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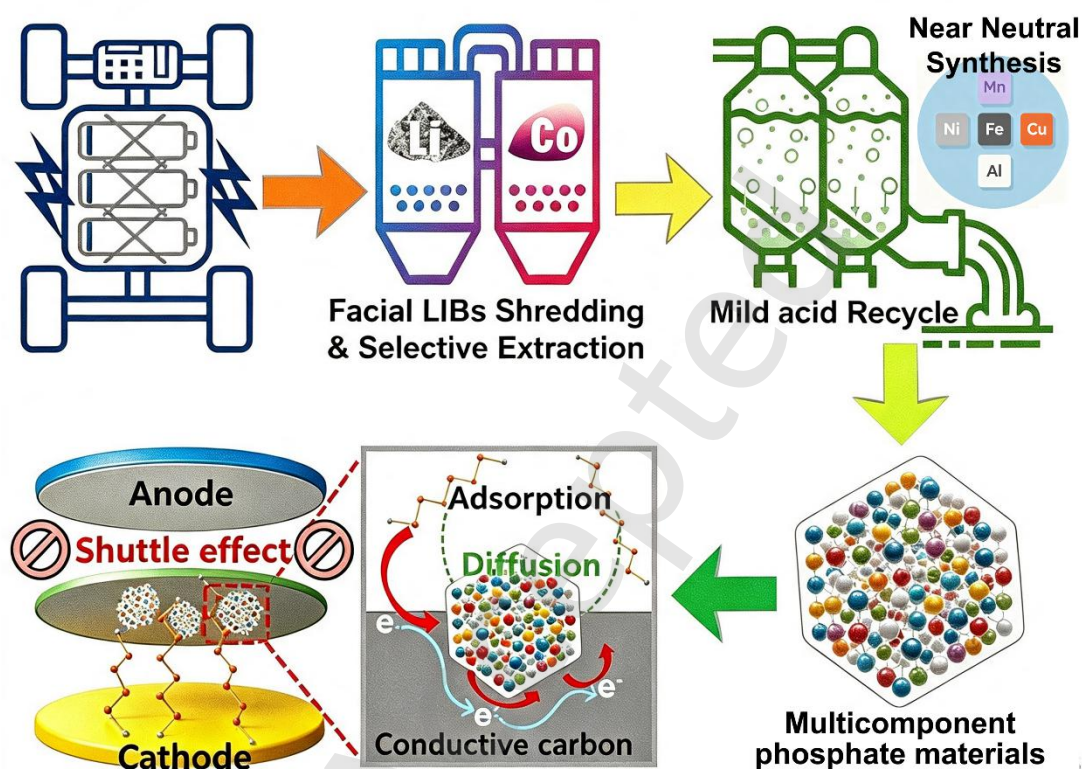
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TOC for **Upcycling Spent Lithium-Ion Batteries into Multicomponent Phosphate**
Catalysts for Enhanced Sulfur Redox Kinetics in Lithium-Sulfur Batteries



A mild-acid, non-dismantling strategy to selectively separate and upcycle spent LIBs into multi-metal phosphates was reported. Benefiting from synergistic electronic modulation, the obtained cathode enables high-loading Li-S cells with exceptional capacity and ultra-stable cycling.

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Abstract

The growing accumulation of spent lithium-ion batteries (LIBs) presents significant environmental challenges, while the complex composition of battery waste complicates efficient resource recovery. Herein, a phosphoric acid-assisted upcycling strategy is developed to recover multimetallic constituents from spent LIBs and reconstruct them into multicomponent phosphate (R-MCP) catalysts for lithium-sulfur batteries, reducing the need for extensive component separation. The resulting R-MCP, containing Ni, Mn, Fe, Cu, and Al, exhibits favorable polysulfide adsorption and sulfur-conversion behavior compared with recycled Ni-Mn-Fe phosphate (R-NMP). Experimental characterizations and density functional theory calculations provide insights into the electronic interactions and favorable sulfur redox kinetics of R-MCP. Consequently, the R-MCP modified separator delivers an initial capacity of

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1075 mAh g⁻¹ at 0.5 C and stable cycling over 2000 cycles at 1 C, with a capacity

decay rate of 0.029% per cycle. Stable cycling is also achieved at a sulfur loading of 10.14 mg cm⁻². This work demonstrates a practical route for converting multimetallic battery waste into functional catalytic materials.

Keywords : Spent lithium-ion batteries; Waste upcycling; Multicomponent phosphates; Lithium-sulfur batteries; Polysulfide conversion.

1.Introduction

The rapid expansion of electric vehicles and energy storage systems has substantially increased the demand for lithium-ion batteries (LIBs), inevitably generating growing quantities of spent batteries.[1-3] The accumulation of end-of-life LIBs poses significant environmental challenges while creating opportunities for resource recovery. Conventional recycling approaches, mainly including pyrometallurgical and hydrometallurgical processes, generally involve high energy consumption, chemical-intensive treatments, and complicated metal separation procedures. Moreover, the presence of multiple transition metals and impurities originating from current collectors further increases the complexity of recovering valuable components.[4-8] Therefore, developing effective strategies for the high value utilization of compositionally complex battery waste is of considerable importance.

Recent advances in spent LIBs recycling have shifted increasing attention toward direct regeneration and functional material upcycling. Chen et al. regenerated degraded Nickel-Cobalt-Manganese cathodes through structural restoration and surface engineering, achieving improved electrochemical performance.[9] Wang et al. further revealed the thermally induced structural reconstruction of degraded LiCoO_2 , providing insights into cathode regeneration.[10] Beyond restoring conventional cathode materials, Zhang et al. converted spent LiCoO_2 into $\text{CoP}_2/\text{Co}_3\text{O}_4$ electrocatalysts for water electrolysis, demonstrating the potential of waste-derived materials for alternative energy applications.[11] Nevertheless, existing strategies frequently emphasize the recovery of individual metals or the restoration of original electrode structures. The intrinsic multimetallic composition of spent LIBs provides an alternative opportunity for constructing functional materials with diverse metal coordination environments, potentially extending their value beyond conventional recycling.

Lithium–sulfur (Li-S) batteries have attracted considerable attention owing to their high theoretical specific capacity (1675 mAh g^{-1}), high energy density (2600 Wh kg^{-1}), and abundant sulfur resources.[12] However, sluggish sulfur redox kinetics and the shuttle effect of soluble lithium polysulfides (LiPSs) severely hinder their practical applications. Functional separator modification has emerged as an effective strategy to immobilize LiPSs and accelerate their conversion. Recently, multicomponent catalysts have demonstrated promising performance in regulating sulfur redox reactions. Raza et al. developed multimetallic oxide and sulfide catalysts that facilitated LiPS conversion and improved cycling stability.[13, 14] Related advances have further highlighted the potential of compositionally complex materials for Li-S batteries.[15] Guo et al. demonstrated that metal-phosphorus orbital interactions could regulate sulfur conversion kinetics, while Qiu et al. further improved catalytic activity by tailoring electronic coupling in multimetallic phosphides.[16, 17] Similarly, Zhu et al. developed a single-atom alloy catalyst for separator modification, emphasizing the importance of interfacial electronic interactions in LiPS conversion.[18] Despite these advances, the utilization of spent LIBs-derived multimetallic phosphates for regulating sulfur electrochemistry remains relatively underexplored. Their diverse metal-oxygen coordination environments offer opportunities to investigate composition-dependent electronic interactions and catalytic behavior.[19, 20]

Herein, we present a resource valorization strategy to convert multimetallic constituents from spent LIBs into phosphate based functional materials for Li–S battery separators. A recycled multicomponent phosphate (R-MCP) containing Ni, Mn, Fe, Cu, and Al is prepared and compared with a recycled Ni-Mn-Fe phosphate (R-NMP). Combined experimental characterization and density functional theory calculations suggest that compositional and structural differences between R-MCP and R-NMP are associated with variations in their local electronic environments and sulfur-conversion behavior. In the investigated computational models, R-MCP exhibits a lower calculated Li_2S decomposition energy barrier than R-NMP.

Benefiting from improved polysulfide regulation and conversion kinetics, the R-MCP-modified separator enables an initial discharge capacity of 1075 mAh g⁻¹ at 0.5 C and prolonged cycling over 2000 cycles at 1 C, with a reported capacity decay rate of 0.029% per cycle. This work provides a promising approach for converting compositionally complex battery waste into functional catalytic interfaces for advanced energy storage systems.

2. Result and discussion

2.1 Upcycling Strategy and Structural Characterization of Waste-Derived Phosphates

A phosphoric-acid-assisted upcycling strategy was developed to convert multimetallic constituents from spent LIBs black mass into phosphate-based functional materials for Li-S battery separators (Figure 1a). Following thermal pretreatment and selective phosphoric acid leaching, the recovered metal-containing residues were subjected to hydrothermal reconstruction in the presence of graphene oxide. This approach enables the utilization of compositionally complex waste-derived metal species without requiring complete separation of individual transition metals. To further contextualize the proposed upcycling strategy, representative approaches for the recycling and high-value utilization of spent LIBs cathode materials are summarized in (Table S2).[21-25] Unlike conventional strategies primarily focused on metal recovery or cathode regeneration, the present work explores the conversion of waste-derived multimetallic constituents into functional phosphate-based materials for Li-S battery separators. By utilizing the compositional complexity of spent battery waste, this approach provides an alternative pathway for resource valorization without requiring complete separation of individual transition metals.

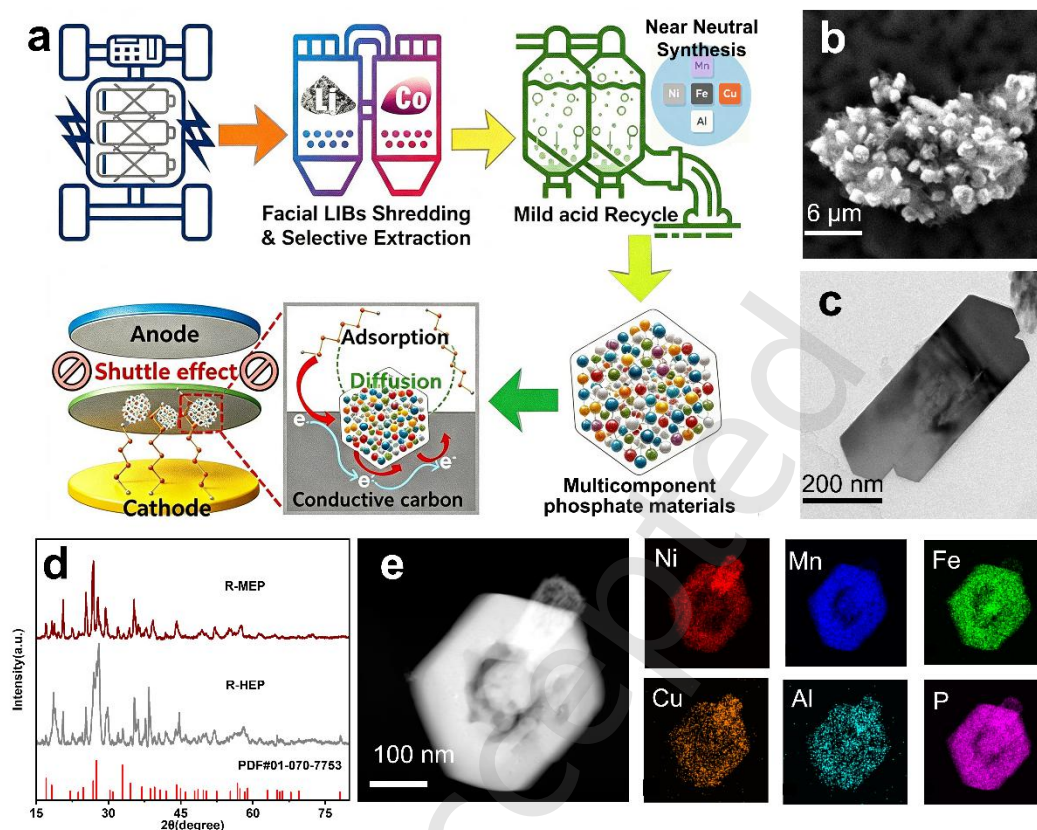


Figure 1. Upcycling strategy and structural characterization of R-MCP. (a) Schematic illustration of the phosphoric-acid-assisted recovery and reconstruction process for converting spent LIBs-derived multimetallic constituents into phosphate-based separator materials for Li-S batteries. (b) SEM image of R-MCP. (c) TEM image showing the faceted crystalline morphology. (d) XRD patterns of R-MCP and R-NMP. (e) HRTEM image and corresponding elemental mapping of Ni, Mn, Fe, Cu, Al and P.

The crystalline structures were further characterized by X-ray diffraction (XRD, Figure 1d). The major diffraction reflections are consistent with the reference phosphate structure (PDF#01-070-7753), indicating the formation of crystalline phosphate phases. Notably, additional reflections at approximately 20.5° and 34.7° are observed. The reflection near 20.5° may be associated with minor manganese-containing phosphate phases, while the peak around 34.7° may originate from spinel-type transition-metal oxides, such as Fe_3O_4 , MnFe_2O_4 , and NiFe_2O_4 . [26,

27] Given the overlap of characteristic diffraction peaks among these possible phases, their precise identification remains uncertain. These observations suggest that the recycled products predominantly contain crystalline phosphate phases, accompanied by possible minor secondary crystalline components. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Figures 1b, 1c, S3, and S4) reveal faceted particles with well-defined morphologies. The corresponding high-resolution transmission electron microscopy (HRTEM) images further exhibit lattice fringes, supporting local crystalline ordering in the reconstructed materials. These structural observations provide morphological information on the recovered phosphates, although the contribution of particle morphology to electron transport requires separate electrochemical evaluation

To examine the carbon-related surface chemistry of the reconstructed materials, C 1s X-ray photoelectron spectroscopy (XPS) spectra were collected for R-MCP and R-NMP (Figure S10). Both samples exhibit a dominant C-C/C=C component near 284.8 eV and additional oxygen containing carbon components, consistent with the presence of carbonaceous species in the final products. As graphene oxide (GO) was introduced during hydrothermal synthesis, these signals may be associated with retained GO derived carbonaceous constituents. Thermogravimetric analysis (TGA) measurements under nitrogen (Figure S11) further reveal differences in the mass-loss behavior of R-MCP, R-NMP, and pristine GO. These results provide complementary information about the surface carbon species and thermal characteristics of the materials, although the degree of GO reduction and its quantitative contribution to the final products cannot be established from these measurements alone.

