



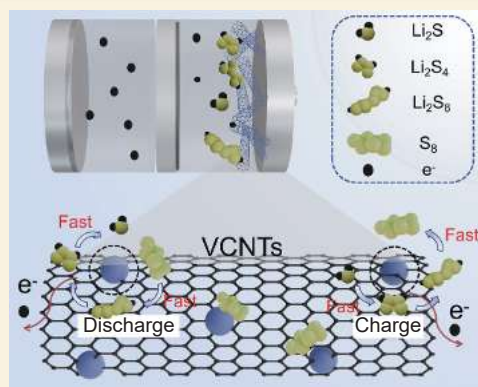
# The formation of vanadium carbide/carbon nanotube functional additives for promoting the sulfur redox kinetics in lithium-sulfur batteries

Hu Pingping, Xu Peng\*, Shao Jiaojing\*

(College of Materials and Metallurgy, Guizhou University, Guiyang 550025, China)

**Abstract:** Although lithium-sulfur batteries have a high theoretical specific capacity and high energy density, their practical performance is severely restricted by the shuttle effect, the sluggish kinetics of the conversion of sulfur-species, and severe volume expansion. We have produced VC/CNT composites using acid-treated multi-walled carbon nanotubes as a conductive scaffold and glucose as a carbon precursor, with vanadium carbide (VC) active sites formed on the nanotube surfaces using a hydrothermal reaction followed by high-temperature carbonization. The as-prepared VC/CNT composite was further mixed with sulfur and other electrode components to fabricate the modified sulfur cathode. Acidification improved the dispersibility and interfacial reactivity of CNTs, thereby facilitating the uniform anchoring of the VC which provides polar adsorption sites and catalytically active centers, thereby enhancing the capture of lithium polysulfide and promoting its redox conversion. Electrochemical measurements showed that the VC/CNT-modified sulfur cathode had a lower charge-transfer resistance and electrochemical polarization, while retaining a discharge specific capacity of  $531.3 \text{ mAh g}^{-1}$  after 400 cycles at 1 C. These results indicate that the VC-modified CNT network is an effective functional additive and catalyst for improving the reaction kinetics and cycling stability of sulfur cathodes in lithium-sulfur batteries.

**Key words:** Lithium-sulfur batteries; Vanadium carbide; Carbon nanotubes; Functional modification; Electrocatalysis



## 1 Introduction

Lithium-sulfur batteries are considered promising next-generation high-energy-density energy storage systems because sulfur cathodes offer high theoretical specific capacity, abundant resource availability, and environmental compatibility<sup>[1-2]</sup>. However, their practical application remains hindered by several critical challenges, including the poor intrinsic conductivity of sulfur and its discharge products<sup>[3-4]</sup>, the shuttle effect induced by the dissolution and migration of lithium polysulfides in the electrolyte<sup>[5-6]</sup>, and the pronounced volume variation of sulfur cathodes during charge-discharge processes<sup>[7]</sup>. These factors are mutually coupled and collectively lead to accelerated capacity fading and reduced Coulombic efficiency, thereby impeding the practical application of lithium-sulfur batteries.

Constructing rational sulfur cathode host materials is considered an effective strategy for mitigating the above-mentioned issues<sup>[8]</sup>. Carbon materials have been widely employed in lithium-sulfur battery cathodes owing to their large specific surface area, good electrical conductivity, and relatively stable structure<sup>[9-11]</sup>. Among them, carbon nanotubes (CNT), owing to their excellent electron transport capability and high aspect ratio, can form a continuous conductive network within the electrode, thereby improving the overall electronic conductivity of the cathode and partially buffering the volume variation of sulfur spe-

Received: May 21, 2026

Revised: July 27, 2026

Accepted: July 28, 2026



cies during repeated conversion processes<sup>[12]</sup>. Therefore, CNTs are regarded as promising carbon-based host materials for lithium-sulfur batteries<sup>[10,13–14]</sup>. However, strong van der Waals interactions among pristine CNTs readily induce aggregation, thereby limiting their dispersion uniformity and structural stability in composite electrodes<sup>[12,15]</sup>. Meanwhile, the relatively inert surface chemistry and weak polarity of CNTs result in insufficient interfacial interactions with sulfur species and polar active components, which is unfavorable for the uniform loading of active materials and the subsequent regulation of interfacial reactions<sup>[16]</sup>. Therefore, appropriate surface functionalization of CNT is an effective approach to improving their dispersibility, interfacial binding capability, and structural stability in composites. Acid treatment can introduce oxygen-containing functional groups, such as hydroxyl and carboxyl groups, onto CNT surfaces, which not only weakens intertube aggregation and improves wettability and dispersion stability but also enhances surface polarity and chemical activity, thereby providing favorable conditions for the adsorption, anchoring, and uniform deposition of metal precursors on CNT surfaces<sup>[17–19]</sup>. Previous studies have reported that oxygen-functionalized carbon nanotubes can serve as both conductive fibrous frameworks and functional interlayers for sulfur cathodes<sup>[20]</sup>. Their surface oxygen-containing functional groups can improve electrolyte wettability and enhance the adsorption and blocking of lithium polysulfides through interfacial interactions, indicating that CNT surface functionalization is an effective means of improving interfacial regulation capability<sup>[21–24]</sup>. Therefore, introducing uniformly dispersed polar active sites while preserving the continuous conductive CNT network and enabling these sites to participate effectively in polysulfide adsorption and conversion remains a key challenge in the modification design of CNT-based sulfur cathodes.

Nevertheless, relying solely on the physical confinement effect of functionalized carbon frameworks is insufficient to effectively suppress polysulfide shut-

tling and accelerate sluggish sulfur-species conversion kinetics. Introducing polar transition metal compounds into carbon frameworks is an effective strategy for further enhancing polysulfide adsorption and accelerating their conversion in sulfur cathodes<sup>[25–27]</sup>. Compared with conventional nonpolar carbon materials, transition metal carbides possess high electrical conductivity, good structural stability, and strong chemical affinity toward polysulfides<sup>[28–30]</sup>. Among these compounds, vanadium carbide (VC) has been reported to enhance polysulfide adsorption and promote bidirectional sulfur redox conversion when coupled with conductive carbon nanotube frameworks<sup>[31]</sup>. Wang et al.<sup>[32]</sup> constructed a  $V_2O_5@V_2C$  vanadium-based heterostructure and demonstrated that the synergy between vanadium-based polar sites and the conductive framework significantly enhanced polysulfide adsorption and reduced the reaction barrier for their conversion into  $Li_2S/Li_2S_2$ , further highlighting the potential of vanadium-based active components for sulfur cathode design in lithium-sulfur batteries.

In this work, acidified multi-walled carbon nanotubes were employed as conductive scaffolds and supporting substrates, and VC active sites were constructed in situ on their surface through a hydrothermal reaction followed by high-temperature carbonization, yielding VC/acidified carbon nanotube composites (VCNTs). The acidified carbon nanotubes not only facilitate precursor dispersion and interfacial compatibility but also provide a continuous conductive network and stable anchoring sites for VC growth. The in situ generated VC introduces polar adsorption and catalytic centers, thereby strengthening the chemical anchoring of lithium polysulfides and promoting the reversible conversion of sulfur species. Through the synergistic integration of an acid-functionalized carbon framework with polar carbide active sites, VCNTs enable effective interfacial regulation and provide a feasible strategy for designing CNT-based functional additives for lithium-sulfur battery cathodes.

