

Review Article

Integrated Design, Fundamental Insights, and Strategic Engineering of Carbon-Based Materials for Next-Generation Lithium–Sulfur Energy Storage Systems

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Lithium–sulfur batteries (LSBs) have garnered significant attention as next-generation energy storage systems due to their exceptionally high theoretical capacity and superior gravimetric and volumetric energy densities. However, their widespread adoption remains hindered by persistent challenges, including polysulfide (PS) shuttling, low sulfur utilization, volume expansion, sluggish reaction kinetics, and insufficient sulfur loading. Carbon-based materials have emerged as promising sulfur hosts, offering structural, morphological, and functional tunability to address these limitations. Various strategies have been explored, including the integration of carbon materials with separators, binders, nanoparticles, and nanosheets; sulfur encapsulation within hollow scaffolds; anchoring of N₄-coordinated single atoms (SAs); self-assembled biomaterials; functional group engineering; hybridization with polar nanoparticles and gel-based matrices; biomass-derived carbon sources; advanced structural modifications. This review provides a comprehensive analysis of recent advancements in carbon-based material design for LSBs, highlighting key behavioral characteristics, novel approaches, and material optimization strategies. Furthermore, it outlines current performance benchmarks and offers insights into future research directions for the continued advancement of LSB technology.

Keywords: carbon; energy storage; heteroatom; hierarchical; lithium–sulfur batteries; porous; sulfur

1. Introduction

The continuous advancement in technology, coupled with the growing energy demands across various emerging sectors such as transportation, military, and aviation, has highlighted the critical need for the development of advanced battery technologies. These technologies are essential for efficiently supplying the energy required by these high-demand applications. Compared to the theoretical limits of current state-of-the-art lithium-ion batteries (LIBs), which offer gravimetric energy density (200–300 W h kg^{−1}) and volumetric energy density (640 W h L^{−1}), next-generation lithium–sulfur batteries (LSBs) present a promising solution to meet future energy

demands. LSBs offer significantly higher theoretical specific capacity (1675 mA h g^{−1}), gravimetric energy density (2600 W h kg^{−1}), and volumetric energy density (2800 W h L^{−1}), making them a strong candidate for fulfilling the increasing energy requirements in the sector (Figure 1) [1–4].

The abundance of sulfur on Earth (constituting 3% of Earth's mass), along with its low cost and nontoxicity, strongly supports the development of LSBs as an advanced energy storage system. Sulfur's multivalency and lightweight nature facilitate efficient redox reactions with alkali lithium (Li) polysulfides (Li₂S_x, 2 < x ≤ 8), preventing thermal runaway due to its wide temperature window and intrinsic overcharge protection [5]. From a cell component perspective, LSBs require an

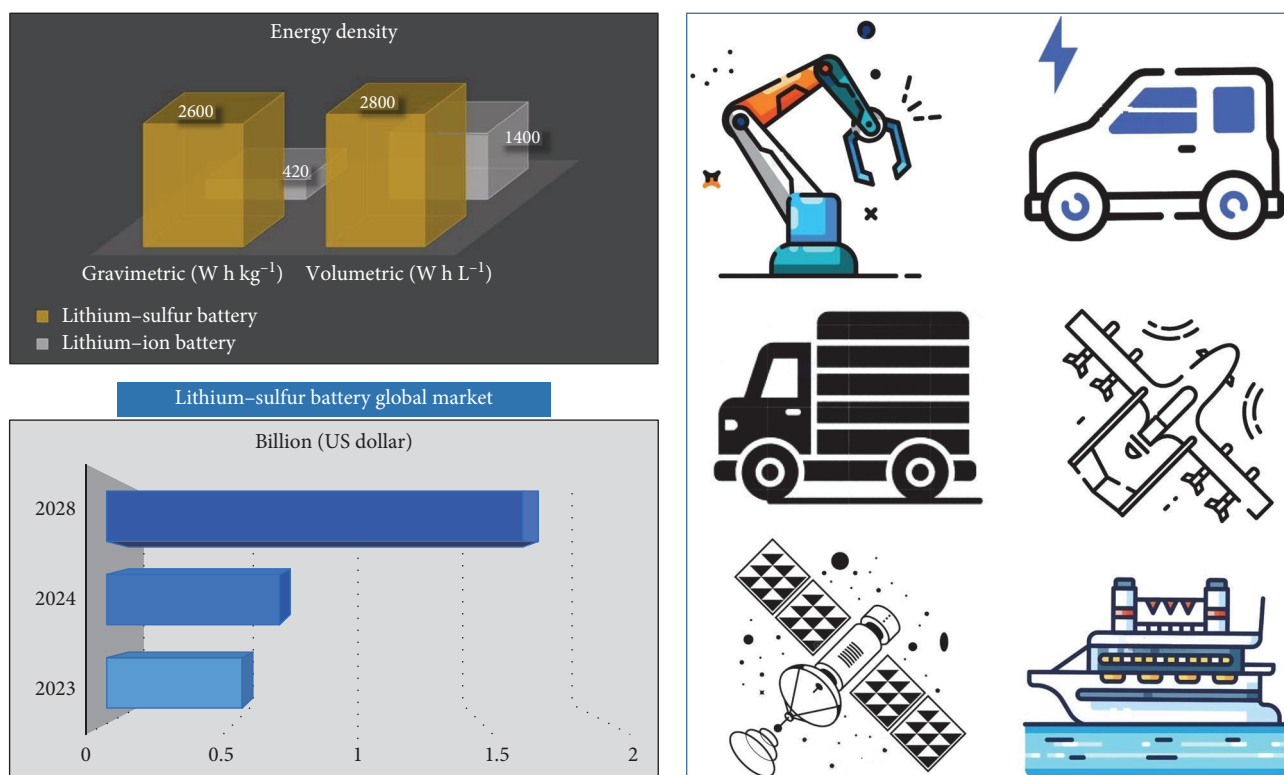


FIGURE 1: Comparative energy densities of lithium-sulfur batteries, global market growth forecast, and potential future application areas.

areal capacity higher than that of commercial LIBs ($\sim 4 \text{ mA h cm}^{-2}$) to be considered for advanced high-performance devices [6, 7]. The operational potential of LSBs is 2.1 V vs. Li/Li^+ , approximately half that of LIBs, which operate at 3.5–4.0 V vs. Li/Li^+ . An areal sulfur loading of 6–8 mg cm^{-2} achieves a sulfur utilization efficiency of 60%–80% [8, 9]. In contrast, a lower sulfur loading of 2 mg cm^{-2} provides an areal capacity of 3.35 mA h cm^{-2} , even at 100% sulfur utilization. The energy density gap between LSBs and LIBs becomes evident, underscoring the need for high sulfur loading on the cathode to fully realize the theoretical potential of LSBs [5–7]. From the perspective of gravimetric energy density, an electrolyte volume-to-sulfur weight (E/S) ratio greater than 3 poses a significant obstacle to increasing the energy density of LSBs. Achieving an optimal E/S ratio is crucial for establishing proper electronic and ionic contact areas. The sulfur loading and its efficient utilization depend on various material design strategies aimed at optimizing these parameters [10–12].

Several key challenges have significantly hindered the development of LSBs. First, sulfur's inherently low electrical conductivity ($5 \times 10^{-30} \text{ S cm}^{-1}$ at 25°C) limits electron transfer efficiency within the battery [13]. Additionally, the dissolution of polysulfides (PSs) in the electrolyte, known as the "shuttle effect," leads to the loss of active sulfur and reduces the battery's overall efficiency and stability. Moreover, the substantial volume change of sulfur during the charge/discharge process compromises the structural integrity of the

battery over repeated cycles. High sulfur loading, while desirable for increasing energy density, exacerbates these issues by enhancing the passivation of the Li metal anode with stoichiometric amounts of Li_2S , further reducing the efficiency and stability of high-energy density LSBs [5, 14, 15].

To fully realize the potential and theoretical performance of LSBs, it is essential to design materials that can address several critical challenges. These include supporting the inherently low electrical conductivity of sulfur, accommodating high sulfur loading, ensuring high sulfur utilization, mitigating the diffusion and dissolution of PSs, and effectively buffering the volume expansion that occurs during charge/discharge cycles [7]. Carbon-based materials, including porous carbon, hierarchical carbon, hollow carbon, heteroatom-doped carbon, carbon nanofibers (CNFs), carbon nanotubes (CNTs), graphene, and carbon black, have been extensively utilized in various roles—such as host materials, conductive networks, buffering mediums, and catalytic supports—to maximize sulfur utilization efficiency [16, 17]. Significant research efforts have focused on engineering carbon-based materials for the cathodes of LSBs, aiming to overcome these challenges and enhance battery performance. This review article provides a comprehensive analysis of current research efforts, examining fundamental strategies, trends, and findings, with a focus on performance outcomes (summarized in Tables 1 and 2). The review also discusses future research directions, offering insights into the continued development of effective and efficient materials for LSB technology.

TABLE 1: Summary and comparison of various review articles with the present review, highlighting the significance of this work.

Review article	Scope	Limitations
Manthiram et al. [18]	LSB configuration and synthesis only	No fundamental discussions on the carbon-based development
Li et al. [19]	Focus on different structured and phase carbon	Vague in theoretical perspective and fundamental critical discussions of current research
Wang et al. [20]	Focus on textural properties of carbon-based materials	No discussion on functional carbon or clear view of development strategy
Deng et al. [21]	Focus only shuttle effects	Absent of integrated development strategy
Xiao et al. [22]	Focused on different carbon-based materials	Limited to synthesis strategy and fabrications, no discussions on theoretical critical factors or correlation
Xiang et al. [17]	Focused on template-based synthesis carbon	Absent of other synthesis route and carbon materials engineering
This review	Fundamental insight of carbon-based integrated development strategy and systematic discussions, materials engineering, understanding conceptual computational analysis, and critical factors	—

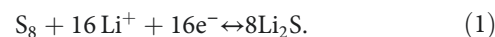
2. Fundamental of LSBs and Critical Issues

The LSBs consist of elemental sulfur (S_8) at the cathode and Li at the anode (Figure 2). It functions via reversible redox reactions between sulfur species and Li ions during charge and discharge cycles (Equations (1) and (2)). In general, a porous and conductive carbon material is used as the sulfur host in the cathode, a separator, and a stoichiometric amount of Li metal as the anode. The core electrochemical process during discharge releases energy and the reverse process stores energy. In the discharge process, a multistep reduction occurs through the reaction of Li ions from the anode with the elemental sulfur in the cathode, known as the lithiation of sulfur. Multistep reduction process ($S_8 \rightarrow Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4 \rightarrow Li_2S_2 \rightarrow Li_2S$) in the discharge categorized into three stage such as: (i) formation of the long chain Li PSs (Li_2S_8 and Li_2S_6) from cyclo-octasulfur, occurred at approximately 2.3 V, which is soluble in the electrolyte, (ii) further reduction of Li_2S_6 to Li_2S_4 at approximately 2.3 V, and (iii) formation of the insoluble PSs (Li_2S_2 and Li_2S) at approximately 2.1 V [21, 36]. Stages (i) and (ii) are characterized by faster reaction kinetics (Equations (3)–(5)). In the Stage (iii), the reduction kinetics slow down as insoluble short-chain Li sulfides form at a lower voltage plateau of approximately 2.1 V, through the decomposition of PSs (Equation (6)). During the charge process, the reactions proceed with slow kinetics. Initially, Li sulfides are oxidized to Li polysulfides (LiPSs) at 2.3–2.4 V (Equations (6), (7)), followed by further oxidation at 2.45–2.5 V (Equations (3)–(5)). This slow oxidation is evidenced by a broad anodic peak [77, 78].

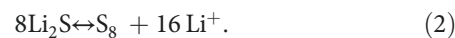
Designing efficient LSBs presents several significant challenges that must be addressed. Sulfur's insulating nature, with its extremely low electrical conductivity ($5 \times 10^{-30} \text{ S cm}^{-1}$ at 25°C) and Li_2S 's low conductivity ($10^{-14} \text{ S cm}^{-1}$), impedes effective electron transport within the battery. The dissolution of PSs into the electrolyte creates the “shuttle effect,” where these soluble PS intermediates diffuse through the separator and accumulate on the Li anode. This results in the passivation of the anode, leading to poor cycling life and

drastic performance degradation. The low exposure of active surfaces further hinders sulfur utilization, slows reaction kinetics, and reduces overall efficiency [30, 79, 80].

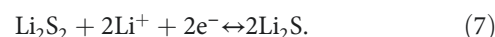
Overall discharge reaction:



Overall charging reaction:



PS interconversion reactions:



The cathode faces specific challenges, including sulfur's low electrical conductivity and the easy dissolution of PS intermediates (Li_2S_n , $4 < n < 8$) in the electrolyte, which migrate to the anode (loss of active sulfur), exacerbating the shuttle effect. During discharge, dissolved PS intermediates form concentration gradients and electrochemical potential triggers the diffusion towards the Li anode. This leads to serious irreversible side reactions between the shuttling PSs and Li metal, the formation of an insulating layer of Li_2S_2 or Li_2S on the Li anode by chemical reduction, resulting in low Coulombic efficiency. LSB design factors, such as electrolyte composition, solvent polarity, and high porosity of the separator, accelerate the diffusion of PSs and poorly confined sulfur host intensifies the shuttling effects. Various strategic approaches may mitigate the shuttle effects of physical confinement, chemical

TABLE 2: Comparison of performances of different materials on lithium–sulfur batteries.

Components	Materials	Performances	Ref.
Separator	G@PC	DC of G@PC/PP 1186 mA h g ⁻¹ (92% CE); PP 412 mA h g ⁻¹ (39% CE)	[23]
Binder	PQ	Initial capacity 9 mA h cm ⁻² , cycling capacity 7 mA h cm ⁻²	[24]
Cathode	Al@S/AB@CC–CoS ₂	DC 1481 mA h g ⁻¹ at 0.1 C, Tafel slope 39 mV dec ⁻¹ , CE 90%	[25]
Cathode	Co ₃ S ₄ coated on N–doped C nanofiber	DC 710 mA h g ⁻¹ at 1 C after 200 cycles, CE 97.8% (1.7 mg cm ⁻²), 4.1 mA h cm ⁻² at 0.1 C (6.8 mg cm ⁻¹ , 100 cycles)	[26]
Cathode	N, P co–doped C sphere	DC 814 mA h g ⁻¹ at 1 C after 500 cycles	[27]
Cathode	Mo–N–doped carbon	DC 1248 mA h g ⁻¹ at 0.2 C (715 mA h g ⁻¹ at 5 C), 4.2 mA cm ⁻² (400 cycles, 5.1 mg cm ⁻² S loading)	[28]
Separator	SnS/porous C nanosheet	Initial DS 1270 mA h g ⁻¹ at 0.5 C; decay rate 0.039% at 1 C each cycle, DC 955.3 mA h g ⁻¹ (6 mg cm ⁻² S loading) at 0.5 C	[29]
Cathode	CoS ₂ @N–doped graphitic C	DC 1300 mA h g ⁻¹ at 0.1 C, 903 mA h g ⁻¹ (100 cycles, 0.1 C)	[30]
Cathode	C fiber/vanadium nitride array	DC 1310 mA h g ⁻¹ at 0.1 C, 1052 mA h g ⁻¹ (250 cycles, 0.1 C)	[31]
Cathode	O, N–doped C	DC 540 mA h g ⁻¹ (300 cycles, 1.6 C)	[32]
Interlayer	CNT–OH/THPP/TDI/PP	Reversible capacity 734 mA h g ⁻¹ at 5 C; reversible capacity 419 mA h g ⁻¹ decay rate 0.029%	[33]
Cathode	N–doped hollow C	DC 1263 mA h g ⁻¹ at 0.2 C, decay rate 0.07% per cycle	[34]
Cathode	N, O–doped C	DC 804 mA h g ⁻¹ at 0.5 C at 200 cycles at 2.5 mg cm ⁻² S loading	[35]
Cathode	S–CoO/Co ₉ S ₈ /NC	DC 1470 mA h g ⁻¹ at 0.1 C, capacity attenuation 0.03% per cycle	[16]
Cathode	C–hemp/CMC/S	Specific capacity 18 mA h cm ⁻² at 28 mg cm ⁻² S mass loading	[36]
Cathode	RHCF/SAC/V ₂ O ₃	DC 578 mA h g ⁻¹ at 5 C, capacity retention 94% after 200 cycles at 0.1 C	[37]
Cathode	N, O–doped C	DC 1549 mA h g ⁻¹ at 0.05 C, DC 5.4 mA h cm ⁻² at 0.2 C (7.4 mg cm ⁻² S loading) for 50 cycles, capacity retention 97.2% after 100 cycles at 0.2 C	[38]
Cathode	Ni _{SA} –Ni _{NP} –CD _S @CNF	DC 66 mA h cm ⁻² at 0.02 C capacity retention 86.1% after 100 cycles at 0.12 C (50 mg cm ⁻² S loading, E/S 5 μ L mg ⁻¹)	[39]
Cathode	MnO ₂ @HCB	DC 1142 mA h g ⁻¹ at 1 A g ⁻¹ , DC ~200 mA h g ⁻¹ at 1 A g ⁻¹ after 60 cycles	[40]
Cathode	AB/S@PPY	DC 1207 mA h g ⁻¹ at 0.2 C, DC 884 mA h g ⁻¹ at 0.2 C after 100 cycles	[41]
Cathode	N–OSC/S	DC 1387 mA h g ⁻¹ at 0.1 C, DC 750 mA h g ⁻¹ after 200 cycles (416 mA h g ⁻¹ after 1000 cycles) at 2 C, decay rate 0.05% per cycle	[42]
Cathode	SA–Co/BNC	DC 1106 mA h g ⁻¹ at 0.2 C after 100 cycles, decay rate 0.03% per cycle	[43]
Cathode	PtHCNB/MWNCT/S	Specific areal capacity 9.8 mA h cm ⁻² (7.3 mA h cm ⁻² after 60 cycles) at 0.1 C (S loading 7.6 mg cm ⁻²)	[44]
Cathode	HNMSCMs	DC 682 mA h g ⁻¹ after 200 cycles (542 mA h g ⁻¹ after 400 cycles) at 1 C	[45]
Cathode	N–rich C with SA–Ni	DC 778 mA h g ⁻¹ at 1 C; capacity decay rate 0.07% per cycles after 600 cycles at 0.5 C	[46]
Cathode	Co/Fe–N/MCFS/S	DC 1523 mA h g ⁻¹ at 0.2 C (891 mA h g ⁻¹ at 5 C; decay rate 0.05% after 1000 cycles at 1 C)	[47]
Cathode	CoSnO ₃ @CNFs/S	DC 554 mA h g ⁻¹ at 0.2 C (300 mA h g ⁻¹ after 200 cycles at 0.2 C)	[48]
Cathode	PC/Cu ₃ P	DC 1205 mA h g ⁻¹ at 0.1 C, decay rate 0.03% per cycle after 1000 cycle at 1 C; DC 545 mA h g ⁻¹ at 1 C at 150°C	[49]
Cathode	Porous C polyhedron–CNT	Decay rate 0.005% per cycle after 500 cycle; volumetric capacity 960 A h L ⁻¹ ; rate capability up to 10 C	[50]
Separator	Fe–NHC/PP	DC 1079 mA h g ⁻¹ at 0.2 C, decay rate 0.07% per cycle	[51]
Cathode	TI–NHCNS	DC 1200 mA h g ⁻¹ at 0.2 C; decay rate 0.04% per cycle after 1000 cycles at 1 C; 75% S loading	[52]
Cathode	S/C@PDA	DC 1135 mA h g ⁻¹ at 0.2 C (965 mA h g ⁻¹ after 200 cycles at 0.2 C); 1135 mA h g ⁻¹ at 5 C	[53]
Cathode	CNT@Bi ₂ O ₃ /S	DC 1232 mA h g ⁻¹ at 0.1 C (639 mA h g ⁻¹ after 150 cycles at 0.5 C)	[54]
Cathode	Pelletized C@CN–CNT	Volumetric energy density 440 W h L ⁻¹ ; areal capacity 24.9 mA h g ⁻¹ at 0.47 mA cm ⁻² at 24 mg cm ⁻² S loading	[6]
Cathode	CdS@NG–CNT/S//CB–PP	DC 1493 mA h g ⁻¹ at 0.2 C (479 mA h g ⁻¹ after 1050 cycles at 1.0 C); decay rate 0.05% at 1.0 C; 75.7 % S loading (3.4 mg cm ⁻²)	[55]
Cathode	Mo–N–C@S	Rate capability 515 mA h g ⁻¹ at 5 C; decay rate 0.03% at 1.0 C after 1000 cycles	[56]
Cathode	N, S–doped C	DC 1290 mA h g ⁻¹ at 0.1 C (608 mA h g ⁻¹ after 100 cycles)	[57]
Cathode	N, O, S–co–doped C	DC 1598 mA h g ⁻¹ at 0.2 C, 1012 mA h g ⁻¹ at 1 C, 84% intial capacity after 500 cycles	[58]

TABLE 2: Continued.

Components	Materials	Performances	Ref.
Cathode	Porous C/CNT	DC 1226 mA h g ⁻¹ at 0.1 C after 100 cycles; DC 900 mA h g ⁻¹ at 20 mg cm ⁻² S loading	[59]
Cathode	Mesoporous N-doped C/CNT	DC 1480 mA h g ⁻¹ (1200 mA h g ⁻¹ at 0.84 mA cm ⁻² after 200 cycles); areal capacity 6 mA h cm ⁻² at 5 mg cm ⁻² S loading	[60]
Cathode	MnO ₂ at HCF	DC 1161 mA h g ⁻¹ at 0.05 C at 3.5 mg cm ⁻² S loading	[61]
Cathode	FeOOH nanorod on CC	DC 820 mA h g ⁻¹ at 0.1 C at 7.9 mg cm ⁻² S loading, 86% capacity retention after 100 cycles	[62]
Cathode	O-functionalized single walled C nanotubes	DC 1090 mA h g ⁻¹ at 0.1 C at 3.4 mg cm ⁻² S loading (806 mA h g ⁻¹ after 100 cycles), overpotential 212 mV	[63]
Cathode	Hollow mesoporous C/CeO ₂ C ₂	DC 728 mA h g ⁻¹ at 0.5 C at 4.7 mg cm ⁻² S loading after 500 cycles, decay rate 0.056% per cycle, area capacity 3.18 mA h cm ⁻²	[64]
Cathode	N-doped C	DC 1265 mA h g ⁻¹ at 0.1 C, decay rate 0.16% per cycle over 300 cycles	[65]
Cathode	CoS ₂ /N-doped C	DC 1324 mA h g ⁻¹ at 0.1 C, decay rate 0.047% per cycle over 1000 cycles at 1 C, DC 533 mA h g ⁻¹ at 3 C	[66]
Cathode	N-doped porous C	DC 1368 mA h g ⁻¹ at 0.5 C (1007 mAh g ⁻¹ after 200 cycles)	[67]
Cathode	N, P-co-doped C decorated CNT	DC 610 mA h g ⁻¹ at 0.3 C after 200 cycles (3.84 mg cm ⁻²), (510 mA h g ⁻¹ at -10°C)	[68]
Separator	CoFe/C with CNT embedded with Co ₃ Fe ₇ /Co _{5.47} N	DC 1136 mA h g ⁻¹ at 0.5 C (692 mA h g ⁻¹ at 3 C) capacity decay 0.061% over 900 cycles at 1 C	[69]
Cathode/separator	Ru quantum dot on C	DC 960 mA h g ⁻¹ at 0.5 C	[70]
Separator	CNF/CoS _{2-x}	DC 1056 mA h g ⁻¹ at 0.2 C (840 mA h g ⁻¹ after 100 cycles)	[71]
Cathode	Co on S, N-co-doped hollow C	DC 1273 mA h g ⁻¹ at 0.1 C, capacity decay 0.024% per cycle over 1700 cycles	[72]
Separator	K ₃ PW ₁₂ O ₄₀ /CNT	DC 813 mA h g ⁻¹ at 0.5 C (526 mA h g ⁻¹ after 300 cycles), DC 630 mA h g ⁻¹ at -10°C (10 mg cm ⁻²)	[73]
Cathode	CoP/Co/N-doped C polyhedron/CNT	DC 1479 mA h g ⁻¹ at 0.1 C (793 mA h g ⁻¹ after 500 cycles at 2 C)	[74]
Cathode	Fe _{1-x} S/N, S-co-doped C	DC 971 mA h g ⁻¹ at 0.2 C (75% retention rate after 100 cycles)	[75]
Separator	Encapsulated C on MXene (Ti-N-Ti ₃ C ₂ Cl-C)	DC 889 mA h g ⁻¹ at 0.3 C (79.5% retention rate after 100 cycles)	[76]

Abbreviations: C, carbon; CC, carbon cloth; CE, coulombic efficiency; CNT, carbon nanotube; DC, discharge capacities; N, nitrogen; O, oxygen; P, phosphorus; S, sulfur.

adsorption by employing a polar host, introducing catalytic accelerators of PSs redox reactions, electrolyte engineering, and separator modifications [27, 68].

The large volume change of sulfur during lithiation (~80%)—due to the density difference between sulfur (2.03 g cm⁻³) and Li₂S (1.66 g cm⁻³)—triggers mechanical stress and pulverization of the cathode, leading to significant capacity fading and further reducing Coulombic efficiency [25, 81, 82]. In the discharge process, sulfur reacts with Li ions and electrons form Li₂S_n intermediates, which causes the particles to swell and requires structural adjustment. Then, finally, insoluble Li₂S precipitates on the host surface within the intrinsic pores. In the charging process, shrinkage occurs due to Li₂S conversion to sulfur. Such reversible expansion–shrinkage in every charge–discharge process causes the structural cracking or pulverization that results in the loss of electrical contact between the sulfur and conductive matrix [64, 66].

A major challenge in LSB development is fabricating cathodes with high mass and areal sulfur loading to achieve high energy density while maintaining stable cycle performance. Additionally, the aluminum foil current collector is prone to cracking during the charge/discharge process. At the same

time, the increased thickness of active materials can block Li⁺ transport and increase resistance, ultimately deteriorating the electrochemical performance of the battery [22]. To address the challenge of low electrical conductivity or insulating behavior in sulfur cathodes, the incorporation of electrically conductive materials such as graphene, CNTs, carbon black, conductive polymers, metals, and porous carbon has been employed. This approach significantly enhances the utilization of active materials and improves discharge capacity by maintaining efficient contact between conductive components and sulfur particles [36, 83].

In LSBs, redox reaction involves solid–liquid–solid phase transitions and multiple electron transfer steps. In comparison to the LIB system, the kinetics of LSBs are intrinsically slow. The slow kinetics of the Li–sulfur (Li–S) are due to the poor electronic conductivity of sulfur, sluggish PS redox conversion, high activation energy for Li₂S nucleation and decomposition, and mass transport limitations. Insulation characteristics of sulfur and Li₂S limit electron transfer, cause higher polarization, hinder full sulfur utilization, and slow charge–discharge rates. Li sulfide formation and decomposition require breaking and formation of the S–S and Li–S bond, which bears a high

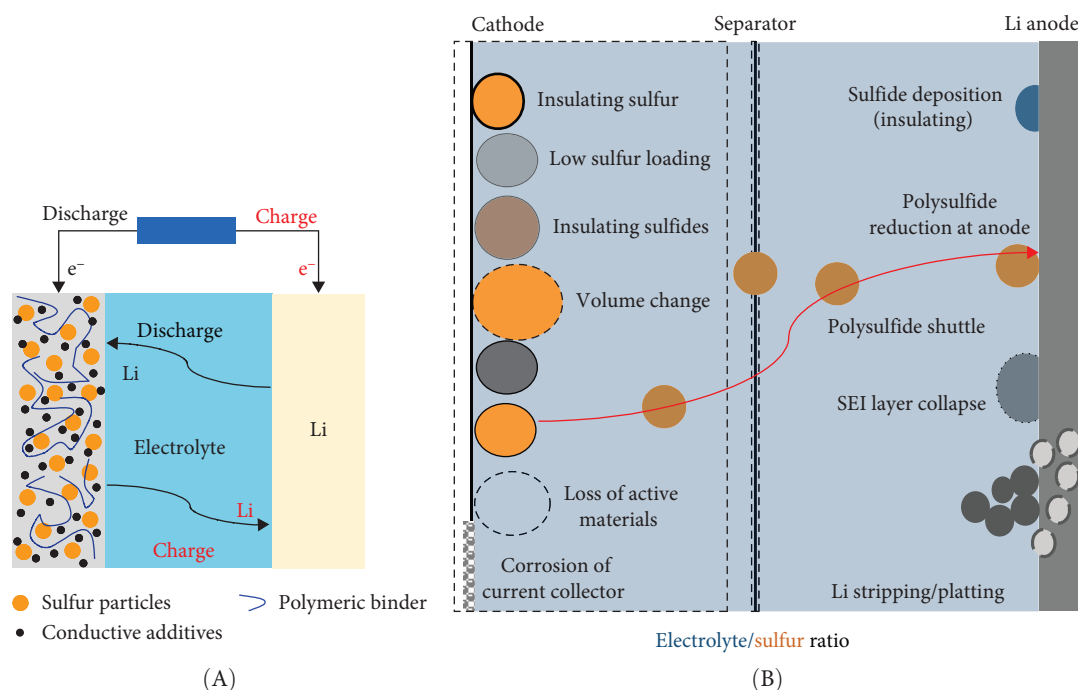


FIGURE 2: (A) Schematic of lithium-sulfur cell charging and discharging. (B) Intrinsic challenges of lithium-sulfur cell.

energy barrier (0.5–1.0 eV). Multistep electron transfer and bond rearrangement result in slow interconversion kinetics of the LiPS due to limited catalytic sites for the redox reaction, electrolyte diffusion control behavior, and weak electronic coupling among the conductive matrix and intermediates. In the PS interconversion mechanism, intrinsically solid-liquid-solid phase transformation occurred that generates the interfacial barrier and nonuniform ion flux, as well as a Li ion diffusion hindered due to thick sulfur layers or accumulated Li_2S film layers [24, 69].