The electrolyte wettability of the modified separators was subsequently evaluated by contact-angle measurements (Figure S7). The R-MCP-coated separator exhibits a contact angle of only 25.2°, substantially smaller than those of R-NMP (41.4°) and the pristine polypropylene (PP) separator (48.0°), indicating significantly enhanced electrolyte affinity. The separator thickness is approximately 40 μm, while the

functional coating possesses a thickness of about 15 μm (Figure S8). The improved electrolyte wettability ensures sufficient exposure of catalytically active sites on the R-MCP surface, enabling rapid adsorption and conversion of soluble LiPSs, suppressing reaction polarization, and ultimately contributing to enhanced rate capability and long-term cycling stability.

The textural properties of the reconstructed phosphates were further characterized by Brunauer-Emmett-Teller (BET) (Figure S9). Both R-MCP and R-NMP exhibit adsorption features associated with mesopores and interparticle voids, as also suggested by their corresponding pore-size distributions. Notably, R-MCP exhibits a higher N_2 uptake of $42.84 \text{ cm}^3 \text{ g}^{-1}$ (STP) at a relative pressure (P/P_0) of approximately 0.99, compared with $24.66 \text{ cm}^3 \text{ g}^{-1}$ (STP) for R-NMP, suggesting a larger accessible pore volume. Combined with its improved electrolyte wettability, the favorable porous characteristics of R-MCP may enhance electrolyte penetration and facilitate interfacial contact between soluble lithium polysulfides (LiPSs) and catalytic surfaces during sulfur redox reactions.

2.2 Polysulfide Adsorption Behavior and Catalytic Conversion Mechanism

To evaluate the capability of the reconstructed phosphates to immobilize soluble LiPSs, visual adsorption experiments combined with ultraviolet-visible (UV-vis) spectroscopy were performed (Figure 2a). After introducing R-MCP into the Li_2S_6 solution, the originally dark-yellow solution became nearly colorless, whereas only partial decolorization was observed for R-NMP. Consistently, the characteristic absorption bands of soluble LiPSs in the UV-vis spectra were dramatically suppressed after adsorption by R-MCP, indicating its substantially stronger affinity toward LiPS species. The pronounced decrease in the characteristic LiPSs absorption signals indicates that R-MCP exhibits stronger apparent polysulfide uptake than R-NMP under the investigated conditions, suggesting its potential to reduce the concentration of soluble sulfur intermediates.

To elucidate the origin of the enhanced adsorption behavior, XPS was carried out before and after Li_2S_6 adsorption (Figures 2b–2d). Pronounced binding-energy shifts were observed for the Ni, Mn, and Fe species after adsorption, indicating strong electronic interactions between the transition-metal active centers and sulfur-containing intermediates. Similar binding-energy shifts were also detected for Cu and Al (Figure S12). The binding-energy variations of Ni, Mn, Fe, Cu, and Al following Li_2S_6 exposure suggest changes in their local electronic environments, consistent with interactions between the R-MCP surface and sulfur-containing species. Compared with R-NMP, the more pronounced spectral changes observed for R-MCP suggest differences in interfacial interactions. These observations are consistent with the stronger apparent polysulfide uptake of R-MCP, although the independent contributions of individual metal species cannot be isolated from the present XPS results.

Density functional theory (DFT) calculations were further performed to quantitatively evaluate the interaction between the catalyst surface and sulfur intermediates (Figure 2e). Throughout the complete sulfur reduction pathway, including Li_2S_8 , Li_2S_4 , Li_2S_2 , and Li_2S , R-MCP consistently exhibits more negative adsorption energies than R-NMP, confirming its intrinsically stronger chemical affinity toward LiPSs. Such optimized adsorption strengths not only suppress the dissolution and migration of soluble sulfur intermediates during long-term cycling but also stabilize reaction intermediates at the catalyst surface, thereby creating favorable interfacial environments for subsequent electrocatalytic conversion.

The catalytic activity toward sulfur conversion was subsequently investigated through Li_2S nucleation experiments (Figure 2f). Among all investigated samples, R-MCP delivers the largest Li_2S precipitation capacity together with the fastest nucleation kinetics. Specifically, the deposited Li_2S capacity reaches $203.31 \text{ mAh g}^{-1}$, which is substantially higher than that of R-NMP (11.86 mAh g^{-1} , Figure S14). The substantially higher Li_2S deposition capacity observed for R-MCP suggests more

favorable Li_2S precipitation behavior under the investigated conditions, consistent with its enhanced sulfur conversion performance.

The influence of R-MCP on lithium deposition behavior was further evaluated using symmetric $\text{Li}||\text{Li}$ cells (Figure 2g). The cell with R-MCP-modified separator maintains remarkably stable voltage polarization for over 1500 h, significantly outperforming R-NMP (1000 h) and the pristine Polypropylene (PP) separator (750 h). The prolonged cycling stability indicates that R-MCP effectively homogenizes Li-ion flux and promotes uniform lithium deposition, thereby suppressing the formation of lithium dendrites and enhancing the interfacial stability of lithium metal anodes.

To investigate the evolution of sulfur species during discharge, in situ Raman spectroscopy was performed using cells equipped with R-MCP and R-NMP-modified separators (Figures 2h–2j). The characteristic Raman bands near 150, 210, and 470cm^{-1} are associated with elemental sulfur (S_8). As discharge proceeds, the intensities of these bands gradually decrease, accompanied by the appearance of a signal near 410 cm^{-1} , which is assigned to soluble polysulfide intermediates. Compared with the R-NMP based cell, the R-MCP based cell exhibits an earlier but less pronounced intermediate related Raman signal, together with faster attenuation of the S_8 bands. These observations suggest differences in the evolution and accumulation of soluble sulfur species during discharge, consistent with more favorable polysulfide regulation and conversion behavior in the presence of R-MCP.

The combined adsorption experiments, XPS analysis, DFT calculations, Li_2S precipitation measurements, and in situ Raman characterization suggest that R-MCP exhibits favorable polysulfide immobilization and sulfur-conversion behavior under the investigated conditions.

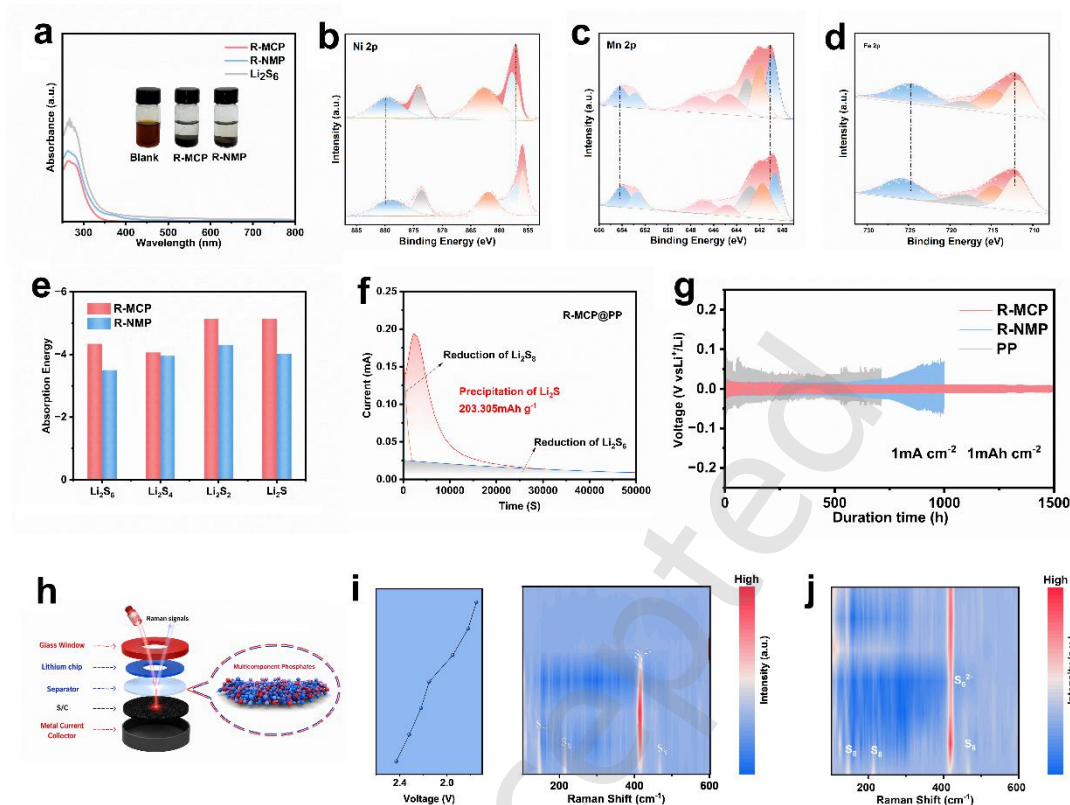


Figure 2. Polysulfide adsorption behavior and electrochemical conversion characteristics of R-MCP and R-NMP. (a) Visual adsorption test and corresponding UV-Vis absorption spectra of Li_2S_6 solutions after treatment with R-MCP and R-NMP. (b–d) High-resolution XPS spectra of Ni 2p, Mn 2p and Fe 2p before and after Li_2S_6 adsorption. (e) DFT-calculated adsorption energies of Li_2S_8 , Li_2S_4 , Li_2S_2 and Li_2S on R-MCP and R-NMP. (f) Li_2S nucleation test of the R-MCP@PP separator. (g) Galvanostatic cycling performance of Li symmetric cells assembled with R-MCP, R-NMP and PP. (h) Schematic illustration of the in-situ Raman configuration. (i) In situ Raman spectra of R-MCP during discharge; (j) In situ Raman spectra of R-NMP during discharge.

2.3 Electronic-Structure Modulation and Catalytic Mechanism Revealed by Density Functional Theory

To investigate the differences in sulfur-conversion behavior between R-MCP and R-NMP, DFT calculations were performed to examine their interfacial electronic interactions and reaction energetics. As shown in Fig. 3a, the charge-density difference (CDD) distributions and Bader charge analysis reveal distinct charge

redistribution upon the adsorption of Li_2S , Li_2S_2 , Li_2S_4 , and Li_2S_6 on the two catalyst surfaces. Overall, R-MCP exhibits larger calculated charge-transfer magnitudes than R-NMP for the investigated sulfur-containing species, suggesting stronger interfacial electronic interactions in the representative R-MCP model.

To further investigate the local electronic environments of the two phosphate models, Bader charge and electron localization function (ELF) analyses were performed. As illustrated in Figs. 3c, d, f, and g, the R-MCP model contains 16 oxygen atoms with an average Bader net charge of $-0.650 |e|$, corresponding to a total net charge of approximately $-10.40 |e|$. The average Bader net charges of Al, Mn, Fe, Ni, and Cu atoms in R-MCP are $+1.459$, $+0.695$, $+0.608$, $+0.385$, and $+0.253 |e|$, respectively. Notably, the three oxygen atoms coordinated to Al exhibit net charges ranging from -0.795 to $-0.875 |e|$. The calculated ELF values at the Al-O, Fe-O, Ni-O, Mn-O, and Cu-O bond midpoints are 0.81 , 0.42 , 0.39 , 0.32 , and 0.27 , respectively, indicating distinct degrees of local electron localization among different metal-oxygen bonds.

In comparison, the R-NMP model contains 12 oxygen atoms with an average Bader net charge of $-0.778 |e|$, corresponding to a total net charge of approximately $-9.33 |e|$. The average Bader net charges of Mn, Fe, and Ni atoms are $+0.663$, $+0.435$, and $+0.172 |e|$, respectively, while the corresponding ELF values at the Mn-O, Fe-O, and Ni-O bond midpoints are 0.28 , 0.37 , and 0.36 . These results reveal composition-dependent differences in local charge distributions and metal-oxygen bonding characteristics. In particular, the additional Al- and Cu-containing coordination environments in R-MCP contribute to a more diverse local electronic environment. Such electronic heterogeneity may influence the interfacial interactions with sulfur-containing intermediates, consistent with the distinct charge redistribution observed in the adsorption calculations.

The calculated sulfur-conversion energetics further reveal differences between the two catalyst models. As shown in (Fig. 3b), the climbing-image nudged elastic band (CI-NEB) calculations yield Li_2S decomposition barriers of 0.44 and 0.79 eV for R-MCP and R-NMP, respectively, suggesting a kinetically more favorable Li_2S decomposition pathway on R-MCP. The Gibbs free-energy profiles in Fig. 3e provide additional insights into the thermodynamics of sulfur reduction. For R-MCP, the Li_2S_4 to Li_2S_2 and Li_2S_2 -to- Li_2S steps involve uphill free-energy changes of 0.62 and 0.59 eV, respectively. In contrast, R-NMP exhibits a free-energy decrease of 0.55 eV during Li_2S_4 to Li_2S_2 conversion, followed by a larger uphill change of 1.35 eV for the subsequent Li_2S_2 to Li_2S step. The smaller free energy increase in the final reduction step on R-MCP suggests more favorable thermodynamics for Li_2S formation from Li_2S_2 . Together, these results indicate distinct reaction energetics for sulfur conversion on the two representative catalyst surfaces.