## 2 Experiment

### 2.1 Chemicals

The main reagents used in this work were as follows: multi-walled carbon nanotubes (MWCNTs, 99.99% purity) were purchased from Hangzhou Handan Optoelectronic Technology Co., Ltd.; concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and concentrated nitric acid ( $\text{HNO}_3$ ) were obtained from Chuandong Chemical; glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) and ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) were purchased from Aladdin Reagent Co., Ltd.; and anhydrous ethanol was obtained from Tianjin Fuyu Fine Chemical Co., Ltd.

### 2.2 Preparation of acidified multi-walled carbon nanotubes (AT-CNTs)

A total of 1.0 g of multi-walled carbon nanotubes was used as the starting material. Concentrated sulfuric acid and concentrated nitric acid were mixed at a volume ratio of 3 : 1 to prepare 100 mL of mixed acid solution<sup>[33]</sup>. Subsequently, the carbon nanotubes were added to the mixed acid solution and magnetically stirred at a rate of 500 r/min in a water bath at 65 °C for 8 h. After the reaction, the obtained suspension was repeatedly washed with deionized water and vacuum-filtered until the filtrate became nearly neutral ( $\text{pH} \approx 7$ ). Finally, the product was freeze-dried and ground for further use, and the resulting acidified carbon nanotubes were denoted as AT-CNTs.

### 2.3 Preparation of VCNTs, A-CNTs and CNTs

VCNTs were prepared through a hydrothermal reaction followed by high-temperature carbonization. First, 2.0 g of glucose was dissolved in deionized water under magnetic stirring for 1 h. Meanwhile, 0.6 g of ammonium metavanadate and 0.2 g of AT-CNTs were dispersed in anhydrous ethanol and ultrasonicated at 60 °C for 1 h to obtain a homogeneous suspension. Subsequently, the two solutions were mixed and further stirred at 60 °C for 0.5 h. The resulting mixture was transferred into a Teflon-lined autoclave and subjected to hydrothermal treatment at 180 °C for 12 h. After the reaction, the autoclave was naturally cooled to room temperature, and the precipitate was

collected and freeze-dried. The dried sample was thoroughly ground and then placed in a tube furnace, where it was heated to 500 °C at a rate of 3 °C/min and maintained for 2 h under an argon atmosphere, and then further heated to 900 °C at a rate of 5 °C/min and held for 2 h, yielding the VCNTs composite. The sample prepared using the same procedure but without ammonium metavanadate was denoted as A-CNTs. The sample prepared using the same procedure without ammonium metavanadate and using pristine MWCNTs instead of AT-CNTs was denoted as CNTs.

### 2.4 Preparation of cathode electrodes

Preparation of the sulfur/carbon composite (S/C): sulfur powder (S) and Ketjen black (KB) were thoroughly ground and mixed at a mass ratio of 7 : 3, followed by melt-diffusion treatment at 155 °C for 12 h under an argon atmosphere to obtain the sulfur/carbon composite (S/C). After cooling, the sample was sealed and stored in an oven at 60 °C for further use.

The S/C composite, VCNTs and poly (vinylidene fluoride) (PVDF) were weighed at a mass ratio of 8 : 1 : 1. First, the S/C composite and VCNTs were thoroughly ground and mixed in an agate mortar. An appropriate amount of N-methyl-2-pyrrolidone (NMP) was then added as the solvent for grinding and dispersion, followed by the addition of PVDF, and the mixture was further ground until a homogeneous electrode slurry was obtained. The slurry was uniformly coated onto an aluminum foil current collector using a doctor blade and dried in a vacuum oven at 60 °C for 12 h to completely remove the solvent. Subsequently, the dried electrode sheets were punched into circular electrodes with a diameter of 12 mm, and the sulfur areal loading in the electrodes was 0.9-1.2 mg  $\text{cm}^{-2}$ . For the control electrodes, VCNTs were replaced with A-CNTs or CNTs, respectively, using the same mass ratio and preparation procedure, while all other conditions were kept unchanged.

### 2.5 Characterization

The crystalline structures of the samples were characterized using an X-ray diffractometer (XRD, D8 Discover, Bruker). The surface morphology and microstructure of the samples were examined using

field-emission scanning electron microscopy (SEM, SU8600, HITACHI) and a high-resolution transmission electron microscope (TEM, JEM-F200). The surface elemental compositions and chemical states of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Nexsa). Raman spectroscopy (XploRA PLUS, Horiba) was used to evaluate the graphitization degree and defect structure of the carbon framework. Fourier-transform infrared spectroscopy (FTIR, Nicolet iS5) was employed to identify changes in the surface functional groups of the samples.  $N_2$  adsorption-desorption measurements were performed using a surface area and porosity analyzer (ASAP 2460) to determine the specific surface area and pore-structure parameters of the samples. To further evaluate the interfacial wettability between the materials and the electrolyte, contact angle measurements were conducted using a contact angle meter (JC2000D1).

### 2.6 Electrochemical performance testing

The prepared cathode electrodes were assembled into CR2032 coin cells in a glovebox filled with high-purity argon, using lithium metal foil as the anode, a polypropylene membrane (Celgard 2400) as the separator, and  $1.0 \text{ mol L}^{-1}$  LiTFSI dissolved in a DOL/DME mixed solvent (volume ratio of 1 : 1) with 2%  $LiNO_3$  as an additive as the electrolyte. In the experiment, the electrolyte volume was  $60 \mu\text{L}$ , corresponding to an  $E/S$  ratio of approximately 35–46  $\mu\text{L/mg}$ . After assembly, the cells were allowed to rest for 12 h to ensure sufficient infiltration of the electrolyte into the electrodes and separator. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (CHI760), with the CV voltage range set to 1.7–2.8 V and the scan rate set to  $0.1 \text{ mV s}^{-1}$ . The galvanostatic intermittent titration technique (GITT) test was conducted at 0.1 C, with a pulse duration of 10 min and a relaxation time of 20 min. Galvanostatic charge-discharge tests, rate performance tests, and cycling performance tests were carried out using a NEWARE battery testing system (NEWARE-CT-4008T).

## 3 Results and discussion

The VCNTs composite was prepared through a hydrothermal reaction followed by high-temperature carbonization, and the schematic illustration of the preparation process is shown in Fig. 1a. The detailed acidification process of the carbon nanotubes is provided in the Supporting Information (Fig. S1). For comparison, the sample prepared using the same procedure but without ammonium metavanadate was denoted as A-CNTs, whereas the sample prepared without ammonium metavanadate and using pristine MWCNTs instead of AT-CNTs was denoted as CNTs. The CNTs retained an intact fibrous structure after acidification, while intertube aggregation was markedly reduced, resulting in a more uniform distribution (Fig. S2a, b). As shown in the dispersion photograph after standing in ethanol for 30 min (Fig. S2c), the acidified CNTs exhibited better suspension stability, indicating that acid treatment effectively improved their surface wettability and dispersibility, which is beneficial for the subsequent uniform loading of vanadium species on the nanotube surface. The SEM images in Fig. 1b, c show that the composite retained an interwoven three-dimensional network framework. Compared with A-CNTs, VCNTs exhibited a rougher surface with relatively uniform particle attachment, indicating that the CNT network was markedly modified after the introduction of the vanadium precursor and subsequent high-temperature carbonization. The EDS elemental mapping results (Fig. S3) further show that V was uniformly distributed throughout the CNT network without obvious large-scale aggregation, suggesting that the vanadium-containing component was successfully introduced and well dispersed within the composite structure. The TEM image (Fig. 1d) shows that the sample was still dominated by a carbon nanotube network, with uniformly dispersed nanoparticles attached to the nanotube surface. The enlarged HRTEM image in Fig. 1e shows a distinct carbon coating layer around the particles, indicating the formation of a closely integrated interface between the VC particles and the car-