Carbon-based materials design and strategic development are considered an integrative approach to addressing the sulfur insulation constraint, PS shuttle reduction, buffering volume expansion-contraction, and sluggish reaction kinetics. Structural, morphological, and textural properties engineering is critical to control the trapping of PS, buffering volume expansions, and creating an efficient transport channel. The design of hierarchical structure containing micro-/meso-/macropores and hollow structure may accommodate sulfur amount, buffer volume alteration, and PS confinement. Micropores (<2 nm) are efficient to confine sulfur and PS to reduce the shuttle effect. Mesopores range from 2 to 50 nm, capable of ion/electron transport, and amount of sulfur loading. Macropores facilitate the electrolyte reserve and buffer stress, and a hollow structure may help to buffer inward volume expansions. Morphological engineering or nanostructure design may facilitate the fast reaction dynamics, effective ion transport, and structural integrity. Nanoparticles provide a high surface area, effective for high sulfur impregnation and higher catalytic sites. Three-dimensional (3D) carbon networks based on aerogels or foams are effective for ion transport. Surface chemical engineering incorporating N, O, S,

P-doping induces polar functional groups that effectively suppress shuttle effects, increasing redox kinetics and electrochemical stability by enhancing chemical adsorption and wettability, boosting catalytic sites, and increasing binding energy to PSs. Also, the generation of carbon of multifunctional interface hybridization with catalytic and polar materials such as metal oxide, sulfide, nitrides, single atom (SA) doping, and composite may enhance the redox kinetics by reducing energy barriers and reducing the charge-transfer resistance [1, 72, 84].

Chronologically, early strategies focused on the confinement of sulfur within carbon matrices and the surface functionalization of carbon materials. These were followed by the incorporation of metal oxides, sulfides, and functional polymer binders. Functional groups in binders, such as those in polyvinylpyrrolidone (PVP), poly(amidoamine) (PAMAM), polyacrylonitrile (PAN), polyfluorene-derived polymers, and gum Arabic, were utilized to immobilize soluble PSs through the formation of C-S, N-Li, and O-Li bonds [14, 85]. The evaluation of polar amino groups demonstrated their effectiveness in reducing PS dissolution, while polyquaternium cationic polymers, with their quaternary ammonium groups, attract the negatively charged PSs (S_x^{2-}) via electrostatic forces. Subsequent advancements involved encapsulating sulfur within various carbon matrices, strengthening sulfur chemical bonds with metal oxide additives, and wrapping sulfur with conducting polymers like poly(3,4-ethylenedioxythiophene) (PEDOT). Conducting polymers and amphiphilic polymers, including PEDOT, polypyrrole-polyethylene glycol (PPY-PEG), and PVP, have been found to form robust membranes that can resist the significant volume expansion during discharge, thereby preventing sulfur from coming into

direct contact with the electrolyte and mitigating the dissolution of PSs in organic electrolytes [86, 87]. In addition, the migration of PSs from the cathode to the anode can be hindered by the introduction of a barrier layer within the separator. However, it is important to consider the high weight density of this barrier layer (typically $> 0.3 \text{ mg cm}^{-2}$), as it can reduce the overall sulfur content in the battery [22, 82].

Carbon-based host materials exhibit high electrical conductivity, large specific surface areas, and porous structures, which enhance conductivity, facilitate high sulfur loadings, and mitigate the impact of volume expansion. Various forms of carbon, including porous carbon, heteroatom-doped carbon materials, mesoporous carbon, hollow and double-shelled hollow carbon spheres (HCSs), aligned CNTs, CNFs, and graphene-based composites, have been investigated as cathode materials for LSBs [31, 88–91]. However, carbon materials suffer from poor rate capability and cycling performance due to insufficient physical adsorption between nonpolar carbonaceous materials and soluble PSs. This insufficient adsorption fails to prevent the shuttle effect, leading to low sulfur utilization efficiency. The introduction of polar metal compounds into the carbon host can reduce PS shuttling. This strategy leverages both physical confinement and chemical adsorption of PSs as promising approaches to improve performance [92]. Various strategic approaches adopted by combining polar materials with good electrical conductivity, such as MXene, TiN, MoS_2 , Ti_4O_7 , CoS_2 , and Co_3S_4 , have been combined with carbonaceous materials to serve as sulfur hosts to enhance chemisorption with LiPSs [26, 82, 90].

As previously mentioned, LSB has a lower operating potential than the LIB; a higher sulfur utilization is required to maintain the comparable energy output. Considering a sulfur utilization efficiency of 60%–80%, sulfur loadings of $6\text{--}8 \text{ mg cm}^{-2}$ are required [5, 93]. To date, the basic strategy to reduce PS shuttling has been investigated mostly with sulfur loadings of approximately 2 mg cm^{-2} . The findings or suggestions from these studies need validation under high loading conditions. It is highly plausible and assumed that under high loading conditions, the PS shuttling effects will intensify. High sulfur loading is likely to exacerbate the passivation of the Li metal anode by Li_2S [9, 94, 95].

3. Strategic Approaches to Modifying Separators and Binders

An effective interlayer is essential for preventing LiPS diffusion while maintaining a high rate of Li^+ transmission. Carbon-based materials such as porous carbon, graphene, CNTs, and CNFs are commonly used for the interlayer [96–98]. These materials not only hinder the diffusion of LiPS but also act as secondary collectors, trapping PSs for reuse and thereby reducing capacity loss. However, carbon materials' weak physical adsorption properties are often insufficient to prevent LiPS diffusion effectively [99, 100].

Inorganic materials offer stronger adsorption for LiPS, but suffer from poor conductivity. Integrating inorganic materials like TiO_2 , SiO_2 , and Al_2O_3 into carbon structures can enhance

adsorption capabilities [13, 101]. Additionally, the slow reaction kinetics of PSs contribute to the shuttle effect. Catalytic compounds such as Ni, Pt, and Co, and conductive compounds like CoS_2 , MoS_2 , and TiN can effectively catalyze the transformation of PSs. These catalytic compounds' conductivity lies between nonpolar carbon and polar inorganic materials [102–104]. Thus, designing an interlayer that can effectively adsorb PSs, limit their diffusion, and simultaneously maintain electronic and ionic conductivity is necessary. This interlayer should also facilitate efficient redox reactions of PSs and contain abundant catalytic active sites.

A collaborative group from Shanghai University of Electric Power and Fudan University designed a SnS-modified porous carbon (SnS/PCNS) separator for LSBs to intensify PS adsorption and enhance the redox reactions of PSs (Figure 3) [29]. Previous studies utilized SnS_2 , which improved PS adsorption and catalyzed transport. However, the wide band gap of SnS_2 (1.99 eV) resulted in poor conductivity ($3.82 \times 10^{-3} \text{ S cm}^{-1}$) [105]. In contrast, SnS, with its narrower band gap (1.04 eV), provides better conductivity ($1.32 \times 10^{-2} \text{ S cm}^{-1}$). SnS/PCNS promotes rapid nucleation and uniform deposition of Li_2S , thereby improving discharge capacity and cyclic stability. Specifically, it achieves a reversible capacity of 655 mA h g^{-1} at 0.5 C with a sulfur loading of 6 mg cm^{-2} and a decay rate of 0.039% at 1 C.

While additional layers may reduce Li^+ transport capacity through the separator, it was found that SnS/PCNS/Celgard provides approximately the same Li^+ conductivity (0.35 mS cm^{-1}) as the Celgard separator. The Li^+ transference number of SnS/PCNS/Celgard is approximately 0.64, compared to the pure Celgard separator's 0.75. Density functional theory (DFT) calculations reveal the phenomena and mechanisms of the bonding properties of S_8 and Li_2S_8 with SnS (001) and SnS_2 (001). The adsorption energy of $\text{S}_8/\text{Li}_2\text{S}_4$ is stronger for SnS (001) ($-0.61/-1.09 \text{ eV}$) than for SnS_2 (001) ($-0.40/-0.97 \text{ eV}$), which significantly improves the limitation of PS diffusion [29].

The Zheng group coated N-doped two-dimensional (2D) porous carbon nanosheets on commercial polypropylene separators (G@PC) to effectively inhibit the migration of PSs through the separators (Figure 4A–C) [23]. The functional barrier thickness and weight density were maintained at $0.9 \mu\text{m}$ and 0.075 mg cm^{-2} , respectively. N-doping enhances the PSs' binding capability via chemisorption. The close-packed assembly of the laminar structure of 2D nanosheets decreases the weight of the barrier layer while the ultrahigh surface area and porous structure provide abundant physical adsorption sites for PSs.

Importantly, the coated 2D nanosheets expand the current-collecting functionality, which facilitates enhanced electrochemical reuse of the trapped PSs on the separators. This improvement is evident in the stability after 100 cycles at 0.2 C, where the discharge capacities reach 1186 mA h g^{-1} , maintaining 92% of the initial capacities of N-doped carbon nanosheet-coated polypropylene, compared to 412 mA h g^{-1} (39% of initial capacity) for polypropylene alone (Figure 4D) [23].

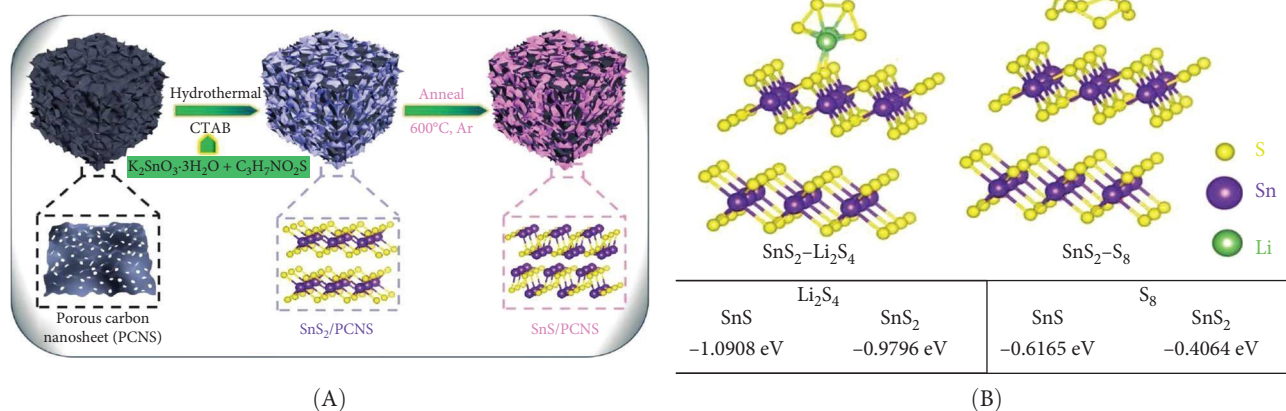


FIGURE 3: (A) Schematic of synthesis of SnS/PCNS. (B) Adsorption energy for S_8 and Li_2S_4 adsorbed on SnS (001) and SnS₂ (001). Reproduced with permission: Copyright 2020, Wiley-VCH GmbH [29].

The Yu group synthesized and employed atomic Fe and N co-doped hollow carbon nanospheres (FeNHC) with Fe-N_x sites for use in commercial PP separators [51]. Their study demonstrates that the positively charged N-sites effectively adsorb negatively charged soluble PSs, while the atomically dispersed Fe catalyzes the conversion of these PSs. The thin mesoporous carbon shell facilitates short mass diffusion paths, enhances adsorption and catalytic conversion, and improves electrolyte infiltration. The HCS structure ensures full exposure of the N-doped and SA catalytic sites. The Fe-NHC/PP separator exhibits a capacity of 1079 mAh g⁻¹ with a capacity decay of only 0.07% per cycle over 500 cycles.

Nonpolar carbon interlayers, such as CNT, graphene, conductive carbon black, and CNFs, have been utilized to anchor migrating PSs, thereby enhancing the cycling performance of LSBs. While nonpolar carbon surfaces can serve as physical barriers to some extent, they are not highly effective at adsorbing PSs. Recent research has addressed this limitation by incorporating organic molecules into carbon-based interlayers, improving the polarity and effectiveness of these materials [106–108]. However, simply mixing organic molecules with a carbon matrix often leads to the loss of organic electrolytes [109–111]. To overcome this, a research group from Wenzhou University emphasized that organic molecules should be tightly bound to the carbon matrix to enhance the catalytic conversion of PSs and maintain structural integrity during charge and discharge cycles (Figure 5) [33]. Their study incorporated toluene diisocyanate (TDI) with organic tris(hydroxypropyl)phosphine (THPP) into hydroxylated multiwalled CNTs (CNT-OH). The THPP catalyst was found to be highly effective in catalyzing the conversion of PSs,

thereby inhibiting shuttle effects and contributing to the formation of solid electrolyte interphase (SEI) layers. The designed interlayer demonstrated a reversible capacity of 734 mA h g⁻¹ at 5 C, with an attenuation rate of 0.029% per cycle after 1500 cycles. Additionally, when tested at a low temperature of $-10^\circ C$, the interlayer exhibited an initial capacity of 951 mA h g⁻¹ at 1 C, with an attenuation rate of 0.036% per cycle after 1700 cycles [33].

Liu's group utilized the cationic poly[bis(2-chloroethyl) ether-alt-1,3-bis[3-(dimethylamino) propyl] urea] quaternized (PQ), which contains quaternary ammonium cations, as a binder to effectively reduce shuttle effects through electrostatic interactions between quaternary ammonium cations and LiPSs, termed trapped LiPSs [24]. The predominant PS species, Li_2S_6 , is highly soluble in the electrolyte. The binding energy of PQ- Li_2S_6 is 1.89 eV, which is higher than that of DOL- Li_2S_6 (0.79 eV) and DME- Li_2S_6 (0.77 eV). Additionally, the binding energies of various functional groups, such as ester, ketone, amide, imine, ether, nitrile, fluoroalkane, chloroalkane, bromoalkane, and alkane, are lower than that of PQ- Li_2S_6 , with values of 1.10, 0.96, 0.95, 0.88, 0.71, 0.60, 0.40, 0.26, 0.23, and 0.23 eV, respectively. This demonstrates that the PQ-based binder provides substantial performance and a higher initial capacity compared to the traditional PVDF binder (initial capacity 2 mA h cm⁻²), with an initial capacity of 9 mA h cm⁻² and a cycling capacity of 7 mA h cm⁻².

Zhang and coworkers engineered a cobalt-iron (CoFe) composite integrated into a carbon matrix, featuring one-dimensional CNTs (1D CNTs) embedded with uniformly dispersed Co₃Fe₇ and Co_{5.47}N nanoparticles [69]. The twisted 1D CNTs anchored onto a 3D cross-linked carbon architecture

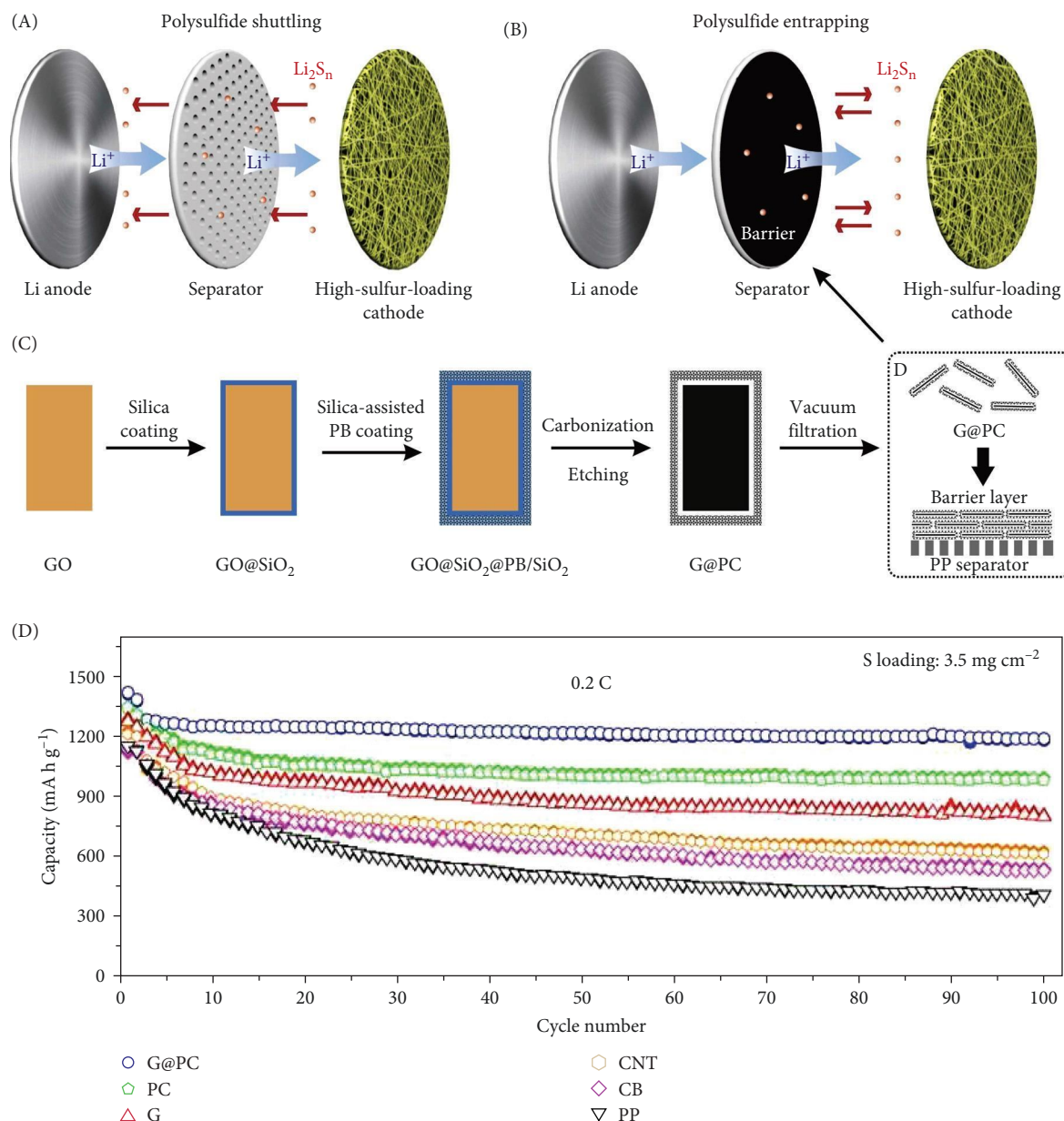


FIGURE 4: Schematic illustration of the Li-S batteries. (A) Shutting effect. (B) Polysulfide entrapment by barrier layer. (C) Fabrication of N-doped 2D porous carbon on the polypropylene separator. (D) Cycling performance comparisons at 0.2 C. Reproduced with permission: Copyright 2017, Elsevier [23].

created a unique 1D/3D hierarchical structure. This design significantly enhances Li⁺ diffusion, provides a greater number of electrochemically active sites, and increases the availability of space for electrolyte infiltration. The CNTs not only contribute additional surface area but also enable enhanced interfacial reactions, improving overall electrochemical performance. Within this architecture, Co₃Fe₇ acts as an efficient electrocatalyst, accelerating the conversion of long-chain PSs into shorter chains, while nitrogen doping in Co_{5.47}N introduces electronic heterogeneity across the carbon surface, promoting faster electron and Li⁺ transfer. The homogeneous distribution of Co₃Fe₇/Co_{5.47}N nanoparticles synergistically suppresses the PS shuttle effect, further stabilizing the battery

system. As a result of these combined enhancements, the CoFe@C-modified separator, when assembled into a LSB, delivered an significant initial specific capacity of 1136 mA h g⁻¹ at 0.5 C and retained 692 mA h g⁻¹ at 3 C. Moreover, the cell exhibited outstanding cycling stability, with a minimal capacity degradation rate of only 0.061% per cycle over 900 cycles at 1 C, underscoring the effectiveness of the hierarchical design in advancing high-performance LSB technologies [69]. A recent study by a research group from Shandong University developed the fluorine-free MXene encapsulated by the N-doped carbon (Ti-N-Ti₃C₂Cl-C) employed for the separator of LSB [76]. The established structure between Ti and N facilitates phase reconfiguration. Hierarchical porous nitrogen

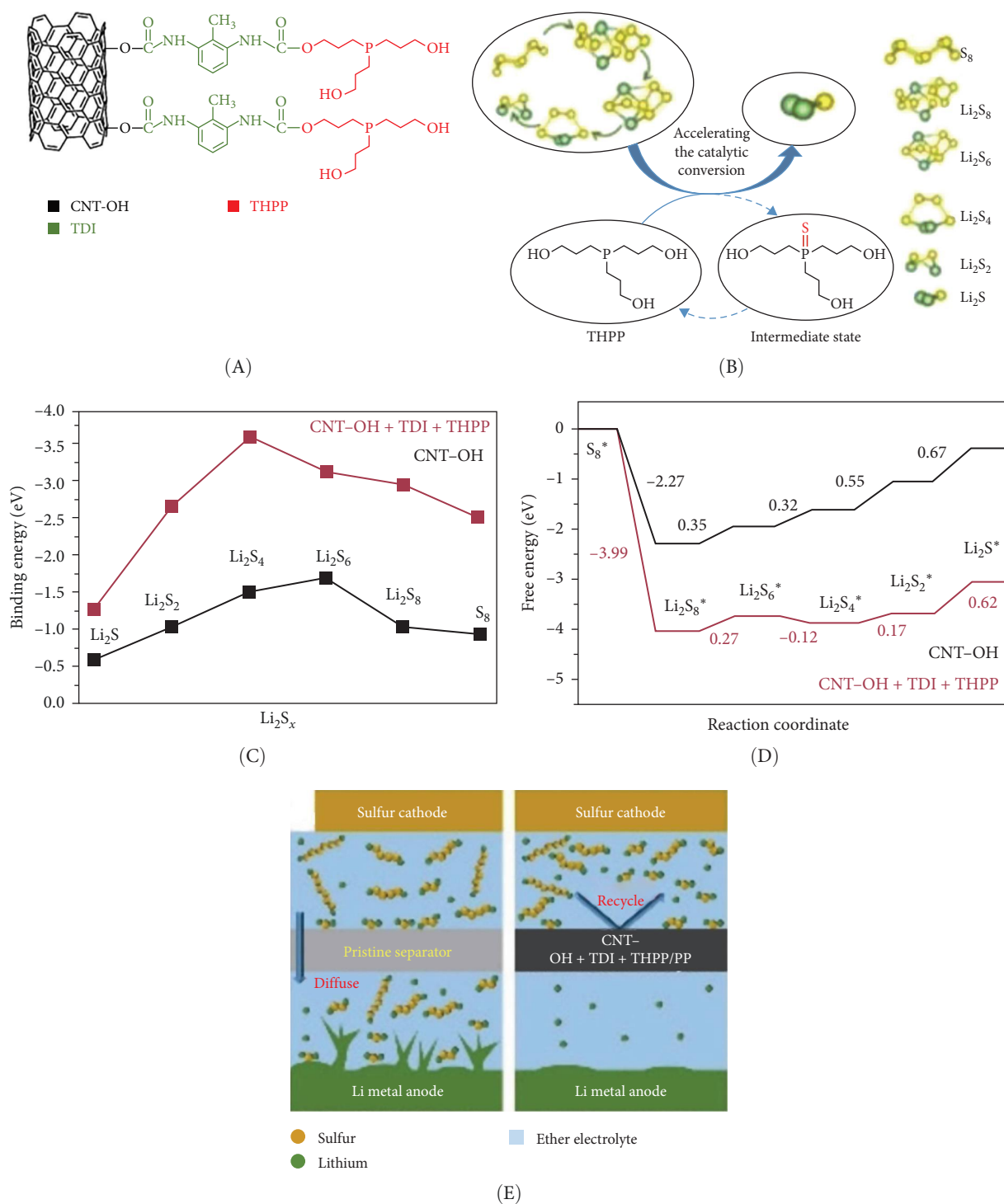


FIGURE 5: (A) Schematic of the grafted THPP onto the CNT-OH. (B) Schematic of polysulfides conversions. (C) Adsorption energy of polysulfides. (D) Free energy of S_8 conversion to Li_2S . (E) Schematic of polysulfides diffusions and Li ion deposition. Reproduced with permission: Copyright 2022, Wiley-VCH GmbH [33].

doped carbon on MXene surface enhance the surface area multifold due to induced micro-/mesopores. Here, Ti coordination with N increases the binding energy, which reduces the energy barrier and accelerates LiPSs redox kinetics. Simultaneously, Ti-N-Ti₃C₂Cl-C intensifies the LiPSs immobilization. From the DFT analysis it shows that Ti-N-Ti₃C₂Cl

shows a lower energy barrier (0.71 eV) than the Ti₃C₂Cl (0.96 eV), as transformation of Li_2S_2 to Li_2S is considered the rate-limiting step. In here, Ti coordinated with N sites are thermodynamically favorable and facilitate the liquid-solid transformation to improve reaction kinetics. This developed separator gives LSB with a reversible capacity

of 889 mA h g^{-1} , maintaining the 79.5% capacity after 100 cycles at 0.5 A g^{-1} [76].

4. Strategic Design of Advanced Carbon-Based Materials

Carbon-based materials have been strategically utilized as host materials in the cathodes of LSBs through various approaches. Fundamental strategies focus on structural modifications aimed at maximizing sulfur loading while ensuring optimal sulfur utilization efficiency. These modifications are designed to maintain electrical and ionic conductivity, accelerate redox kinetics, inhibit PS dissolution and diffusion, and buffer the volume expansion within the cathode. Section 4 discusses the fundamental developments, intrinsic findings, and technical evaluations from various perspectives related to these approaches.

The choice principle of carbon materials is focused on balancing the performance of LSBs as follows: (i) high electrical conductivity, (ii) PS adsorption (physical/chemical), (iii) efficient ion/electron transport, (iv) hierarchical structure, (v) structural integrity, and (vi) efficient catalytic activity. To achieve a multidimensional continuous conductive network, a combination of 2D (graphene sheets), 1D (CNTs), or 0D (carbon blacks) forms the interconnected pathways. The approach helps to rapid charge transport and facilitates electrochemical performance at high sulfur loading. Hierarchical structure of activated carbon combination of micro-/meso-/macropores, plays a crucial role in managing the PSs properties. Micropores less than 2 nm facilitate the PS trapping by the physical adsorption, and mesopores buffer the volume expansion. Macropores greater than 50 nm are essential for the ion diffusion and electrolyte penetration. Also, the continuous volume expansion could destroy the structural integrity of the host materials. Flexible CNTs or graphene sheets with a combination of mesoporous carbon could maintain the mechanical strength and elastic buffering capability of the structure. High loading of sulfur and efficient utilization can be achieved through 3D structural frameworks with conductive networks for efficient charge and electrochemical performance. Hybridization of the 3D graphene and porous carbon framework can provide a high energy density by facilitating the high sulfur loading. A catalytically active carbon metal hybrid could intensify the PS redox reaction, helping to enhance the conversion efficiency and coulombic efficiency. A rational integration of the carbon allotropes and catalytic component could balance the required properties of the LSBs.

4.1. Pure Carbon as Sulfur Host. In LSBs, sulfur is the main active cathode materials, but core drawbacks sulfur insulating nature ($\sigma \approx 5 \times 10^{-30} \text{ S cm}^{-1}$), high volume expansion nature ($\sim 80\%$), and solubility nature PSs (Li_2S_n , $n = 4-8$) demands a conductive structural host which is well served by pure carbon materials such as activate carbon, carbon black, mesoporous carbon, graphene, CNT. Such pure carbon forms a conductive network and provides a continuous electron transport pathway, 2–50 nm in size, termed mesoporous, effective for hosting or trapping sulfur molecules, as well as efficiently buffering volume expansion during lithiation/delithiation [112, 113].

Carbon materials effectively improve the cycle stability, active sulfur utilization, and rate capability of the sulfur cathode due to good electrical conductivity, large pore volume, and strong adsorption capability on the surface. Active sulfur is loaded (at least over 60%) on the intrinsic porous structure of carbon, which improves the electrochemical performance of sulfur cathodes in various electrolyte systems. A large sulfur loading is essential for enhancing the capacity of the sulfur cathode and the energy density of LSBs. To increase the sulfur loading of the host materials, a group from Nankai University activated commercial conductive carbon black with KOH to enhance its porosity [114]. They have examined the sulfur loading with 64 and 73 wt% on activated conductive carbon black. It is found that 73 wt% sulfur loading could not utilize the active sulfur efficiently (Figure 6). Due to the pore blockage of inside sulfur hampers the electrochemical reaction, as some crystalline nanoparticles block the pore mouth. In the case of the 64 wt% loading, the mouth of the pores remains open, causing high utilization efficiency by the indispensable penetration and transportation of electrolyte and soluble LiPSs during the electrochemical reaction process [114]. Similar types of strategy, another group synthesized the activated carbon from the natural plant by KOH activation, achieving the specific surface area $3164 \text{ m}^2 \text{ g}^{-1}$ and pore volume $1.88 \text{ cm}^3 \text{ g}^{-1}$ [115]. The composite of sulfur and carbon shows the 1105 mA h g^{-1} capacity at 60 wt% sulfur loading at 200 mA g^{-1} current density. At the current density of 800 mA g^{-1} , the composite shows a 51% capacity retention after 800 cycles, fade rate of 0.06% per cycle. The study shows that increasing sulfur loading from 60% to 68% gives a similar capacity value, but lowers the Coulombic efficiency to 92% due to dissolution of PSs into the electrolyte [115]. Such findings emphasize that large surface area and pore volume not only increase the sulfur loading but also ensure the well-dispersed elemental sulfur on the carbon structure. The strategy helps with sulfur utilization. Nanopores in the structure inhibit the diffusion of PSs in organic electrolytes. It demands to design of carbon materials that can achieve high S loading and low dissolution of PSs for efficient capacity performance. The design strategy for carbon textural properties was based on the fundamental requirement of pore shape and distribution in the carbon structure. To improve cycling stability, it is essential to induce micropores ($< 2 \text{ nm}$) in the structure homogenously that are capable of anchoring soluble intermediates, PSs, due to strong interaction [116]. To achieve efficient rate capability, it is essential to design optimization of mesopores (2–50 nm) and macropores ($> 50 \text{ nm}$) that enables fast Li^+/e^- transport by shortening the diffusion path length in the structure. Different strategies and morphological engineering of pure carbon scaling up the performance in terms of energy density and cycle life [116].