The projected density of states (PDOS) analysis was further performed to investigate the electronic structures of R-MCP and R-NMP (Figure 3h and Figure S17). The two models exhibit distinct distributions of metal-derived electronic states, reflecting differences in their local coordination environments. Notably, the calculated d-band center of R-MCP (-0.75 eV) is closer to the Fermi level than that of R-NMP (-0.90 eV), indicating a relative shift in the distribution of metal d states. Such electronic-structure differences may influence the interfacial interactions with sulfur-containing intermediates, consistent with the calculated charge redistribution and adsorption behavior. Overall, the DFT results reveal differences in local electronic environments and sulfur-conversion energetics between the two representative catalyst models, which are qualitatively consistent with the experimentally observed electrochemical kinetic trends.

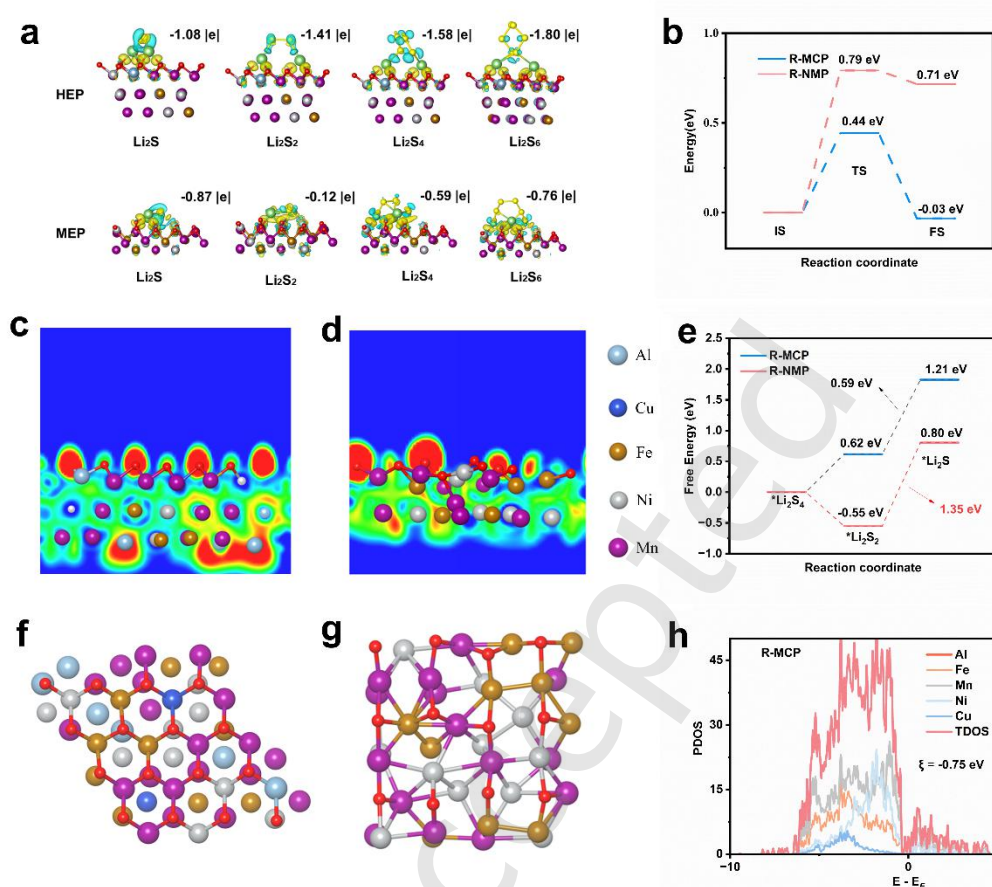


Figure 3. DFT calculations for understanding the catalytic mechanism of R-MCP and R-NMP. (a) Charge-density difference distributions of Li_2S , Li_2S_2 , Li_2S_4 and Li_2S_6 adsorbed on R-MCP and R-NMP surfaces; the corresponding charge-transfer values are labeled. (b) Energy profiles for the Li_2S decomposition reaction on R-MCP and R-NMP. (c, d) Cross-sectional two-dimensional electron density distribution of R-MCP and R-NMP systems. (e) Gibbs free-energy diagrams for the sulfur reduction reaction on R-MCP and R-NMP. (f, g) Molecular configuration of the Bader charge for R-MCP (left) and R-NMP (right). (h) Projected density of states (PDOS) of R-MCP.

2.4 Electrochemical Kinetic Evaluation of R-MCP-Modified Separators

To further evaluate the electrochemical kinetic behavior of R-MCP-modified separators, cyclic voltammetry (CV), galvanostatic intermittent titration technique (GITT), and temperature-dependent electrochemical impedance spectroscopy (EIS) were conducted.

The electrochemistry (EC) behavior of the cells was first investigated over a scan-rate range of 0.1-0.5 mV s⁻¹ (Figure S18). All cells exhibit two cathodic peaks and one anodic peak, corresponding to the stepwise reduction of elemental sulfur to soluble LiPSs, followed by the formation of insoluble Li₂S₂/Li₂S and the subsequent oxidation process during charging.[28, 29] As the scan rate increases, the oxidation and reduction peak positions of the R-MCP cell remain remarkably stable, whereas substantially larger peak shifts are observed for both R-NMP and the pristine PP separator, indicating reduced electrochemical polarization in the R-MCP based cell. These observations are fully consistent with the two-dimensional CV contour plots shown in (Figures 4a-4c), where R-MCP maintains the smallest peak displacement throughout the entire scan-rate range, demonstrating substantially faster sulfur redox kinetics.

To further evaluate the electrochemical kinetics, the relationship between the CV peak currents and the square root of the scan rate was analyzed using the Randles-Ševčík relationship (Figure S19). Considering the complex multiphase sulfur conversion reactions, the fitted slopes were used as semi-quantitative indicators of apparent electrochemical kinetic behavior rather than direct measures of intrinsic Li⁺ diffusion coefficients. The oxidation peak of the R-MCP cell exhibits the highest absolute fitting slope of 335.62, exceeding those of R-NMP (301.23) and PP (151.69), suggesting more favorable oxidation kinetics during the charging process. Similar trends are observed for both reduction peaks, with fitting slopes of -133.15 and 190.13 for R-MCP, compared with -116.94 and -151.80 for R-NMP and -77.81 and -74.02 for PP, respectively. These results indicate more favorable scan-rate-dependent redox responses for the R-MCP-based cell during both reduction and oxidation processes. Such electrochemical behavior may be associated with differences in the porous structure, electrolyte accessibility, and interfacial interactions of the reconstructed phosphate materials.[30]

The dynamic lithium-ion diffusion behavior was further examined using the galvanostatic intermittent titration technique Galvanostatic intermittent titration technique (GITT) (Figures 4d-4f), the R-MCP cell consistently exhibits the smallest voltage polarization throughout both discharge and charge processes, suggesting significantly reduced kinetic resistance during sulfur conversion. The corresponding Li^+ diffusion coefficients calculated from the GITT profiles are summarized in (Figure S20). Across nearly the entire discharge process, R-MCP maintains the highest diffusion coefficients among all investigated samples, followed by R-NMP and the pristine PP separator. The GITT results reveal differences in the apparent ion-transport behavior among the investigated cells, which are broadly consistent with the electrochemical trends observed in the CV analysis. Such enhanced diffusion kinetics are particularly beneficial for sustaining rapid EC reactions under high current densities.

To further evaluate the interfacial charge-transfer kinetics, temperature-dependent EIS measurements were conducted over a wide temperature range (Figures 4g–4i). As shown in (Figure S21), the apparent activation energies (E_a) were derived by fitting the temperature-dependent curves of $\log(1/R_{ct})$ versus $1/T$ according to the Arrhenius relationship. The calculated E_a values for R-MCP, R-NMP, and PP are 50.449, 61.498, and 70.416 kJ mol^{-1} , respectively. Notably, R-MCP exhibits the lowest E_a , corresponding to a reduction of approximately 28.4% compared with the pristine PP separator. This lower activation energy indicates a reduced kinetic barrier for interfacial charge transfer, thereby contributing to more favorable sulfur redox kinetics.

Overall, the CV, GITT, and temperature-dependent EIS results indicate more favorable electrochemical kinetics in the R-MCP-based cells, with the experimental trends being qualitatively consistent with the theoretical predictions.

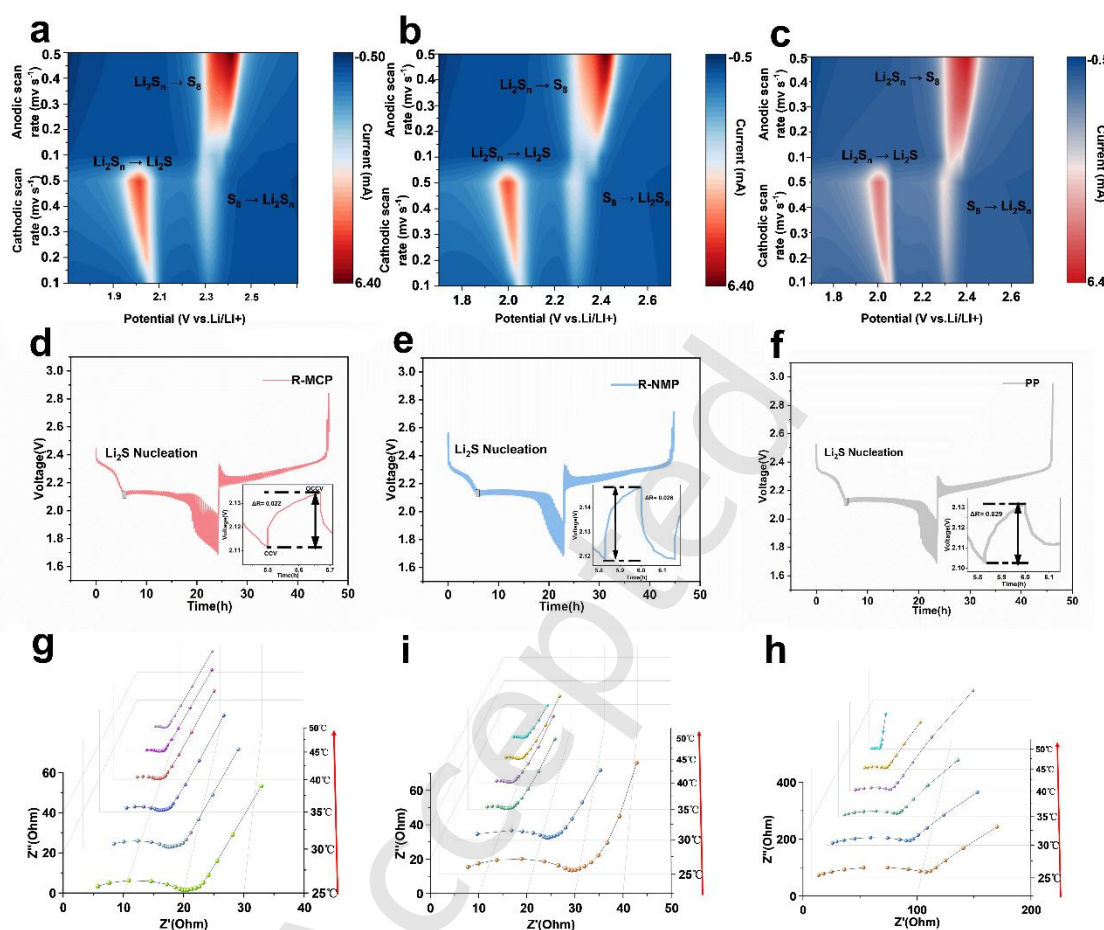


Figure 4. EC kinetics analysis of Li-S batteries with different separators. (a-c) Cyclic voltammetry (CV) contour maps of cells employing R-MCP, R-NMP and PP separators at different scan rates. (d-f) Galvanostatic intermittent titration technique (GITT) profiles of the corresponding cells, with enlarged voltage regions shown in the insets. (g-i) Temperature-dependent EIS Nyquist plots of cells with R-MCP, R-NMP, and PP separators, respectively.

2.5 EC Performance under Practical Operating Conditions

The electrochemical performance of Li-S batteries employing different separators was systematically evaluated to investigate the effects of the R-MCP-modified separator on polysulfide regulation, sulfur redox conversion, and interfacial electrochemical behavior. Figure 5a compares the long-term cycling performance at 0.5 C. Benefiting from the synergistic LiPSs immobilization and catalytic conversion

enabled by R-MCP, the corresponding cell delivers an initial discharge capacity exceeding $1075.14 \text{ mAh g}^{-1}$ and retains approximately $707.29 \text{ mAh g}^{-1}$ after 300 cycles, significantly outperforming both R-NMP and the pristine PP separator. More importantly, the Coulombic efficiency remains consistently close to 100% throughout the entire cycling process, indicating highly reversible sulfur redox reactions and effective suppression of the LiPSs shuttle effect. These results indicate that R-MCP functions beyond a conventional physical barrier, instead serving as an active catalytic interface that continuously regulates sulfur species during cycling.

The corresponding galvanostatic charge–discharge profiles are presented in Figure 5b. All cells exhibit the characteristic two-stage discharge plateaus associated with the sequential reduction of elemental sulfur to soluble LiPSs and finally to insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$. Notably, the R-MCP cell displays a considerably smaller charge–discharge voltage gap (ΔE) than the comparison cells, reflecting substantially reduced EC polarization. The reduced polarization observed for the R-MCP-based cell is consistent with its favorable polysulfide adsorption and sulfur-conversion behavior, as indicated by the complementary electrochemical and characterization results. Consistently, the initial charge–discharge profiles at 0.1 C (Figure S22) show that the R-MCP-based cell delivers a higher discharge capacity and a more extended discharge plateau than the R-NMP, GO, and PP counterparts. The favorable voltage characteristics are consistent with the reduced polarization observed in Figure 5b, further supporting the beneficial role of R-MCP in sulfur redox reactions.

