

An active bifunctional natural dye for stable all-solid-state organic batteries

Received: 9 October 2024

Accepted: 17 July 2025

Published online: 24 September 2025



Qihang Yu^{1,2,8}, Yang Hu^{3,8}, Sixu Deng¹, Mohsen Shakouri⁴, Jingye Chen⁴, Vinicius Martins⁵, Heng-Yong Nie^{6,7}, Yining Huang⁵, Yang Zhao³, Karim Zaghib¹, Tsun-Kong Sham⁵ & Xia Li¹✉

Sustainable and cost-effective organic electrode materials are promising for next-generation lithium-ion batteries but are hindered by severe shuttle effects. While all-solid-state batteries offer a potential solution, chemical and mechanical incompatibility between organic electrode materials and inorganic solid electrolytes limit areal capacity and cycling stability, falling short of practical requirements. Here, we report a bifunctional indigo natural dye that serves as both an active material and a solid molecular catalyst in sulfide-based all-solid-state batteries, addressing these compatibility challenges. Contrary to the prevailing view that chemical reactions between organic electrode materials and sulfide solid electrolytes are detrimental, our study reveals that controlled reactions between indigo and $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte catalyze their synergistic redox process after optimizing electrode microstructures. This strategy enables a high reversible capacity of 583 mAh g^{-1} ($\text{Li}_6\text{PS}_5\text{Cl}$ contribution: 379 mAh g^{-1}) at 0.1 C , a high areal capacity of 3.84 mAh cm^{-2} , and good cycling stability at an operation temperature of 25°C . These findings highlight the potential of bifunctional organic electrode materials in sulfide-based all-solid-state batteries to overcome the key challenges of organic electrode materials in practical applications.

Organic electrode materials (OEMs) have attracted considerable research attention for next-generation sustainable lithium-ion batteries (LIBs) due to their eco-friendliness, cost-effectiveness, and versatile structures, especially when compared to transition metal oxides (TMOs) containing scarce elements such as cobalt and nickel^{1–3}. The exploration of OEMs dates back to the 1960s when Williams et. al. first reported the application of carbonyl compounds, dichloroisocyanuric acid, in primary LIBs⁴. In subsequent decades, a variety of OEMs featuring diverse redox functional groups have been explored^{5–7}, including nitrile compounds⁸, imine compounds^{9,10}, organosulfur compounds^{11,12}, organic radicals^{13,14},

and conductive polymers^{15,16}. However, OEMs face a significant challenge due to the severe shuttle effect caused by the dissolution in polar liquid electrolytes, leading to unsatisfactory electrochemical performance^{17,18}. While most research has focused on synthesizing molecular structures with higher molecular weight to mitigate their dissociation by liquid electrolytes^{19,20}, this approach often demands intricate organic synthesis, contrary to the original aim of utilizing cost-effective OEMs as active materials. Alternatively, other research endeavors have focused on physically or chemically confining OEMs to mitigate the shuttle effect^{21–23}. However, completely preventing the dissolution of OEMs, particularly

¹Department of Chemical and Materials Engineering, Concordia University, Montreal, Quebec, Canada. ²Department of Mechanical, Industrial & Aerospace Engineering, Concordia University, Montreal, Quebec, Canada. ³Department of Mechanical and Materials Engineering, University of Western Ontario, London, Ontario, Canada. ⁴Canadian Light Source Inc., University of Saskatchewan, Saskatoon, Saskatchewan, Canada. ⁵Department of Chemistry, University of Western Ontario, London, Ontario, Canada. ⁶Surface Science Western, University of Western Ontario, 999 Collip Circle, London, Ontario, Canada. ⁷Department of Physics and Astronomy, University of Western Ontario, 1151 Richmond St, London, Ontario, Canada. ⁸These authors contributed equally: Qihang Yu, Yang Hu. ✉e-mail: xia.li@concordia.ca

organic small molecules, using conventional methods such as carbon coating and separator engineering^{24–26}, remains challenging, resulting in unsatisfactory long-term cycling stability of OEMs. Despite these challenges, the research direction towards battery configuration engineering in Li-organic batteries adopting organic small molecules as active material is promising. Compared with oligomers, hybrids, and polymers, organic small molecules offer advantages in terms of cost and intrinsic flat redox plateaus owing to their simple molecular structures^{27–29}.

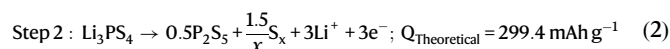
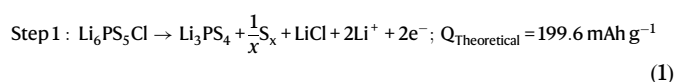
With the development of solid-state battery technology, incorporating inorganic solid electrolytes (SEs) has emerged as a promising strategy to fundamentally address the dissolution challenges of OEMs, thereby unlocking the full potential of organic small molecules as active materials³⁰. Additionally, using OEMs as active materials can alleviate the interfacial resistance of solid-solid contact in all-solid-state batteries (ASSBs) due to their lower Young's moduli compared to TMOs³¹. Among various inorganic SEs, sulfide SEs stand out for their high ionic conductivity and favorable mechanical properties, including softness and plasticity^{32,33}. Pioneering work from Yao's group has showcased prototype sulfide-based ASSBs utilizing two typical OEMs as active materials, Na₂C₆O₆ and pyrene-4,5,9,10-tetraone (PTO)^{31,34}, inspiring further exploration in this system^{35–38}. Despite these achievements, state-of-the-art sulfide-based ASSBs using OEMs as active materials still face challenges such as limited rate capability, low areal capacity, and short cycle life at an average temperature of 25 °C, with most examples operating at elevated temperatures (>50 °C). Furthermore, concerns about the chemical compatibility between OEMs, particularly carbonyl-based types, and sulfide SEs question the feasibility of using OEMs in sulfide-based ASSBs. For instance, potential nucleophilic addition reactions between α -hydrogen in carbonyl-based monomers and PS₄³⁻ polyanions in sulfide SEs remain a concern³⁹. Thus, the chemical compatibility between OEMs and sulfide SEs remains unclear, highlighting the pressing need for chemistries or design strategies.

Here we report bifunctional indigo ((E)-[2,2'-biindolinylidene]-3,3'-dione, C₁₆H₁₀N₂O₂), a historically natural organic small-molecule dye, serving as both the redox active material and an efficient solid molecular catalyst in sulfide-based ASSBs to resolve the compatibility challenges between OEMs and inorganic SEs. As the active material, indigo demonstrates rapid redox kinetics in ASSBs attributed to its semiconductor nature and planar molecular configuration. As the solid molecular catalyst, indigo could chemically oxidize S²⁻ anions in Li₆PS₅Cl (LPSC) SE during the charging process, thus circumventing the typically sluggish electrochemical oxidation of LPSC SE, known as the inner-sphere redox pathway. This distinctive catalytic process, referred to as the outer-sphere redox pathway, facilitates the synergistic redox between indigo and LPSC SE. Therefore, the bifunctionality of indigo natural dye can enable both high areal capacity and good cycling stability in ASSBs. After systematic microstructure engineering of positive electrode composites, ASSBs could deliver a high capacity of 583 mAh g⁻¹ (LPSC contribution: 379 mAh g⁻¹) at 0.1 C (1 C = 204 mA g⁻¹) rate at 25 °C, corresponding to the specific energy of 1224.3 Wh kg⁻¹ (583 mAh g⁻¹ × 2.1 V) based on the mass of indigo and 244.9 Wh kg⁻¹ based on the total electrode mass. The efficient homogeneous catalytic reaction and ionic/electronic percolation network within the positive electrode composites facilitate good rate performance and cycling stability, whether under high specific current (86% capacity retention after 600 cycles at 2 C rate) or low temperature (92% capacity retention after 200 cycles at -10 °C). Additionally, the fabricated ASSBs exhibit a maximum areal capacity of 3.84 mAh cm² with good cycling performance (95% capacity retention after 100 cycles at 0.2 C). This study demonstrates the effectiveness of incorporating bifunctional indigo natural dye into ASSBs as a strategic solution to overcome the bottlenecks faced by OEMs in the practical applications.

