Multifunctional Effects of Sulfonyl-Anchored, Dual-Doped Multilayered Graphene for High Areal Capacity Lithium Sulfur Batteries

Masud Rana,† Qiu He,‡ Bin Luo,⁎† Tongen Lin,† Lingbing Ran,† Ming Li,† Ian Gentle,* and Ruth Knibbe*†

¹Materials Engineering, School of Mechanical and Mining Engineering, ²Nanomaterials Centre, School of Chemical Engineering and Australian Institute for Bioengineering and Nanotechnology, and ³School of Chemistry and Molecular Biosciences, Faculty of Science, The University of Queensland, St Lucia, Queensland 4072, Australia

²State School Key Laboratory of Silicate Materials for Architectures, International School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, Hubei, China

Supporting Information

ABSTRACT: Li–S batteries (LSBs) require a minimum 6 mAh cm⁻² areal capacity to compete with the state-of-the-art lithium ion batteries (LIBs). However, this areal capacity is difficult to achieve due to a major technical issue—the shuttle effect. Nonporc carbon materials limit the shuttle effect through physical confinement. However, the polar polysulfides (PSs) only provide weak intermolecular interactions (0.1–0.7 eV) with these nonporc carbon materials. The physically encapsulated PSs inside the nonporc carbon scaffold eventually diffuses out and starts shuttling. Chemically interactive hosts are more effective at interacting with the PSs due to high binding energies. Herein, a multifunctional separator coating of nitrogen-doped multilayer graphene (NGN) and −SO₃⁻ containing Nafion (N-NGN) is used to mitigate PS shuttling and to produce a high areal capacity LSB. The Nafion is used as a binder instead of PVDF to provide an additional advantage of −SO₃⁻ to chemically bind the PS. The motive of this research is to investigate the effect of highly electronegative N and −SO₃⁻ (N-NGN) in comparison with the −OH, −COOH, and −SO₃⁻ groups from a hydroxyl graphene and Nafion composite (N-OHGN) to mitigate PS shuttling in LSBs. The highly conductive doped graphene architecture (N-NGN) provides efficient pathways for both electrons and ions, which accelerates the electrochemical conversion at high sulfur loading. Moreover, the electron-rich pyridine N and −SO₃⁻ show strong chemical affinity with the PS through polar–polar interactions, which is proven by the superior electrochemical performance and density functional theory calculations. Further, the N-NGN (5 h) produces a maximum areal capacity of 12.0 and 11.0 mAh cm⁻², respectively, at 15 and 12 mg cm⁻² sulfur loading. This areal capacity limit is significantly higher than the required areal capacity of LSBs for commercial application, which shows the significant strength of N-NGN as an excellent separator coating for LSBs.

1. INTRODUCTION

The successful application of rechargeable batteries for portable electronics and electric vehicles depends a number of factors including their power density, energy density, areal capacity, environmental friendliness, and manufacturing costs. Lithium-ion batteries (LIBs) are the most common commercial rechargeable battery used for portable electronic and electric vehicles.¹,² Over the years, there has been an increased demand for portable energy storage with a high energy density. The requirement of this energy density is anticipated to be beyond the gravimetric (240 Wh kg⁻¹) and volumetric (670 Wh L⁻¹) energy density of LIBs.³ Among the different alternatives, lithium sulfur batteries (LSBs) are a promising option with a high theoretical gravimetric (2600 Wh kg⁻¹) and volumetric (2800 Wh L⁻¹) energy densities, which is approximately 3–5 times that of commercialized LIBs cathodes, such as LiMn₂O₄, LiCoO₂, and LiFePO₄.⁴–⁶ Moreover, the LSBs are environmentally friendly and cost-effective (~$150 per ton) as compared to transition-metal oxide cathodes of LIBs, such as LiCoO₂ (~$10 000 per ton).²,⁷ However, LSBs are not commercially available yet due to one major technical drawback known as the shuttle effect.³ This effect can be simply defined as the dissolution of higher order polysulide (PS) intermediates in the liquid electrolyte, which can then freely diffuse from the cathode to the anode and vice versa during battery cycling.⁸,⁹ This results in insignificant irreversible capacity loss; inferior cycling stability; low sulfur utilization; lithium metal corrosion, and severe self-discharge.¹⁰,¹¹ Furthermore, sulfur (~5 × 10⁻¹⁰ S cm⁻¹) and its...
end discharge product Li$_2$S ($\sim 10^{-14}$ S cm$^{-1}$) are electronically and ionically insulating. This limits Li$^+$ and electron access to sulfur, leading to poor sulfur utilization. All of these drawbacks impede LSBs market penetration.12

The most recent research for LSBs has focused on the impregnation of sulfur into the internal spaces in porous carbon, hollow carbon spheres, carbon nanotubes, and graphene.3–26 These carbon materials mitigate the shuttle effect through physical confinement of PSs in their high surface area. However, because of weak intermolecular interactions of PS (0.1–0.7 eV) with these nonpolar carbon hosts,27 the PS eventually migrates out of the porous carbon and starts shuttling. This limits the cycling stability of the LSB. In addition, the pore sizes in the porous structures may not be appropriate to effectively prevent PS diffusion.28 More specifically, mesopores (2–50 nm) and macropores $\geq$50 nm are much larger than the soluble PS species (max $\sim$2 nm). This PS diffusion out of the cathode is expected to be more severe at high sulfur loadings.29,30 Nevertheless, advanced LSB electrode fabrication focuses on a high sulfur loading to meet the practical energy density and areal capacity of LSB.3,31 Therefore, there is a lot of interest in controlling PS shuttling through chemical interactions rather than only relying on physical confinement in porous host materials. Chemically interactive functional groups have a strong binding affinity with the PS.29,30,32 Different functional heteroatoms (N, S, O, B, F)33 or functional groups such as sulfonate (SO$_3^-$), hydroxyl (–OH), nitrile (–C≡N), carboxyl (–COOH), imine (–N═), or amine (–NH$_2$) can provide promising solutions to chemically attract PSs to produce LSBs with a high sulfur loading.27,32,34 Introducing these functional polar groups in a highly conductive carbon matrix could be an effective solution to capture PS through both chemical and physical trapping.

