Design Multifunctional Catalytic Interface: Toward Regulation of Polysulfide and Li₂S Redox Conversion in Li–S Batteries

Shuang Fan, Shaozhuan Huang, Mei Er Pam, Song Chen, Qingyun Wu, Junping Hu, Ye Wang, Lay Kee Ang, Congcong Yan, Yumeng Shi,* and Hui Ying Yang*

DOI: 10.1002/smll.201906132

However, the development of Li–S batteries for practical applications is still impeded by the insulating sulfur and discharged product (Li₂S),[4,5] volume expansion of the electrode,[6–8] and lithium polysulfide (LiPS) dissolution during cycling.[9,10] The shuttling effect caused by the LiPS migration between the cathode and anode, induces the Li anode corrosion, electrode decomposition, solid products (S/Li₂S) redistribution on electrode/electrolyte interfaces, finally resulting in low sulfur utilization and rapid capacity degradation.[11–13] Therefore, significant efforts have been devoted into cathode,[14–17] electrolyte system,[18,19] and separator modification,[20,21] from the view of polysulfide trapping and conversion.

The modification of the separators has attracted great attention to suppress the shuttle effect and improve the redox kinetics of sulfur species.[22–26] Many researchers focus on physical barriers with porous carbon materials[27–30] and chemical barriers with transition metal compounds and organic polymers[3,31–34] to effectively inhibit polysulfide shuttling. However, only favorable anchoring for diffusive polysulfides is rather limited for improving the battery performance because of the inefficient reuse of sulfur species at the three-phase boundary.
between cathode, electrolyte, and modified separator. The interface chemistry at these boundaries governs the redox kinetics of sulfur species and the level of sulfur reutilization.\[23\] The complicated kinetic mechanisms of the redox reactions for these sulfur species mainly involved have been revealed.\[25\] First, the sluggish reduction reaction of longer chain sulfur species to lower polysulfides of Li$_2$S critically impedes the complete use of active sulfur species. Second, the final discharged products of Li$_2$S are highly interfacial electronic resistive and need large activation energies to be oxidized in the conversion reactions. Based on these fundamental studies, a range of catalytic materials including organometallic redox mediators and transition metal compounds (metal oxides, sulfides, nitrides, and so on) can effectively regulate the kinetic behaviors of these sulfur species.\[25,26,32\] For example, Nazar and co-workers found that a few layers of MnO$_2$ coated with newly formed insoluble S$_2$O$_3^{2-}$ can facilitate the soluble long chain polysulfides species to low chain Li$_2$S during the reduction process.\[35\] Cui and co-workers reported that metal sulfides (CoS$_2$, VS$_2$, and TiS$_2$) can significantly reduce the potential barrier for insulate Li$_2$S decomposition under oxidation process.\[36\] However, it is difficult to demonstrate a comprehensive design for functional separators to strongly interact with polysulfides and deal all the sluggish redox reaction for these sulfur species.

Herein, we introduce a multifunctional catalytic interface by anchoring niobium nitrides homogeneously on hierarchical porous N-doped graphene nanosheets (NbN/NG) between the diffusive polysulfides, cathodes and electrolyte, which can promote the polysulfide redox conversion and regulate the Li$_2$S nucleation–growth–decomposition through strong chemisorption and electrocatalysis. A schematic diagram of a Li–S battery with the NbN/NG barrier is displayed in Figure 1. The polysulfides generated from shuttle effect are highly soluble and polar, and then a conventional separator can hardly block polysulfides migration. For the NbN/NG barrier, which combines the advantages of both N-doped graphene nanosheets and NbN to effectively inhibit the shuttle effect of polysulfides. The metallic NbN with high electrical conductivity (up to 4.6 $\times$ 104 S m$^{-1}$)\[37\] can provides abundant exposed active sites for intimate chemisorption for sulfur species and catalyzes the polysulfides reduction and Li$_2$S decomposition to enhance the sulfur species reutilization.\[38,39\] Moreover, the numerous NbN nanodots uniformly dispersed in NG nanosheets can govern the uniform distribution of polysulfides species followed by uniform nucleation and growth of Li$_2$S. Additionally, the graphene support with N dopant can afford a stable interconnected network to enable anisotropic electron and Li-ion transport.\[40,41\] Through this rational design, the functional NbN/NG interface can afford the synergistic effects for effective prevention the shuttle of polysulfides, significant enhancement redox kinetics for sulfur species, and uniform regulation the sulfur species distribution, finally leading to good performance. With these advantages, the Li–S batteries show high rate performance (621.2 mAh g$^{-1}$ at 3 C), superior cycling stability (81.5% capacity retention after 400 cycles) and high sulfur utilization.