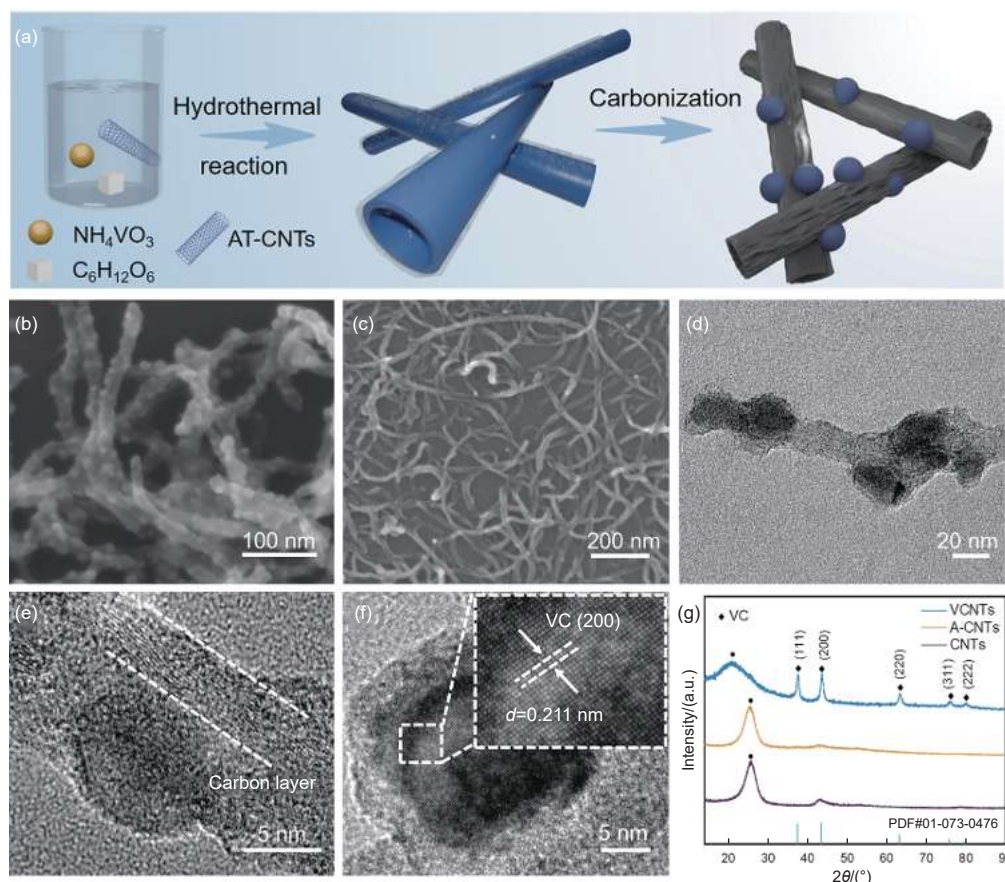


Fig. 1 Preparation procedure and morphological/structural characterization of the VCNTs composite: (a) Schematic illustration of the preparation procedure of VCNTs. (b) SEM image of VCNTs. (c) SEM image of A-CNTs. (d) TEM image of VCNTs. (e, f) High-resolution TEM images of VCNTs. (g) XRD patterns

bon framework. As shown in Fig. 1f, the measured lattice spacing of 0.211 nm corresponds to the (200) plane of VC, confirming the successful formation of a well-crystallized VC phase. The XRD pattern (Fig. 1g) is consistent with the microscopic structural analysis; in addition to the characteristic diffraction peaks of carbon materials, VCNTs exhibited diffraction peaks attributable to the VC phase, further confirming the successful introduction of VC. To further quantify the VC content in the VCNTs composite, thermogravimetric analysis (TGA, Fig. S4) was performed on the sample. Based on the test results, the mass fraction of VC in the VCNTs was determined to be approximately 35.1%, while the CNT content was about 38.55%. This quantitative result indicates that VC accounts for a significant mass proportion in the composite, providing abundant catalytic active sites for the electrode, while the CNT network ensures efficient electron transport, thereby achieving a good balance between catalytic activity and overall electrode

conductivity.

Fourier-transform infrared spectroscopy (FTIR, Fig. 2a) shows that CNTs, A-CNTs and VCNTs all retained the characteristic absorption signals of the carbon framework, with peaks corresponding to O—H ( $3430$  and  $1380\text{ cm}^{-1}$ ), C—H ( $2920$  and  $2850\text{ cm}^{-1}$ ), C=O ( $1720\text{ cm}^{-1}$ ), and C—O ( $1100\text{ cm}^{-1}$ ). Compared with pristine CNTs, A-CNTs exhibited enhanced absorption peaks associated with oxygen-containing functional groups, indicating that acidification modified the surface chemical environment of CNTs. However, subsequent high-temperature carbonization may have caused partial decomposition or reconstruction of these oxygen-containing functional groups. The changes in the corresponding absorption peaks of VCNTs further indicate that the introduction of VC altered the surface chemical environment. In the Raman spectra (Fig. 2b), all three samples exhibited typical *D* bands at  $1340\text{ cm}^{-1}$  and *G* bands at  $1580\text{ cm}^{-1}$ , corresponding to disordered/defective carbon and

