Stabilizing sulfur cathodes using nitrogen-doped graphene as a chemical immobilizer for Li-S batteries

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Abstract

Lithium–sulfur (Li–S) battery, as a high energy-density storage system, has attracted great attention for next generation rechargeable battery applications. However, the fast capacity decay caused by lithium polysulfides (LiPSs) dissolution impedes its prospect for commercialization. In this work, nitrogen-doped graphene, as a chemical immobilizer, was designed to bind LiPSs and stabilize sulfur in the cathode for high performance Li-S batteries. The incorporated nitrogen dopants in the graphene network were found to have a strong binding effect on the LiPSs to improve electrochemical stability and promote fast electrochemical reaction kinetics. As a result, the nitrogen doped graphene-based sulfur electrode could deliver an initial capacity of $\sim 1200 \text{ mAh g}^{-1}$ at 0.3 A g^{-1} , and exhibit good capacity retention with only 0.05% capacity decay per cycle after 300 cycles at 0.75 A g^{-1} .

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1. Introduction

Lithium–sulfur (Li–S) battery is a promising candidate for next generation energy storage systems due to its high theoretical specific capacity (1675 mAh g^{-1}) and energy density ($\sim 2600 \text{ Wh kg}^{-1}$). Moreover, the low cost, environmental friendliness and wide availability of sulfur makes it attractive for battery applications [1-4]. However, the practical application of the Li–S batteries has been impeded due to a series of obstacles such as low electrical conductivity of sulfur/lithium sulfides, low Coulombic efficiency caused by the dissolving and shuttling of soluble lithium polysulfides (LiPSs), and large volume expansion/shrinkage of sulfur during lithiation/delithiation processes [5-8].

To address the above issues, graphene based electrodes have attracted considerable interest for applications in Li–S batteries due to their high electrical conductivity and large surface area [9], such as graphene wrapped sulfur cathode [10], three-dimensional hierarchical graphene network encapsulated sulfur electrode [11], unstacked double-layer graphene confined sulfur cathode [12], and graphene sandwiched sulfur structure [13]. As a high conductivity, porous and flexible framework, graphene was incorporated into the electrodes to overcome the shortcomings of Li–S batteries, such as the insulating nature of sulfur, “shuttle effect” of LiPSs during repeated electrochemical charge/discharge cycles, and large volume expansion problems. However, these designs are still limited by the weak interactions (related to physical adsorption/confinement) between the graphene matrix and the sulfur species, which are not sufficient for alleviating polysulfides dissolution into the

electrolyte. Besides hetero-atoms doping in the carbon materials as the strategy to bring chemical binding with lithium polysulfides, other promising chemical adsorbents such as transition metal oxides or sulphides have recently been introduced into Li-S battery system to immobilize lithium polysulfides [14-17]. However, the use of non-conductive metal oxides as polysulfide immobilizers will affect the rate performance of the electrodes. Therefore, an ideal conductive substrate should not only host non-polar sulfur, but also strongly adsorb (or bind) polar polysulfide species to extend the battery cycle life and achieve high utilization of active sulfur.

Generally, chemically-derived graphene from graphene oxide (GO) is decorated with abundant oxygen-containing functional groups (e.g. hydroxyl (C–OH), carboxyl (–COOH), carbonyl (–C=O), epoxyl (–C–O–C–)), and lattice defects (e.g. atom vacancy, distortion, and dangling bonds) on the lateral surface or at edges [18, 19]. It is well demonstrated that non-metal heteroatoms can be easily incorporated into the graphene network, which has proven to be a very effective approach to tune the electrical and chemical environment of the carbon surface for electrochemical reactions [20]. Among different non-metal heteroatoms, nitrogen (N) is a very popular doping element that could act as a Lewis base in the lattice of graphene and interacts with other molecules [21], such as LiPSs and final discharge lithium sulfides, to significantly improve the electrochemical performance of Li–S batteries. For example, N-doped porous carbon [22, 23], N-doped carbon nanotubes [24, 25] and N-doped graphene [26-28] were applied as the conductive substrates to improve the performance of Li-S batteries. In these studies, Wang's group proposed that the