Results and Discussion

Design principle of bifunctional indigo in sulfide-based ASSBs

LPSC SE crystallizes in the cubic F $\bar{4}3m$ space group, consisting of two inequivalent S²⁻ sites: one identified as “free” S²⁻ anion, exclusively binding with Li⁺ cations, and the other as “terminal” S²⁻ anion within the PS₄³⁻ tetrahedra (Supplementary Fig. 1)⁴⁰. Many studies have reported additional capacity provided by the direct electrochemical redox of LPSC SE in ASSBs (Fig. 1a)^{41–43}, referred to as the inner-sphere redox pathway (blue, step 1–2). In the charging process, “free” S²⁻ anions initially undergo oxidation, resulting in the formation of amorphous Li₃PS₄, LiCl, and S_x species (Step 1). Subsequently, the “terminal” S²⁻ anions in Li₃PS₄ undergo oxidation to yield P₂S₅ and S_x species as final products (Step 2). The theoretical specific capacity of LPSC, utilizing the S²⁻ redox center, is 499 mAh g⁻¹, with step 1 contributing 199.6 mAh g⁻¹ and step 2 providing 299.4 mAh g⁻¹. First-principle computations utilizing the Li grand potential phase diagram reveal the thermodynamically favorable reactions of LPSC SE, alongside their corresponding voltage profiles and phase equilibria upon oxidation and reduction (Fig. 1b). According to the calculations, the oxidation of “free” S²⁻ anions (Step 1) occurs at 2.01 V vs. Li⁺/Li, while the oxidation of “terminal” S²⁻ anions occurs at 2.31 V vs. Li⁺/Li (Step 2). Although “free” or “terminal” S²⁻ anions have a relatively low thermodynamic oxidation potential, the redox activity of LPSC SE via an inner-sphere pathway is often hindered by sluggish kinetics of the electrochemical oxidation from S²⁻ to S_x in ASSBs⁴⁴. Consequently, there is ongoing debate over whether inhibiting or promoting the redox activity of LPSC SE is more important for achieving superior ASSB performance.

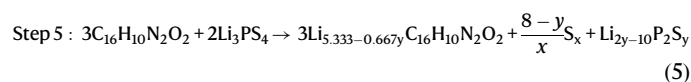
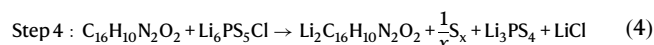
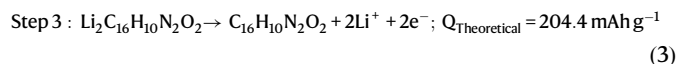


Introducing bifunctional indigo natural dye into sulfide-based ASSBs creates a distinct catalyzed redox pathway for LPSC SE, diverging from the traditional inner-sphere electrochemical redox pathway (blue) and referred to as the outer-sphere redox pathway (orange, step 3–5) (Fig. 1a). This synergistic reversible redox between indigo and LPSC SE significantly improves the redox kinetics and reversibility of LPSC SE, thereby enhancing the obtained reversible capacities and cycling stability of ASSBs. For an ideal molecular catalyst to catalyze the outer-sphere redox of LPSC SE, two prerequisites are essential in theory: the higher thermodynamic electrode potential than S²⁻ anions in LPSC SE, and good redox kinetics of its own. For simplicity, the Gibbs free energy change (ΔG) of indigo, Li₂S (representing “free” S²⁻ anions), and Li₃PS₄ (representing “terminal” S²⁻ anions) before and after oxidation reactions were calculated to determine their thermodynamic electrode potentials using the formula $\Delta G = -nFE$. In this equation, n is the number of electrons transferred, F is the Faraday constant, and E is the standard electrode potential. A higher absolute value of ΔG corresponds to a higher thermodynamic electrode potential. Based on density functional theory (DFT) calculation results, the ΔG absolute value of indigo is higher than that of Li₂S and lower than that of Li₃PS₄, suggesting that indigo can chemically oxidize “free” S²⁻ anions in LPSC while unable to directly oxidize “terminal” S²⁻ anions in PS₄³⁻ tetrahedra to P₂S₅ (Fig. 1c)⁴⁵. However, there still exists the possibility that indigo partially chemically oxidizes “terminal” S²⁻ anions to form linked or oligomerized thiophosphate units like P₂S_y (P₂S₇⁴⁻ and P₂S₆²⁻), which will be proved in the following sections. Furthermore, indigo demonstrates inherent rapid redox kinetics due to its semiconductor characteristics. The highest occupied molecular orbital (HOMO) and the

lowest unoccupied molecular orbital (LUMO) of indigo were calculated using DFT (Supplementary Fig. 2, Supplementary Data 1). The energy gap between the HOMO and LUMO orbitals shows a relatively low value of 2.69 eV among reported OEMs⁴⁶, attributed to its rapid intramolecular electron mobility within the planar molecular configuration. Therefore, indigo, as a small-molecule OEM, meets all the requirements for an ideal molecular catalyst to LPSC SE, offering a comparable areal density to typical TMOs while significantly reducing the overall cost of ASSBs (Supplementary Fig. 3, Supplementary Table 1).

The highly reversible synergistic redox process between indigo and the outer-sphere redox of LPSC SE can be described as follows: during 1st discharge, indigo is electrochemically reduced (step 3). In the subsequent 1st charge, LPSC SE is expected to undergo initial oxidation prior to reduced indigo due to the lower thermodynamic electrode potential of “free” S²⁻ anions. However, the intrinsic sluggish kinetics of LPSC SE cause its real electrochemical oxidation sequence in ASSBs to lag behind that of reduced indigo. After oxidation is finished, indigo subsequently chemically oxidizes the “free” S²⁻ anions (Step 4) and partially oxidizes “terminal” S²⁻ anions (Step 5) in PS₄³⁻ tetrahedra, returning to its reduced state to complete a catalytic cycle. In a typical catalytic cycle, the oxidized indigo molecular catalyst provides the necessary electron holes for the transition from S²⁻ anions to S_x species, effectively circumventing the sluggish inner-sphere redox of LPSC SE. After completing the outer-sphere oxidation of LPSC SE, indigo undergoes electrochemical oxidation to fulfill one charge process. Subsequently, during 2nd discharge, indigo and S_x species undergo reversible synergistic reduction, resulting in high reversible capacities

for ASSBs. Notably, since the outer-sphere redox of LPSC SE (Steps 3-5) is not an electrochemical process, the average charge potential of the synergistic oxidation between indigo and LPSC should remain the same as that of indigo rather than LPSC.



The sluggish redox kinetics of the inner-sphere redox pathway, as well as the enhanced redox kinetics of LPSC SE via the outer-sphere redox pathway, are evident in cyclic voltammetry (CV) curves. In liquid cells, the electrochemical reduction peak of indigo occurs at 2.15 V vs. Li⁺/Li and the electrochemical oxidation peak arises at 2.45 V vs. Li⁺/Li, with an average redox potential of 2.3 V, which surpasses the calculated thermodynamic electrode potential of 2.01 V vs. Li⁺/Li for “free” S²⁻ anions and 2.15 V vs. Li⁺/Li of Li₂S in liquid cells⁴⁷, providing further evidence that indigo can chemically oxidize LPSC SE in theory (Fig. 1d). Additionally, the CV profile of pure LPSC SE reveals two distinct oxidation peaks at 2.55 V and 2.8 V vs. Li⁺/Li, corresponding to the electrochemical oxidation of “free” S²⁻ anions and “terminal” S²⁻ anions, respectively, which are notably higher than the calculated