Graphene is a promising and versatile material owing to its excellent electronic conductivity and mechanical strength. Recently, hydroxyl graphene has been explored as a promising LSB material.35 Our research is the first to report a multiarchitectural graphene with chemically interactive functional groups (–O, –OH, –COOH) through the H$_2$O$_2$ treatment. To improve the electronic conductivity and facilitate the chemical affinity, this material was further treated at high temperature under a NH$_3$ environment to produce electronegative N groups (pyridinic, pyrrolic, and graphitic) in the graphene structure (NGN). It has been proposed by other groups that this highly electronegative N (3.07) facilitates Li$^+$ transport during LSB cycling and hinders PS migration.36 For the Celgard PP coating, the OHGN/Nafion (N–OHGN) and NGN/Nafion (N-NGN) composite was used without any additional PVDF binder (Figure 1A). The NGN graphene provides an interconnected conductive framework to facilitate fast electron transport and facilitate electrochemical reactions—encouraging sulfur utilization and reducing polarization losses. It is proposed that the shuttling is significantly reduced through a combination of polar–polar trapping of the PS (Figure 1B). The reduced polarization losses can also be attributed to the catalytic effect of both the N and –SO$_3^-$, which enhances the electrochemical kinetics.37 The pyridinic, pyrrolic, and graphitic N in the NGN36 and the –SO$_3^-$ from the Nafion traps the PS through polar–polar interactions. In addition, the NGN $d$-spacing (0.32 nm) is significantly less than the maximum PS dimension ($\sim$2 nm)35 but higher than the Li$^+$ ($\sim$0.14 nm).38 Hence, the NGN could also physically block PS migration while maintaining continuous Li$^+$ trans-
N-NGN (3 h) and the N-OHGN coated separators were investigated by the microscopy analysis. The SEM and TEM images of OHGN and NGN (3 h) powders are also shown in Figure S1. Figure 2A,C shows the surface morphologies of the N-NGN and N-OHGN coated separators, respectively, before cycling. The composite layer is uniformly dispersed on the surface of the Celgard PP separator. Their corresponding cross section SEM images are shown in Figure 2B,D, which shows an intimate contact between the coatings and the Celgard PP separator without any additional PVDF. Post-mortem analysis of the N-NGN and N-OHGN coated separators were carried out after LSB discharge (Figure S2). After operation, the N-NGN and N-OHGN coating surfaces have changed. Unusual phases are also identified on the N-NGN and N-OHGN surface, as marked by the red circle. EDS mapping indicates that this is a solid sulfur compound, strongly indicating the presence of solid Li2S phases could be well adhered on the graphene architecture. During electrochemical reaction, the PS phases escape from the carbon matrix of the electrode due to the weak intermolecular interactions between the nonpolar carbon and the PS phases.40 These PS phases can bind onto the surface of the N-NGN coating through polar–polar interactions and physical trapping, thereby suppressing the PS shuttling. In regard to this, the theoretical adsorption energy of PSs with the N-NGN is confirmed by the DFT calculation (Figure 6a–e).

To further understand the multilayered architectures, TEM analysis was used to characterize the NGN and OHGN materials. Figure 2E,G shows the TEM micrographs of OHGN and NGN (3 h), respectively. From HRTEM images, both the OHGN and NGN (3 h) show multilayer architectures (Figure 2F,H). The NGN shows a larger number of graphene layers with a slightly smaller interlayer spacing in comparison to the OHGN (Table 1). The NH3 annealing leads to the decomposition of the hydroxyl and oxygen groups in the OHGN and increases the number of stacking layers, which agrees with other reported results.41 This N doping also increases the electronic conductivity, which also can improve

Table 1. Materials Properties of OHGN, NGN (3 h), and NGN (5 h)

| samples     | d-spacing (nm) | \( L_C \) | stacking layers (n) | conductivity (S cm\(^{-1}\)) |
|-------------|----------------|----------|---------------------|-----------------------------|
| OHGN        | 0.33           | 18.5     | 56                  | 0.17                        |
| NGN (3 h)   | 0.32           | 26.5     | 82                  | 3.12                        |
| NGN (5 h)   | 0.32           | 38.5     | 120                 | 4.33                        |
electrochemical reaction kinetics. The uniform distribution of N, C, and O in the graphene structure is confirmed by the STEM-EDS mapping of NGN (3 h) (Figure 2I–L).

The surface area of the graphenes was obtained using the Brunauer–Emmett–Teller (BET) method. The OHGN shows a BET of 17 m² g⁻¹ with both a microporous and mesoporous structure with pore sizes ranging from 0.7 to 10 nm. The NGN materials still maintain the microporous/mesoporous structure, with a pore size distribution ranging from 0.07 to 10 nm. However, the surface area is slightly decreased to 13 m² g⁻¹ (Figure S3). The micropores (≤2 nm) are suitable to enable strong physical adsorption of PS (∼2 nm), and the mesopores ensure sufficient ionic pathways for Li⁺ migration.

To further explore the crystallinity of the NGN materials, XRD was used to characterize the bulk structure of the OHGN and NGN (3 h) (Figure 3A). For OHGN, a weak peak at 26.83 (d-spacing = 0.33 nm) indicated that graphene oxide was reduced through the hydroxylation process. After the NH₃ treatment at 850 °C, the XRD peak shifted to 27.03 (d-spacing = 0.32 nm). The peak also narrowed and became stronger. The decrease in d-spacing suggests a deoxygenation from OHGN to form the NGN. The incorporation of a smaller radius N into the graphitic sp² structure reduces the lattice constant and also results in tensile stresses between the NGN layers. The decrease in the full width half-maximum (fwhm) of the peak suggests that the crystallinity of the NGN is enhanced during high temperature treatment. Further exploring the thickness of the materials the crystallite parameters L_C of the OHGN and NGN (3 h) and NGN (5 h) were calculated from the XRD peak position and their fwhm using the Scherrer equation:

\[ L_C = \frac{k\lambda}{\beta \cos \theta} \]

where K is the crystallite constant (0.89), λ is the fwhm, and θ is the angle between incident and the scattered ray. The thicknesses of the OHGN, NGN (3 h), and NGN (5 h) is calculated as 18.5, 26.5, and 38.5 nm, respectively. This corresponds well with the TEM results shown in Figure 2F,H, where it is observed that the NGN has more layers than the OHGN. The film thickness also plays an important role in the mechanically robustness and electronic conductivity of the graphene. The number of stacking layers (n) is further calculated from the thickness (L_C) as follows:

\[ n = \frac{L_C}{d \text{-spacing}} \]

The number of layers obtained for the OHGN, NGN (3 h), and NGN (5 h) is 56, 82, and 120, respectively. The details of some properties of OHGN, NGN (3 h), and NGN (5 h) are shown in Table 1.

