultralow capacity decay rate of 0.089% over 300 cycles. This work proposes a strategic design of a
multifunctional electrode structure endowed with targeted functions for high-performance Li-S batteries,
which inspires rational design of electrodes for analogous electrochemical conversion reactions.

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