4.2. Nanoparticle/Nanosheets With Carbon. To enhance the chemisorption of carbonaceous materials with LiPSs, various polar conductive nanoparticles are combined with carbon materials. Co sulfides are considered highly promising due to their strong polarity and electrical conductivity. Co sulfides, such as nanotubes and nanoboxes with CNTs, have been

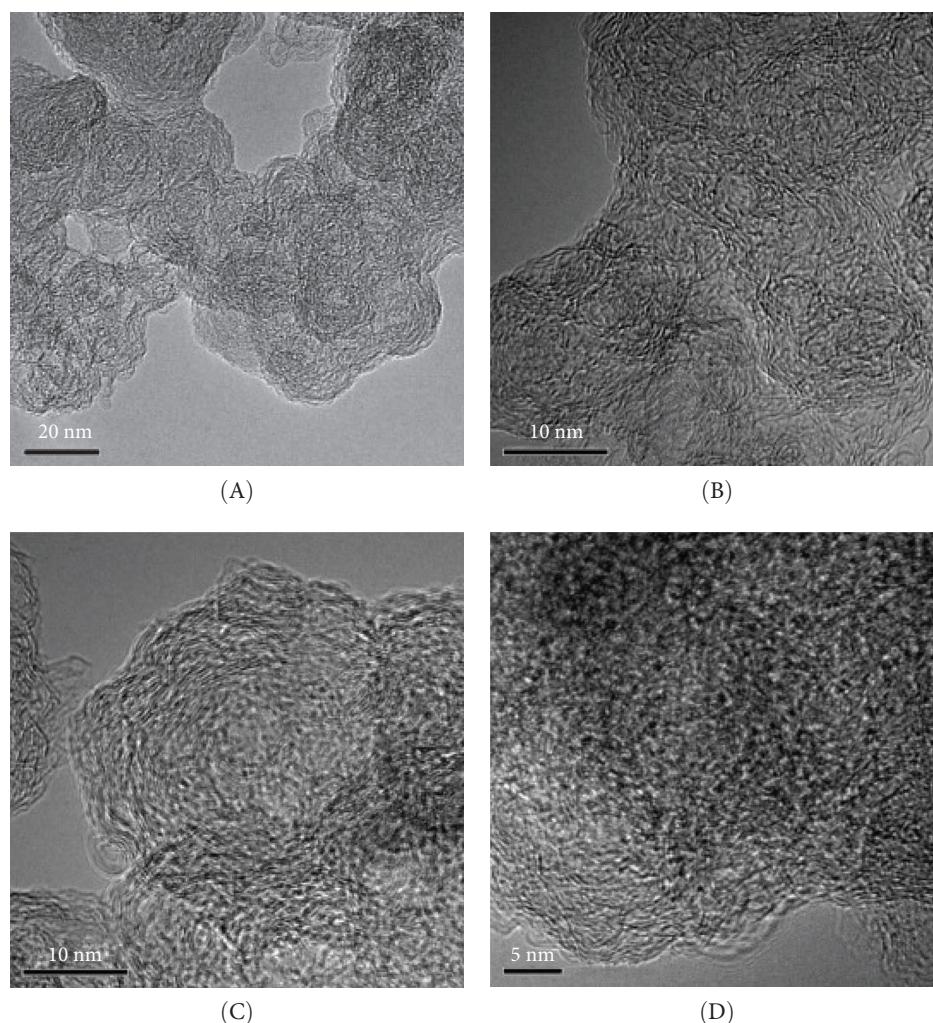


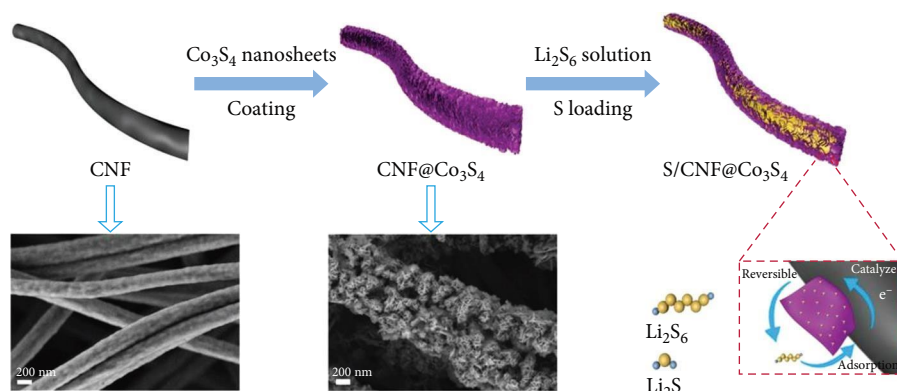
FIGURE 6: TEM images of the (A, B) activated conductive carbon black and sulfur-loaded activated conductive carbon black composites (C) 64 wt% S, and (D) 73 wt% S. Reproduced with permission: Copyright 2013, 2013 Elsevier B.V [114].

explored as sulfur hosts [117]. Zhou group investigated N-doped CNFs coated with 2D Co_3S_4 nanosheets ($\text{CNF@Co}_3\text{S}_4$) for sulfur hosting (Figure 7) [26, 118]. Their study shows that N-doped carbon and Co_3S_4 provide polar sites that are effective for LPS chemisorption. N-doped carbon eliminates the need for aluminum foil and binder, which significantly reduces the invalid weight load on LSBs. The $\text{CNF@Co}_3\text{S}_4$ composite exhibited an areal capacity of 4.1 mA h cm^{-2} at 0.1 C with a high sulfur loading of 6.8 mg cm^{-2} for 100 cycles. The distinct roles of Co_3S_4 and N-doped carbon in enhancing LPS chemisorption were confirmed through a Li_2S_6 adsorption test. UV-vis spectra revealed that the peak intensity at 425 nm for S_4^{2-} and the lower wavelengths for S_6^{2-} , and S_8^{2-} were significantly reduced in the supernatant solution of Li_2S_6 after adsorption by $\text{CNF@Co}_3\text{S}_4$ for 24 h. X-ray photoelectron spectroscopy (XPS) spectra further confirmed chemisorption, showing that the Co $2p_{1/2}$ and Co $2p_{3/2}$ doublet shake-up satellite peaks shifted to lower binding energies than 798.6 and 782.7 eV, respectively. Additionally, the N 1s spectra identified Li–N and S–N bonds at 407.5 and 399.3 eV, respectively, for $\text{CNF@Co}_3\text{S}_4$ after adsorption. These results confirm

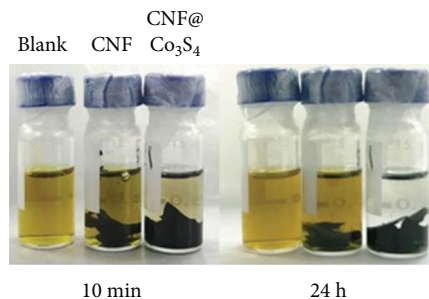
the importance of both components in mitigating the LPS shuttling effect, with their relative significance demonstrated by the adsorption images of Li_2S_6 after 24 h [26].

A joint research from the Hefei University of Technology, China University of Petroleum, and Hefei Normal University group utilized carbon cloth coated with CoS_2 nanoparticles (CC-CoS_2) as cathodes (Figure 8) [25]. The carbon cloth serves as a robust 3D current collector with excellent and rapid electrical conductivity. This 3D structure, with its abundant void space, efficiently increases sulfur loading and buffers the volume expansion during the lithiation/delithiation process. The uniformly distributed nanosized CoS_2 provides polarity on the surface of the carbon cloth, mimicking strong localized chemical binding with LiPSs and facilitating fast interfacial charge transfer. The CC-CoS_2 acts as a permselective barrier, functioning as a physical block, offering strong chemical adsorption, efficient catalytic conversion of LPS, and fast Li^+ transport properties [25, 119].

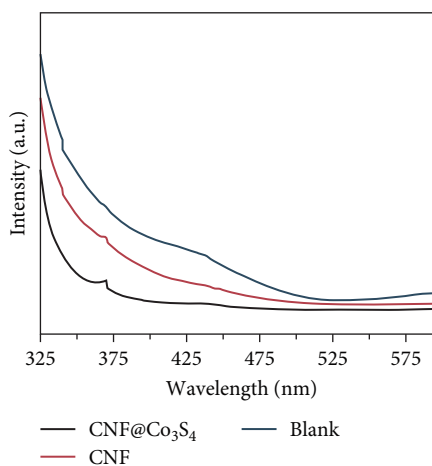
The Al@S/AB@CC-CoS_2 cathode demonstrated a specific capacity of 1481 mA h g^{-1} at 0.1 C. A high voltage plateau around 2.3 V exhibited discharge capacities of 419 mA h g^{-1}



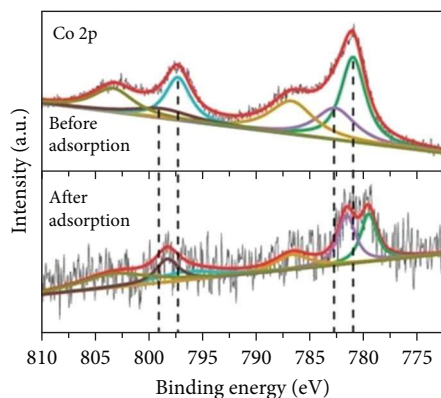
(A)



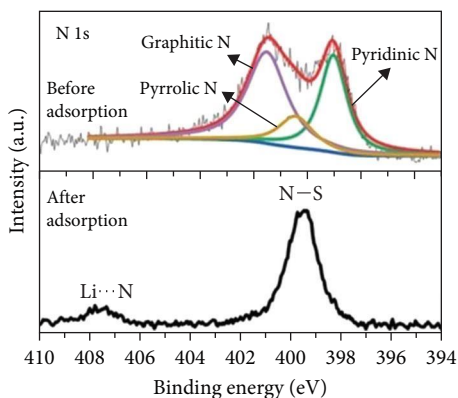
(B)



(C)



(D)



(E)

FIGURE 7: (A) Schematic of synthesis of Co₃S₄ coated on carbon nanotube (CNF@Co₃S₄). (B) Adsorption test of Li₂S₆. (C) UV-vis spectra. (D) XPS of Co 2p peak of CNF@Co₃S₄. (E) XPS of N 1s peak of CNF@Co₃S₄. Reproduced with permission: Copyright 2020, Wiley-VCH GmbH [26].

for the conversion from S₈ to Li₂S_n ($4 \leq n \leq 8$), while a low voltage plateau around 2.1 V showed discharge capacities of 1256 mA h g⁻¹ for the conversion from Li₂S₄ to Li₂S₂/Li₂S. DFT investigations of the binding energy of LPS on the CoS₂ (111) plane compared to the carbon basal plane revealed that the binding energies of soluble Li₂S_n ($n = 8, 6$, and 4) on CoS₂ were -1.06 , -1.12 , and -1.26 eV, respectively,

significantly higher than the carbon plane values of -0.54 , -0.61 , and -0.56 eV, respectively. This phenomenon is attributed to the abundant charge accumulation and distribution on the CoS₂ substrate, leading to more stable adsorption of Li₂S_n on CoS₂ compared to the carbon surface [25]. The Lin group developed a CoS₂-incorporated nitrogen-doped ultrathin wall mesoporous carbon electrode, where the mesoporous

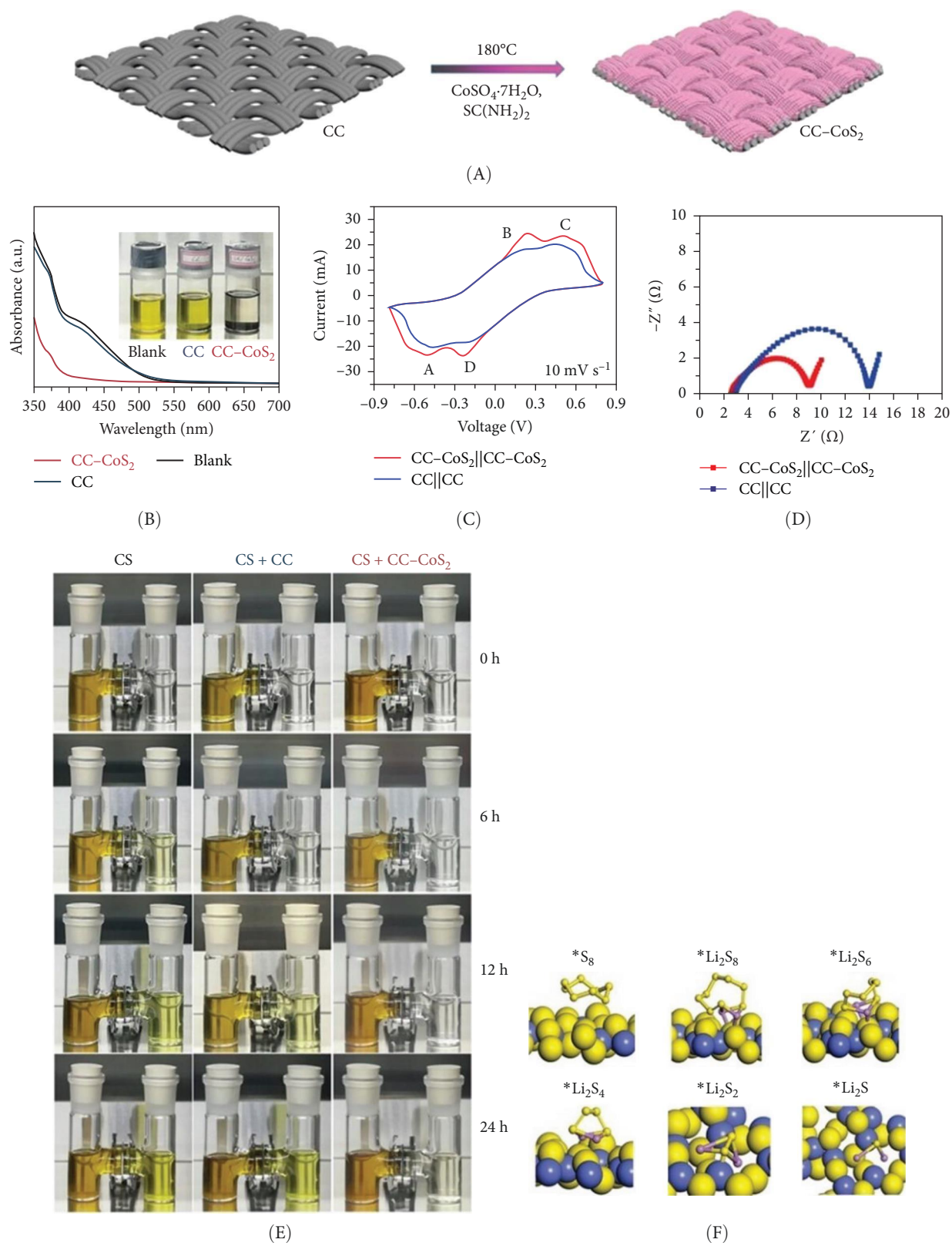


FIGURE 8: Continued.

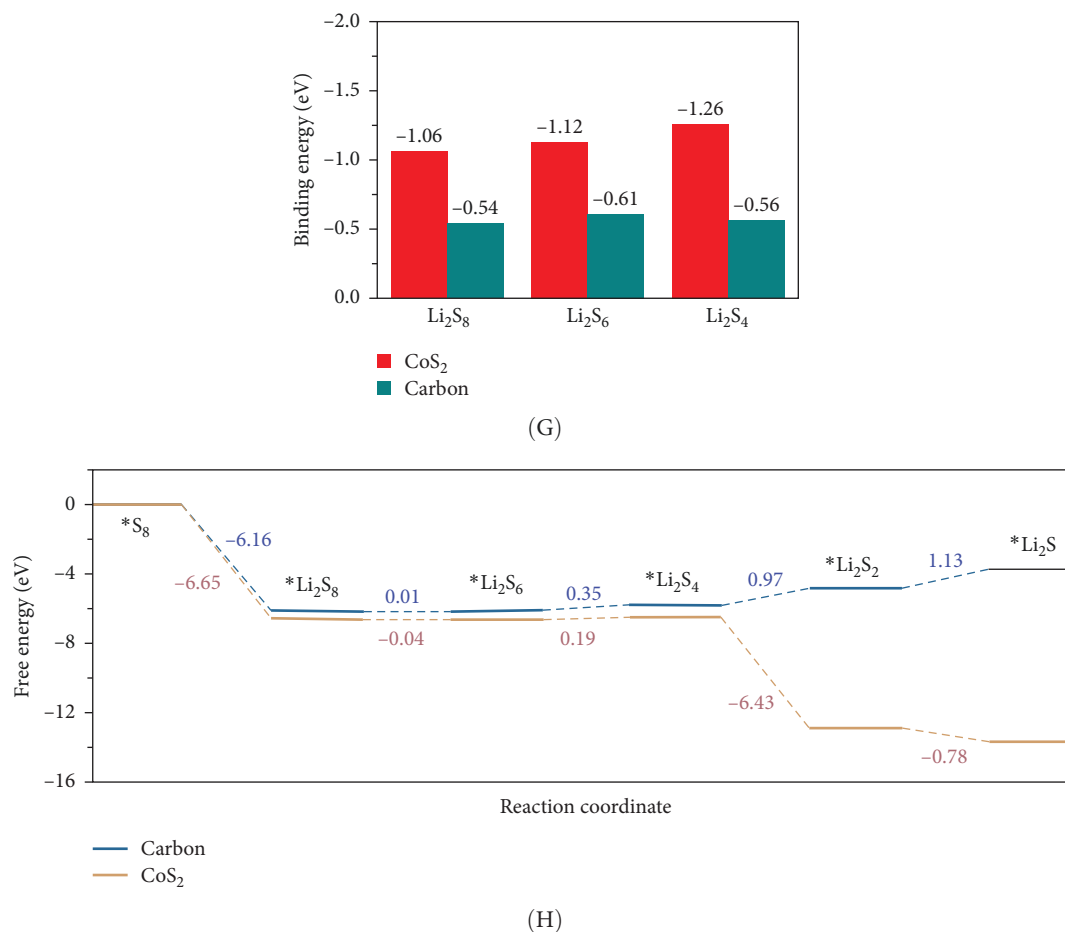


FIGURE 8: (A) Schematic of synthesis of CoS₂ coated on carbon cloth (CoS₂-CC). (B) UV-vis spectra of Li₂S₆ in DOL/DME solutions in blank, mixed with carbon cloth (CC), and CoS₂-CC for 12 h (inset: image of the solutions). (C) CV of symmetric cell of CC and CoS₂-CC at 10 mV s⁻¹ (0.2 M Li₂S₆ electrolyte). (D) Nyquist plot of symmetric cell of CC and CoS₂-CC. (E) Optical image of H-glass cell separated with Celgard separator (CS), CS + CC, and CC-CoS₂ film in left Li₂S₆ with DOL/DME and in right DOL/DME solution only. (F) Adsorption configuration on CoS₂ (111) plane of S₈ to Li₂S_n (4 ≤ n ≤ 8). (G) Comparison of binding energy with CoS₂ and carbon surface with LSP. (H) Free energy diagram of reduction of Li₂S_n on CoS₂ and carbon catalytic surface. Reproduced with permission: Copyright 2021, Wiley-VCH GmbH [25].

structure enhances the availability of active reaction sites and facilitates ion diffusion, thereby improving the reaction kinetics and cycling lifespan [66]. The strong adsorption of LiPSs on CoS₂ effectively suppresses the shuttle effect, leading to improved PS conversion efficiency and enhanced electrochemical performance. The CoS₂-based electrode exhibited an initial discharge capacity of 1324 mA h g⁻¹ at 0.1 C, with a remarkably low capacity decay rate of 0.047% per cycle over 1000 cycles at 1 C, significantly outperforming the ultrathin wall mesoporous carbon electrode, which exhibited a higher decay rate of 0.093% per cycle [66].

Ahn's group explored a dual-function strategy by utilizing carbon cloth as an interlayer to mitigate LiPS shuttle effects while enhancing the utilization of active charge-discharge products [62]. In this approach, a FeOOH nanorod-assisted carbon cloth (FeCC) was employed to construct a sandwiched, self-supporting cathode (FeCC/S-FeCC), where FeCC functioned both as a sulfur host and an interlayer. The vertically aligned FeOOH nanorods uniformly integrated into the 3D carbon cloth network exhibited strong LiPS trapping

capability and catalytic activity. Additionally, the carbon cloth effectively anchored the nanorods, preventing their aggregation and facilitating the exposure of redox-active sites. The FeCC interlayer significantly improved contact between the active material and the electrode, enabling high sulfur loading (7.9 mg cm⁻²) while simultaneously suppressing LiPS diffusion. This design resulted in an initial discharge capacity of 820 mAh g⁻¹ at 0.1 C, maintaining 86% capacity retention after 100 cycles, demonstrating enhanced electrochemical stability and efficiency [62].

PS accumulation is a primary cause of shuttle effects, resulting from the slow conversion kinetics of PSs to insoluble sulfides. Thus, it is essential to utilize a catalytic surface that can rapidly convert PSs to insoluble sulfides. CNFs are effective for high sulfur loading and low electrolyte-to-sulfur (*E/S*) ratios, while also providing high conductivity. However, confining catalytic particles within CNF is challenging due to large voids (> 50 nm). Loaded catalytic particles are highly susceptible to agglomeration and loss during high-temperature treatment, which diminishes their catalytic properties [120, 121].

The Lu group designed CNF with carbon dots (CDs) containing nickel SA (Ni_{SA}) sites and nickel nanoparticles (Ni_{NP}) that are uniformly dispersed ($\text{Ni}_{\text{SA}}\text{-Ni}_{\text{NP}}\text{-CDS@CNF}$) [39]. The CDs act as confinement agents, reducing the agglomeration and loss of Ni_{NP} during high-temperature carbonization. The functional groups of CDs adsorb metal ions, while the crystalline core of the CDs restricts space for metal growth. $\text{Ni}_{\text{SA}}\text{-Ni}_{\text{NP}}\text{-CDS@CNF}$ demonstrated a capacity of $66.5 \text{ mA h cm}^{-2}$ at 0.02 C , with good cycle stability and 86.1% capacity retention after 100 cycles at 0.12 C . This performance was achieved with a high sulfur loading of 50 mg cm^{-2} and a low E/S ratio of $5 \mu\text{L mg}^{-1}$.

A research group from the University of Science and Technology, Shanghai utilized macroporous multichannel CNFs embedded with Co/Fe-N electrocatalysts (Co/Fe-N/MCFs) to enhance LiPSs conversions in LSBs [47]. The CNFs facilitate sulfur dispersion and accommodation while maintaining close contact with sulfur species as a conductive substrate. The macropores on the outer and inner surfaces of the CNFs enable efficient sulfur transport into the core of the material and promote fast Li^+ transport. The embedded Co/Fe-N in the inner channels restrict PS species and catalyze their rapid conversion. The Co/Fe-N/MCFs/S cathode exhibits an initial capacity of 1523 mA h g^{-1} at 0.2 C and maintains a specific capacity of 1523 mA h g^{-1} at 5 C , with a decay rate of 0.05% per cycle over 1000 cycles at 1 C . The study differentiates between Co/Fe-N/MCFs and MCFs without embedded Co/Fe-N, which are meso/macroporous and micro/mesoporous, respectively. Both types show a similar initial discharge capacity of approximately 1500 mA h g^{-1} . The findings suggest that meso/macroporous structures are more crucial than micropores, as they allow for volume expansion. Embedding Co/Fe-N restricts LiPSs, resulting in a lower decay rate for Co/Fe-N/MCFs (0.05%) compared to MCFs (0.07%) per cycle at 0.2 C [47]. The Kong group employed another strategy by wrapping CoSnO_3 nanocubes with CNF, which can host 60% sulfur [48]. In this configuration, CoSnO_3 serves as polar active sites that restrain the dissolution of PSs. The $\text{CoSnO}_3\text{@CNF/S}$ cathode exhibits a capacity of 554 mA h g^{-1} at 0.2 C , retaining a capacity of 300 mA h g^{-1} after 200 cycles.

4.3. Encapsulating Sulfur Cathode by Carbon Matrix. The utilization of micro/mesoporous carbons, hollow carbon nanospheres, CNFs, or nanotubes for encapsulating the sulfur cathode is a promising strategy to hinder the migration of PSs to the Li anode [122, 123]. Hollow spheres are particularly advantageous due to their rational design, which accommodates a large amount of sulfur and its volume changes, while also providing abundant contact area for rapid electrolyte permeation and ion transport [7, 123, 124]. The Shen group uniquely designed double-shell structures to maximize utilization efficiency, confining the outward diffusion of PSs and buffering volume changes during intensive operation cycles (Figure 9) [27]. Double-shelled carbon spheres are beneficial for high sulfur loading (5.8 mg cm^{-2} , 72.4 wt%) due to their empty spaces, which also accommodate volume changes during charge/discharge cycles. Dual-doped nitrogen and phosphorus co-doped porous carbon (NPDSCS) serves as a physical

confinement to limit the diffusion of LiPSs, acting as an active center for PS trapping through chemical interactions. Phosphorus doping enhances electrochemical reaction kinetics by catalyzing the redox reactions of sulfur species. NPDSCS functions as a dual PS trapping center, providing both physical and chemical confinement, thereby retaining LiPSs within the carbon sphere. The porous shell and hollow structure facilitate short diffusion distances for Li ions, resulting in rapid ion and electrolyte diffusion. The study demonstrates that theoretical simulations based on DFT methods reveal that nitrogen and phosphorus co-doped carbon exhibit higher binding energies compared to nitrogen-doped carbon and pristine carbon. The binding energies of Li_2S_4 on pyridinic nitrogen (N_{PD}) and pyrrolic nitrogen (N_{PL}) are 0.67 and 0.59 eV, respectively, which are significantly lower than those at the N_{PDP} and N_{PLP} sites, which are 1.03 and 0.78 eV, respectively. This suggests that pyridinic nitrogen on carbon is the most effective nitrogen configuration for inhibiting PSs. Moreover, this effectiveness could be enhanced if the carbon structure is co-doped with other types of atoms [27].

When encapsulating sulfur within hollow carbon host materials, it is crucial to consider the sulfur utilization rate and the potential agglomeration of sulfur within the host, which can hinder the confinement of PSs [125, 126]. Addressing this concern, Wang's group tailored the inner structure of carbon hollow spheres to evenly disperse sulfur, optimizing sulfur reaction kinetics [127]. They designed a carbon flower at the core of a carbon nanosphere, creating a walnut-like yolk-shell structure (WSYCS) to accommodate sulfur. Controlling the buffer space—the gap between the hollow sphere and the inner carbon flowers—is vital, as it influences volume expansion and electrolyte capacity during the sulfur reaction process. The study emphasizes the importance of buffer spaces (15, 30, and 45 nm) and the cavity of buffer chambers for the electrochemical reaction kinetics of sulfur and its dispersion within the internal carbon sphere (Figure 10). A 30 nm buffer space was found to effectively disperse sulfur, enhancing its adsorption and loading capacity. Host materials for sulfur significantly impact sulfur storage, dispersion, PS binding, reaction intermediates, ion diffusion rate, and stress. The study categorizes the carbon structures into microporous HCSs, mesoporous carbon nanospheres (CNF), and a combination of carbon spheres and carbon flower nanospheres with a 15 nm buffer space (WSYCS2), evaluating their individual roles in the overall process. The HCS wall effectively migrates Li^+ , but hinders PS migration through its micropores, resulting in low utilization efficiency of internally stored and agglomerated sulfur. Mesoporous CNF improves sulfur utilization due to multistage pore channels formed by cross-linking carbon sheets, which uniformly disperse sulfur.

