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batteries

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A sufficient areal capacity is necessary for achieving high-energy lithium sulfur battery, which requires high enough sulfur loading in cathode materials. Therefore, kinetically fast catalytic conversion of polysulfide intermediates is especially important for full utilization of sulfur. Herein, $Co_9S_{8,x}/N$ -doped graphene ($Co_9S_{8,x}/N$ -G) is used as sulfur host material and electrocatalyst in a high sulfur-loading cathode, in which sulfur vacancies are generated by hydrogen reduction of stoichiometric Co_9S_8 . The produced sulfur vacancies in $Co_9S_{8,x}/N$ -G effectively improves the adsorption ability for polysulfide anions, and theoretical calculation indicates that $Co_9S_{8,x}$ has lower adsorption energy for polysulfides than Co_9S_8 . Furthermore, electrochemical experiments reveal the electrode process kinetics for catalytic conversion of polysulfides is enhanced by sulfur vacancies. As a results, the $S/Co_9S_{8,x}/N$ -G cathode with a high sulfur loading of 14.6 mg cm⁻² delivers a high areal capacity of 12.9 mAh cm⁻², and a long cycle stability with a slow decay rate of 0.035% per cycle during 1000 cycles at 1C. Besides, the pouch cell shows foldable flexibility and stable areal capacity of 5.9 mAh cm⁻² under sulfur loading of 7.1 mg cm⁻². The results show that enhancing polysulfide conversion process kinetics by sulfur vacancies could be an effective approach to high-performance lithium sulfur battery.

1. Introduction

With increasing demand for electric vehicles and mobile electronics, rechargeable batteries with high energy density, long cycle life and low cost are eagerly needed.¹⁻³ It is considered that lithium-sulfur battery is one of the most promising alternatives for meeting the demands.⁴⁻⁶ However, lithium-sulfur batteries are facing a series of challenges including insulation of sulfur, shuttle effect of lithium polysulfide intermediates, volume strain of lithium sulfides, etc., resulting in low sulfur utilization, capacity decay, and poor cycle lifespan.⁷⁻⁹ In particular, to realize the final high energy density, high enough sulfur-loading and sufficient areal capacity are necessary for sulfur cathodes.^{10, 11} Certainly, the high sulfur loading in the cathode materials can aggravate the above problems.

A lot of efforts have been made on the issues. Typically, various carbon-based materials are used as host for sulfur to improve conductivity and adsorb polysulfides.¹² Afterwards, some transition metal compounds such as sulfides,¹³ nitrides,¹⁴ phosphides,¹⁵ carbides¹⁶ and borides¹⁷, are investigated as host materials for sulfur, in which electrocatalytic activity of the transition metal compounds for conversion of polysulfides is usually effective for improving

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Recently, surface defects engineering e.g. oxygen vacancy and sulfur vacancy, provides a possible strategy to enhancing catalytic conversion of polysulfides in lithium-sulfur batteries. Surface oxygen-deficient $Fe_2O_{3,x}^{20}$ and sulfur-deficient MOS_2^{21} have shown enhancement of catalytic conversion process of polysulfide intermediates. Because surface defects could change electron structure of the host materials, favouring adsorption and conversion of polysulfides.^{22, 23} Besides, some heterostructured materials are also concerned for enhanced catalytic ability due to electron state change and interface formation,^{24, 25} such as VSe₂-Graphene,²⁶ CNT@TiO_{2-x}²⁷ WS₂/ZnS.²⁸ In addition, a synergistically catalytic mechanism of metal-semiconductor based on Mott-Schottky effect is also proposed to improve the catalytic ability for conversion of polysulfide.²⁹⁻³¹

In this work, N-doped graphene (N-G) supported $Co_9S_{8\cdot x}$ is prepared and used as host for sulfur to obtain cathode materials with high sulfur-loading, in which surface sulfur vacancies are rationally generated by hydrogen reduction of stoichiometric Co_9S_8 . Co_9S_8 exhibits good thermodynamic stability and relatively high electrical conductivity, and provides coupled interaction with polysulfides like $Sn^{2-}-Co^{\delta+}$ and $Li^+-S^{\delta-}$ (of Co_9S_8).³² Surface sulfur vacancies in $Co_9S_{8\cdot x}$ could be helpful for reducing electron transition energy barrier and enhancing electrophilic adsorption.^{22, 33} Based on the density functional theory (DFT) calculation and electrochemical experiments, enhancement effect of sulfur vacancies in $Co_9S_{8\cdot x}$ for electrochemical