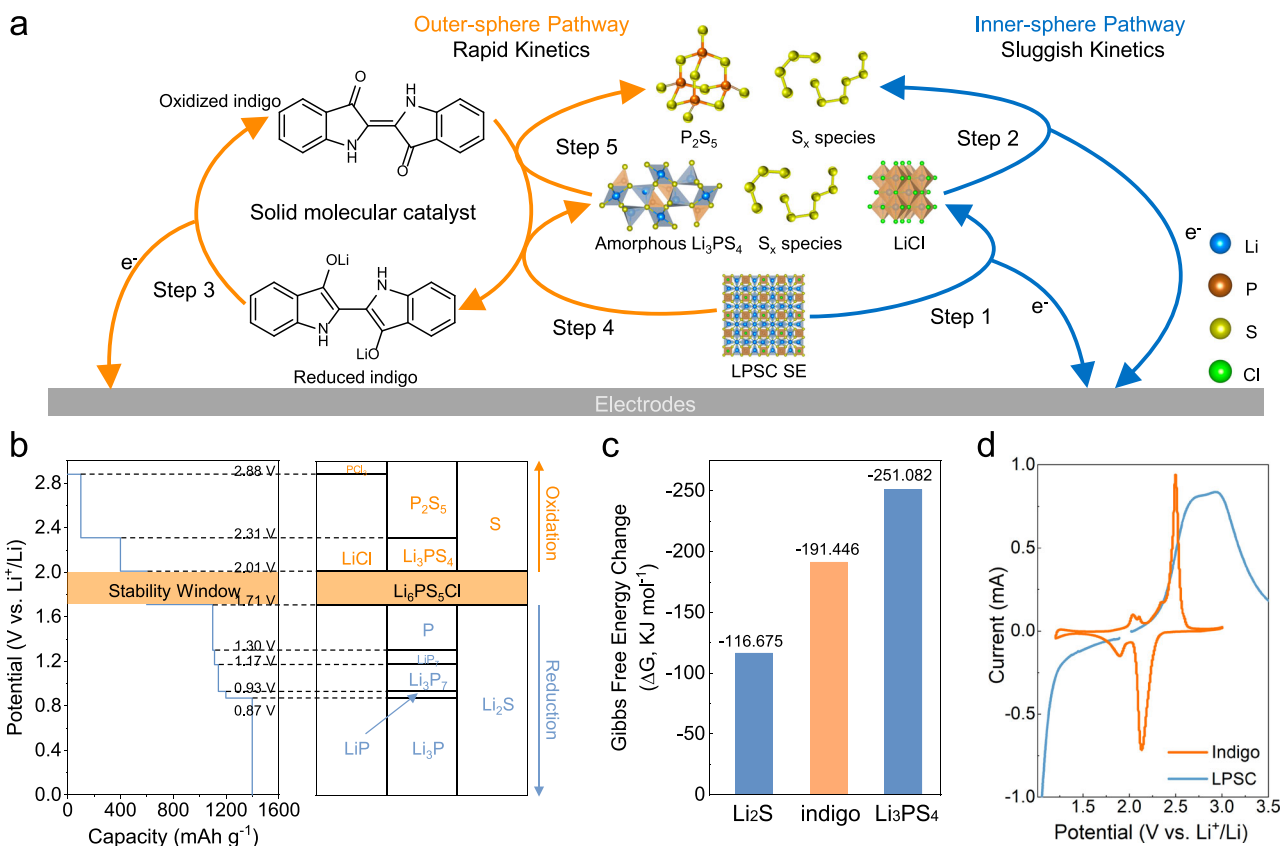


Fig. 1 | Working mechanism of indigo natural dye as both the active material and the molecular catalyst in sulfide-based ASSBs. a Schematic illustration of the outer-sphere redox pathway (catalyzed by the indigo molecular catalyst) and the typical inner-sphere redox pathway (electrochemical reaction) of LPSC SE. **b** Density functional theory (DFT) calculations of voltage profile and phase

equilibria of LPSC SE upon oxidation and reduction generated by pymatgen. **c** The calculated Gibbs free energy change of reaction step 1, step 2 and step 3. **d** CV curves of LPSC SE in ASSBs and indigo in liquid cells. Source data for this figure are provided as a Source Data file.

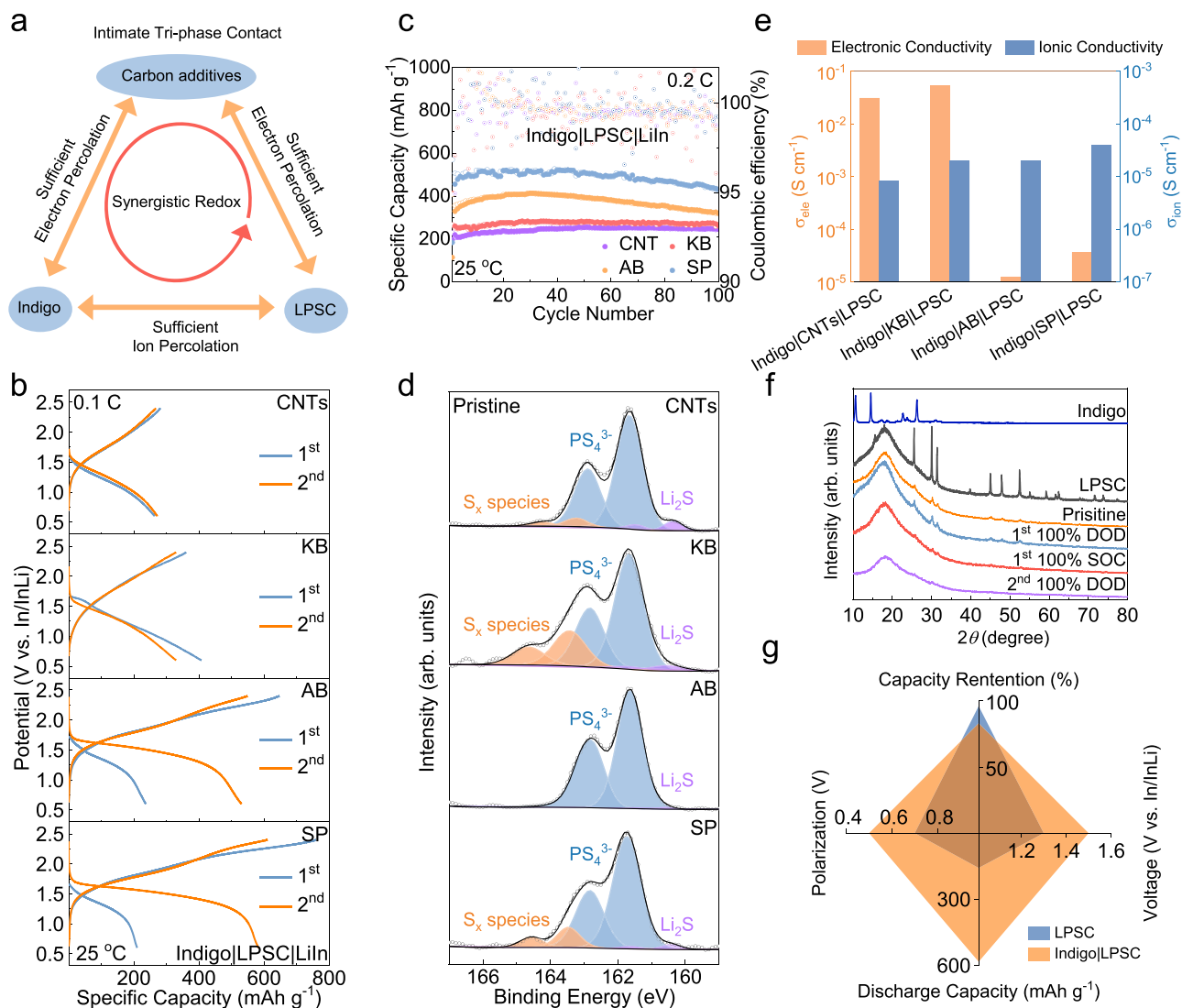


Fig. 2 | Different redox behavior in positive electrode composites with various carbon additives in sulfide-based ASSBs. **a** Schematic illustration of the optimization protocol for microstructure engineering of positive electrode composites. **b** Galvanostatic charge-discharge curves of positive electrode composites with various carbon additives at 0.1 C rate (1 C = 204 mA g⁻¹). **c** Comparison of cycling profiles between positive electrode composites with various carbon additives at 0.2 C rate. **d** High-resolution S 2p XPS spectra of pristine positive electrode composites with various carbon additives. **e** Electronic and ionic conductivity of positive electrode composites with various carbon additives measured via DC

polarization. **f** Ex situ XRD patterns of indigo|SP|LPSC positive electrode composite at 1st 100% DOD (achieved capacity -210 mAh g⁻¹), 1st 100% SOC (achieved capacity -759 mAh g⁻¹), and 2nd 100% DOD (achieved capacity -583 mAh g⁻¹), along with LPSC and indigo standards. **g** Comparison of inner-sphere and outer-sphere redox of LPSC SE in terms of capacity retention over 100 cycles, polarization, discharge capacity, and working voltage. The reversible specific capacity of the inner-sphere redox of LPSC SE was calculated based on the same weight as the outer-sphere redox for comparison. Source data for this figure are provided as a Source Data file.

