Long-Life and High-Areal-Capacity Li–S Batteries Enabled by a Light-Weight Polar Host with Intrinsic Polysulfide Adsorption

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ABSTRACT: Lithium–sulfur batteries are attractive electrochemical energy storage systems due to their high theoretical energy density and very high natural abundance of sulfur. However, practically, Li–S batteries suffer from short cycling life and low sulfur utilization, particularly in the case of high-sulfur-loaded cathodes. Here, we report on a light-weight nanoporous graphitic carbon nitride (high-surface-area g-C₃N₄) that enables a sulfur electrode with an ultralow long-term capacity fade rate of 0.04% per cycle over 1500 cycles at a practical C/2 rate. More importantly, it exhibits good high-sulfur-loading areal capacity (up to 3.5 mAh cm⁻²) with stable cell performance. We demonstrate the strong chemical interaction of g-C₃N₄ with polysulfides using a combination of spectroscopic experimental studies and first-principles calculations. The 53.5% concentration of accessible pyridinic nitrogen polysulfide adsorption sites is shown to be key for the greatly improved cycling performance compared to that of N-doped carbons.

KEYWORDS: lithium–sulfur battery, graphitic carbon nitride, long cycle life, polysulfide adsorption, light-weight

The increasing demand for sustainable but intermittent energy sources such as solar or wind energy has created massive markets for advanced energy storage devices. Lithium–sulfur (Li–S) batteries are considered as one of the most promising next-generation batteries for electric vehicle (EV) applications, due to the high theoretical specific capacity (1675 mA h g⁻¹) and gravimetric energy density (2600 Wh kg⁻¹) of sulfur. Additional advantages of low cost and high natural abundance make this element an apparently ideal electrode material. However, Li–S batteries still face problems including low sulfur utilization, poor cycle life, and an inability to achieve good capacity at high sulfur loading. These difficulties originate mainly from the low conductivity of the end-member products (sulfur and Li₂S), a large volume change upon discharge, early precipitation of insulating Li₂S in highly concentrated media, and the shuttling of lithium polysulfide (LiPS) intermediates between the two electrodes.

In order to address these problems, various approaches have been proposed that fall into three categories: (i) confining LiPSs within the cathode through material or electrode design, (ii) modifying the liquid electrolyte or employing solid electrolytes, and (iii) protecting the anode via coatings and electrolyte additives. Most efforts have focused on designing carbon-based cathodes, such as micro/mesoporous carbons, porous hollow carbon nanospheres, carbon nanofibers/nanotubes, and graphene nanosheets. These sulfur hosts provide electronic conductivity and physical confinement of LiPSs within the nonpolar carbon frameworks. More recently, in light of the ineffectiveness of physical interactions of nonpolar carbons with polar LiPSs, researchers have explored highly modified carbon surfaces in order to better adsorb the LiPSs. Examples of such materials include graphene oxide and N-doped carbons. However, there is a threshold for the N concentration doped in carbon lattices (14.5 atom %). Practically, what is achieved is usually less than 5%, which places a constraint on the density of active sites for LiPS adsorption. In a deviation from carbonaceous materials, metal oxides (SiO₂, TiO₂, VOₓ, MnO₂) and metal–organic frameworks, which are inherently polar materials, have been shown to strongly adsorb and entrap LiPSs. Also, highly conductive materials such as Ti₃O₇, indium tin oxide, and MXene phases have been reported to provide a sulphilic and conductive surface for enhanced redox of LiPSs. Nonetheless, an ultrahigh surface area of such relatively heavy materials is needed to...
fully realize the promise of the chemical interactions. A light-weight sulfur host material that contains a very high accessible fraction of LiPS chemisorption sites well-suited to realize a long-life and high-loading Li–S battery.

