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Tungsten phosphide on nitrogen and phosphorus-doped carbon as a functional membrane coating enabling robust lithium-sulfur batteries

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G R A P H I C A L A B S T R A C T

Tungsten phosphide (WP) nanoparticles supported on nitrogen and phosphorus co-doped carbon nanosheets (WP@NPC) provide outstanding performance as a multifunctional separator in lithium-sulfur batteries, enabling higher sulfur utilization and exceptional rate capability. Its excellent performance is associated with the abundance of lithium polysulfide (LiPS) adsorption and catalytic conversion sites and swift ion transport within the separator. Key to these features is the sulfophilic character of W and the lithiophilicity of nitrogen and phosphorus, as well as the capability of WP to regulate the LiPS catalytic conversion, accelerating the Li-S redox kinetics.



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ABSTRACT

Lithium-sulfur batteries (LSBs) hold great potential as future energy storage technology, but their widespread application is hampered by the slow polysulfide conversion kinetics and the sulfur loss during cycling. In this study, we detail a one-step approach to growing tungsten phosphide (WP) nanoparticles on the surface of nitrogen and phosphorus co-doped carbon nanosheets (WP@NPC). We further demonstrate that this material provides outstanding performance as a multifunctional separator in LSBs, enabling higher sulfur utilization and exceptional rate performance. These excellent properties are associated with the abundance of lithium polysulfide (LiPS) adsorption and catalytic conversion sites and rapid ion transport capabilities. Experimental data and density functional theory calculations demonstrate tungsten to have a sulfophilic character while nitrogen and phosphorus provide lithiophilic sites that prevent the loss of LiPSs. Furthermore, WP regulates the LiPS catalytic conversion, accelerating the Li-S redox kinetics. As a result, LSBs containing a polypropylene separator coated with a WP@NPC layer show capacities close to 1500 mAh/g at 0.1C and coulombic efficiencies above 99.5 % at 3C. Batteries with high sulfur loading, 4.9 mg cm⁻², are further produced to validate their superior cycling stability. Overall, this work demonstrates the use of multifunctional separators as an effective strategy to promote LSB performance.

1. Introduction

Lithium-sulfur batteries (LSBs) are one of the most promising technologies for the new generation of energy storage systems. Their interest arises from the abundance and low cost of the cathode active material and its high theoretical specific capacity (1675 mAh/g) and energy density (2600 Wh kg⁻¹) [1–3]. Nevertheless, several limitations hamper their commercialization, including the insulating nature of the charged and discharged cathode active material, S₈ and Li₂S [4,5], and the loss of this active material upon cycling in the form of soluble lithium polysulfides (LiPSs) generated during the charge–discharge process. The migration of LiPSs to the LSB anode causes its corrosion and eventually the complete LSB failure [6,7]. To overcome the electrical conductivity limitation, carbon-based materials are generally used as sulfur hosts [8,9]. To prevent the LiPS migration, mechanisms to trap these polysulfides and at the same time accelerate their conversion need to be considered [10].

The separator is an essential component of LSBs. It is generally an inactive element that mechanically separates the sulfur cathode and the lithium anode, allowing ion transport while preventing electrical short circuits [11,12]. The most common separator type is based on polyolefin materials including polypropylene (PP). Conventional polyolefin membranes have nonpolar surfaces, being unable to block the migration of LiPSs. To take advantage of this inactive but necessary element in LSBs,

the cathode side of the separator can be functionalized with a polar material able to capture the LIPSs [13]. This coating can also contribute to the electron transport at the cathode side and even accelerate the redox reaction taking place during the charge–discharge process. Compared with the modification of the cathode host material, the use of multifunctional separators has advantages in terms of simplicity and cost-effective manufacturing [14–16].

As the membrane coating material, carbon-based materials, including graphene, carbon nanotubes, and porous carbon, have been proposed owing to their large surface area and high electrical conductivity [17–20]. However, the nonpolar surface of carbon shows limited affinity for LiPS, making it unable to meet long-term stability requirements. Enhancement in the trapping of LiPS by carbon materials has been achieved through the introduction of heteroatoms to increase the surface polarity [5,9,21–23]. Besides, transition metal oxide/chalcogenide particles, offering stronger LiPS chemical anchoring and simultaneously improving the kinetics of the Li-S reaction, have been also postulated as additives in the separator or cathode [8,24]. However, improved electrical conductivities, electrocatalytic activities, and stabilities are still required to ensure the long-term performance of the produced devices [25].

In recent years, transition metal phosphides have emerged as highly active and stable materials in several electrochemical fields [26,27]. Metal phosphides show excellent electrocatalytic activity, high

electrical conductivities, and outstanding chemical and electrochemical stabilities against corrosion. Besides, transition metal phosphides offer polar surfaces to trap LiPSs and highly active sites to catalytically activate the Li-S conversion process. As an example, cobalt phosphide exhibits the best catalytic performance among several cobalt-based compounds, associated with the effect of the non-metal anions (P) that enhance the sulfur cathode redox kinetics [28]. We also recently demonstrated that the charge redistribution taking place upon combining CoFeP with C3N4 effectively reduces the reaction barrier and promotes the LiPSs catalytic conversion [29]. As a drawback, the preparation of efficient phosphide-based catalysts often involves complex synthesis steps and toxic gases such as phosphine (PH₃), e.g. when using sodium hypophosphite as a phosphorus source during hightemperature synthesis processes [30], or the waste of high-boilingpoint solvents, e.g. when using colloidal synthesis methods [31,32]. Therefore, developing simpler and more effective approaches to produce metal phosphide nanoparticles holds significant value in promoting the development of phosphide catalysts.

In terms of the transition metal, tungsten-based catalysts have demonstrated unique application value in photocatalysis and electrocatalysis [33,34]. Tungsten-based layered materials, including tungsten oxide (WO₃), tungsten nitride (WN), tungsten carbide (WC), and tungsten selenide (WSe₂) [21], also show excellent performance towards the activation of the Li-S reaction [35,36]. Nevertheless, despite the demonstrated potential of both phosphide and W-based compounds, WP has not been explored as a functional membrane coating material within LSBs.

In this work, we detail a simple one-step thermal annealing process to prepare WP nanoparticles embedded within nitrogen and phosphorus co-doped carbon nanosheets (WP@NPC). We further explore this WPbased composite coated on the cathode side of PP membranes as an inhibitor of the LiPS migration and as a catalyst of the complex Li-S multi-electron conversion reactions involving 16 electrons [29]. Using both experimental measurements and density functional theory (DFT) calculations, we evaluate the capacity of W, N, and P sites to capture LiPSs and promote the Li-S redox reaction thus improving the battery performance and its cycling stability.

2. Experimental section

2.1. Chemicals

Sodium tungstate dihydrate (Na₂WO₄·2H₂O, \geq 99 %), dicyanocobinamide (\geq 93 %), D-(+)-glucose (\geq 99.5 %), ammonium phosphate monobasic (NH₄H₂PO₄, ACS reagent, \geq 98 %), sulfur power (\geq 99.98 %), and lithium sulfide (Li₂S) were bought from Sigma. Polyvinylidene fluoride (PVDF), *N*-methylpyrrolidone (NMP), 1,3-dioxolane (DOL), 1,2-dimethoxyethane (DME), and Super P were purchased from Fisher. These chemicals were used as received, without additional purification.

2.2. Synthesis of WP@NPC and NPC

0.275~g of $Na_2WO_4\cdot 2H_2O$, 0.1~g of glucose, 2 g of dicyandiamide, and 0.405~g of $NH_4H_2PO_4$ were ground into a homogeneous white powder in a mortar. The mixture was then placed into a porcelain boat. The boat was placed in a tube furnace and annealed at 800 °C for 2 h under an inert atmosphere. The resulting product was collected and dispersed in deionized water and anhydrous ethanol through ultrasonic treatment and centrifugation several times. Subsequently, the centrifuged product was placed in a vacuum oven at 80 °C overnight to collect the black powder, which is referred to as WP@NPC. Similarly, nitrogen and phosphorus co-doped three-dimensional carbon nanosheets (NPC) materials were synthesized using similar steps, except that sodium tung-state was not added.