Nonmetal heteroatoms (N, S, O, B, and F) are known to enhance the electrochemical kinetics and mitigate the PS shuttle in LSBs through chemical interactions. These heteroatoms also can easily be incorporated into the graphene structure to tune the electrical and chemical properties of the graphene materials for electrochemical storage applications. For example, NGN graphene exhibits three common bonding configurations in the carbon lattice of graphene: graphitic N, pyridinic N, and pyrrolic N. These N dopants are highly attractive to PSSs due to their high electronegativity (3.07). To reveal the intrinsic chemical interactions, the graphene structures were analyzed using an XPS survey and high resolution scans (Figure 3B–F). Figure 3D is the XPS survey scan for OHGN, NGN (3 h), NGN (5 h), and N-NGN (3 h) after operation. As anticipated, the C peak is present in all XPS scans (Figure 3B). Also, S and Li peaks are found in the N-NGN (3 h) sample after operation. The O peak is also present in all samples. The O peak increases for the NGN (3 h) sample after operation. The N peak is found in NGN (3 h), NGN (5 h), and NGN (3 h) after operation. This confirms that N-doping is introduced to the OHGN sample during NH₃ treatment at high temperature. During the longer treatment time of 5 h, the intensity of the N peaks increases. The three configurations of the N in the NGN (3 h) sample (Figure 3C) were deconvoluted into three different binding energies at 399.1, 400.0, and 401.8 eV, corresponding to pyridinic N, pyrrolic N, and graphitic N, respectively. The integration of electronnegative nitrogen into the graphene structure increases the graphene electrical conductivity and the PS binding ability through chemical interactions. However, all these potential activities rely on the concentration of nitrogen containing functional groups in the graphene structure. From the N high resolution scan, the concentration of pyridinic N is higher in comparison to the pyrolic and graphitic N. Pyridinic N provides the strongest PS binding, which is also proven through DFT calculations (Figure 6A). The pyridinic N has an extra pair of electrons. This electron-rich donor with filled p-orbitals naturally interacts with the Li in the PS. It also coordinates Li cations and helps immobilize PS to enhance the
electrochemical kinetics. The pyrrolic N and graphitic N also can chemically interact with PS. However, both of these dopants form three σ bonds and one π bond in the graphene lattice. As such, they have no lone pair electrons to create intermolecular Keesom interactions.51

The high resolution XPS spectrum of Li 1s in the N-NGN (3 h) operated sample is also deconvoluted (Figure 3D). The dominant Li 1s peak at 55.5 eV is attributed to the Li-S. The slight asymmetry to this peak is attributed to a small Li-N peak at 56.5 eV, which suggests that the Li is bonding to the N in the NGN.52 It has been previously reported that these Li bonds formed during electrochemical reactions promote electrochemical kinetics.36 The C 1s and O 1s high resolution XPS scan of the OHGN are shown in Figure 3, panels E and F, respectively. The main peak at 285.5 eV in Figure 3E correspond to the O−C−O bonding. This refers to O atoms incorporating into the graphene ring after H2O2 treatment. The π−π* (291.1 eV) is attributed to the satellite peak of C in aromatic compounds due to π−π interaction. The presence of different oxygen containing functional groups such as −COOH (288.9 eV), C−OH (287.5 eV), and C−COO (285.5 eV) are anticipated to be from the carboxyl and hydroxyl functional groups. The presence of −COOH also was confirmed by FTIR analysis (Figure S11). These functional groups can trap PSs through polar−polar interactions.8,32

2.2. Electrochemical Performance. The electrochemical cycling performances of N-NGN and N-OHGN contained LSBs are shown in Figure 4A–C followed by their charge/discharge profiles (Figure 4D–F) and areal capacities at initial and 100th cycles (Figure 4G–I). In order to rationally evaluate the performance of all LSBs, a lean electrolyte loading of 8 μL/ mg was used. To understand the electrochemical performances of the 70 wt % N-NGN (3 h) and 70 wt % N-OHGN coated separators, the galvanostatic cycling profiles were observed at a current density of 0.1 C (1 C = 1675 mAh g−1) shown in Figure 4A. The sulfur and coating loadings of these LSBs are (6.0 mg cm−2, 0.4 mg cm−2 for 70 wt % N-NGN (3 h), black), (5.4 mg cm−2, 0.3 mg cm−2 for 70 wt % N-NGN (3 h) red), and (4.5 mg cm−2, 0.4 mg cm−2 for 70 wt % N-OHGN, blue). The 70 wt % N-OHGN delivered a low initial specific capacity of 628 mAh g−1 and was retained to 296 after 200 cycles with 26% capacity loss (Figure 4A, blue). The initial capacity is pretty low; however, it shows stable cycling performance until 200 cycles. This is attributed to the abundant hydroxyl groups on the N-OHGN which serve as a PS adsorption sites. As the residual hydroxyl groups attract PSs during cycling through polar−polar interactions, they contribute to capacity retention and morphology conservation.33 The chemical interactive nature of the hydroxyl groups with the PS is also supported by the DFT calculations shown in Figure 6.

The 70 wt % N-NGN (3 h) (Figure 4A, red) with a low coating loading exhibited an initial specific capacity of 836 mAh g−1 and was retained to 358 mAh g−1 after 200 cycles with a capacity loss of 58%. Even though the capacity loss is higher, the initial and final performance is also higher as compared to 70 wt % N-OHGN (Figure 4A, blue). The 70 wt % N-NGN (3 h) with a higher coating loading and higher sulfur loading exhibited an initial specific capacity of 683 mAh g−1 and was retained to 449 mAh g−1, showing a capacity loss
of 17% (Figure 4A, black). As such, increasing the N-NGN coating loading from 0.3 mg cm\(^{-2}\) to 0.4 mg cm\(^{-2}\) improves the cycling stability despite the slight increase in the sulfur loadings between these two samples (sulfur loading increased from 5.4 to 6.0 mg cm\(^{-2}\)). The N-NGN coated separators are capable of immobilizing the soluble PS to produce a low LSB cycling degradation by the mutual effect of the N dopants and the \(-\text{SO}_3^-\). The higher initial specific capacity of the N-NGN in comparison to the N-OHGN is attributed to the higher electronic in-plane conductivity of NGN (3 h) (Figure 5C). This encourages a higher sulfur utilization through the electrode. Furthermore, the chemical adsorption of PSs promotes electrochemical kinetics on the N-NGN (3 h).