Here, we describe a strategy of chemically confining the LiPSs in a light-weight polar host material, graphitic carbon nitride (g-C3N4). It is a highly ordered polymeric material consisting of continuous tri-s-triazine building blocks, with a structure analogous to layered graphite.47 The intrinsic high charge polarity of g-C3N4 embraces enriched LiPS binding sites (pyridinic N) as we demonstrate with first-principles calculations. This provides superior LiPS adsorptivity, which leads to controlled precipitation not only of the discharge product Li2S upon reduction of LiPSs but also of the charge product (elemental sulfur) formed upon their oxidation, as shown previously.48,49 Additionally, the polymeric nature of g-C3N4 allows for structural elasticity that can aid in accommodating the volume expansion upon formation of Li2S on discharge.49 We note that Zhang et al. recently reported g-C3N4 and oxygenated C3N4 (o-C3N4) prepared by pyrolysis of urea and glucose as sulfur host materials. However, these are quite different materials, and their approach is very different than ours. Their synthesized g-C3N4 exhibits a very low accessible surface area (73 m² g⁻¹), thus leading to rapid capacity fading. The o-C3N4 structure is described as carbon-nitride-supported oxygenated carbon, with a low nitrogen content of 15–20 wt %. Thus, the stable cycling of the sulfur cathode at a lower sulfur content (56 wt %) and low-areal sulfur loading was ascribed to the surface oxygen groups instead of the cathode at a lower sulfur content (56 wt %) and low-areal sulfur loading.

RESULTS AND DISCUSSION

Nanoporous g-C3N4 was synthesized by polycondensation of cyanamide (CN2H2) based on a hard-template (colloidal silica) approach,50 as shown schematically in Figure 1a. Upon heat treatment of cyanamide at 550 °C, graphitic C3N4 is formed via a stepwise condensation of the melamine units with the release of NH3 gas. The product is reported to be thermally stable up to 600 °C under air. The graphitic nature of g-C3N4 is confirmed by its XRD pattern (Figure S1a, Supporting Information), where the two reflections at 27.6 and 13.1° correspond to the interlayer stacking (002) and in-plane (100) repeating motifs of the tri-s-triazine network (see Figure 1a). The structure of g-C3N4 was confirmed by Fourier transform infrared spectroscopy (FTIR, Figure S1b). The bands at 810, 1200–1600, and 3200 cm⁻¹ correspond to the s-triazine units, the tri-s-triazine units, and the residue surface amino groups, respectively.50 X-ray photoelectron spectroscopy (XPS) studies provide detailed information on the chemical environment of the N and C sites. The N 1s spectrum (Figure 1b) shows three components, of which the major is pyridinic N (398.2 eV) and two others are tertiary nitrogen in N–(C)3 groups (399.8 eV) and amino groups (400.8 eV). The corresponding C–N–C component (287.7 eV) is observed in the C 1s spectrum (Figure S1d), where the peak at 284.8 eV is attributed to adventitious carbon. The O 1s spectrum (Figure S1e) suggests that g-C3N4 also contains a small fraction of surface oxygen groups (C=O and C–O) formed by exposure of dangling bonds on the surface to ambient atmosphere. We note that both surface amino and oxygen groups are reported to bind LiPSs/Li2S species, which adds to the advantages of the g-C3N4 material.27,51 This concept has been employed in the fabrication of microporous oxygenated carbon nitride prepared by a completely different route, which contains about 4-fold less nitrogen in its structure.49

