Grafting polysulfides into a functional *N*-halo compound for high-performance lithium–sulfur battery

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ABSTRACT Due to its high energy density, lithium-sulfur (Li-S) battery is considered as the most promising candidate for the energy storage systems, but its practical application is hindered by the dissolution of lithium polysulfides in the electrolyte. In this work, *N*-bromophthalimide ($C_8H_4NO_2Br$, NBP), an aromatic molecule with carbophilic, sulfiphilic, lithiophilic, and solvophilic nature, is introduced into active graphene (AG) to fabricate the sulfur composite cathode. The carbophilic NBP is anchored readily on the AG surface *via* π - π stacking interaction. During discharging, the dissolved lithium polysulfide anion (LiS_n^-) is grafted into the sulfiphilic NBP spontaneously *via* S_N2 substitution reaction to form $C_8H_4NO_2S_nLi$, which brings the dissolved LiS_n^- back to the AG surface in the composite cathode. Moreover, the lithiophilic and solvophilic nature of NBP improve the wettability of the porous composite cathode, and the electrolyte molecule is easily penetrated into the micro-mesopores of AG to facilitate the diffusion of the electrolyte. Thus, NBP, as a multi-functional compound in Li-S battery, can immobilize LiS_n^- and enhance the diffusion of the electrolyte. The above features of NBP endow the sulfur composite cathode with improved electrochemical performance in the cycling stability.

Keywords: Li-S battery, sulfur cathode, multi-functional materials, *N*-bromophthalimide, polysulfides, *ab initio* calculation

INTRODUCTION

Lithium-sulfur (Li-S) battery has attracted more and more attention, due to the high theoretical specific capacity (1675 mA h g^{-1}) [1] of sulfur (S_8), which is capable of being discharged to lithium sulfide (Li_2S) with two electrons gained by each S atom [2–5]. However, due to S_8 and its intermediate products lithium polysulfides (Li_2S_n ,

$n = 2-8$) as well as the final product Li_2S , are all electron insulating [3], a composite cathode with electron conducting host has to be adopted for the practical applications of Li-S battery [6]. The composite cathode could be composed of an electron conducting material with a high specific surface area, such as micro-mesoporous carbon (MMC) as a sulfur host material [7–10], in order to achieve high loading of sulfur with high energy density. Thus, the redox of sulfur or its discharged products, accompanied by the association/dissociation of Li^+ during cycling [11], occurs at the interface with good contact to facilitate electron transportation for the redox process, between the active Li_2S_n and the inactive electron conducting host materials.

For the practical applications of Li-S battery, one of the major issues is that high-order Li_2S_n ($n = 4-8$) is soluble in the electrolyte [11]. During the discharging process, Li^+ near the cathode is consumed rapidly, and the dissolution of Li_2S_n , formed upon reduction, is unavoidable owing to the lack of Li^+ [12]. The effect of such dissolution may be of two folds. On one hand, the dissolution is in a certain sense welcome, especially for the high loading sulfur cathode, because it can leave room to sulfur that is not in good contact with the electron conducting host, and thus promoting complete reductions [13]; on the other hand, the dissolved LiS_n^- [12] may shuttle to the lithium metal anode with undesirable side reactions [11]. Moreover, once the dissolved LiS_n^- diffuses into the bulk electrolyte, it causes capacity decay with low coulombic efficiency over long-term cycling [5,9,10]. Thus, it is essential to encapsulate S_8 and its discharging products in an electron conducting host material, while establishing a strategy to immobilize the dissolved LiS_n^- before diffusing into the

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bulk electrolyte, in order to maintain a good balance of the dissolution-precipitation cell chemistry [14,15].

Since both LiS_n^- and the electrolytes are polar, the polar and sulfiphilic sites are often introduced in the otherwise non-polar electron conducting host, in order to increase the attraction of LiS_n^- and thus suppress its dissolution. Ji and co-workers [16] employed partially reduced graphene oxide (rGO) as host to encapsulate sulfur, and the resultant cathode was found to immobilize LiS_n^- with high reversible capacity, thanks to the chemical bonding of the S-atom to the C-C bonds around the functional hydroxyl and epoxy groups. Wang *et al.* [17] synthesized ethylenediamine-functionalized rGO, in which the lithiophilic N-atom on the amino group acted as Lewis base to donate the lone electron pair to the Li-atom and immobilized the polar Li_2S_n on the carbon host, with 80% capacity retention over 350 cycles. Such strong Lewis acid-based interaction with LiS_n^- is often employed in the heteroatom-doped polar carbon-based hosts. For example, the nitrogen-doped carbon can act as electron donor that binds to Li^+ [18], the boron-doped carbon can act as electron acceptor onto which the sulfur chain of LiS_n^- is grafted [19], while N- and S-atom dual-doped carbon takes advantage of both strong $\text{Li}\cdots\text{N}$ and $\text{S}\cdots\text{S}$ interactions with double Li_2S_n absorptivity [20]. Recently, host materials with ultrahigh concentrations of electron donors or acceptors, such as graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) [21] and early transition metal type MXene such as Ti_2C [22] and TiC [23], are also employed in the sulfur cathode with relatively high energy density, thanks to the strong Lewis acid-based interaction bonds to LiS_n^- . Thus, the key feature of good carbon-based hosts is adequate polar sites that are capable of immobilizing LiS_n^- with high electron conductivity. Besides carbon-based hosts, Nazar and coworkers [24] recently directly grafted the dissolved polysulfides into a $\delta\text{-MnO}_2$ host to form thiosulfate for further catenations, and achieved a remarkable long-term cycling performance. For comprehensive discussions on the chemical modification of the polar sulfur host, we refer to the review articles and the references cited therein [15,22,25,26].