The multifunctional barrier material was fabricated by in situ growing NbN nanocrystals on mesoporous NG network through a spatially confined nitriding route. First, the abundant oxygen functional groups on GO chemically adsors the niobium ions to promote the confined growth of nanocrystalline Nb$_2$O$_5$ on graphene nanosheets (Nb$_2$O$_5$/G) by a solvothermal method (see the corresponding scanning electron microscopy (SEM), transmission electron microscopy (TEM) images, and X-ray powder diffraction (XRD) pattern in Figure S1 in the Supporting Information). The Nb$_2$O$_5$ nanodots with an average size of $\approx$3–6 nm are uniformly anchored on the mesoporous and interconnected graphene network due to the confinement effect. Further nitriding of Nb$_2$O$_5$@G was carried out at 850 °C by using urea as the nitrogen source, in which Nb$_2$O$_5$ was converted to NbN nanodots and graphene was functionalized with N dopant. During the heat-treat procedure, high conductive NbN nanodots and N-doped graphene improve the overall conductivity of the composite. As revealed by XRD patterns, the NbN nanodots shows well-defined characteristic (111), (200), and (220) peaks of cubic NbN phase (JCPDS No. 03-065-9399)

---

**Figure 1.** Schematic for Li–S batteries with different separators: with a routine separator (left) and with an NbN/NG modified separator (right).
Figure 2. Morphology of the NbN@NG composite and NbN@NG separator: a) XRD pattern, b) SEM images, c,d) TEM images, and e) HRTEM images. f) SEM images of pristine PP separator, g,h) SEM images of the multilayered NbN@NG separator, and i) digital photos of the NbN@NG separator under various mechanical stresses. (Inset image of (e): SAED of NbN@NG composites.)
or NbN@NG/PP separator shows a higher conductivity than that of NG and NG@PP separator, resulting in enhanced the kinetic behaviors of soluble lithium polysulfides. Moreover, the NbN@NG hybrid coating on PP separator has good mechanical properties to withstand stress caused by bending, wrinkling and folding (Figure 2i).

To illustrate the advantage of NbN@NG hybrid for trapping polysulfides, adsorption test was conducted by adding the bare NG and NbN@NG composites (with the same surface area) separately to 3 mmol L\(^{-1}\) Li\(_2\)S\(_6\) solution (Figure 3a). Although the nitrogen dopant in NG (about 3.6%) could provide chemical adsorption sites for polysulfides, the limited heterodoping is still insufficient to capture a certain amount of LiPSs (Figure S7, Supporting Information).\(^{[43,44]}\) After adsorption for 12 h, NbN@NG composite displays more obvious color fading than that of NG, demonstrating that the polar NbN can offer strong chemical adsorption for LiPSs. To further confirm the chemical interaction between NbN@NG and LiPSs, X-ray photoelectron spectroscopy (XPS) was conducted. As shown in XPS spectrum of Nb (Figure 3b), the 3d peaks can be divided into three principal peaks with bonding energies of 204.6, 205.6, and 207.5 eV, corresponding to the Nb–N, Nb–N–O, and Nb–O bonds, respectively. Recently, it was illustrated that the surface oxidation layers on the metal compounds could activates the surface metal sites for polysulfides binding via strong chemical bonding.\(^{[45]}\) After adsorbing Li\(_2\)S\(_6\), the characteristic peaks of Nb slightly shift to lower binding energies, relating to the strong chemical interaction between NbN and polysulfide that results in the electron transfer from polysulfides to Nb atoms.\(^{[138]}\) In the S 2p spectrum after adsorption, the two S 2p\(_{3/2}\) contributions at 162.1 and 163.8 eV correspond to the terminal (S\(_\text{f}^{-1}\)) and bridging sulfur (S\(_\text{b}^{0}\)) atoms of Li\(_2\)S\(_6\), respectively. The S 2p\(_{3/2}\) peak at 167.1 and 168.4 eV is in precise related to the binding energy of thiosulfate and polythionate complex, which may be ascribed to the surface redox reaction between the Li\(_2\)S\(_6\) and NbN@NG and further reaction between long-chain LiPSs and thiosulfate.\(^{[6]}\) To gain further insight into the chemical interaction between the NbN, NG and polysulfides, density