existence of N in the mesoporous carbon will promote the formation of bonds between sulfur atoms and nitrogen-related functional groups on the carbon [22]. However, the effect of N-dopants on the soluble LiPSs that are generated during the electrochemical reaction of a Li-S battery are not well-understood. Further, it is still ambiguous as to which types of N-dopants are the most effective immobilizers to restrict the dissolution of LiPSs and what is the detailed interaction mechanism between N-dopants and LiPSs.

Herein, we propose a facile strategy towards high-performance Li-S battery by using N-doped graphene as chemical immobilizer to stabilize sulfur and its discharge products. To provide the proof-of-the-concept, the raw material of GO was annealed in ammonia atmosphere serving as sulfur host (denoted as N-G), in side-by-side comparison to GO treated in argon (denoted as A-G). The results lead to insights about the roles played by the doped N heteroatom in graphene network on the electrochemical reaction. As a result, a high capacity of $\sim 1200 \text{ mAh g}^{-1}$, excellent cycling stability, and good rate capability of a N-G-based Li-S battery are achieved.

2. Experimental

2.1 Synthesis of GO

GO was fabricated using natural graphite flakes by a modified Hummers' method [29]. The concentration of the GO suspension obtained was 1.8 mg mL^{-1} .

2.2 Synthesis of N-G and A-G

N-G was prepared by annealing GO at $400 \text{ }^{\circ}\text{C}$ under NH_3 gas flow. Briefly, 100 mg of GO was put in the middle of a quartz tube furnace in NH_3 flow of 50 sccm. It

was then heated to 400 °C with a ramp of 5 °C min⁻¹ and held at this temperature for 2 h. The resultant N-G samples were obtained after the furnace was naturally cooled to room temperature. In order to prepare the A-G sample, GO was thermally reduced by a similar procedure under 400°C at argon atmosphere.

2.3 Synthesis of sulfur/graphene composites (N-G-S and A-G-S)

N-G-S and A-G-S were fabricated *via* a melt-diffusion method. The mass ratio of graphene based material (N-G or A-G) and sulfur is 3:7. The mixtures were co-heated at 155 °C in a sealed flask for 4 h to obtain the N-G-S and A-G-S.

2.4 Materials Characterisation

Scanning electron microscopy (SEM) observations were performed on a FEI Nova NanoSEM 430 operated at 15 kV. Transmission electron microscopy (TEM) and STEM were performed using a Tecnai F20 (200 kV). Energy-dispersive X-ray spectroscopy (EDS) was used for elemental analysis. X-ray photoelectron spectroscopy (XPS) analysis was performed by using an ESCALAB 250 instrument with Al K α radiation (15 kV, 150 W) under a pressure of 4 $\times$ 10⁻⁸ Pa. X-ray diffraction (XRD) was conducted with a D-MAX/2400 diffractometer (Cu K α , λ =0.154056 nm). Raman spectra were collected with a 632.8 nm He-Ne laser with a Jobin Yvon LabRam HR800 micro-Raman system at room temperature. Thermogravimetric analysis (TGA) was performed with a NETZSCH STA 449C thermo-balance in argon with a heating rate of 10 °C min⁻¹ to 500 °C. Zeta potential was measured by the ZETASIZER Nano series (Nano-ZS90). 10 mg N-G and A-G powders were dispersed in 50 mL distilled water and sonicated by a tip sonicator (SCIENITZ-IID) for 0.5 h. The obtained graphene dispersion was then used to measure the Zeta potential. Fourier transform infrared spectroscopy (FTIR) spectra were obtained using a Bruker

TENSOR 27 spectrometer. The samples were collected using the KBr-pellet method and the obtained spectra were normalized using OPUS 6.5 software.