To further evaluate the feasibility of R-MCP under practically relevant conditions, EC tests were performed using high sulfur loading and lean electrolyte configurations. As shown in Figure 5c, when the sulfur loading reaches 10.14 mg cm^{-2} with an electrolyte-to-sulfur (E/S) ratio as low as $3.94 \text{ }\mu\text{L mg}^{-1}$, the R-MCP cell still maintains a capacity retention of 83.64% after 120 cycles at 0.2 C, demonstrating remarkable EC stability under stringent operating conditions. When the sulfur loading is adjusted

to approximately 9.05 mg cm^{-2} , the cell delivers even higher reversible capacities while maintaining excellent cycling stability, further demonstrating the electrochemical stability of the R-MCP-modified separator under the investigated conditions.

To verify the durability of the catalyst under high sulfur loading, additional cycling tests were conducted at both 1 C (Figure S23) and 0.5 C (Figure S24). Even under these demanding conditions, the R-MCP-modified separator sustains stable cycling for 200 cycles at 1 C and 120 cycles at 0.5 C while maintaining high capacity retention. Furthermore, the corresponding rate capability and galvanostatic charge–discharge profiles shown in (Figures S25) demonstrate highly reversible voltage plateaus with only limited polarization over a broad current density range. These results indicate that the catalytic interface remains highly active even when both sulfur loading and current density are simultaneously increased.

The favorable electrochemical performance observed under relatively lean-electrolyte and high-sulfur-loading conditions highlights the potential of R-MCP-based separator modification for Li-S batteries operated under more demanding conditions. Under practical operating conditions, sluggish sulfur conversion and severe LiPSs accumulation are generally intensified because of the limited electrolyte supply and increased sulfur utilization. Nevertheless, the R-MCP catalyst effectively overcomes these challenges through its integrated adsorption–catalysis mechanism. The adsorption affinity of R-MCP may help reduce the migration of soluble LiPSs, while its interfacial interactions with sulfur intermediates are consistent with the improved electrochemical conversion behavior.

Consequently, rapid electron transfer, efficient Li^+ transport, and highly reversible sulfur chemistry can be simultaneously maintained, allowing the battery to preserve excellent EC performance even under practically relevant conditions.

These results demonstrate that the superior catalytic activity of R-MCP is not limited to conventional low loading laboratory tests but remains effective under realistic electrode configurations with high sulfur loading and lean electrolyte supply. These results indicate that the R-MCP-modified separator retains favorable electrochemical performance across the investigated sulfur-loading and electrolyte conditions, providing a basis for further evaluation of its long-term cycling and rate capabilities.

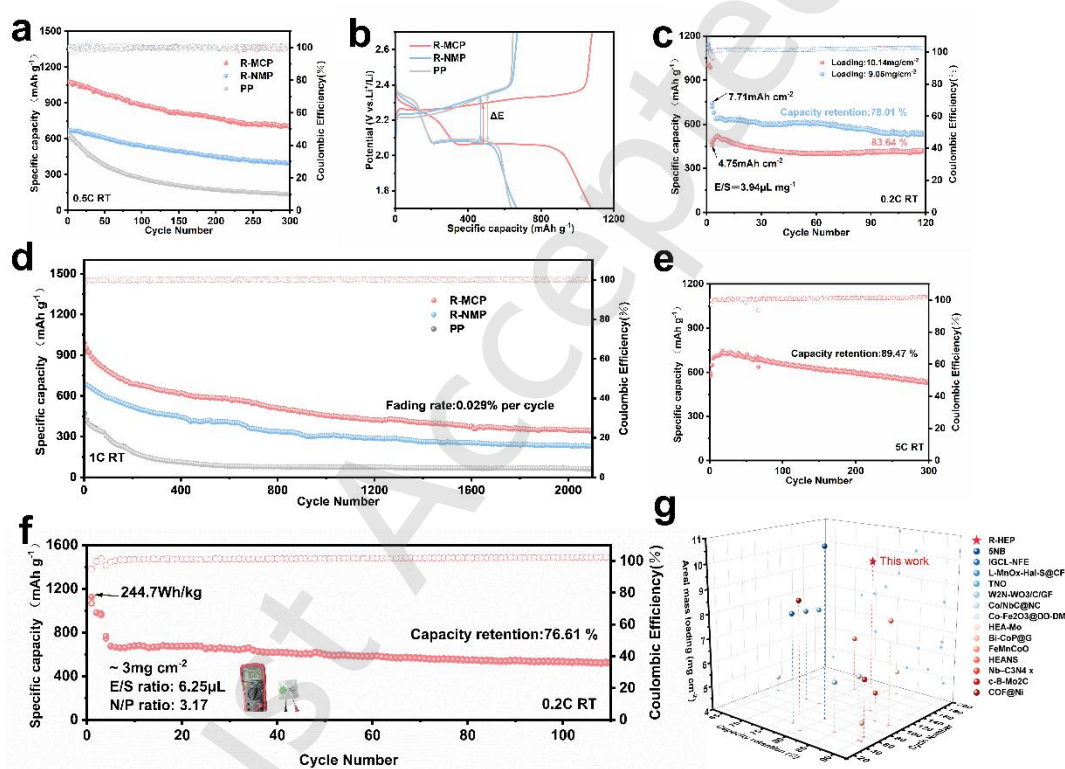


Figure 5 (a) Cycling performance at 0.5 C. (b) Charge–discharge profiles of the first cycle at 0.5 C. (c) Cycling performance of R-MCP at 0.2 C of LSB with a high sulfur load of 10.14 mg cm⁻² and 9.05 mg cm⁻². (d) Long-term cycling performance at 1 C. (e) Cycling performance at 5 C. (f) Cycling stability of the R-MCP-based Li-S pouch cell (insert map: The digital photographs of pouch cell). (g) Comparison of the EC performance of R-MCP with reported systems.

The long-term cycling durability of the R-MCP-modified separator was further evaluated under a current density of 1 C (Figure 5d). Remarkably, the cell maintains stable operation over 2000 consecutive cycles with an ultra-low capacity fading rate of only 0.029% per cycle while preserving a Coulombic efficiency consistently approaching 100%. The prolonged cycling stability of the R-MCP-based cell suggests that the modified separator maintains favorable electrochemical functionality during repeated charge–discharge operation. The persistent suppression of shuttling, together with the accelerated sulfur redox kinetics, effectively minimizes the loss of active sulfur species and stabilizes the electrode/electrolyte interface, thereby ensuring highly reversible EC reactions over thousands of cycles.

Beyond long-term durability, the EC behavior under high current densities was further investigated to evaluate the rate capability of the catalytic separator. Even at an ultrahigh current density of 5 C (Figure 5e), the R-MCP cell exhibits excellent cycling stability, retaining 89.47% of its capacity after 300 cycles. This high-rate cycling performance is consistent with the favorable sulfur redox kinetics observed for the R-MCP-based cell. The strong electronic coupling between catalytic active sites and LiPSs, together with accelerated Li^+ transport through the open mesoporous framework, enables efficient sulfur conversion even under extremely short charge/discharge durations. Consequently, polarization remains effectively suppressed, allowing the cell to maintain high sulfur utilization over a wide range of operating rates.

To further demonstrate the scalability of the proposed strategy, pouch-type Li-S batteries were assembled using the R-MCP-modified separator (Figure 5f). The pouch cell retains 76.61% of its initial capacity after 110 cycles at 0.2 C while maintaining stable EC operation throughout cycling. More importantly, the assembled pouch battery is capable of continuously powering external electronic devices, providing direct evidence of its practical applicability. These results demonstrate the feasibility of employing waste-derived R-MCP materials as functional separator coatings in both

coin-cell and pouch-cell configurations, although further evaluation is required to establish their practical cell level performance.

To benchmark the EC performance of the present work, a comprehensive comparison with representative Li-S batteries reported in recent literature was performed (Figure 5g).[30-43] Benefiting from its favorable polysulfide adsorption behavior and sulfur-conversion performance, the R-MCP-modified separator exhibits competitive electrochemical characteristics, including high reversible capacity, ultra-long cycling life, excellent high-rate capability, stable operation under high sulfur loading, and lean-electrolyte compatibility. These comprehensive advantages place the present system among the leading separator-modification strategies reported to date and demonstrate the potential of integrating waste-derived multicomponent phosphate materials with functional separator engineering for Li-S batteries.

Overall, the electrochemical results indicate that the R-MCP-modified separator improves sulfur-conversion behavior and supports stable battery operation under the investigated testing conditions. The outstanding cycling durability, exceptional rate capability, excellent tolerance toward high sulfur loading and lean electrolyte operation, together with successful pouch-cell validation, collectively highlight the potential of waste-derived R-MCP materials for developing functional separator interfaces in Li-S batteries.

3. Conclusion

In summary, we have developed a phosphoric-acid-assisted upcycling strategy to convert multimetallic constituents from spent lithium-ion batteries into functional phosphate-based materials for lithium–sulfur battery separators. The recycled multicomponent phosphate (R-MCP), containing Ni, Mn, Fe, Cu, and Al, exhibits favorable polysulfide adsorption and sulfur-conversion behavior compared with the recycled Ni–Mn–Fe phosphate (R-NMP). Experimental characterization and theoretical calculations suggest that differences in local electronic environments and

interfacial interactions contribute to the distinct electrochemical responses of the investigated materials. The R-MCP-modified separator enables an initial discharge capacity of 1075 mAh g⁻¹ at 0.5 C and stable cycling over 2000 cycles at 1 C, with an average capacity decay rate of 0.029% per cycle. The material also demonstrates promising performance under increased sulfur loading in a pouch-cell configuration. This study highlights the potential of compositionally complex spent battery materials as resources for constructing functional catalytic interfaces in advanced energy storage systems.

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Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Materials. Additional data related to this paper may be requested from the corresponding author upon request.

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Upcycling spent lithium-ion batteries into multicomponent phosphate catalysts for enhanced sulfur redox kinetics in lithium-sulfur batteries

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Experimental Details

Pre-separation and synthesis of R-MCP and R-NMP

The black powders of spent lithium-ion batteries (LIBs) were obtained from Henan Ruisai New Material Technology Co., Ltd. Both batches contained a mixture of cathode materials, including lithium Nickel-Cobalt-Manganese oxide (NCM) with nominal compositions of NCM811 ($\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$), NCM532 ($\text{LiNi}_{0.5}\text{Co}_{0.3}\text{Mn}_{0.2}\text{O}_2$), and NCM622 ($\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$), lithium iron phosphate (LiFePO_4), and unidentified transition-metal-containing cathode materials. Two batches of spent LIB black mass with different preprocessing histories were used for the synthesis of recycled multicomponent phosphate (R-MCP) and recycled Ni-Mn-Fe phosphate (R-NMP). The precursor used for R-MCP contained Ni, Mn, Fe, Cu, and Al-bearing constituents, whereas the precursor used for R-NMP mainly contained Ni, Mn, and Fe bearing constituents. The differences in precursor composition and

preprocessing history were considered when interpreting the comparative material and electrochemical results.

First, 1000 mg black powder was calcined in a tubular furnace under an argon atmosphere at 500 °C for 2 h to remove residual organic solvents and Polyvinylidene fluoride (PVDF). Phosphoric acid was added followed by filtration treatment. In detail, 50 mL 10 wt% phosphoric acid aqueous solution was added and the reaction lasted for 2 h at 40 °C. When the leaching is completed, dark slurry was subjected to separation via centrifuging. The leachate that enriched in lithium and cobalt and the residue enriched in nickel, manganese, iron, copper and aluminum were collected separately. The residue was washed repeatedly with deionized water and then dried in a vacuum drying oven.

Subsequently, 20 mg graphene oxide (GO) and 5 mL 20 wt% phosphoric acid solution was added followed by ultrasonication. The suspension was transferred into a 50 mL polytetrafluoroethylene-lined stainless-steel autoclave for hydrothermal treatment. The hydrothermal parameters were set to 180 °C and 24 hours reaction duration. The products were collected by centrifugation, washed repeatedly with deionized water and absolute ethanol to eliminate residual phosphate species and soluble impurities. The sample was vacuum-dried to acquire the recycled R-MCP. Another batch of black powder without Cu, Al current collector was treated via the identical procedure to produce R-NMP. The GO control sample was also hydrothermally treated at 180 °C for 24 h before being coated onto a PP separator for comparative galvanostatic charge–discharge measurements.

Inductively Coupled Plasma Optical Emission Spectrometry Analysis

The elemental compositions of the recycled precursors before and after selective phosphoric acid treatment were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 5110, U.S.). For the R-MCP, the concentrations of Li, Co, Ni, Mn, Fe, Cu, and Al before leaching were 238.6, 208.4, 104.2, 132.8, 63.7, 7.1, and 13.5 $\mu\text{g mL}^{-1}$, respectively. After leaching, the concentrations of Li and Co decreased to 5.9 and 0.8 $\mu\text{g mL}^{-1}$. In contrast, Ni, Mn,

Fe, Cu, and Al remained at 57.74, 113.7, 49.43, 6.76, and 12.84 $\mu\text{g mL}^{-1}$, indicating that most transition-metal species were retained. For the R-NMP, the initial concentrations of Li, Co, Ni, Mn, and Fe were 242.5, 212.7, 265.3, 149.6, and 145.2 $\mu\text{g mL}^{-1}$, respectively. After selective phosphoric acid leaching, Li and Co decreased to 7.1 and 2.5 $\mu\text{g mL}^{-1}$, while Ni, Mn, and Fe remained at 120.1, 89.3, and 98.6 $\mu\text{g mL}^{-1}$, respectively. The ICP-OES measurements indicate a pronounced decrease in the reported Li and Co concentrations following phosphoric acid treatment, while Ni, Mn, Fe, Cu, and Al remain detectable in the investigated samples. These observations suggest preferential Li and Co removal under the experimental conditions. Quantitative elemental retention or recovery efficiencies, however, require normalization to the corresponding sample mass and solution volumes.