Figure 5. (A) OCV profiles of 56 wt % N-NGN (3 h), 70 wt % N-OHGN and Celgard contained LSBs during 20 h resting time before the cycling operation. (B) EIS spectra of 56 wt % N-NGN (3 h) and 70 wt % N-OHGN contained LSBs for before and after cycling operation. (C) Electrical conductivity of 70 wt % N-OHGN, 56 wt % N-NGN (3 h), and 56 wt % N-NGN (5 h) coated Celgard PP separator. (D) Voltage interruption test of 56 wt % N-NGN (3 h) contained LSBs followed by 5 h resting time after charge and discharge cycles, respectively. (E) Zoom in view of first cycle to show the charging closed circuit voltage (CCCV), charging open circuit voltage (OCOV), discharging closed circuit voltage (DCCV), and discharging open circuit voltage (DOCV). (F) \(r + i\eta\) loss for the all discharge and charge cycles shown in panel (d) from eqs 3 and 4.

Figure 4B represents the cycling performances of 70 wt % N-NGN (3 h) and 56 wt % N-NGN (3 h) contained LSBs in comparison with the Celgard PP separator at 0.2 C. The sulfur and coating loadings of these LSBs are (3.6 mg cm\(^{-2}\) for Celgard PP, green), (4.9 mg cm\(^{-2}\), 0.3 mg cm\(^{-2}\) for 70 wt % N-NGN (3 h), blue), and (5.4 mg cm\(^{-2}\), 0.3 mg cm\(^{-2}\) for 56 wt % N-NGN (3 h), black). The LSB with the pristine Celgard delivered a maximum specific capacity of 420 mAh g\(^{-1}\) with a rapid degradation of 45% after 143 cycles with a 3.6 mg cm\(^{-2}\) sulfur loading. This rapid degradation is caused by the migration of highly soluble PSs through the pores of the Celgard PP separator and the subsequent electrochemical conversion at the anode. It results in specific capacity loss in LSBs. In addition, most of the sulfur associated with Li,S in the anode is considered lost as they do not return to the cathode.

In contrast to the Celgard PP, the capacity loss is remarkably reduced to 12% after 200 cycles, when 70 wt % N-NGN (3 h) is implemented (Figure 4B, blue). This N-NGN coated Celgard PP with the negatively charged \(\text{SO}_3^-\) promotes the Li\(^+\) transport and hinders the PS migration through charge repulsion. As a result, the low degradation is achieved. However, Naion has a low electronic conductivity, which is not promising for the active material utilization during cycling. Therefore, to elevate the electrochemical performances of the LSBs, the amount of concentrated Naion solution was reduced to 56 wt % and mixed with 44 wt % Naion, nominally presented as 56 wt % N-NGN (3 h) (Figure 4B, black). Interestingly, with a coating loading of 0.3 mg cm\(^{-2}\), this LSB introduces an initial specific capacity of 862 mAh g\(^{-1}\) and is maintained to 604 mAh g\(^{-1}\) after 200 cycles with a 14% capacity loss. The improved electrochemical performance and stability are a good indication that the higher electronic conductivity facilitates sulfur utilization.

Realizing this improved electrochemical performances of Naion reduced 56 wt % N-NGN (3 h) (Figure 4B, blue), focus was given to NGN (5 h) with 56 wt % Naion (56 wt % N-NGN (5 h)) to produce LSBs at high sulfur loading (Figure 4C). However, a high sulfur loading is difficult to obtain using the conventional doctor blade slurry coating process on the conventional aluminum current collector. For sulfur loadings higher than 8 mg cm\(^{-2}\), the electrode becomes brittle, and most of the active composites peel off from the cathode while punching. Taking these drawbacks into consideration, the high sulfur loading electrodes were prepared through drop coating. The details of the drop casting process are illustrated in the Figure S4. The electrochemical performance of 56 wt % N-NGN (5 h) with the drop cast electrodes is shown in Figure 4C. The 56 wt % N-NGN (5 h) containing LSBs with a high sulfur loading of 15 mg cm\(^{-2}\) and 12 mg cm\(^{-2}\) shows an initial specific capacity of 808 mAh g\(^{-1}\) and 914 mAh g\(^{-1}\) with 32% and 34% losses after 200 cycles respectively at 0.1 C. The enhanced initial sulfur utilization and electrochemical performance are attributed to the electrical conductivity and the strong PS affinity of the 56 wt % N-NGN (5 h) coating. Specially, the Li bond forms with the electronegative N dopants and the \(\text{SO}_3^-\). These species facilitate intermolecular binding and charge transfer which enhances the sulfur and PS conversion kinetics (Figure 6).

However, these LSBs with high sulfur loadings produce undesirable Coulombic efficiencies with some cycling instability. The unstable Coulombic efficiency could be due to unwanted side reactions and the lack of electrons and Li\(^+\) to facilitate electrochemistry in the LSB during cycling. During cycling, the PS agglomerates at the sandwich interface between the coating layer and the electrode. This interrupts Li\(^+\) conduction and electron access to the sulfur. This phenomenon becomes more severe as the sulfur loading is increased. As a result, the Coulombic efficiency is interrupted. This loss of discharge capacity could be due to the polarization that occurs when a high load current passes through the electrodes. In a more specific way, these losses can be regarded as the activation polarization due to the electrochemical reactions and the concentration polarization owing to the concentration differences of the reactants and products at the electrode surface. These polarization effects mostly consume the loss of charge energy and are given off as waste heat. As a result, not...
all of the theoretically available energy stored in electrodes is fully converted into useful discharge energy.

2.2.1. Charge/Discharge Profiles. LSB charge–discharge profiles provide information on the electrochemical kinetics and voltage losses. For an ideal electrochemical reaction, the LSB needs the following: continuous supply of Li⁺; electrons to activate the sulfur; functional host to bind the PS in the between cathode and coated separators and their reactivation. During discharge, the soluble PSs undergo multiple conversion steps to insoluble Li₂S. The poor chemical affinity of the host materials with the PS prevents efficient charge transfer and slows down the reaction kinetics. Therefore, a PS mediator with a strong chemical affinity to the PSs is required to facilitate the sulfur electrochemistry. Moreover, the electrocatalytic conversion of the PS products during cycling requires a conductive scaffold to maintain the electrochemical reactions.

In our research, the highly conductive NGN acts not only as a PS trap, but also as a promising electrocatalyst to accelerate the electrochemical kinetics of intermediate PSs.