Besides the chemical modifications of the carbon-based hosts, there is also the physical mixing of small dipolar aromatic molecules to the non-polar carbon hosts. Helms and co-workers [27] introduced the aromatic benzo[ghi]peryleneimide (BPI) in the carbon fibers with $\pi\text{-}\pi$ stacking interactions between them, and found that BPI acted as a redox mediator to facilitate the reduction of the dissolved LiS_n^- , with 6-folds increase in Li_2S formation compared with the neat carbon host. Recently, Li *et al.*

[28] introduced anthraquinonoid (AQ), a natural abundant organic molecule, into the rGO host. Due to the aromatic ring, AQ is evenly distributed and anchored on the graphitic carbon *via* $\pi\text{-}\pi$ interactions. Furthermore, the keto group of AQ forms strong Lewis acid-based chemical bond with LiS_n^- , and such effect effectively suppresses the dissolution of the latter, and the resultant rGO/AQ/S composite cathode shows long cycling stability [28]. Indeed, the sulfur chain of the dissolved LiS_n^- may be grafted onto a polar aromatic molecule that is anchored on the otherwise non-polar MMC surface. The benefits are (1) immobilizing the dissolved LiS_n^- ; and (2) providing a polar electrode surface with better wettability, and thus enhancing Li^+ transportation. The above studies orientated a strategy of the design of a polar host *via* simply physical mixing of small polar aromatic molecules with carbon materials with proper functional groups.

In this study, we follow the physical mixing strategy by introducing a small aromatic organic molecule *N*-bromophthalimide ($\text{C}_8\text{H}_4\text{NO}_2\text{Br}$, NBP) into active graphene (AG) as host of sulfur to form AG/NBP/S composite cathode for Li-S batteries. It is of interest to note that phthalimide derivatives, including NBP, has been recently investigated computationally as electrolyte additives in Li-ion batteries for its capability to form solid electrolyte interphase (SEI) layer on the graphite anode [29]. Here, we show that the AG/NBP/S composite cathode, with the aromatic NBP binding on the graphene surface *via* $\pi\text{-}\pi$ stacking, can exchange its Br with LiS_n^- *via* bimolecular nucleophilic substitution ($\text{S}_\text{N}2$) reaction, and thus inhibits the dissolution of the latter. The electron-rich carbonyl ($\text{C}=\text{O}$) group acts as Lewis base binding to Li^+ , while the polar nature of NBP is expected to strongly interact with solvents and thus facilitates the transportation of Li^+ . The composite cathode shows good reversibility, high rate capability, and long-term cycling stability. In order to explore the mechanism of NBP, a series of experiments and *ab initio* calculations were employed in this study.

EXPERIMENTAL SECTION

Preparation of AG/NBP, AG/NBP/S, AG/S composite and Li_2S_6 solution

The AG/NBP was synthesized through mixing 180 mg of AG (The Six Element) and 120 mg of NBP (Alfa, 98.0%) (wt/wt, 3:2) into a crucible, then sealed up in a 200-mL autoclave with a Teflon liner and heated to 170°C for 15 h and the total weight of AG/NBP was about 297 mg. AG/NBP/S was synthesized *via* a facile melting method. Briefly, 297 mg of AG/NBP and 552 mg of sulfur (wt/wt,

3.5:6.5) were fully mixed and added into a crucible, then sealed up in a 200-mL autoclave with a Teflon liner and heated to 155°C for 15 h. Finally, the AG/NBP/S sample about 806 mg was obtained. AG/S was prepared through the melting method with the mixing weight ratio 1:3 of AG:S. Stoichiometric sulfur and Li₂S (5:1) were dissolved in 1,3-dioxolane/1,2-dimethoxyethane solvent (*v/v*, 1:1) and stirred at 60°C for 48 h in the glove box to obtain Li₂S₆ solution (0.1 mol L⁻¹).

Materials characterization

X-ray photoelectron spectra (XPS) were conducted on an X-ray photoelectron spectrometer (PHI5000 Versa-Probe) with a monochromator of Al-K α (1486.8 eV) radiation. X-ray diffraction (XRD) patterns were achieved via X-ray powder diffractometer (Rigaku MiniFlex II, Monochrome Cu-K α rays) in the diffraction angle range of 5°–85° with the scanning speed of 4° min⁻¹. Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (Mettler-Toledo) in Ar with a heating rate of 10°C min⁻¹ from ambient temperature to 600°C. Fourier transform infrared (FTIR) spectroscopy was conducted by Nicolet 6700 using KBr pellets with the transmission mode. The microstructure and morphology of the as-prepared materials were acquired from field-emission scanning electron microscope (SEM, JSM-7800) with an elemental mapping apparatus and transmission electron microscope (TEM, FEI, Tecnai F20). UV-vis spectra were measured on a UV-vis spectrophotometer (CARY 100 Conc). N₂ sorption/desorption isotherm were measured on a surface area porosity analyzer (JW-BK122F). The resistivity was measured on a power resistivity analyzer (ST-2722) at different pressures.