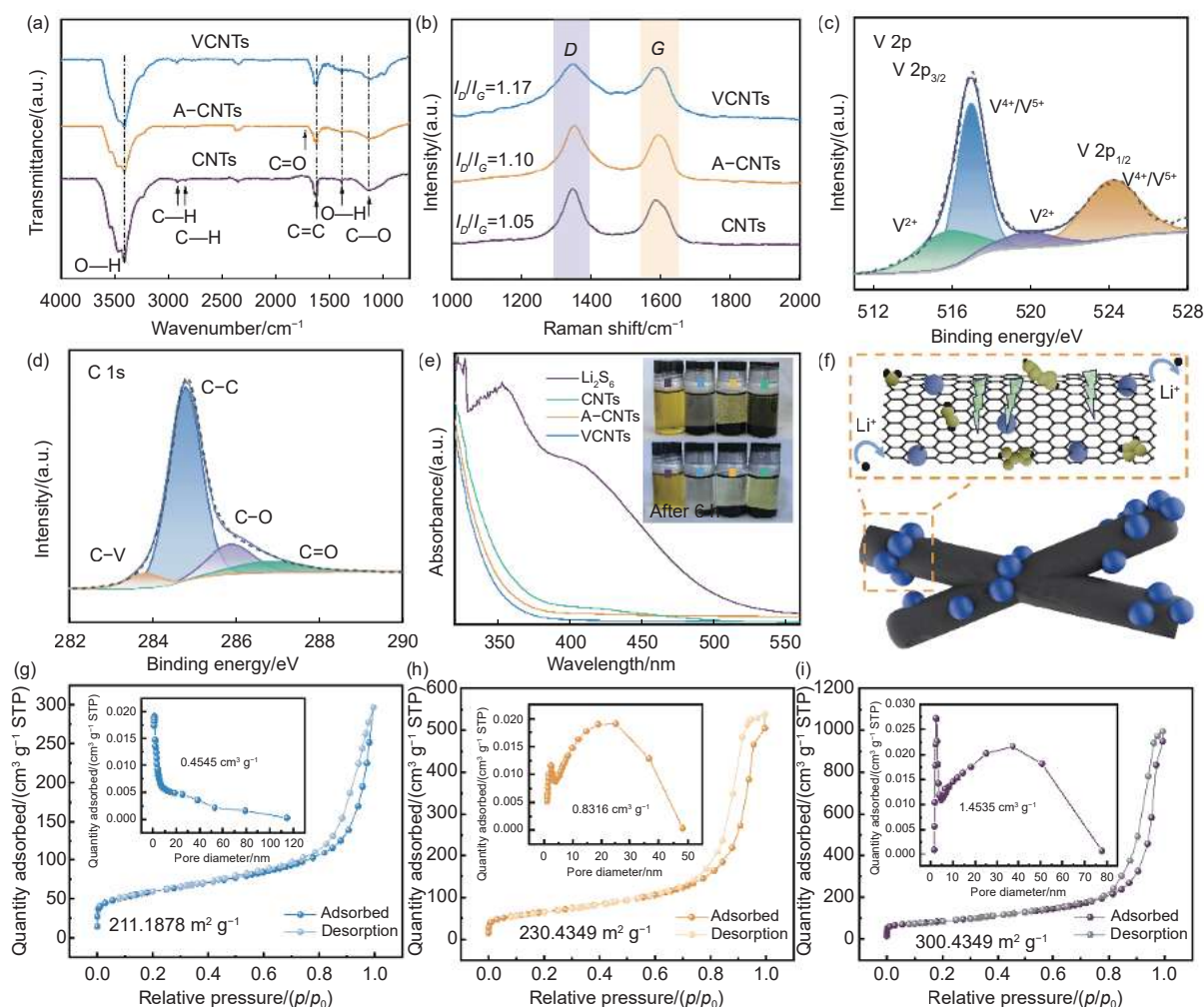


Fig. 2 (a) FTIR spectra of CNTs, A-CNTs, and VCNTs; (b) Raman spectra of CNTs, A-CNTs, and VCNTs; high-resolution XPS spectra of VCNTs: (c) V 2p spectrum and (d) C 1s spectrum; (e) adsorption photographs of CNTs, A-CNTs, and VCNTs toward  $\text{Li}_2\text{S}_6$  solution and the corresponding UV-vis absorption spectra; (f) schematic illustration of the LiPS adsorption and catalytic conversion mechanism in the VCNTs electrode;  $\text{N}_2$  adsorption-desorption isotherms and pore size distribution curves of (g) VCNTs, (h) A-CNTs, and (i) CNTs

graphitized carbon structures, respectively<sup>[34,35]</sup>. The  $I_D/I_G$  value increased successively from CNTs (1.05) to A-CNTs (1.10) and then to VCNTs (1.17), indicating an increased degree of defects and structural disorder in the carbon framework, which may provide additional active sites for polysulfide adsorption and interfacial reactions. In addition, contact angle measurements (Fig. S5) further demonstrate that VCNTs possessed improved electrolyte wettability, which is conducive to sufficient electrolyte penetration into the electrode interior and to increasing the effective reaction interface.

To further investigate the surface chemical states of VCNTs, X-ray photoelectron spectroscopy (XPS) was performed. As shown in Fig. 2c, the fitted peak at

515.6 eV can be assigned to V—C bonding, indicating the successful formation of VC active sites. The components at approximately 516.9 and 524.1 eV can be attributed to oxidized vanadium species, suggesting the presence of surface vanadium oxides that may originate from slight oxidation of VC upon air exposure. Since no characteristic diffraction peaks of any vanadium oxides other than the VC phase were observed in the XRD results, these surface oxides are merely an extremely thin native oxide layer rather than an independent crystalline byproduct phase. The C 1s spectrum (Fig. 2d) can be deconvoluted into C—V (283.8 eV), C—C (284.8 eV), C—O (285.9 eV), and C=O (286.8 eV) components, among which the C—V peak further confirms interfacial

bonding between VC and the carbon framework. In the O 1s spectrum (Fig. S6), the peaks at 530.1 and 531.7 eV correspond to V—O and O—H/C—O species, respectively, indicating the presence of oxygen-containing surface structures on VCNTs. These XPS results, together with the XRD and HRTEM analyses, indicate that VC-related active sites were successfully introduced into the CNT network and formed polar surface interfaces favorable for polysulfide adsorption.

The static  $\text{Li}_2\text{S}_6$  adsorption experiment and UV-vis spectroscopy (Fig. 2e) further confirm that VCNTs exhibit a stronger polysulfide adsorption capability than the control samples. This result indicates that the polar VC sites in VCNTs play an important role in polysulfide capture, while the mesoporous structure and CNT network provide physical confinement and mass-transfer channels. Fig. 2f presents a schematic illustration of the synergistic adsorption-catalysis mechanism of the VCNTs-modified sulfur cathode in lithium-sulfur batteries. The VC active sites on the carbon nanotube surface can anchor and confine soluble lithium polysulfides through polar interactions, thereby mitigating the shuttle effect. These sites can also serve as electrocatalytic centers to accelerate polysulfide redox kinetics, thus improving the rate capability and cycling stability of the sulfur cathode.  $\text{N}_2$  adsorption-desorption measurements (Fig. 2g-i, corresponding to VCNTs, A-CNTs and CNTs, respectively) show that all 3 samples exhibited typical type IV isotherms with H3-type hysteresis loops, indicating mesoporous structural characteristics. The BET specific surface area and total pore volume followed the order of VCNTs < A-CNTs < CNTs, and the decrease in pore parameters can be attributed to pore occupation caused by carbon-layer coating and VC loading. This result suggests that the improved electrochemical performance of VCNTs does not simply arise from an increased specific surface area, but is more likely associated with the synergistic effect of VC polar sites, defect structures, and the conductive CNT network.

Fig. 3a shows that, at a scan rate of  $0.1 \text{ mV s}^{-1}$ ,

the CNTs, A-CNTs and VCNTs electrodes all exhibited typical redox peaks of lithium-sulfur batteries. The two reduction peaks correspond to the stepwise reduction of elemental sulfur to long-chain lithium polysulfides (LiPSs) and then to solid  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ , whereas the 2 oxidation peaks correspond to the reversible oxidation of  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$  to higher-order LiPSs and finally to elemental sulfur<sup>[36–37]</sup>. In comparison, the VCNTs electrode displayed higher redox peak current densities, more distinct peak profiles, and smaller peak potential separations, indicating that the introduction of VC active sites reduced electrochemical polarization during sulfur-species conversion and improved the interfacial conversion kinetics of LiPSs. The Tafel analysis results in Fig. 3b, c further confirm this conclusion. The Tafel slopes of the VCNTs electrode for the reduction and oxidation processes were as low as 35.5 and  $115.1 \text{ mV dec}^{-1}$ , respectively, which were markedly lower than those of the A-CNTs and CNTs electrodes, demonstrating faster interfacial reaction kinetics and superior electrocatalytic conversion activity. Cyclic voltammetry measurements (Fig. S7) showed that the first 3 CV curves of the VCNTs electrode nearly overlapped, with no obvious shifts in redox peak positions or peak currents, indicating excellent reversibility of the electrode reactions.