The corresponding charge/discharge profiles for all the tested LSBs for the 10th cycle are displayed in Figure 4D–F. To produce discharge capacity, the S₈ undergoes two voltage plateaus. During these plateaus, the S₈ forms into liquid and then solid PS (Li₂Sₓ, n = 1–8). In Figure 4D–F, two distinct discharge plateaus are observed. In the high voltage plateau, the elemental sulfur (S₈) reduces to long-chain PS (Li₂Sₓ, n = 4–8). At the low voltage plateau, the long-chain PS reduces to LiₓSₓ/LiₓS. The theoretical capacity of the high and low voltage plateaus is 419 and 1256 mAh g⁻¹, respectively. The first and second plateau region of the 70 wt % N-OHGN provides specific capacities of 117 mAh g⁻¹ and 406 mAh g⁻¹ (Figure 4D), which is 27% and 23% of the theoretical capacity of these plateaus. The N-OHGN has a large voltage loss, which also leads to sluggish electrochemical kinetics and low sulfur utilization. However, after the 70 wt % N-NGN (3 h) coating is introduced, the capacity of the first and second plateau is promoted to 57% and 46% of the theoretical limits despite the higher sulfur loading (Figure 4D, red). The voltage is also reduced for the 70 wt % N-NGN (3 h) sample (Figure S5). This clearly indicates improved electrokinetics, which is attributed to the higher electronic conductivity of the N-NGN (3 h) (Figure SC) and the chemical affinity of the N dopants and the SO₃⁻ which facilitates charge transfer (Figure 6).

Turning back to Figure 4E, the LSB with the pristine Celgard PP shows a high voltage loss, indicating sluggish electrochemical kinetics. As a result, this LSB only achieves 16% and 13% of the theoretical capacity at the first and second plateau, respectively. This large voltage loss is predominately due to sluggish oxidation and reduction kinetics of the solid PS during cycling. On the contrary, the 56 wt % N-NGN (3 h) promoted the electrochemical kinetics with 50% and 37% of the theoretical limit even at a high sulfur loading of 5.3 mg cm⁻² (Figure 4E, black). Interestingly, this voltage loss is more significantly reduced when the 56 wt % N-NGN (5 h) is introduced even at a high sulfur loading of 12 and 15 mg cm⁻² (Figure 4F). At 12 mg cm⁻² sulfur loading (Figure 4F, red), the N-NGN (5 h) produced 71% and 45% of the theoretical capacity at the first and second plateau. The underlying reason for the promising electrochemical performance of 56 wt % N-NGN (5 h) at high sulfur loading could be attributed to the Li atoms captured by the electronegative N-dopants in NGN with different doping configurations. The chemical interaction of PS can happen strongly with the pyridinic N, and additional binding can form between the S anions in PS and Li ions captured by the N dopants. As such, the higher electronic conductivity coupled with the strong chemical bonding sites for the PSs increases electrochemical kinetics of the N-NGN (5 h) which reduces the voltage losses (Figure S5).

2.2.2. Areal Capacity. The practical applications of LSBs in electric vehicles requires an increased sulfur loading to achieve a high areal capacity (mAh cm⁻²). The areal capacity of commercial LIBs is 4 mAh cm⁻² for electric vehicle applications. Comparing the lower average voltage of LSBs (2.2 V) to LIBs (3.5 V), the LSB areal capacity will need to be around ~6 mAh cm⁻² to compete with the state-of-the-art LIBs. However, at a high sulfur loading, the shuttle effect becomes more prominent. In the presence of chemically interactive hosts, such as N and SO₃⁻, the PS shuttleting can be mitigated even at a high sulfur loading. Hence, chemically interactive hosts are key to accessing the active materials, which leads to a high areal capacity at a high sulfur loading.

In our research, the areal capacities at the initial and 100th cycles of all LSBs (Figure 4A–C) are compared in Figure 4G–I. The 56 wt % N-NGN (5 h) produces a maximum areal capacity of 12.0 mAh cm⁻² and 11.0 mAh cm⁻², respectively, at 12.0 mg cm⁻² and 15.0 mg cm⁻² sulfur loading. This areal capacity limit is even higher than the required areal capacity of LSBs for commercial application (Figure 4I). Interestingly, both of these LSBs also retain an areal capacity of more than 6 mAh cm⁻² after 100 cycles. The remarkable electrochemical performance of the N-NGN can be attributed to

(1) the oxygen and hydroxyl dopants of graphene in N-OHGN. This enables stable cycling chemical binding of the PS onto the functional groups. However, the initial capacity is compromised due to the reduced electronic conductivity of this coating layer. In addition, the multilayered structure of the OHGN ensures physical separation of the PSs.

(2) The high electronic conductivity of the N-NGN, which affords fast electron transport to accelerate the electrochemical reactions. In addition, the N-NGN both chemically binds and physically blocks the PS migration. The chemical binding is provided through the electronegative N dopants, and the physical blocking is provided through the multilayered structure.

(3) The presence of the Nafion in both NGN and OHGN provides a chemically interactive −SO₃⁻ group to chemically attract the PSs and also facilitates Li⁺ conductivity of the coating. ²⁻

2.2.3. Anode Observation. From the anode photographs, it is clear that the N-NGN contained LSB provides better protection to the anode than the Celgard PP and the N-OHGN contained LSBs (Figure S6). However, some Coulombic efficiency instabilities are noticed at a high sulfur loading (Figure 4C). Typically, the cracks in the high sulfur loaded electrode will reduce in-plane electronic conduction and electron access to the active sulfur, leading to the breakdown of the conductive matrix. In addition to this issue, the lithium metal degradation may be encouraged through unstable solid-electrolyte interface growth and uncontrolled dendrite growth. To understand the Li anode degradation in the current cells, the SEM-EDS mapping was carried out of the cycled Li anode used for 12 mg cm⁻² and 15 mg cm⁻² sulfur loading (Figure S7). The SEM images show a corroded Li
surface for both electrodes. Here, the anode with 15 mg cm$^{-2}$ is more porous and cracked—suggesting severe corrosion during plating and depleting of Li$^+$. In addition, the EDS elemental analysis reveals the presence of sulfur on the Li anode surface, indicating PS migration at high sulfur loading causing the cycling instability.

2.2.4. OCV and IR Loss Analysis. The open circuit voltage (OCV) is the potential difference between the two electrode terminals when no external load is connected. Monitoring the OCV before using the LSB provides a good indication of the cell stability and the defensive nature of the coated separators when no current is being drawn. The OCV will change due to the shuttling of PSs during rest. In our research, to understand when no current is being drawn. The OCV gradually drops for the Celgard PP LSB, and the N-OHGN shows OCV fluctuations during resting, indicating PS shuttling. However, the N-NGN (3 h) LSB shows a very stable OCV, indicating that the PS shuttling is mitigated during the resting time.