2.5 Electrochemical Measurements

The N-G-S and A-G-S electrodes were prepared by mixing 80 wt % active material with 10 wt % conductive carbon black (super P) as a conducting agent and 10 wt % polyvinylidene fluoride dissolved in N-methyl-2-pyrrolidone as a binder to form a slurry, which was then coated onto a Al foil and dried under vacuum at 60°C for 12 h. The obtained sulfur electrodes were shaped into a circular pellet with a diameter of 12 mm and was used as a cathode. The mass loading of the sulphur cathode was $\sim 2 \text{ mg cm}^{-2}$. The electrolyte was 1.0 M lithium bis-trifluoromethanesulphonylimide in DOL and DME (1:1 by volume) with 0.5 wt% LiNO_3 additive. 2032-type stainless steel coin cells were used to assemble test batteries. Lithium metal foil was used as the anode, and Celgard 2400 (thickness: 25 mm, porosity: 41%) was used as the separator. The coin-type cell was assembled in an Ar-filled glove box (MBraun Unilab). A LAND galvanostatic charge–discharge instrument was used to perform the measurements. The current density set for tests was referred to the mass of sulfur in the cathode and was varied from 0.3 to 6 A g^{-1} . The charge/discharge voltage range was 1.5-2.8 V. The cyclic voltammetry (CV) was measured using a VSP-300 multichannel potentiostat/galvanostat (Bio-Logic, France) workstation operated in the voltage range of 1.5-2.8 V (vs. Li^+/Li) at a scan rate of 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of 100 kHz to 0.01 Hz with an AC voltage amplitude of 10 mV at the open-circuit potential or discharge to 2.3 V after five cycles.

3. Results and discussion

The graphene-sulfur composites were prepared by thermal-diffused sulfur into N-G and A-G samples at 155°C [30, 31]. SEM images reveal that both N-G-S and A-G-S have a curly morphology with a thin, wrinkled laminated structure (**Figure 1a,c** and **Figure S1a**). The elemental composition was analyzed by EDS that shows the presence of C, O, and S in the N-G-S and A-G-S composites (**Figure 1b**, **Figure S2**), while N element only appears in the N-G-S sample, indicating the successful incorporation of N atoms into the carbon framework. The elemental distribution results obtained by the EDS elemental mappings (**Figure S1b-d**) and STEM (**Figure 1d-g**) further confirm the existence and homogeneous distribution of C, O, S and C, O, S, N atoms on the surface of A-G-S and N-G-S composites. The uniform dispersed sulfur without obvious agglomeration suggests the well mixed state of sulfur in the composites, which will be beneficial for improving sulfur utilization.

Figure 1. (a) SEM image of the N-G-S composite. (b) EDS spectrum of the N-G-S

composite (unit: keV). (c) TEM image of the N-G-S composite. (d-g) Corresponding elemental mappings of the N-G-S composite in (c).

XRD patterns of the GO, A-G, N-G, A-G-S and N-G-S samples are shown in **Figure S3**. GO shows a typical diffraction peak at around 12° [32]. After the heat treatment, this peak disappears while a broad diffraction peak emerges between 22 and 28° in the XRD patterns for both N-G and A-G samples, suggesting the reduction reaction of GO. After impregnating sulfur through melt-diffusion strategy, all the pronounced diffraction peaks observed in the N-G-S and A-G-S composites, except for the broad one at around 26° , could be assigned to the orthorhombic sulfur (JCPDS card No. 08-0247) [33]. To verify the doping of nitrogen on the graphene surface, XPS was used to elucidate the surface chemical composition of the A-G, N-G, A-G-S and N-G-S samples. **Figure 2a** demonstrates the presence of C 1s, N 1s, and O 1s peaks in the N-G while only C 1s and O 1s peaks existing in the A-G sample, indicating the incorporation of nitrogen into the sp^2 carbon network of N-G. After impregnating sulfur, S 2s and S 2p peaks could be detected in the A-G-S and N-G-S samples [34]. Based on the N1s peak that appeared at about 400 eV after NH_3 treatment, it is estimated that ~ 7.1 wt% nitrogen was doped into the carbon framework, accompanied with a decrease in the oxygen content. The C/O ratios are also investigated as shown in **Figure 2b**. The C/O ratios are 2.5, 7.6 and 9.6 for GO, A-G, and N-G, respectively, which suggest a more efficient reduction process by using NH_3 to treat GO than employing argon. The binding energy peaks observed in the high-resolution N 1s profile of the N-G-S at ~ 398.3 , ~ 399.8 and ~ 401.7 eV (**Figure**