However, the open channels cannot fully prevent the shuttle effect (PS migration). Finite element method (FEM) simulations using COMSOL software verified these hypotheses. Sulfur loading on HCS showed minimal conversion to PSs due to low utilization rates of aggregated sulfur at discharge voltage, while CNF exhibited higher conversion

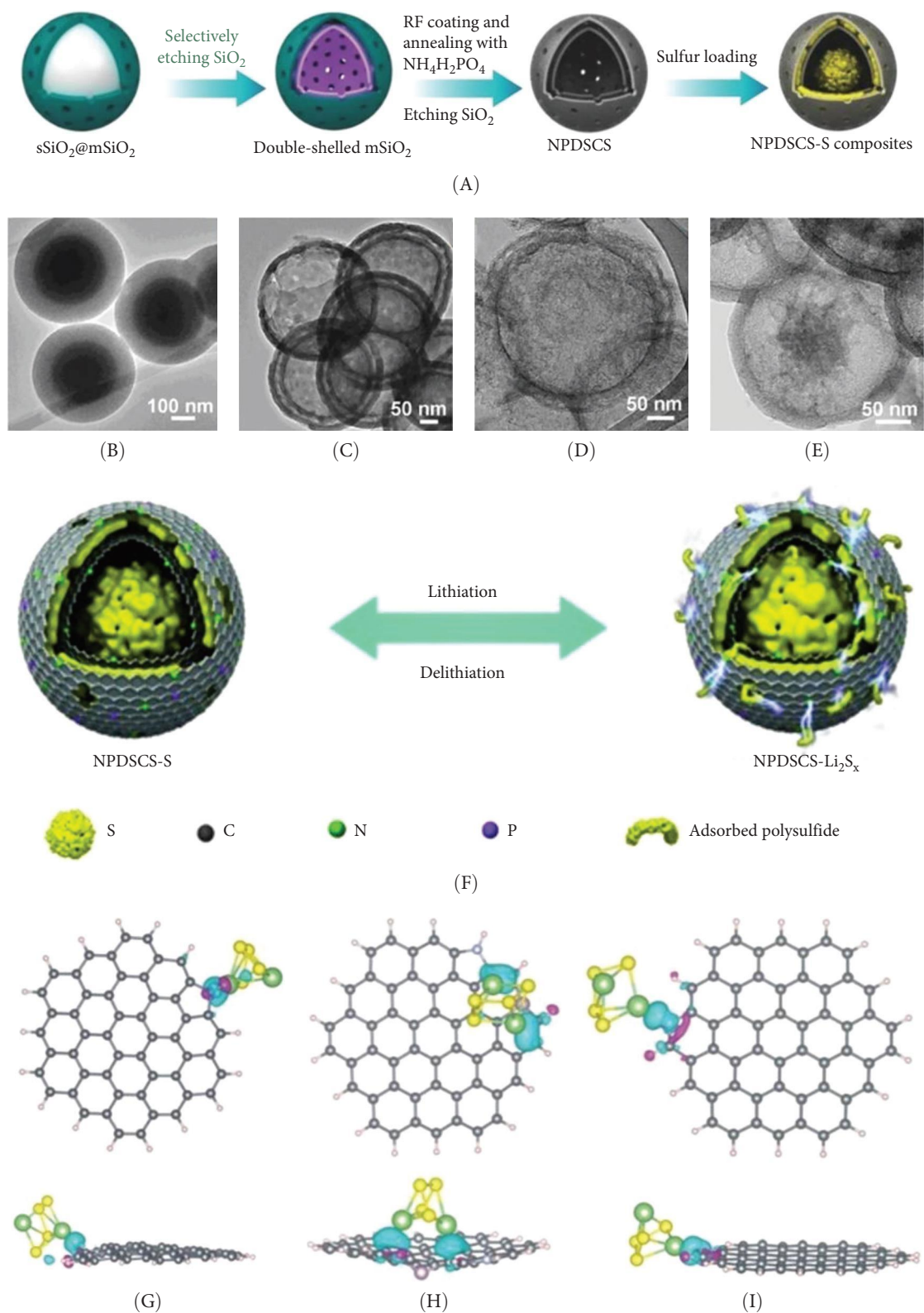


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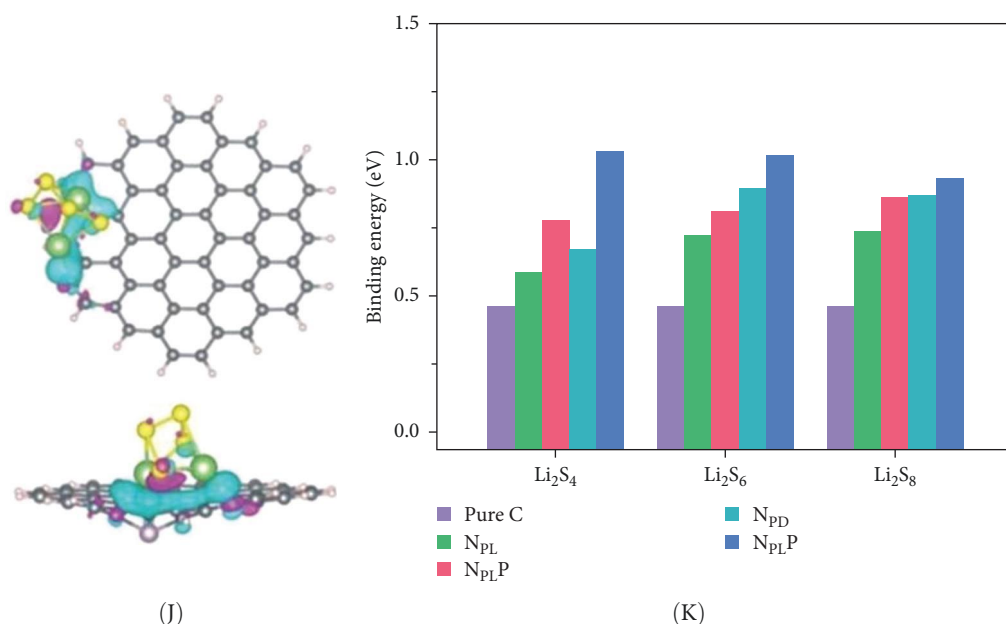


FIGURE 9: (A) Schematic of the fabrication of NPDSCS-S. TEM image of (B) $\text{sSiO}_2@\text{mSiO}_2$. (C) Double-shelled mSiO_2 . (D) NPDSCS. (E) NPDSCS-S. (F) Schematic of the trapping mechanism of sulfide and polysulfide species. First-principles calculation of carbon host-sulfur containing guest interactions, showing the top views and side views of the optimized molecular configuration. The binding of the Li_2S_4 molecule with (G) N_{PL} . (H) N_{PLP} . (I) N_{PD} . (J) N_{PD} . Here, yellow, green, blue, purple, and pink spheres represent sulfur, lithium, nitrogen, phosphorus, and hydrogen atoms, respectively. (K) DFT calculated binding energies between LiPSs and various heteroatom-doped carbon. Reproduced with permission: Copyright 2018, Wiley-VCH GmbH [27].

efficiency at various discharge voltages. WSYCS2 demonstrated a combined effect of hindering shuttle effects and uniformly dispersing sulfur, resulting in high efficiency in transforming sulfur to PSs at various discharge voltages. The correlation between maximum electric field and current density at different current densities showed that WSYCS2 had a much lower electric field strength than HCF and CNF, indicating excellent structural stability [127].

4.4. Anchoring N_4 -Coordinate SA on Carbon Matrix. A strategic approach has been developed to immobilize PSs onto carbon surfaces by engineering “lithophilic” or “sulfiphilic” surfaces. “Lithophilic” surfaces (Li-X) are created by doping heteroatoms such as N, O, B, and S, while “sulfiphilic” surfaces are formed by introducing metal oxides, hydroxides, sulfides, carbides, and similar compounds onto the carbon host [128–130]. A higher loading of nanostructural metal compounds improves the adsorption and catalysis of PSs. However, although significant loading of these metals enhances adsorption and catalysis properties, it compromises the surface area and pore volume. Additionally, it deteriorates the conductivity and Li^+ migration rate of the materials, consequently reducing the performance of LSBs [131–134]. Introducing SAs into the carbon configuration modifies the polarity, offering high exposure sites for enhanced physical adsorption and catalytic conversion of PSs without deteriorating the surface area and pore volume. However, the high surface free energy of SAs makes them chemically unstable, leading to self-aggregation into nanoparticles, which reduces catalytic activity and slows reaction kinetics. A strategic engineering approach involves coordinating single metal atoms

with adjacent dopants such as C, O, N, and S to fix monoatomic agglomeration. This method can tune catalytic activity in a controlled manner by customizing the coordination type and number. A multidisciplinary collaborative research group from Wenzhou University, Zhengzhou University, and Nankai University synthesized N_4 -coordinated SAs of molybdenum (Mo) anchored on N-doped carbon nanoflowers (Mo-N-CNF) as a host for the cathode electrode of LSBs (Figure 11) [28]. Single Mo atoms on a carbon structure act as a host for sulfur, balancing the chemical and physical adsorption of LiPSs. The adsorption energies (E_{ads}) for various PSs are as follows: S_8 (−2.64 eV), Li_2S_8 (−3.36 eV), Li_2S_6 (−3.66 eV), Li_2S_4 (−3.09 eV), Li_2S_2 (−3.43 eV), and Li_2S (−4.21 eV). This configuration provides fast redox kinetics, resulting in high sulfur loading (5.1 mg cm^{-2}) and an areal specific capacity of 3.18 mA cm^{-2} at a current density of 4.2 mA cm^{-2} over 400 cycles, with an attenuation rate of 0.004% per cycle [28].

The binding energy between Mo atoms and N-doped graphene is −6.11 eV, which is more negative than the adsorption energies of PSs on Mo-N-CNF. The cohesive energies of MoS_2 , Mo_2S_2 , and Mo_3S_4 are −3.30, −3.62, and −3.74 eV, respectively. Consequently, the stability of the Mo-N-C configuration is ensured, as the formation of Mo sulfides from the reaction of single Mo atoms with PSs or sulfur is unlikely.

The ratio of coordinated Mo in N-doped CNF is crucial for hindering PS dissolution. The ratios of Mo to Mo-N-CNF were maintained at 4.7%, 9.4%, and 23.0% for Mo-N-CNF-1, Mo-N-CNF-2, and Mo-N-CNF-3, respectively, as calculated from thermal gravimetric analysis. Ex situ adsorption measurements showed that the UV absorbance peaks at

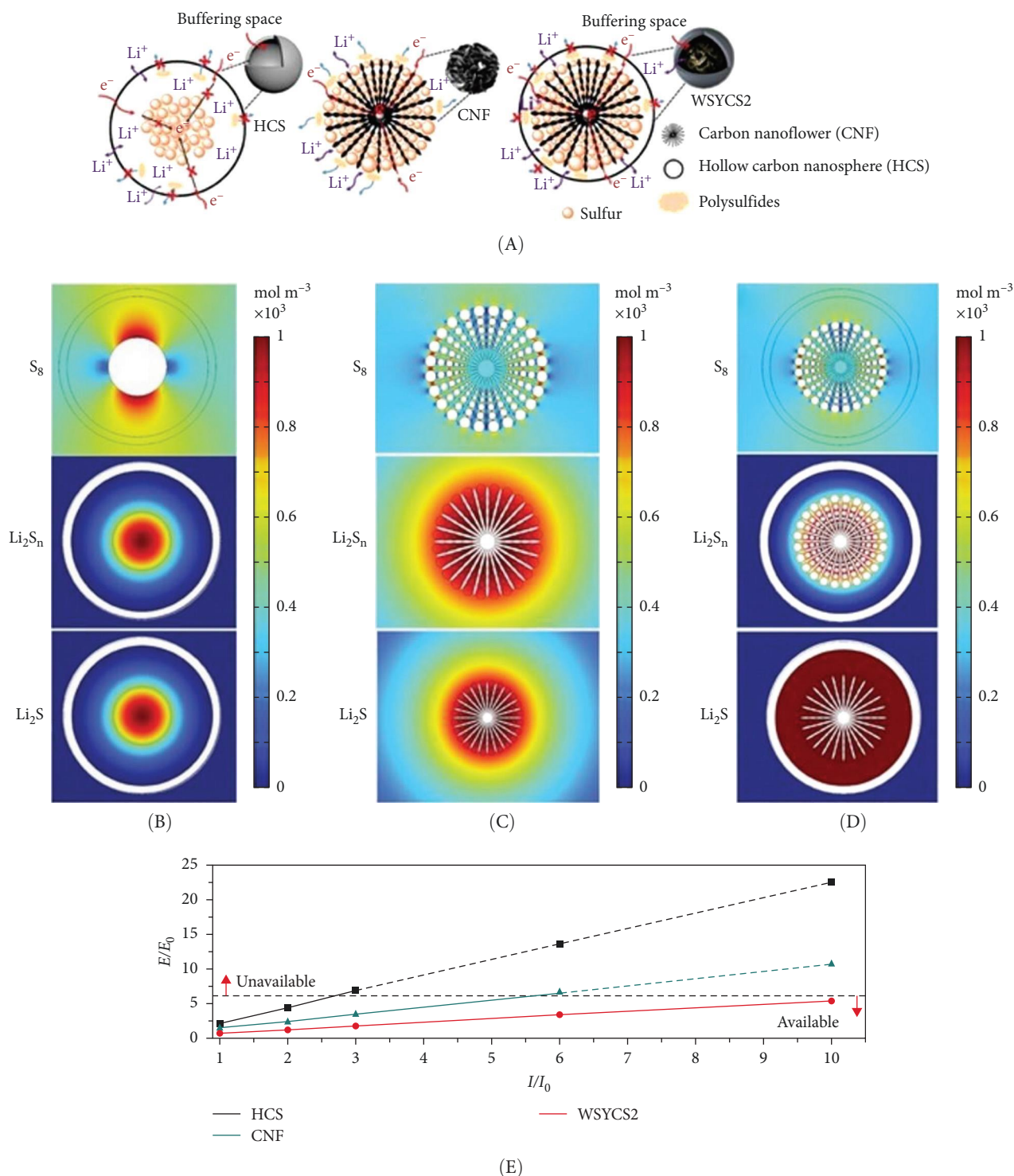


FIGURE 10: Structural analysis. (A) Schematic illustration of the internal dispersion of active sulfur in various materials. The finite element method (FEM) simulation of COMSOL software is used to simulate the polysulfide concentration in (B) HCS. (C) CNF. (D) WSYCS2 structures at different discharge voltages. (E) The maximum electric field intensity of all sample models under different current densities, where the purple dotted line is the threshold and the dotted line above the purple line is the failure zone. Reproduced with permission: Copyright 2023, Wiley-VCH GmbH [127].

400–450 cm^{-1} for Mo–N–CNF–2 exposed to Li_2S_6 PS solution were weakest, indicating strong chemical adsorption. XPS spectra further confirmed this with a negative shift to lower binding energy in the S 2p peaks after Li_2S_6 adsorption. The

Mo 3d spectra demonstrated the chemical bonding of Mo–S from the S atom of PSs, while the broadening of the Li 1s spectra of Mo–N–CNF soaked in Li_2S_6 solution indicated electron injection from the N atom to Li, highlighting the

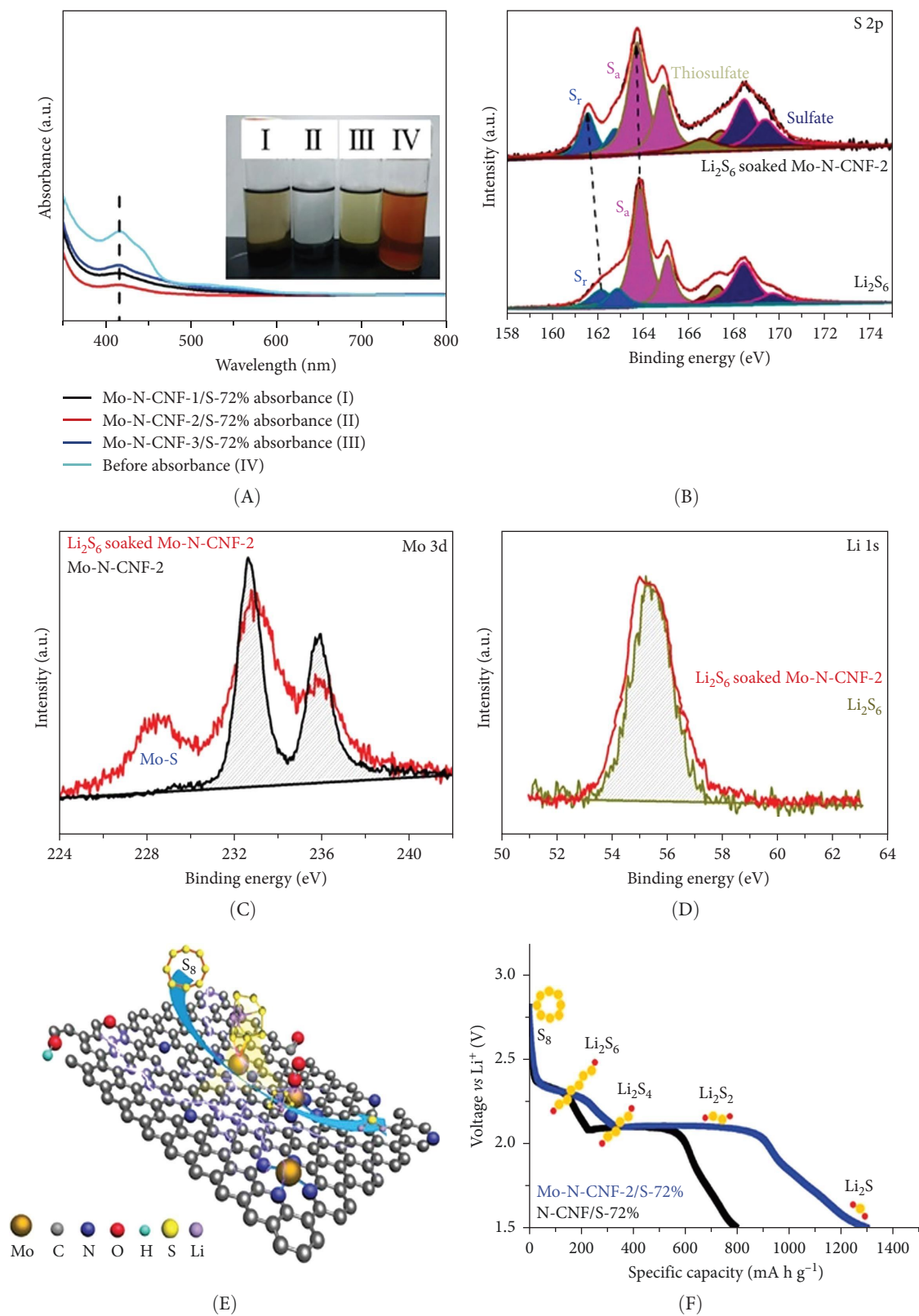


FIGURE 11: (A) UV-vis spectra (inset image of solution). XPS spectra of Li_2S_6 and the Li_2S_6 wet on Mo-N-CNF-2. (B) S 2p. (C) Mo 3d. (D) Li 1s. structures at different discharge voltages. (E) Electro catalytic process of LPS on the M-N-CNF. (F) Discharge capacity at 0.2 C. Reproduced with permission: Copyright 2022, Wiley-VCH GmbH [28].

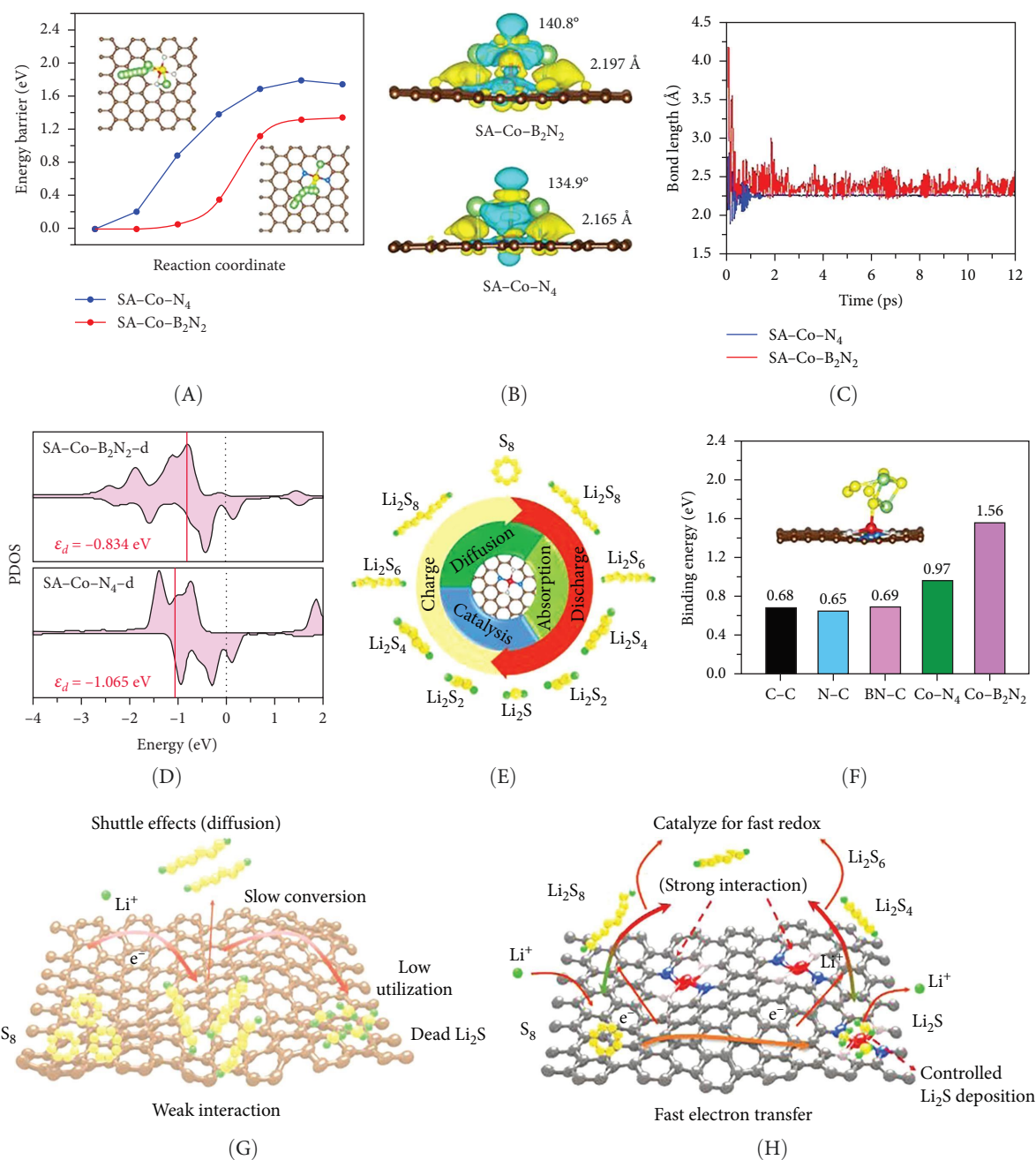


FIGURE 12: (A) Decomposition barrier of Li₂S. (B) Side view for charge density difference of Li₂S adsorption on the SA-Co/BNC and SA-Co/NC (accumulate (yellow) and lose (blue) regions of electrons). (C) Li-S bond length over time. (D) PDOS for SA-Co/BNC and SA-Co/NC. (E) Schematic diagram of LiPS changes during charge and discharge of Li-S batteries. (F) Binding energy of Li₂S₆. (G) Schematics of the conversion process on carbon. (H) Schematics of the conversion process on SA-Co/BNC. Reproduced with permission: Copyright 2023, Wiley-VCH GmbH [43].

beneficial effects of N-doping and Li affinity. Ultimately, the specific capacities of Mo-N-CNF are higher than those of N-doped CNF without Mo anchoring [28].

Several studies have concentrated on the SA N₄ coordination; however, the Chen group explored SA material coordination in alternative environments (Figure 12) [43]. Specifically, their study investigates Co SAs (SA-Co) with B₂N₂ (BN) coordination anchored on CNT arrays (C) (SA-Co/BNC). This configuration demonstrates a lower

Li₂S decomposition barrier and higher binding energy for Li₂S₆. Notably, the decomposition barrier of Li₂S in SA-Co/BNC (1.35 eV) is significantly lower than in SA-Co/NC (1.79 eV), indicating that SA-Co-BN active sites are more effective in breaking the Li-S bond, thus, facilitating rapid delithiation during the charging process. Additionally, charge density difference calculations reveal that the bond length and bond angle of Li₂S on SA-Co-BNC are greater (2.197 Å, 140.8°) compared to SA-Co-NC (2.165 Å, 134.9°). Projected density

of states (PDOSs) analysis shows more pronounced d-orbital splitting and a rise in the d-band center around -1.065 eV for SA-Co/BNC, indicative of strong metal-adsorbent interactions. Experimentally, SA-Co/BNC exhibited a specific capacity of 1106 mA h g^{-1} at 0.2 C after 100 cycles, with a decay rate of only 0.03% per cycle. Furthermore, after 1000 cycles at 1 C and a sulfur loading of 1.2 mg cm^{-2} , SA-Co/BNC maintained a reversible capacity of 684 mA h g^{-1} , surpassing that of SA-Co/NC (532 mA h g^{-1}) and BNC (308 mA h g^{-1}) [43].

4.5. Hollow Scaffold. As a sulfur container porous carbon pore size, distribution and volume direct the electrochemical properties of sulfur and carbon composites. The size range of $2\text{--}50$ nm of mesopores and over 50 nm of macropores gives the sulfur loading and volume expansion opportunity. But it is need to be consider in this pore range PSs dissolution becomes pronounced. The size range of less than 2 nm of micropores is effective for the hinder PS diffusion as a physical barrier but an obstacle for the sulfur loading on the host materials [135–137]. In this context, in general hollow carbon with microporous core and micro-/mesopores shell considered for the LSB. Internal core cavities will accommodate the high amounts of sulfur and keeps spaces for the volume expansion on the lithiation. Micro-/mesopores shell act as physical barrier for the LPS diffusion as well maintain the efficient path of the electrolyte and ion penetrations [100, 138]. Excessive narrower pores in the shell could hinder the sulfur penetration through the shell to the core and over larger pores in the shell could allows the excessive host of the sulfur to the core that fills the core and keeps the unviable spaces for the volume expansions [40]. As a concern it is required a tradeoff management of pores size controls in the shell which is quite tricky. Though the infusion the polar materials in the carbon utilized to chemical confinement effects to block the LPS diffusion to prevent shuttling effects. It is may be concerning that polar materials in the mesoporous shell in the hollow carbon make it difficult to infuse of sulfur the shell to the core. Also, excessive polar materials will enhance the sulfur host may not be able to contribute in the energy storage [90, 139, 140]. All this consideration it needs to be design a precise way of materials configuration with proper pores size of shell with the internal cores and rights amount of polar materials incorporation that can homogenize distribute the sulfur into the shell and cavity and maintain and a proper redox reaction without a shuttling effect.

Hou group utilized polar MnO_2 nanosheets as chemical entrapment agents, coating them with carbon to form hollow nanoboxes termed $\text{MnO}_2\text{@HCB}$ [40]. These nanoboxes are designed to maximize sulfur loading and buffer the volume expansion during lithiation. Additionally, the nanoboxes act as physical barriers, containing soluble PSs within the carbon boxes. The MnO_2 nanosheets provide resistance to PS migration out of the carbon nanoboxes through strong chemical interactions. The hierarchical porous structure of the coated nanoboxes ensures efficient ionic and electronic transport, effectively utilizing the loaded sulfur. The $\text{MnO}_2\text{@HCB/S}$ hybrid nanoboxes, with a sulfur loading of $67.9 \text{ wt}\%$, exhibit a specific capacity of 1042 mA h g^{-1} at a current density of 1

A g^{-1} . However, the approach shows that after 60 cycles, the discharge capacity reaches approximately 200 mA h g^{-1} at a current density of 1 A g^{-1} [40].

The Dong–Wan group has innovatively designed dual hollow scaffolds consists of polar CoS_2 on N-doped graphitic carbon nanoshells (NGCNs) comprising a core of approximately 600 nm in macrohollow structure surrounded by a shell of around 50 nm in microhollow configuration (Figure 13) [30]. This design proves effective for accommodating sulfur in LSBs. The CoS_2 polar groups hinder the LPS mobilization by chemical interaction. Mesoporous surface in the shells effectively provide the diffusion of the sulfur to the hollow core and center of the cavity remain enough empty to buffer the volume expansions at the time of lithiations. Sulfur infiltrated in the carbon shell remains near the conductive carbon shell as consequence it may optimally utilized conductive path of the carbon. The mesoporous hollow $\text{CoS}_2\text{@NGCNS}$ effectively hosts a high sulfur loading of $75 \text{ wt}\%$, utilizing ample void spaces within its structure. The mesopores in the shell facilitate easy penetration of electrolytes and ions, while the macrohollow voids within the core serve to buffer volume expansions during cycling. The mesoporous hollow $\text{CoS}_2\text{@NGCNS}$ shows the 903 mA h g^{-1} cycle performance at 0.1 C after 100 cycles [30].

The Kemin group employed CeO_2 as a catalytic material for LSBs, leveraging its moderate band gap and multiple valence states [64]. By embedding CeO_2 into mesoporous hollow carbon, they introduced oxygen vacancies, which enhanced electrical conductivity and provided additional active sites, thereby improving adsorption capacity, catalytic activity, and overall electrochemical performance. The synergy between HCSs and oxygen-deficient CeO_2 contributed to multiple advantages: efficient sulfur penetration, enhanced electron and ion transport through the mesoporous framework, and hollow inner cavities that acted as sulfur reservoirs while mitigating volume expansion. This integrated design significantly improved sulfur redox kinetics, leading to a high retention capacity of 728 mA h g^{-1} after 500 cycles, with a minimal capacity decay rate of 0.056% per cycle under a sulfur loading of 4.7 mg cm^{-2} . Furthermore, the system maintained a substantial reversible areal capacity of 4.7 mA h cm^{-2} , demonstrating its potential for high-performance LSB applications [64].

Considering the importance of hollow carbon for volume buffering, the Huang group inserted or doped nitrogen (N) groups into hollow porous carbon to increase its polarity and suppress the diffusion of PSs via chemical interactions [34].