Within the scan-rate range of  $0.1\text{--}0.5 \text{ mV s}^{-1}$ , the redox peak currents of all 3 electrodes increased with increasing scan rate, accompanied by varying degrees of peak shifts, indicating that the electrochemical reactions were jointly governed by Li-ion diffusion and charge-transfer processes. Among the three electrodes, the VCNTs electrode consistently maintained distinct redox peak profiles and smaller peak shifts over the entire scan-rate range, suggesting lower electrochemical polarization and faster sulfur-species conversion kinetics (Fig. 3d-f). In addition, the VCNTs electrode consistently exhibits 2 well-separated oxidation peaks at all scan rates. This is attributed to the multifunctional catalytic roles of VC, which include weakening the S—Li bonds through polar adsorption, providing metallic-like conductive pathways to accelerate charge transfer, and facilitating  $\text{Li}^+$  extraction.

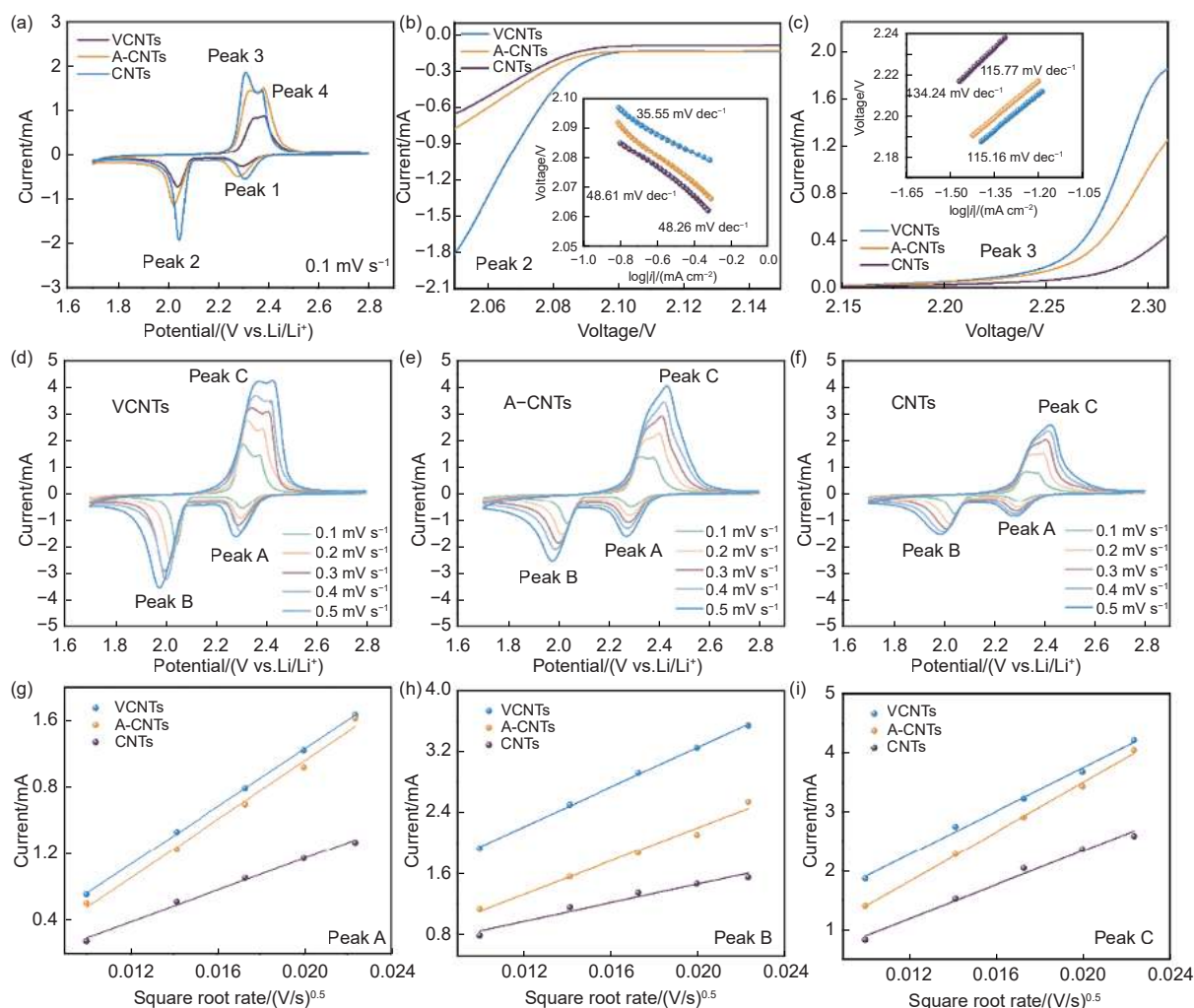


Fig. 3 Kinetic characterization of redox reactions on VCNTs, A-CNTs and CNTs electrodes: (a) Cyclic voltammetry (CV) curves of the 3 electrodes at a scan rate of  $0.1 \text{ mV s}^{-1}$ . (b) Tafel plot corresponding to the reduction peak of Peak 2. (c) Tafel plot corresponding to the oxidation peak of Peak 3. (d-f) CV curves of VCNTs, A-CNTs and CNTs electrodes at different scan rates ranging from  $0.1$  to  $0.5 \text{ mV s}^{-1}$ , respectively. (g-i) Linear fitting curves of peak current versus square root of scan rate for characteristic peaks Peak A, Peak B and Peak C, respectively

These functions enable both oxidation steps to proceed rapidly at low overpotentials, and even at high scan rates, the characteristic potentials of each step remain distinct, thus ensuring clear peak separation throughout. In contrast, the CNTs and A-CNTs electrodes, lacking polar catalytic sites, suffer from relatively large overpotentials for both oxidation steps, causing them to approach each other on the potential axis. Moreover, as the scan rate increases, the sluggish solid-phase oxidation kinetics fail to keep up with the rapid potential changes, resulting in temporal/potential coupling of the two-step reaction, which eventually merges into a single broad peak. Based on the linear fitting plots of peak current ( $I_p$ ) versus the square root of the scan rate ( $v^{0.5}$ ) (Fig. 3g-i), all three

electrodes exhibited good linear relationships at the three characteristic redox peaks, indicating that diffusion processes play an important role in the redox reactions. Notably, the fitted curves of the VCNTs electrode exhibited larger slopes for each characteristic peak, demonstrating faster apparent ion diffusion/mass-transfer behavior, which can be attributed to the transport pathways provided by the mesoporous structure and conductive CNT network.

To further analyze the polarization behavior of different electrodes during sulfur-species conversion, galvanostatic intermittent titration technique (GITT) measurements were performed to compare their voltage responses during discharge and charge processes. As shown in Fig. 4a-c, during discharge, the