The scanning electron microscopy image (SEM, Figure 1d) of g-C3N4 reveals a morphology of interconnected nanoparticles with interparticle pores. This is confirmed by the bright- and dark-field transmission electron microscopy (TEM) images (Figure 1e), where disordered pores are evident, evenly distributed over the framework. Nitrogen adsorption/desorption measurement confirms that the nanostructured g-C3N4 consists of mostly mesopores (~5 nm) and some micropores formed by SiO2 nanoparticle templating and NH3 gas evolution upon condensation, respectively (Figure 1c). A high surface area of 615 m² g⁻¹ with a pore volume of 0.97 cm³ g⁻¹ is achieved. The energy-dispersive spectroscopy (EDS) mapping (Figure S2) shows a uniform distribution of C and N, with a nitrogen concentration of 53.5 atom %. This value is more than 10-fold higher than that of most reported N-doped carbons.28,30,32 The high nitrogen concentration and surface area is crucial for interface-based LiPS binding. To prove this, a N-doped carbon (NdC) synthesized using a similar hard-template approach and a commercial carbon—Vulcan carbon (VC)—were used as comparisons in this study. The NdC contains pyridinic N, pyrrolic N, and graphitic N, with a total nitrogen concentration of 3.1 atom %. This value is more than 10-fold higher than that of most reported N-doped carbons.28,30,32 The high nitrogen concentration and surface area is crucial for interface-based LiPS binding. To prove this, a N-doped carbon (NdC) synthesized using a similar hard-template approach and a commercial carbon—Vulcan carbon (VC)—were used as comparisons in this study. The NdC contains pyridinic N, pyrrolic N, and graphitic N, with a total nitrogen concentration of 3.1 atom % (Figure S1f,g). The NdC and VC also exhibit nanoparticle morphology, as shown in Figure S3. The surface area (and pore volume) of NdC and VC are 922 m² g⁻¹ (1.42 cm³ g⁻¹) and 260 m² g⁻¹ (0.87 cm³ g⁻¹), respectively.

The adsorptivity of the host materials toward LiPSs was quantified using a potentiostatic titration method by measuring the residual LiPS concentration upon contact with the respective host materials in an ether-based solution.52 The medium chain-length polysulide Li2S4 was used as the representative LiPS. The adsorptivities of g-C3N4, NdC, VC, a commercial mesoporous TiO2 (meso-TiO2), and Super P...
were evaluated (Figure 2a). The NdC adsorbs 20-fold LiPS compared to that of VC or Super P (comparable to mesoporous TiO₂), while g-C₃N₄ adsorbs almost twice that of NdC (i.e., 4.25 mg of polysulphide per 10 mg of material) even with a 33% lower surface area. This demonstrates the beneficial effect of the increased pyridinic N active site fraction.

The underlying factors responsible for the superior LiPS adsorptivity of g-C₃N₄ were investigated using FTIR and XPS. The spectrum of the g-C₃N₄/Li₂S₄ solid powder recovered from the titration experiment described above was compared to that of g-C₃N₄ and Li₂S₄ alone. Li₂S₄ exhibits a prominent FTIR peak at 1620 cm⁻¹, corresponding to a Li–S component at 169 eV in g-C₃N₄/Li₂S₄. The downward shift indicates electron transfer to Li⁺ due to the thiosulfate and polythionate species formed by reaction between Li₂S₄ and the residual surface oxygen functional groups, as we reported for graphene oxide.50

To fully understand the nature and strength of the interaction of g-C₃N₄ with LiPSs, first-principles calculations based on the density functional theory framework were performed. In order to quantitatively compare the substrates in terms of their ability to bind LiPSs, the g-C₃N₄ and doped/pristine carbons were, respectively, modeled by a monolayer 2 × 2 g-C₃N₄ and a 6 × 6 graphene supercell to create the same substrate supercell size (only 4.0% difference).54 The number of pyridinic N atoms per supercell was varied (0, 1, 2, and 3) to model the N-doped carbon and achieve different N concentrations (0, 0.4, 2.9, and 4.4%; here denoted as NOC, N1C, N2C, and N3C). The Li₂S₂ molecule was mainly used as the representative polysulphide for simplicity. The number of Li₂S₂ molecules adsorbed on the substrates was varied to quantify the Li₂S₂ binding capacity of the respective substrate. Long-chain Li₂S₄ and the end-member LiS were also examined (see Table 1).