2.3. Synthesis of WP@NPC@PP and NPC@PP

WP@NPC was mixed with PVDF in NMP solvents with a mass ratio of 9:1. Then, it was sonicated for 1 h to form a uniform viscous liquid. The mixture was then vacuum filtered onto a PP membrane and dried in a vacuum oven at 60 °C overnight. Similarly, NPC@PP was prepared using the same method. The loading of the material on the PP membrane was 0.5 mg/cm^2 .

2.4. Synthesis of S@Super P

Super P was mixed with sulfur power with a weight ratio of 2:8. The mixture was then heated to 155° C overnight in a sealed glass bottle under argon. The redundant sulfur was removed by a 3 mL CS₂ and ethanol solution (1:4, volume ratio).

2.5. Physicochemical characterization

X-ray diffraction (XRD) patterns were obtained by a Bruker D8 Advance X-ray diffractometer with Cu K radiation ($\lambda = 1.5106$ Å) operating at 40 kV and 40 mA. The morphology and microstructure of samples were investigated by transmission electron microscopy (TEM, JEOL JEM-2100HR) and field emission scanning electron microscopy (FESEM, ZEISS Auriga) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector operated at 20 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out by the Thermo Scientific K-Alpha XPS instrument. The spot size of the X-ray beam was set at 400 µm, with a working voltage of 12 kV and a filament current of 6 mA. The Brunauer-Emmett-Teller equation and Barret-Joyner-Halenda (Tristar II 3020 Micromeritics) analysis were used to determine the specific surface area and pore size distribution. The WP content, sulfur amount, and thermal stability of the as-prepared materials were examined by thermogravimetric analysis (TGA, STA209PC) under an air or N₂ atmosphere from 30 °C to 800 °C at a heating rate of 10 °C min⁻¹. UV-vis absorption spectra were identified by a PerkinElmer LAMBDA 950 UV-vis spectrophotometer. To determine wettability, the contact angle between the electrolyte and separator was measured by a contact angle system (JC2000C, China). Electrical conductivities were measured using a four-point probe station (Keithley 2400, Tektronix), by pressing the sample into a square slice of 1 cm x 1 cm x 1 mm and placing it between two temperature probes, then adjusting the electric probe to align with the sample and closing the test chamber to keep them under argon environment. For testing, the program included raising the temperature from ambient to 100 °C at a heating rate of 5 °C min⁻¹. The resistivity(ρ) was measured every 10°, then the conductivity σ can be obtained through the equation of $\sigma = 1/\rho$.

2.6. WP content calculation

The WP content was determined from TGA in air atmosphere and calculated based on this formula: $2WP + 11/2 O_2 \rightarrow 2WO_3 + P_2O_5$ There is a weight gain in going from tungsten phosphide to tungsten oxide due to larger molecular weight of tungsten oxide than tungsten phosphide. Assuming that the carbon material is X, the overall calculation is X-(184 + 16*3–184-31)/(184 + 31)*(1-X) = 10 %, X = 16.7 %, 1- X = 83.3 %. Taking into account TGA data displayed in the results section.

2.7. Lithium-ion transference number (t_{Li}^+) measurement

The lithium-ion transference number (t_{Li}^{-}) of different modified separators was determined using an electrochemical working station (CHI660E) from coin-type cells produced by sandwiching each membrane between two lithium metal electrodes. The constant step potential was set as 20 mV and the lithium-ion transference number was calculated from the ratio of steady-state current to initial state current according to the following equation: $t_{Li}^{+}=I_s/I_o$, where t_{Li}^{+} is the lithium-ion

transference number, and $I_{\rm s}$ and $I_{\rm o}$ represent the current at the steady state and initial state, respectively.

2.8. Lithium ionic conductivity measuremen

The ionic conductivity of different separators was measured using an EIS (10–100 KHz) method. The separator saturated with electrolyte was sandwiched between two stainless steel electrodes, and its ionic conductivity was determined according to the following equation: $\sigma = L/(R_b*A)$. where σ is the ionic conductivity (S cm⁻¹), and L, Rb, and A represent the thickness of the separator (cm), bulk resistance (Ω), and area of the stainless-steel electrode (cm²), respectively.

2.9. Electrochemical characterization

Li-S battery performance was tested at ambient temperature (with no climatic chamber) in CR2032 coin-type cells. The assembly process, in which a lithium foil was used as the anode, the produced membranes as the separator, and S@Super P composites as the cathode was conducted in a glovebox filled with argon. The cathode was obtained by doctoral blade methods. Briefly, S@SuperP composites, conductive carbon, and PVDF binder (weight ratio = 8:1:1) were well mixed into *N*-methyl pyrrolidone (NMP, 99.5 %, Acros Organics) to form a black slurry, and then coated it on Al foils and dried at 60 °C overnight. After drying the foil was punched into small disks with a diameter of 12.0 mm. Sulfur loading was about 1.0 mg cm^{-2} . The electrolyte was prepared by dissolving 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (99 %, Acros Organics) into a solution of 1,2-dimethoxy ethane (DME, 99 %, Honeywell) and 1,3-dioxolane (DOL,99.5 %, Alfa Aesar) (v/v = 1/1) and containing 1 % of LiNO₃. Unless otherwise specified, the standard amount of electrolyte used was¹³ mL/g_{Sulfur}. The Li-S cells were galvanostatically cycled at a voltage window of 1.7-2.8 V on a Neware BTS4008 battery tester with different C rates Low current activation was conducted before the cycling test. Cyclic voltammetry (CV) measurements were performed on a battery tester BCS-810 from BioLogic at a scan rate of 0.1–0.4 mV s⁻¹ and electrochemical impedance spectroscopy (EIS) tests were conducted with a voltage amplitude of 10 mV in the frequency range 100 kHz to 10 mHz. All electrochemical tests were repeated three times and the data error was controlled within 6 %.

2.10. Preparation of Li₂S₆ solutions for adsorption test

Sulfur and Li₂S were mixed with a molar ratio of 5:1, and then the powder was poured into appropriate amounts of DME/DOL (volume ratio of 1:1) solution under vigorous magnetic stirring overnight until a dark brown solution was obtained. 10 mg of NPC, WP@NPC poured into 3.0 mL 5 mM Li₂S₆ solution, respectively. All the steps were conducted under Ar atmosphere.

2.11. Symmetric cell assembly and measurements

The preparation of the symmetrical battery is similar to the preparation of the LSBs but uses NPC and WP@NPC as the working and the counter electrode, respectively. 40 μ L of electrolyte containing 0.5 M Li₂S₆ and 1 M LiTFSI dissolved in DOL/DME (V/V = 1:1) was added into the coin cells. The loading of each electrode is about 0.5 mg cm⁻². The prepared symmetrical battery was tested at a scan rate of 10 mV s⁻¹.

2.12. Measurement of nucleation of Li₂S

Different active materials of Super P, NPC, and WP@NPC were dispersed into an ethanol solution, and coated onto carbon paper as working electrodes. Lithium foil was used as the counter electrode. 0.25 M Li₂S₈ with 1.0 M LiTFSI in tetraethylene glycol dimethyl ether solution and 1.0 M LiTFSI solution without Li₂S₈ were used as catholyte and anolyte respectively. The prepared battery was first discharged to 2.06 V

at 0.112 mA, and then a constant voltage deposition experiment was carried out at a voltage of 2.05 V.