Their study demonstrated that Li_2S_6 interacts more strongly with N-doped hollow carbon than with graphene or CNTs, suggesting that N-doping can enhance PS immobilization through chemical adsorption. The study also identified and classified the functionalities of the N-groups using deconvolution of XPS spectra, identifying pyridinic N, graphitic N, pyrrolic N, and oxidized N. However, the research did not determine which specific N-group is most effective for PS immobilization or elucidate the mechanisms by which the polarity of the host material influences chemical interactions with PSs. Further investigation is required to fully understand

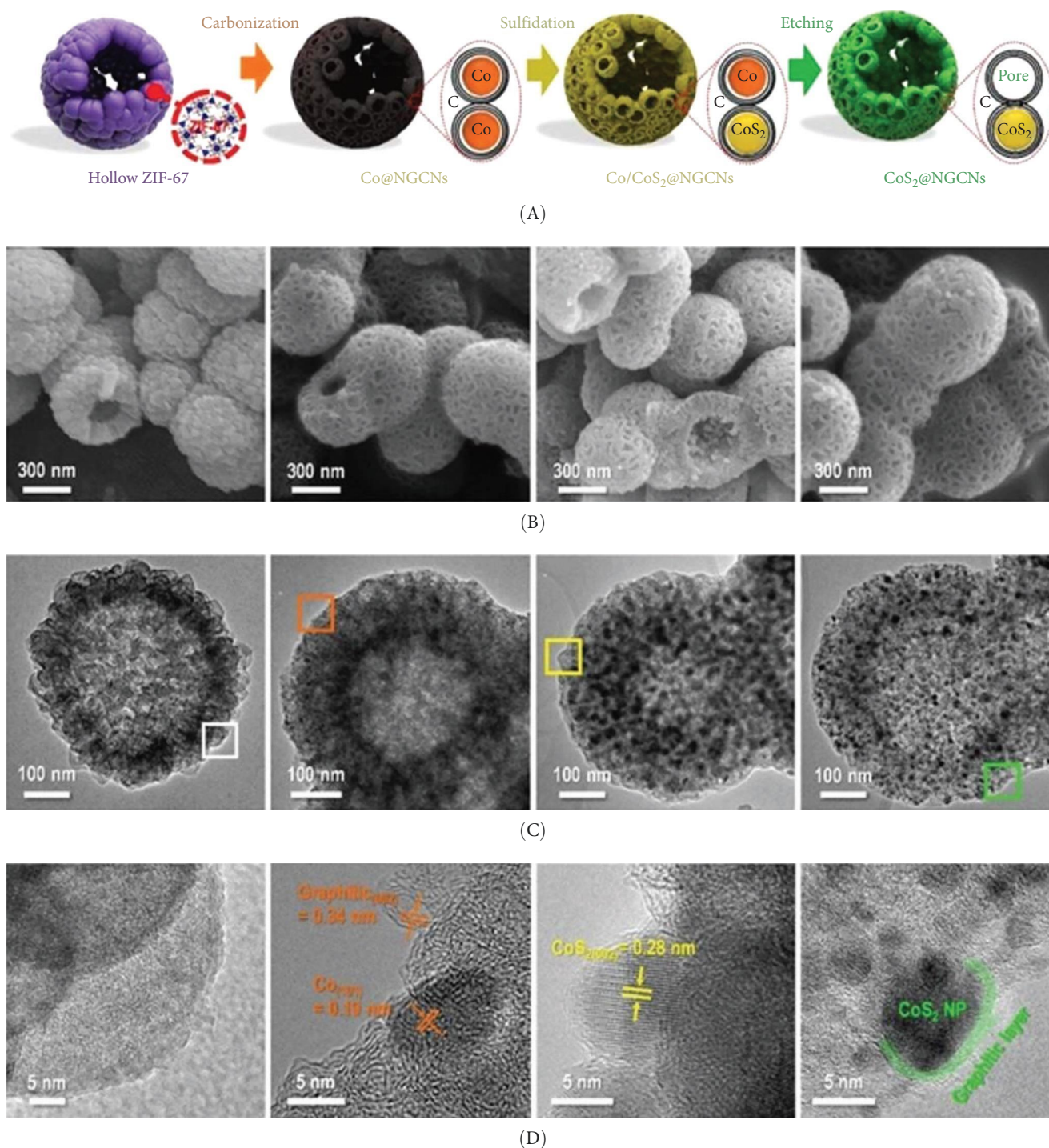


FIGURE 13: Structural analysis. (A) Scheme of the mesoporous hollow CoS_2 @N-doped graphitic carbon nanoshells (NGCNs) preparation. (B) SEM Image. (C) TEM image. (D) HRTEM image. Reproduced with permission: Copyright 2019, Wiley-VCH GmbH [30].

these mechanisms and advance the fundamental development of this process.

Several studies have focused on multiphase construct heterostructures due to their provision of abundant active sites and enhanced conductivity, which play a crucial role in maximizing the utilization of sulfur and mitigating the capacity degradation of LSBs to some extent [141, 142]. In contrast, single-phase metal oxides, metal sulfides, and metal nitrides

exhibit strong chemisorption on polar materials but suffer from low ionic and electronic conductivity as well as weak redox kinetics [143]. Heterostructures improve adsorption capability, redistribute charge density, enhance immobilization, and promote the conversion kinetics of LiPSs [144, 145]. The Jiang group designed a hollow polyhedron $\text{CoO}/\text{Co}_9\text{S}_8/\text{nitrogen-doped carbon}$ ($\text{CoO}/\text{Co}_9\text{S}_8/\text{NC}$) heterostructure as a sulfur host for LSBs [16]. In this design, CoO , a

p-type semiconductor, facilitates strong adsorption of LiPSs, while n-type Co_9S_8 supports fast redox kinetics for LiPSs. The p–n heterojunction provides additional active sites, thereby enhancing ion and electron transport. Nitrogen-doped carbon (N-doped C) aids in the physical capture of LiPSs and improves electronic conductivity. Anchoring sulfur on the hollow polyhedron $\text{CoO}/\text{Co}_9\text{S}_8/\text{nitrogen-doped carbon}$ ($\text{S-CoO}/\text{Co}_9\text{S}_8/\text{NC}$) cathode achieves a capacity of 1470 mA h g^{-1} at 0.1 C , with a capacity attenuation of 0.03% per cycle [16].

The Wang group from Wenzhou University designed and produced radially inwardly aligned, hierarchically N-doped hollow carbon nanospheres (TI-NHCNS) from the glucose padding on the urchin-like SiO_2 [52]. This strategic design incorporates an interior cavity among the ribs, creating nanochannels that enable efficient sulfur infusion, while the central void spaces act as a buffering zone to accommodate volume expansion. The internal inwardly aligned ribs maximize sulfur utilization and facilitate shorter ion diffusion lengths. The N-doped shell enhances both the chemical and physical confinement of PSs. The prepared cathode, which hosts 75% sulfur, demonstrated performance integrity with a decay rate of 0.04% per cycle over 100 cycles at 1 C [52].

4.6. Structural Engineering. Structural configuration and textural properties play a significant role in the overall functionality of LSBs. Micropores effectively inhibit the dissolution of S_8 , Li_2S_2 , and Li_2S_4 . Mesopores accelerate Li ion transport and the conversion reactions of LiPSs. Macropores are effective in confining long-chain PSs within the pore walls [146–148]. Lee and colleagues evaluated the importance of different pore morphologies, alongside heteroatom doping, to address the challenges in LSB operation [35]. The study differentiated three types of porous carbon structures: micropores less than 2 nm , micropores with 3 nm mesopores, and micropores with $2\text{--}7 \text{ nm}$ mesopores, all of which contained nitrogen and oxygen functional groups. The results indicated that the micro-mesopores (2 to 7 nm) structure exhibited enhanced performance compared to the micropores and micro-mesopores (2 nm), with specific capacities of 804 , 821 , and 672 mA h g^{-1} , respectively. The presence of nitrogen and oxygen functional groups efficiently reduced the loss of active sulfur materials and accelerated the conversion kinetics of LiPSs [35].

The Liu group designed a honeycomb-like, regular, and uniform N, O-doped carbon structure with the perspective of high sulfur loading and heteroatom retention of PSs on the cathodes [38]. This design also promotes the catalytic conversion of PSs. The honeycomb-like hollow structure facilitates high sulfur loading and accommodates volume expansion during lithiation. Additionally, the N, O dual-doped carbon can reduce the diffusion of LiPS. The honeycomb structure is expected to ensure efficient infiltration of electrolytes, maintaining low E/S (electrolyte/sulfur) ratios ($4.8 \mu\text{L mg}^{-1}$). A modified template method (using SiO_2 , 20 nm with furfuryl alcohol) was utilized to synthesize the honeycomb-like structure, enhancing the pore size to a range of $10\text{--}40 \text{ nm}$. The designed material shows an initial capacity of 1549 mA h g^{-1}

at 0.05 C , with a capacity retention of 97.2% after 100 cycles at 0.2 C , and 5.4 mA h cm^{-2} capacity after 50 cycles at 0.2 C with 7.4 mg cm^{-2} loadings [38].

High sulfur loading ($\geq 6 \text{ mg cm}^{-2}$) significantly exacerbates PS shuttling and electrode passivation, posing challenges for maintaining electrical and ionic conductivity. Large pore volumes are necessary to accommodate the substantial sulfur content and its associated volume expansion. Specifically, at a sulfur loading of 6 mg cm^{-2} with $70 \text{ wt}\%$ sulfur and $10 \text{ wt}\%$ carbon support, a pore volume of $2.4 \text{ cm}^3 \text{ g}^{-1}$ is required to achieve 70% sulfur utilization. To fully convert the sulfur to Li_2S , the pore volume must increase to $4.3 \text{ cm}^3 \text{ g}^{-1}$ [149, 150]. Achieving this high pore volume necessitates expanding the pore diameter from a few nanometers to tens of nanometers. However, the pore diameter must be carefully optimized to ensure that sulfur, PSs, and Li_2S remain in close proximity to the carbon surface, thereby maintaining efficient ionic and electrical conductivity. The carbon support can inadvertently enhance PS shuttling, reducing cycle life and the utilization efficiency of active materials [18, 151]. The Young-Si group addressed these challenges by employing mesoporous carbon (C@CN) derived from the molecular cooperative assembly of glucose and triazine as a sulfur host (Figure 14) [6]. By adjusting the glucose-to-triazine ratio, they engineered a pore structure and chemical composition that provided a considerable pore volume ($1.96 \text{ cm}^3 \text{ g}^{-1}$) and large pore diameters ($20\text{--}60 \text{ nm}$). Additionally, a highly conductive carbon buckypaper or CNT was used as the primary host and current collector, adding an extra pore volume of $0.87 \text{ cm}^3 \text{ g}^{-1}$. When combined with carbon buckypaper, the pelletized C@CN electrode demonstrated areal capacities of 24 and 17 mA h cm^{-2} at current densities of 0.47 and 4.7 mA cm^{-2} , respectively, at a sulfur loading of 24 mg cm^{-2} . The optimized pelletized C@CN -based LSB achieved a total energy density of 39 mWh and a volumetric energy density of 440 Wh L^{-1} at a sulfur loading of 24 mg cm^{-2} , with a sulfur fraction of 70% and a utilization fraction of 61% [6].

The Li group designed a MoN-C-MoN trilayer architecture, featuring a sandwich structure with continuous 2D catalysis-conduction interfaces [56]. In this configuration, the metal nitrides, with overlapping d-orbitals, exhibit ultra-high electronic conductivity, surpassing that of metals alone, and serve as a polar host for sulfur species [152–154]. The multiple valence states of Mo (Mo^{6+} , Mo^{4+} , Mo^{3+} , and Mo^{2+}) provide advantageous properties for maintaining electrochemical stability in electrodes [155, 156]. The two-sided MoN layer strongly adsorbs PSs, while the carbon interlayer facilitates charge transfer and supplies sufficient electrons to the MoN layers. This 3D design intensifies the conductive and catalytic network. Even, the phase separation between C and MoN preserves contact between the conductive substrate and catalytic sites, akin to the 2D interface contact between MoN and C lattices (Figure 15). The nitride host is capable of supporting a sulfur loading of $75.7 \text{ wt}\%$. The cathode, based on this design strategy, demonstrated a high-rate capacity of 515 mA h g^{-1} at 4 C and long-cycle stability, with a decay rate of 0.03% per cycle at 1 C after 1000 cycles [56].

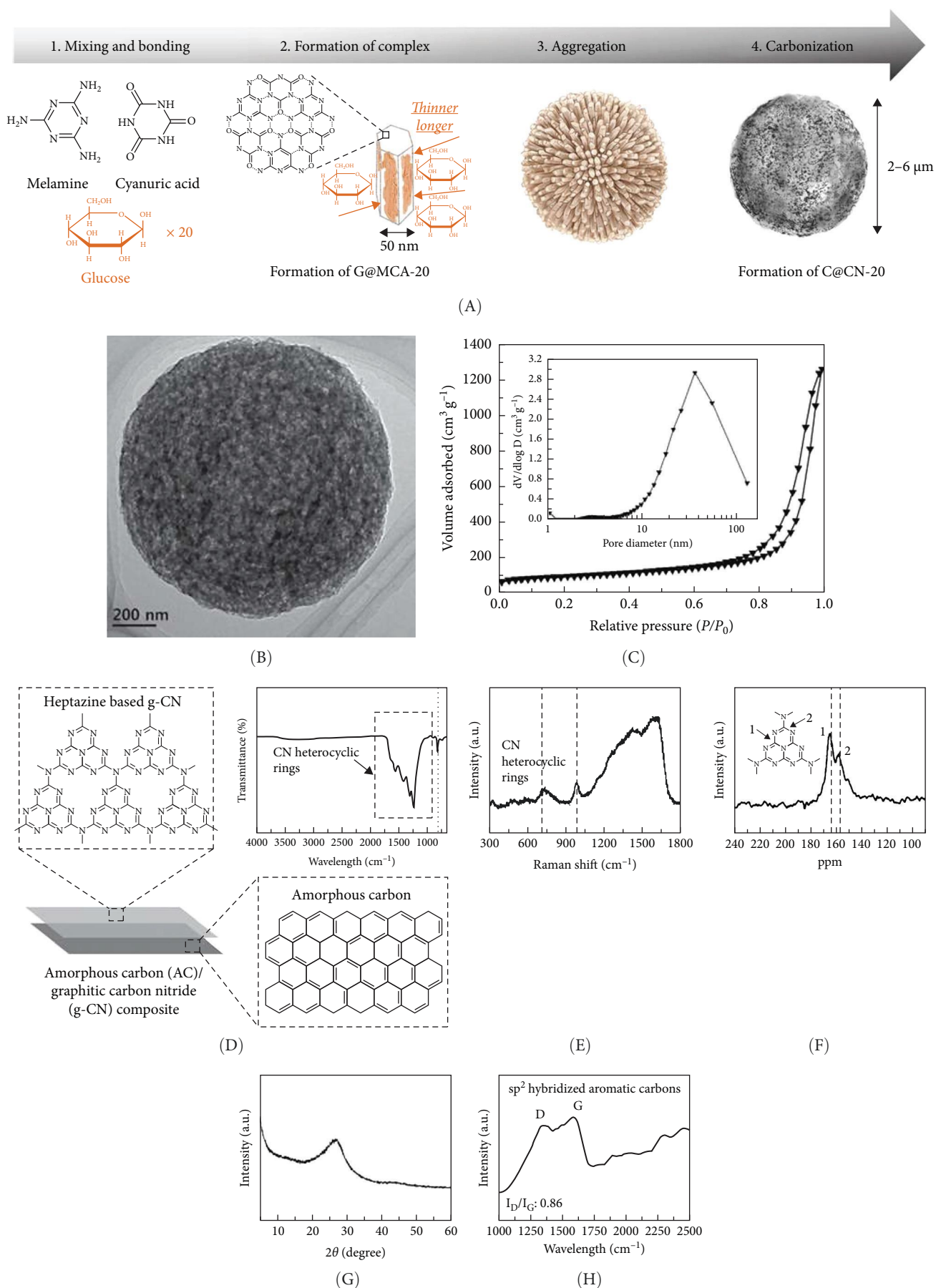


FIGURE 14: (A) Molecular cooperative assembly–based synthesis of carbon. (B) TEM Image. (C) N_2 isotherm (inset: NLDFT pores size distribution). (D) FTIR spectrum. (E) UV–Raman spectrum. (F) Solid state ^{13}C NMR. (G) XRD spectra. (H) Visible Raman spectra. Reproduced with permission: Copyright 2021, The authors, Wiley & Sons [6].

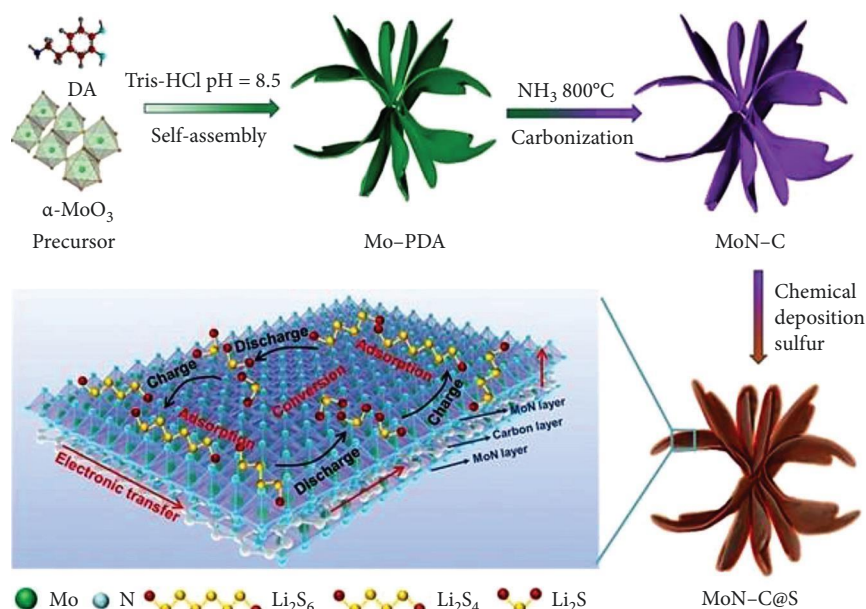


FIGURE 15: Scheme of the preparation of the MoN-C@S and adsorption–conversion–conduction effects of polysulfides. Reproduced with permission: Copyright 2020, The authors, Wiley & Sons [56].

4.7. Gel Composite With Polar Nanoparticles. Incorporating polar metal oxide nanoparticles into a carbon host maximizes sulfur utilization through spatial confinement and enhanced chemical interactions. However, a large mass of nanoparticles can reduce the overall loading mass of active sulfur. Reduced-size polar nanoparticles, including metal oxides, nitrides, carbides, and phosphides, are beneficial for the adsorption of soluble LiPSs and the enhancement of catalytic conversion kinetics [157, 158]. Carbon-supported Co catalysts have demonstrated utility in PS conversions, with single Co atoms showing optimal charge transfer and sulfur redox kinetics. Although nanoscale designs offer significant advantages in terms of active adsorption sites and reaction kinetics, they often face aggregation issues during reactions, are challenging to scale up, and result in high production costs [159–161].

The Zhou group utilized *Rhizopus* hyphae as a support skeleton, where sodium alginate gel was polymerized through multivalent metal cations (V_2O_3 , 2–5 nm) to form an alginate gel-filled hyphae complex (RHCF/SAC/ V_2O_3 ; Figure 16) [37]. Upon carbonization, RHCF acted as a 3D microfiber network for the sulfur host, providing good electrical conductivity, mechanical stability, and N, P, O heteroatom doping (Figure 16). The designed material's complex pore structure, heteroatom doping, and polar V_2O_3 limited the diffusion and loss of PSs through physical inhibition and physical and chemical adsorption. V_2O_3 played a crucial role in the catalytic conversion kinetics of PSs [37].

DFT calculations revealed that the adsorption energy of PSs on the V_2O_3 (104) crystal plane was significantly higher than on pure graphene surfaces (Figure 16). Electronic density of states (DOSs) analysis showed the interfacial charge regulation mechanisms of the sulfur host during the redox transformation of PSs. N, P co-doping phenomena were compared by observing changes in the total DOSs (TDOS) before and

after Li_2S_6 probe molecule adsorption on N, P-doped graphene. It was observed that quaternary-N, pyridinic-N, and P-doped graphene exhibited significantly shortened band gap distances compared to pure graphene, indicating the generation of s and p hybridization orbitals [37].

The catalytic conversion of LiPS on V_2O_3 (104) was further evaluated by DOS analysis (Figure 16). PDOSs investigations of the V-d and S-p orbitals before and after Li_2S_6 adsorption on V_2O_3 showed enhanced electron concentration near the Fermi level (E_F) for both V-d and S-p orbitals after chemical interaction. Moreover, the d-band of the V atom entered the adsorbed Li_2S_6 , resulting in increased d-p orbital hybridization, reduced energy band gap between the V d-band and S p-band, enhanced charge compensation effects, and ultimately improved interfacial redox and conversion kinetics. This 3D hierarchical carbon network of RHCF/SAC/ V_2O_3 exhibited 94% capacity retention after 200 cycles at 0.1 C and a specific capacity of 578 mA h g^{-1} at 5 C [37].

4.8. Biomass Derived Porous Carbon. The development of carbon materials such as micro/mesoporous carbon, hierarchical porous carbon, hollow sphere carbon, carbon fibers (CFs), nanotubes, and graphene involve complex processing steps, is relatively expensive, and poses significant challenges for large-scale production [123, 162]. Biomass-derived porous carbon from common plants, seeds, and bio-waste is considered an alternative for synthesizing activated carbon for LSBs due to its low cost, facile synthesis routes, large specific surface area, well-developed porosity, abundant raw material sources, good electrical conductivity, and strong mechanical integrity [163, 164].

The Yan group developed N-doped biomass-derived carbon from okra shells for LSBs [42]. This material exhibits a large specific surface area ($2702 \text{ m}^2 \text{ g}^{-1}$) and abundant

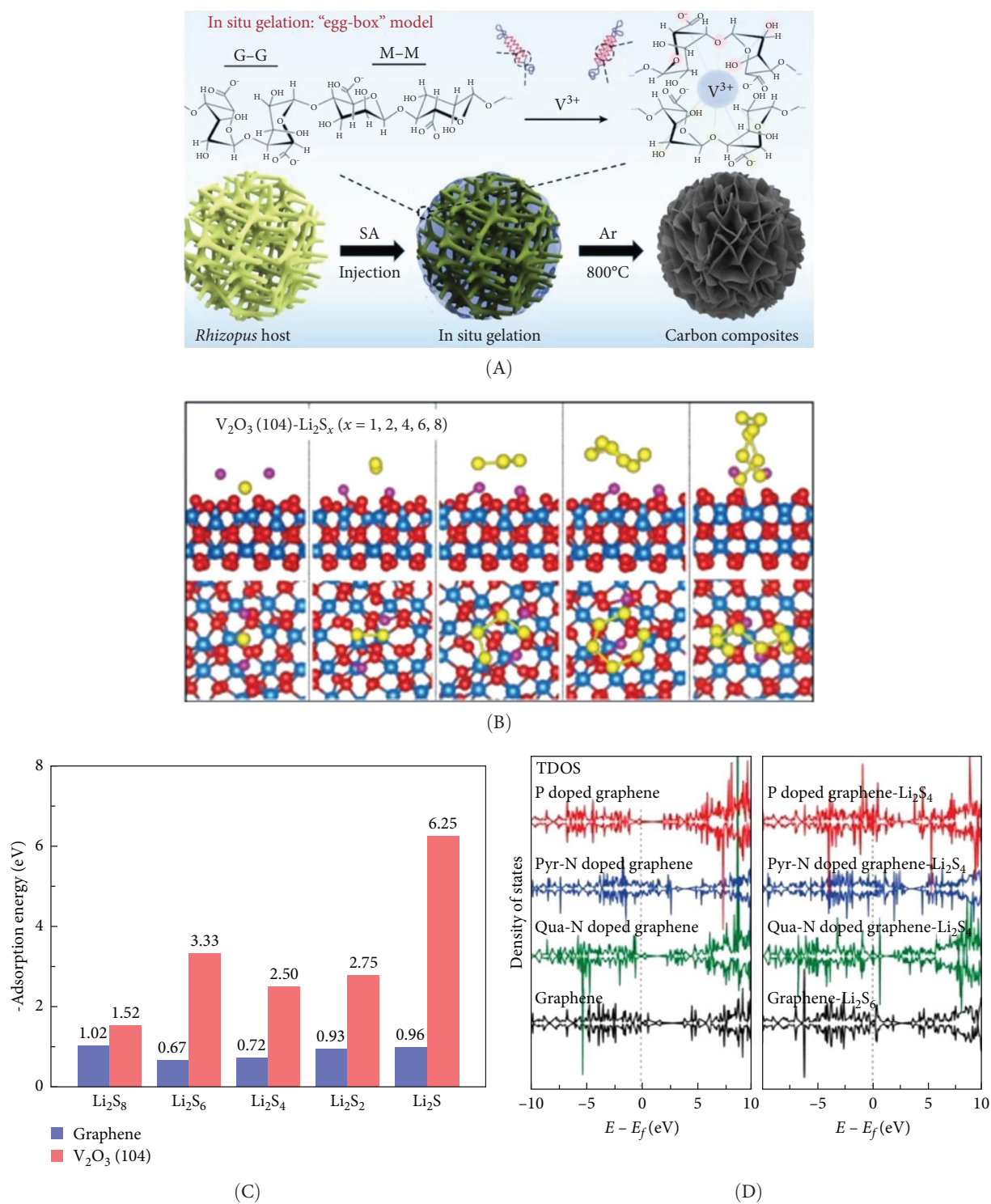


FIGURE 16: Continued.

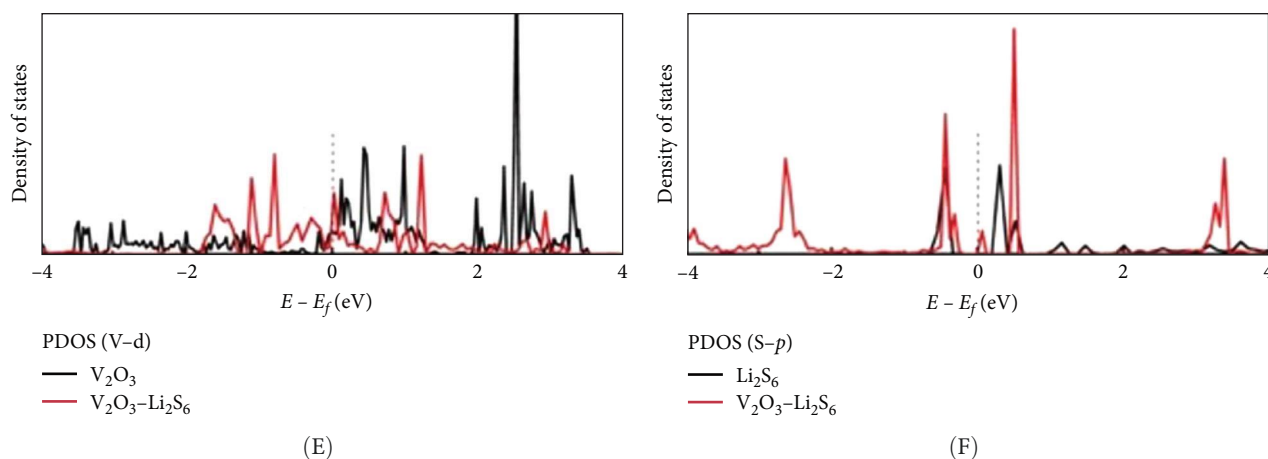


FIGURE 16: (A) Schematic of the structural formation of multilayer carbon. (B) DFT calculations of adsorption energies of LiPS on V_2O_3 (104). (C) Comparisons of adsorption energy. (D) TDOS. (E) PDOS analysis of V_2O_3/Li_2S_6 interactions, V-d orbital. (F) PDOS analysis of V_2O_3/Li_2S_6 interactions S-p orbital. Reproduced with permission: Copyright 2023, Wiley-VCH GmbH [37].

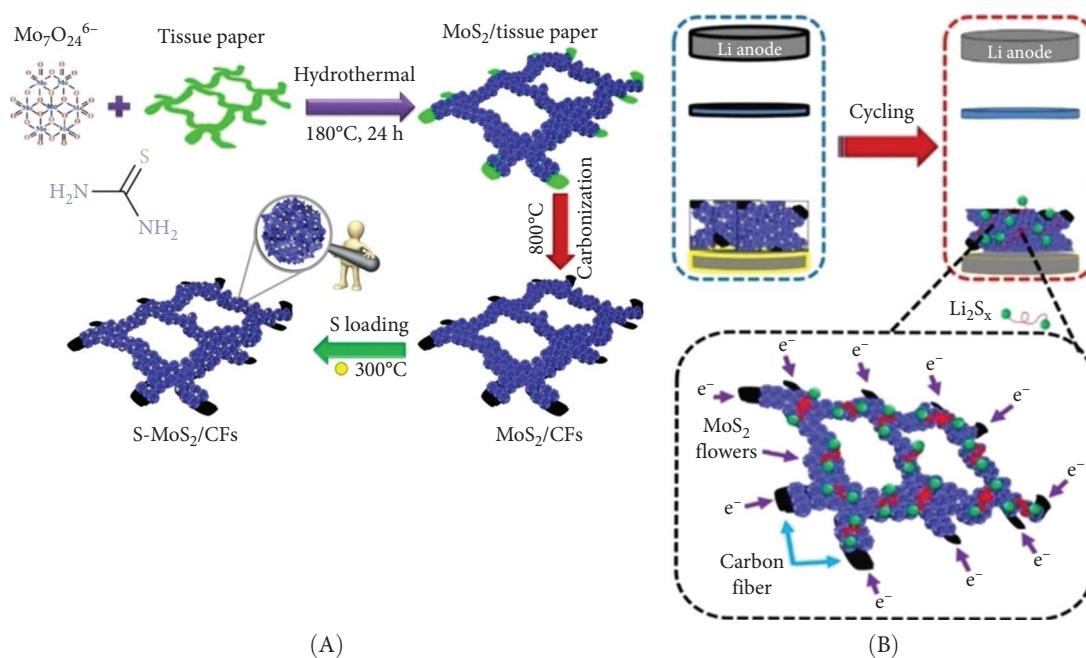


FIGURE 17: (A) Schematic of MoS_2/CFs preparation and the sulfur loading. (B) Illustration of the redox reaction mechanisms. Reproduced with permission: Copyright 2020, Wiley-VCH GmbH [165].

porosity ($0.17 \text{ cm}^3 \text{ g}^{-1}$), which allows for high sulfur loading (69.71%) and numerous adsorption sites, thereby minimizing the dissolution of LiPS. N-doping of the carbon was achieved through NH_3 gas treatment during carbonization, which creates defects that promote more active sites, facilitate electron conduction from sulfur, and favor the reduction reaction of Li_2S_x ($8 \leq x \leq 4$) to Li_2S . The cathode designed with the carbon-sulfur composite demonstrated a discharge capacity of 1387 mA h g^{-1} at 0.1 C and 750 mA h g^{-1} at 0.5 C after 200 cycles, with a decay rate of 0.05% per cycle [42].