For the S 2p spectrum, Li₂S₄ shows two components that correspond to terminal sulfur S²⁻ and bridging sulfur S⁰ at 161.5 and 163.1 eV, respectively (Figure 2d).52 The S 2p spectrum exhibits 2p₁/₂ and 2p₃/₂ doublets due to the splitting of 2p energy levels, and only the peak positions of 2p₃/₂ components are cited here. Upon contact with g-C₃N₄, the S 2p spectrum shifts by more than 0.5 eV toward lower binding energy, with the S²⁻ affected more than the S⁰ (Figure 2f). This shows that the terminal sulphide groups acquire a more negative charge as a result of charge polarization; a finding confirmed by DFT calculations discussed in the next section. Very minor components at 166–169 eV in g-C₃N₄/Li₂S₄ are due to the thiosulfate and polythionate species formed by reaction between Li₂S₄ and the residual surface oxygen functional groups, as we reported for graphene oxide.50

The charge density distribution maps of the host substrates are shown in the top panels in Figures 3 and S4a,b. The pristine carbon NOC shows a uniform distribution of the charge over the carbon lattice, whereas the pyridinic N in N-doped carbon bears a negative charge (electron-rich), represented by the red electron density contour curves (Figure 3a,b). Similarly, for all of the N positions in g-C₃N₄, the N atoms bear a negative charge as expected (Figure 3c). The most stable geometrical configurations of the respective substrates—binding 2 Li₂S₂ per supercell—are representatively shown in Figures 3 and S4b,c. The binding energy values are normalized by the number of Li₂S₂ adsorbed. There is no specific binding of Li₂S₄ with the pristine carbon substrate (Figure 3a), consistent with its low binding energy of 0.51 eV. For both N-doped carbon N3C and g-C₃N₄, the Li₂S₄ is bonded to the substrate via a favorable Li⁺–N⁰ bonding, indicated by the shortened bond distance (the average Li–N bonding is 2.14 and 2.06 Å, respectively, as compared to 2.46 Å for pristine carbon, Figure 3b,c). This is further confirmed by the geometries of g-C₃N₄ binding 1 or 4 Li₂S₄ molecules shown in Figure S4e,f. More importantly, we clearly observed charge transfer (by Bader charge analysis) onto

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**Figure 2.** (a) Polysulfide (Li₂S₄) adsorptivity of g-C₃N₄ and NdC, with comparison to Super P, Vulcan carbon, and a commercial mesoporous TiO₂, as evaluated by the electrochemical titration method. (b) FTIR spectrum of g-C₃N₄, g-C₃N₄/Li₂S₄ and Li₂S₄, with the dotted lines and asterisk, respectively, showing the peak shifts and new peak for g-C₃N₄/Li₂S₄. (c) High-resolution XPS (c,e) Li 1s and (d,f) S 2p spectra of (c,d) Li₂S₄ and (e,f) g-C₃N₄/Li₂S₄.

**Table 1. Summary of Binding Energies for Different Polysulfides on the Surface of Pristine Carbon, Doped Carbons (at Different Concentrations), and g-C₃N₄**

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>pristine carbon</th>
<th>N1C</th>
<th>N2C</th>
<th>N3C</th>
<th>g-C₃N₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂S₄</td>
<td>0.47</td>
<td>0.73</td>
<td>1.83</td>
<td>1.55</td>
<td>4.08</td>
</tr>
<tr>
<td>Li₂S₂</td>
<td>0.51</td>
<td>0.63</td>
<td>0.84</td>
<td>1.57</td>
<td>1.73</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>0.06</td>
<td>0.40</td>
<td>0.42</td>
<td>0.54</td>
<td>1.70</td>
</tr>
</tbody>
</table>

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the $S_2^{2−}$ cluster upon contact with the substrate (Figure S4a), further lending support to the XPS S 2p studies discussed above. The calculated charge transfer of Li$^+$ ions is too small to measure, due to the few valence electrons included in the pseudopotential models. The variation of the binding energy values with respect to the N concentration in doped carbons and g-C$_3$N$_4$ is shown in Figure 3d. The superior binding ability of g-C$_3$N$_4$ is even more apparent at high concentrations of Li$_2$S$_2$. This is because g-C$_3$N$_4$ has more pyridinic N active sites available for adsorption, whereas N-doped carbon does not, as shown for the N3C binding of 4 Li$_2$S$_2$ molecules in Figure S4d. The charge transfer number for S$_2^{2−}$ clusters shows the same relationship with respect to the binding energy values (Figure S4a).