thermodynamic values of 2.01 V and 2.31 V vs. Li⁺/Li (Fig. 1b). This notable disparity between experimental and theoretical values highlights the sluggish redox kinetics of LPSC SE via the inner-sphere redox pathway in ASSBs. In contrast, the CV profile of positive electrode composites incorporating indigo exhibits different electrochemical behavior, with a broad redox peak and reduced polarization compared to pure LPSC SE, indicating the role of indigo in facilitating the outer-sphere redox of LPSC SE and enhancing overall redox kinetics.

Microstructure engineering of positive electrode composites

Achieving highly reversible synergistic redox between indigo and LPSC SE requires intimate tri-phase contact among indigo, carbon additives, and LPSC SE, emphasizing the critical role of microstructure engineering in positive electrode composites (Fig. 2a). Therefore, positive electrode composites with four different representative carbon additives, including carbon nanotubes (CNTs), Ketjenblack (KB), acetylene

black (AB), and Super P varying in morphology, specific surface area, and particle size are selected to investigate the effect of microstructures (Supplementary Fig. 5-6, Supplementary Table 2). Among them, CNTs and KB have relatively large specific surface areas (-1400.94 and -1379.01 m² g⁻¹, respectively), while AB and SP exhibit a spherical morphology with moderate specific surface areas (-79.7 and -61.1 m² g⁻¹, respectively). The mass ratio of different components in positive electrode composites was optimized (Supplementary Fig. 7), and all full cells were tested within the potential range of 0.6 V to 2.4 V vs. In/Li-In to avoid the reduction of P³⁺ cations in LPSC SE (Supplementary Fig. 4)⁴⁴.

Interestingly, galvanostatic charge-discharge curves of four positive electrode composites show very different profiles in the first two cycles (Fig. 2b). For indigo|AB|LPSC and indigo|SP|LPSC positive electrode composites, an initial specific capacity of ~200 mAh g⁻¹ is observed after the 1st discharge, followed by a large specific capacity

exceeding 600 mAh g⁻¹ after the 1st charge. In the subsequent discharging process, the observed specific capacities are significantly higher than those in the 1st discharge cycle. This electrochemical behavior aligns with the proposed synergistic redox reactions between indigo and LPSC SE via an outer-sphere redox pathway. During the 1st discharge, indigo and a small amount of S_x species, which are oxidized by indigo during positive electrode composite mixing, are reduced. In the 1st charge, the outer-sphere redox of LPSC SE is activated, leading to a large oxidation capacity, which is then reversible in the 2nd discharge. Notably, the indigo|SP|LPSC positive electrode composite exhibits a reversible discharge capacity of 583 mAh g⁻¹ after 2nd discharge at 0.1 C (1 C = 204 mA g⁻¹), nearly three times higher than the theoretical capacity of indigo (204 mAh g⁻¹). This suggests that the outer-sphere redox reaction of the LPSC SE, catalyzed by indigo, provides an additional capacity of 379 mAh g⁻¹. In contrast, the SP|LPSC composite achieves only 158 mAh g⁻¹ (calculated based on the same weight as indigo|SP|LPSC) in 2nd cycle (Supplementary Fig. 8), less than half the capacity from the indigo|SP|LPSC composite. The average working potential of the indigo|SP|LPSC composite is 1.45 V vs. In/Li-In, significantly higher than the 1.22 V vs. In/Li-In observed in SP|LPSC, suggesting that the synergistic redox between indigo and LPSC SE can mitigate sluggish redox kinetics effectively.

In contrast, indigo|CNTs|LPSC and indigo|KB|LPSC positive electrode composites exhibit different electrochemical behavior. They exhibit much lower reversible specific capacities and no significant increase in charge capacity over discharge capacity in the 1st cycle, indicating limited synergistic redox activity between indigo and LPSC SE. Moreover, their 1st discharge capacities are notably high, particularly for indigo|KB|LPSC, which reaches nearly 407 mAh g⁻¹. These results are interesting, as carbon additives with large surface areas, like CNTs and KB, typically enhance the performance of OEMs in liquid cells⁴⁴, but appear to have the opposite effect in sulfide-based ASSBs. In liquid cells, the electrolyte can flow into the microstructure of OEM-carbon composites to achieve efficient ionic and electronic transport. In ASSBs, however, the large surface area of CNTs and KB hinders effective penetration at the interface between indigo and LPSC SE, resulting in their excessive dual-phase contact. Therefore, the large 1st discharge capacity observed in indigo|CNTs|LPSC and indigo|KB|LPSC positive electrode composites is likely due to the high formation of S_x species, produced by the chemical reaction between indigo and LPSC SE during mixing, resulting from poor tri-phase contact, as will be demonstrated by the following characterizations. Additionally, the comparison of cycling profiles at a 0.2 C rate also illustrates that indigo|SP|LPSC and indigo|AB|LPSC positive electrode composites achieve notably higher reversible capacities compared to indigo|CNTs|LPSC and indigo|KB|LPSC positive electrode composites within 100 cycles, with indigo|SP|LPSC demonstrating the highest value (Fig. 2c, and Supplementary Fig. 9). In conclusion, carbon additives with moderate surface area and spherical morphology are more effective than those with larger surface areas in promoting intimate tri-phase contact in solid positive electrode composites, thereby facilitating synergistic redox between indigo and LPSC SE.

To better understand the differences in electrochemical behavior, various characterizations were conducted for the four positive electrode composites. X-ray photoelectron spectroscopy (XPS) was employed to analyze the compositional differences in the four pristine positive electrode composites (Fig. 2d). In high-resolution S 2p spectra, the presence of doublet peaks corresponding to PS₄³⁻ tetrahedra (blue, 161.74/162.96 eV) and Li₂S (green, 160.53/161.83 eV) in all four positive electrode composites suggests that the primary component in each positive electrode composite remains LPSC SE (Supplementary Fig. 10). Moreover, the emerging doublet peaks (orange, 163.47/164.57 eV) belong to S_x species shows the highest relative intensity in the indigo|KB|LPSC positive electrode composite, confirming the excessive dual-phase contact rather than intimate tri-phase contact

mentioned above. In the high-resolution P 2p XPS spectra, all four positive electrode composites show only doublet peaks (132.05/132.95 eV) corresponding to PS₄³⁻ tetrahedra, indicating that the observed S_x species in the pristine positive electrode composites primarily originate from the oxidation of “free” S²⁻ anions in LPSC SE by indigo (Supplementary Fig. 11).