---

**Figure 3.** Demonstration of the strong interaction of NbN@NG composite with polysulfides. a) A photograph of a Li\(_2\)S\(_6\) solution with the addition of NG and NbN@NG after 12 h; b) XPS spectra of Nb 3d in NbN@NG before and after mixing with Li\(_2\)S\(_6\) XPS spectra; c) XPS spectra of S 2p in NbN@NG/Li\(_2\)S\(_6\) composites; d) side view of a Li\(_2\)S\(_4\) molecule on a nitrogen-doped graphene surface and NbN (200) surface; e) permeation experiment with the double-L permeation device for the PP, NG, and NbN@NG/PP separator.
functional theory (DFT) calculations were conducted, as shown in Figure 3d. Herein, Li₂S₄ was chosen as the representative LiPSs. As shown in Figure 3d, the strong polar–polar interaction between Li₂S₄ and NbN leads to the deformation of Li₂S₄ molecule, producing the S\(\rightarrow\)Nb and Li\(\rightarrow\)N bonds. The binding energy of Li₂S₄ on NbN (200) and NG were calculated to be 3.54 and 0.89 eV, respectively, demonstrating that NbN possesses superior anchoring ability for LiPSs.[39]

To prove the advantage of NbN/NG barrier to suppress the polysulfides migration, the polysulfide permeability test was examined with several separators, as identified by the H-type cell in Figure 3e. In three H-type cells, 0.3 m of Li₂S₆ DOL/DME (v:v = 1:1) solution and pure DOL/DME (v:v = 1:1) solution were separated by NbN@NG/PP, NG/PP, and PP separators, respectively. The H-type cell with the pristine PP separator displays an obvious dark yellow color in the right glass bottle due to the Li₂S₆ diffusion after standing for 10 h. For NG/PP separator, only light-yellow color was observed after 10 h due to a certain amount of Li₂S₆ blocking by NG/PP separator. In contrast, there is a negligible color change based on the NbN@NG/PP separator after 10 h, indicating the superior polysulfides entrapment by the NbN@NG barrier. These results reveal the good affinity and strong chemical interaction of NbN@NG interfaces for polysulfide.