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Figure 1. Preparation process, morphology and microstructure of the samples. a) Schematic illustration of the preparation process for Co_9S_{8-x}/N -doped graphene. b) SEM image, c, d) TEM images, and e, f) HRTEM images of Co_9S_{8-x}/N -doped graphene; g) Elemental mapping images of Co_9S_{8-x}/N -doped graphene; h) XRD patterns of the as-prepared Co_9S_8/N -doped graphene and Co_9S_{8-x}/N -doped graphene; i) Raman spectra of Co_9S_{8-x}/N -doped graphene, Co_9S_8/N -doped graphene and N-doped graphene; j) Electron spin resonance spectra of Co_9S_8/N -doped graphene and Co_9S_8/N -doped graphene.

kinetics, in particular adsorption and catalytic conversion of polysulfides is confirmed. $S/Co_9S_{8-x}/N-G$ shows excellent cycling stability and a record areal capacity in the metal sulfide cases of 12.9 mAh cm⁻² with a sulfur loading up to 14.6 mg cm⁻².

2. Results and discussion

$2.1 \ Co_9 S_{8\text{-x}} / \text{N-doped graphene}$

The preparation process of the sulfur-defective $Co_9S_{8-x}/N-G$ host material is shown schematically in **Figure 1a**. In the solvothermal reaction, thioacetamide (TAA) and cobalt nitrate are used as sulfur source and cobalt source, respectively, and stoichiometric Co_9S_8 precipitate can be generated by the reaction of cobalt and S^{2-} anions

released from hydrolysis of TAA, in which PEG is introduced to retard hydrolysis of TAA for obtaining small and dispersive Co_9S_8 particles. The subsequent annealing in 5% H₂/Argon makes the formation of surface sulfur vacancies in Co_9S_{8-x} . As shown in **Figure 1b** and **1c**, Co_9S_{8-x} particles are well dispersed on N-G (**Figure S1a**), and most of Co_9S_{8-x} particles have a size of 10–50 nm with irregular morphologies. Moreover, the higher magnification TEM image (**Figure 1d**) shows that the Co_9S_{8-x} particles have an apparent surface layer, indicating absence of surface sulfur atoms, which is consistent with the reported results.^{21, 34} Actually, it is clearer from the comparison between Co_9S_{8-x} and Co_9S_8 that has more regular morphology without the special surface layer (**Figure S1b and S1c**). In the HRTEM images (**Figure 1e, 1f**), the lattice spacing of 4.95 Å and 2.98 Å is indexed to (200) and (311) plane, respectively, of cubic Fm³m Co₉S₈

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(PDF#65-6801), agreeing with the results in X-ray diffraction (XRD) patterns (Figure 1h); this also indicates that Co₉S_{8-x} keeps the same crystalline phase as the stoichiometric Co₉S₈. Moreover, surface element analysis results from XPS in Figure S2a and S2b displays that the atomic ratio of Co to S for Co_9S_8 and Co_9S_{8-x} is 9:8.01 and 9:7.16, respectively, implying absence of 10% of surface sulfur atoms. And the content of Co_9S_{8-x} is 74 wt% based on the EDS analysis results (Figure S3, S4 and Table S1). Element mapping of energy dispersive spectroscopy (EDS) for Co_9S_{8-x}/N -G verifies existence of cobalt sulfide as a compound and doping of nitrogen in graphene (Figure 1g). In the Raman spectra (Figure 1i), the peaks of Eg (468 cm⁻¹), F2g (513 and 609 cm⁻¹) and A1g (671 cm⁻¹) correspond to various vibrational modes of Co,³⁵ and the peaks located at 1353 and 1585 cm⁻¹ point to D-band (disorder induced) and G-band (graphitic) of carbon, respectively. 36 In all the cases, the ratio of I_D/I_G is kept at about 0.993, demonstrating no obvious structure change for graphene during the annealing treatment. In addition, electron spin resonance (ESR) spectra also verify sulfur vacancies in the sample with Co_9S_{8-x} , in which the ESR signal g=2.002 is indexed to sulfur vacancies for Co₉S₈₋ $_x$ /N-G (Figure 1j).^{22, 34} Furthermore, the existence of sulfur vacancies in Co_9S_{8-x}/N -G can be proven from the comparison of XPS spectra of the two samples without or with the treatment by H_2/Ar (Figure 2). In Co2p spectra, Co-S is dominant for Co₉S_{8-x}/N-G, while for Co₉S₈/N-G the inevitable surface pollution from moisture in air occurs. From S2p spectra, it is clear that the binding energy for S2p3/2 assigned to Co-S shifts positively about 0.6 eV (from 161.7 to 162.3 eV) for Co₉S₈₋ $_{\rm x}$ /N-G compared to Co₉S₈/N-G. This indicates the formation of sulfur vacancies in the surface of $Co_9S_{8\text{-x}}/N\text{-}G.^{22}$ Additionally, with the partially reduction by H₂/Ar, the proportion of pyridinc-N increases for the N-doped graphene in Co_9S_{8-x}/N -G (Figure S3). The formation of sulfur vacancies is the result of surface reconstruction at equilibrium state of thermodynamics, and the defects can be kept in sulfur electrode. .21, 34