2.13. Theoretical calculation

All DFT calculations were conducted using the VASP package, with post-processing of the calculated data carried out using the VASPKIT code. The exchange–correlation energy was treated using the Perdew-Burke-Ernzerhof functional within the generalized gradient approximation (GGA) framework. The interaction between core and valence electrons was described by the projected augmented wave (PAW) basis set. A convergence cutoff of 500 eV was employed. Weak intermolecular interactions were investigated using the zero-damping DFT-D3 method. These heterointerfaces were constructed to minimize crystal parameter mismatch, maintaining it below 5.0 %. In the geometry optimization step, the force convergence criterion was set below 0.02 eV/Å. The Monkhorst-Pack K-point mesh density (threshold: 0.04) and the k-path for band structure calculations followed the recommendations of the VASPKIT code. A vacuum layer of 20 Å was added along the z-axis for each model to mitigate periodic layer effects.

The binding energy of LiPS intermediate species was determined using the following equation: $E_{LiSx} = E_{slab} + E_{LiSx} - E_{LiSx} - slab$, Where E_{LiSx} represents the binding energy of the LiPS species, E_{slab} is the DFT energy of the slab, E_{LiSx} is the corrected energy (at 300 K) of isolated LiPS molecules in vacuum, and $E_{LiSx} - slab$ is the total energy after the slab absorbs the intermediate Li-S_x species. Here, x represents the stoichiometry number of sulfur atoms in a Li-S_x-like molecule.

3. Results and discussion

A schematic diagram of the synthesis of WP@NPC is depicted in Fig. 1a. In simple terms, WP nanoparticles embedded in nitrogen and phosphorus dual-doped carbon nanosheets (WP@NPC) were obtained through a one-step annealing process at 800 °C from a mixture of sodium tungstate, dicyandiamide, and ammonium dihydrogen phosphate as precursors (see details in the Supporting Information, SI). As shown by SEM, the WP@NPC composite consists of a nanosheet-based threedimensional (3D) porous structure (Fig. 1b and Fig. S1). EDS elemental maps confirm the uniform distribution of C, N, P, and W (Fig. 1c,d) [37]. TEM general view images show a uniform dispersion of elongated WP particles (darker regions) in the nanometer size regime throughout the NPC nanosheets (Fig. 1e and Fig. S2). Fast Fourier transform (FFT) structural analysis obtained on the high-resolution TEM (HRTEM) images (Fig. 1f) confirms the orthorhombic crystal phase, Pnma space group, of the WP nanoparticles (Fig. 1f and Fig. S2e). High-angle annular dark-field scanning TEM (HADDF-STEM) images (Fig. 1g and Fig. S3) show a high dispersion of WP nanoparticles that appear as bright structures due to HAADF-STEM Z-contrast, due to the high atomic number of W, in contrast to the light contrast of the N- and P-doped carbon nanosheets. Electron energy loss spectroscopy (EELS) further confirms the uniform distribution of W and P within each nanoparticle (Fig. 1g). XRD patterns (Fig. 1h) confirm the presence of the orthorhombic WP phase (90-029-1364) with diffraction peaks at 31.04°, 43.20°, and 44.58° corresponding to the (011), (112), and (211) crystal planes of WP, respectively [37]. Thermogravimetric analysis (TGA, Fig. 1i) shows the WP weight content in the composite material WP@NPC is approximately 83.3 % (the calculation details can be seen in the experiment section). Overall, these experimental results demonstrate the formation of WP nanoparticles supported on N- and P-doped carbon nanosheets (WP@NPC).

As a reference sample, nitrogen and phosphorus carbon nanosheets (NPC) without WP, were also produced. SEM and TEM characterization (Figs. S4 and S5) confirmed the NPC to present the same nanosheet structure as WP@NPC. EDS elemental maps further confirmed the uniform distribution of N, P, and C elements and their relative content (Fig. S5). The XRD pattern of NPC (Fig. S6) shows a broad diffraction



Fig. 1. (a) Schematic illustration of the process used to produce WP@NPC. (b,c) SEM images at different magnifications and (d) EDX compositional mapping of WP@NPC. (e) HRTEM image of WP@NPC. (f) HRTEM image and corresponding indexed power spectrum and (g) HAADF STEM image and EELS chemical composition maps of WP@NPC. (h) XRD pattern of WP@NPC. (i) TGA profile of WP@NPC under air atmosphere.

peak around 24° corresponding to the (002) planes of graphite. This peak is significantly shifted to lower angles with respect to the pure graphite peak (26.4°), which is associated with the expansion of the interlayer structure due to the presence of N and P [21].

Four-point probe measurements showed WP@NPC to be characterized by a high electrical conductivity of 2.61 S cm⁻¹, well above that of NPC, at 0.65 S cm⁻¹ (Fig. S7). The nitrogen adsorption–desorption isotherms and Barret-Joyner-Halenda (BJH) pore size distribution for NPC and WP@NPC are shown in Fig. S8. Type IV isotherms were obtained for all samples and the related pore size distributions confirmed the presence of both micro and mesopores [38]. The Brunauer-Emmett-Teller (BET) specific surface area of NPC was estimated at 79 m² g⁻¹ and that of WP@NPC was 52 m² g⁻¹.

A slurry prepared by the mixing of WP@NPC (or NPC) and PVDF in NMP was coated onto a PP membrane using vacuum filtration. The prepared WP@NPC@PP (or NPC@PP) membrane contains a layer of black material that will face the sulfur cathode (**Fig. S9a**). SEM surface inspection and EDX elemental maps (**Fig. S9b**) show C, N, P, and W elements are uniformly distributed on the membrane. Similarly, SEM and EDX maps show N, P, and C elements are homogeneously distributed within the NPC@PP membrane, as shown in **Fig. S10**. Cross-section SEM images (**Fig. 2a**) show the thickness of the WP@NPC layer to be approximately 20 µm. Upon folding and heating at 140 °C, the WP@NPC@PP membrane shows excellent mechanical stability (**Fig. 2b**). In contrast, the PP and NPC@PP membranes shrink when heated at 140 °C in **Fig. S11**. This different behavior is associated with the significant inhibition of PP membrane shrinkage at high temperatures by the robust inorganic WP particles.

The electrolyte permeability of the membrane is a critical performance indicator [39]. Contact angle measurements of the three different separators were conducted with the LSB electrolyte to evaluate their wettability (Fig. 2c). WP@NPC@PP exhibits the smallest contact angle, at 22°, well below that of the unmodified PP membrane (36°) and NPC@PP (30°) which indicates that the WP@NPC coating significantly enhances the electrolyte wetting, promoting its diffusion within the separator. To further elucidate the impact of different coatings on Li⁺ transport, the ion conductivity and Li+ transference number of the different membranes were assessed. As shown in Fig. 2d, the WP@NPC@PP separator shows an excellent Li⁺ transference number, at 0.88, well above that of PP at 0.82, and NPC@PP at 0.85. Fig. 2e shows the Nyquist plots of the electrochemical impedance spectroscopy (EIS) spectra of symmetric cells based on the different separators. The fitting results (see details in the SI) show the cells based on WP@NPC@PP separators to exhibit significantly higher ion conductivity (6.5 \times 10⁻¹ mS cm $^{-1}$) than pure PP (0.9 \times 10 $^{-1}$ mS cm $^{-1}$) and NPC@PP (1.1 \times 10 $^{-1}$ mS cm⁻¹) [40]. These outstanding Li⁺ transport properties of WP@NPC@PP arise from the high lithium affinity of the polar WP nanoparticles and nitrogen and phosphorus heteroatoms.

The ability to trap polysulfides, thus suppressing LiPS migration [41], is an important indicator for evaluating the functional membrane performance. As shown in Fig. 3a, similar amounts of NPC and WP@NPC were immersed in the same volume of a 5 mM Li₂S₆ solution. After 20 h, the vial containing NPC showed the dark orange-colored Li₂S₆ solution to have significantly lightened due to the Li₂S₆ adsorption on N and P atoms through dipole–dipole interactions [42]. The vial containing WP@NPC exhibited more effective Li₂S₆ adsorption attributed both to the N and P heteroatoms and the WP nanocrystals. UV–visible spectroscopy data confirmed the visual inspection results (Fig. 3a) [43].