Electrochemical measurements

Cathodes were prepared by casting *N*-methyl-2-pyrrolidone (NMP) slurry containing 70 wt% of the as-prepared cathode materials, 20 wt% of conductive carbon Super-P, 10 wt% of binder polyvinylidene fluoride (PVDF) on an aluminium foil using a doctor blade and dried at 60°C overnight in drying oven. The obtained electrode foil was pressed and cut into circular disks with a diameter of 10 mm, where the areal mass loading of sulfur was around 0.8–1.0 mg cm⁻². Coin cells (2032) were assembled with lithium metal as the anode and Celgard 2300 as the separator with electrolyte volume in the electrolyte volume/sulfur mass (E/S) ratio of 10–15 μ L mg⁻¹. The electrolyte contained 1.0 mol L⁻¹ lithium bis(trifluoromethane) sulfonamide (LiTFSI, 98.0%, TCI) and 0.2 mol L⁻¹ LiNO₃ (99.9%, Alfa Aesar) in a co-

solvent of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (*v/v*, 1:1). Galvanostatic discharge and charge tests were conducted on the LAND battery test system (CT2001C). All specific capacity was calculated based on the mass of sulfur. Cyclic voltammetry (CV) was performed by the electrochemical analyzer (CHI600E). Electrochemical impedance spectra (EIS) were measured by an electrochemical workstation (ZAHNER elektrik IM6ex) for the frequency range from 100 kHz to 10 mHz, with 5 mV alternating current (AC) amplitude. Chronoamperometry was performed on an electrochemical analyzer (LK2005a) from open circuit potential in the fully charged state and terminated at 2.15 V vs. Li/Li⁺.

Computational methods

Ab initio calculations were performed with Gaussian 09 [30] on the B3LYP/6-311G(d) level of theory. The normal mode analyses of all species were calculated at the same level to confirm the minima or transition states and evaluate zero-point energies (ZPE). The Gibbs free energies were calculated at 298.15 K and 1 atm. The electrostatic potential (ESP) was calculated on the isoelectron density surface of 0.001 electrons/bohr³, in which more than 95% of the molecular electronic charge was encompassed. The Gibbs free energies were calculated at 298.15 K and 1 atm with the IEFPCM [31] implicit solvent model using the dielectric constant of DOL ($\epsilon = 7.1$).

RESULTS AND DISCUSSION

We first performed *ab initio* calculations to characterize NBP. The optimized structure, as well as the electrostatic potential of NBP, is shown in Scheme 1a. This molecule has an electronegative region on C=O groups as well as an electronegative “belt” around the covalent N–Br bond, while an electropositive region, i.e., a “ σ -hole” [32], on the outermost surface of halogen along the N–Br bond. Thus, NBP can be considered as an amphiphilic compound with the O-atom of the C=O group as Lewis base, and the N-atom of the N–Br bond as Lewis acid. Moreover, Br⁻ is a common leaving group that can easily be substituted by nucleophilic groups via an S_N2 reaction [33]. Such features make the O-atom of NBP easily bind to the Li⁺, while the Br-atom of NBP is ready to be substituted by the dissolved strong Lewis base LiS_n⁻ in the electrolyte to form C₈H₄NO₂S_nLi via S_N2 reaction, leaving the Br⁻ in the solution. Furthermore, the electron-withdrawing C=O groups of NBP induce an electron-deficient region in the center of the pyrrole ring, which is expected to interact with the π -electron-rich aromatic core of the hexagonal carbon ring of graphene, and thus forms a face-centered

Scheme 1 Schematic illustration of the mechanism of NBP in sulfur composite cathode. (a) The optimized structure of NBP and the corresponding electrostatic potential (ESP) on the electronic isodensity surface of 0.001 electrons/bohr³. The *ab initio* calculations were performed at the B3LYP/6-311G(d) level of theory; (b) scene of the electrode/electrolyte interface, in which carbophilic NBP was anchored on the AG surface *via* π - π stacking, the active materials S₈ were loaded in the micro-mesopores of AG, and Li⁺, the dissolved LiS_n⁻, and DOL electrolyte molecules were on the solution side; (c) scene of the formation of C₈H₄NO₂S₈Li on the AG surface. During the discharging process, the dissolved LiS_n⁻, a strong Lewis base, was grafted onto the anchored NBP *via* S_N2 reaction to form N-S bond, with Br⁻ the leaving group in the solution, according to the chemical reaction in the scene; (d) scene of the solution side, highlighting the presence of the polar NBP on AG resulted in strong charge-dipole interaction between NBP and Li⁺ and dipole-dipole interaction between NBP and DOL. Such interactions make both Li⁺ and DOL approach the AG surface more closely with better wettability of AG.