2.2 S/Co₉S_{8-x}/N-doped graphene

Sulfur is loaded into the as-prepared Co₉S_{8-x}/N-G, as well as Co₉S₈/N-G and N-G for comparison, using the typical melt-diffusion method.¹⁰ XRD results show that sulfur exists in the host materials as monoclinic sulfur (**Figure. S6a**). Thermogravimetric analysis (TGA) results indicate that all the three samples have the same sulfur content of



Figure 2. XPS spectra of $Co_{9}S_{8,x}/N$ -doped graphene and $Co_{9}S_{8,N}/N$ -doped graphene. The narrow scan of a) Co 2p, b) S 2p and c) N 1s, respectively.

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72 wt% (Figure S6b). The SEM images and EDS element maps in Figure S7 reveals that the two-dimensionab morphology based on graphene is kept, and the loaded sulfur is homogeneously distributed on the host materials. Specific surface area and pore distribution of $C_{0_3}S_{8.x}/N$ -G, $C_{0_3}S_8/N$ -G, N-G, and after loading sulfur are determined N₂ adsorption-desorption isotherms (Figure S8, Table S2). N-G has a much higher specific surface area than $C_{0_3}S_{8.x}/N$ -G and $C_{0_3}S_8/N$ -G, and the latter two are close, 327 and 273 m² g⁻¹, respectively. Especially, the follow-up sulfur-contained S/ $C_{0_3}S_{8.x}/N$ -G and S/ $C_{0_3}S_8/N$ -G provide specific surface area of 191 and 118 m² g⁻¹, respectively, and equal average pore size. The results means that $C_{0_3}S_{8.x}/N$ -G obtained by hydrogen reduction has increased specific, beneficial for dispersion of sulfur.

2.3 Interaction with polysulfides

Adsorption of polysulfides on a catalytically active host material is always the initial stage for catalytic conversion. Influence of sulfur vacancies in Co₉S_{8-x}/N-G on polysulfide adsorption are investigated by static adsorption experiment and the density functional calculation (DFT). After Co₉S_{8-x}/N-G, Co₉S₈/N-G and N-G as adsorbent are immersed in the Li_2S_6 solution for 10 h, the liquid supernatants are separated and analysed with UV-vis adsorption spectra (Figure 3a and 3b). According to the fundamental understanding of lithium polysulfides in ether-based electrolyte, Li₂S₆ exists two molecular conformations and is partially dissociated into LiS₆⁻ with detectable free radicals LiS₃.³⁷ In the UV-Vis spectrum of Li₂S₆ solution, the absorption bands at 295~340 nm are assigned to Li₂S₆, and LiS₆⁻ has some contribution to the signal at ~340 nm; the strong absorbance at ~405 nm is derived from LiS_6^- ; the absorption band at ~ 245 nm is contributed by excitation of all the species; and at ~620 nm is solely contributed by LiS₃ (Figure 3a). Obviously, LiS₆ anions are adsorbed by the host materials more easily. More importantly, $Co_9S_{8-x}/N-G$ with anionic sulfur vacancies has stronger adsorption ability for polysulfides than Co₉S₈/N-G and N-G (Figure 3b). Compared to N-G, Co₉S₈/N-G shows stronger polysulfide adsorption though the latter has a much higher surface area. The results can be understood from the discovering that the adsorption of polysulfides on a polarity surface could elongate S-S bonds to facilitate the bond splitting in reduction. 38 Co_9S_{8-x} with sulfur vacancies is more strongly apt to adsorb polysulfide anions than stoichiometric Co_9S_8 because the partial sulfur absence increases its electrophilicity. In addition, the sulfur deficiencies in the Co₉S_{8-x} surface could also facilitate the formation of metastable free radicals as an important intermediate in the polysulfide reduction and oxidation.³⁴