To illustrate the catalytic effects of NbN@NG interfaces for Li–S batteries, the polysulfide redox reaction was investigated by the symmetric cells and Li₂S nucleation. As revealed previously by symmetric cells, the low capacity and large polarization potentials also due to the sluggish redox of polysulfide intermediates. Analogous symmetric cells composed of Li₂S₆ electrolyte between two identical working and counter electrodes were assembled. The EIS of the symmetric cells reveal that NbN@NG shows a 41.7% decrease in charge transfer resistance compared to NG (Figure 4a). Due to the advantageous lithium-free feature of the symmetric cells, such a decrease is related to the enhanced interfacial affinity between NbN@NG interfaces and polysulfides, and quick charge transfer along the interfaces.[46] As shown in Figure 4b, the CV curve of the NbN@NG electrode in the Li₂S₆ electrolyte displays two evident reduction peaks at 0.09, 0.49 eV and distinct oxidation peaks at −0.09, −0.49 eV, as well as the narrow peak separation. The two reduction peaks related to the reduction of Li₂S₆ to short chain polysulfides and Li₂S, respectively. On the contrary, the two oxidation peaks represent the oxidation of Li₂S to polysulfide and sulfur element, respectively.[6] In contrast, the NG shows only one pair of redox peaks, and deliver lower current intensity in comparison with that with NbN/NG composite. It indicates the enhanced electrochemical reversibility and
quicker reaction kinetics with NbN@NG interfaces, suggesting that NbN@NG interfaces can afford abundant catalytic sites toward polysulfide redox conversion. To further investigate the role of NbN@NG interfaces in regulating the Li$_2$S deposition, Li$_2$S precipitation experiments were performed on different substrates including carbon fiber (CF), CF/NG and CF/NbN@NG, by using Li$_2$S$_6$ tetraglyme solution as electrolyte. The galvanostatic discharge was first conducted to 2.09 V to consume most high-order polysulfides, followed by apply a 0.01 V overpotential to drive the nucleation of Li$_2$S. Figure 4c exhibits the nucleation and growth of Li$_2$S for the aforementioned electrodes at 2.08 V. The contributions of progressive reduction of polysulfides (Li$_2$S$_6$/Li$_2$S$_4$) and Li$_2$S precipitation experiments were mathematically modeled and distinguished by dark and light colors, respectively. The quantity of the Li$_2$S precipitation on CF, CF/NG and CF/NbN@NG are calculated to be 89.4, 175.4, and 256.8 mAh g$^{-1}$, respectively. Obviously, NbN@NG composites have the highest activity toward Li$_2$S precipitation. The morphology of the initial precipitation on different substrates was characterized by SEM. As shown in Figure 2f, barely observable Li$_2$S deposits on CF surface, owing to the low affinity of nonpolar carbon for lithium polysulfides.\cite{47} The deposition type is related to a high energy barrier for the conversion reaction of LiPSs on the CF. The amounts of Li$_2$S deposited on the NG/CF are slightly improved but insufficient owing to the limited number of initial nucleation sites of NG nanosheets. Excitingly, after introduction NbN@NG composites, the CF/NbN@NG manifests a significantly improved uniform and dense Li$_2$S deposition, which is mainly associated with numerous and well-distributed nucleation sites of NbN nanocrystals on the conductive graphene matrix. The enhanced precipitation of Li$_2$S attributed to the strong affinity between the LiPSs and conductive polar NbN@NG interfaces, thus enhancing the nucleation sites and reducing the precipitation energy barriers. The above results reveal that NbN nanocrystals of NbN@NG interfaces indeed display a significant catalytic role in accelerating the LiPSs redox reaction and regulating the Li$_2$S nucleation.\cite{23} This is mainly ascribed to effective d-band structure derived from metal d-orbits of niobium nitrides, which would cause a greater density of states (DOS) similar to group noble metals, imparting the catalysis characteristics equivalently to d-band of noble metal.\cite{48–50} Thus, the NbN@NG is an ideal functional material to improve the electrochemical performance for Li–S batteries.