The binding strength of the end-member discharge product (Li$_2$S) shows the same trend as Li$_2$S$_2$: the binding energy increases with increasing concentration of doped N, with g-C$_3$N$_4$ exhibiting the highest binding energy of 4.08 eV (Table 1). For the larger molecule Li$_2$S$_4$, the binding energy on doped carbons is higher than that on pristine carbon, although the values for Li$_2$S$_4$ are lower than the respective values for Li$_2$S (consistent with results reported in ref 55). However, the binding energy for Li$_2$S$_4$ is still very close to Li$_2$S, namely, 1.70 eV. Thus, we believe that the high N concentration of 53.5 atom % in g-C$_3$N$_4$ along with its very high surface area, contributes to its high LiPS adsorptivity. Based on a back-of-the-envelope calculation, we also note that the 53.5 atom % N concentration is sufficient to adsorb all the polysulfide of a sulfur cathode containing 75 wt % sulfur (see Supporting Information for details).

Sulfur electrodes were fabricated to evaluate the practical effects of high N concentration and superior LiPS adsorptivity of g-C$_3$N$_4$ on the cycling performance of a Li–S battery. Sulfur composites with 75 wt % sulfur were prepared by the melt-diffusion method for g-C$_3$N$_4$, NdC, and VC (Figure S5), denoted as g-C$_3$N$_4$/S75, NdC/S75, and VC/S75, respectively. First, cells with a “typical” low sulfur loading of 1.5 mg cm$^{-2}$ and an electrolyte/sulfur ratio of 15:1 (μL/mg) were examined in galvanostatic mode to enable comparison with previously published work. Higher loading cathodes are described in the next section. All Li–S cells were cycled at a slow C/20 (1C = 1675 mAh g$^{-1}$) rate for the first cycle to enable electrode conditioning prior to increasing the rate for the duration of cycling. Cells constructed with g-C$_3$N$_4$ alone as a cathode versus...
Li metal exhibit no electrochemical redox reaction during the 1.8−3 V (vs Li/Li+) window, contributing to a negligible capacity of only ~1 mA h g⁻¹ (Figure S6). This confirms that the as-synthesized g-C₃N₄ does not participate in the redox reaction during the cycling of a Li−S cell.

Figure 4a shows the first-cycle galvanostatic voltage profiles of the g-C₃N₄/S₇₅ electrode at variable rates, which all exhibit typical two-plateau discharge curves. A high discharge capacity of 1170, 900, 855, and 785 mA h g⁻¹ (based on the mass of sulfur) was achieved at C/20, C/5, C/2, and C rates, respectively. The specific capacity reported here is slightly lower than that for other electrodes we have reported, due to the poorly semiconducting nature of g-C₃N₄.⁵⁶ However, the addition of 15 wt % Super P carbon in the electrode guarantees good rate capability, as indicated by the negligible polarization increase upon increasing the rate. Cycling tests at different rates (C, C/2, C/5) of the g-C₃N₄/S₇₅ electrodes all show only a slight capacity loss over 200 cycles (Figure 4b). For example, a discharge capacity of 730 mA h g⁻¹ that corresponds to 93% of the initial capacity was retained over 200 cycles at a C rate. Long-term cycling of the electrodes was carried out to demonstrate the superior lifetime of g-C₃N₄ over N-doped/pristine carbon-based electrodes. At a practical intermediate current density corresponding to C/2 (Figure 4d), an ultralow capacity fade rate of 0.04% per cycle for 1500 cycles was achieved over 3 months of cycling for the g-C₃N₄/S₇₅ electrode, while the NdC/S₇₅ and VC/S₇₅ electrodes faded rapidly to low capacities of 280 mA h g⁻¹ over 500 and 150 cycles, respectively.