From the UV-Vis spectra, the difference in adsorption of neutral Li_2S_6 molecules of the different host materials is not as distinct as in adsorption of LiS_6^- anions. DFT calculations are used to confirm the chemisorption capacity and charge distribution of the Binding-Energy-state. Co_9S_{8-x} and Co_9S_8 are simulated by slab models of the (311) in **Figure 3c** and **3d** based on crystal characteristics from actual experimental results (**Figure 1h**). The optimized configurations for the binding Li_2S_6/Co_9S_{8-x} (311) are shown, with selected bond lengths listed in **Table S3**. The coupled interaction of Co_9S_8 with Li_2S_n corresponding to S_n^{2-} — Co^{5+} and Li^+ — S^5 -(of Co_9S_8 .) binding.³² Obviously strong bonding energy of $E_b = -4.138$ eV in Co_9S_8 . (311), confirming

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Figure 3. Chemical interactions with polysulfides. a) Assignment of absorption bands in UV-Vis spectrum of Li_2S_6 DOL/DME solution; b) UV-Vis spectra of the Li_2S_6 solution and after static adsorption of the different host materials; c, d) DFT of Li_2S_6 on Co_9S_8 and Co_9S_{8-x} (311) surface.

a strong anchoring polysulfide attributing to enhanced chemisorption bond from sulfur vacancy. **Figure S9** shows a visual analysis of the charge difference in the Binding-Energy-state by using Bader charge analysis.³⁹ A striking difference is that a profound charge transfer of 0.682e from Li_2S_6 to the Co_9S_{8-x} (311) surface, which is about two times higher than that to the Co_9S_8 (311) surface (0.353e). Such intense charge transfer from correlates with the stronger chemical binding in the presence of the vacancy on the Co_9S_{8-x} (311) surface. Therefore, the existence of sulfur vacancy can significantly enhance the binging energy of Co_9S_{8-x} (311) with lithium polysulfides, and enhance the chemical bonding ability by strengthening the electron migration number, which can reduce the concentration of polysulfide intermediates in the electrolyte and inhibiting the shuttle effect in lithium-sulfur batteries.

After adsorption of polysulfides on the host materials, the subsequent step is electron transfer from the host to the adsorbed polysulfides for completing electrocatalytic conversion of polysulfides. The catalytic ability of $Co_9S_{8-x}/N-G$, $Co_9S_8/N-G$ and N-G is investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and potentiostatic precipitation of Li₂S. In **Figure 4a**, the three cathodic peaks present the reduction processes of from S_8 to $S_6^{2-}(0.05 \text{ V})$, S_6^{2-} to $S_4^{2-}(-0.33 \text{ V})$, S_4^{2-} to Li_2S (-0.42 V), respectively; and the three anodic peaks are attributed to the oxidation processes from Li₂S to S_4^{2-} (-0.05 V), S_4^{2-} to S_6^{2-} (0.33 V), S_6^{2-} to S_8 (0.42 V), respectively. The higher current density and sharper current peaks for $Co_9S_{8-x}/N-G$ can be observed in the CV curves compared to $Co_9S_8/N-G$ and N-G, demonstrating a fast redox kinetic process of polysulfide conversion reactions. Actually the

relatively fast redox kinetics is also shown in the CV measurements of the sulfur electrodes, $S/Co_9S_{8-x}/N-G$, $S/Co_9S_8/N-G$ and S/N-G. The $S/Co_9S_{8-x}/N-G$ electrode presents stronger and sharper current peaks and lower potential difference between anodic and catholic processes, compared to $S/Co_9S_8/N-G$ and S/N-G, showing faster conversion reaction for polysulfides and lower polarization in the $Co_9S_{8-x}/N-G$ than in the $Co_9S_8/N-G$ and N-G (**Figure S11**). In the EIS Nyquist plots shown in **Figure 4b**, the semicircle at high-frequency region and the line at low-frequency region correspond to interface charge transfer impedance (R_{ct}) and Warburg diffusion resistance (W_o), respectively. Clearly, in the case of $Co_9S_{8-x}/N-G$, R_{ct} is much smaller than that of $Co_9S_8/N-G$ and N-G, confirming the faster interface process between $Co_9S_{8-x}/N-G$ and polysulfides.⁴⁰