2c) correspond to pyridinic, pyrrolic and graphitic nitrogen, respectively [27, 35]. The C 1s spectra of the N-G-S sample consists of component peaks at ~284.6 eV and ~285.9 eV, corresponding to the carbon species of C-C and C-N, respectively, which also confirms nitrogen doping into the carbon network (**Figure 2d**). **Figure S4** presents the FTIR spectra of the GO, A-G-S and N-G-S samples. Consistent with the XPS analysis, the infrared vibration intensities of oxygen-containing bonds (C-O-C bonding at 1045 cm^{-1} , C-O bonding at 1215 cm^{-1} and 1394 cm^{-1} , and C=O bonding at 1725 cm^{-1}) [36, 37] of A-G-S and N-G-S show a pronounced decrease due to the reduction of oxygen-containing functional groups heated in argon and ammonia atmosphere. The C-N bonding (1575 cm^{-1}) appears in the spectrum of the N-G-S sample [38], further indicating the successful incorporation of nitrogen into the carbon network.

Figure 2. (a) XPS spectra of the surface chemical composition of the A-G, N-G, A-G-S and N-G-S samples. (b) Weight percentage of the C, O, N, and C/O ratios for the GO, A-G and N-G. (c) N 1s XPS spectrum of the N-G-S. (d) C 1s XPS spectrum of the N-G-S.

Raman spectroscopy is highly sensitive to the subtle structural variations in the carbon network and can be used to study the structural differences of the composite before and after reduction (GO, A-G and N-G), and after mixing sulfur in the composite (A-G-S and N-G-S). All the samples display two distinct Raman peaks at ~ 1335 and ~ 1580 cm^{-1} , which correspond to the D band and G band of sp^2 carbon materials, respectively [32]. As shown in **Figure 3a**, the intensity ratios of D band to G band (I_D/I_G) of the A-G ($I_D/I_G = 1.12$) and N-G ($I_D/I_G = 1.17$) are higher than that of

GO ($I_D/I_G = 1.07$), which is possibly due to the increase of the number of C atoms at graphene edges or defects during the reduction process [39]. Owing to the nitrogen atoms doped in the network of the graphene, the ratio of I_D/I_G of N-G is higher than that of A-G. Moreover, we have analyzed G peaks of the A-G, N-G, A-G-S and N-G-S samples in **Figure 3a**, the red shift (shift to higher frequency) of G peaks in the N-G and N-G-S samples compared to the un-doped A-G and A-G-S samples, further confirming the successfully N-doping in the samples [40]. After adding sulfur in the A-G and N-G, more defects lead to a higher intensity ratio between D band and G band in the A-G-S and N-G-S composites. The absence of the sulfur peaks (in the range of $100\text{-}500\text{ cm}^{-1}$) which stem from S-S bond vibration in sulfur crystals, suggest that sulfur is well-dispersed in the A-G-S and N-G-S composites without long-range ordering [41]. TGA shows that the A-G-S and N-G-S composites (**Figure 3b**) have similar sulfur content ($\sim 67.1\%$ and $\sim 68.6\%$, respectively). However, compared with the A-G-S composite, the sulfur of N-G-S composite evaporates at an elevated temperature ($\sim 223^\circ\text{C}$ compared to $\sim 192^\circ\text{C}$ of A-G-S), which is likely due to the strong interaction between nitrogen-doped graphene and sulfur [33]. Besides, we measured the Zeta potential of A-G and N-G, to be $+0.254\text{ mV}$ and -1.951 mV , respectively, which suggest that N-G should exhibit a better adsorption ability to Li_2S_x ($4 \leq x \leq 8$) [27].