A joint research group from the Shenyang Normal University, University of Jinan, and Shanghai JiaoTong University

employed interwoven cellulose fibers from commercial tissues as a biomass source for CFs (Figure 17) [165]. 2D MoS_2 nanoflakes were integrated into the CFs (MoS_2/CFs), where MoS_2 provided ample anchoring sites for the adsorption of LiPSs and facilitated their redox conversion. The hydrothermal formation of MoS_2 into a 3D flower-like structure on the woven network prevented the lamellar aggregation of the 2D MoS_2 nanoflakes while maintaining high electronic conductivity, abundant electrode/electrolyte interaction, and rapid electron and Li^+ transport. The S- MoS_2/CFs cathode demonstrated a capacity of 1149 mA h g^{-1} at 0.2 C and 608 mA h g^{-1} at 4 C , with approximately 75% capacity retention at 2 C after 500

cycles, indicating a capacity fading rate of 0.05% per cycle. The 3D MoS₂ flower provided abundant nanoflakes and nanovoids for LiPSs retention, enhanced Li⁺ diffusion, and facilitated catalytic conversions [165].

The Luo group successfully synthesized hollow nitrogen-doped mesoporous carbon microspheres (HNMCs) utilizing dairy products, specifically milk and tetrabutylorthosilicate, as biomass sources [45]. The synthesis process involved spray drying a silica template, followed by carbonization at 800°C, and subsequent template removal using a NaOH etchant. The spray drying technique produced microscale spherical droplets ranging from 1 to 5 μm, with the formation of hollow spheres being regulated by the evaporation rate. Upon removing the silica template, the resulting HNMCs featured pore diameters of 2.8–4 nm, a surface area of 872 m² g^{−1}, and a pore volume of 0.84 cm³ g^{−1}. Electrochemical performance tests revealed that the HNMCs demonstrated an initial discharge capacity of 682 mA h g^{−1}, maintaining a capacity retention of 79.4% after 400 cycles at a current rate of 1 C. The Fellingner group employed a molten salt templating method (ZnCl₂) to produce hierarchically porous, heteroatom-doped carbon gels from glucose, with a volume of approximately 1 cm³ g^{−1} [57].

The porous carbon gel, doped with 5.6 wt% N and 1.8 wt% S, can accommodate 50 wt% sulfur within the material. The resulting carbon gel exhibited an initial capacity of 1290 mA h g^{−1}, retaining 608 mA h g^{−1} after 100 cycles at 0.1 C. The Lu group utilized pollen (bee) with nanoscale germinating pores on its wall to provide a 3D structure after carbonization [49]. The presence of phosphorus and nitrogen in the pollen resulted in the formation of P, N-co-doped carbon. A hybrid material of porous carbon and cuprous phosphide (Cu₃P; PC/Cu₃P) was prepared, where Cu₃P exhibited a high adsorption energy of PSs (−6.52 eV). The PC/Cu₃P cathode, when loaded with sulfur, demonstrated a capacity of 1205 mA h g^{−1} at 0.1 C, with a decay rate of only 0.03% per cycle over 1000 cycles at 1 C. Notably, the designed PC/Cu₃P LSB was tested under high-temperature conditions, maintaining a capacity of 545 mA h g^{−1} at 1 C even at 150°C [49].

The Sharma group developed nitrogen-doped carbon (N-doped carbon) derived from tamarind peel, an abundant biomass waste with an annual production of approximately 162,000 tons in India as of 2023 [65]. The resulting N-doped carbon/sulfur composite electrode demonstrated a high initial discharge capacity of 1265 mA h g^{−1} at 0.1 C, with a capacity decay rate of 0.16% per cycle over 300 cycles [65]. This study highlights the potential of biomass-derived carbon materials for sustainable and high-performance LSBs.

4.9. Self-Assembled Biomaterials. Biological self-assembled nanotechnology has been utilized to develop multidimensional building blocks with hierarchical ordering across various scales, favoring multifunctionality. *Rhizopus*, a self-assembled biomaterial with a unique structure and multifunctional properties, is produced in hyphae balls via liquid culture. Carbonization of these hyphae balls generates interwoven hyphae carbon nanobelts (HCNBs), which serve as electrodes for LSBs. These self-supporting materials are highly useful for high sulfur loading, eliminating the need

for binders, conductive additives, and current collectors. HCNBs are advantageous for heteroatom doping (e.g., N, O, and P), providing a porous structure, high conductivity, and chemical stability [166–168].

The Wu group designed Pt-doped HCNBs/multiwalled CNT (PtHCNB/MWCNT) composites (Figure 18) [44]. The inclusion of Pt nanoparticles modulates the local electronics of O, P, and N heteroatoms in HCNBs through chemical bonding (Pt–O), generating more active sites and accelerating the redox kinetics of LiPSs via synergistic catalytic effects. The incorporation of MWCNTs enhances the conductivity of the cathode.

The PtHCNB/MWCNT/S cathode demonstrates stable cycle performance, with a capacity retention of 77% over 400 cycles at 0.5 C (S loading 4.6 mg cm^{−2}) and a specific areal capacity of 9.8 mA h cm^{−2} at 0.1 C (S loading 7.6 mg cm^{−2}). Tafel slope analysis evaluated the reaction kinetics between PtHCNB/MWCNT/S and HCNB/MWCNT/S. The results indicate slower kinetics for the conversion of S₈ to Li₂S₄ (144 mV dec^{−1}) when Pt is added to the cathode materials, compared to the materials without Pt (124 mV dec^{−1}). However, the reduction process from Li₂S₄ to Li₂S is faster with Pt incorporation. The Tafel slope for PtHCNB/MWCNT/S (279 mV dec^{−1}) is lower than that for HCNB/MWCNT/S (396 mV dec^{−1}) during the conversion of Li₂S to S₈. The discharge capacity during the S₈ to Li₂S₄ conversion (Q_H, 363 mA h g^{−1}) at approximately 2.3 V is similar for both PtHCNB/MWCNT/S and HCNB/MWCNT/S. However, at the approximately 2.1 V plateau, PtHCNB/MWCNT/S shows a higher capacity (Q_L, 1053 mA h g^{−1}) due to the more efficient conversion of Li₂S₄ to Li₂S. The synergistic effects of Pt on O, N, and P heteroatoms contribute to faster kinetics for the reduction of Li₂S₄ to Li₂S and the oxidation of Li₂S to S₈. Additionally, the high discharge capacity for Li₂S₄ to Li₂S indicates efficient adsorption of LiPSs on the cathode materials, minimizing polysulfide shuttle effects. Operando Raman spectroscopy shows initial S₈ peaks at 80, 146, 213, and 446 cm^{−1} at open-circuit voltage (OCV). New peaks at 398, 446, and 503 cm^{−1}, corresponding to Li₂S_n formation, appear at 2.26 V. These peaks decrease significantly at the second plateau (~2.1 V) and vanish at 1.7 V. Conversely, upon charging the PtHCNB/MWCNT/S cathode to 2.5 V, Li₂S rapidly converts to Li₂S_n and S₈. Complete conversion is observed at 2.8 V for the PtHCNB/MWCNT/S cathode. The Pt catalyst on the cathode materials enhances the adsorption of S₈, acts as a selective catalytic conversion process, and slows the conversion of S₈ to Li₂S₄ while accelerating the conversion of Li₂S₄ to Li₂S. Additionally, the oxidation conversion of Li₂S to S₈ is expedited [44].

4.10. Roles of Functional Group Configuration. To suppress the shuttle effect, heteroatom doping is employed to increase the binding energy of PSs through various nitrogen configurations. Understanding the binding of PSs and the associated binding energies with the catalyst surface is crucial. A DFT analysis conducted by the Tianjin University of Technology–Nanyang Technological University a joint research group compares the binding energies of Li₂S_x (x = 4–8) with graphene and nitrogen configurations, including pyrrolic and

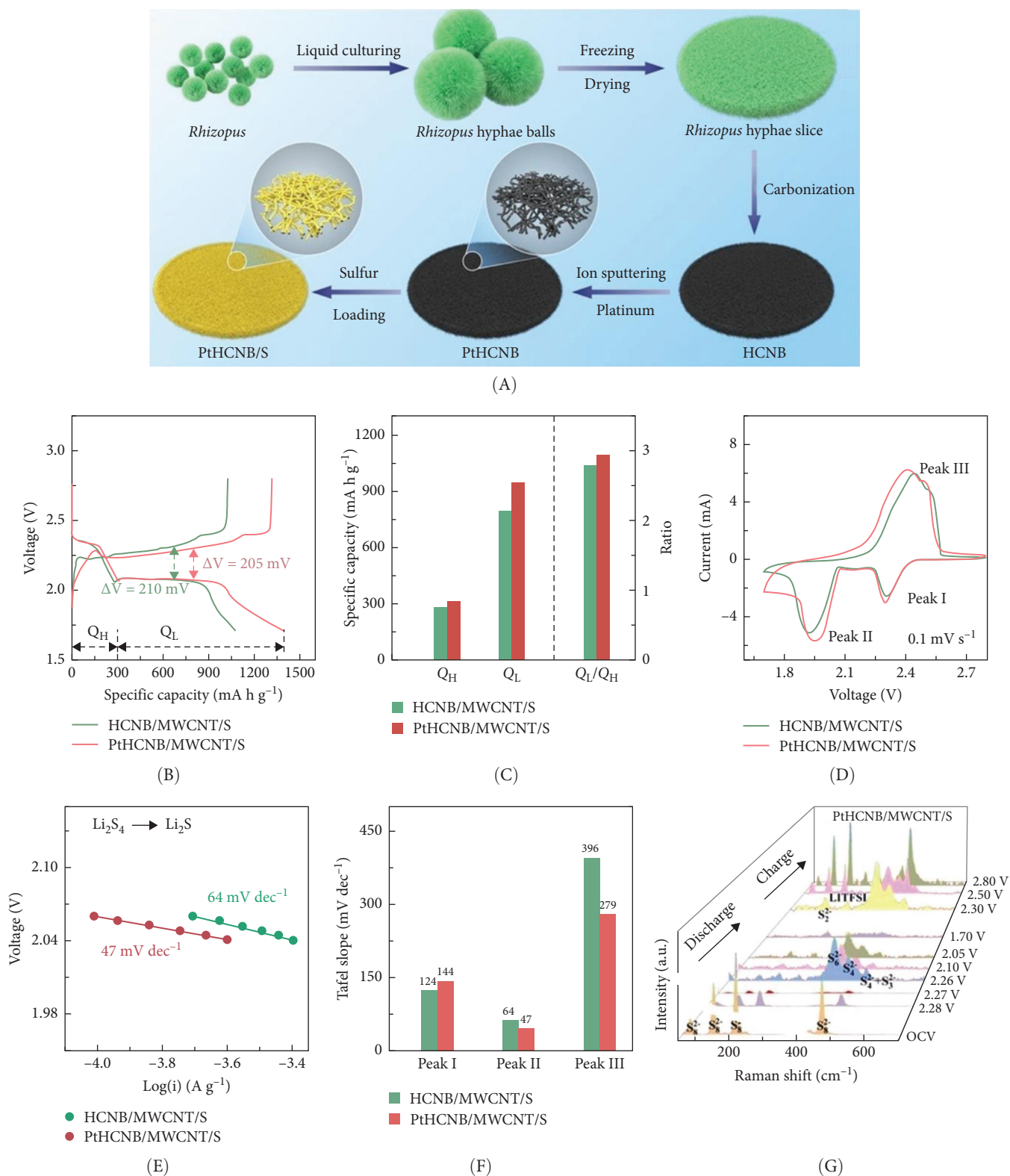


FIGURE 18: (A). Schematic of the synthesis of the PtHCNB/MWCNT/S. (B) GCD profiles (S loadings 4.6 mg cm^{-2} , 0.1 C). (C) Values of Q_H , Q_L , and Q_L/Q_H . (D) CV curves (0.1 mV s^{-1}). (E) Tafel slopes. (F) Comparison of Tafel slope. (G) Operando Raman spectra of PtHCNB/MWCNT/S cathodes (1st cycle at 0.1 C). Reproduced with permission: Copyright 2023, Wiley–VCH GmbH [44].

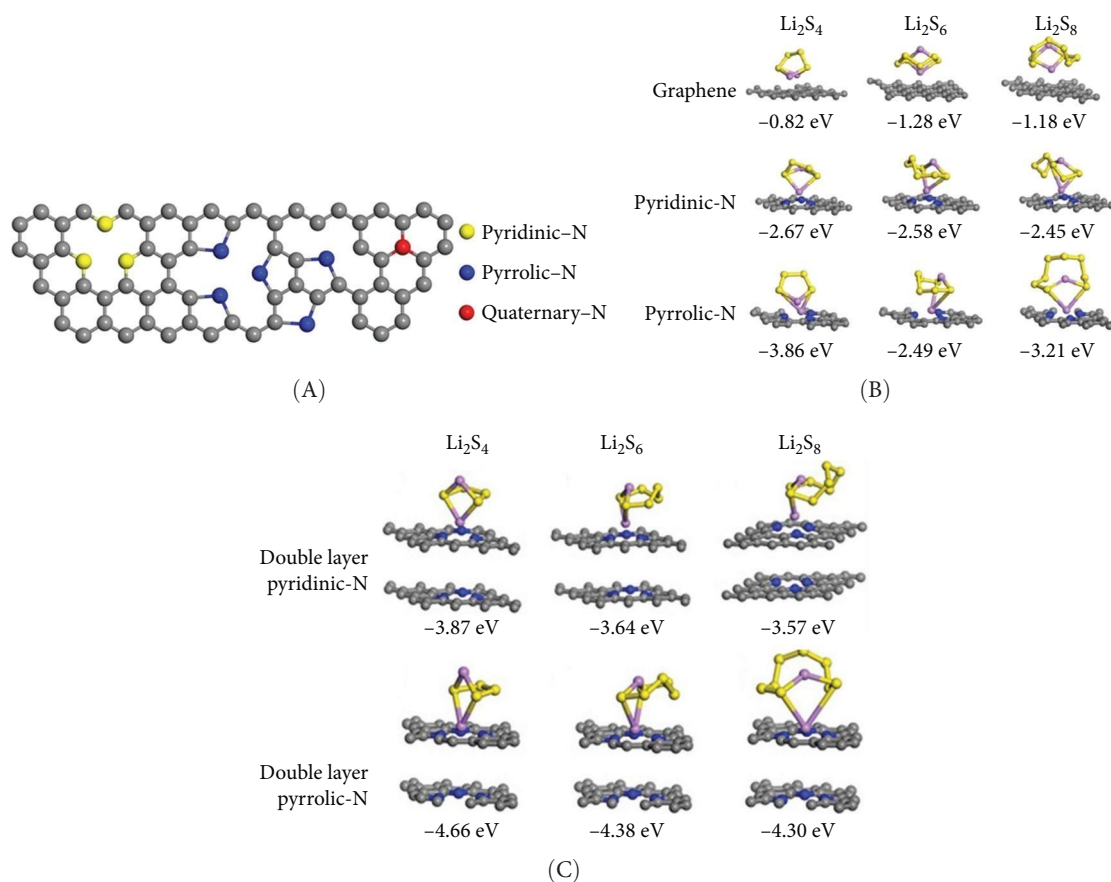


FIGURE 19: (A). Schematic of the nitrogen configuration on carbon. (B) DFT theoretical calculation of adsorption binding energy for Li₂S_x ($x = 4-8$) (gray, blue, yellow, and purple represents C, N, S, and Li). (C) DFT theoretical calculation of adsorption binding energy for Li₂S_x ($x = 4$ to 8) for double layer N configured carbon (gray, blue, yellow, and purple represents C, N, S, and Li). Reproduced with permission: Copyright 2018, Wiley-VCH GmbH [169].

pyridinic nitrogen (Figure 19) [169]. The study theoretically demonstrates that nitrogen-doped carbon exhibits significantly higher adsorption energy for Li₂S_x compared to a pure graphene layer. Among the nitrogen configurations, pyrrolic nitrogen (Li₂S₄, Li₂S₆, Li₂S₈: -3.86, -2.49, -3.21 eV, respectively) shows considerably higher adsorption binding energy than pyridinic nitrogen (Li₂S₄, Li₂S₆, Li₂S₈: -2.67, -2.58, -2.45 eV, respectively) for Li₂S_x. Furthermore, the study reveals that when a double layer of pyrrolic and pyridinic nitrogen is considered, the adsorption binding energy is nearly 1 eV higher than that of a single-layer carbon for PSs (Li₂S_x) [169]. Niu and colleagues functionalized CNTs with nitrogen and phosphorus dopants to enhance LiPS adsorption and redox kinetics in LSBs [68]. The nitrogen doping configurations were systematically categorized into pyridinic, pyrrolic, and graphitic forms. Among these, pyridinic and pyrrolic nitrogen exhibited superior PS adsorption capabilities due to their higher electronegativity and lone-pair electron interactions. Phosphorus doping also played a significant role in LiPS immobilization, as evidenced by the formation of a P—S bond, identified at 134.85 eV in the XPS spectra. To quantify Li ion transport behavior, the Li ion diffusion coefficients were calculated using the Randles–Ševčík equation:

$$I_p = (2.69 \times 10^5) n^{1.5} A D_{Li^+}^{0.5} C_{Li^+} \nu^{0.5}, \quad (8)$$

where I_p is the peak current, n the number of electrons transferred, A the effective electrode area, D_{Li^+} the diffusion coefficient, C_{Li^+} the analyte concentration, and ν the scan rate. Results indicated significantly enhanced ion diffusion kinetics in N, P co-doped CNTs compared to pristine CNTs. The calculated diffusion coefficients (in cm²s⁻¹) for N, P co-doped CNTs were: S₈ to Li₂S_n (8.64×10^{-11}), Li₂S_n to Li₂S (2.02×10^{-10}), and Li₂S_n to S₈ (3.00×10^{-10}); whereas the values for pristine CNTs were: S₈ to Li₂S_n (7.62×10^{-11}), Li₂S_n to Li₂S (1.90×10^{-10}), and Li₂S_n to S₈ (2.42×10^{-10}). These findings conclusively demonstrate that N, P co-doping of carbon frameworks significantly accelerates Li ion diffusion, enhances redox kinetics, and provides strong chemisorption and catalytic conversion of PSs—highlighting a promising strategy for improving the electrochemical performance and stability of LSBs [68].

Jun-Woo's group functionalized single-walled CNTs (SWCNTs) with oxygen-containing groups (C=O, C—O) to suppress LiPS precipitation by hindering the diffusion of Li₂S_x toward the anode (Figure 20) [63]. This was achieved by forming smaller nanotube bundles through Li—O bonding. The functionalized SWCNTs exhibited an initial

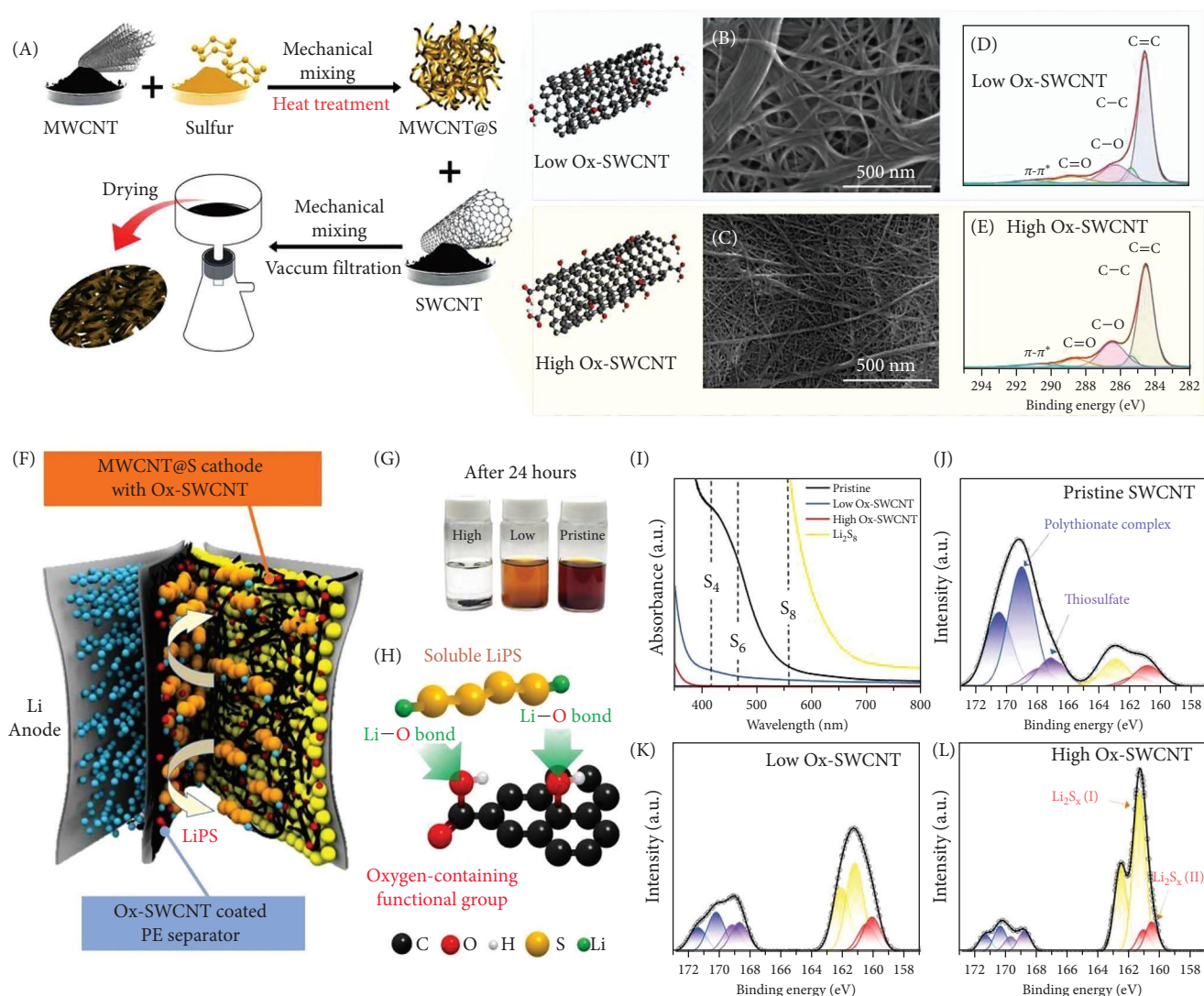


FIGURE 20: (A) Schematic representation of the synthesis process for MWCNT@S powder and the fabrication of an oxidized SWCNT-based sulfur cathode. SEM image: (B) low-oxidized SWCNTs and (C) high-oxidized SWCNTs. XPS spectra: (D) low-oxidized SWCNTs (C1s) and (E) high-oxidized SWCNTs (C1s). (F) Schematic of the Li-S battery configuration and lithium polysulfide shuttle effect. (G) Photograph of the DOL/DME/Li₂S₈ solution after 24 h of exposure to pristine SWCNTs, low-oxidized SWCNTs, and high-oxidized SWCNTs. (H) Illustration depicting the chemical interactions between soluble LiPS and oxygen functional groups in SWCNTs. (I) UV-vis absorption spectra of Li₂S₈ solutions after the addition of different SWCNT variants. XPS spectra of S2p for three SWCNT types: (J) pristine SWCNTs, (K) low-oxidized SWCNTs, and (L) high-oxidized SWCNTs after interaction with Li₂S₈. Reproduced with permission: Copyright 2024, Wiley-VCH GmbH [63].

discharge capacity of 1090 mA h g⁻¹, retaining 805 mA h g⁻¹ after 100 cycles at 0.1 C, whereas pristine SWCNTs demonstrated a lower initial capacity of 656 mA h g⁻¹ with a retention of approximately 67% after 100 cycles. The study highlighted the crucial role of oxygen functionalization, showing that the extent of oxidation significantly influenced electrochemical performance. Cycling tests at various C-rates (0.1, 0.2, 0.5, and 1 C) revealed that highly oxidized SWCNTs maintained a superior capacity of 630 mA h g⁻¹ at 1 C, compared to 300 mA h g⁻¹ for low-oxidized SWCNTs and 180 mA h g⁻¹ for pristine SWCNTs. These findings underscore the effectiveness of oxygen functionalization in enhancing LSB performance by improving LiPS immobilization and electrochemical stability [63]. However, the study did not

systematically categorize the configurations of oxygen functional groups or evaluate their individual roles in electrochemical performance. A comprehensive understanding of how specific functional group arrangements influence LiPS interactions would be valuable for further optimization and rational material design.

4.11. All Solid-State Approaches. Replacing flammable and leakage-prone organic solvents with solid electrolytes has significantly enhanced the safety, thermal stability, and operational lifespan of LSBs. Moreover, several challenges persist, including the dissolution of reaction intermediates, which leads to capacity fading and electrode degradation, as well as the intrinsically low electronic conductivity of sulfur and

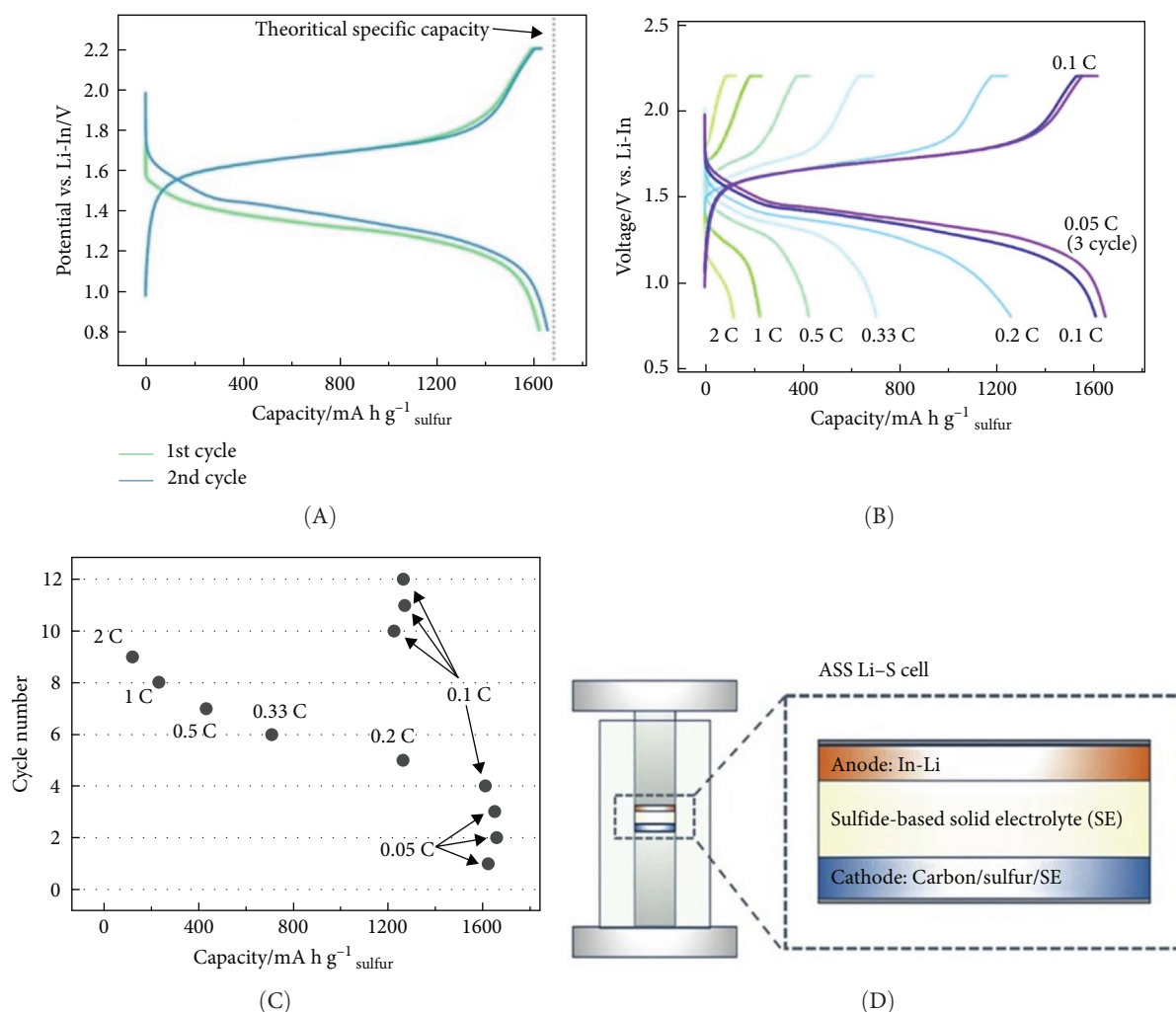


FIGURE 21: (A) Voltage profiles of the all solid-state (ASS) Li-S cell during the first (green solid line) and second (blue solid line) charge-discharge cycles. (B) Comparison of charge-discharge characteristics and rate performance of different ASS Li-S cell samples. (C) Sulfur-specific capacities measured during the discharge process. (D) Schematic representation of the ASS Li-S battery configuration. Reproduced with permission: Copyright 2025, Springer Nature [175].

sluggish redox kinetics [170, 171]. To address these issues, carbon-sulfur composites have been synthesized via melt diffusion, where sulfur is effectively confined within porous carbon frameworks [172]. This strategy enhances electronic conductivity, sulfur utilization, and overall electrochemical performance by providing an optimized reaction environment for Li ions and electrons while increasing the electrochemically active surface area [173, 174].