Lower rate C/5 cycling was also examined (Figure 4c). The g-C₃N₄/S₇₅ electrode retained 620 mA h g⁻¹ capacity after 500 cycles, corresponding to a capacity fade rate of 0.06% per cycle, whereas NdC/S₇₅ and VC/S₇₅ electrode cells both experienced very rapid capacity fading. We also note that the as-prepared g-C₃N₄/S₇₅ electrode shows a cycling performance far superior to that of previously reported oxygenated carbon-nitride-based cathodes (i.e., 0.10% fade per cycle over 500 cycles, with only 56 wt% sulfur content).⁴⁹ To further probe the effectiveness of the chemical interaction of g-C₃N₄ on the inhibition of the LiPS shuttle, C₃N₄/S₇₅ cells identical to those above were run in a LiNO₃-free electrolyte. Figure S7a,b shows that almost negligible first-cycle overcharge was observed for the g-C₃N₄/S₇₅ electrode. This is in sharp contrast to the very significant overcharge exhibited by both NdC/S₇₅ and VC/S₇₅ along with low Coulombic efficiencies of 76 and 25%, respectively. Much higher average Coulombic efficiency for the g-C₃N₄/S₇₅ cell was obtained over 100 cycles compared to NdC/S₇₅ (~92% vs ~81%), indicative of a significantly reduced polysulphide shuttle. In order to evaluate the potential of g-C₃N₄/S₇₅ electrodes in high-power energy storage applications, the electrode was also subjected to high rate cycling at a C rate (Figure S7c). A discharge capacity of 370 mA h g⁻¹ was retained over 1000 cycles with a fade rate of 0.05% per cycle, indicative of very good rate capability. The morphology of an electrode after 200 cycles at a discharged state was examined (Figure S8). No glassy Li₂S layer is evident on the cathode surface nor on the individual bulk monoliths, which is further evidence of effective confinement of polysulfides within the porous cathode.

Achieving high sulfur loading is critical in order for high-areal capacity and volumetric energy density.⁵⁶,⁵⁷,⁵⁸ Compared with traditional graphene nanosheets or carbon nanosphere-based sulfur composites, the bulk monolithic architecture of g-C₃N₄—that nonetheless still contains highly interconnected nanoporous channels—allows better particle packing and thus thicker electrodes to be fabricated.⁵⁸ Here, thick electrodes were prepared at different sulfur loadings (3−5 mg cm⁻², thickness = 90−150 μm), with the addition of 5 wt % of graphene (total carbon additive 10 wt %) during slurry preparation. The graphene additive was used to create a 3D electron conducting pathway and to promote electrolyte wetting across the thick electrodes.⁵⁷ This was successful, as demonstrated by the negligible variation in the voltage polarization for electrodes with different loadings (Figure 5a).

All high-areal loading cells were conditioned by cycling at C/20 for the first cycle. As shown in Figure 5b, an areal discharge capacity of 3.15 mA h cm⁻² was achieved at C/20 for a 3.0 mg cm⁻² electrode, which increases to 4.27 mA h cm⁻² for the 5.0 mg cm⁻² loading. The cycling performance for the thick electrodes at C/5 is displayed in Figure 5c, where all electrodes show very stable cycling. The longer-term cycling of the 3.0 mg cm⁻² electrode is extremely stable following the first 20 cycles of conditioning (Figure 5d). Although the areal capacity of 4.27 mA h cm⁻² (at a rate of 0.42 mA cm⁻²) 3.35 mA h cm⁻² (1.67 mA cm⁻²) reported here (Figure 5b,c) is not as high as that of some recently reported well-architected carbon-based electrodes,²⁸,³⁴,³⁵,³⁹ we consider our slurry-derived electrodes to exhibit reasonably high-areal capacity, and especially, we are able to show outstanding cycling stability over 175 cycles. Work is ongoing to construct a smart architecture that incorporates a g-C₃N₄ composite and provides conductive pathways and better volume accommodation.