Separator modification and cathode fabrication

In a typical procedure, R-MCP, Super P, and PVDF were mixed at a weight ratio of 8:1:1 using N-methyl-2-pyrrolidone (NMP) as the solvent. The resulting slurry was uniformly coated onto a Celgard 2500 polypropylene (PP) separator and subsequently vacuum-dried to obtain the R-MCP-modified separator. The total areal mass loading of the functional coating was approximately 1.0 mg cm^{-2} . The R-NMP-modified separator was prepared following the same procedure with an identical coating mass loading.

Typically, Sulfur powder and Ketjen Black (8:2 in weight) were mixed and sealed in a Teflon contain filled with argon, followed by heating to 155 °C in an oven for 12 h. In the standard procedure, a mixture containing 80% S/KB, 10% Super P, and 10% PVDF was dissolved in NMP, coated on aluminum foil, and dried in vacuum at 60 °C for 24 h.

Fabrication of pouch cells

For pouch cells assembly, the cathode, separator, and anode were stacked sequentially to assemble the pouch cells. Aluminum and nickel tabs were welded onto the cathode and anode, respectively, serving as current collector tabs. After electrolyte injection, the cell was vacuum-sealed in an aluminum-plastic pouch. The electrolyte consisted of 1.0 M LiTFSI and 2 wt.% LiNO_3 in a 1:1 (v/v) mixture of 1,3-dioxolane

(DOL) and Dimethoxyethane (DME). The electrolyte-to-sulfur (E/S) ratio was maintained at 6.25 $\mu\text{L mg}^{-1}$, with a sulfur loading of 3 mg cm^{-2} . Galvanostatic charge–discharge cycling was conducted using a LAND battery testing system within a voltage window of 1.7–2.7 V at a current density of 0.2 C (1 C = 1675 mAh g^{-1}). The electrode-level specific energy ($E_{\text{sp,electrode}}$) was calculated according to the following equation:

$$E_{\text{sp,electrode}} = \frac{m_s \times C_{\text{sp}} \times U_{\text{ave}}}{m_{\text{cathode}} + m_{\text{anode}}}$$

where m_s is the mass of sulfur active material (0.04951 g). C_{sp} is the first discharge specific capacity based on sulfur mass (1066.19 mAh g^{-1}), and U_{ave} is the average discharge voltage (2.1 V). m_{cathode} is the total mass of the cathode electrode (sulfur composite and Al current collector (126.87 mg)), and m_{anode} is the total mass of the lithium metal anode (Li foil and Cu current collector, 326.19 mg). In this calculation, the N/P capacity ratio was set to 3.17, and the corresponding mass of lithium foil was (68.11 mg). Tabs, separator, electrolyte and Al-plastic pouch were excluded from the mass calculation. The calculated electrode-level specific energy was 244.7 Wh kg^{-1} .

Electrochemical measurements

CR2032 coin-type Li-S batteries were assembled using S/KB composite cathodes, lithium metal anodes, and pristine PP, R-MCP-modified, or R-NMP-modified separators. For routine electrochemical measurements, the sulfur areal loading was approximately 1.0 mg cm^{-2} , and the electrolyte-to-sulfur (E/S) ratio was maintained at 18 $\mu\text{L mg}^{-1}$. The total areal mass loading of the functional separator coating was approximately 1.0 mg cm^{-2} . Unless otherwise specified, the cells were tested within a voltage window of 1.7–2.7 V.

Cyclic voltammetric (CV) measurements were under a VMP3 multichannel electrochemical workstation (BioLogic, France). Temperature-dependent electrochemical impedance spectroscopy (EIS) measurements were carried out on Li-S batteries at different temperatures. The batteries were tested at 25, 30, 35, 40, 45, and 50 $^{\circ}\text{C}$ using a temperature-controlled chamber. Before each measurement, the batteries were held at

he target temperature for 30 min to ensure thermal equilibration. EIS spectra were collected over a frequency range of 10^6 to 0.1 Hz with an AC perturbation amplitude of 5 mV. The impedance spectra were fitted using the equivalent circuit. The fitted charge-transfer resistance values at each temperature are summarized in Table S1. The apparent activation energy was evaluated from the temperature dependence of the fitted resistance using an Arrhenius-type relationship. All measurements were performed under identical electrochemical conditions. Nitrogen adsorption-desorption isotherm (SBET, Micromeritics ASAP 2460) is used to calculate the Brunauer–Emmett–Teller (BET) specific surface area of the sample. UV-Vis spectra were acquired to evaluate the polysulfide adsorb abilities of different samples.

Materials Characterization

X-ray diffraction (XRD, Ultima IV Rigaku) analysis using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) at a voltage of 40 kV and a current of 40 mA was carried out. Scans were conducted with a step size of 0.02° in the 2θ range of $15\text{--}80^\circ$. As for scanning electron microscopy (SEM), an accelerating voltage of 10 kV was utilized, and the samples were analyzed using a JSM-7900F instrument. Elemental analysis was performed in conjunction with energy-dispersive X-ray spectroscopy (EDS). Transmission electron microscopy (TEM) was conducted using a Talos F200S instrument at an acceleration voltage of 200 kV. The chemical composition of the products was investigated using X-ray photoelectron spectroscopy (XPS) with a Thermo Scientific K-Alpha+ instrument. The in-situ Raman spectra were recorded using a LabRAM HR Evo spectrometer from HORIBA at room temperature, with an excitation wavelength of 532 nm.

Visual Encapsulation of LiPSs

The Li_2S_6 solution was prepared by stirring Li_2S and sulfur at a molar ratio of 1:5 overnight in a mixture of DOL and DME ($v/v = 1:1$). The experiments were conducted within an argon-filled glove box. An H-shaped glass cell containing tubes on two sides was used for the Li_2S_6 solution permeation tests. Separators (with/without R-MCP and R-NMP) divided the two tubes. A certain amount of Li_2S_6 solution was placed on the left side, and an equal volume of DOL/DME solvent was

placed on the other side. Simultaneous photographs were taken during different time periods to record infiltration.

Li₂S Precipitation Measurement

The electrode material and lithium foil are used to assemble the battery, and 25 μ L

blank electrolyte (1.0 M LiTFSI in tetreglyme) is dripped on one side of the lithium foil

and 25 μ L Li₂S₈ catholyte (0.2 M Li₂S₈, 1.0 M LiTFSI in tetreglyme) is dripped on one side of the electrode material. The Li-S batteries were galvanostatically discharged at

0.112 mA to 2.06 V, and then potentiostatically discharged at 2.05 V for 50000 s.

Assembly of Li || Li symmetric cells

All Li-Li symmetric cells were assembled in an Argon-filled glove box (< 1 ppm of O₂ and H₂O). The electrolyte was consistent with that used in conventional Li-S batteries, and R-MCP and R-NMP modified separators and pristine PP separators were used, respectively.

Analysis of Scan-Rate-Dependent CV Peak Currents (D_{Li^+})

$$I_p = 2.69 \times 10^5 n^{1.5} A D_{Li^+}^{0.5} C_{Li^+} v^{0.5} \#$$

where the I_p refers to the peak current, n refers to the number of electrons, A is the geometric area of the corresponding electrode, D_{Li^+} corresponds to the lithium-ion diffusion coefficient, C_{Li^+} corresponds to the change in Li-ion concentration in the chemical reaction, and v is the scan rate.

Density functional theory (DFT) calculations

The quasi-crystalline structure of the R-MCP and R-NMP was generated using the MCSQS (Monte Carlo Simulated Quenching) method¹ implemented in the Alloy Theoretic Automated Toolkit (ATAT) package. [1, 2] With the acceptance probability for each Monte Carlo step governed by the Metropolis-Hastings algorithm. Following the Monte Carlo optimization of R-MCP and R-NMP structures, density functional theory (DFT) calculations were conducted using the Vienna ab initio Simulation

Package (VASP) to predict the material's catalytic properties. [3-7]The Perdew-Burke-Ernzerh of (PBE) exchange-correlation functional within the generalized gradient approximation (GGA) was adopted to describe the exchange-correlation interaction. A plane-wave cutoff energy of 450 eV was employed to ensure convergence. A vacuum

layer of 15 Å was inserted along the z-axis to eliminate periodic image interactions. The adsorption energy was calculated using the formula:

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{catalyst}} - E_{\text{adsorbate}}$$

Here, E_{total} , E_{catalyst} , and $E_{\text{adsorbate}}$ denote the total energy of the adsorbed system, the energy of the clean catalyst, and the energy of the isolated adsorbate, respectively.[8-10]

The Gibbs free energy (ΔG) for each step was computed as follows:

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S$$

where ΔE , ΔZPE , and ΔS represent the electronic energy, zero-point energy, and entropy differences between the corresponding reaction states, respectively. The free-energy profiles were referenced to the Li_2S_4 state of each model. The differences between adjacent reaction states were interpreted as thermodynamic free-energy changes rather than kinetic activation barriers.

The charge-density difference was calculated as:

$$\Delta \rho = \rho(\text{total}) - \rho(\text{substrate}) - \rho(\text{adsorbate})$$

where $\rho(\text{total})$, $\rho(\text{substrate})$, and $\rho(\text{adsorbate})$ represent the electron densities of the adsorption system, catalyst substrate, and adsorbed lithium polysulfides, respectively.

The d-band centers were calculated from the projected density of states (PDOS), considering the summed d-orbital contributions of all metal atoms in the respective catalyst models. The d-band center was determined using the following equation:

$$\varepsilon_d = \frac{\int E \times Dd(E) dE}{\int Dd(E) dE}$$

Here, $Dd(E)$ represents the summed d-orbital projected density of states of all metal atoms in the corresponding catalyst model, and the energy is referenced to the Fermi

level ($E_F = 0$ eV). The same integration procedure was applied to both models to evaluate their respective d-band centers.

Electron Localization Function (ELF) Analysis.

The electron localization function was employed to examine the spatial distribution and localization characteristics of electrons in the optimized catalyst structures. The ELF is a dimensionless quantity ranging from 0 to 1, where values approaching 1 indicate highly localized electrons and a value close to 0.5 corresponds to electron localization characteristics similar to those of a homogeneous electron gas. The resulting ELF distributions were used to qualitatively compare the local electronic environments of R-MCP and R-NMP.

Bader Charge Analysis

Bader charge analysis was used to quantify the electronic charge redistribution associated with the interaction between lithium polysulfide intermediates and the catalyst surfaces. The atomic net charge was defined as:

$$q_i = Z_i - N_i^{Bader}$$

where Z_i is the nuclear charge of atom i , and N_i^{Bader} represents the number of electrons assigned to that atom through Bader partitioning. The charge redistribution upon adsorption was evaluated by comparing the corresponding atomic charges before and after adsorption. A positive net charge indicates electron deficiency, whereas a negative net charge indicates electron enrichment.

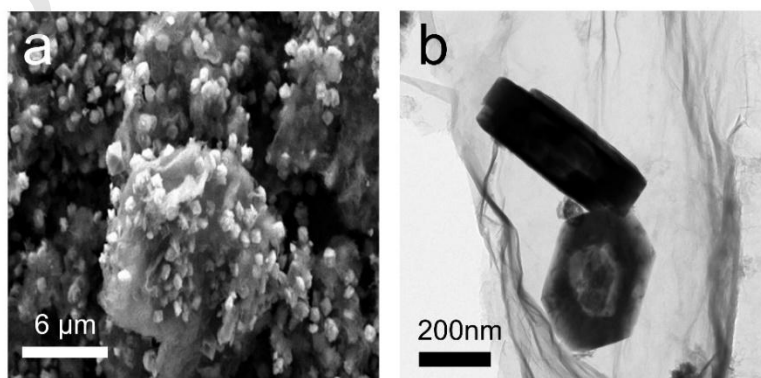


Figure S1. (a) Scanning electron microscopy (SEM) and (b) Transmission electron microscopy (TEM) images of R-NMP.

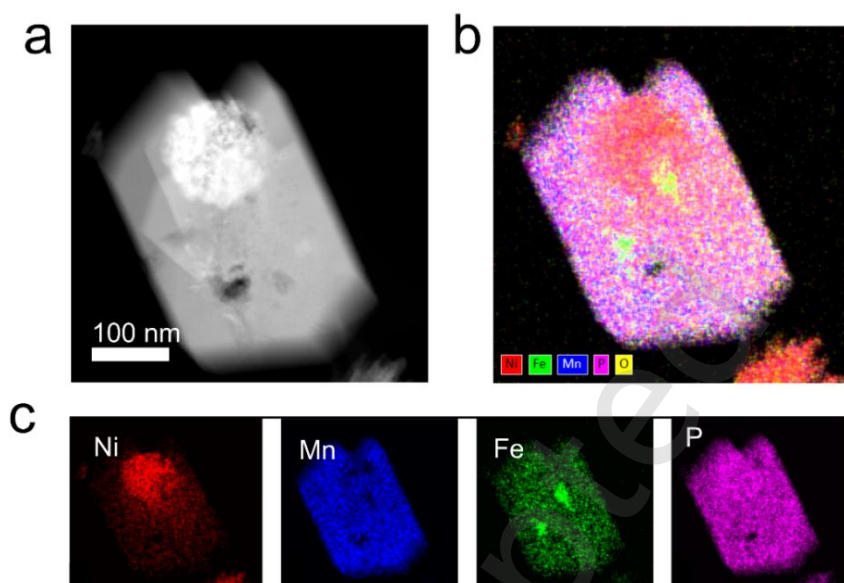


Figure S2. Characterizations of R-NMP: (a) TEM images, (b) and (c) Energy-dispersive X-ray spectroscopy (EDS) elemental distribution in the TEM system.