In respect of catalytic conversion process of polysulfides, it is believed the step from Li₂S₂ to Li₂S is decisive for performance of lithium-sulfur batteries due to insolubility of Li₂S.⁴¹ Therefore, the situation of Li₂S deposition on host materials can reflect electrode process of catalytic conversion of polysulfide to a certain extent, which is basically related to energy barrier of nucleation and growth of Li₂S on host materials. In the measurements, 10 mV overpotential is potentiostatically used to trigger nucleation of Li₂S. As shown in **Figure 4c-e**, the result confirms that Co₉S_{8-x}/N-G takes a shorter deposition time but has a larger deposition amount than Co₉S₈/N-G and N-G. The shorter deposition time means faster nucleation rate of Li₂S, basically a reduced energy barrier for Li₂S deposition on the host surface.^{35, 41} On the other hand, Co₉S_{8-x}/N-G calculated capacities of Li₂S conversion is 159.46 mAh g⁻¹, more than that of

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Figure 4. Interaction and kinetics analysis of polysulfides with Co_9S_{8-x}/N -doped graphene as well as Co_9S_8/N -doped graphene and N-doped graphene. a) CV curves and b) EIS spectra of the symmetric configuration with Li_2S_6 solution; c-e) Potentiostatic discharge curves of Li_2S_8 /tetraglyme solution at 2.05 V on various surfaces of Co_9S_{8-x}/N -doped graphene, Co_9S_8/N -doped graphene and N-doped graphene.

 Co_9S_8/N -G (130.08 mAh g⁻¹) and N-G (97.38 mAh g⁻¹), on basis of Faraday's law,⁴² demonstrating an enhanced catalytic deposition capability for Li₂S. The results strongly support the above point that Co_9S_{8-x}/N -G with sulfur vacancies offers fast kinetic process for conversion of lithium polysulfides.

2.4 Electrochemical performance

Electrochemical performance of S/Co₉S_{8-x}/N-G, S/Co₉S₈/N-G and S/N-G electrodes are compared in Figure 5. The host materials are electrochemically inactive and have negligible capacity contribution under the used test conditions (1.7-2.8 V, Figure S12). The initial charge-discharge curves in Figure 5a show that the S/Co₉S_{8-x}/N-G electrode deliveries an initial discharge capacity of 1198 mAh g⁻¹, higher than 1097 mAh g⁻¹ of the S/Co_9S_8 /N-G electrode, while that of the S/N-G electrode is only 767 mAh g⁻¹. The relatively low potential difference between charge and discharge for S/Co₉S_{8-x}/N-G and $S/Co_9S_8/N-G$ also proves the electrocatalytic effect of cobalt sulfide. S/Co₉S_{8-x}/N-G retains a capacity of 850.4 mAh g⁻¹ after 100 cycles at 0.2 C with a coulombic efficiency of 99.1%, superior to 744.6 mAh g $^{\rm -1}$ of Co $_9S_8/N\text{-}G$ (coulombic efficiency 98.3%) and 642.1 mAh g $^{\rm -1}$ (coulombic efficiency 94.7%) of S/N-G, in which S/N-G presents a gradually activated process in the initial few cycles due to the partial aggregation of the graphene host material (Figure 5b). Besides, Figure 5c presents more stable discharge curves and with a smaller polarization potential drop that is calculated by subtracting the

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median potential at the midpoint of discharge capacity from the counterpart of charge curve. (Figure 5d, Figure S13). Figure 5e shows the outstanding rate performance of $S/Co_9S_{8-x}/N-G$. The average discharge capacities delivery 1296.6, 1074.3, 976, 910, and 878 mAh g⁻¹ at 0.1, 0.2, 0.5, 1 and 2 C. For S/Co₉S₈/N-G, the data are 1175.5, 966.9, 875, 807.6 and 755 mAh g⁻¹ at the same current densities. At 2C rate, a sharp capacity drop can be seen for S/N-G with the second discharge plateau entirely disappearing. However, a typical multistep discharge profile can still be observed at the current rate of 2 C for S/Co₉S_{8-x}/N-G, showing improved rate capacity. More remarkably, $S/Co_9S_{8-x}/N-G$ shows a lower charge-discharge potential gap than $Co_9S_8/N-G$ and S/N-G, and the potential gap presents smaller rise with increasing rates. S/Co₉S_{8-x}/N-G shows an excellent long cycle performance at 1C rate, as shown in Figure 5h. After 1000 cycles, the discharge capacity still reaches 661.9 mAh $g^{\mbox{-}1}$ with a coulombic efficiency of 99.7%, and the fading rate is only 0.035% per cycle at 1C rate. As references, S/Co₉S₈/N-G and S/N-G have capacity of 357.9 mAh g⁻¹ and 63.8 mAh g⁻¹ after 1000 cycles with obviously lower coulombic efficiency of 97.6% and 92.5%, and faster capacity decay of 0.067% and 0.094%, respectively.