Figure 3. (a) Raman spectra of the GO, A-G, A-G-S, N-G and N-G-S samples. (b) TGA and differential thermogravimetry (DTG) curves of similar sulfur loading in the A-G-S and N-G-S composites.

In order to prove the effect of the doped nitrogen atoms on the electrochemical performance of Li-S batteries, the A-G-S and N-G-S electrodes were tested in coin cells with a lithium-metal anode. Firstly, electrochemical impedance spectroscopy (EIS) was used to test the reaction kinetics of these cathodes. The Nyquist plots of these two battery systems at the open-circuit voltage are composed of a depressed semicircle in the high-medium frequency range, corresponding to the charge-transfer resistance (R_{ct}) and a sloped tail in the low-frequency region, corresponding to the Warburg impedance related to the ion-diffusion process (**Figure 4**) [13, 42]. The R_{ct} of the N-G-S electrode (295.7 Ω) is much lower compared to A-G-S (939.4 Ω) electrode, which can be attributed to the favorable charge- and ion-transfer processes from the graphene network and N dopants (**Figure 4a**). After five cycles and discharge to 2.3 V, the curve for N-G-S consists two semicircles, the first semicircle (at high frequency) can be ascribed to the solid electrolyte interface (SEI) film resistance during cycling

process and the second semicircle is due to the R_{ct} . [43] The SEI film resistance and R_{ct} of N-G-S electrode are much smaller compared with A-G-S electrode due to the improved electronic transport process by N-doping, the electrochemical conditioning effects such as better contacts and distribution of the polysulfide species on the graphene sheets (**Figure 4b**).

Figure 4. Nyquist plots of the (a) N-G-S and (b) A-G-S electrodes at the open-circuit potential and discharge to 2.3 V after five cycles with a frequency range of 100 kHz to 0.01 Hz by using an AC voltage amplitude of 10 mV.

Figure 5a and **b** show the CV curves of the N-G-S and A-G-S electrodes scanned at a rate of 0.1 mV s^{-1} . Two well-defined reduction peaks for N-G-S electrode exist distinctly in the first scan, which are located at 2.27 and 2.02 V, corresponding to the two step conversions of sulfur to high-order LiPSs ($\text{Li}_2\text{S}_x, 4 \leq x \leq 8$) and high-order LiPSs to $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$, respectively [44]. Only one broad oxidation peak located at around 2.46 V is observed, showing the transformation of the lithium sulfides to soluble LiPSs and to the final sulfur [13, 45]. At the same time, the reduction and

oxidation peaks of A-G-S electrode are much broader than those of N-G-S electrode, which suggest the slower reaction kinetics, implying the sluggish and incomplete utilization of active materials. By comparing **Figure 5a** and b, we come to the conclusion that nitrogen-doped graphene plays an important role in suppressing the diffusion of polysulfide species and minimizing the mass loss of active materials during cycling. From the second cycle in **Figure 5a**, the cathodic peaks shift to a higher potential of about 2.32 and 2.05 V, while the oxidation peaks also shift to a lower potential of about 2.42 V and the CV curves exhibit similar shapes, indicating that the reacting kinetics have been improved for the subsequent cycles and good reversibility is achieved for the N-G-S electrode. To better understand the reaction dynamics, we also depicted the peak potential and onset potential of N-G-S electrode and A-G-S electrode, as shown in **Figure S5**. The peak potential obtained from the second cycle of CV curve indicates the increased redox kinetics and smaller polarization for the N-G-S electrode due to the higher reduction peaks and lower oxidation peak. The onset potential also reveals that the existence of heteroatom will help to accelerate the oxidation reaction. Besides, the intensity of redox peaks from the A-G-S electrode drops constantly, indicating the occurrence of irreversible reactions (**Figure 5b**).