XPS spectra of the solid samples before and after Li_2S_6 adsorption are shown in Fig. 3b-d. The N 1s XPS spectrum of the WP@NPC sample shows four peaks at 398.2 eV, 399.45 eV, 400.53, and 402.65 eV corresponding to pyridinic nitrogen, pyrrolic nitrogen species, graphitic nitrogen, and oxidized nitrogen, respectively. After adsorption, due to



Fig. 2. (a) Cross-section SEM image of the WP@NPC layer on the PP separator. (b) WP@NPC@PP under different folding and at 140 °C. (c) Contact angle test of PP, NPC@PP, WP@NPC@PP using Li-S electrolyte (1 mol/L LiTFSI dissolved in DOL/DME (v/v = 1/1) containing 1 % LiNO₃). (d) Chronoamperometric curves and (e) Nyquist plots of the EIS spectra showing lithium ion conductivity behaviors of symmetric cells with various separators.

the influence of Li_2S_6 , the pyridinic nitrogen shifted from 398.2 to 397.8 eV, and pyrrolic nitrogen shifted from 399.45 to 399.1 eV. According to previous research reports, this shift is attributed to the unpaired electrons of pyridinic/pyrrolic nitrogen sites serving as Lewis basic active centers, forming dipole–dipole interactions with Li atoms in LiPS, which possess Lewis acidic characteristics, leading to chemical anchoring of LiPS [29].

As shown in Fig. 3c, in the P 2p XPS spectrum of WP@NPC before Li_2S_6 adsorption, six peaks located at 129.2, 130.07, 132.02, 132.93, 133.98, and 134.94 eV were attributed to three P 2p doublets assigned to P-W, P—C, and P—O chemical environments, respectively. After LiPS adsorption, all the P components shifted to higher binding energies, which is related to the interaction between P sites and the terminal Li atoms in Li_2S_6 [29].

Fig. 3d displays the W 4f spectra of the WP@NPC sample before and after Li_2S_6 adsorption. Before LiPS adsorption, the W 4f peaks at 31.35 and 33.49 eV are attributed to the W $4f_{7/2}$ and $4f_{5/2}$ orbitals of W within a W-P bond, while W 4f peaks at 35.32 and 37.48 eV are assigned to the W $4f_{7/2}$ and $4f_{5/2}$ orbitals of W within a WO₃ chemical environment. The presence of this oxidized component is related to the inevitable exposure of the sample to trace amounts of oxygen during manipulation and

transportation, before XPS characterization. After the Li_2S_6 adsorption test, the W 4f binding energies of the W-P component in the WP@NPC- Li_2S_6 sample blue shift. We associate this positive binding energy shift with the formation of W-S bonds, taking into account the higher electronegativity of sulfur (2.58) compared with phosphorus (2.19) [21].

To gain an understanding of the interaction with LiPS, DFT calculations were carried out. A configuration model combining N@C, P@C, and WP (211) with Li₂S_x (x = 1,2,4,6,8) was first used to study the adsorption of various sulfur-containing species by different adsorbents, as shown in Fig. S12. In Fig. 3e, Li₂S₆ is bound on the N@C and P@C surfaces through Li-N and Li-P bonds. The calculated binding energies (E_b) are -1.8 eV and -1.3 eV, which are significantly larger values (in absolute terms) than binding energies reported for graphene (~ -1 eV) [6]. This result shows that P and N heteroatoms have a stronger chemical affinity with LiPS. The calculated E_b of the Li₂S₆ geometric configuration on the WP (211) surface is -2.80 eV by the formation of W – S bonds, which is higher than calculated for the N and P dopants. Similarly, the binding energy of polar WP for different LIPS species is greater than that of N- or P-doped graphene (Fig. 3f).

Overall, DFT calculations and experimental results show that: i) Within NPC, the presence of N and P provides lithiophilic polar sites able



Fig. 3. (a) UV–vis spectra and optical images of the polysulfide solutions after interaction with different adsorbents overnight. (b,c,d) N 1s, P 2p, and W 4f XPS spectra before and after WP@NPC interaction with Li_2S_6 . (e) Relaxed Li_2S_6 -adsorbed structures on the surface of N@C, P@C, and WP. (f) Binding energies between LiPS (Li_2S_2 , Li_2S_4 , Li_2S_6 , and Li_2S_6) and N@C, P@C and WP(211).

to create Li-N or Li-P bonds. ii) Within WP@NPC, in addition to the N and P lithiophilic sites, WP nanoparticles show a strong sulfur affinity that further promotes the LiPSs capture.

To assess the electrocatalytic activity of the different materials toward the conversion of polysulfides, symmetric cells containing $\rm Li_2S_6$ were assembled and tested using cyclic voltammetry (CV) in the voltage range of -1 to 1 V (Fig. 4a) [44,45]. The symmetric cell based on two WP@NPC electrodes exhibited larger current densities than those based on NPC, indicating that the highly conductive polar WP nanoparticles enhanced the electrochemical activity for the conversion of polysulfides.

Subsequently, the performance of LSBs with a S@Super P cathode (Fig. S13-S14), a Li anode, and the three different separators (PP, NPC@PP, and WP@NPC@PP) were tested. In the constant current charge-discharge test shown in Fig. 4b, the three cells showed one charge and two discharge plateaus. The first discharge plateau provides a capacity Q1 in the range from 2.4 to 2.1 V, corresponding to the reduction of S8 receiving electrons to form soluble long-chain Li2S4 (S8 $+ 4Li^+ + 4e^- \rightarrow 2Li_2S_4$). The second discharge plateau, in the range of 2.1-1.7 V, provides a capacity Q2 and is associated with the 12 electron reduction reaction to form insoluble lithium sulfide $(2Li_2S_4 + 12Li^+ +$ $12e^- \rightarrow 8Li_2S$ [46]. As shown in Fig. 4b, the cell based on the PP separator shows a discharge capacity of 892 mAh/g, the cell containing the NPC@PP separator has a discharge capacity of 1087 mAh/g, and the cell assembled with the WP@NPC@PP separator exhibits the highest discharge specific capacity at 1444 mAh/g. These capacities are primarily provided by sulfur, as demonstrated by the negligible discharge capacity within the voltage range of 1.7-2.8 V obtained for the cell based on an electrode made of WP@NPC (Fig. S15).

Typically, the potential difference ΔE between the charge and discharge curves at 50 % discharge capacity is defined as the LSB polarization potential. This value is used as a quantitative measure of the LiPS conversion kinetics [47]. The battery containing the WP@NPC@PP separator showed a low polarization voltage of $\Delta E = 138$ mV, significantly below that of cells based on NPC@PP ($\Delta E = 163$ mV) and PP ($\Delta E = 172$ mV) separators. The low polarization voltage obtained with the

WP@NPC@PP separator is attributed not only to the promoting effect of the highly conductive WP@NPC interlayer material but also to the catalytic activity of WP@NPC towards LiPS conversion.

We further quantified the electrocatalytic activity of the different catalysts using the capacity ratio of the two plateaus in the reduction process, Q2/Q1 [48]. Theoretically, the ratio Q2/Q1 should be 3 because Q1 corresponds to a 4-electron reduction reaction and Q2 involves a 12-electron reduction reaction. However, in practice, lower Q2/ Q1 ratios are always obtained due to the incomplete Li₂S reduction process, usually accompanied by the formation of incompletely discharged Li₂S₂ products and the migration of Li₂S₄ to the negative electrode that reduces the amount of cathode active material. As shown in Fig. 4c, the LSB equipped with the WP@NPC@PP separator exhibits an exceptionally high Q2/Q1 ratio of 2.99, well above that of the cells based on the PP (2.07) and the NPC@PP (2.15) separators. These results indicate that the synergistic effect of WP and NPC, as a composite interlayer material, not only effectively and almost completely blocks LiPS migration but also enhances the redox kinetics of the Li-S reaction as a catalyst, promoting the LiPS conversion process.