During cycling, the LSB OCV depends on state of charge (SOC) and the depth of discharge (DOD). In the ideal scenario, at the end of charge the active material should all be sulfur, and at the end of discharge the active material should be Li$_2$S and Li$_2$S. As such, the OCV is different after the charge and discharge cycles. However, the migration of the soluble PS through the coated separators and the consequent loss of solid Li$_2$S to the anode would change the OCV after discharge and charge cycles. To understand the OCV after charge and discharge cycles, the N-NGN (3 h) contained LSB were monitored through voltage interruptions test as shown in Figure S8. The first few cycles of this test are shown in Figure 5D. For this experiment, the charge/discharge profiles of LSB were operated in the galvanizatic land system followed by 5 h resting time after each charge/discharge cycle to capture the OCV’s. The identical OCV’s of the LSB after charge/discharge upon cycling indicates there is minimal PS shuttling during LSB cycling.

Figure 5E is a zoomed in view of the first cycle and shows the close circuit voltage (CCV) and open circuit voltage OCV during charge and discharge, presented as CCCV, COCCV, DCCV, and DOCV, respectively. The internal resistance of the LSB is another important parameter which combines losses from electrochemical and ohmic resistance in the system. It captures information about the voltage losses, which consumes part of the useful energy. The voltage drop due to internal resistance is proportional to the current drawn from the system. The CCV of the N-NGN (3 h) contained LSB is quantified based on the following equations:\cite{57}

$$V_{\text{charge}}(\text{CCCV}) = V_{\text{OCOV}} + [(\eta_{\text{ct}}) + (\eta_{\text{i}})] + [(\eta_{\text{ct}}C) + (\eta_{\text{i}}C)] + \hat{i}_{\text{charge}}R_{\text{charge}}$$

$$V_{\text{discharge}}(\text{DCCV}) = V_{\text{OCOV}} - [(\eta_{\text{ct}}) + (\eta_{\text{i}})] - [(\eta_{\text{ct}}C) + (\eta_{\text{i}}C)] - \hat{i}_{\text{discharge}}R_{\text{discharge}}$$

Here, $V_{\text{charge}}(\text{CCCV})$ and $V_{\text{discharge}}(\text{DCCV})$ are the closed circuit voltages/operating voltages during charging and discharging, respectively; $V_{\text{OCOV}}$ is the OCV, $[(\eta_{\text{ct}}) + (\eta_{\text{i}})]$ are the charge-transfer overpotential at the anode and cathode, respectively, $(\eta_{\text{ct}}C)$ and $(\eta_{\text{i}}C)$ are the concentration overpotential at the anode and cathode, respectively. $\hat{i}_{\text{charge}}$ and $\hat{i}_{\text{discharge}}$ are the electronic current during charging and discharging. $R_{\text{charge}}$ and $R_{\text{discharge}}$ are the ohmic resistances during charging and discharging, respectively. It is understandable from the above equations that both the charge ($V_{\text{charge}}(\text{CCCV})$) and discharge voltage ($V_{\text{discharge}}(\text{DCCV})$) predominantly depend on the OCV and overpotential and ohmic resistance of the LSBS. From the above equations, the overpotential ($\eta$) and iR loss ($\eta + iR$) is calculated for both the charge and discharge curves as shown in Figure 5E. Upon repetitive cycles, the ($\eta + iR$) loss for both the charge (0.46 V) and the discharge (0.44 V) cycles are constant. This indicates there is no increase in the internal resistance of the cell during cell operation. This combined with the stable OCVs indicates that the N-NGN (3 h) LSB mitigates PS migration and also maintains a constant internal resistance. It is well-known that the voltage losses during charging are higher during cycling. This is due to the slow kinetics of converting the Li$_2$S and Li$_2$S. These voltage losses are undesirable as they are responsible for poor energy efficiency.\cite{64} In addition, a larger voltage loss typically provides slower kinetics that reduces sulfur utilization, leading to larger specific capacity loss.

2.3. Electrochemical Impedance and Conductivity Analysis. Electrochemical impedance spectroscopy (EIS) was further employed to understand the electrochemical behavior of the N-OHGN LSB and the N-NGN (3 h) LSBS before and after cycling. The EIS for the 70 wt % N-OHGN and 56 wt % N-NGN (3 h) before and after operations incorporates an ohmic resistance of the electrolyte and electrode, a high-frequency charge-transfer process ($R_a$), and a sloping straight line in the low-frequency region that represents a semi-infinite Warburg diffusion process. The $R_a$ demonstrates electrochemical kinetics, which rely on both surface polarity and intrinsic conductivity.\cite{56} The $R_a$ is remarkably smaller for the 56 wt % N-NGN (3 h) LSB in comparison to the 70 wt % N-OHGN LSB after cycling. This is attributed to the faster Li$^+$ diffusion and improved PS pinning, which encourages improved charge transfer. The ohmic resistance of the 56 wt % N-NGN (3 h) LSB is also lower than the 70 wt % N-OHGN LSBS. This indicates that the highly conductive NGN (3 h) has a better contact resistance between the coating and the electrode in comparison to the N-OHGN.

A key metric for LSB performance is the electronic conductivity of the coating film.\cite{65} A high electronic conductivity improves sulfur utilization due to improved redox kinetics. Therefore, the favorable in plane electronic conductivity of 56 wt % N-NGN (3 h) coating can assist in reactivating these solid and liquid PS during cycling. In regard to this, the physical electronic conductivities of 70 wt % N-OHGN, 56 wt % N-NGN (3 h), and 56 wt % N-NGN (5 h) coated Celgard PP separators were confirmed by the four point probe analysis (Figure 5C). Interestingly, the value of electronic conductivities of these coated Celgard PP is in good agreement with the cycling performance presented in Figure 4A–C. The low electronic conductivity of 70 wt % N-OHGN could be attributed to the C/O ratios due to the presence of abundant oxygen contents after the H$_2$O$_2$ treatment.\cite{69} Contrary, the higher conductivity of 70 wt % N-NGN (3 h) and 56 wt % N-NGN (5 h) is comparatively higher in comparison to 70 wt % N-OHGN (Table 1), indicating the presence of abundant electronegative N dopants. In LSBS, the discharged products (Li$_2$S and Li$_2$S) could be easily precipitated onto the surface of N-NGN matrix and form a passivation layer. Such an insulated passivation layer hinders.
the fast diffusion of active species and slows down the electrochemical reaction. Because of this higher electronic conductivity, the N-NGN acts as a second current collector layer. This facilitates electron transport and improves electrode kinetics.