CONCLUSIONS

Targeting high-energy-density Li−S batteries with controlled polysulphide shuttling and a long cycling life, a light-weight nanoporous graphitic carbon nitride material shows much promise as a sulfur host. In addition to low mass, high-surface-area g-C₃N₄ is advantageous for containing a high N concentration of up to 53.5 atom %, giving rise to its superior

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LiPS adsorptivity over N-doped carbons. The nature of the interaction between g-C3N4 and LiPS, revealed for the first time by FTIR and XPS studies, shows a favorable Li+–Nδ− interaction. First-principles calculations not only confirm this but also provide a quantitative evaluation of the significant effect of high pyridinic N concentration on improving the LiPS adsorptivity for g-C3N4. We have demonstrated the excellent long-term cycling performance of the g-C3N4/S75 electrode in a Li–S cell, with as low as 0.04% fade per cycle over 1500 cycles at a C/2 rate. More importantly, high-sulfur-loading electrodes with up to 4.2 mAh cm−2 capacity and stable cycling performance were also demonstrated. This paves the way for future exploration of new Li–S host materials, embracing improved cathode architecture with these guidelines in mind.

EXPERIMENTAL SECTION

Synthesis of g-C3N4 and NdC. The nanoporous g-C3N4 was synthesized using a hard-template approach. Typically, cyanamide and Ludox (AS-30) silica nanoparticle (12 nm) colloid solutions with a cyanamide/SiO2 weight ratio of 1:1.5 were mixed by stirring at 60 °C for 6 h. The as-formed dispersion was dried in vacuo at 60 °C overnight to form the white composite powder. The g-C3N4 powder was obtained by thermal condensation of the precursor powder at 550 °C for 4 h (4 °C/min ramping) and HF (5 wt %) etching. The sample was washed and dried at 90 °C in vacuo before use.

N-doped carbon was synthesized in the same way, except that polydopamine was used for the N and C source. Polymerization of dopamine was carried out in the presence of tris(hydroxymethyl)aminomethane in aqueous solution at 25 °C overnight (w/w 2:1).

Synthesis of Sulfur Composites. The g-C3N4/S75 sulfur composite was prepared via a melt-diffusion method. The g-C3N4 powder was mixed with elemental sulfur in the desired ratio, and the mixture was heated under ambient atmosphere at 155 °C for 12 h. The NdC/S75 and VC/S75 composites were prepared by the same general route.

Synthesis of LiSx and LiS2x Composite. The LiSx was synthesized by reacting Li2S and lithium superhydride (LiEtBH) in the desired ratio in anhydrous tetrahydrofuran at room temperature for 1 h inside an argon glovebox (<2 ppm of O2 and H2O). The resulting solid was washed with toluene and vacuum-dried. To study the interaction of g-C3N4 with LiSx, by XPS and FTIR, the LiSx solutions were prepared by dissolving 8 mg of Li2S4 in 10 mL of 1,2-dimethoxyethane (DME) and then centrifuged. The solid was recovered and dried in vacuo. All procedures were carried out in an argon-filled glovebox with <3 ppm of H2O and O2.

Polysulfide Adsorptivity Measurements. Polysulfide adsorptivity was evaluated by electrochemical titration that determines the amount of residual LiPS in solution after contact with the respective host cathode materials.25 Sample solutions were prepared by stirring a known mass of materials (g-C3N4, NdC, VC, Super P, meso-TiO2) in a known concentration of LiSx in tetraethylglycol dimethyl ether (TEGDME), respectively. The mixtures were stirred overnight, and after centrifugation, the supernatant was collected. It was diluted using 1 M LiClO4 in TEGDME, and the solution was electrochemically titrated to determine residual polysulfide content. The potential was held at 3.0 V for a complete oxidation (vs Li metal anode), and the capacity was determined based on the integrated current passed until it reached 0 mA. The actual adsorption was determined by extrapolation from a calibration curve using standard materials.26 All procedures were performed in a H-type cell in an argon-filled glovebox.