π - π stacking between them [34,35]. Thus, C₈H₄NO₂S_nLi is anchored on the graphene surface for the following cationations [15].

Based on the above characterizations on the NBP molecules, we propose the mechanism of NBP in the sulfur composite cathode of Li-S battery, as illustrated in Scheme 1b. With the presence of the carbophilic NBP *via* π - π stacking on AG, the dissolved strong Lewis base LiS_n⁻ can spontaneously react with NBP to form C₈H₄NO₂S_nLi precipitates *via* an S_N2 reaction, as highlighted in Scheme 1c. Such reaction effectively prevents LiS_n⁻ from diffusing into the bulk of electrolyte, and thus maintains cycling stability. The improved performance with the presence of NBP can be attributed to two factors, i.e., more electron transfer between sulfur and graphene, which facilitates the electron transfer reaction from the electrode side, as well as Li⁺ transportation from the so-

lution side (Scheme 1d). The former can be attributed to the π - π interaction between AG and NBP, as well as the S_N2 reaction between NBP and LiS_n⁻. The latter results from the dipole-dipole interaction between NBP (3.8 Debye) and DOL (1.5 Debye) in Fig. S1, as well as the charge-dipole interaction between NBP and Li⁺, which makes both DOL and Li⁺ approach the graphene surface more closely with better wettability. Such multi-functional effects, thanks to NBP, are expected to promote the improved electrochemical performance, as is presented and analyzed below.

The specific surface area of AG is 2082 m² g⁻¹ and the pore size distribution of micropores and mesopores is 0.66 and 2.3 nm, respectively, based on Brunauer-Emmett-Teller (BET) measurement in Fig. S2. AG is composed of 3-dimensional corrugated layers, which is beneficial to accommodate sulfur, as shown in the SEM image of AG/NBP composite of Fig. 1a. NBP and AG were mixed and heated at 170°C for 15 h to achieve homogeneous distribution of NBP in the AG/NBP composite materials, which can be demonstrated by the element mappings of C, N, O, Br in Fig. 1b-e as well as TEM and XRD in Fig. S3. Besides, sulfur distributes uniformly in the fabricated AG/NBP/S composite as shown in the sulfur element mapping in Fig. S4. The sulfur and NBP contents of the AG/S and AG/NBP/S composite were determined by TGA tests in Fig. S5. Briefly, the weight ratio of AG:S is 24:76 in the AG/S composite and that of AG:NBP:S is 21:14:65 in the AG/NBP/S composite. Therefore, the AG:S ratios are close to 1:3 in both composites.

FTIR spectra on neat NBP and the AG/NBP composite show a red-shift of the characteristic peak of C=O bond, from 1724 cm⁻¹ of the neat NBP to 1637 cm⁻¹ of the AG/NBP, as shown in Fig. 1f and Table S1. Such red-shift highlights the charge transfer effects due to the π - π stacking interactions between NBP and AG. As shown in the optimized NBP/graphene complex in Fig. 1g, a polyaromatic hydrocarbon molecule consisting of 48 C atoms and 18 H atoms is adopted to mimic single-layered graphene. The face-centered stacking between the two aromatic planes, with an inter-plane distance of 3.5 Å, signifies the π - π stacking interaction between NBP and AG with a binding energy -0.18 eV. In addition, certain charge transfers from the C=O groups of NBP to the model graphene compound, suggesting the C=O bond is weakened with a red-shift, in accord with the FTIR result in Fig. 1f. Such charge transfer also manifests in the electric conductivity of AG and the AG/NBP composite, measured at different pressures by the four-probe meth-

Figure 1 (a) SEM image of the AG/NBP composite; (b–e) element mapping of C, N, O, Br of the AG/NBP composite; (f) FTIR spectra of the neat NBP and the AG/NBP composite, in which the arrows denote the characteristic vibrational peak of the C=O group of NBP. It shows apparent redshift of the C=O group for the AG/NBP composite, due to π - π stacking interaction between them. (g) The electron density map of the optimized AG/NBP complex, in which $C_{48}H_{18}$ is adopted to mimic AG. The green and blue isosurfaces represent the electron accepting and donating regions, respectively, which suggests the charge transfer effect from the C=O group of NBP to AG. Such an effect, altogether with the inter-plane distance of 3.5 Å, highlights the π - π stacking interaction between NBP and AG. The binding energy of the π - π stacking in (g) is -0.18 eV. The geometrical optimization was performed with ONIOM (B3LYP/6-311G(d):PM6), in which NBP was at the B3LYP/6-311G(d) and $C_{48}H_{18}$ at the PM6 level, while the electron density difference was performed at the B3LYP/6-311G(d) level of theory.

od, as shown in Fig. S6. It can be seen that the conductivity of the AG/NBP is higher than that of AG, similar to the co-crystal formed by the donor-acceptor charge transfer complex with high conductivity [36].