Both low electrolyte/sulfur ratio (E/S) and high sulfur areal loading are very important for lithium-sulfur rechargeable batteries to achieve finally high energy density.⁴³ In this work, with gradually reducing E/S to 6 μ L mg⁻¹, the discharge plateau descends obviously due to electrolyte viscosity increasing and barrier of Li⁺ transfer

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Sulfur loading (mg cm⁻²) Cycle number **Figure 5**. Electrochemical performance of Co_9S_{8-x}/N -doped graphene, Co_9S_8/N -doped graphene, and N-doped graphene. a) The initial chargedischarge curves at 0.2 C; b) Cycling performance at 0.2 C; c) Charge-discharge curves at various rates of Co_9S_{8-x}/N -doped graphene; d) comparison of the corresponding overpotential; e) Various rate capacities; f) Cycling performance of the lithium-sulfur cells with sulfur mass loading of 7.0 and 14.3 mg cm⁻²; g) Comparison of areal capacity of the reported lithium–sulfur batteries involving metal sulfide as host materials (The number is the order number of the references listed in Table S3 in Supporting Informant); and h) Long cycling performances and coulombic efficiency at 1 C rate.

raising (Figure S14a). The reversible capacities of 876.7 , 804.3 and 530.6 mAh g⁻¹ can be obtained at 0.1 C rate after 100 cycles with the E/S ratios of 10 , 8 and 6 μ L mg⁻¹, respectively (Figure S14b). Moreover, sulfur areal loading is raised from1.5 mg cm⁻² to 7.0 and14.6 mg cm⁻² (E/S=5.8 μ L mg⁻¹). As shown in Figure 5f, the discharge areal capacity in the case of 7.0 mg cm⁻² presents 4.9 mAh cm⁻² after 100 cycles (corresponding to 614.3 mAh g⁻¹) at a current density of 0.1 C (activation for three laps in front at 0.05 C). To the higher sulfur loading of 14.6 mg cm⁻², a discharge areal capacity of 12.9 mAh cm⁻² is delivered and 8.5 mAh cm⁻² is retained after 50cycles with a very low E/S of 5.8 μ L mg⁻¹. Compared to the reports in recent years, this result should be a record capacity for lithium-sulfur batteries with sulfide as host materials (Figure 5g and Table S4).

In addition, to further demonstrate the practical potential of $S/Co_9S_{8-x}/N-G$, the test data from the pouch cell are shown in **Figure 6**. Herein, the areal loading of sulfur is 7.1 mg cm⁻², and the electrode area is 20 cm² (4×5cm, the ratio of negative to positive, N/P = 1.7). The pouch cell has a typical initial charge-discharge curve (**Figure 6a**) and stable cycling capability, and still delivers a capacity of 5.6 mAh cm⁻² after 50 cycles (with a current density of 0.05 C, the ratio of

electrolyte to sulfur, E/S=10 μ L/mg), which is obvious higher than typical commercial lithium ion batteries (4.0 mA h cm⁻²) (**Figure 6b**). Moreover, the pouch cell provides continuous energy output in despite a series of folded operations from 0°to 180°. These are very encouraging results for the potential practical use of Co₉S_{8-x}/N-G in lithium-sulfur batteries.

3. Conclusion

Sulfur vacancies are technically generated for $Co_9S_{8,*}/N$ -G by partially reduction of stoichiometric Co_9S_8/N -G by hydrogen. The surface sulfur-defective $Co_9S_{8,*}/N$ -G shows enhanced adsorption ability for polysulfide anions and reduced adsorption energy for polysulfides, compared to the stoichiometric Co_9S_8/N -G. Moreover, the generated sulfur vacancies generally accelerate the electrode process kinetics of the electrocatalytic conversion of polysulfides. The S/Co₉S_{8,*}/N-G cathode with a high sulfur loading of 14.6 mg cm⁻² delivers a high areal capacity of 11.7 mAh cm⁻², and an excellent cycle stability with a decay rate of 0.035% during 1000 cycles at 1C. Besides, the assembled pouch cell shows foldable flexibility and stable areal capacity of 5.9 mAh cm⁻² with areal loading 7.1 mg cm⁻². It is

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Figure 6. Pouch cell performance with Co_9S_{8-x}/N -doped graphene electrode. a) The first charge-discharge curve at room temperature; b) Size, areal capacity and cycling performance; c) Photographs of LED illumination test driven by the assembled pouch cell at various folding state.

encouraging that the generation of surface vacancies improve the electrochemical kinetics of cobalt sulfide host materials to the outstanding performance for lithium-sulfur batteries with high sulfur loading.