Such an approach has demonstrated high efficiency, achieving a specific capacity of 1488 mA h g⁻¹, which corresponds to 89% of the theoretical capacity for all solid-state LSB [170]. To further understand the structural evolution of sulfur within carbon pores and its influence on battery performance, Koji's group employed pair distribution function (PDF) analysis to investigate the local atomic structure of sulfur in porous carbon [175]. Their results indicate that in all solid-state Li-S cells, sulfur impregnation through melt diffusion retains an amorphous phase, where sulfur molecules interact with carbon surfaces. During the first and

second discharge cycles, the cells exhibited specific capacities of 1625 and 1658 mA h g⁻¹, respectively, validating the theoretical capacity expectations. PDF analysis at 2.1, 3.4, and 4.5 Å confirmed that sulfur maintains an S₈ ring-like structure within the carbon pores, forming stable molecular interactions with carbon walls (Figures 21 and 22) [175].

To further probe the molecular configuration, Gaussian modeling of S₈ rings and a linear intermolecular correlation model were employed (Figure 22) [175]. The open-chain sulfur model did not align with the experimental data, confirming that sulfur predominantly exists in an S₈ ring-shaped molecular configuration within the carbon pores [175]. Additionally, the study emphasized that pore size and carbon type play a crucial role in determining sulfur's molecular structure, which could significantly impact battery performance. This fundamental investigation into the local sulfur structure within carbon matrices provides key insights into material design strategies and has the potential to accelerate advancements in next-generation LSB technology.

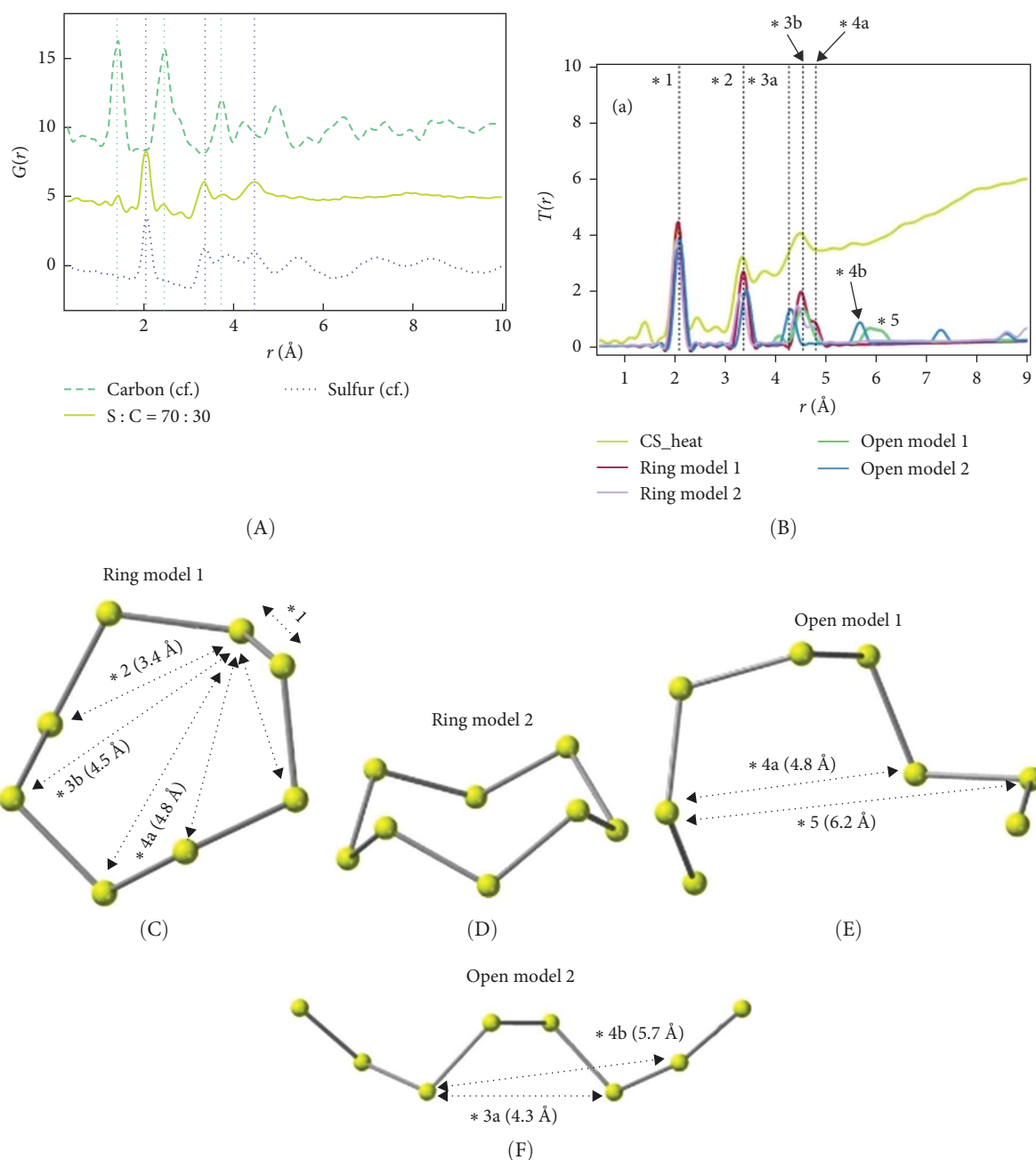


FIGURE 22: (A) Comparison of pair distribution functions (PDFs): The upper dashed line represents carbon (cf.), the yellow solid line corresponds to carbon–sulfur composites (CS_heat), and the lower dotted line denotes sulfur (cf.). (B) Analysis of $T(r)$ by comparing experimental data with different structural models. (C) Representation of S_8 ring model 1. (D) Representation of S_8 ring model 2. (E) Visualization of S_8 open-ring model 1. (F) Visualization of S_8 open-ring model 2. Reproduced with permission: Copyright 2025, Springer Nature [175].

5. Summary and Future Research Perspectives

Integrating carbon-based interlayers with polar inorganic materials presents a promising strategy for mitigating PS diffusion, providing catalytic active sites for efficient redox reactions, and maintaining electronic and ionic conductivity. Nanofibers and nanoparticles are particularly effective in promoting the uniform distribution of catalytic sites, thereby enhancing redox reactions and reducing the agglomeration of catalytic centers. The incorporation of nanoparticles with CNTs or nanofibers enhances the

localized chemical binding of LiPSs, facilitating rapid charge transfer and efficient catalytic conversions. Moreover, it has been demonstrated that certain catalytic phases of inorganic materials are more effective than others. Therefore, it is crucial to investigate the performance and mechanisms associated with different nanoparticle phases and crystalline planes.

Additionally, the crystalline fraction of carbon materials warrants careful evaluation, as evidence suggests that the crystalline cores of CDs can inhibit metal growth, reduce agglomeration, and maintain the efficient distribution of redox sites.

Regarding pore structure, while mesopores and macropores are generally considered favorable for accommodating volume expansion, there remains a need to evaluate which pore system—whether micro/mesoporous or meso/macroporous—is optimal from a kinetic perspective. This evaluation should consider factors such as hosting capacity, ion diffusion, kinetics, volume buffering, and surface catalytic interactions.

Heteroatom doping in carbon has been shown to improve catalytic performance in various contexts. It is essential to delineate the individual and combined roles of different heteroatoms, to design heteroatom combinations that optimize the binding of PSs and enhance catalytic conversions.

Maximizing sulfur utilization efficiency is critical. Hosting large amounts of sulfur without ensuring proper utilization can accelerate the degradation of cycle life, as sulfur diffuses into the anode and passivates it. Therefore, research must focus on determining the most effective particle size and shape for sulfur hosting, ensuring efficient catalytic sulfur dispersion, ion diffusion, PS binding, and stress management.

Polar materials hold significant potential for enhancing the performance of sulfur-based materials. However, it is crucial to consider their direct contribution to energy storage. The challenge lies in optimizing the precise amount of polar material infused into host materials, balancing the need to act as a barrier against LiPS diffusion without obstructing the pores essential for sulfur infusion into the internal structure. To accurately determine this optimal amount, *in situ* studies (Operando) should be conducted on various material design strategies, focusing on understanding material properties, and refining optimization and modification techniques.

Current research efforts and fundamental findings concerning the mechanisms and validation of performance predominantly focus on sulfur loadings of 2 mg cm^{-2} or lower. For LSBs to achieve their full potential, it is imperative to evaluate their performance under high sulfur loading conditions. Under such conditions, the intrinsic properties, cell component optimization, degradation processes, and PS shuttling effects are expected to become more pronounced, requiring deeper investigation.

As a consequence, future research should prioritize the evaluation and validation of LSB performance at higher sulfur loadings. Establishing a minimum sulfur loading standard is necessary to guide sustainable development and to fully exploit the theoretical capacity of LSBs. This approach will ensure the advancement of LSB technology in the right direction, maximizing its practical applications and energy storage potential.

Based on the above findings and strategic understanding, the present study suggests the rational development plan as follows: Phase I—Bench scale optimization: Development of carbon–sulfur composite with a high amount of sulfur loading based on hierarchical structure and porosity ($> 70 \text{ wt\%}$). Phase II—Materials engineering: Development of catalytic carbon frameworks to achieve a fast kinetics and minimum shuttle (areal sulfur loading $> 5 \text{ mg S cm}^{-2}$, areal capacity $4\text{--}10 \text{ mA h cm}^{-2}$, cathode utilization—fraction of S turned into $\text{Li}_2\text{S} \geq 80\%\text{--}90\%$). Phase III—Full cell design: Integrate

a full cell based on carbon–sulfur cathode and a Li anode, develop the catalytic performances by optimization of electrolyte–carbon interface chemistry ($E/S \text{ ratio} < 2.4 \mu\text{L mg}^{-1} \text{ S}$), operando analysis, and kinetics observations.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflicts of interest.

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References

- [1] S. H. Lin, P. W. Chen, C. C. Cheng, et al., “Cobalt Sulfide Nanoparticles Embedded Carved Carbon Nanoboxes Dispersed in Iron Single-Atom Decorated Multiwalled Carbon Nanotube Porous Structure as a Host Material for Lithium–Sulfur Batteries,” *ACS Sustainable Chemistry & Engineering* 11, no. 31 (2023): 11645–11659.
- [2] L. Bai, Z. Guan, J. Nie, and B. Du, “Bimetallic Nanoparticles Decorated Porous Carbon as the Host Material to Enhance the Performance of Lithium–Sulfur Batteries,” *Chemical Engineering Journal* 466 (2023): 143187.
- [3] M. Armand, “Issues and Challenges Facing Rechargeable Lithium Batteries,” *Nature* 414, no. 6 (2001): 359–367.
- [4] Y. Son, J. S. Lee, Y. Son, J. H. Jang, and J. Cho, “Recent Advances in Lithium Sulfide Cathode Materials and Their Use in Lithium Sulfur Batteries,” *Advanced Energy Materials* 5, no. 16 (2015): 1–14.
- [5] Y.-S. Kang, J.-W. Park, H. J. Hwang, et al., “Electrocatalytic and Stoichiometric Reactivity of 2D Layered Siloxene for High-Energy-Dense Lithium–Sulfur Batteries,” *Carbon Energy* 3, no. 6 (2021): 976–990.
- [6] Y.-S. Kang, T.-G. Lee, H. Kim, et al., “Thick Free-Standing Electrode Based on Carbon–Carbon Nitride Microspheres With Large Mesopores for High-Energy-Density Lithium–Sulfur Batteries,” *Carbon Energy* 3, no. 3 (2021): 410–423.
- [7] F. Pei, L. Lin, D. Ou, et al., “Self-Supporting Sulfur Cathodes Enabled by Two-Dimensional Carbon Yolk-Shell Nanosheets for High-Energy-Density Lithium–Sulfur Batteries,” *Nature Communications* 8, no. 1 (2017): 1–10.
- [8] Y. S. Su and A. Manthiram, “Lithium–Sulphur Batteries With a Microporous Carbon Paper as a Bifunctional Interlayer,” *Nature Communications* 3, no. 1 (2012): 1–6.
- [9] S. H. Chung, C. H. Chang, and A. Manthiram, “Hierarchical Sulfur Electrodes as a Testing Platform for Understanding the High-Loading Capability of Li–S Batteries,” *Journal of Power Sources* 334 (2016): 179–190.

- [10] S. H. Chung and A. Manthiram, "Carbonized Eggshell Membrane as a Natural Polysulfide Reservoir for Highly Reversible Li-S Batteries," *Advanced Materials* 26, no. 9 (2014): 1360–1365.
- [11] X. Ji, K. T. Lee, and L. F. Nazar, "A Highly Ordered Nanostructured Carbon-Sulphur Cathode for Lithium-Sulphur Batteries," *Nature Materials* 8, no. 6 (2009): 500–506.
- [12] N. B. Emerce and D. Eroglu, "Effect of Electrolyte-to-Sulfur Ratio in the Cell on the Li-S Battery Performance," *Journal of the Electrochemical Society* 166, no. 8 (2019): A1490–A1500.
- [13] X. Meng, Y. Liu, Y. Cao, Y. Ren, W. Lu, and J. W. Elam, "High-Performance High-Loading Lithium–Sulfur Batteries by Low Temperature Atomic Layer Deposition of Aluminum Oxide on Nanophase S Cathodes," *Advanced Materials Interfaces* 4, no. 17 (2017): 1–11.
- [14] W. Li, G. Zheng, Y. Yang, Z. W. Seh, N. Liu, and Y. Cui, "High-Performance Hollow Sulfur Nanostructured Battery Cathode Through a Scalable, Room Temperature, One-Step, Bottom-up Approach," *Proceedings of the National Academy of Sciences* 110, no. 18 (2013): 7148–7153.
- [15] Y. V. Mikhaylik and J. R. Akridge, "Polysulfide Shuttle Study in the Li/S Battery System," *Journal of the Electrochemical Society* 151, no. 11 (2004): A1969.
- [16] H. Liu, X. Yang, B. Jin, et al., "Coordinated Immobilization and Rapid Conversion of Polysulfide Enabled by a Hollow Metal Oxide/Sulfide/Nitrogen-Doped Carbon Heterostructure for Long-Cycle-Life Lithium–Sulfur Batteries," *Small* 19, no. 32 (2023): 1–14.
- [17] Y. Xiang, L. Lu, A. G. P. Kottapalli, and Y. Pei, "Status and Perspectives of Hierarchical Porous Carbon Materials in Terms of High-Performance Lithium–Sulfur Batteries," *Carbon Energy* 4, no. 3 (2022): 346–398.
- [18] A. Manthiram, Y. Fu, S. H. Chung, C. Zu, and Y. S. Su, "Rechargeable Lithium–Sulfur Batteries," *Chemical Reviews* 114, no. 23 (2014): 11751–11787.
- [19] S. Li, B. Jin, X. Zhai, H. Li, and Q. Jiang, "Review of Carbon Materials for Lithium–Sulfur Batteries," *ChemistrySelect* 3, no. 8 (2018): 2245–2260.
- [20] M. Wang, X. Xia, Y. Zhong, et al., "Porous Carbon Hosts for Lithium–Sulfur Batteries," *Chemistry – A European Journal* 25, no. 15 (2019): 3710–3725.
- [21] C. Deng, Z. Wang, S. Wang, and J. Yu, "Inhibition of Polysulfide Diffusion in Lithium–Sulfur Batteries: Mechanism and Improvement Strategies," *Journal of Materials Chemistry A* 7, no. 20 (2019): 12381–12413.
- [22] Q. Xiao, J. Yang, X. Wang, et al., "Carbon-Based Flexible Self-Supporting Cathode for Lithium–Sulfur Batteries: Progress and Perspective," *Carbon Energy* 3, no. 2 (2021): 271–302.
- [23] F. Pei, L. Lin, A. Fu, et al., "A Two-Dimensional Porous Carbon-Modified Separator for High-Energy-Density Li-S Batteries," *Joule* 2, no. 2 (2018): 323–336.
- [24] M. Ling, W. Yan, A. Kawase, et al., "Electrostatic Polysulfides Confinement to Inhibit Redox Shuttle Process in the Lithium Sulfur Batteries," *ACS Applied Materials & Interfaces* 9, no. 37 (2017): 31741–31745.
- [25] J. Xu, L. Yang, S. Cao, et al., "Sandwiched Cathodes Assembled From CoS₂-Modified Carbon Clothes for High-Performance Lithium–Sulfur Batteries," *Advanced Science* 8, no. 16 (2021): 2101019.
- [26] X. Zhang, C. Shang, E. M. Akinoglu, X. Wang, and G. Zhou, "Constructing Co₃S₄ Nanosheets Coating N-Doped Carbon Nanofibers as Freestanding Sulfur Host for High-Performance Lithium–Sulfur Batteries," *Advanced Science* 7, no. 22 (2020): 2002037.
- [27] Z. X. Wang, H. Yang, Z. Chen, et al., "Double-Shelled Phosphorus and Nitrogen Codoped Carbon Nanospheres as Efficient Polysulfide Mediator for High-Performance Lithium–Sulfur Batteries," *Advanced Science* 5, no. 11 (2018): 1800621.
- [28] D. Guo, X. Zhang, M. Liu, et al., "Single Mo–N₄ Atomic Sites Anchored on N-Doped Carbon Nanoflowers as Sulfur Host With Multiple Immobilization and Catalytic Effects for High-Performance Lithium–Sulfur Batteries," *Advanced Functional Materials* 32, no. 35 (2022): 2204458.
- [29] Z. Li, F. Zhang, T. Cao, et al., "Highly Stable Lithium–Sulfur Batteries Achieved by a SnS/Porous Carbon Nanosheet Architecture Modified Celgard Separator," *Advanced Functional Materials* 30, no. 48 (2020): 1–10.
- [30] D. Seo, D. Park, and S. Park, "Brain-Coral-Like Mesoporous Hollow CoS₂@N-Doped Graphitic Carbon Nanoshells as Efficient Sulfur Reservoirs for Lithium–Sulfur Batteries," *Advanced Functional Materials* 29, no. 38 (2019): 1903712.
- [31] Y. Zhong, D. Chao, S. Deng, et al., "Confining Sulfur in Integrated Composite Scaffold With Highly Porous Carbon Fibers/Vanadium Nitride Arrays for High-Performance Lithium–Sulfur Batteries," *Advanced Functional Materials* 28, no. 38 (2018): 1–9.
- [32] K. Mi, S. Chen, B. Xi, et al., "Sole Chemical Confinement of Polysulfides on Nonporous Nitrogen/Oxygen Dual-Doped Carbon at the Kilogram Scale for Lithium–Sulfur Batteries," *Advanced Functional Materials* 27, no. 1 (2017): 1604265.
- [33] B. Yang, D. Guo, P. Lin, et al., "Hydroxylated Multi-Walled Carbon Nanotubes Covalently Modified With Tris(hydroxypropyl) Phosphine as a Functional Interlayer for Advanced Lithium–Sulfur Batteries," *Angewandte Chemie International Edition* 61, no. 28 (2022).
- [34] Y. Xiao, S. Guo, D. Li, et al., "Confining Sulfur in N-Doped Hollow Porous Carbon Spheres for Improved Lithium–Sulfur Batteries," *Zeitschrift für anorganische und allgemeine Chemie* 647, no. 6 (2021): 629–634.
- [35] W. S. Heo, W. Kwon, T. Lee, et al., "Structural Engineering of Carbon Host Derived From Organic Pigment Toward Physicochemically Confinement and Efficient Conversion of Polysulfide for Lithium–Sulfur Batteries," *Small Methods* 8, no. 9 (2024): 1–14.
- [36] P. Wang, Z. Gong, K. Ye, et al., "Design and Construction of a Three-Dimensional Electrode With Biomass-Derived Carbon Current Collector and Water-Soluble Binder for High-Sulfur-Loading Lithium–Sulfur Batteries," *Carbon Energy* 2, no. 4 (2020): 635–645.
- [37] B. L. Huang, H. Zhang, Z. Qiu, et al., "Hyphae Carbon Coupled With Gel Composite Assembly for Construction of Advanced Carbon/Sulfur Cathodes for Lithium–Sulfur Batteries," *Small* 20, no. 16 (2024): 1–9.
- [38] K. Zou, W. Jing, X. Dai, et al., "A Highly Efficient Sulfur Host Enabled by Nitrogen/Oxygen Dual-Doped Honeycomb-Like Carbon for Advanced Lithium–Sulfur Batteries," *Small* 18, no. 17 (2022): 2107380.
- [39] H. Pei, Q. Yang, J. Yu, et al., "Self-Supporting Carbon Nanofibers With Ni-Single-Atoms and Uniformly Dispersed Ni-Nanoparticles as Scalable Multifunctional Hosts for High Energy Density Lithium–Sulfur Batteries," *Small* 18, no. 27 (2022): 2202037.
- [40] S. Rehman, T. Tang, Z. Ali, X. Huang, and Y. Hou, "Integrated Design of MnO₂@Carbon Hollow Nanoboxes to

- Synergistically Encapsulate Polysulfides for Empowering Lithium Sulfur Batteries,” *Small* 13, no. 20 (2017): 1–8.
- [41] L. Zhu, R. Hu, Y. Xiang, et al., “Enhanced Performance of Li-S Battery by Constructing Inner Conductive Network and Outer Adsorption Layer Sulfur-Carbon Composite,” *International Journal of Energy Research* 45, no. 4 (2021): 6002–6014.
 - [42] Y. Li, L. Liu, R. Shi, et al., “Natural Okra Shells Derived Nitrogen-Doped Porous Carbon to Regulate Polysulfides for High-Performance Lithium–Sulfur Batteries,” *Energy Technology* 7, no. 12 (2019): 1900165.
 - [43] Z. Wang, Y. Yan, Y. Zhang, et al., “Single-Atomic Co-B₂N₂ Sites Anchored on Carbon Nanotube Arrays Promote Lithium Polysulfide Conversion in Lithium–Sulfur Batteries,” *Carbon Energy* 5, no. 11 (2023).
 - [44] F. Han, L. Fan, X. Ma, et al., “Conversion of LiPSs Accelerated by Pt-Doped Biomass-Derived Hyphae Carbon Nanobelts as Self-Supporting Hosts for Long-Lifespan Li-S Batteries,” *Energy & Environmental Materials* 7, no. 3 (2024): e12623.
 - [45] R. Luo, Y. Lu, X. Hou, et al., “Evolution of Hollow N-Doped Mesoporous Carbon Microspheres From Outdated Milk as Sulfur Cathodes for Lithium-Sulfur Batteries,” *ChemistrySelect* 3, no. 14 (2018): 3952–3957.
 - [46] Y. Li, Y. Zeng, Y. Chen, D. Luan, S. Gao, and X. W. Lou, “Mesoporous N-Rich Carbon With Single-Ni Atoms as a Multifunctional Sulfur Host for Li-S Batteries,” *Angewandte Chemie International Edition* 61, no. 47 (2022).
 - [47] Z. Zhang, J. Xu, W. Ahmed, et al., “Macroporous Multichannel Carbon Nanofibers Embedded With Co/Fe-N Electrocatalyst as the Sulfur Host for Boosting Polysulfides Conversion in Lithium-Sulfur Batteries,” *ChemistrySelect* 6, no. 24 (2021): 5932–5940.
 - [48] J. Shi, S. Zhang, J. Wang, et al., “CoSnO₃ Nanocubes Wrapped by Carbon Nanofibers for Improving Lithium-Sulfur Battery Performances,” *ChemistrySelect* 6, no. 35 (2021): 9453–9457.
 - [49] Y. Guo, R. Khatoun, J. Lu, et al., “Regulating Adsorption Ability Toward Polysulfides in a Porous Carbon/Cu₃P Hybrid for an Ultrastable High-Temperature Lithium–Sulfur Battery,” *Carbon Energy* 3, no. 6 (2021): 841–855.
 - [50] Y. Liu, G. Li, J. Fu, Z. Chen, and X. Peng, “Strings of Porous Carbon Polyhedrons as Self-Standing Cathode Host for High-Energy-Density Lithium–Sulfur Batteries,” *Angewandte Chemie International Edition* 56, no. 22 (2017): 6176–6180.
 - [51] Z.-Z. Zhang, C.-Y. Yang, J. Qu, et al., “Constructing Atomic Fe and N Co-Doped Hollow Carbon Nanospheres With a Polymer Encapsulation Strategy for High-Performance Lithium-Sulfur Batteries With Accelerated Polysulfide Conversion,” *Chemistry – A European Journal* 28, no. 31 (2022): e202200363.
 - [52] Z. Yu, M. Liu, D. Guo, et al., “Radially Inwardly Aligned Hierarchical Porous Carbon for Ultra-Long-Life Lithium–Sulfur Batteries,” *Angewandte Chemie - International Edition* 59, no. 16 (2020): 6406–6411.
 - [53] X. Zhang, D. Xie, Y. Zhong, et al., “Performance Enhancement of a Sulfur/Carbon Cathode by Polydopamine as an Efficient Shell for High-Performance Lithium–Sulfur Batteries,” *Chemistry – A European Journal* 23, no. 44 (2017): 10610–10615.
 - [54] X. Zeng, Y. Tang, L. Liu, Y. Zhang, Y. Gao, and M. Qian, “Oxygen-Doped Porous Carbon Nanotubes Encapsulated Bismuth Oxide to Enhance the Performance of Lithium-Sulfur Battery,” *ChemElectroChem* 11, no. 12 (2024): e202400010.
 - [55] Y. Li, J. Xu, D. Xu, et al., “A Synergistic Strategy With 3D Highly Conductive Carbon Matrix-Decorated With Low Loading of CdS Quantum Dots as a Sulfur Host for Advanced Li–S Batteries,” *ChemElectroChem* 8, no. 9 (2021): 1642–1652.
 - [56] R. Li, H. Peng, Q. Wu, et al., “Sandwich-Like Catalyst–Carbon–Catalyst Trilayer Structure as a Compact 2D Host for Highly Stable Lithium–Sulfur Batteries,” *Angewandte Chemie - International Edition* 59, no. 29 (2020): 12129–12138.
 - [57] F. Schipper, A. Vizintin, J. Ren, R. Dominko, and T.-P. Fellingner, “Biomass-Derived Heteroatom-Doped Carbon Aerogels From a Salt Melt Sol–Gel Synthesis and Their Performance in Li–S Batteries,” *ChemSusChem* 8, no. 18 (2015): 3077–3083.
 - [58] S. Chen, G. Du, D. Han, et al., “One-Step Pyrolysis Route to N, O, S Co-Doped Hierarchical Carbon as Multi-Functional Separator for Lithium-Sulfur Batteries,” *Journal of Alloys and Compounds* 1010 (2025): 177268.
 - [59] Q. Sun, X. Fang, W. Weng, et al., “An Aligned and Laminated Nanostructured Carbon Hybrid Cathode for High-Performance Lithium–Sulfur Batteries,” *Angewandte Chemie International Edition* 54, no. 36 (2015): 10539–10544.
 - [60] J. Song, M. L. Gordin, T. Xu, et al., “Strong Lithium Polysulfide Chemisorption on Electroactive Sites of Nitrogen-Doped Carbon Composites For High-Performance Lithium–Sulfur Battery Cathodes,” *Angewandte Chemie International Edition* 54, no. 14 (2015): 4325–4329.
 - [61] Z. Li, J. Zhang, and X. W. Lou, “Hollow Carbon Nanofibers Filled With MnO₂ Nanosheets as Efficient Sulfur Hosts for Lithium-Sulfur Batteries,” *Angewandte Chemie International Edition* 54, no. 44 (2015): 12886–12890.
 - [62] H. Shang, R. Yang, P. Li, et al., “FeOOH Nanorod-Assisted Carbon Cloth Sandwich Cathodes for Lithium-Sulfur Batteries,” *ACS Applied Nano Materials* 8, no. 7 (2025): 3487–3496.
 - [63] J. Heo, J.-W. Hong, H. W. Gu, et al., “A Promising Approach to Ultra-Flexible 1 Ah Lithium–Sulfur Batteries Using Oxygen-Functionalized Single-Walled Carbon Nanotubes,” *Advanced Science* 12, no. 4 (2025): 2406536.
 - [64] X. Hu, C. Han, Y. Liang, Y. Yang, Y. Zhang, and K. Shen, “Nanosized CeO₂/C₂ With Rich Oxygen Vacancies Embedded in Hollow Mesoporous Carbon as a Multifunctional Sulfur-Loaded Matrix for Lithium-Sulfur Batteries,” *Journal of Alloys and Compounds* 1010 (2025): 177182.
 - [65] A. Dharmesh, P. Rani, and A. K. Sharma, “Tamarind Peel-Derived Nitrogen-Doped Porous Carbon: A Sustainable Sulfur Host for Enhanced Lithium–Sulfur Battery Performance,” *Journal of Power Sources* 634 (2025): 236429.
 - [66] T. Bi, J. Zhang, J. Li, W. Cui, and Q. Lin, “A CoS₂-Loaded N-Doped Ultrathin-Wall Mesoporous Carbon With Three-Dimensional Fluffy Network Structure as Desirable Sulfur-Loading Host for Lithium-Sulfur Battery,” *Journal of Alloys and Compounds* 1020 (2025): 179386.
 - [67] D. Lee, J. Yang, W. C. Yun, and J. W. Lee, “Nitrogen-Doped Hierarchical Porous Carbon Derived From CO₂ for the High-Performance Cathode of Lithium-Sulfur Battery,” *Electrochimica Acta* 520 (2025): 145867.
 - [68] D. Li, H. Sun, C. Ma, et al., “Nitrogen/Phosphorus Co-Doped Honeycomb Carbon Decorated Carbon Nanotubes as a Free-Standing Cathode for High Performance Lithium-Sulfur Batteries,” *Journal of Energy Storage* 113 (2025): 115698.