Electrochemical evaluations were conducted to systematically confirm the functions of NbN@NG/PP separator in Li–S batteries. The S/ketjen black (KB) composite with sulfur content of 70.8 wt% was employed as the cathode material (Figure S8, Supporting Information). The areal sulfur loading in the whole cathode is about 1.5 mg cm$^{-2}$. Typical cyclic voltammetry (CV) of the Li–S batteries using different functional separators was first examined in a voltage range of 1.7–2.8 V at a scan rate of 0.1 mV s$^{-1}$ (Figure 5a). For the NbN@NG/PP separator, the two distinct cathodic peaks at 2.27 and 2.02 V are ascribed to reduction conversion of sulfur to high-order lithium polysulfide (Li$_2$S$_{x}$, 4 < x < 8) and the subsequent conversion to insoluble lithium sulfide (Li$_2$S/Li$_2$S$_4$), respectively. The two oxidation peaks are related to the reversible conversion of short-chain lithium polysulfides to high-order lithium polysulfides and cyclo-S$_8$, respectively.\cite{7} Notably, the reduction and oxidation peaks of NbN@NG/PP exhibit a much smaller potential polarization than those of PP and NG/PP, suggesting the enhanced redox reaction kinetics between soluble polysulfides of NbN@NG/PP induced by the catalytic effect of NbN@NG interfaces. In addition, the higher peak current of NbN@NG/PP suggests the enhanced sulfur utilization due to the effective polysulfides trapping and reusing by the NbN@NG interfaces. Importantly, the CV curves of NbN@NG/PP in the following cycles overlap well, demonstrating the good reversibility (Figure S9, Supporting Information). These findings support solid evidences for the strong immobilization of LiPSs by the NbN@NG in modified separator. As shown in Figure 5b, the cyclic stability of the cells with NbN@NG/PP, NG/PP, and pristine PP separators was measured at a low current density of 0.2 C (1 C = 1673 mAh g$^{-1}$). The Li–S cells with NG/PP separators display an initial discharge capacity of 1081.3 mAh g$^{-1}$ and a 100th capacity of 639.2 mAh g$^{-1}$, corresponding to a capacity retention of 59.1%, which is higher than that of the pristine Celgard PP separator (only 19.3% capacity retention). With multifunctional catalytic NbN@NG interfaces, the NbN@NG/PP shows a much higher capacity of 1206.3 mAh g$^{-1}$ and it remains at 979.5 mAh g$^{-1}$ after 100 cycles, corresponding to an improved capacity retention of 81.2%. In addition, the smaller capacity degradation of the NbN@NG/PP is also evidenced by its higher Coulombic efficiencies over entire cycles (~98% for NbN@NG/PP separator). Considering the same electrodes for Li–S batteries, it is proven that the superior cyclic performances of NbN@NG/PP are related to the improved redox reaction kinetics and polysulfide entrapment caused by NbN@NG interfaces. Besides, the capacity contribution of the NbN@NG barrier was also conducted in a voltage range of 1.7–2.8 V by using it as the cathode. A low discharge capacity of only 9.2 mAh g$^{-1}$ at 0.1 C are shown, which contributes negligible capacity to the Li–S battery (Figure S10, Supporting Information). After cycling, the surface morphologies of lithium anodes with different separators were conducted to further investigate the PS blocking effect in cells (Figure S11, Supporting Information). The pristine lithium anodes display the smooth and flat surface; however, the lithium anode with PP separator shows a rough surface accompanied by numerous bulges and cracks. In comparison, the lithium anode with NbN@NG/PP separator displays smoother surface than those with pristine Celgard and NG/PP separators, demonstrating the much improved anode protection by the effective LiPSs entrapment of NbN@NG composite. Moreover, energy dispersive X-ray spectroscopic (EDX) analysis of NbN@NG barrier after cycling reveals the presence of S signal, suggesting the impressive chemical bonding to polysulfides by NbN@NG (Figure S12, Supporting Information). The EIS spectra of the Li–S cells with NbN@NG/PP, NG/PP, and pristine PP separators after 10 cycles are shown in Figure 5c. It is noteworthy that the charge-transfer resistance ($R_{ct}$) of NbN@NG/PP is much lower than those of PP and NG/PP, implying a more rapid electrochemical reaction kinetics. The role of NbN@NG interfaces can be more clearly revealed by rate capability under various current densities, which involves faster charge transfer and higher conversion reaction kinetics during the charge/discharge process. As shown in Figure 5d, the reversible capacities with NbN@NG/PP separator are...
1345.2, 1149.3, 983.5, 854.6, 736.2, and 621.2 mAh g\(^{-1}\) under 0.1, 0.2, 0.5, 1, 2, and 3 C, respectively. In contrast, the cells employing NG/PP and PP exhibit much lower capacities under the same rate cycling conditions. In particular, when the current density switches back to the C/10 rate, a high capacity of 1183.7 mAh g\(^{-1}\) is recovered, confirming its good mechanical stability and the strong immobilization of LiPSs by NbN@NG/PP separator. To further demonstrate the role of NbN@NG interfaces in catalytic conversion of Li\(_2\)S, the decomposition energy barrier of Li\(_2\)S is systematically investigated with the Li–S cells with the NbN@NG/PP, NG/PP, and pristine PP separators (Figure 5e). The decomposition of Li\(_2\)S usually result in a high overpotential at the initial charging to overcome the high energy barrier due to low electrical conductivity and low lithium ion diffusivity of Li\(_2\)S. Thus, the cathode with PP separator display a high potential barrier at about 2.34 V, further demonstrating a sluggish activation process about the decomposition of Li\(_2\)S.[36] In comparison, the cathode with NG/PP separator exhibits a lower potential at 2.30 V during the activation process due to conductive nature of NG. Significantly, the cathode with the NG/PP separator shows a larger voltage jump to lowest potential at 2.23 V, indicating the lower potential barrier for decomposition of Li\(_2\)S to soluble LiPSs catalyzed by the NbN@NG interfaces. Moreover, the discharge/charge profiles with NbN@NG/PP separator exhibit longer and flatter plateaus with lower polarization as compared with the NG/PP and PP, also indicating improved polysulfide redox kinetics by the multifunctional catalytic property of the NbN@NG interfaces in Li–S batteries.[51]