2.4. PS Adsorption Energy Calculation through DFT Analysis. PS adsorption is more prominent on polarized surfaces of the host materials. To reveal the impact of the pyridinic NGN graphene, −OH-doped graphene, and −SO3̶ graphene on the cycling performance of LSBs, the theoretical adsorption energies between PS Li2Sn (n = 1, 2, 3, 4, 6, 8) with N, −OH, −COOH, and −SO3̶ graphene were calculated using density functional theory (DFT) (Figure 6).

The molecular structures of the NGN (5 h), NGN (3 h), −OH doped graphene (OHGN), sulfonated graphene (SGN), and −COOH graphene with their adsorption configurations are shown in Figure 6a–e. These configurations were obtained by a CASTEP simulation package in the framework of DFT. In the adsorption structure (Figure 6a–e), the most favorable binding terminals of the Li2Sn are the Li atoms which tend to bond with the N, −OH, −COOH, and −SO3̶. The interactions of the Li and the Sn anions from the PS species with these functional groups can be denoted as a chemical interaction and physical van der Waals (vdW) interactions. It can be understood from Cui’s work that the Sn molecule has almost no chemical interaction, and the adsorption is dominated by physical vdW interaction with a low adsorption energy. The adsorption of long-chain PSs mainly depends on the vdW interactions, while the anchoring of short-chain PSs depends on the chemical bonding. With the lithiation of PSs, the weak physical adsorption gradually exchanges to strong chemical binding. In our study, the adsorption energy of PSs to the functional groups shows a gradually decreasing tendency as the number of S increases, which is similar to those of the two-dimensional moderate anchoring materials (MS2, M = Ti, Zr, V, Nb, Mo). The details of the synergistic adsorption energies of all these elements are depicted in Figure 6f. These adsorption energies are predominantly higher than the weak intermolecular interactions (0.1−0.7 eV) of the polar PS with the nonpolar carbon materials. The PSs prefer to be adsorbed on the polar surface caused by a newly formed Li−O bond between the Li2Sn and the O atoms in the hydrophilic −OH group. The Li−O bond not only stabilizes the PS but also accelerates the charge transfer on the OHGN due to its covalent character, promoting the cycling stability of the OHGN LSB (Figure 4A, blue). The interfacial adsorption energy of PS on OHGN is further increased for Li2S2 and Li2S due to the shorter bond lengths. This stronger adsorption energy can also be attributed to the higher overall fraction of the positively charged Li+ ions. Therefore, the stable cycling performance of N-OHGN could be attributed to the oxidants of OHGN after the H2O2 treatment (Figure 4A, blue). The ability of PS to nucleate on the N-OHGN and N-NGN surface was confirmed by EDS mapping, Figure S3. However, the overall worse performance of the OHGN is attributed to the reduced electronic conductivity despite the relatively good binding energies with the PS (Figures 5C and 6a).

The PS adsorption energies of N dopants for NGN (3 h) is comparatively higher than the −OH and −COOH and SO3̶ species. The adsorption energies of N with the PSs from the NGN (5 h) even outperform the other functional groups in Figure 6a–e. The cycling performances also in line
with this theoretical DFT calculation. The higher concentration of N-dopants in the NGN (5 h) could be key to the enhanced electrochemical performance at high sulfur loadings.\(^{38}\) Additionally, the \(-\text{SO}_3^-\) group of the Nafion plays a crucial role in confining the PS species through polar–polar interaction. Therefore, the combined synergistic effect of pyridinic N and \(-\text{SO}_3^-\) of the N-NGN exhibits a higher areal capacity at a high sulfur loading. The strong interaction between the surface functional dopants, and the PS is essential to limit the shuttle effect, which is also confirmed by the OCV and voltage interruption tests shown in Figure S5A-D.

### 3. CONCLUSION

In conclusion, we have employed N-NGN as a promising separator coating for LSBs. These cells produced an impressive specific capacity and a long life cycle. The unique multilayer structure of the N-NGN coating not only physically blocks the PSs but also chemically binds the PSs through polar–polar interactions of the pyridinic N and \(-\text{SO}_3^-\). Furthermore, the electronic conductivity of the NGN enhances the sulfur utilization of LSBs. The N-NGN coating with the electrode 70 wt % sulfur content ensured a high areal capacity of 12.0 and 11.0 mAh cm\(^{-2}\), respectively, at 12 and 15 mg cm\(^{-2}\) sulfur loading. This areal capacity is promising and higher than the required areal capacity of LSBs to be applicable in electric vehicles and portable devices.

### 4. MATERIALS PREPARATION

Graphene oxide was synthesized from graphite by the modified Hummers method. In order to enhance the hydroxyl groups and oxide content, the graphene oxide powders were further treated in the presence of H\(_2\)O\(_2\) liquid 35% and water. This was mixed using a mechanical stirrer for 8 h. The viscous gray slurry was heated to 60 °C for 8 h. The purification and neutralization processes were conducted using an excess of demineralized water multiple times until a pH of 7 was achieved. The products were filtered and washed with an excess amount of double distilled water, followed by acetone washing and dried at 100 °C for 24 h. The obtained sample, hydroxyl graphene (OHGN), was further dried in the oven at 110 °C for 24 h. The H\(_2\)O\(_2\) was used due to its low cost and effectiveness as a reagent. In addition, the hydroxyl (-OH) and oxygen (-O) radicals generated from the water oxidation open up the graphene edges and facilitate ion intercalation to form graphene multilayers.\(^{26,69}\) In the next synthesis procedure, the OHGN was treated at 850 °C under NH\(_3\) atmosphere to decompose the oxygen and hydroxyl functional groups to form the C–N bond and establish N doping in the graphene lattice. To achieve this, the OHGN was heated to 850 °C at a heating rate of 5 °C min\(^{-1}\) and was held at 850 °C for 3 h and 5 h in NH\(_3\) to produce NGN (3 h) and NGN (5 h). The sample was then cooled down to ambient temperature at a cooling rate of 5 °C min\(^{-1}\).