Moreover, measuring the ionic and electronic conductivities of the four positive electrode composites using the direct-current (DC) polarization technique provides further insights (Fig. 2e, and Supplementary Fig. 12–13). While the ionic conductivities of the four positive electrode composites are similar, with the indigo|SP|LPSC composite slightly higher than the others, the electronic conductivities vary significantly between carbon additives with large surface areas and those with spherical morphologies. According to percolation theory, high electronic conductivity typically indicates the formation of a long-range electron transport network. In indigo|CNTs and indigo|KB mixtures without LPSC, the large surface area of CNTs and KB facilitates indigo encapsulation within their micropores, disrupting long-range electron conduction. As a result, the electronic conductivity of indigo|CNTs and indigo|KB mixtures is nearly one order of magnitude lower than that of indigo|AB and indigo|SP mixtures (Supplementary Fig. 14, Supplementary Table 3), despite the intrinsically higher conductivity of CNTs and KB compared to AB and SP. However, the introduction of LPSC alters this trend: indigo|AB|LPSC (1.3×10^{-5} S cm⁻¹) and indigo|SP|LPSC (3.6×10^{-5} S cm⁻¹) composites exhibit electronic conductivity three orders of magnitude lower than indigo|CNTs|LPSC (3.2×10^{-2} S cm⁻¹) and indigo|KB|LPSC (5.5×10^{-2} S cm⁻¹). This reversal in electronic conductivity is attributed to excessive dual-phase contact between indigo and LPSC in CNT- and KB-based composites, which limits contact with carbon additives and reduces interfacial electronic percolation, thereby enhancing long-range electron transport. In contrast, the spherical morphologies of AB and SP promote more effective tri-phase contact, improving interfacial electron conduction in indigo|AB|LPSC and indigo|SP|LPSC composites but limiting overall long-range electronic conductivity. The outer-sphere redox behavior of LPSC SE catalyzed by indigo can also be observed in ex situ X-ray diffraction (XRD) patterns (Fig. 2f). In the pristine positive electrode composite, the characteristic peaks of indigo are not observed, and those of cubic LPSC SE are weakened due to the homogeneous ball-milled process. While the characteristic peaks of cubic LPSC SE maintain the same intensity as the pristine positive electrode composite after 1st 100% depths of discharge (DOD), they become barely observable after 1st 100% state of charge (SOC) and 2nd 100% DOD, indicating the formation of amorphous species due to deep redox reactions of LPSC SE via the outer-sphere redox pathway (Step 3-5).

In summary, compared to typical inner-sphere redox pathway, the outer-sphere redox of LPSC SE catalyzed by bifunctional indigo showcases higher reversible capacity, higher average working voltage, and reduced polarization in ASSBs, despite a slightly lower capacity retention (Fig. 2g, and Supplementary Fig. 8). In this section, we highlight the critical role of microstructure engineering in achieving highly reversible synergistic redox between indigo and LPSC SE. This study also provides the first evidence of using carbonyl-based OEMs as effective molecular catalysts to overcome the persistent interface challenge between OEMs and sulfide SEs, offering a promising pathway to enhance the energy density of sulfide-based ASSBs employing OEMs as active materials.

Synergistic redox mechanism between indigo and LPSC SE

Characterizing the component variations in different positive electrode composites during the charge-discharge process provides deeper insights into the synergistic redox mechanism. We first investigated the four positive electrode composites at 1st 100% SOC. S K-edge X-ray absorption spectroscopy (XAS) reveals distinct features in the four positive electrode composites after 1st charge, compared to

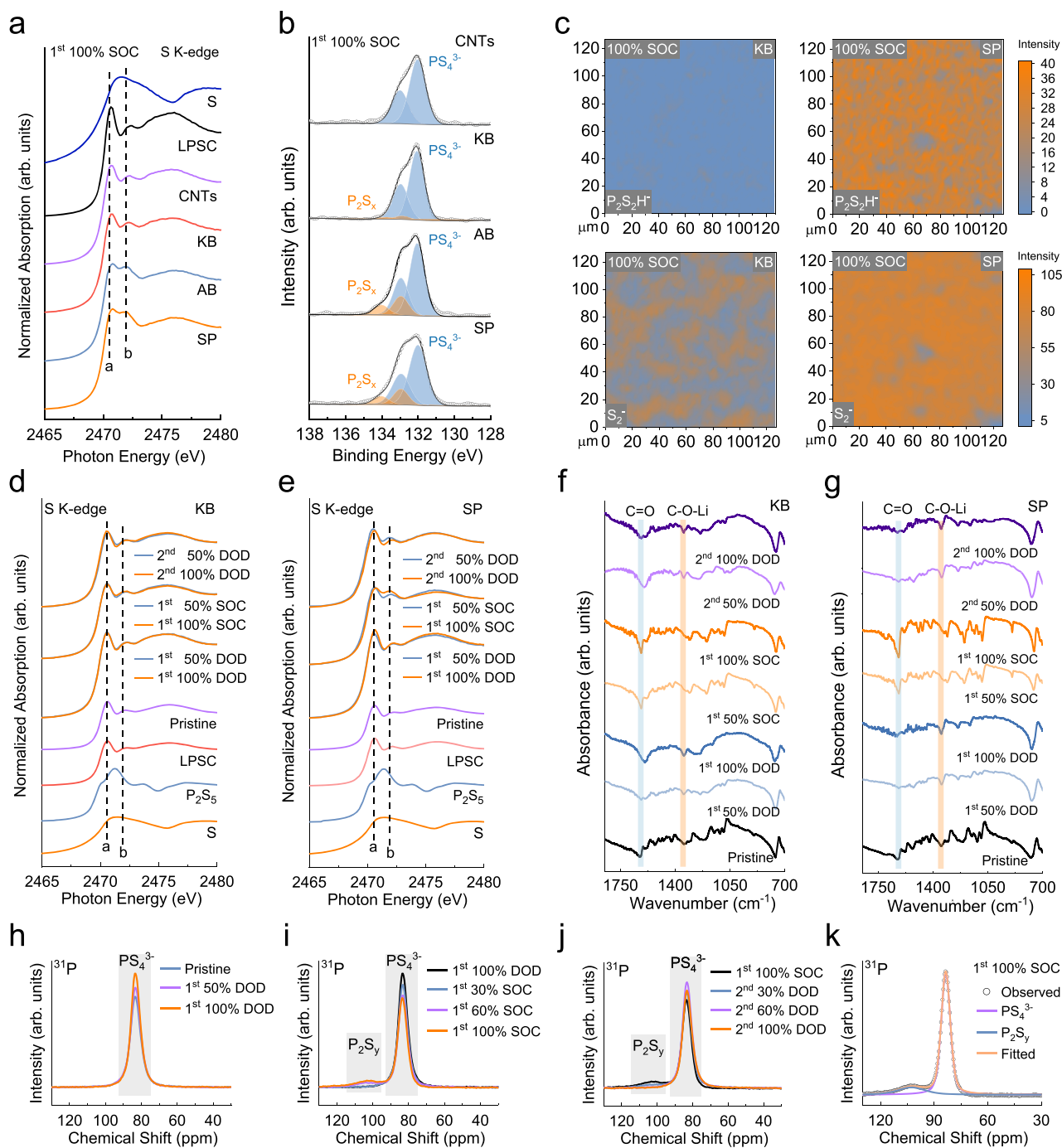


Fig. 3 | Characterization of synergistic redox behavior between indigo and LPSC SE in four positive electrode composites. **a** S K-edge XAS of sulfur, LPSC and four positive electrode composites with different carbon additives at 1st 100% SOC (achieved capacity $\sim 759 \text{ mAh g}^{-1}$ at 0.1 C). **b** High-resolution P 2p XPS spectra of four positive electrode composites with different carbon additives at 1st 100% SOC (achieved capacity $\sim 759 \text{ mAh g}^{-1}$ at 0.1 C). **c** 2D distribution of $\text{P}_2\text{S}_2\text{H}^+$ and S_2^- TOF-SIMS negative secondary ions in indigo|KB|LPSC and indigo|SP|LPSC positive electrode composites at 1st 100% SOC (achieved capacity $\sim 759 \text{ mAh g}^{-1}$ at 0.1 C). **d, e** Ex situ S K-edge XAS of indigo|KB|LPSC and indigo|SP|LPSC positive electrode

composites (ASSBs at various SOC and DOD were tested at 0.1 C). **f, g** Ex situ FT-IR of indigo|KB|LPSC and indigo|SP|LPSC positive electrode composites. **h–j**, ^{31}P MAS NMR spectra of indigo|SP|LPSC positive electrode composite at different charge-discharge states. **k** Fitted curve of ^{31}P MAS NMR spectra at 1st 100% SOC state. All the battery were tested at an average temperature of 25 °C. Source data for this figure are provided as a Source Data file. XAS normalization involves subtracting the pre-edge background and scaling the post-edge region so the absorption edge step is standardized to unity for accurate comparison.