4. Experimental

4.1 Materials preparation

All chemicals were of analytical grade and used without further purification. The Co₉S_{8-x}/N-G were prepared using a solvothermal method and annealing process, as shown in **Figure 1a**. In details, Co(NO₃)₂·GH₂O (68 mM) and Thioacetamide (TAA) (0.67 M) were dissolved in an aqueous solution of PEG-20000 (0.28 mM , 30 mL), followed by vigorous stirring for 0.5 h, and then commercial N-doped graphene (0.32 M) was added with intense ultrasonic process. After that, the solution was transferred into a 60 ml Teflon-lined autoclave, and kept at 200 °C for 20 h in an oven. The obtained precipitation was collected and washed with deionized water and alcohol for three times, respectively, and then freeze drying overnight. Finally, sulfurdefective Co₉S_{8-x}/N-G was obtained by calcining the dried production at 600 °C for 6 h in (5 %) H₂/Ar mixture. The Co₉S₈/N-G as reference was prepared by the same procedure except for calcined in Argon.

S/Co₉S_{8-x}/N-G composite was prepared with a conventional meltdiffusion method. Firstly, the as-prepared Co₉S_{8-x}/N-G and sulfur (99.5% commercial, Aladdin) were mixed with the mass ratio of 28:72 by grind continuously for 0.5 h. Then the mixture was heated at 155 °C for 12 h in an Argon encapsulated autoclave. S/ Co₉S₈/N-G and S/N-G as references were prepared by the same method except for Co₉S₈/N-G and the commercial N-G as host materials.

4.2 Materials characterization

Morphology and microstructure of the prepared materials were characterized by scanning electron microscopy (SEM, JSM-7800F) and transmission electron microscopy (TEM, JEM-2800). X-ray diffraction (XRD) analyses were carried out using X-ray diffractometer (Rigaku mini Flex II) with Cu K α radiation. N₂ adsorption and desorption isotherms were used to determine specific surface area and pore volume of the samples with Brunauer-Emmett-Teller (BET) model, and pore size distribution were calculated with BJH method (JW-BK112 instrument). Sulfur content was identified with thermogravimetric analyzer (Mettler Toledo, TGA/DSC) under an Ar atmosphere, and the temperature programming was set as 10 °C min⁻¹ (30-600°C). Surface chemical state were analysed by X-ray photoelectron spectra (XPS, ESCALAB 250Xi, Thermo Scientific) with Al K α source. Electron spin resonance (ESR) spectra were tested on a BRUKER A300 machine.

4.3 Electrochemical measurements

To prepare sulfur electrodes, 70 wt% the as-prepared composites, 20 wt% Super P conductive agent and 10 wt% polyvinyldifluoride (PVDF) were blended in N-methyl-2-pyrrolidone (NMP) to obtain a homogeneous slurry. The slurry was then coated onto a carboncoated Al foil current collector and dried at 60 °C for 12 h before punched into disks with a diameter of 10 mm for the routine tests with areal sulfur-loading of 1.3-1.5 mg cm⁻². For the tests with a higher areal sulfur loading of 7-14.6 mg cm⁻² and pouch cell, the electrodes were fabricated with the same method except for using carbon cloth as current collector. 2032-type coin cells were assembled in an Ar-filled glove box using Celgard 2325 membrane as a separator and lithium foil as the reference/counter electrode. The electrolyte was consisted of 1.0 M LiTFSI in dimethyl ether (DME) and 1,3-dioxolane (DOL) (v/v, 1:1) with 0.2 M LiNO₃ additive. The ratio of electrolyte to sulfur (E/S) was controlled to be 12 µL mg⁻¹ for typical tests, but 7 μ L mg⁻¹, 5.8 μ L mg⁻¹ for the tests with higher sulfur loading. The galvanostatic discharge/charge tests were performed in a potential window of 1.7-2.8 V (vs. Li+/Li) with LAND-CT2001A instruments. Cyclic voltammetry (CV) measurements were performed on a CHI600E electrochemical workstation between 1.7-2.8 V at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectra (EIS) were carried out on a Zahner IM6ex electrochemical workstation with a frequency range from 10 mHz to 100 KHz.