Electrochemistry Measurements. For the preparation of electrodes with 1.5 mg cm−2 sulfur loading, sulfur composites with Super P and PVDF binder were dispersed in dimethylformamide in a weight ratio of 7:5:1.5:1. For the preparation of electrodes with 3–5 mg cm−2 sulfur loading, sulfur composites with Super P, graphene (ACS Materials), styrene butadiene rubber aqueous binder, and carboxymethyl cellulose binder were dispersed in a mixture solvent of deionized water and dimethylformamide (2:1 v/v) in a weight ratio of 8:0.5:0.5:0.5:0.5. The slurry was doctor-blade coated onto carbon paper (AvCarb PS0) to prepare the cathodes. The PS0 paper was used as received without any pretreatment and cut into 16 cm diameter disks. The electrodes were dried at 60 °C overnight and assembled into 2325 coin cells in an Ar-filled glovebox. A lithium foil anode and an electrolyte comprising 1 M bis(trifluoromethanesulfonyl)imide lithium in a mixture of 1,2-dimethoxyethane and 1,3-dioxolane (v/v 1:1) was used. A 2 wt % of LiNO3 was added for LiNO3-containing electrolyte. The cells were operated in a voltage window of 1.8–3.0 V (or 1.7–3.0 V, 1.9–3.0 V, depending on rates) using a BT2000 battery cycle (Arbin Instruments).

Materials Characterization. XRD patterns were obtained on a Bruker D8-Advance X-ray diffractometer, operating at 40 kV/30 mA with Cu Kα radiation. LEO 1530 field emission SEM (Zeiss) was used for SEM studies and EDX elemental mapping. Electrodes were retrieved after cycling by dispersing the cells in the glovebox and washing them with DME. Electrodes were transferred to the SEM chamber under argon atmosphere protection. The TEM samples were imaged using a JEOL 2100F TEM/STEM operating at 200 keV. The surface area and pore volume were measured using a Quantachrome Autosorb-1 system at 77 K. Surface areas and pore size distribution were calculated using the Brunauer–Emmett–Teller method and quenched solid density functional theory method, respectively. Temperature conductance analysis was conducted at a heating rate of 10 °C/min under a N2 flow, using a TA Instruments SDT Q600. FTIR spectra were obtained using a Bruker Tensor 37 spectrometer. XPS analysis was performed on a Thermo ESCALAB 250 instrument, using a monochromatic or non-monochromatic Al Kα source for conductive composite and nonconductive materials, respectively. The samples were transported under an argon atmosphere and transferred into the chamber anaerobically. All spectra were fitted with Gaussian–Lorentzian functions and a Shirley-type background. For S 2p spectra with 2p3/2 and 2p1/2 doublets, fitting constraints of a splitting of 1.2 eV, a peak area ratio of 2:1, and equal full width at half-maximum were applied. The binding energy values were all calibrated using the C 1s peak at 284.8 eV.

Computational Methods. First-principles calculations were performed using the plane-wave-based VASP code. Projector-augmented wave (PAW) pseudopotentials were applied to describe electron–ion interactions, and the Perdew–Burke–Ernzerhof version of the generalized gradient approximation was used for the electronic exchange correlation effect.60,61 The Li sub sv version of the PAW potential was used for Li atoms. A cutoff energy of 500 eV was used for the plane wave basis to ensure convergence. Spin-polarized calculations were employed. A single-layer graphene of a 6 × 6 supercell size was adopted as the platform for pristine and N-doped carbon. Variable numbers of pyridinic nitrogen atoms per supercell (1–3) were incorporated to model the doped carbon. For modeling g-C3N4, a 2 × 2 supercell size was used to achieve the same supercell size for both carbon and g-C3N4. A vacuum layer of 15 Å was used in the vertical direction in order to exclude the interaction between the layer and its images. The conjugate gradient algorithm was used for ionic relaxation. The binding energy (Ebind) of lithium polysulfides on the substrates is defined as

\[ E_{\text{bind}} = \left( E_{\text{tot}} - E_{\text{sub}} \right) / n \]

where Esub, Eps, and Esub+ps represent the ground-state energies of the substrate, respective polysulfide, and substrate polysulfide, and n is the number of respective polysulfides employed. A larger positive value is indicative of greater binding ability.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b07347.

Characterization of g-C3N4/ND SEI images, variation of charge transfer onto S2− anion clusters, back-of-the-
envelope calculations of polysulfide absorptivity, and supporting electrochemical studies (PDF)

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Notes
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