For the separator coating, Nafion was used as a binder and chemically interactive nature with the PSs. Two coating slurries were produced: OHGN/Nafion (N-OHGN) and NGN/ Nafion (N-NGN) slurry. The slurry was prepared in two steps. First, the 30 wt % OHGN and NGN (3 h), respectively were mixed with 70 wt % concentrated Nafion solution and mixed via stirring for 30 min at 500 rpm and 80 °C to produce 70 wt % N-OHGN and 70 wt % N-NGN (3 h). Second, 44 wt % of NGN (3 h) and NGN (5 h), respectively, was mixed with 56 wt % concentrated Nafion solution followed by the same process to produce 56 wt % N-NGN (3 h) and 56 wt % N- NGN (5 h). The heat treatment (80 °C) was used for both of these processes and to encourage a homogeneous slurry formation.\(^{39}\) The slurry was coated onto one side of the Celgard PP-2500. After deposition, the slurry coated Celgard PP separators were dried at 60 °C for 12 h in a vacuum oven at 0.08 MPa. Finally, the dried OHGN and N-NGN coated separators were punched into 16 mm diameter discs to use for LSBs.

The conventional sulfur electrodes were prepared using a conventional slurry coating doctor blade process. To prepare the cathode, the conventional CNTs/sulfur composite with 70 wt % sulfur so-called CNT-70 was prepared through the infiltration process at 155 °C. The 80 wt % CNT-70 with the 10 wt % conductive Super P and 10 wt % PVDF were mixed for electrodes preparation followed by slurry coating doctor blade process on the carbon coated aluminum foil. The sulfur cathode was cut into a circular pellet with a diameter of 10 mm. For the high sulfur loading research, a drop casting process was used.\(^{34}\)

The electrolyte solution was prepared using a 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) at the volumetric ratio of 1:1, 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and 0.1 M LiNO\(_3\). The electrolyte was prepared inside a glovebox, supplied with Ar, with O\(_2\) and H\(_2\)O levels below 0.1 ppm to avoid air and moisture contamination.

### 5. MATERIALS CHARACTERIZATION

Field emission transmission electron microscopy (FE-TEM F20) was used to investigate the NGN and OHGN materials. The morphology and composition of the N-doped graphene (NGN) and OHGN samples before and after battery operation were characterized using a scanning electron microscope (SEM) (SU-3500) equipped with an Oxford X-MAXX energy-dispersive X-ray spectroscopy (EDS) detector. Fourier transform infrared (FTIR) spectra were recorded using a NICOLET 6700 from 500 to 4500 cm\(^{-1}\) under 4 cm\(^{-1}\) resolution. XPS survey data were acquired using a Kratos Axis ULTRA X-ray photoelectron spectrometer incorporating a 165 mm hemispherical electron energy analyzer. The incident radiation was monochromatic Al K\(_{\alpha}\) X-rays (1486.6 eV) at 150 W (15 kV, 10 mA). Survey (wide) scans were taken at an analyzer pass energy of 160 eV and multiplex (narrow) high resolution scans at 20 eV. Survey scans were carried out over 1200–0 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow high-resolution scans were run with 0.05 eV steps and at a dwell time of 250 ms. Base pressure in the analysis chamber was 1.0 × 10\(^{-9}\) Torr and during sample analysis 1.0 × 10\(^{-8}\) Torr. Atomic concentrations were calculated using the CasaXPS version 2.3.14 software and a Shirley baseline with Kratos library relative sensitivity factors (RSFs). Peak fitting of the high-resolution data was also carried out using the CasaXPS software. The Brunauer, Emmett, and Teller (BET) surface area of the NGN and OHGN was determined using a Tristar II (Micromeritics Vac prep-061). Thermal gravimetric analysis (PerkinElmer, Diamond TG) (TGA) for CNT-70 was performed in nitrogen atmosphere to measure wt % mass loss at a heating rate of 10 °C min\(^{-1}\) until 800 °C.

X-ray diffraction (XRD) of N-doped graphene (NGN) and hydroxyl graphene (OHGN) samples were analyzed on a Bruker D8 Advance Powder X-ray diffractometer equipped...
with a Cu source, operated at 40 kV and 40 mA, and an energy discriminating 2D array detector that minimizes a fluorescent background. Data were collected using a Bragg–Brentano geometry with a 0.12 deg divergence slit from 5 deg to 80 deg two-theta at a resolution of 0.02 deg and at 1.2 s per step. The four point probe with probe diameter 81 μm and probe spacing 1.6 mm (Agilent B1500A) was used to measure the electrical conductivity of coated Celgard PP by the composition of OGHN, NGN (3 h), and NGN (5 h), respectively, with 70 wt % of NaTf2SO4 electrolyte.

5.1. DFT Simulation for Adsorption Energies of PS Species. The immobilization ability of the different functionalized graphene materials was evaluated through density functional theory (DFT) calculations. The pristine 2D graphene was constructed with the dimension of ~13 × 13 Å, containing 60 carbon atoms and fully optimized. DFT calculations for structural optimizations and PS adsorption energies were carried out using the Dmol3 module in the Materials Studio software.17 The Grimme method72 was used to correct for the van der Waals (vdW) force in these structures. For structural optimization, the electronic self-convergence field (SCF) tolerance was set to be 1.0 × 10−6 eV/atom, and the energy convergence was 1.0 × 10−8 eV/atom. The adsorption energies (\(E_a\)) are calculated by following equations:

\[
E_a = E(\text{graphene} - Li_xS_y) - E(Li_xS_y) - E(\text{graphene})
\]

\(1 \leq x \leq 8\)

5.2. Battery Assembly. The LSBs were assembled inside an Ar-filled glovebox. An electrolyte/sulfur ratio of 8 μL/mg was used to assemble the LSBs. Consequently, after construction, the LSBs were sealed using a hydraulic crimping machine (MSK-110 Crimper) inside the glovebox under 0.1 ppm of H2O and O2 pressure.

5.3. Electrochemical Measurements. The LSBs battery performance was tested in a galvanostatic mode using a LAND system with a voltage window of 1.7–2.8 V (Li/Li+) at 0.1, 0.2, and 0.5 C rates. Before and after battery testing, the cell impedance was measured using a Biologic VSP. The electrochemical impedance spectroscopy (EIS) tests were conducted at 200 kHz to 100 mHz by applying a small AC potential (10 mV) between the working and reference electrodes.

5.4. Safety Statement. No unexpected or unusually high safety hazards were encountered.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.9b01005.

SEM and TEM characterizations, EDS mapping, drop slurry casting process, handset pictures of the cycled anodes, EDS mapping of cycled anodes, voltage interruptions tests, XRD and TGA analysis, FTIR analysis, table to compare our research with the existing literature (PDF)
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