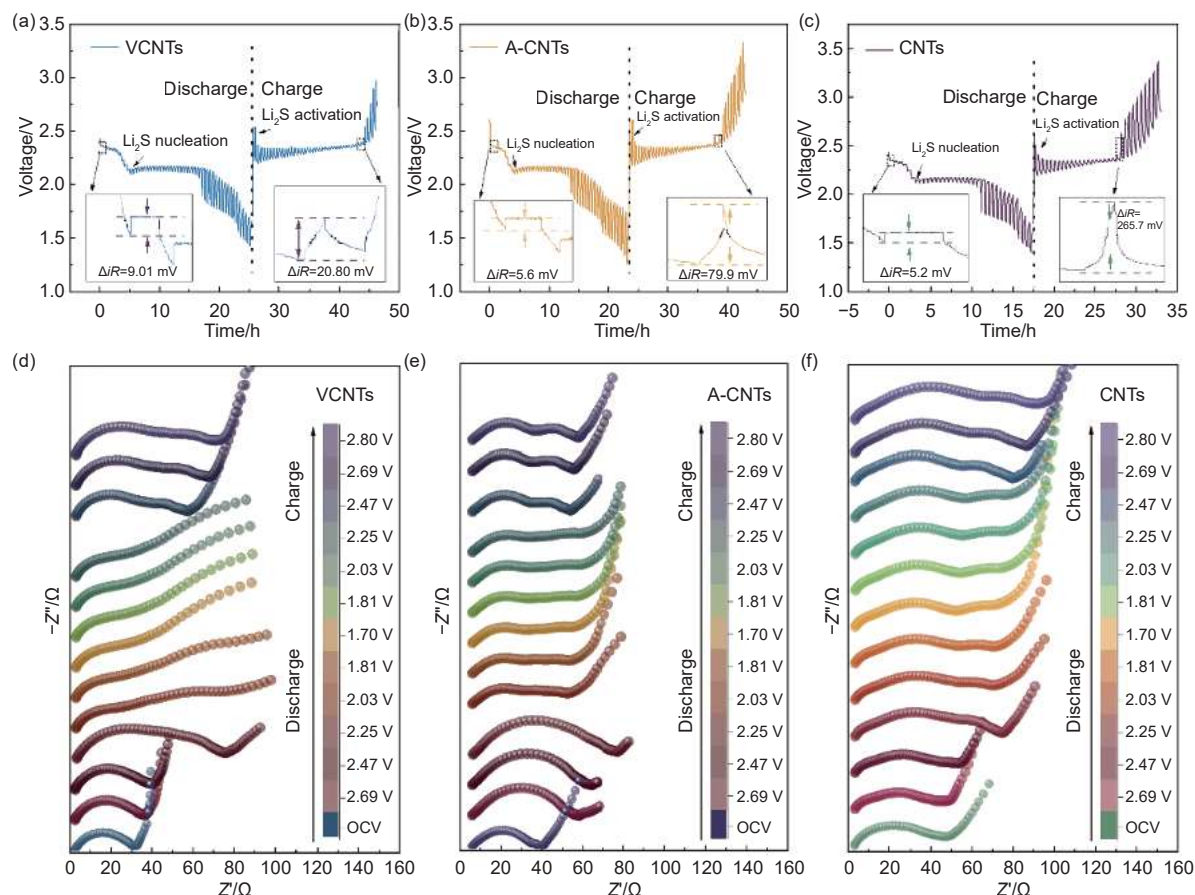


Fig. 4 (a-c) Represent the Galvanostatic Intermittent Titration Technique (GITT) test curves for VCNTs, A-CNTs and CNTs electrodes, respectively (the inset shows an enlarged view of the polarization voltage during the formation stage of solid lithium sulfide during discharge and the oxidation conversion stage of solid lithium sulfide during charge). (d-f) Represent the in-situ electrochemical impedance spectra of VCNTs, A-CNTs and CNTs electrodes at different charge-discharge voltages, respectively

polarization differences among the three electrodes were relatively small in the stage associated with the formation of solid lithium sulfides. In contrast, during charge, particularly in the stage associated with the oxidative conversion of solid lithium sulfides, the voltage polarization ( $\Delta iR$ ) of the VCNTs electrode was only 20.8 mV, which was much lower than those of the A-CNTs (79.9 mV) and CNTs (265.7 mV) electrodes. This result indicates that the VCNTs electrode exhibited reduced voltage hysteresis during solid lithium sulfide conversion, suggesting that it can alleviate kinetic sluggishness in the formation and oxidation of solid-phase products. As shown in Fig. 4d-f, compared with the A-CNTs and CNTs electrodes, the VCNTs electrode maintained a smaller impedance semicircle radius and a more gradual impedance evolution throughout the entire charge-discharge process. Particularly during deep discharge and charge stages,

the increase in interfacial impedance for the VCNTs electrode was markedly lower than those of the control samples, indicating lower interfacial charge-transfer resistance.

Fig. 5a shows that the VCNTs electrode consistently delivered the highest discharge specific capacities at current densities of 0.2, 0.5, 1, 2 and 3 C, reaching 1123.2, 909.9, 816.4, 717.0, 649.4 mAh g<sup>-1</sup>, respectively. When the current density was returned to the initial 0.2 C, the discharge specific capacity rapidly recovered to 938.2 mAh g<sup>-1</sup>, demonstrating excellent rate capability and electrochemical reversibility. As shown in Fig. 5b, c, all three electrodes exhibited the typical two-plateau discharge behavior of lithium-sulfur batteries at a current density of 0.1 C. Among the three electrodes, the VCNTs electrode showed more stable charge-discharge plateaus, with a charge-discharge potential difference ( $\Delta E$ ) of only 190.8 mV,