To gain an understanding of the electrochemical process during battery cycling, Fig. 4d displays the CV curves obtained from cells based on WP@NPC@PP, NPC@PP, and PP separators. All curves exhibit one oxidation peak (Peak III) and two reduction peaks (Peak I and Peak II) corresponding to the S/Li₂S conversion process [49], consistent with the measured charge–discharge curves. Among the three separators, the cell based on WP@NPC@PP exhibits the highest peak current density and the highest/lowest onset potentials for reduction/oxidation (Fig. 4d,e), which is also consistent with the polarization voltage results.

When the scanning rate is increased from 0.1 to 0.4 mV s⁻¹ (Fig. 4f), the two reduction peaks shift to more negative potentials, while the oxidation peak shifts to more positive potentials, resulting in an overall increase in polarization voltage. Batteries equipped with WP@NPC@PP membranes exhibit significantly higher current densities and lower polarization voltage compared to those with NPC@PP and PP membranes (Fig. S16a,b). The linear relationship between the peak current



Fig. 4. (a) CV profiles of symmetrical cells with three different host materials using an electrolyte containing 0.5 mol/L Li₂S₆ and 1 mol/L LiTFSI dissolved in DOL/ DME (v/v = 1/1). (b) Charging/discharging curves of different separators at the current rate of 0.1C. (c) ΔE and Q2/Q1 values obtained from charging/discharging curves. (d) CV profiles of Li-S coin cells with different separators. (e) Peak voltages obtained from CV curves with different separators. (f) CV curves of WP@NPC@PP at various scan rates. (g) The CV peak current for peaks I, II, and III versus the square root of the scan rates in WP@NPC@PP Li-S coin cells. (h) Potentiostatic discharge profile of Li₂S nucleation at 2.05 V on different materials with Li₂S₈ catholyte.

and the square root of the scanning rate shows that the reaction is diffusion-controlled. Therefore, the classical Randles-Sevcik equation is used to calculate the ${\rm Li}^+$ diffusion coefficient during the process [18].

$$I_p = (2.69^*10^5) n^{1.5} A D_{Li^+}^{0.5} C_{Li^+} v^{0.5}$$

Where I_p is the peak current, n is the charge transfer number, A is the geometric electrode area, D_{Li+} is the Li⁺ diffusion coefficient, C_{Li+} is the concentration of Li^+ in the electrolyte, and ν is the scan rate. At a given n, A, and C_{Li+} , sharper $Ip/\nu^{0.5}$ slopes denote faster Li^+ diffusion. As shown in Fig. 4g and Fig. S16c,d, the cells based on WP@NPC@PP exhibit the steepest slopes among the three reaction peaks, indicating the highest Li⁺ diffusion rate during the redox reactions. In peaks I, II, and III, the Li⁺ diffusion coefficients corresponding to WP@NPC@PPbased batteries are 0.61 \times 10⁻⁷, 0.96 \times 10⁻⁷, and 1.49 \times 10⁻⁷ cm² $s^{-1}\text{,}$ significantly higher than those of cells based on NPC@PP (0.35 \times $10^{-7},\,0.5\,\times\,10^{-7},\,0.61\,\times\,10^{-7}~cm^2~s^{-1})$ and PP (0.27 $\times\,10^{-7},\,0.43\,\times\,$ $10^{-7},~0.56~\times~10^{-7}~cm^2~s^{-1}$). Li^+ diffusivity strongly depends on the electrolyte viscosity that increases with the accumulation of LiPS and on the presence of insulating Li₂S/Li₂S₂ on the electrodes. Thus, the higher Li⁺ diffusion coefficients measured in the presence of WP@NPC@PP membranes confirm that the WP@NPC promotes the Li-S reaction and effectively traps LiPS.

 ${\rm Li}_2 S$ deposition experiments were used as an additional quantitative measure of the catalytic activity of different active materials. In this

direction, WP@NPC was tested as electrode material. Compared with Super P and NPC, WP@NPC exhibits a higher current response during constant potential polarization at 2.05 V, as shown in Fig. 4h. According to Faraday's law (Q = It, where Q, I, and t represent capacity, discharge current, and time, respectively) [50], the deposition capacity of WP@NPC (270.4 mA h g⁻¹) is significantly larger than that of NPC (124.4 mA h g⁻¹) and Super P (83.1 mA h g⁻¹). Thus, nucleation experiments clearly indicate that the WP@NPC materials effectively reduce the reaction barrier during Li₂S nucleation, thereby promoting the complete conversion of LiPS.

Fig. 5a displays the rate performance of cells based on the three different membranes. As the current increases from 0.1C to 5C, electrodes equipped with the WP@NPC@PP membrane consistently exhibit the highest discharge specific capacities. Notably, the WP@NPC@PP-based cell displays a remarkable capacity of up to 1494 mAh/g in the initial discharge at 0.1C, and maintains a high specific capacity of 636 mAh/g even at a high current density of 5C. When the current rate is reverted to 0.2C, the cell still delivers a substantial specific capacity of 1120 mAh/g, demonstrating excellent stability.

Constant current charge–discharge curves measured on cells based on WP@NPC@PP at different current rates are shown in Fig. 5b. All discharge curves exhibit two distinct discharge plateaus, even at a current density of 5C. In contrast, the cell equipped with the NPC@PP membrane displays a similar shape but with a significantly lower specific capacity, and the cell containing the PP membrane exhibits higher



Fig. 5. (a) Rate performances of PP, NPC@PP, and WP@NPC@PP separators. (b) Charging/discharging curves of WP@NPC@PP separators at current rates from 0.1 to 5C. (c) EIS plot of WP@NPC@PP separators before and after 100 cycles at 1C. (d) Capacity retention of different separators at 1C over 500 cycles. (e) Cycling stability of WP@NPC@PP-based cell at 3C over 1000 cycles. (f) Energy efficiency of three different separators at various current rates. (g,h) SEM image of lithium foil recovered from a coin cell based on PP (g) and WP@NPC@PP separators (h). (i,j) EDX sulfur maps from the Li foil recovered from a coin cell based on PP (i) and WP@NPC@PP separators (j).

polarization potentials and virtually no capacity release at currents above 3C (Fig. S17). These results suggest that the presence of WP nanoparticles plays a positive role in modulating the LiPS conversion kinetics.

To gain an understanding of the changes within the electrodes during cycling, EIS tests were conducted. Fig. **5c and Fig. S18** depict the Nyquist plots of the cells before and after 100 cycles at 1C. Fresh cells

exhibit a semicircle in the high-frequency region, corresponding to the charge transfer resistance (Rct) at the electrode–electrolyte interface, followed by a linear dependence in the low-frequency region, corresponding to lithium-ion diffusion [21]. Based on the equivalent circuit diagrams and fitting data in Fig. S18a,b, the WP@NPC@PP-based battery exhibits a lower Rct (35 Ω) compared to NPC@PP (75 Ω) and PP (125 Ω). This lower Rct in the WP@NPC@PP-based battery is

consistent with WP@NPC facilitating a rapid charge transfer at the electrode–electrolyte interface. After 100 charge–discharge cycles, an additional semicircle (Rp) appears in the high-frequency region due to the formation of insoluble Li₂S₂/Li₂S passivation layers during cycling [6]. Compared to the other two batteries, the cell equipped with the WP@NPC@PP membrane shows a significantly lower Rp value (8 Ω), indicating that the presence of the WP@NPC interlayer limits the formation of the Li₂S₂/Li₂S layer during cycling. In addition, the analysis of the Rct results shows a significant reduction in the electrode equipped with the WP@NPC@PP membrane compared to the pre-cycling results. This can be attributed to the activation of the electrode during the cycling process [51].

Fig. 5d depicts the cycling performance of cells with different membranes at a 1C current rate. The cell based on a WP@NPC@PP separator exhibits an initial discharge capacity of approximately 732 mAh/g at 1C, and it retains 84.4 % of its initial capacity after 500 cycles. Similarly, after 1000 cycles at 3C, the WP@NPC@PP-based battery still delivers a discharge specific capacity of 308 mAh/g, corresponding to an average decay rate of 0.09 % per cycle. Furthermore, the corresponding Coulombic efficiency reaches 99.6 % (Fig. 5e). In contrast, the cell equipped with the NPC@PP membrane shows a significantly lower discharge capacity at 1C, with a capacity retention of 57 % after 500 cycles at 1C, and the cell based on the PP membrane retains just 38 % of its initial capacity after 500 cycles at 1C.