The rate capability of the N-G-S and A-G-S electrodes was investigated as shown in **Figure 5c**. The results show that N-G-S electrode exhibits a capacity above 1150 mA h g⁻¹, much higher than that of the A-G-S electrode (839 mA h g⁻¹) in the first five cycles at 0.3 A g⁻¹. Upon increasing the current density, the capacities of the

N-G-S electrode are much better than A-G-S electrode, and the specific capacity of the N-G-S electrode still remains at $\sim 330 \text{ mA h g}^{-1}$ under a very high current density (6 A g^{-1}). We have also depicted the galvanostatic charge/discharge curves for the N-G-S and A-G-S electrodes, respectively, at different current densities. As shown in the **Figure S6**, we can see the difference that the polarization between charge and discharge curves of the A-G-S electrode is obviously larger than that of the N-G-S electrode under the same current density. These results indicate the introduction of heteroatoms not only creates much active sites for trapping lithium polysulfides, but also significantly reduces the charge transfer resistance. The cyclic stability of the samples was also investigated at a current density of 0.3 A g^{-1} , as shown in **Figure 5d**. The initial capacity of both electrodes is similar, however, A-G-S electrode showed a significant capacity decrease after only the initial few cycles. After 100 cycles, the N-G-S electrode exhibits good cyclic performance and retained a capacity of $\sim 880 \text{ mA h g}^{-1}$. **Figure 5e** shows the long cycling performance and Coulombic efficiency of A-G-S and N-G-S electrodes at a current density of 0.75 A g^{-1} . After 300 cycles, the Coulombic efficiency of N-G-S electrode is still around 95% and the specific capacity is maintained above 700 mA h g^{-1} with only $\sim 0.051\%$ capacity decay per cycle, much higher than A-G-S electrode with a Coulombic efficiency of only 85% and a capacity of 230 mA h g^{-1} (0.201% capacity decay per cycle) under the same test condition. These results demonstrate that electrodes with nitrogen doping in the graphene network: (a) improve electron transport pathways with decreased resistance and increased reaction kinetics, and (b) provide strong binding between doped functional

groups and Li_2S /LiPSs to suppress polysulfide dissolution. The interactions between LiPSs and N-G with different doping configurations by density functional theory calculations were carried out in our group [46]. It was found that, among all different N-doping configurations in N-G, only the clustered pyridinic N-dopants can strongly attract LiPSs with large enough binding energies to effectively anchor the soluble LiPSs, due to (i) an enhanced attraction between Li ions in LiPSs and pyridinic N-dopants and/or (ii) an additional attraction between S anions in LiPSs and Li ions captured by pyridinic N-dopants.

Figure 5. CVs of the (a) N-G-S electrode and (b) A-G-S electrode at a scan rate of 0.1 mV s⁻¹. (c) Rate performance, (d) cycling performance at a current density of 0.3 A g⁻¹ and (e) long term cycling test at a current density of 0.75 A g⁻¹ showing specific capacity and Coulombic efficiency of the Li-S batteries with N-G-S and A-G-S electrodes.

4. Conclusion

In summary, a stabilized sulfur cathode was achieved by using nitrogen modified graphene as chemical immobilizer for Li-S batteries. The N-doped graphene cathode with ~70% of sulfur exhibits a high specific capacity, fast reaction dynamics, good rate performance, and stable cycling performance with only 0.051% capacity decay per cycle up to 300 cycles. When the current density increased to 6 A g^{-1} , the specific capacity is still retained up to $\sim 330 \text{ mA h g}^{-1}$. The enhanced performance can be attributed to the facilitated electron and ion transportation, and the strong interactions between the doped graphene network and LiPSs, thereby reducing polysulfide dissolution. The related chemical adsorption insight obtained in this work could also pave the way in developing novel types of doped carbon frameworks as cathodes in Li-S batteries.

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Graphical Abstract:

High performance Li-S batteries was designed by using nitrogen-doped graphene as a chemical immobilizer to bind lithium polysulfides and stabilize sulfur in the cathode.