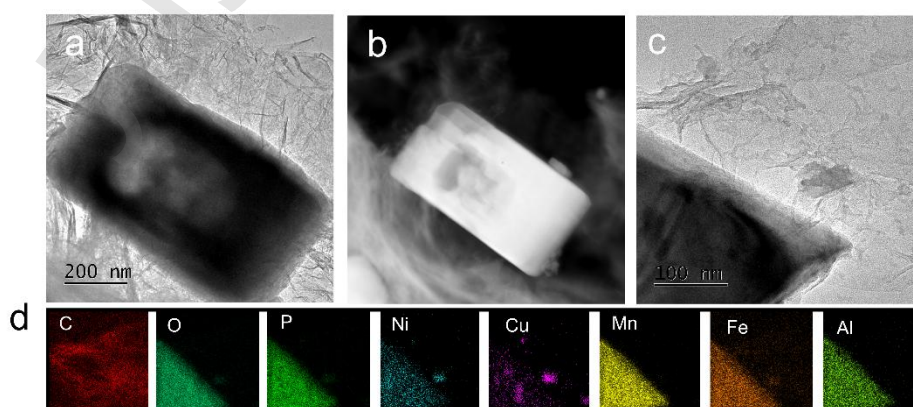


Figure S3. TEM characterization and elemental mapping of R-MCP: (a-d) TEM/STEM images and corresponding elemental distributions.

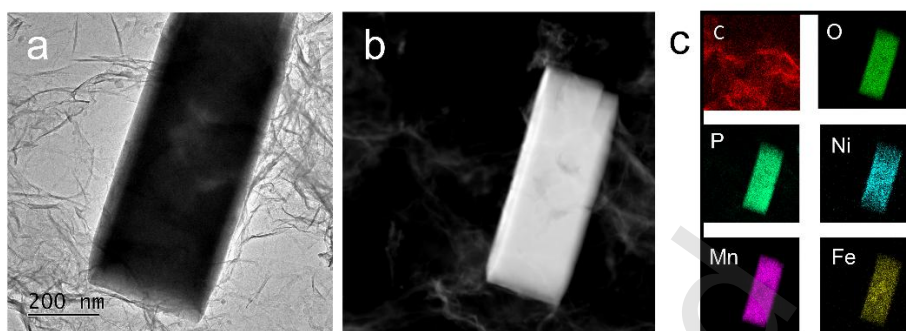


Figure S4. TEM characterization and elemental mapping of R-NMP: (a-c) TEM/STEM images and corresponding elemental distributions.

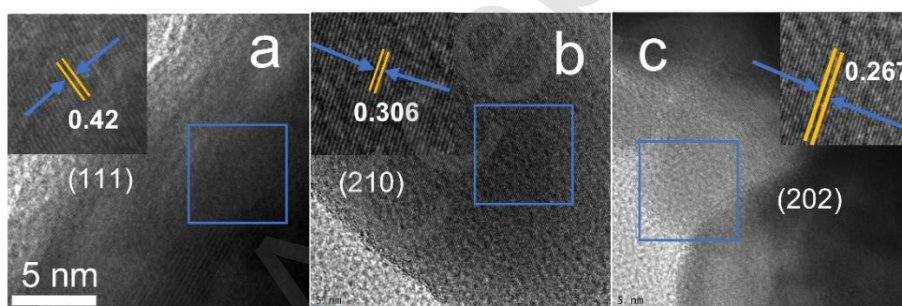


Figure S5. (a-c) High-resolution transmission electron microscopy (HRTEM) image with corresponding inverse fast Fourier transform (IFFT) pattern of R-MCP.

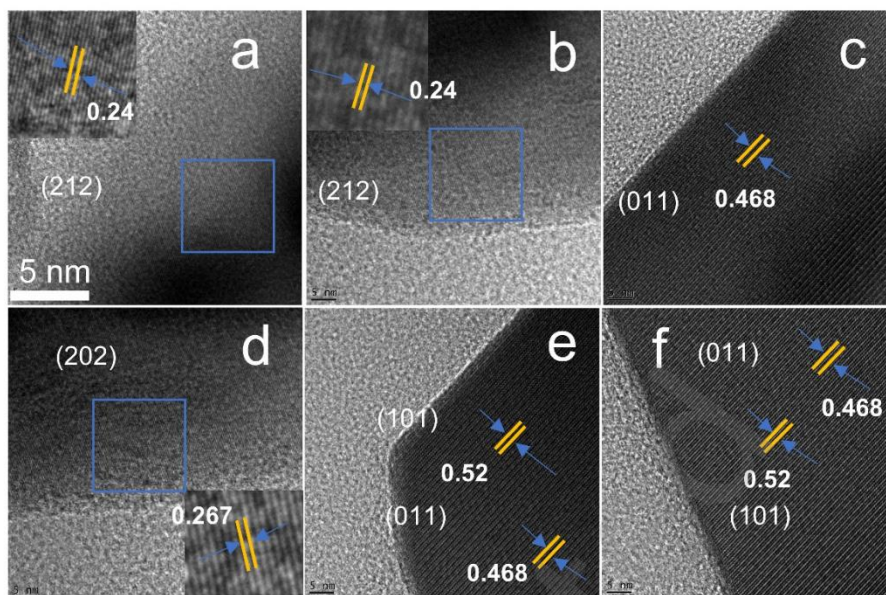


Figure S6. (a-f) HRTEM image with corresponding IFFT pattern of R-NMP.

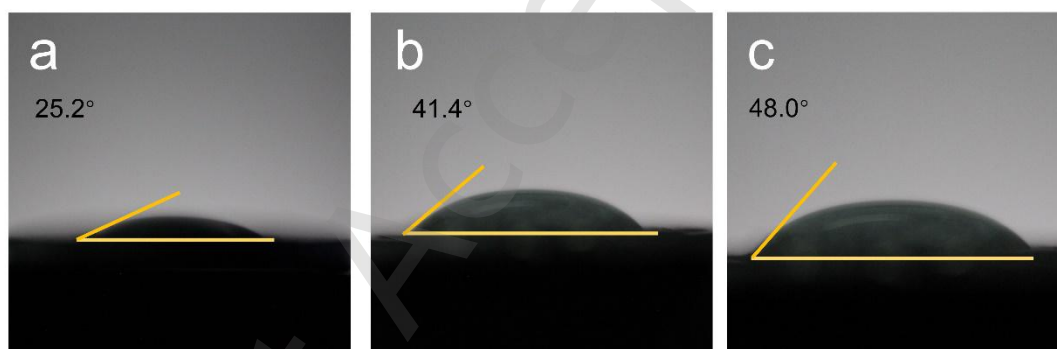


Figure S7. Contact angle between separators and electrolyte. (a) R-MCP (b) R-NMP and (c) PP.

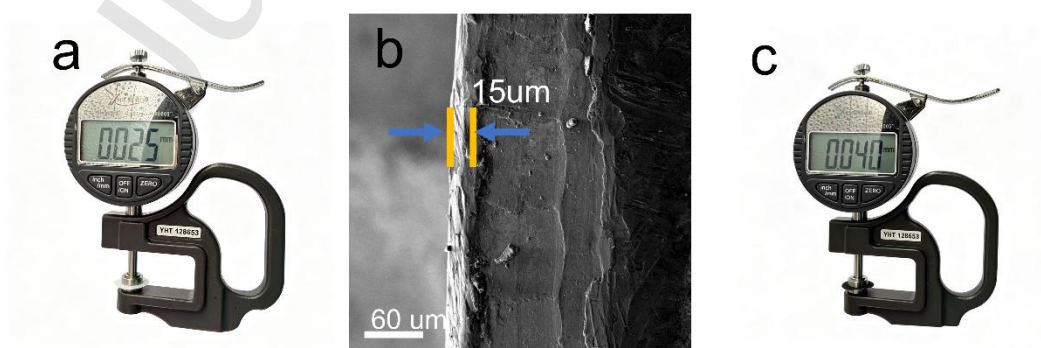


Figure S8. (a) Thickness of the PP, (b) SEM cross-section of the modified separator, and (c) modified separator measured by a thickness gauge.

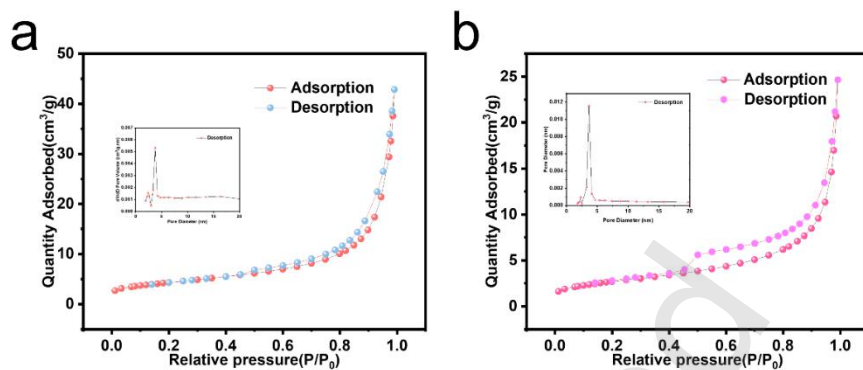


Figure S9. (a) R-MCP and (b) R-NMP nitrogen adsorption–desorption isotherms with inset of pore size distribution.

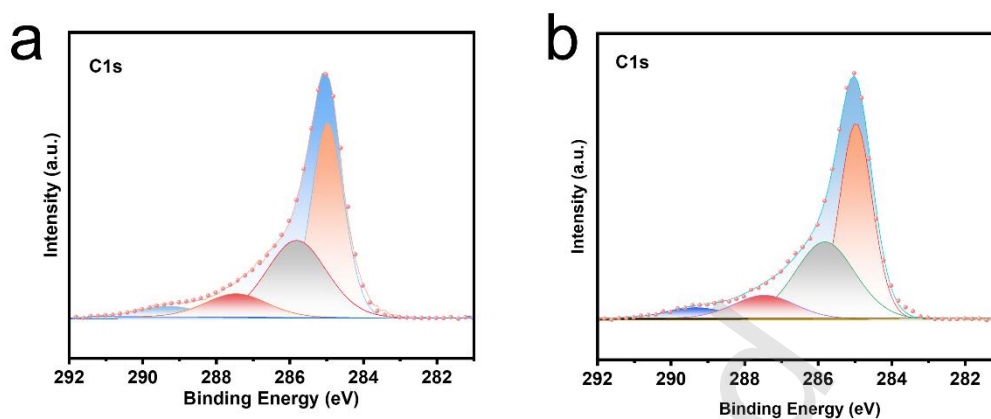


Figure S10. High-resolution C 1s XPS spectra of (a) R-MCP and (b) R-NMP.

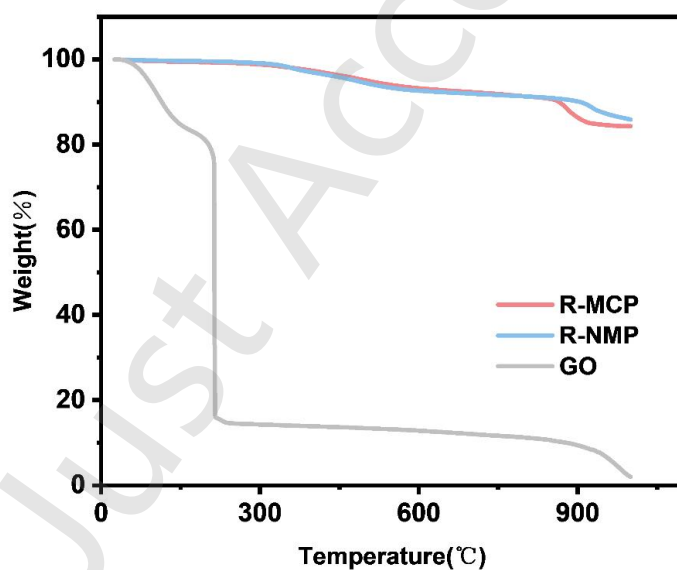


Figure S11. Thermogravimetric analysis (TGA) curves of GO, R-MCP and R-NMP under nitrogen atmosphere.

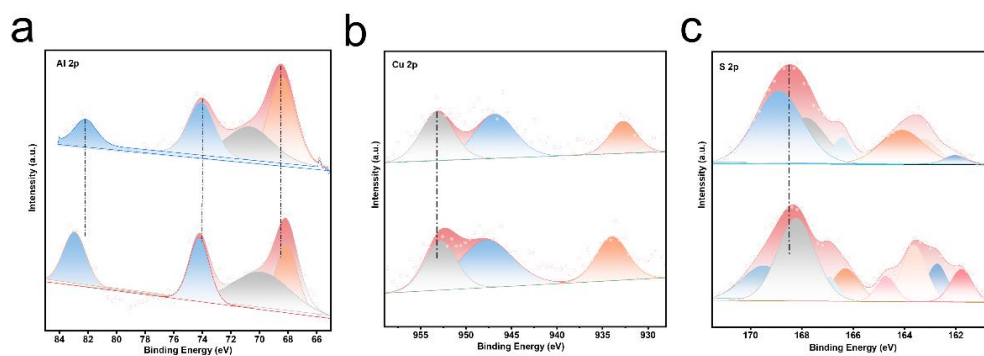


Figure S12. (a-c) XPS of Al 2p, Cu 2p, S 2p of R-MCP before and after adsorption of Li_2S_6 .