4.4 Polysulfide adsorption

Li₂S₆ as adsorbate was used to evaluate adsorption ability of the prepared host materials for sulfur. Li₂S₆ solution (2 mM) was obtained by dissolving stoichiometric S and Li₂S (5:1) in a DOL/DME (v/v, 1:1) mixed solvent, and then vigorous stirring at 60 °C for 48 h. 30 mg of the prepared materials, Co₉S_{8-x}/N-G, Co₉S₈/N-G or N-G, were dried in a vacuum oven at 60 °C and added into Li₂S₆ solution (5 mL), respectively. All the operations were carried out in an Ar-filled glovebox. After immersion for 10 h, the liquid supernatants were separated for UV-vis adsorption spectra measurement (Varian Cary 100 Conc.), and the residual solids were dried for XPS analysis.

4.5 Symmetric cell cyclic voltammetry

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Symmetric cell cyclic voltammetry was used to evaluate catalytic ability of the prepared host materials. A symmetric cell configuration with two identical electrodes with Co₉S_{8-x}/N-G, Co₉S₈/N-G or N-G, respectively, were tested in 40 μ L of electrolyte containing 0.2 mol L⁻¹ Li₂S₆ in 1:1 DOL/DME (v/v), and the CV tests were performed from -1 to 1 V at a rate of 3 mV s⁻¹.

4.6 Li₂S nucleation

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Nucleation. Li₂S₈ solution as catholyte was prepared by adding Li₂S and S at a molar ratio of 1:7 into the electrolyte containing 1.0 mol L⁻¹ LiTFSI in tetraglyme solvent. Co₉S_{8-x}/N-G, Co₉S₈/N-G and N-G (1.5 mg cm⁻²) were, respectively used as cathode while lithium foil as anode. 20 mL Li₂S₈ (0.2 M) catholyte was added into the cathode side, while 20 mL of the origin electrolyte without Li₂S₈ was added in the anode side. The cell was first galvanostatically discharged until the voltage reached 2.06 V at the rate of 0.03 C, then the voltage was held at 2.05 V with keeping a current of lower than 10⁻⁵ A for nucleation and growth of polysulfide.

4.7 Computational Details

The density functional (DFT) calculations were performed by employing the *Vienna ab initio* simulation package (VASP),⁴⁴ with Projector augmented plane wave (PAW)⁴⁵ and Perdew, Burke, and Ernzerh (PBE)⁴⁶ functional, and DFT-D3 correction⁴⁷ was applied for the correlation of dispersion interactions. The PBE+U method5 was employed for the d orbitals of the Co atoms to add on-site potentials for properly simulating the electronic states, with Ueff = U-J parameters of 3 eV imported for the Co atoms.⁴⁸ A slab model was adopted to simulate the Co₉S₈ (311) surface, and 42 atoms were included in supercell of 4 frozen atom layers with a 3 × 3 × 1 Gamma type k-point grid. A 20 Å vacuum layer and a 1×2 supercell is employed to the interaction energy between a LiPS and the slab. A cutoff of 400 eV was chosen for the plane wave basis set in all the calculations.

The adsorption of Li₂S₆ on Co₉S_{8-x} surface consists of following steps: Firstly, Li₂S₆ is attracted by the Co₉S_{8-x} surface by the dispersion interactions,⁴⁹ and is anchored on the surface. The result is that Li₂S₆ is pulled from the solvent phase to the solid-liquid interface, and thus enable the adsorption of Li₂S₆ on the Co₉S_{8-x} (311) surface. During the anchoring process, Li₂S₆ maintains its molecular structure. The second process is decomposition and forming chemical bond on the Co₉S_{8-x} (311) surface. The S atoms of the adsorbed Li₂S₆ are gradually pulled toward the surface, and form chemical bonds with the Co atoms. Such process results in the breakage of the S-S bonds of Li₂S₆ and formation of S-Co bond, and thus forms Li₂S₆+Co₉S_{8-x} complex. The binding energy (Eb) can be calculated by

$$E_{\rm b} = E_{\rm LiPS+surface} - E_{\rm surface} - E_{\rm LiPS} \tag{1}$$

in which $E_{LiPS+surface}$ is the energy of the chemical bonded $Li_2S_6+Co_9S_{8-x}$ complex, and $E_{surface}$ and E_{LiPS} are the energies of the individually optimized Co_9S_{8-x} (311) surface and Li_2S_6 , respectively.

Conflicts of interest

There are no conflicts to declare.

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