In order to validate the proposed reaction between NBP and LiS_n^- in Scheme 1, UV-vis absorption spectra and visual observation were conducted on the 5 mmol L^{-1} Li_2S_6 solution. As presented in Fig. 2a, such a solution is initially yellow-colored with an absorption peak near 425 nm in the UV-vis spectrum, attributed to the excitation of the dissolved LiS_n^- . On the other hand, the above solution becomes colorless immediately as 5 mmol L^{-1} NBP is added, along with the disappearance of the 425 nm absorption in UV-vis spectra as depicted in Fig. 2a. Such a phenomenon is accompanied by the formation of a precipitate, which was further subjected to XPS to investigate the composition, as shown in Fig. 2b. The high-resolution S $2p_{3/2}$ core spectrum of the precipitate shows three peaks at 161.7, 163.1, and 163.7 eV, ascribed to the terminal sulfur of S–Li bond (S_T^-), the bridging sulfur of S–S bond (S_{B1}^0), and the bridging sulfur

of S–N bond (S_{B2}^0), respectively [24,37]. Furthermore, the characteristic FTIR peaks of the precipitate is assigned based on *ab initio* normal mode vibrational frequency analyses and compared with that of the neat NBP [38], as shown in Fig. 2c. The FTIR peak of the neat NBP at 677 cm^{-1} (vs. cal. 679 cm^{-1}), attributed to the characteristic stretching mode of Br–N bond of NBP, diminished in the precipitate, accompanied by the appearance of the characteristic stretching mode of S–N at 847 cm^{-1} (vs. cal. 842 cm^{-1}). In addition, the characteristic stretching mode of O–Li bond at 648 cm^{-1} (vs. cal. 620 cm^{-1}) in the precipitate indicates the Li of LiS_6^- is bonded to the O of the carbonyl group (C=O) of NBP, which hinders the motion of C=O bending and thus causes a notable blue-shift from 702 cm^{-1} (vs. cal. 709 cm^{-1}) of NBP to 715 cm^{-1} (vs. cal. 718 cm^{-1}) of the precipitate. Detailed vibrational normal mode assignments observed in FTIR are listed in Table S2.

The above observations demonstrate that an S_N2 reaction of Br by LiS_6^- indeed occurs in the electrolyte solution, i.e.,

Figure 2 (a) UV-vis spectra of Li_2S_6 and $\text{NBP/Li}_2\text{S}_6$ (supernatant) solution. The inset shows the individual samples of Li_2S_6 (left) and $\text{NBP/Li}_2\text{S}_6$ (right) solution. (b) S 2p XPS core spectrum of the $\text{C}_8\text{H}_4\text{NO}_2\text{S}_6\text{Li}$. (c) FTIR spectra of the neat NBP and the $\text{C}_8\text{H}_4\text{NO}_2\text{S}_6\text{Li}$ precipitate. ν_{BrN} represents the stretching mode of N-Br bond, ν_{OLi} represents the stretching mode of O-Li, δ_{OCC} represents the bending mode of C=O, and ν_{SN} represents the stretching mode of N-S, which are assigned based on the *ab initio* calculations. (d) The critical configurations on the potential energy surface of the $\text{S}_{\text{N}}2$ reaction between NBP and Li_2S_6 . Complex 1 represents the separated NBP and Li_2S_6 , 2 is the pre-reaction complex, 3 is the transition state, 4 is the post-reaction complex, 5 is $\text{C}_8\text{H}_4\text{NO}_2\text{S}_6\text{Li}$. The bond lengths (Å) of N-S and N-Br in this complex are marked with and without parentheses, respectively. The *ab initio* calculations in (b) and (d) were performed at the B3LYP/6-311G(d) level of theory.

in which the lithium 6-(phthalimidy) hexasulfide ($\text{C}_8\text{H}_4\text{NO}_2\text{S}_6\text{Li}$) precipitate is formed. *Ab initio* calculations in Fig. 2d shows that the dissolved LiS_6^- forms a frontside pre-reaction complex with NBP through halogen-bond between the Lewis base terminal S and the σ -hole of Br, with a nearly linear $\text{S} \cdots \text{Br} \cdots \text{N}$ bond, of a binding free energy -0.89 eV. On the other side, the Lewis acid Li^+ is attached to the O on the C=O group of NBP, and also in contact with the electronegative belt on Br (c.f. Fig. S1). Such Li-O bond was also observed in the nitrogen-doped carbon material that contains C=O or COOH groups [39]. The transition state is characterized by the approaching of Br to Li, accompanied by the attack of S to the N of NBP, with a free energy barrier of 0.68 eV. In the post-reaction complex, Br is in close contact with Li^+ and

the Br-N bond is replaced by the S-N bond with a binding free energy of -0.95 eV, more stable than that of the pre-reaction complex, and the final product is the $\text{C}_8\text{H}_4\text{NO}_2\text{S}_6\text{Li}$ precipitation with Br^- left in the electrolyte instead. Such potential energy surface is represented by a double-well of the $\text{S}_{\text{N}}2$ reaction, with the S of the dissolved LiS_6^- acting as the frontside attacking nucleophile and Br as the leaving group [40,41]. The relative configuration parameters are listed in Table S3. In the AG/NBP/S cathode, since NBP is absorbed on the graphene surface *via* π - π stacking interaction, we expect that the adsorbed NBP molecules are ready to capture the dissolved LiS_n^- and produce $\text{C}_8\text{H}_4\text{NO}_2\text{S}_n\text{Li}$ that is in good contact with the AG surface. Furthermore, once the dissolved LiS_n^- is grafted onto NBP to produce $\text{C}_8\text{H}_4\text{NO}_2\text{-S}_n\text{Li}$, it is immobilized on the AG surface all the time, and the following electrochemical reaction takes place on the AG

surface, because the S_nLi chains are now chemically bonded to NBP *via* N–S bond.