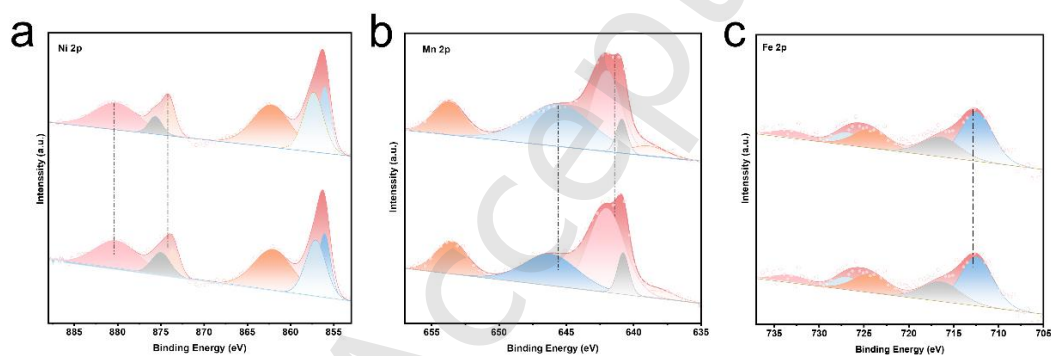


Figure S13. High resolution XPS of Ni 2p (a), Mn 2p (b), and Fe 2p (c) of R-NMP before and after adsorption of Li_2S_6 .

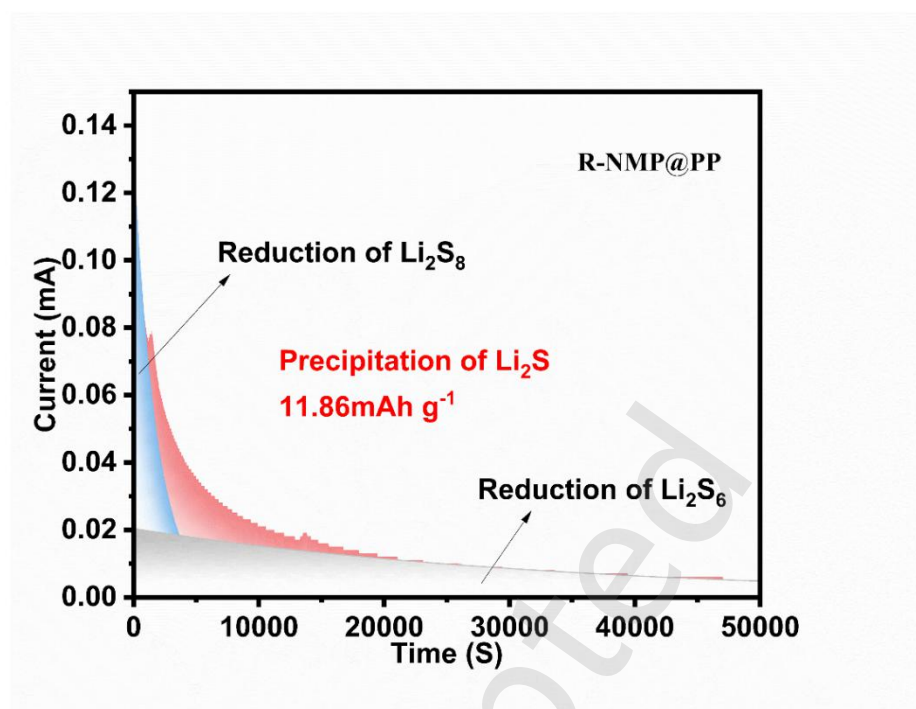


Figure S14. Li_2S deposition measurements for R-NMP, with potentiostatic discharge profile of 2.05 V.

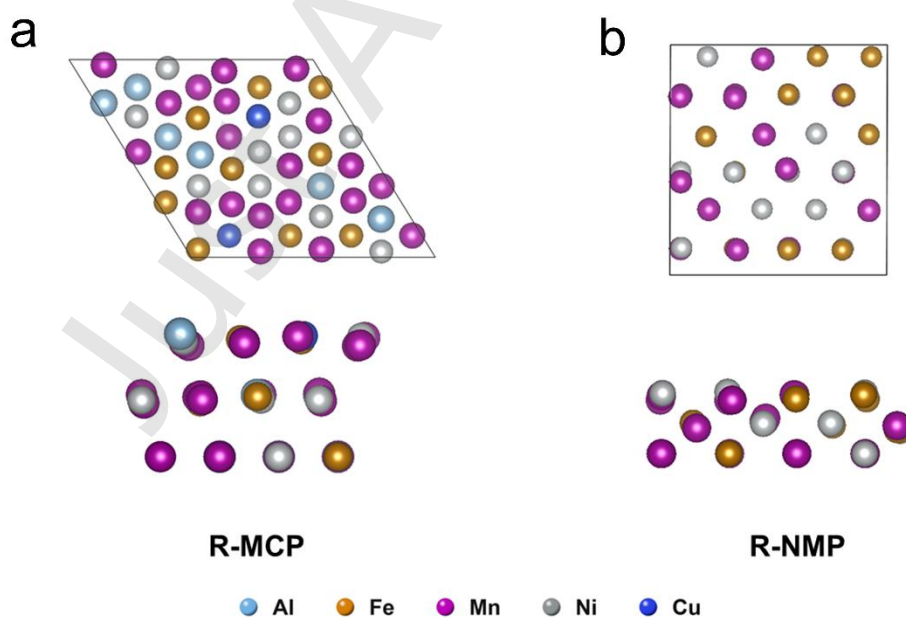


Figure S15. Initial configurations of (a) R-MCP and (b) R-NMP.

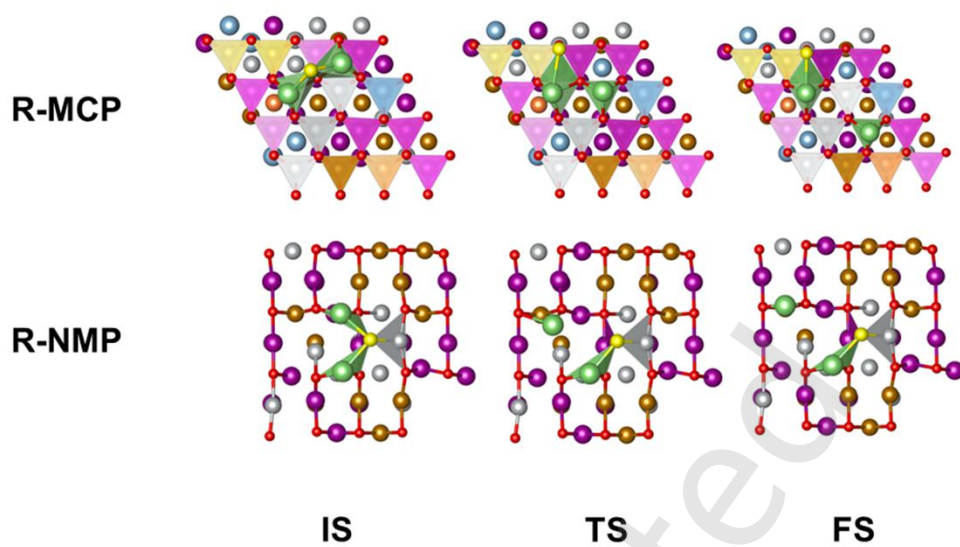


Figure S16. Optimized adsorption geometries of sulfur species adsorbed on the surface of R-MCP and R-NMP.

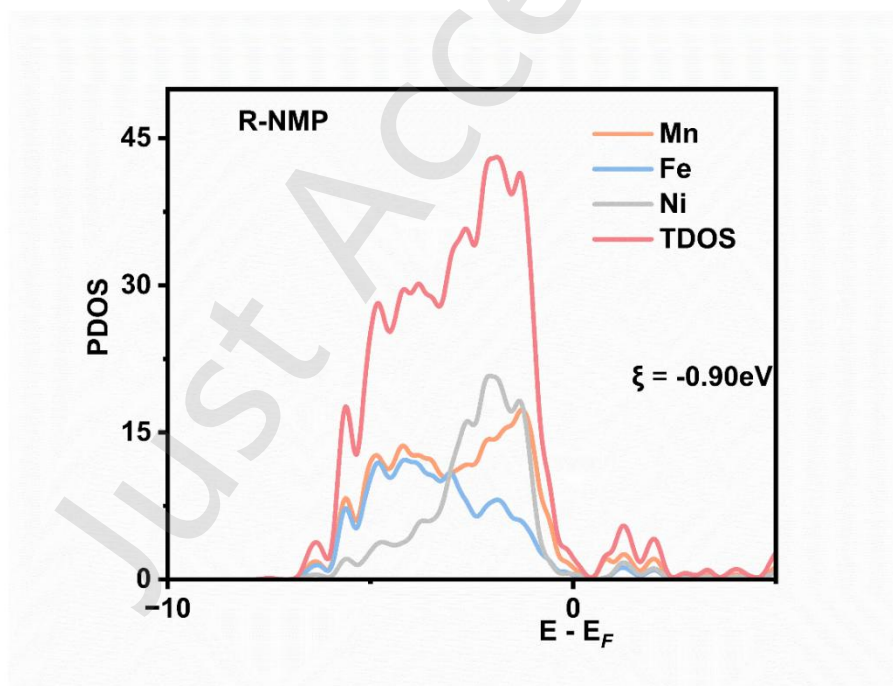


Figure S17. Projected density of states (PDOS) of R-NMP.

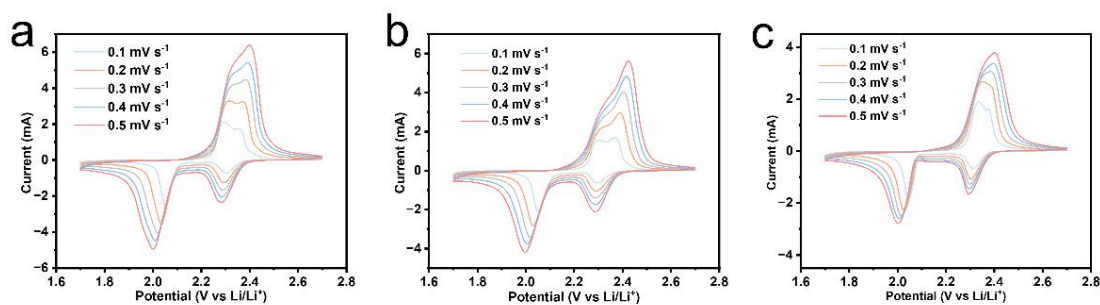


Figure S18. CV curves for (a) R-MCP, (b) R-NMP, and (c) PP at various scan rates at 0.1-0.5 mV s⁻¹.

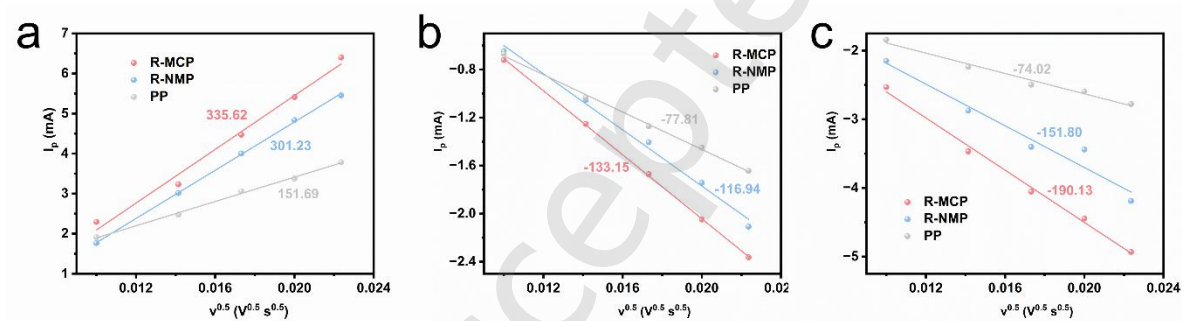


Figure S19. Calculated lithium ions diffusion coefficients of R-MCP, R-NMP and PP.

Analysis of Scan-Rate-Dependent CV Peak Currents

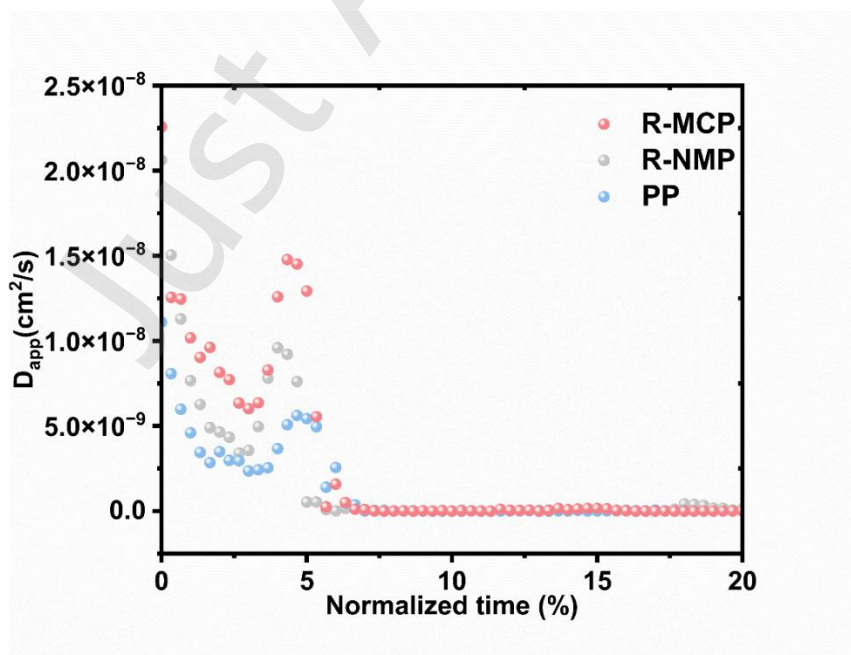


Figure S20. Li⁺ diffusion coefficients of R-MCP, R-NMP, and PP.

Calculation of Apparent Li⁺ Diffusion Coefficients

The apparent Li⁺ diffusion coefficients were estimated from galvanostatic intermittent titration technique (GITT) measurements using the following equation:

$$D_{app} = \frac{4}{\pi\tau} \left(\frac{n_m V_m}{S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2$$

where τ is the duration of the constant-current pulse (s), n_m is the number of moles of active material (mol), V_m is its molar volume (cm³ mol⁻¹), and S is the effective electrode/electrolyte contact area (cm²). ΔE_s represents the quasi-equilibrium potential change during relaxation, and ΔE_t is the voltage change during the current pulse after excluding the instantaneous IR drop. Considering the multiphase nature of sulfur conversion, the calculated values are regarded as apparent diffusion coefficients.