As shown in Fig. 5f, in the current density range of 0.1C to 1C, both NPC@PP- and WP@NPC@PP-based cells maintain energy efficiencies exceeding 90 %. In contrast, the efficiency of the PP-based cell drops to 81 % at 1C. As the current density continues to increase, up to 5C, the cell equipped with the WP@NPC@PP separator still maintains a high conversion efficiency of 83.4 %. On the other hand, the NPC@PP-based cell based on the PP separator cannot release capacity due to excessive polarization.

To further demonstrate the effective role played by WP@NPC, the batteries cycled at 1C for 100 cycles were disassembled and characterized (Fig. 5g-j). SEM characterization revealed a very rough and cracked surface of the lithium metal recovered from the PP-based cell, which was

attributed to the growth of lithium dendrites and the LiPS-related erosion. In contrast, the surface of the lithium metal electrode recovered from the WP@NPC@PP-based cell was smooth and even, with minimal cracks. Subsequent EDX compositional maps revealed that the amount of sulfur on the surface of the Li foil obtained from the cell equipped with the WP@NPC@PP membrane was significantly lower than that on the lithium foil extracted from the cell equipped with the PP separator, as shown in Fig. 5i-j.

To achieve the high energy density required for practical applications, it is necessary to increase the sulfur loading. Therefore, a series of electrochemical tests were conducted on cells equipped with WP@NPC@PP separators and high sulfur loading conditions. Fig. 6a,b shows the rate performance results for batteries produced with a high sulfur loading of 4.5 mg cm⁻². The WP@NPC@PP-based battery exhibits a high initial discharge capacity of 1263 mAh/g, equivalent to an areal capacity of 5.2 mAh cm^{-2} , significantly higher than commercial lithium-ion batteries at about 4 mAh cm^{-2} [29]. Besides, as shown in Fig. 6b, all constant current charge/discharge curves at different current rates clearly exhibit a charging plateau and two discharging plateaus, indicating that even under high sulfur loading, the cells equipped with WP@NPC@PP separators can still effectively reduce polarization during LiPS conversion. For the high sulfur-loaded cells with WP@NPC@PP separators, an impressive Q2/Q1 value of 2.9 is still maintained at a 0.1C current rate. Fig. 6c shows the cycling performance of cells that combine high sulfur loading (4.9 mg cm^{-2}) and lean electrolyte conditions of 9.2 mL g_{Sulfur}^{-1} . After 120 long cycles at 0.25C, the discharge capacity of the cell based on the WP@NPC@PP separator remains 725 mAh/g, with a capacity retention of 75.9 % (Fig. 6d), demonstrating the potential of the WP@NPC@PP separator in practical LSBs.

4. Conclusions

High surface area and porous composites comprising tungsten phosphide (WP) nanoparticles embedded in nitrogen- and phosphorusdoped carbon (WP@NPC) were synthesized using a simple one-step calcination process. These composites were then integrated onto one side of polypropylene (PP) membranes. The resulting WP@NPC@PP



Fig. 6. (a) Rate performance of WP@NPC@PP separators with a 4.5 mg cm⁻² sulfur loading and (b) charging/discharging curves. (c) Cycling performance of WP@NPC@PP separators with a 4.9 mg cm⁻² sulfur loading and (d) charging/discharging curves at 0.25C with lean electrolyte.

membranes underwent comprehensive evaluation as multifunctional separators in lithium-sulfur batteries (LSBs), showcasing their potential. This study represents the first demonstration of employing such sophisticated yet straightforwardly synthesized materials as exceptional candidate for multifunctional separators in LSBs. Both experimental results and DFT calculations show WP@NPC to provide strong anchoring of LiPS through W-S, Li-P, and Li-N bonds with large binding energies. During the LiPS conversion process, the high catalytic activity of WP nanoparticles significantly promotes the deposition and oxidation of Li2S, effectively enhancing the reaction kinetics during the LiPS conversion. The WP@NPC interlayer reduces the loss of active materials during the conversion process and the polarization voltage of the conversion, thereby significantly improving energy efficiency. Besides, the WP@NPC multifunctional interlayer improves the sulfur cathode utilization at different cycling rates. Overall, our results indicate that the WP@NPC composite material supported on the cathode side of a PP membrane provides excellent rate performance (636 mAh/g at 5C) and outstanding cycling stability, with a coulombic efficiency of 99.6 % after 1000 cycles at 3C. Even with a 4.9 mg cm^{-2} sulfur loading, robust electrochemical performance results were obtained. In conclusion, the readily accessible WP@NPC interlayer material acting as a highconductivity current distributor, LiPS adsorber, as well as Li-S catalyst offers a new opportunity to enhance the performance of LSBs.

CRediT authorship contribution statement

Canhuang Li: Writing - original draft, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Jing Yu: Software, Methodology. Chaoqi Zhang: Writing - review & editing, Validation, Resources, Methodology. Dawei Yang: Validation, Investigation, Data curation. Jian Wang: Software, Methodology, Investigation, Formal analysis, Data curation. Hao Li: Software, Methodology, Investigation, Data curation. Chen Huang: Software, Methodology, Investigation, Data curation. Ke Xiao: Software, Methodology, Data curation. Yapeng Cheng: Software, Resources, Methodology, Investigation, Data curation. Yuchuan Ren: Software, Project administration, Methodology, Formal analysis, Data curation. Xuede Qi: Resources, Methodology, Data curation. Tianxiang Yang: Formal analysis, Data curation. Junshan Li: Resources, Methodology. Jiaao Wang: Software, Methodology, Investigation, Formal analysis, Data curation. Graeme Henkelman: Software, Data curation, Conceptualization. Jordi Arbiol: Methodology, Funding acquisition, Formal analysis, Conceptualization. Junmin Nan: Visualization, Validation, Resources, Methodology, Data curation. Andreu Cabot: Writing - review & editing, Visualization, Supervision, Project administration, Investigation, Funding acquisition, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References