- [69] S. Li, S. Jing, X. Peng, et al., "Three-Dimensional Decussated Superstructure Consisting of Carbon Nanotubes Wrapped With $\text{Co}_3\text{Fe}_7/\text{Co}_{5.47}\text{N}$ Nanocrystals for Super Lithium Sulfur Batteries," *Materials Today Chemistry* 43 (2025): 102488.
- [70] S. Liang, G. Feng, X. Ding, et al., "Ru Quantum Dots Modified Mucor-Derived Carbon Submicroribbons for Advanced Lithium-Sulfur Batteries," *Advanced Functional Materials* 35, no. 25 (2025): 2420162.
- [71] X. Men, T. Deng, X. Li, L. Huang, and J. Wang, "Electrospun Carbon Nanofibers Loaded With Sulfur Vacancy CoS_2 as Separator Coating to Accelerate Sulfur Conversion in Lithium-Sulfur Batteries," *Journal of Colloid and Interface Science* 678 (2025): 345–354.
- [72] Y. Sun, Y. Wang, C. Li, et al., "Heteroatom-Doping Modulates Metal-Support Interactions in Carbon-Supported Cobalt Catalysts to Accelerate Polysulfide Redox for Lithium-Sulfur Batteries," *Advanced Functional Materials* 35, no. 27 (2025): 2421780.
- [73] R. Wang, C. Ma, C. Li, et al., "Keggin-Type Potassium Phosphotungstate Modified Functionalization of Carbon Nanotubes Hybrid Materials for Capture and Boost Conversion of Polysulfides in Lithium-Sulfur Batteries," *Journal of Energy Storage* 109 (2025): 115168.
- [74] H. Xing, K. Zhang, R. Chang, Z. Wen, and Y. Xu, "Integrating CoP/Co Heterojunction Into Nitrogen-Doped Carbon Polyhedrons as Electrocatalysts to Promote Polysulfides Conversion in Lithium-Sulfur Batteries," *Journal of Colloid and Interface Science* 677 (2025): 181–193.
- [75] Z. Zhao, H. Dou, X. Xu, et al., "Magnetopyrite $\text{Fe}1-x\text{S}$ Modified With N/S-Doped Carbon as a Synergistic Electrocatalyst for Lithium-Sulfur Batteries," *Journal of Colloid and Interface Science* 684 (2025): 180–191.
- [76] X. Zhang, Z. Ni, X. Bai, et al., "Hierarchical Porous N-Doped Carbon Encapsulated Fluorine-Free MXene With Tunable Coordination Chemistry by One-Pot Etching Strategy for Lithium-Sulfur Batteries," *Advanced Energy Materials* 13, no. 29 (2023): 2301349.
- [77] S. Chen, X. Huang, H. Liu, et al., "3D Hyperbranched Hollow Carbon Nanorod Architectures for High-Performance Lithium-Sulfur Batteries," *Advanced Energy Materials* 4, no. 8 (2014): 130176.
- [78] G. C. Li, G. R. Li, S. H. Ye, and X. P. Gao, "A Polyaniline-Coated Sulfur/Carbon Composite With an Enhanced High-Rate Capability as a Cathode Material for Lithium/Sulfur Batteries," *Advanced Energy Materials* 2, no. 10 (2012): 1238–1245.
- [79] Q. Pang, X. Liang, C. Y. Kwok, and L. F. Nazar, "Advances in Lithium-Sulfur Batteries Based on Multifunctional Cathodes and Electrolytes," *Nature Energy* 1, no. 9 (2016): 1–11.
- [80] J. W. Park, H. J. Hwang, H. J. Kang, et al., "Hierarchical Porous, N-Containing Carbon Supports for High Loading Sulfur Cathodes," *Nanomaterials* 11, no. 2 (2021): 1–12.
- [81] Y. Yang, G. Zheng, and Y. Cui, "Nanostructured Sulfur Cathodes," *Chemical Society Reviews* 42, no. 7 (2013): 3018–3032.
- [82] H. S. Kang and Y. K. Sun, "Freestanding Bilayer Carbon-Sulfur Cathode With Function of Entrapping Polysulfide for High Performance Li-S Batteries," *Advanced Functional Materials* 26, no. 8 (2016): 1225–1232.
- [83] Y. Song, L. Zou, C. Wei, Y. Zhou, and Y. Hu, "Single-Atom Electrocatalysts for Lithium-Sulfur Chemistry: Design Principle, Mechanism, and Outlooks," *Carbon Energy* 5, no. 4 (2023): e286.
- [84] Z. Sun, M. Xiao, S. Wang, et al., "Electrostatic Shield Effect: An Effective Way to Suppress Dissolution of Polysulfide Anions in Lithium-Sulfur Battery," *Journal of Materials Chemistry A* 2, no. 38 (2014): 15938–15944.
- [85] M. Zhao, B. Q. Li, X. Q. Zhang, J. Q. Huang, and Q. Zhang, "A Perspective Toward Practical Lithium-Sulfur Batteries," *ACS Central Science* 6, no. 7 (2020): 1095–1104.
- [86] J. Balach, T. Jaumann, M. Klose, S. Oswald, J. Eckert, and L. Giebeler, "Functional Mesoporous Carbon-Coated Separator for Long-Life, High-Energy Lithium-Sulfur Batteries," *Advanced Functional Materials* 25, no. 33 (2015): 5285–5291.
- [87] H. Pan, Z. Cheng, Z. Zhou, et al., *Boosting Lean Electrolyte Lithium-Sulfur Battery Performance With Transition Metals: A Comprehensive Review* (Springer Nature Singapore, 2023).
- [88] B. Zhang, X. Qin, G. R. Li, and X. P. Gao, "Enhancement of Long Stability of Sulfur Cathode by Encapsulating Sulfur Into Micropores of Carbon Spheres," *Energy & Environmental Science* 3, no. 10 (2010): 1531–1537.
- [89] C. Ye, L. Zhang, C. Guo, et al., "A 3D Hybrid of Chemically Coupled Nickel Sulfide and Hollow Carbon Spheres for High Performance Lithium-Sulfur Batteries," *Advanced Functional Materials* 27, no. 33 (2017): 1–9.
- [90] L. Hu, C. Dai, H. Liu, et al., "Double-Shelled $\text{NiO-NiCo}_2\text{O}_4$ Heterostructure@Carbon Hollow Nanocages as an Efficient Sulfur Host for Advanced Lithium-Sulfur Batteries," *Advanced Energy Materials* 8, no. 23 (2018): 2–9.
- [91] H.-J. Kang, G. A. K. M. R. Bari, T.-G. Lee, et al., "Microporous Carbon Nanoparticles for Lithium-Sulfur Batteries," *Nanomaterials* 10, no. 10 (2020): 1–17.
- [92] Z. Hu, C. Geng, L. Wang, W. Lv, and Q. H. Yang, "Revisiting the Roles of Carbon in the Catalysis of Lithium-Sulfur Batteries," *Advanced Energy and Sustainability Research* 5, no. 1 (2024).
- [93] P. Kumar Nema, K. Mohanty, and R. Thangavel, "Bio-Mass Derived Hierarchically Porous and High Surface Area Carbon as an Efficient Sulfur Host for Lithium-Sulfur Batteries," *Journal of Industrial and Engineering Chemistry* 121 (2023): 235–241.
- [94] Q. Z. Peng, J.-Q. Huang, and X.-B. Cheng, "Review on High-Loading and High-Energy Lithium-Sulfur Batteries," *Advanced Energy Materials* 7, no. 24 (2017): 1700260.
- [95] W. Liu, M. Liu, H. Shen, et al., "Insights Into Nickel Nanoparticles Modified Porous Biomass-Derived Carbon as Sulfur Host Matrix for Advanced Rechargeable Lithium-Sulfur Battery," *Journal of Alloys and Compounds* 937 (2023): 168459.
- [96] H. J. Peng, D. W. Wang, J. Q. Huang, et al., "Janus Separator of Polypropylene-Supported Cellular Graphene Framework for Sulfur Cathodes With High Utilization in Lithium-Sulfur Batteries," *Advanced Science* 3, no. 1 (2016): 1–11.
- [97] Y. Pang, J. Wei, Y. Wang, and Y. Xia, "Synergetic Protective Effect of the Ultralight MWCNTs/NCQDs Modified Separator for Highly Stable Lithium-Sulfur Batteries," *Advanced Energy Materials* 8, no. 10 (2018): 1–11.
- [98] G. Gnana Kumar, S.-H. Chung, T. Raj Kumar, and A. Manthiram, "Three-Dimensional Graphene-Carbon Nanotube-Ni Hierarchical Architecture as a Polysulfide Trap for Lithium-Sulfur Batteries," *ACS Applied Materials & Interfaces* 10, no. 24 (2018): 20627–20634.
- [99] X. Fan, W. Sun, F. Meng, A. Xing, and J. Liu, "Advanced Chemical Strategies for Lithium-Sulfur Batteries: A Review," *Green Energy & Environment* 3, no. 1 (2018): 2–19.

- [100] Z. Li, H. B. Wu, and X. W. Lou, "Rational Designs and Engineering of Hollow Micro-/Nanostructures as Sulfur Hosts for Advanced Lithium-Sulfur Batteries," *Energy & Environmental Science* 9, no. 10 (2016): 3061–3070.
- [101] D. Fang, Y. Wang, X. Liu, et al., "Spider-Web-Inspired Nanocomposite-Modified Separator: Structural and Chemical Cooperativity Inhibiting the Shuttle Effect in Li-S Batteries," *ACS Nano* 13 (2019): 1563–1573.
- [102] Z. Cheng, H. Pan, J. Chen, X. Meng, and R. Wang, "Separator Modified by Cobalt-Embedded Carbon Nanosheets Enabling Chemisorption and Catalytic Effects of Polysulfides for High-Energy-Density Lithium-Sulfur Batteries," *Advanced Energy Materials* 9, no. 32 (2019): 1–10.
- [103] T. Zhou, W. Lv, J. Li, et al., "Twinborn TiO₂-TiN Heterostructures Enabling Smooth Trapping-Diffusion-Conversion of Polysulfides Towards Ultralong Life Lithium-Sulfur Batteries," *Energy & Environmental Science* 10, no. 7 (2017): 1694–1703.
- [104] H. Lin, S. Zhang, T. Zhang, et al., "Simultaneous Cobalt and Phosphorous Doping of MoS₂ for Improved Catalytic Performance on Polysulfide Conversion in Lithium-Sulfur Batteries," *Advanced Energy Materials* 9, no. 38 (2019): 1–9.
- [105] B. Moorthy, S. Kwon, J. H. Kim, P. Ragupathy, H. M. Lee, and D. K. Kim, "Tin Sulfide Modified Separator as an Efficient Polysulfide Trapper for Stable Cycling Performance in Li-S Batteries," *Nanoscale Horizons* 4, no. 1 (2019): 214–222.
- [106] M. Zhao, B. Q. Li, X. Chen, J. Xie, H. Yuan, and J. Q. Huang, "Redox Mediation With Organopolysulfides in Working Lithium-Sulfur Batteries," *Chem* 6, no. 12 (2020): 3297–3311.
- [107] P. Chen, Z. Wu, T. Guo, et al., "Strong Chemical Interaction Between Lithium Polysulfides and Flame-Retardant Polyphosphazene for Lithium-Sulfur Batteries With Enhanced Safety and Electrochemical Performance," *Advanced Materials* 33, no. 9 (2021): 1–11.
- [108] H. Gao, S. Ning, J. Lin, and X. Kang, "Molecular Perturbation of 2D Organic Modifiers on Porous Carbon Interlayer: Promoted Redox Kinetics of Polysulfides in Lithium-Sulfur Batteries," *Energy Storage Materials* 40 (2021): 312–319.
- [109] W. Hua, Z. Yang, H. Nie, et al., "Polysulfide-Scission Reagents for the Suppression of the Shuttle Effect in Lithium-Sulfur Batteries," *ACS Nano* 11, no. 2 (2017): 2209–2218.
- [110] H. Chen, M. Ling, L. Hencz, et al., "Exploring Chemical, Mechanical, and Electrical Functionalities of Binders for Advanced Energy-Storage Devices," *Chemical Reviews* 118, no. 18 (2018): 8936–8982.
- [111] S. Li, H. Zhang, W. Chen, et al., "Toward Commercially Viable Li-S Batteries: Overall Performance Improvements Enabled by a Multipurpose Interlayer of Hyperbranched Polymer-Grafted Carbon Nanotubes," *ACS Applied Materials & Interfaces* 12, no. 23 (2020): 25767–25774.
- [112] Z. Sun, M. Xiao, S. Wang, et al., "Specially Designed Carbon Black Nanoparticle-Sulfur Composite Cathode Materials With a Novel Structure for Lithium-Sulfur Battery Application," *Journal of Power Sources* 285 (2015): 478–484.
- [113] D.-L. Vu, J.-S. Seo, H.-Y. Lee, and J.-W. Lee, "Activated Carbon With Hierarchical Micro-Mesoporous Structure Obtained From Rice Husk and Its Application for Lithium-Sulfur Batteries," *RSC Advances* 7, no. 7 (2017): 4144–4151.
- [114] G. C. Li, J. J. Hu, G. R. Li, S. H. Ye, and X. P. Gao, "Sulfur/Activated-Conductive Carbon Black Composites as Cathode Materials for Lithium/Sulfur Battery," *Journal of Power Sources* 240 (2013): 598–605.
- [115] S. Zhang, M. Zheng, Z. Lin, et al., "Activated Carbon With Ultrahigh Specific Surface Area Synthesized From Natural Plant Material for Lithium-Sulfur Batteries," *Journal of Materials Chemistry A* 2, no. 38 (2014): 15889–15896.
- [116] F. L. Lama, V. Marangon, Á. Caballero, J. Morales, and J. Hassoun, "Diffusional Features of a Lithium-Sulfur Battery Exploiting Highly Microporous Activated Carbon," *ChemSusChem* 16, no. 6 (2023): e202202095.
- [117] J. He, Y. Chen, and A. Manthiram, "MOF-Derived Cobalt Sulfide Grown on 3D Graphene Foam as an Efficient Sulfur Host for Long-Life Lithium-Sulfur Batteries," *iScience* 4 (2018): 36–43.
- [118] T. Chen, Z. Zhang, B. Cheng, et al., "Self-Templated Formation of Interlaced Carbon Nanotubes Threaded Hollow Co₃S₄ Nanoboxes for High-Rate and Heat-Resistant Lithium-Sulfur Batteries," *Journal of the American Chemical Society* 139, no. 36 (2017): 12710–12715.
- [119] J.-N. Zhang, *Carbon-Based Nanomaterials for Energy Conversion and Storage* (Springer Nature Singapore, 2022).
- [120] Y. C. Ho and S. H. Chung, "A Design of the Cathode Substrate for High-Loading Polysulfide Cathodes in Lean-Electrolyte Lithium-Sulfur Cells," *Chemical Engineering Journal* 422 (2021): 130363.
- [121] Y. Song, H. Zhou, X. Long, et al., "Dual-Heterostructures Decorated Interweaved Carbon Nanofibers Sulfur Host for High Performance Lithium-Sulfur Batteries," *Chemical Engineering Journal* 418 (2021): 129388.
- [122] J. S. Lee, J. Jun, J. Jang, and A. Manthiram, "Sulfur-Immobilized, Activated Porous Carbon Nanotube Composite Based Cathodes for Lithium-Sulfur Batteries," *Small* 13, no. 12 (2017): 1–7.
- [123] R. Fang, S. Zhao, P. Hou, et al., "3D Interconnected Electrode Materials With Ultrahigh Areal Sulfur Loading for Li-S Batteries," *Advanced Materials* 28, no. 17 (2016): 3374–3382.
- [124] G. Zhou, Y. Zhao, and A. Manthiram, "Dual-Confined Flexible Sulfur Cathodes Encapsulated in Nitrogen-Doped Double-Shelled Hollow Carbon Spheres and Wrapped With Graphene for Li-S Batteries," *Advanced Energy Materials* 5, no. 9 (2015): 1402263.
- [125] J. Li, Z. Xiong, Y. Sun, et al., "Balanced Capture and Catalytic Ability Toward Polysulfides by Designing MoO₂-Co₂Mo₃O₈ Heterostructures for Lithium-Sulfur Batteries," *Nanoscale* 13, no. 37 (2021): 15689–15698.
- [126] Y. Zhu, Y. Zuo, X. Jiao, et al., "Selective Sulfur Conversion With Surface Engineering of Electrocatalysts in a Lithium-Sulfur Battery," *Carbon Energy* 5, no. 2 (2023): 1–13.
- [127] H. Ma, Z. Yu, H. Li, et al., "Tandem Carbon Hollow Spheres With Tailored Inner Structure as Sulfur Immobilization for Superior Lithium-Sulfur Batteries," *Advanced Functional Materials* 34, no. 12 (2024): 1–11.
- [128] Z. Sun, J. Zhang, L. Yin, et al., "Conductive Porous Vanadium Nitride/Graphene Composite as Chemical Anchor of Polysulfides for Lithium-Sulfur Batteries," *Nature Communications* 8, no. 1 (2017): 14627.
- [129] D. Guo, Z. Zhang, B. Xi, Z. Yu, Z. Zhou, and X. Chen, "Ni₃S₂ Anchored to N/S Co-Doped Reduced Graphene Oxide With Highly Pleated Structure as a Sulfur Host for Lithium-Sulfur Batteries," *Journal of Materials Chemistry A* 8, no. 7 (2020): 3834–3844.
- [130] C. Zu and A. Manthiram, "Hydroxylated Graphene-Sulfur Nanocomposites for High-Rate Lithium-Sulfur Batteries," *Advanced Energy Materials* 3, no. 8 (2013): 1008–1012.

- [131] D. Xie, Y. Xu, Y. Wang, et al., "Poly(ionic Liquid) Nanovesicle-Templated Carbon Nanocapsules Functionalized With Uniform Iron Nitride Nanoparticles as Catalytic Sulfur Host for Li-S Batteries," *ACS Nano* 16, no. 7 (2022): 10554–10565.
- [132] W. Bao, L. Liu, C. Wang, S. Choi, D. Wang, and G. Wang, "Facile Synthesis of Crumpled Nitrogen-Doped MXene Nanosheets as a New Sulfur Host for Lithium–Sulfur Batteries," *Advanced Energy Materials* 8, no. 13 (2018): 1–11.
- [133] H. Zhao, P. Chen, Y. Fan, et al., "Co,N-Co-Doped Graphene Sheet as a Sulfur Host for High-Performance Lithium–Sulfur Batteries," *RSC Advances* 12, no. 3 (2022): 1375–1383.
- [134] D. Luo, G. Li, Y. P. Deng, et al., "Synergistic Engineering of Defects and Architecture in Binary Metal Chalcogenide Toward Fast and Reliable Lithium–Sulfur Batteries," *Advanced Energy Materials* 9, no. 18 (2019): 1–10.
- [135] X. Q. Zhang, B. He, W. C. Li, and A. H. Lu, "Hollow Carbon Nanofibers With Dynamic Adjustable Pore Sizes and Closed Ends as Hosts for High-Rate Lithium–Sulfur Battery Cathodes," *Nano Research* 11, no. 3 (2018): 1238–1246.
- [136] R. Kumar, J. Liu, J. Y. Hwang, and Y. K. Sun, "Recent Research Trends in Li-S Batteries," *Journal of Materials Chemistry A* 6, no. 25 (2018): 11582–11605.
- [137] H. J. Peng, W. T. Xu, L. Zhu, et al., "3D Carbonaceous Current Collectors: The Origin of Enhanced Cycling Stability for High-Sulfur-Loading Lithium–Sulfur Batteries," *Advanced Functional Materials* 26, no. 35 (2016): 6351–6358.
- [138] J. S. Yeon, S. Yun, J. M. Park, and H. S. Park, "Surface-Modified Sulfur Nanorods Immobilized on Radially Assembled Open-Porous Graphene Microspheres for Lithium–Sulfur Batteries," *ACS Nano* 13, no. 5 (2019): 5163–5171.
- [139] H. Wu, Y. Li, J. Ren, et al., "CNT-Assembled Dodecahedra Core@Nickel Hydroxide Nanosheet Shell Enabled Sulfur Cathode for High-Performance Lithium–Sulfur Batteries," *Nano Energy* 55 (2019): 82–92.
- [140] W. Cai, G. Li, D. Luo, et al., "The Dual-Play of 3D Conductive Scaffold Embedded With Co N Codoped Hollow Polyhedra Toward High-Performance Li–S Full Cell," *Advanced Energy Materials* 8 (2018): 1–9.
- [141] W. Yao, W. Zheng, J. Xu, et al., "ZnS-SnS@NC Heterostructure as Robust Lithiophilicity and Sulphilicity Mediator Toward High-Rate and Long-Life Lithium–Sulfur Batteries," *ACS Nano* 15, no. 4 (2021): 7114–7130.
- [142] R. Chu, T. T. Nguyen, Y. Bai, N. H. Kim, and J. H. Lee, "Uniformly Controlled Treble Boundary Using Enriched Adsorption Sites and Accelerated Catalyst Cathode for Robust Lithium–Sulfur Batteries," *Advanced Energy Materials* 12, no. 9 (2022): 1–15.
- [143] S. Wang, S. Feng, J. Liang, et al., "Insight Into MoS₂–MoN Heterostructure to Accelerate Polysulfide Conversion Toward High-Energy-Density Lithium–Sulfur Batteries," *Advanced Energy Materials* 11, no. 11 (2021): 1–10.
- [144] W. Li, Z. Gong, X. Yan, et al., "In Situ Engineered ZnS-FeS Heterostructures in N-Doped Carbon Nanocages Accelerating Polysulfide Redox Kinetics for Lithium Sulfur Batteries," *Journal of Materials Chemistry A* 8, no. 1 (2020): 433–442.
- [145] C. Jin, P. Zhai, J. Tang, et al., "Ultrathin NiO/Ni₃S₂ Heterostructure as Electrocatalyst for Accelerated Polysulfide Conversion in Lithium–Sulfur Batteries," *Energy and Environmental Materials* 6, no. 6 (2023): 1–9.
- [146] K. A. See, Y. S. Jun, J. A. Gerbec, et al., "Sulfur-Functionalized Mesoporous Carbons as Sulfur Hosts in Li-S Batteries: Increasing the Affinity of Polysulfide Intermediates to Enhance Performance," *ACS Applied Materials & Interfaces* 6, no. 14 (2014): 10908–10916.
- [147] D. Gueon, J. T. Hwang, S. B. Yang, et al., "Spherical Macroporous Carbon Nanotube Particles With Ultrahigh Sulfur Loading for Lithium–Sulfur Battery Cathodes," *ACS Nano* 12, no. 1 (2018): 226–233.
- [148] L. Gao, J. Yang, X. Lu, H. Ren, E. Sheng, and J. Huang, "Hierarchical Porous Carbon Doped With High Content of Nitrogen as Sulfur Host for High Performance Lithium–Sulfur Batteries," *Journal of Electroanalytical Chemistry* 878 (2020): 114593.
- [149] J. Schuster, G. He, B. Mandlmeier, et al., "Spherical Ordered Mesoporous Carbon Nanoparticles With High Porosity for Lithium–Sulfur Batteries," *Angewandte Chemie International Edition* 51, no. 15 (2012): 3591–3595.
- [150] J. Balach, T. Jaumann, M. Klose, S. Oswald, J. Eckert, and L. Giebeler, "Mesoporous Carbon Interlayers With Tailored Pore Volume as Polysulfide Reservoir for High-Energy Lithium - Sulfur Batteries," *The Journal of Physical Chemistry C* 119, no. 9 (2015): 4580–4587.
- [151] S. Imtiaz, J. Zhang, Z. A. Zafar, et al., "Biomass-Derived Nanostructured Porous Carbons for Lithium–Sulfur Batteries," *Science China Materials* 59, no. 5 (2016): 389–407.
- [152] Y. Zhong, X. H. Xia, F. Shi, J. Y. Zhan, J. P. Tu, and H. J. Fan, "Transition Metal Carbides and Nitrides in Energy Storage and Conversion," *Advanced Science* 3, no. 5 (2016).
- [153] L. Zhang, X. Chen, F. Wan, et al., "Enhanced Electrochemical Kinetics and Polysulfide Traps of Indium Nitride for Highly Stable Lithium–Sulfur Batteries," *ACS Nano* 12, no. 9 (2018): 9578–9586.
- [154] Y. Song, W. Zhao, L. Kong, et al., "Synchronous Immobilization and Conversion of Polysulfides on a VO₂–VN Binary Host Targeting High Sulfur Load Li-S Batteries," *Energy & Environmental Science* 11, no. 9 (2018): 2620–2630.
- [155] E. Cha, M. D. Patel, J. Park, et al., "2D MoS₂ as an Efficient Protective Layer for Lithium Metal Anodes in High-Performance Li-S Batteries," *Nature Nanotechnology* 13, no. 4 (2018): 337–344.
- [156] C. Wu, J. Hu, J. Tian, et al., "Stacking of Tailored Chalcogenide Nanosheets Around MO₂–C Conductive Stakes Modulated by a Hybrid POMCMOF Precursor Template: Composite Conversion-Insertion Cathodes for Rechargeable Mg-Li Dual-Salt Batteries," *ACS Applied Materials & Interfaces* 11, no. 6 (2019): 5966–5977.
- [157] T. Wang, J. He, Z. Zhu, et al., "Heterostructures Regulating Lithium Polysulfides for Advanced Lithium–Sulfur Batteries," *Advanced Materials* 35, no. 47 (2023): 1–32.
- [158] W. Jing, Q. Tan, Y. Duan, et al., "Defect-Rich Single Atom Catalyst Enhanced Polysulfide Conversion Kinetics to Upgrade Performance of Li–S Batteries," *Small* 19, no. 4 (2023): 1–11.
- [159] X. Zhou, R. Meng, N. Zhong, S. Yin, G. Ma, and X. Liang, "Size-Dependent Cobalt Catalyst for Lithium Sulfur Batteries: From Single Atoms to Nanoclusters and Nanoparticles," *Small Methods* 5, no. 10 (2021): 1–10.
- [160] C. Wei, B. Xi, P. Wang, et al., "Situ Anchoring Ultrafine ZnS Nanodots on 2D MXene Nanosheets for Accelerating Polysulfide Redox and Regulating Li Plating," *Advanced Materials* 35 (2023): 1–12.
- [161] Y. Yao, W. Feng, M. Chen, et al., "Boosting the Electrochemical Performance of Li–S Batteries With a Dual

- Polysulfides Confinement Strategy,” *Small* 14, no. 42 (2018): 1–9.
- [162] M. Weinberger, J. Munding, M. Lindén, and M. Wohlfahrt-Mehrens, “Template-Derived Submicrometric Carbon Spheres for Lithium–Sulfur and Sodium-Ion Battery Electrodes,” *Energy Technology* 6, no. 9 (2018): 1797–1804.
- [163] M. Li, P. Hu, X. Wang, et al., “Hierarchical Porous Carbon Derived From Peanut Hull for Polysulfide Confinement in Lithium–Sulfur Batteries,” *Energy Technology* 7, no. 3 (2019): 1–6.
- [164] J. Wang, P. Nie, B. Ding, et al., “Biomass Derived Carbon for Energy Storage Devices,” *Journal of Materials Chemistry A* 5, no. 6 (2017): 2411–2428.
- [165] R. Razaq, N. Zhang, Y. Xin, Q. Li, J. Wang, and Z. Zhang, “Dense MoS₂ Micro-Flowers Planting on Biomass-Derived Carbon Fiber Network for Multifunctional Sulfur Cathodes,” *ChemistrySelect* 5, no. 25 (2020): 7563–7570.
- [166] M. Wang, Z. Bai, T. Yang, et al., “Advances in High Sulfur Loading Cathodes for Practical Lithium–Sulfur Batteries,” *Advanced Energy Materials* 12, no. 39 (2022).
- [167] K. Zou, T. Zhou, Y. Chen, et al., “Defect Engineering in a Multiple Confined Geometry for Robust Lithium–Sulfur Batteries,” *Advanced Energy Materials* 12, no. 18 (2022): 1–13.
- [168] Y. Bai, Q. Luo, and J. Liu, “Protein Self-Assembly: Via Supramolecular Strategies,” *Chemical Society Reviews* 45, no. 10 (2016): 2756–2767.
- [169] M. Zhen, J. Wang, X. Wang, and C. Wang, “Hierarchical N-Rich Carbon Sponge With Excellent Cycling Performance for Lithium–Sulfur Battery at High Rates,” *Chemistry – A European Journal* 24, no. 22 (2018): 5860–5867.
- [170] T. Ando, Y. Sato, T. Matsuyama, A. Sakuda, M. Tatsumisago, and A. Hayashi, “High-Rate Operation of Sulfur/Mesoporous Activated Carbon Composite Electrode for All-Solid-State Lithium–Sulfur Batteries,” *Journal of the Ceramic Society of Japan* 128, no. 5 (2020): 233–237.
- [171] M. Fiedler, M. A. Lange, F. Hippauf, et al., “The Role of Nanoporous Carbon Materials for Thiophosphate-Based All Solid State Lithium Sulfur Battery Performance,” *Carbon* 227 (2024): 119252.
- [172] C. Liang, N. J. Dudney, and J. Y. Howe, “Hierarchically Structured Sulfur/Carbon Nanocomposite Material for High-Energy Lithium Battery,” *Chemistry of Materials* 21, no. 19 (2009): 4724–4730.
- [173] D. S. Jung, T. H. Hwang, J. H. Lee, et al., “Hierarchical Porous Carbon by Ultrasonic Spray Pyrolysis Yields Stable Cycling in Lithium–Sulfur Battery,” *Nano Letters* 14, no. 8 (2014): 4418–4425.
- [174] J. Guo, Y. Xu, and C. Wang, “Sulfur-Impregnated Disordered Carbon Nanotubes Cathode for Lithium–Sulfur Batteries,” *Nano Letters* 11, no. 10 (2011): 4288–4294.
- [175] H. Yamaguchi, Y. Ishihara, Y. Haniu, et al., “Local Structure of Amorphous Sulfur in Carbon–Sulfur Composites for All-Solid-State Lithium–Sulfur Batteries,” *Communications Chemistry* 8, no. 1 (2025): 1–8.