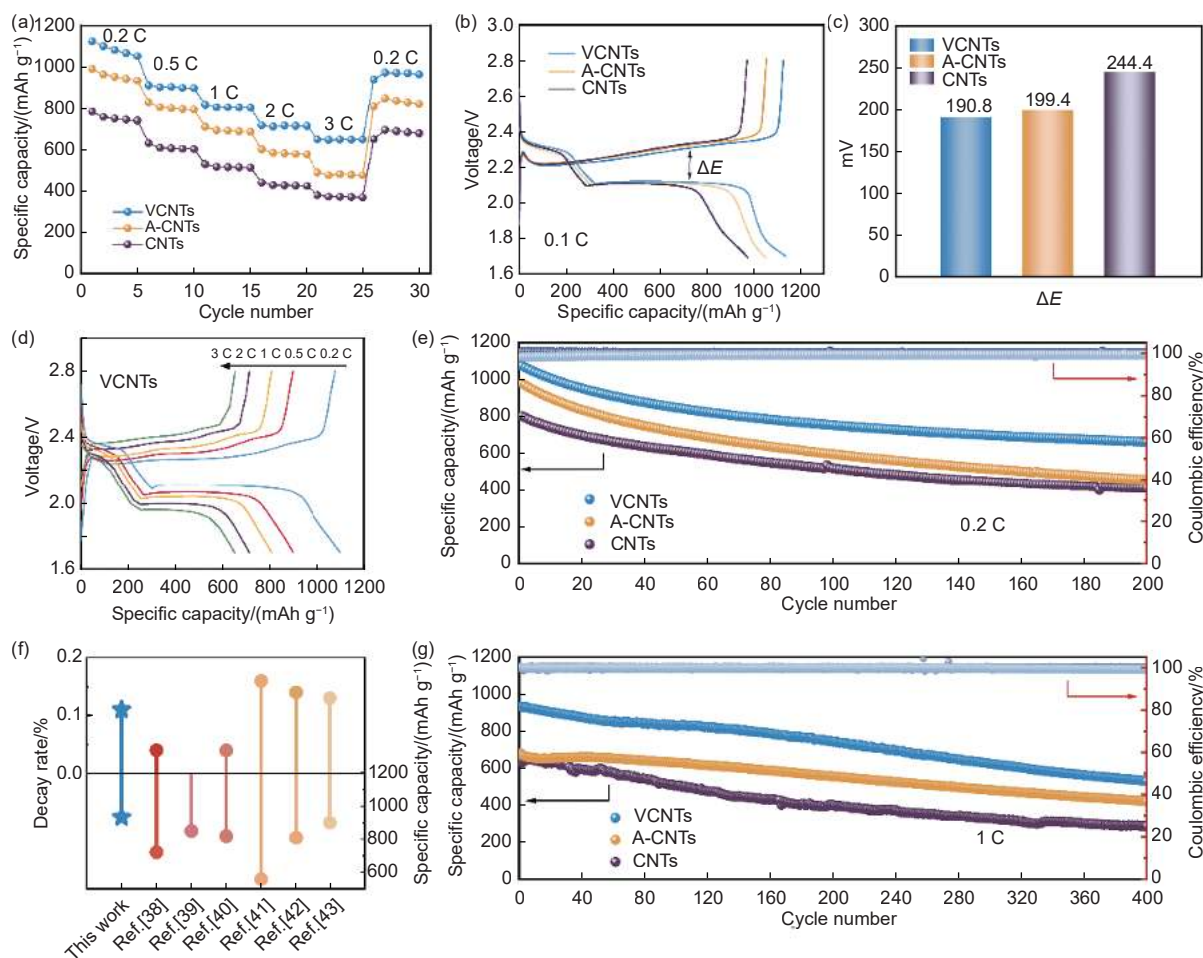


Fig. 5 (a) Rate performance curves of 3 electrodes at current densities ranging from 0.2 C to 3 C. (b) First constant current charge-discharge curves of the three electrodes at a current density of 0.1 C. (c) Comparison bar graph of the charge-discharge platform potential difference  $\Delta E$  of the 3 electrodes. (d) Constant current charge-discharge curves of the VCNTs electrode at different rates. (e) Long-cycle performance and Coulombic efficiency curves of the 3 electrodes at a current density of 0.2 C. (f) Comparison chart of the attenuation rate of the electrode at 1 C with reported literature<sup>[38–43]</sup>. (g) Long-cycle performance and Coulombic efficiency curves of the three electrodes at a current density of 1 C

which was lower than those of the A-CNTs (199.4 mV) and CNTs (244.4 mV) electrodes, indicating lower electrochemical polarization and superior reaction reversibility. Furthermore, the charge-discharge curves at different rates (Fig. 5d and Fig. S8) show that the VCNTs electrode maintained relatively distinct two-plateau discharge profiles and high specific capacities at various rates, whereas the plateau decay of the A-CNTs and CNTs electrodes was more pronounced, and the VCNTs electrode exhibited the smallest impedance (Fig. S9), further confirming the significant enhancement effect of VCNTs on sulfur-species conversion kinetics.

As shown in Fig. 5(e–g), at a current density of 0.2 C, the VCNTs electrode delivered an initial discharge specific capacity of 1075.1 mAh g<sup>−1</sup>, retained

61.8% of its capacity after 200 cycles, and exhibited an average capacity decay rate of only 0.19% per cycle. At a current density of 1 C, the VCNTs electrode delivered an initial discharge specific capacity of 932.9 mAh g<sup>−1</sup> and retained 531.3 mAh g<sup>−1</sup> after 400 cycles, outperforming the A-CNTs and CNTs control electrodes. The Coulombic efficiency of the VCNTs electrode remained close to 100%, indicating good reversibility and partially suppressed shuttle-related side reactions. Overall, the enhanced electrochemical performance of the VCNTs electrode can be attributed to the rapid electron/ion transport enabled by the continuous conductive CNT network and the synergistic LiPS adsorption and electrocatalytic effects provided by the polar VC sites. These features help mitigate polysulfide shuttling and reduce interfa-

cial polarization associated with solid sulfide conversion, thereby promoting more reversible sulfur redox reactions. In contrast, the CNTs electrode exhibited slight fluctuations in Coulombic efficiency during the later stages of cycling ( $\sim 250$ -270 cycles). This phenomenon primarily arises from the lack of polar active sites on the CNTs electrode, which prevents effective anchoring and catalytic conversion of polysulfides, thereby causing dynamic fluctuations in the shuttle effect over prolonged cycling. Specifically, the interplay among polysulfide shuttling, repeated rupture and regeneration of the SEI film on the anode, continuous electrolyte consumption, and uneven passivation of the lithium anode surface collectively contributes to the observed fluctuations in Coulombic efficiency. As shown in Fig. 5f and Table S1, the cycling decay rate of the VCNTs electrode at 1 C is comparable to those of previously reported carbide/CNT-based lithium-sulfur cathode materials, indicating competitive cycling stability and improved sulfur redox kinetics.

## 4 Conclusions

In this study, acidified CNTs were employed as conductive scaffolds, and VC active sites were constructed in situ on their surface through a hydrothermal reaction followed by high-temperature carbonization, yielding VCNTs composites. Structural characterizations showed that VC nanoparticles were successfully anchored on the CNT network surface and formed a closely integrated interface with the carbon framework. The acidified CNTs provide continuous electron transport pathways and a favorable dispersion matrix, while the VC sites enhance polysulfide adsorption and improve the apparent kinetics of sulfur-species conversion. Compared with the A-CNTs and CNTs control electrodes, the VCNTs-modified sulfur cathode exhibited lower electrochemical polarization, smaller interfacial impedance, and superior rate and cycling performance, retaining a discharge specific capacity of 531.3 mAh g<sup>-1</sup> after 400 cycles at 1 C. These results indicate that coupling polar carbide active sites with a conductive CNT network is an ef-

fective modification strategy for improving the reaction kinetics of sulfur cathodes in lithium-sulfur batteries.

## References

- [1] Zhu L, Zhang X, Zhang J, et al. A review on sulfur-based composite cathode materials for lithium-sulfur batteries: Progress and prospects[J]. *Journal of Alloys and Compounds*, 2025, 1010: 178282.
- [2] Carolina P A, Roberto R S, Miguel O S, et al. N-doped activated carbons from leather waste produced by microwave activation for use as the cathode of Li-S batteries[J]. *New Carbon Materials*, 2025, 40(2): 382-396.
- [3] Bongu C S, Tasleem S, Krishnan M R, et al. Carbon nanotubes in lithium-sulfur batteries and photocatalytic hydrogen evolution: From conductive hosts to catalytic interfaces[J]. *Advanced Composites and Hybrid Materials*, 2026, 9(3): 218.
- [4] Agostini M, Matic A. Designing highly conductive functional groups improving guest-host interactions in Li/S batteries[J]. *Small*, 2020, 16(2): 1905585.
- [5] Ma Y, Liu K, Zhu L, et al. Rethinking the shuttle effect: Intrinsic phenomenon and regulatory opportunities in battery design[J]. *Advanced Functional Materials*, 2026, 36(22): e25291.
- [6] Ren W, Ma W, Zhang S, et al. Recent advances in shuttle effect inhibition for lithium sulfur batteries[J]. *Energy Storage Materials*, 2019, 23: 707-732.
- [7] Manthiram A, Fu Y, Chung S H, et al. Rechargeable lithium-sulfur batteries[J]. *Chemical Reviews*, 2014, 114(23): 11751-11787.
- [8] Li Z, Wu H B, Lou X W. Rational designs and engineering of hollow micro-/nanostructures as sulfur hosts for advanced lithium-sulfur batteries[J]. *Energy & Environmental Science*, 2016, 9(10): 3061-3070.
- [9] He X, Zuo H, Xiao R, et al. The use of a ternary metal sulfide loading on carbon fibers as the sulfur host for high performance low-temperature lithium sulfur batteries[J]. *New Carbon Materials*, 2025, 40(1): 167-177.
- [10] Zheng M, Chi Y, Hu Q, et al. Carbon nanotube-based materials for lithium-sulfur batteries[J]. *Journal of Materials Chemistry A*, 2019, 7(29): 17204-17241.
- [11] Wei C, Shao X, Lin F, et al. A review of electrospun carbon-based nanofibers materials used in lithium-sulfur batteries[J]. *Chemistry-A European Journal*, 2024, 30(52): e202401442.
- [12] Li Z, Liu Z, Sun H, et al. Superstructured assembly of nanocarbons: fullerenes, nanotubes, and graphene[J]. *Chemical Reviews*, 2015, 115(15): 7046-7117.
- [13] Wei H, Liu Y, Zhai X, et al. Application of carbon nanotube-based materials as interlayers in high-performance lithium-sulfur batteries: a review[J]. *Frontiers in Energy Research*, 2020, 8: 585795.