The electrochemical tests were performed in the 2032 coin cells, which were assembled with both AG/NBP/S and AG/S cathodes for comparison. As shown in Fig. 3a and b, CV curves for both cathodes present two pairs of redox peaks, corresponding to the reduction of S_8 to high-order Li_2S_n ($n = 4-8$) following by low-order Li_2S_n ($n = 1-3$) and the reverse process [42,43]. After the two initial activation scanning, the reduction peaks of AG/NBP/S at low voltage have a better overlap for the following scanning than that of AG/S, suggesting the better reversibility of AG/NBP/S. Moreover, the reduction current density peaks of AG/NBP/S after the first activation cycles are higher than that of AG/S, indicating faster reaction kinetics of the AG/NBP/S cathode with better contact of $Li_2S_n^-$ and AG. This is expected, because the presence of the polar NBP molecule on the otherwise non-polar AG surface improves the wettability of the electrode, and facilitates the Li^+ transportation with better reversibility and faster kinetics. Since the only difference between the AG/NBP/S and the AG/S cathodes is the presence of NBP in the former, the better performance of the AG/NBP/S cathode may be attributed to the immobilization of the

dissolved $Li_2S_n^-$ by the anchored NBP. It is notable that there is no apparent oxidation peak of Br^- in Fig. 3a. Thus, the leaving Br^- anions are dissolved in the electrolyte and will not affect the subsequent electrochemical reactions. It is also notable that there is a small peak at 1.75 V after the 3rd cycle in the CVs of AG/NBP/S cathode. Since the reduction potential of Br is higher than 3.0 V [44], which is beyond the voltage range of 1.7–2.8 V in this study, it cannot be involved in the electrochemical cycling. Therefore, Br^- is as a leaving group into the electrolyte after S_{N2} reaction and does not contribute to the capacity. On the other hand, the small peak may be caused by NBP, but the contribution to the total capacity is negligible, according to the study of similar compound AQ by Lu and co-workers [28]. Fig. S7 shows the discharge-charge profiles of the AG/NBP/S and AG/S cathode at 0.1 C after two cycles activation in the voltage range of 1.7–2.8 V. These two cathodes have similar shapes, which present a two-stage voltage profile, corresponding to two electrochemical processes that is consistent with the CVs in Fig. 3a and b. It is worth noting that the polarization of AG/NBP/S cathode is smaller than that of AG/S cathode, also indicating that the AG/NBP/S enhances the electrochemical reaction as com-

Figure 3 CVs of (a) AG/NBP/S and (b) AG/S at the potential range of 1.7–2.8 V vs. Li/Li^+ with a scan rate of 0.1 mV s^{-1} . Chronoamperometry of (c) AG/NBP/S, and (d) AG/S electrodes. The solid circles represent the experimental data, while the black curve represents the fitting with Equation (2), and the individual contributions from the reduction of S_8 to high-order Li_2S_n (cyan), the reduction to low-order Li_2S_n (pink), and the deposition of the dissolved $Li_2S_n^-$ (green) are also shown. EIS with Nyquist plot of (e) AG/NBP/S and (f) AG/S cathode after 5 cycles. The red line denotes the fitting against the equivalent circuit in the insets, which consists of series of R_s , and individual components $R_{ct}|CPE1$, $R_{ct}|CPE2$, and CPE3, with fitting parameters in Table S5. 3.3 and 0.8 kHz are the characteristic frequencies of components $R_{ct}|CPE2$ in the AG/NBP/S and AG/S cathodes, respectively.

pared with AG/S.

In order to detect the formation and deposition of LiS_n^- , chronoamperometry was performed on the AG/NBP/S and AG/S electrodes, as shown in Fig. 3c and d. The experiments were performed in the potential range from the initial open circuit potential to 2.15 V vs. Li/Li^+ , which corresponded to the reduction of S_8 to the soluble high-order Li_2S_n^- . The current-time curves can be fitted by the following equation [27,45–47],

$$I(t) = i_1 \exp\left(-\frac{t}{\tau_1}\right) + i_2 \exp\left(-\frac{t}{\tau_2}\right) + i_m \left(\frac{t}{\tau_m}\right)^2 \exp\left[-\frac{2}{3} \left(\frac{t_m^3 - \tau_m^3}{\tau_m^3}\right)\right], \quad (2)$$