standard references (Fig. 3a). The strongest peak ‘a’ (2470.62 eV) corresponds to the typical PS_4^{3-} tetrahedral local environment, while peak ‘b’ (2471.98 eV) represents a more complex combination peak of LPSC, sulfur and P_2S_y species⁴⁸. Notably, indigo|CNTs|LPSC and indigo|KB|LPSC positive electrode composites exhibit peak ‘a’ and peak ‘b’ features similar to LPSC SE, without features of S_x and P_2S_y species,

suggesting limited redox activity of LPSC SE with carbon additives with large specific surface areas in positive electrode composites. In contrast, the intensified peak ‘b’ in indigo|AB|LPSC and indigo|SP|LPSC positive electrode composites support the formation of S_x and P_2S_y species after 1st charge due to the activated redox of LPSC SE via an outer-sphere pathway. It is worth noting that features corresponding

to S_x species observed in the XPS spectra of the pristine indigo|KB|LPSC positive electrode composite cannot be detected in XAS due to the greater detection depth of XAS compared to XPS (Fig. 2d)⁴⁹, indicating only a small amount of these species formed at the interfaces. In contrast, the clear features corresponding to S_x species in the XAS of indigo|AB|LPSC and indigo|SP|LPSC positive electrode composites after the 1st charge suggest a significant amount of oxidized S_x species in the bulk through the outer-sphere redox of LPSC SE. Moreover, high-resolution P 2p XPS spectra reveal emerging doublet peaks at higher binding energies (orange, 132.92/134.02 eV) than the doublet peaks associated with PS_4^{3-} tetrahedra (blue, 132.05/132.95 eV) in indigo|AB|LPSC and indigo|SP|LPSC positive electrode composites after 1st charge. However, these peaks are negligible in indigo|CNTs|LPSC and indigo|KB|LPSC positive electrode composites and in all four pristine positive electrode composites (Fig. 3b, and Supplementary Fig. 10). These emerging peaks correspond to linked or oligomerized thiophosphate units P_2S_y ($P_2S_7^{4-}$, $P_2S_6^{2-}$, or even P_2S_5) as oxidation products of “terminal” S^{2-} anions in LPSC SE, proving indigo can also partially oxidize “terminal” S^{2-} anions during the outer-sphere redox of LPSC SE. Meanwhile, time-of-flight secondary ion mass spectrometry (TOF-SIMS) detects strong signals of negative secondary ions $P_2S_2H^-$ and S_2^- in the indigo|SP|LPSC positive electrode composite after 1st charge cycle, while much weaker intensities are observed in the indigo|KB|LPSC and SP|LPSC positive electrode composites after 1st charge cycle (Fig. 3c, and Supplementary Fig. 15). These analyses confirm that indigo, as a solid molecular catalyst, can catalyze the oxidation of both “free” and “terminal” S^{2-} anions in LPSC SE during charging when intimate tri-phase contact is achieved in the positive electrode composites, resulting in synergistic redox with enhanced kinetics.

Ex situ XAS and Fourier-transform infrared spectroscopy (FT-IR) for indigo|KB|LPSC and indigo|SP|LPSC positive electrode composites are further carried out. The main peak ‘a’ (2470.62 eV) and peak ‘b’ (2471.98 eV) in S K-edge X-ray absorption near-edge structure (XANES) of the indigo|KB|LPSC positive electrode composite exhibit nearly consistent features across different depths of discharge and state of charge in both 1st and 2nd cycles, indicating that the average local structures surrounding sulfur atoms in LPSC SE remain largely unchanged throughout the entire charge-discharge process (Fig. 3d). In contrast, the intensity of peak ‘b’ associated with S_x species in the S K-edge XANES of the indigo|SP|LPSC positive electrode composite remains unchanged during 1st discharge, but gradually increases during 1st charge, and subsequently diminishes during 2nd discharge (Fig. 3e, and Supplementary Fig. 16). In FT-IR, characteristic peaks belonging to the carbonyl group (1617 cm^{-1}) of indigo show minimal variation across different depths of discharge and charge during both 1st and 2nd cycle in the indigo|KB|LPSC positive electrode composite, indicating the limited redox activity of indigo due to poor tri-phase contact (Fig. 3f). Conversely, these peaks in indigo|SP|LPSC positive electrode composite gradually disappear during 1st discharging process, reappear from 50% SOC to 100% SOC during 2nd charging process, and then gradually vanish again from 50% DOD to 100% DOD during 2nd discharging (Fig. 3g). Similarly, characteristic peaks belonging to “C-O-Li” group exhibit a reverse evolution trend. In summary, the evolution of features observed in ex situ XANES and FT-IR analyses supports the correlation between microstructure and the synergistic redox activity between indigo and LPSC SE (Fig. 1a).

To further investigate the synergistic redox behavior between indigo and LPSC SE, ex situ solid-state nuclear magnetic resonance (NMR) measurements were conducted on the indigo|SP|LPSC positive electrode composite. Single pulse ^{31}P magic angle spinning (MAS) NMR was used to probe the structural evolution of P-S polyhedron in the LPSC SE during charge-discharge process. During 1st discharge, the intensity of the peak at 84 ppm, corresponding to PS_4^{3-} tetrahedra, increases (Fig. 3h), likely due to the lithiation of minor corner- or edge-sharing PS_4^{3-} tetrahedra in the thiophosphate glass phase formed

during LPSC synthesis. Upon charging, a new peak emerges at 103 ppm at 1st 60% and 100% SOC, accompanied by a decreased peak intensity at 84 ppm (Fig. 3i). This shift suggests the partial oxidation of “terminal” S^{2-} anions in PS_4^{3-} tetrahedra, leading to the formation of P_2S_y polysulfide species (e.g., $P_2S_7^{4-}$ and $P_2S_6^{2-}$). During 2nd discharge, the peak at 103 ppm diminishes, and the peak at 84 ppm regains intensity (Fig. 3j). Peak fitting at 1st 100% SOC reveals that ~16% of PS_4^{3-} tetrahedra are converted to polysulfide species (Fig. 3k). Furthermore, peak fitting at 2nd 100% DOD confirms the complete recovery of PS_4^{3-} tetrahedra (Supplementary Fig. 17), demonstrating the fully reversible nature of S^{2-} redox in the LPSC SE via an outer-sphere redox pathway. To investigate the interactions between indigo and LPSC SE, ^{31}P cross-polarization magic angle spinning (CP-MAS) NMR was performed (Supplementary Fig. 18). CP-MAS technique enhances the NMR signal of low-abundance nuclei (e.g., ^{31}P) by transferring polarization from abundant ^1H nuclei, providing insights into dipole-dipole interactions and the proximity of functional groups in complex solid materials⁵⁰. The single pulse ^{31}P MAS NMR spectra at 1st 100% SOC reveal two distinct ^{31}P resonances corresponding to PS_4^{3-} tetrahedra and P_2S_y polysulfide species. In contrast, the ^{31}P CP-MAS spectra at 1st 100% SOC, acquired with contact times of 2–6 ms, display only the resonance for PS_4^{3-} tetrahedra, with no detectable signal from P_2S_y species. Since CP efficiency depends on dipole-dipole interaction strength⁵¹, the absence of P_2S_y signals in different contact time suggests that these species are spatially distant from ^1H nuclei in indigo. By comparing the single pulse ^{31}P MAS NMR and CP-MAS spectra, we conclude that indigo specifically interacts with PS_4^{3-} tetrahedra in the LPSC SE but not with the oxidation product P_2S_y species, supporting the role of indigo as a solid molecular catalyst in the oxidation process of LPSC SE. ^7Li MAS NMR measurements were further carried out to provide an overview for the synergistic redox between indigo and LPSC (Supplementary Fig. 19). These solid-state NMR spectra indicate the reversible synergistic redox behavior between indigo and LPSC SE.