- J. Zhang, C. You, H. Lin, J. Wang, Electrochemical kinetic modulators in lithiumsulfur batteries: From defect-rich catalysts to single atomic catalysts, Energy Environ. Mater. 5 (2022) 731–750.
- [2] T. Huang, Y. Sun, J. Wu, J. Jin, C. Wei, Z. Shi, M. Wang, J. Cai, X.T. An, P. Wang, C. Su, Y.Y. Li, J. Sun, A dual-functional fibrous skeleton implanted with singleatomic Co-N(x) dispersions for longevous Li-S full batteries, ACS Nano 15 (2021) 14105–14115.
- [3] J. Wang, L. Jia, J. Zhong, Q. Xiao, C. Wang, K. Zang, H. Liu, H. Zheng, J. Luo, J. Yang, H. Fan, W. Duan, Y. Wu, H. Lin, Y. Zhang, Single-atom catalyst boosts electrochemical conversion reactions in batteries, Energy Storage Mater. 18 (2019) 246–252.
- [4] C. Zhang, J.J. Biendicho, T. Zhang, R. Du, J. Li, X. Yang, J. Arbiol, Y. Zhou, J. R. Morante, A. Cabot, Combined high catalytic activity and efficient polar tubular nanostructure in urchin-like metallic NiCo₂Se₄ for high-performance lithium-sulfur batteries, Adv. Funct. Mater. 29 (2019) 1903842.
- [5] D. Yang, C. Li, M. Sharma, M. Li, J. Wang, J. Wei, K. Liu, Y. Zhang, J. Li, G. Henkelman, Q. Zhang, A. Cabot, Three birds with one arrow: Multifunctional single-atom catalysts enable efficient lithium-sulfur batteries, Energy Storage Mater. 66 (2024) 103240.
- [6] D. Yang, Z. Liang, C. Zhang, J.J. Biendicho, M. Botifoll, M.C. Spadaro, Q. Chen, M. Li, A. Ramon, A.O. Moghaddam, J. Llorca, J. Wang, J.R. Morante, J. Arbiol, S. L. Chou, A. Cabot, NbSe₂ meets C₂N: A 2D–2D heterostructure catalysts as multifunctional polysulfide mediator in ultra-long-life lithium-sulfur batteries, Adv. Energy Mater. 11 (2021) 2101250.
- [7] D. Yang, J. Wang, C. Lou, M. Li, C. Zhang, A. Ramon, C. Li, M. Tang, G. Henkelman, M. Xu, J. Li, J. Llorca, J. Arbiol, D. Mitlin, G. Zhou, A. Cabot, Single-atom catalysts with unsaturated Co–N₂ active sites based on a C₂N 2D-organic framework for efficient sulfur redox reaction, ACS Energy Lett. (2024) 2083–2091.
- [8] C. Huang, J. Yu, C.Y. Zhang, Z. Cui, J. Chen, W.H. Lai, Y.J. Lei, B. Nan, X. Lu, R. He, L. Gong, J. Li, C. Li, X. Qi, Q. Xue, J.Y. Zhou, X. Qi, L. Balcells, J. Arbiol, A. Cabot, Electronic spin alignment within homologous NiS(2)/NiSe(2) heterostructures to promote sulfur redox kinetics in lithium-sulfur batteries, Adv. Mater. (2024) e2400810.
- [9] C. Zhao, F. Huo, Y. Yang, J. Ruan, F. Chai, H. Xu, Y. Liu, L. Zhang, A. Cabot, Z. Sun, Y. Zhang, Development of synergistically efficient Ni–Co pair catalytic sites for enhanced polysulfide conversion in lithium-sulfur batteries, Adv. Funct. Mater. (2024) 2402175.
- [10] D. Yang, Y. Han, M. Li, C. Li, W. Bi, Q. Gong, J. Zhang, J. Zhang, Y. Zhou, H. Gao, J. Arbiol, Z. Shi, G. Zhou, A. Cabot, Highly conductive Quasi-1D hexagonal chalcogenide perovskite Sr8Ti7S21 with efficient polysulfide regulation in lithium-sulfur batteries, Adv. Funct. Mater. (2024) 2401577.
- [11] Y. Xiang, J. Li, J. Lei, D. Liu, Z. Xie, D. Qu, K. Li, T. Deng, H. Tang, Advanced separators for lithium-ion and lithium-sulfur batteries: A review of recent progress, ChemSusChem 9 (2016) 3023–3039.
- [12] C. Li, R. Liu, Y. Xiao, F. Cao, H. Zhang, Recent progress of separators in lithiumsulfur batteries, Energy Storage Mater. 40 (2021) 439–460.
- [13] T. Lei, W. Chen, W. Lv, J. Huang, J. Zhu, J. Chu, C. Yan, C. Wu, Y. Yan, W. He, J. Xiong, Y. Li, C. Yan, J.B. Goodenough, X. Duan, Inhibiting polysulfide shuttling with a graphene composite separator for highly robust lithium-sulfur batteries, Joule 2 (2018) 2091–2104.
- [14] Z.A. Ghazi, X. He, A.M. Khattak, N.A. Khan, B. Liang, A. Iqbal, J. Wang, H. Sin, L. Li, Z. Tang, MoS(2)/celgard separator as efficient polysulfide barrier for long-life lithium-sulfur batteries, Adv. Mater. 29 (2017) 1606817.
- [15] W. Wang, K. Xi, B. Li, H. Li, S. Liu, J. Wang, H. Zhao, H. Li, A.M. Abdelkader, X. Gao, G. Li, A sustainable multipurpose separator directed against the shuttle effect of polysulfides for high-performance lithium-sulfur batteries, Adv. Energy Mater. 12 (2022) 2200160.
- [16] H. Yao, K. Yan, W. Li, G. Zheng, D. Kong, Z.W. Seh, V.K. Narasimhan, Z. Liang, Y. Cui, Improved lithium–sulfur batteries with a conductive coating on the separator to prevent the accumulation of inactive S-related species at the cathode–separator interface, Energ. Environ. Sci. 7 (2014) 3381–3390.
- [17] C. Zhang, R. Du, S. Martí-Sánchez, K. Xiao, D. Yang, C. Zhang, C. Li, G. Zeng, X. Chang, R. He, J. Arbiol, J. Li, J. Jacas Biendicho, A. Cabot, Tubular C₃N₄

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nanotubes as metal-free sulfur hosts toward stable lithium-sulfur batteries, Energies 16 (2023) 4545.

- [18] C. Huang, J. Yu, C. Li, Z. Cui, C. Zhang, C. Zhang, B. Nan, J. Li, J. Arbiol, A. Cabot, Combined defect and heterojunction engineering in ZnTe/CoTe₂@NC sulfur hosts toward robust lithium-sulfur batteries, Adv. Funct. Mater. 33 (2023) 2305624.
- [19] M. Chen, H. Wang, J. Wang, M. Sun, Y. Hu, X. Zhao, Y. Zhou, Efficient degradation of formaldehyde based on DFT-screened metal-doped C(3)N(6) monolayer photocatalysts: Performance evaluation and mechanistic insights, PCCP 25 (2023) 25353–25360.
- [20] M. Chen, H. Zhang, H. Li, Z. Zhao, K. Wang, Y. Zhou, X. Zhao, D.P. Dubal, CxNybased materials as gas sensors: Structure, performance, mechanism and perspective, Coord. Chem. Rev. 503 (2024) 215653.
- [21] C. Zhang, B. Fei, D. Yang, H. Zhan, J. Wang, J. Diao, J. Li, G. Henkelman, D. Cai, J. J. Biendicho, J.R. Morante, A. Cabot, Robust lithium-sulfur batteries enabled by highly conductive WSe2-based superlattices with tunable interlayer space, Adv. Funct. Mater. 32 (2022) 2201322.
- [22] Z. Wei, Y. Ren, J. Sokolowski, X. Zhu, G. Wu, Mechanistic understanding of the role separators playing in advanced lithium-sulfur batteries, InfoMat 2 (2020) 483–508.
- [23] J. Feng, W. Liu, C. Shi, C. Zhang, X. Zhao, T. Wang, S. Chen, Q. Li, J. Song, Enabling fast diffusion/conversion kinetics by thiourea-induced wrinkled N, S Co-doped functional MXene for lithium-sulfur battery, Energy Storage Mater. 67 (2024) 103328.
- [24] C.Y. Zhang, C. Zhang, J.L. Pan, G.W. Sun, Z. Shi, C. Li, X. Chang, G.Z. Sun, J. Y. Zhou, A. Cabot, Surface strain-enhanced MoS₂ as a high-performance cathode catalyst for lithium-sulfur batteries, eScience 2 (2022) 405–415.
- [25] Z. Zhang, Y. Lai, Z. Zhang, K. Zhang, J. Li, Al₂O₃-coated porous separator for enhanced electrochemical performance of lithium sulfur batteries, Electrochim. Acta 129 (2014) 55–61.
- [26] X. Wang, N. Deng, Y. Liu, L. Wei, H. Wang, Y. Li, B. Cheng, W. Kang, Porous and heterostructured molybdenum-based phosphide and oxide nanobelts assisted by the structural engineering to enhance polysulfide anchoring and conversion for lithium-sulfur batteries, Chem. Eng. J. 450 (2022) 138191.
- [27] S. Huang, Y.V. Lim, X. Zhang, Y. Wang, Y. Zheng, D. Kong, M. Ding, S.A. Yang, H. Y. Yang, Regulating the polysulfide redox conversion by iron phosphide nanocrystals for high-rate and ultrastable lithium-sulfur battery, Nano Energy 51 (2018) 340–348.
- [28] Y. Zhong, L. Yin, P. He, W. Liu, Z. Wu, H. Wang, Surface chemistry in cobalt phosphide-stabilized lithium-sulfur batteries, J. Am. Chem. Soc. 140 (2018) 1455–1459.
- [29] C. Zhang, R. Du, J.J. Biendicho, M. Yi, K. Xiao, D. Yang, T. Zhang, X. Wang, J. Arbiol, J. Llorca, Y. Zhou, J.R. Morante, A. Cabot, Tubular CoFeP@CN as a Mott-Schottky catalyst with multiple adsorption sites for robust lithium–sulfur batteries, Adv. Energy Mater. 11 (2021) 2100432.
- [30] J.F. Callejas, C.G. Read, C.W. Roske, N.S. Lewis, R.E. Schaak, Synthesis, characterization, and properties of metal phosphide catalysts for the hydrogenevolution reaction, Chem. Mater. 28 (2016) 6017–6044.
- [31] X. Zhang, J. Yan, F. Zheng, J. Zhao, L.Y.S. Lee, Designing charge transfer route at the interface between WP nanoparticle and g-C₃N₄ for highly enhanced photocatalytic CO₂ reduction reaction, Appl. Catal. B 286 (2021) 119879.
 [32] J. Liu, X. Yu, R. Du, C. Zhang, T. Zhang, J. Llorca, J. Arbiol, Y. Wang, M. Meyns,
- [32] J. Liu, X. Yu, R. Du, C. Zhang, T. Zhang, J. Llorca, J. Arbiol, Y. Wang, M. Meyns, A. Cabot, Chromium phosphide CrP as highly active and stable electrocatalysts for oxygen electroreduction in alkaline media, Appl. Catal. B 256 (2019) 117846.
- [33] WC Nanocrystals Grown on Vertically Aligned Carbon Nanotubes: An Efficient and Stable Electrocatalyst for Hydrogen Evolution Reaction, 9 (5) 2015 5125-5134.
- [34] D. Vadivel, M. Sturini, A. Speltini, D. Dondi, Tungsten catalysts for visible light driven ofloxacin photocatalytic degradation and hydrogen production, Catalysts 12 (2022) 310.
- [35] B. Zhang, C. Luo, Y. Deng, Z. Huang, G. Zhou, W. Lv, Y.B. He, Y. Wan, F. Kang, Q. H. Yang, Optimized catalytic WS₂–WO₃ heterostructure design for accelerated