in which the two exponential decay functions represent the reduction of S_8 to high-order Li_2S_n^- , and from high-order Li_2S_n^- to low-order Li_2S_n^- , successively, with characteristic times τ_1 and τ_2 , respectively. Since the reduction product Li_2S_n^- is soluble, the last term of Equation (2) is Avrami equation [46,47] that characterizes the deposition of the dissolved LiS_n^- , with i_m the peak current density and τ_m the peak time. It can be seen that the experimental chronoamperometry can be well fitted by Equation (2) with the fitting parameters listed in Table S4. The initial fast decay of the current-time curves corresponds to the fast reduction of S_8 to high-order Li_2S_n^- . As shown in Table S4, the characteristic times τ_1 of AG/NBP/S (69 s) and AG/S (68 s) are similar for the two cathodes. Indeed, at the stage of initial discharging, the only electrochemical process is the reduction of S_8 to high-order Li_2S_n^- . On the other hand, the characteristic times τ_2 of AG/NBP/S (1710 s) is shorter than that of AG/S (2490 s), indicating a faster electrode process at the stage of a long-time discharging. Apart from that, there are apparent deposit peaks for both cathodes, with τ_m 960 s for AG/NBP/S and 1350 s for AG/S, respectively. Moreover, i_m of AG/NBP/S (1.89 A g^{-1}) is also higher than that of AG/S (1.20 A g^{-1}), which also suggests the faster kinetics of AG/NBP/S cathode. Therefore, the dissolved LiS_n^- can be effectively captured by NBP with the enhanced electrochemical performance of the AG/NBP/S composite cathode.

In order to further study the kinetics of the electrode process, we conducted EIS measurements of both AG/NBP/S and AG/S cathodes. Fig. 3e and f show the Nyquist plots of AG/NBP/S and AG/S after 5 cycles activation. The above Nyquist plots can be well fitted with the equivalent circuit in the insets, in which R_s represents the internal resistance, and R_{ct} |CPE2 component represents charge transfer process, respectively. For the AG/NBP/S

cathode, an additional process, manifested in the depressed medium frequency semi-circle, is observed. We attribute such process to the response of the adsorbed NBP layer to the external perturbed electric field in EIS, represented by R_L |CPE1 component. It should be noted that the $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ layer for the AG/S cathode can also be formed for longer cycling, but such process does not complete at the 5th cycling [48]. At low frequency, the process is limited by the transportation of Li^+ , represented by CPE3. The fitting parameters of both AG/NBP/S and AG/S are listed in Table S5. It is notable that (1) R_s (1.80Ω) of AG/NBP/S is smaller than that (2.47Ω) of AG/S, indicating the higher ionic conductivity of electrolyte of the AG/NBP/S than that of the AG/S, due to that the presence of NBP in the former inhibits the dissolution of LiS_n^- and thus relieves the electrolyte viscosity; (2) R_{ct} of AG/NBP/S (13.51Ω) is lower than that of AG/S (56.49Ω), as highlighted in the smaller semi-arc of the AG/NBP/S. The reason may be attributed to that the $\text{C}_8\text{H}_4\text{NO}_2\text{S}_n\text{Li}$ brings better contact of the sulfur chain with AG via π - π interaction between NBP and AG, and thus reduces R_{ct} .

Then we compared the cycling performance of the AG/NBP/S and AG/S cathodes. Fig. 4a shows a different rate capability of AG/NBP/S and AG/S cathodes. The specific capacities of both cathodes decrease with higher C-rate, with that of AG/NBP/S remains 150 mA h g^{-1} or higher than that of AG/S at each C-rate. Especially, when the C-rate is back to 0.1 C ($1.0 \text{ C} = 1675 \text{ mA g}^{-1}$), AG/NBP/S returns to the higher specific capacity of 951 mA h g^{-1} and maintains cycling stability in the subsequent cycles. On the other hand, the specific capacity of AG/S is only 720 mA h g^{-1} when the C-rate is back to 0.1 C, with inferior stability in the subsequent cycling. Based on the electrochemical tests in Fig. 4a, the improved reversibility and capability of the AG/NBP/S cathode, thanks to the presence of NBP, are evident. The better rate performance may be attributed to the polar nature of NBP, with strong dipole-charge and dipole-dipole interactions between NBP and Li^+ as well as electrolyte molecules, which brings both Li^+ and electrolyte altogether into the micropores that are not easily penetrated by Li^+ alone (c.f. Scheme 1d). Thus, the presence of the polar NBP on the otherwise non-polar AG surface improves the wettability of the electrode, and such effect is beneficial to the penetration of Li^+ into the porous electrode. The long-term cycling performance of the sulfur composite cathodes was further investigated by the cycling tests at 0.2 C in Fig. 4b. The results show that the AG/NBP/S cathode exhibits long-term cycling stability for 500 cycles with a low ca-

Figure 4 (a) The rate capability of AG/NBP/S and AG/S at different C-rates, with corresponding coulombic efficiency. (b) Long-term cycling of the AG/NBP/S and AG/S at 0.2 C (1.0 C = 1675 mA g⁻¹), and the corresponding coulombic efficiency.