- [ 14 ] He J, Chen Y, Li P, et al. Three-dimensional CNT/graphene-sulfur hybrid sponges with high sulfur loading as superior-capacity cathodes for lithium-sulfur batteries[J]. *Journal of Materials Chemistry A*, 2015, 3(36): 18605-18610.
- [ 15 ] Choi C, Yun T G, Hwang B. Dispersion stability of carbon nanotubes and their impact on energy storage devices[J]. *Inorganics*, 2023, 11(10): 383.
- [ 16 ] Ansari R, Rouhi S, Ajori S. On the interfacial properties of polymers/functionalized single-walled carbon nanotubes[J]. *Brazilian Journal of Physics*, 2016, 46(3): 361-369.
- [ 17 ] Nurettin Sezer, Muammer Koç. Oxidative acid treatment of carbon nanotubes[J]. *Surfaces and Interfaces*, 2019, 14: 1-8.
- [ 18 ] Chiang Y C, Lin W H, Chang Y C. The influence of treatment duration on multi-walled carbon nanotubes functionalized by  $\text{H}_2\text{SO}_4/\text{HNO}_3$  oxidation[J]. *Applied Surface Science*, 2011, 257(6): 2401-2410.
- [ 19 ] Osorio A G, Silveira I C T, Bueno V, et al.  $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{HCl}$ -functionalization and its effect on dispersion of carbon nanotubes in aqueous media[J]. *Applied Surface Science*, 2008, 255(5): 2485-2489.
- [ 20 ] Banerjee S, Hemraj-Benny T, Wong S S. Covalent surface chemistry of single-walled carbon nanotubes[J]. *Advanced Materials*, 2005, 17(1): 17-29.
- [ 21 ] Kim G H, Raza A, Lee Y J, et al. Enhanced lithium host performance of multi-walled carbon nanotubes through acidic functionalization for lithium-sulfur batteries[J]. *Heliyon*, 2024, 10(16): e35969.
- [ 22 ] Popov V N. Carbon nanotubes: properties and application[J]. *Materials Science and Engineering: R: Reports*, 2004, 43(3): 61-102.
- [ 23 ] Gupta N, Gupta S M, Sharma S K. Carbon nanotubes: synthesis, properties and engineering applications[J]. *Carbon Letters*, 2019, 29(5): 419-447.
- [ 24 ] Usrey M L, Strano M S. Controlling single-walled carbon nanotube surface adsorption with covalent and noncovalent functionalization[J]. *The Journal of Physical Chemistry C*, 2009, 113(28): 12443-12453.
- [ 25 ] Zhao C X, Wang H F, Li B Q, et al. Multianion transition metal Compounds: synthesis, regulation, and electrocatalytic applications[J]. *Accounts of Materials Research*, 2021, 2(11): 1082-1092.
- [ 26 ] Shan Y H, Li L B, Du J T, et al. High performance lithium-sulfur batteries using three-dimensional hierarchical porous carbons to host the sulfur[J]. *New Carbon Materials*, 2021, 36(6): 1094-1101.
- [ 27 ] Wang H, Zhang W, Xu J, et al. Advances in polar materials for lithium-sulfur batteries[J]. *Advanced Functional Materials*, 2018, 28(38): 1707520.
- [ 28 ] Sun M, Ren X, Gan Z, et al. Nanostructured binary transition-metal-sulfides and nanocomposites as high-performance electrodes for hybrid supercapacitors[J]. *Applied Physics Reviews*, 2024, 11(2): 021318.
- [ 29 ] Xiao Y, Hwang J Y, Sun Y K. Transition metal carbide-based materials: Synthesis and applications in electrochemical energy storage[J]. *Journal of Materials Chemistry A*, 2016, 4(27): 10379-10393.
- [ 30 ] Zhong Y, Xia X, Shi F, et al. Transition metal carbides and nitrides in energy storage and conversion[J]. *Advanced Science*, 2016, 3(5): 1500286.
- [ 31 ] Qi J, Zhai Y, Bethune K, et al. Vanadium carbide nanoflakes as catalysts for  $\text{V}^{3+}/\text{V}^{2+}$  redox reactions[J]. *Electrochimica Acta*, 2025, 511: 145399.
- [ 32 ] Wang Z, Yu K, Gong S, et al. Vanadium based carbide-oxide heterogeneous  $\text{V}_2\text{O}_5@\text{V}_2\text{C}$  nanotube arrays for high-rate and long-life lithium-sulfur batteries[J]. *Nanoscale*, 2020, 12(36): 18950-18964.
- [ 33 ] Wang L, Wang Y, Zhuang Q. Simple self-referenced ratiometric electrochemical sensor for dopamine detection using electrochemically pretreated glassy carbon electrode modified by acid-treated multiwalled carbon nanotube[J]. *Journal of Electroanalytical Chemistry*, 2019, 851: 113446.
- [ 34 ] Zhang Y, Zhang J, Fan M, et al. Exploring a novel approach to fabricate vanadium carbide encapsulated into carbon nanotube (VC@C) with large specific surface area[J]. *Bulletin of Materials Science*, 2013, 36(3): 345-351.
- [ 35 ] Cançado L G, Jorio A, Ferreira E H M, et al. Quantifying defects in graphene via raman spectroscopy at different excitation energies[J]. *Nano Letters*, 2011, 11(8): 3190-3196.
- [ 36 ] Jiao X, Hu J, Zuo Y, et al. Self-recovery catalysts of  $\text{ZnIn}_2\text{S}_4@\text{In}_2\text{O}_3$  heterostructures with multiple catalytic centers for cascade catalysis in lithium-sulfur battery[J]. *Nano Energy*, 2024, 119: 109078.
- [ 37 ] Jiang Y, Yang R, Jiang B, et al. Hierarchical catalysis tailoring  $\text{Li}_2\text{S}_2$  solid-state dissociation for high-energy lithium-sulfur batteries[J]. *Journal of Energy Chemistry*, 2026, 116: 604-616.
- [ 38 ] Wang L, Li J, Chen Y, et al. Recycling two wastes for constructing vanadium nitride/vanadium trioxide dual-decorated carbonfiber interlayer and porous carbon to improve lithium-sulfur batteries[J]. *Journal of Colloid and Interface Science*, 2026, 709: 139934.
- [ 39 ] Guo J, Chen Z, Yan X, et al. Promoting polysulfides conversion by hexagonal-like V-MOF-derived VC-doped carbon nanotubes for lithium-sulfur batteries[J]. *Synthetic Metals*, 2024, 307: 117706.
- [ 40 ] Liu F, Yuan M, Feng P, et al. Synthesis of nitrogen-doped carbon nanotubes from biomass polysaccharides and lignin in waste corn stalk as host materials for lithium-sulfur batteries[J]. *International Journal of Biological Macromolecules*, 2025, 304: 140813.
- [ 41 ] Dharmesh A, Rani P, Sharma A K. Tamarind peel-derived nitrogen-doped porous carbon: A sustainable sulfur host for enhanced lithium-sulfur battery performance[J]. *Journal of Power Sources*, 2025, 634: 236429.