Synergistic redox kinetics between indigo and LPSC SE

The rapid synergistic redox behavior between indigo and LPSC SE is identified by various electrochemical and microscopic techniques. In situ electrochemical impedance spectroscopy (EIS) Nyquist plots and the corresponding distribution of relaxation time (DRT) reveal distinctly different electrochemical behaviors in the indigo|KB|LPSC, SP|LPSC and indigo|SP|LPSC positive electrode composites. For the indigo|KB|LPSC positive electrode composite, the Nyquist plots show only the typical bulk resistance (R_{bulk}) of SEs throughout the charge-discharge process, without clear charge transfer resistance (R_{ct}) (Fig. 4a). This is due to the limited redox activity of indigo and LPSC SE in the indigo|KB|LPSC positive electrode composite, with only S_x species in the pristine positive electrode composite contributing most capacities, as previously discussed. Therefore, the overall decrease in resistance observed in the EIS Nyquist plots during the 1st and 2nd discharging process, and the increase during the 1st charging process, can be attributed to the volume expansion of S_x species during the discharge/lithiation process. Notably, the Nyquist plots of the indigo|KB|LPSC positive electrode composite show very similar features to the widely reported sulfur positive electrodes in ASSBs^{52,53}, further validating the dominant role of S_x species in the indigo|KB|LPSC positive electrode composite during the charge-discharge process. The corresponding DRT during charge-discharge cycles primarily shows characteristic peaks related to charge transfer in the LiIn alloy negative electrode with a time constant ranging from 10^{-3} to 10^{-1} s⁵⁴, while the region with a time constant shorter than 10^{-3} s shows negligible characteristic peaks. In contrast, EIS Nyquist plots of the SP|LPSC positive electrode composite without indigo show clear R_{bulk} and R_{ct} , which are further fitted with equivalent electrical circuits (Fig. 4b, and Supplementary Fig. 20, Supplementary Table 4a). R_{bulk} and R_{ct} remain similar during the 1st discharging process but increase from 55.73 Ω and 7.45 Ω

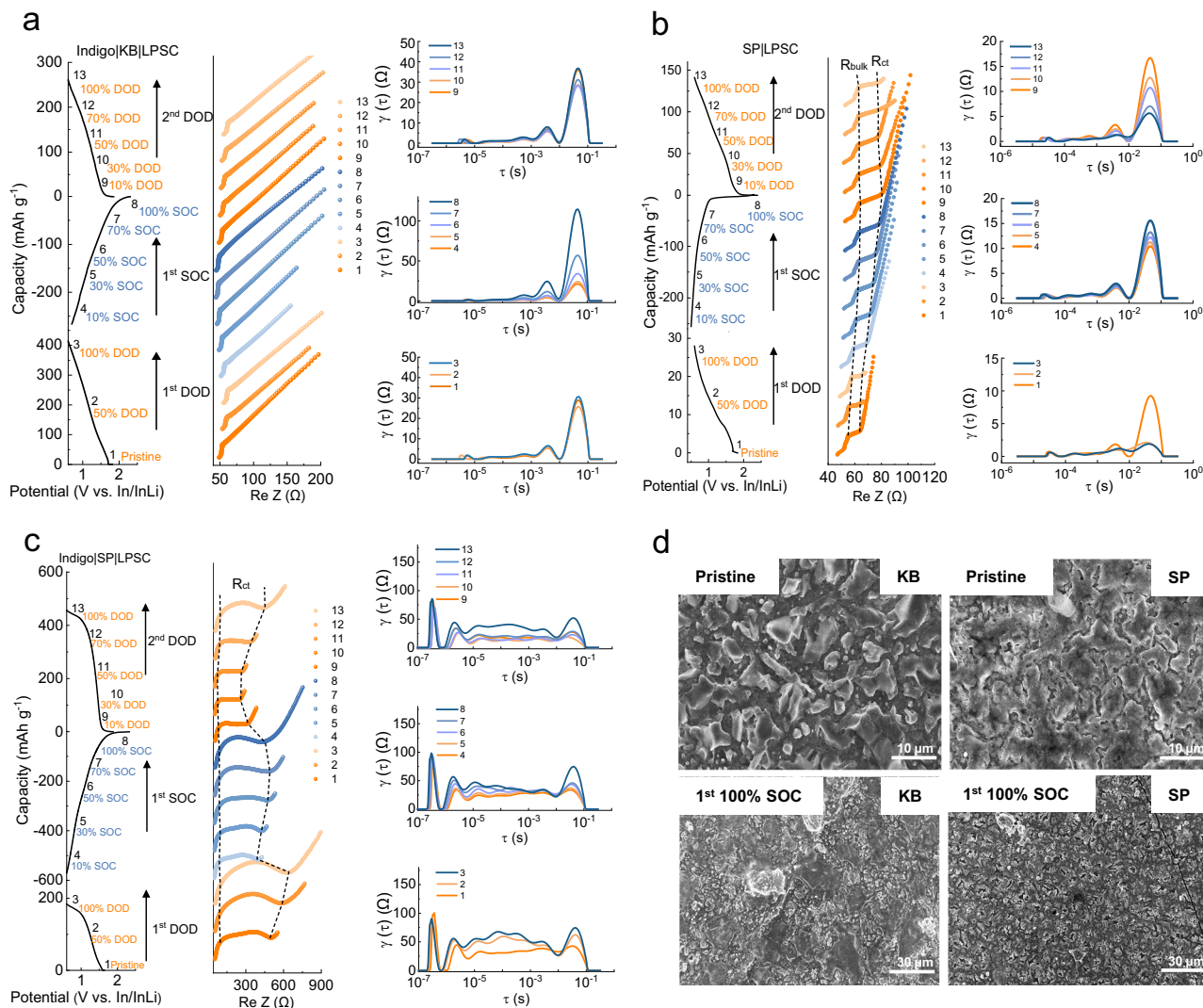


Fig. 4 | Electrochemical and microscopic characterizations of different positive electrode composites during charge-discharge process. In situ EIS Nyquist plots and the corresponding DRT $\gamma(\tau)$ of (a) indigo|KB|LPSC; b SP|LPSC and c indigo|SP|

LPSC positive electrode composites at 0.2 C rate at 25 °C. d, SEM images of indigo|KB|LPSC and indigo|SP|LPSC positive electrode composites before (pristine state) and after 1st charged. Source data for this figure are provided as a Source Data file.

to 63.89 Ω and 17.83 Ω , respectively, after 1st charging, then change slightly to 63.14 Ω and 20.79 Ω after 2nd discharging. The increased R_{bulk} and R_{ct} in the 1st charging and 2nd discharging process are due to the formation of electronically and ionically insulating LiCl, S_x and P_2S_5 species in the electrochemical oxidation of “free” and “terminal” S^{2-} anions in LPSC SE (Step 1-2). From another perspective, the maximum R_{ct} in the SP|LPSC positive electrode composite is only 20.79 Ω , indirectly reflecting the limited electrochemical redox activity of LPSC SE in the inner-sphere pathway, as also evidenced by the negligible peak variation in the DRT, except for the charge transfer resistance in the Li|In negative electrode.