polysulfide conversion in lithium-sulfur batteries, Adv. Energy Mater. 10 (2020) 2000091.

- [36] Y. Wang, Y. Pu, L. Yuan, Y. Zhang, C. Liu, Q. Wang, H. Wu, Synergistic effect of WN/Mo(2)C embedded in bioderived carbon nanofibers: A rational design of a shuttle inhibitor and an electrocatalyst for lithium-sulfur batteries, ACS Appl. Mater. Interfaces 14 (2022) 18578–18588.
- [37] K. Xu, X. Fu, H. Li, Z. Peng, A novel composite of network-like tungsten phosphide nanostructures grown on carbon fibers with enhanced electrocatalytic hydrogen evolution efficiency, Appl. Surf. Sci. 456 (2018) 230–237.
- [38] C. Wu, Y. Zhu, C. Guan, C. Jia, W. Qin, X. Wang, K. Zhang, Mesoporous aluminium manganese cobalt oxide with pentahedron structures for energy storage devices, J. Mater. Chem. A 7 (2019) 18417–18427.
- [39] Y.-H. Liu, L.-X. Li, A.-Y. Wen, F.-F. Cao, H. Ye, A Janus MXene/MOF separator for the all-in-one enhancement of lithium-sulfur batteries, Energy Storage Mater. 55 (2023) 652–659.
- [40] C. Yin, Z. Li, D. Zhao, J. Yang, Y. Zhang, Y. Du, Y. Wang, Azo-branched covalent organic framework thin films as active separators for superior sodium-sulfur batteries, ACS Nano 16 (2022) 14178–14187.
- [41] P. Wang, Z. Zhang, N. Song, X. An, J. Liu, J. Feng, B. Xi, S. Xiong, WP nanocrystals on N, P dual-doped carbon nanosheets with deeply analyzed catalytic mechanisms for lithium-sulfur batteries, CCS Chem. 5 (2023) 397–411.
- [42] J. Huang, N. Wang, J. Wang, N. Huang, M. Bayati, T. Xiaoteng Liu, Nitrogen, phosphorus co-doped porous carbon originated from egg white for advanced lithium-sulfur battery, J. Electroanal. Chem. 894 (2021) 115362.
- [43] D. Yang, M. Li, X. Zheng, X. Han, C. Zhang, J. Jacas Biendicho, J. Llorca, J. Wang, H. Hao, J. Li, G. Henkelman, J. Arbiol, J.R. Morante, D. Mitlin, S. Chou, A. Cabot, Phase engineering of defective copper selenide toward robust lithium-sulfur batteries, ACS Nano 16 (2022) 11102–11114.
- [44] J. Feng, C. Shi, H. Dong, C. Zhang, W. Liu, Y. Liu, T. Wang, X. Zhao, S. Chen, J. Song, Design of ZnSe-CoSe heterostructure decorated in hollow N-doped carbon nanocage with generous adsorption and catalysis sites for the reversibly fast kinetics of polysulfide conversion, J. Energy Chem. 86 (2023) 135–145.
- [45] Z. Chang, W. Liu, J. Feng, Z. Lin, C. Shi, T. Wang, Y. Lei, X. Zhao, J. Song, G. Wang, Cobalt/MXene-derived TiO₂ heterostructure as a functional separator coating to trap polysulfide and accelerate redox kinetics for reliable lithium-sulfur battery, Batteries Supercaps 7 (2024) e202300516.
- [46] M. Li, D. Yang, J.J. Biendicho, X. Han, C. Zhang, K. Liu, J. Diao, J. Li, J. Wang, M. Heggen, R.E. Dunin-Borkowski, J. Wang, G. Henkelman, J.R. Morante, J. Arbiol, S.L. Chou, A. Cabot, Enhanced polysulfide conversion with highly conductive and electrocatalytic iodine-doped bismuth selenide nanosheets in lithium-sulfur batteries, Adv. Funct. Mater. 32 (2022) 2200529.
- [47] H. Pan, Z. Cheng, Z. Zhou, S. Xie, W. Zhang, N. Han, W. Guo, J. Fransaer, J. Luo, A. Cabot, M. Wubbenhorst, Boosting lean electrolyte lithium-sulfur battery performance with transition metals: A comprehensive review, Nanomicro Lett 15 (2023) 165.
- [48] Z. Su, W. Qiu, Y. He, Y. Zeng, D. Xie, X. Xiao, J. Nan, X. Zuo, A strontium ferrite modified separator for adsorption and catalytic conversion of polysulfides for excellent lithium-sulfur batteries, Dalton Trans. 52 (2023) 9032–9041.
- [49] D. Xie, X. Zuo, Z. Su, T. Zhu, S. Liu, X. Xiao, J. Nan, A natural polymer modified separator as a barrier in lithium-sulfur batteries to inhibit the shuttle of polysulfides, Energ. Technol. 10 (2022) 2101142.
- [50] L. Shen, Y.-W. Song, J. Wang, C.-X. Zhao, C.-X. Bi, S.-Y. Sun, X.-Q. Zhang, B.-Q. Li, Q. Zhang, Synergistic catalysis on dual-atom sites for high-performance lithiumsulfur batteries, Small Structures 4 (2022) 2200205.
- [51] C.Y. Zhang, C. Zhang, G.W. Sun, J.L. Pan, L. Gong, G.Z. Sun, J.J. Biendicho, L. Balcells, X.L. Fan, J.R. Morante, J.Y. Zhou, A. Cabot, Spin effect to promote reaction kinetics and overall performance of lithium-sulfur batteries under external magnetic field, Angew. Chem. Int. Ed. Engl. 61 (2022) e202211570.