capacity decay rate of 0.07% per cycle and good coulombic efficiency close to 100%. In contrast, the AG/S cathode shows an uninterrupted capacity decay and a deteriorative coulombic efficiency. On the other hand, it also shows a faster capacity decay for the AG/NBP/S cathode at the initial 30 cycles. As the dissolved LiS_n^- is gradually captured by NBP and finally produces $\text{C}_8\text{H}_4\text{NO}_2\text{SLi}$ on the AG surface, such process is accompanied by a part of capacity loss. The final discharge products of AG/NBP/S cathode may be $\text{C}_8\text{H}_4\text{NO}_2\text{SLi}$ and Li_2S from the reduction of $\text{C}_8\text{H}_4\text{NO}_2\text{S}_n\text{Li}$, since no redox peaks of other species or functional groups can be observed in CV curves of AG/NBP/S. Therefore, the total electrochemical reaction of $\text{C}_8\text{H}_4\text{NO}_2\text{S}_n\text{Li}$ during discharging process may be described by (taking $n=6$ as an example)

The final discharge product $\text{C}_8\text{H}_4\text{NO}_2\text{SLi}$ can deliver only one electron, in contrast to two electron transfer per S atom for the final product Li_2S . Consequently, discharging from S_8 to $\text{C}_8\text{H}_4\text{NO}_2\text{SLi}$ delivers totally 15 electrons, thus inevitably leading to capacity loss, which is similar to the organosulfur cathode with the full discharge products of RSLi and Li_2S , where R represents an organic moiety [49–51]. Once NBP is completely consumed during cycling, this part of capacity loss is terminated, with good cycling stability in the follow-up cycling.

Upon discharging, Li ions in the cathode/electrolyte interface are quickly consumed to form Li_2S_n . As electrons are continuously accumulating on the cathode, the dissolution of Li_2S_n is unavoidable to form the dissolved LiS_n^- with an additional Li^+ to neutralize electron in order to maintain the voltage. The NBP molecules, anchored on the AG surface *via* π - π interaction, provide an alternative route to depress the dissolution of LiS_n^- by grafting it *via* an $\text{S}_\text{N}2$ reaction. This is a good strategy to immobilize the

dissolved LiS_n^- , while bringing the latter in better interaction with the electrode, and lead to improved cycling performance. In addition, thanks to the polar nature of NBP, both Li^+ and polar solvent DOL can be easily pulled into the micro-mesopores of AG with better wettability to assist the redox reaction with lower resistance, as shown in the EIS of Fig. 3e and f. In that case, NBP may be considered as a multi-functional material, which can (1) depress the dissolution of LiS_n^- and improve the interaction of polysulfides with the AG surface, and (2) enhance the diffusion of the electrolyte.

CONCLUSIONS

In summary, we adopted a multi-functional molecule, NBP, and prepared AG/NBP/S composite cathode for Li-S battery with improved electrochemical performance. The mechanism of NBP in the cathode was studied both experimentally and computationally. The current study demonstrates that the carbophilic NBP is anchored on the AG surface *via* π - π stacking interaction. During discharging, the dissolved LiS_n^- is grafted onto NBP *via* $\text{S}_\text{N}2$ reaction to form $\text{C}_8\text{H}_4\text{NO}_2\text{S}_n\text{Li}$ and thus is immobilized on the AG surface. In addition, due to the lithophilic and solvophilic nature of NBP, both Li^+ and DOL electrolyte molecules are easily pulled into the micro-mesopores with better wettability of cathode materials to facilitate the diffusion of the electrolyte. Thus, NBP, as a multi-functional material in Li-S battery, can not only depress the dissolution of LiS_n^- and improve the interaction of polysulfides with the AG surface, but also enhance the diffusion of the electrolyte. The above features of the composite cathode ensure improved electrochemical performance with cycling stability. We hope the finding in this study could deepen the understanding of the dissolution-precipitation process toward the design of better functional materials in Li-S battery.

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嫁接多硫化物到功能化的氮-卤化合物上实现高性能锂硫电池

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摘要 锂硫(Li-S)电池因其能量密度高, 被认为是最有前景的储能系统, 但多硫化锂在电解液中的溶解阻碍了其实际应用. 本工作将 *N*-溴邻苯二甲酰亚胺($\text{C}_8\text{H}_4\text{NO}_2\text{Br}$, NBP), 一种具有亲碳、亲硫、亲锂、亲溶剂性质的芳香分子, 引入到活性石墨烯(AG)中, 制备出了硫复合阴极. 并证实了亲碳的NBP能够很容易地通过 π - π 堆叠的相互作用固定到AG上. 在放电过程中, 溶解的多硫化锂阴离子(LiS_n^-)通过 S_8 取代反应自发地嫁接到亲硫的NBP上, 生成 $\text{C}_8\text{H}_4\text{--NO}_2\text{S}_n\text{Li}$, 从而将溶解的 LiS_n^- 带回到复合阴极的AG表面. 此外, NBP的亲锂性和亲溶剂性提高了多孔复合阴极的润湿性, 电解质分子容易渗透到AG的微孔中, 促进了电解质的扩散. 因此, 在锂硫电池中, NBP作为一种多功能的化合物, 具有固定多硫离子的功能, 并能增强电解质的扩散. NBP的上述特性使得硫复合阴极在循环稳定性方面具有较好的电化学性能.