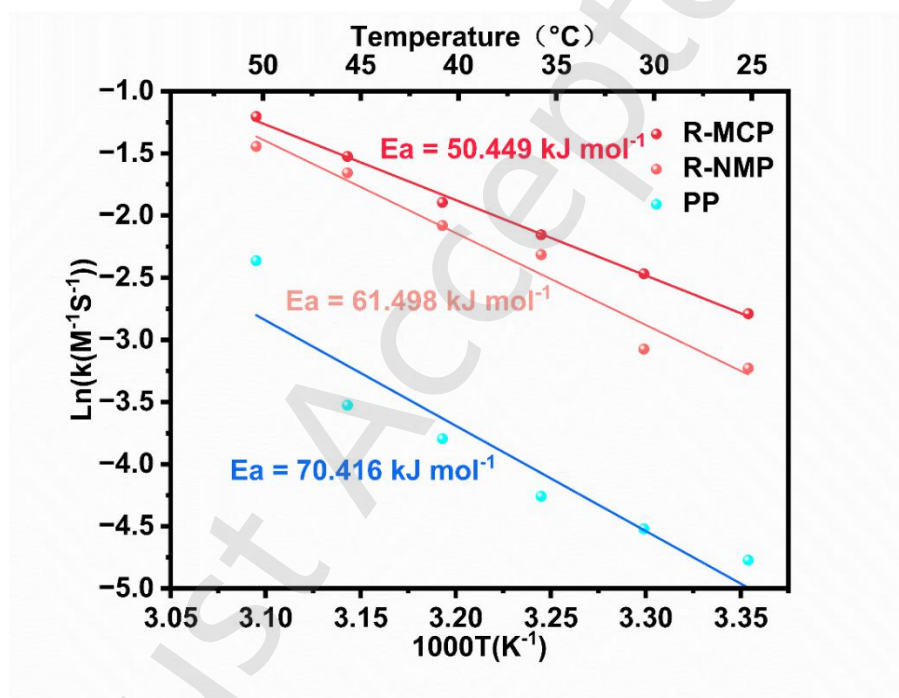
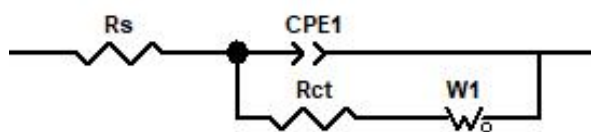


Figure S21. Comparison of activation energy of R-MCP, R-NMP, and PP extracted from (Figure 4 g-i).

Temperature-Dependent EIS Analysis



The temperature-dependent EIS spectra were fitted using the equivalent circuit $R_s -$

$[CPE1 \parallel (R_{ct} + W1)]$, where R_s is the ohmic resistance, $CPE1$ represents the non-ideal interfacial capacitive response, R_{ct} is the charge-transfer resistance, and $W1$ represents the Warburg diffusion element. The apparent activation energy was calculated using the Arrhenius-type relationship:

$$\ln\left(\frac{1}{R_{ct}}\right) = -\frac{E_a}{RT} + C$$

where E_a is the apparent activation energy (J mol^{-1}), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), and C is the fitting constant.

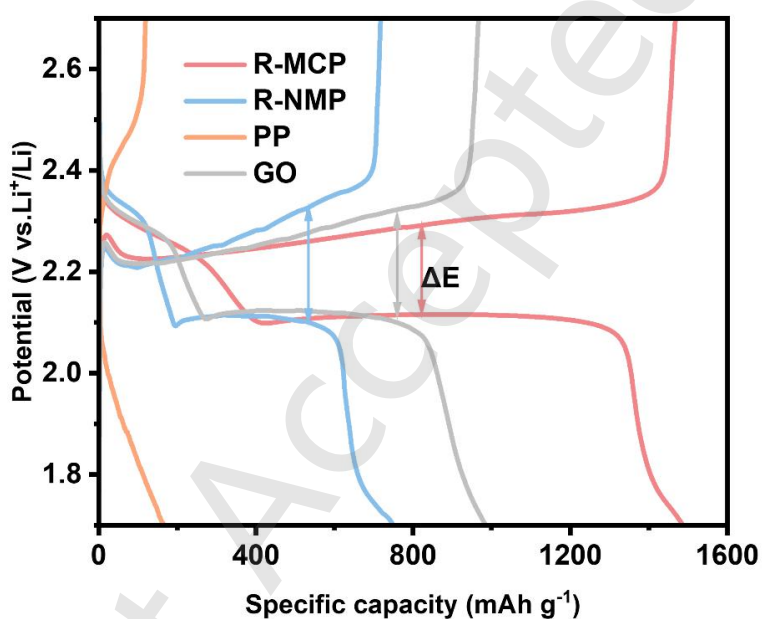


Figure S22. Charge-discharge profiles of the first cycle at 0.1 C

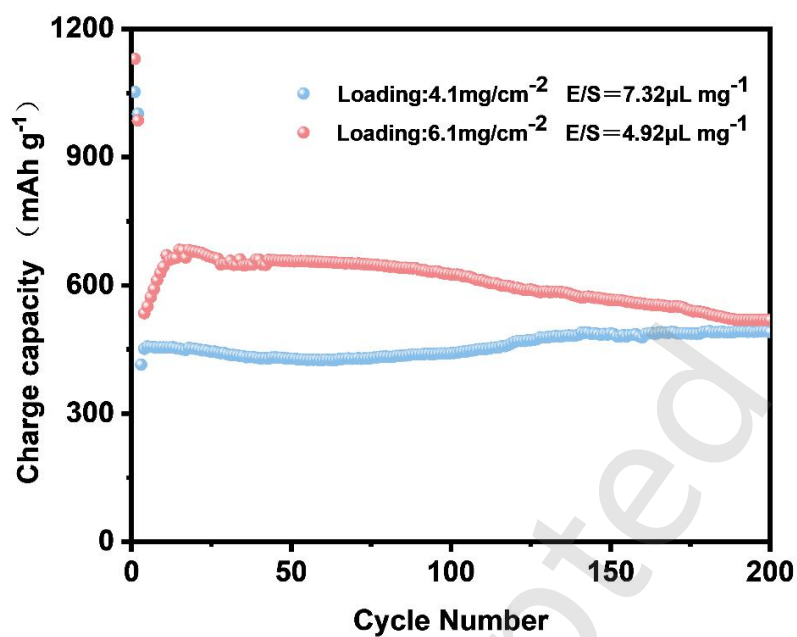


Figure S23. Cycling performance of R-MCP at 1 C with a high sulfur loading of 4.1 and 6.1 mg cm⁻², respectively.

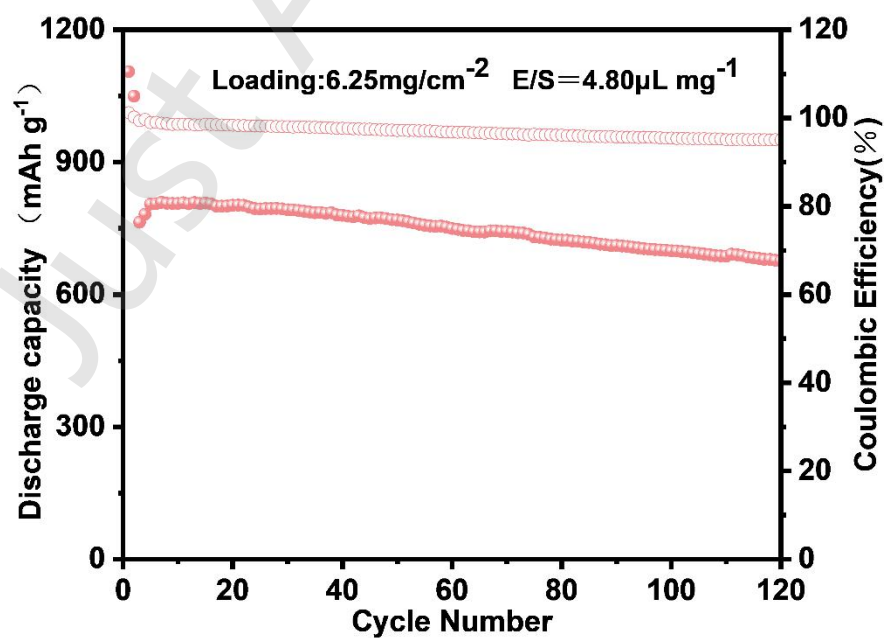


Figure S24. Cycling performance of R-MCP at 0.5C with a sulfur loading of 6.25 mg cm⁻².

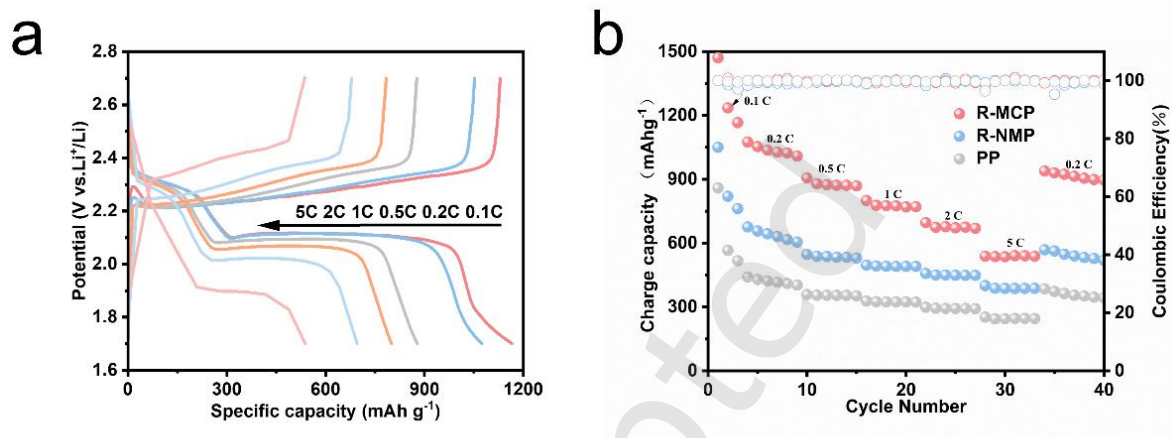


Figure S25. (a) Charge–discharge profiles of the first cycle at various rate capabilities. (b) Rate capability.

Table S1. Fitted charge-transfer resistance (R_{ct}) values of Li–S cells with different separators at various temperatures.

Temperature (°C)	R-MCP (Ω)	R-NMP (Ω)	PP (Ω)
25	16.28	25.22	118.2
30	11.81	21.62	91.88
35	8.622	10.69	70.70
40	6.648	8.007	44.47
45	4.589	5.242	33.97
50	3.333	4.235	10.63

Table S2. Comparison of Representative Spent LIB Recycling and Value-Added Utilizations

Reference	Waste feedstock	Recycling/upcycling strategy	Processing conditions	Final products and applications	Advantages and limitations
Zhu et al., 2024 Adv. Funct. Mater.	Spent LiCoO ₂ and LiMn ₂ O ₄	Acid dissolution followed by high-temperature shock treatment	HNO ₃ dissolution; thermal shock at 1500 °C for approximately 2 s under Ar/H ₂	Co–MnO bifunctional catalysts for Li–S batteries; 0.058% capacity decay per cycle over 400 cycles at 1 C	Effective polysulfide adsorption and catalytic conversion; however, the process involves strong-acid dissolution and high-temperature shock treatment
Gu et al., 2024 Waste Management	Spent NCM523	Carbon-assisted selective sulfidation, water leaching and cathode regeneration	Sulfidation at 800 °C for 60 min; subsequent calcination at 750 °C for 5 h and 950 °C for 15 h	Regenerated NCM cathode materials; Li leaching efficiency > 99%	Selective Li recovery and closed-loop cathode regeneration; however, multiple high-temperature treatments and composition-controlled regeneration are required
Ma et al., 2024 Nat. Commun.	Spent NCM523 and LiMn ₂ O ₄	Selective subtraction of Ni/Co followed by precursor reconstruction	Selective precipitation and coprecipitation, followed by thermal synthesis	Low-Co 5 V-class LiNi _{0.4} Co _{0.1} Mn _{1.5} O ₄ cathode; >99.9% transition-metal reuse	High metal utilization without additional Li/Ni precursor input; however, the process involves composition adjustment and multistage precipitation

Zhao et al., 2025 Chem. Commun.	Spent NCM cathode materials	Deep eutectic solvent- assisted selective metal extraction	Choline chloride/oxalic acid DES; leaching at 120 °C for 10 h, followed by stepwise precipitation and calcination	NiO, Co ₃ O ₄ and Mn ₃ O ₄ electrocatalysts for PET upcycling; maximum formic-acid Faradaic efficiency of 90.6%	Value-added conversion of recovered metals into electrocatalysts; however, multiple metal-separation steps and additional solvent treatment are required
This work	Mixed spent NCM811, NCM532, NCM622, LFP and other cathode components	Selective phosphoric-acid treatment followed by multicomponent phosphate synthesis and functional application	Pretreatment at 500 °C for 2 h; 10 wt.% H ₃ PO ₄ at 40 °C for 2 h; hydrothermal conversion at 180 °C for 24 h	Ni–Mn–Fe–Cu–Al multicomponent phosphate catalysts for Li–S separators; 2000 cycles at 1 C with 0.029% capacity decay per cycle; sulfur loading up to 10.14 mg cm ⁻²	Enables value-added utilization of compositionally complex cathode waste without complete separation of individual transition metals; combines multimetal resource utilization with polysulfide regulation in Li–S batteries

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