Furthermore, the long-term cycling performance is evaluated at 1 C (Figure 5e). Remarkably, the NbN@NG/PP exhibits a high capacity of 714.5 mAh g\(^{-1}\) after 400 cycles, corresponding...
to a high capacity retention of 81.5% (0.04% capacity decay per cycle). However, the NG/PP delivers a low capacity of 248.8 mAh g\(^{-1}\) after 400 cycles. The higher specific capacity and capacity retention of the NbN@NG/PP reveal that the sulfur utilization is greatly improved by the NbN@NG interfaces via trapping and reusing the soluble LiPSs. To build high-energy-density Li–S batteries, the batteries using NbN@NG/PP separator deliver cyclic capacity retentions of 84.3%, 83.5%, and 86.2% after 200 cycles at 1 C at high sulfur loadings of 1.53, 2.34, and 3.27 mg cm\(^{-2}\) (Figure 5h), respectively.

The impressive stability for high sulfur loading cells implies that the NbN@NG interfaces can effectively anchor the soluble LiPSs to inhibit the shuttle effect of thick sulfur cathodes. The results strongly reveal that multifunctional catalytic NbN@NG interface effectively suppresses the outward diffusion of LiPSs and accelerates sulfur species redox reaction kinetics during cycling, finally play pivotal roles in improving the Li–S performance for practical use.

In summary, a multifunctional catalytic NbN@NG interface was constructed to effectively suppress the polysulﬁdes shuttling, accelerate the polysulﬁde redox reaction, and regulate the lithium sulfide deposition followed by the decomposition. The conductive NbN nanodots show a strong anchoring effect for polysulﬁde species and serve as the chemical catalyst to accelerate the trapped polysulﬁde conversion. Significantly, uniform NbN nanodots anchored on N-graphene matrix effectively regulate Li\(_2\)S nucleation–growth–decomposition, enhancing sulfur species conversion kinetics. Therefore, the conductive NbN@NG interfaces with the excellent mechanical properties serve as the shield to block the diffusion of dissolved polysulﬁde intermediates, and act as “the second current collector” to reuse the trapped active polysulﬁdes and signiﬁcantly improve the sulfur reutilization. As expected, the Li–S battery with the NbN@NG barrier exhibits a reversible high capacity of 1086.3 mAh g\(^{-1}\) after 100 cycles at 0.2 C, a high-rate capacity of 714.5 mAh g\(^{-1}\) at 1 C with remarkable capacity retention of near 81.5% after 400 cycles, and a stable operation of high sulfur loading electrode (2.34–3.27 mg cm\(^{-2}\)) 

Keywords

- Li,S nucleation–growth–decomposition
- lithium–sulfur batteries
- multifunctional catalytic interfaces
- niobium nitride electrocatalysis

Received: October 24, 2019
Published online: [link to the article]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Y.S. acknowledges the support from the Thousand Young Talents Program of China. S.F. and Y.S. thank the support from the National Natural Science Foundation of China (Grant Nos. 51602200 and 61874074) and (Grant No. 21603192), the Science and Technology Project of Shenzhen (JCY20170817100100705), and the (Key) Project of Department of Education of Guangdong Province (Grant No. 2016KZDXM008). This project was supported by the Science and Technology Project of Shenzhen (ZDSYS20170727104468) and the Shenzhen Peacock Plan (Grant No. KQTD2016053112042971). Singapore Ministry of Education academic research grant Tier 2 (MOE2018-T2-2-178) is gratefully acknowledged.

Conflict of Interest

The authors declare no conflict of interest.