Interestingly, the evolution of EIS in the indigo|SP|LPSC positive electrode composite is more complex owing to the synergistic redox between indigo and LPSC SE (Fig. 4c, and Supplementary Fig. 21, Supplementary Table 4b). During 1st discharging process, R_{ct} increases up to 505.2 Ω at 100% DOD due to the lithiation of indigo, which is not observed in the EIS Nyquist plot of indigo|KB|LPSC positive electrode composite, further confirming the limited redox activity of indigo in indigo|KB|LPSC positive electrode composite. During the 1st charging process, R_{ct} initially drops from 505.24 Ω at 100% DOD to 323.15 Ω at the beginning of charging process due to the de-lithiation of reduced indigo. However, as charging continues, R_{ct} increases to 353.95 Ω because of the

chemical oxidation of LPSC SE by indigo. After the completion of the outer-sphere redox of LPSC SE, R_{ct} drops again to 334.86 Ω due to the final de-lithiation of indigo. In the subsequent 2nd discharging process, the overall resistance is significantly reduced compared to the 1st cycle, suggesting gradually optimized interfacial characteristics during the synergistic oxidation process. Initially, R_{ct} decreases to 214.25 Ω due to the formation of ionically conductive amorphous Li_3PS_4 phase during the lithiation of S_x species formed in the 1st charging process. However, R_{ct} then increases to 323.43 Ω due to the lithiation of indigo. Unlike indigo|KB|LPSC and SP|LPSC positive electrode composites, the corresponding DRT in the indigo|SP|LPSC positive electrode composite shows strong signals with a time constant in the range of 10^6 to 10^3 s related to the charge transfer resistance in the synergistic redox between indigo and LPSC SE. The evolution trend of DRT aligns well with the EIS Nyquist plot, thus validating the proposed working mechanism of bifunctional indigo in sulfide-based ASSBs. Despite the higher overall resistance of the indigo|SP|LPSC positive electrode composite compared to the indigo|KB|LPSC and SP|LPSC positive electrode composites, galvanostatic intermittent titration technique (GITT) reveals good redox kinetics due to consistently high diffusion coefficients across cycling, supporting its outstanding electrochemical performance in ASSBs (Supplementary Fig. 22), which will be discussed in detail later. Scanning electron

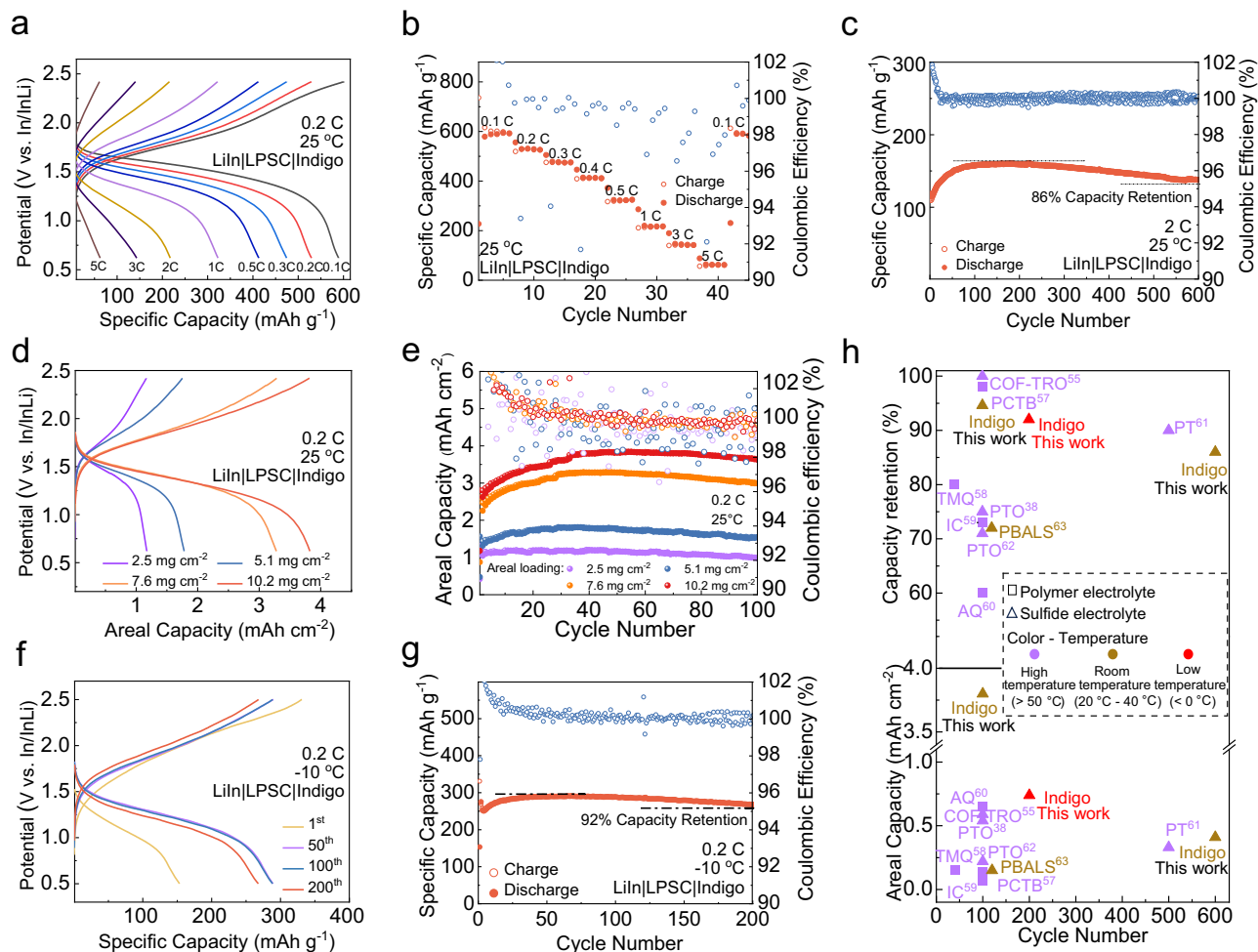


Fig. 5 | Electrochemical performance of indigo|SP/LPSC positive electrode composite in ASSBs. **a** Galvanostatic charge-discharge curves at different specific current at 25 °C. **b** Rate performance at 25 °C. **c** Cycling profile at a specific current of 2 C at 25 °C (1 C = 204 mAh g⁻¹). **d** Galvanostatic charge-discharge curves and (e) cycling profiles with different areal capacities. **f**, Galvanostatic charge-discharge

curves and (g) cycling profiles at a 0.2 C rate under -10 °C. **h** Summary of state-of-the-art ASSBs using OEMs as active materials in terms of cycling performance, areal capacity and operating temperature. HT = high temperature (> 50 °C); RT = room temperature (20 °C–40 °C); LT = low temperature (< 0 °C). Source data for this figure are provided as a Source Data file.

microscope (SEM) images reveal the morphology evolution of indigo|KB|LPSC and indigo|SP|LPSC positive electrode composites during the charge-discharge process (Fig. 4d, Supplementary Fig. 23). The pristine indigo|KB|LPSC positive electrode composite shows large, irregular aggregates with KB carbon encapsulating the indigo and LPSC SE, resulting from the excessive dual-phase contact between indigo and LPSC SE rather than uniform tri-phase contact during the mixing process. Notably, the indigo|KB|LPSC positive electrode composite after 1st charging exhibits even more irregular features. In contrast, the pristine indigo|SP|LPSC positive electrode composite displays a uniform morphology, with the charged electrode showing uniformly distributed ‘flower-like’ particles related to the outer-sphere oxidation products of LPSC SE formed via the homogeneous catalytic reaction. Therefore, we successfully correlate the structural evolution in different positive electrode composites with their electrochemical behavior, further validating the synergistic redox mechanism and confirming its rapid redox kinetics in sulfide-based ASSBs.

Sulfide-based ASSBs with bifunctional indigo natural dye

To demonstrate the application potential of incorporating bifunctional OEMs into sulfide-based ASSBs, we further evaluate the electrochemical performance of the indigo|SP|LPSC positive electrode composite (Supplementary Fig. 24). Rate performance of the ASSBs was investigated over a wide specific current range from 0.1 C to 5 C (1 C = 204 mA g⁻¹) at

25 °C (Fig. 5a, b). Galvanostatic charge-discharge curves of indigo|SP|LPSC positive electrode composite indicate much smaller polarization compared to the redox reactions of LPSC SE in the inner-sphere pathway, attributed to improved kinetics in the synergistic redox process. ASSBs incorporating bifunctional indigo deliver a discharge capacity of 591.2, 525.7, 472.2, 406.6, 323.5, 218.0, 140.2, and 60.8 mAh g⁻¹ at specific current of 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 3.0, and 5.0 C, respectively, recovering to 588.1 mAh g⁻¹ as the specific current is restored back to 0.1 C (1 C = 204 mA g⁻¹). Moreover, the fabricated ASSBs demonstrate stable cycling performance, retaining 86% of their capacity over 600 cycles (0.023% per cycle) at a high specific current of 2 C at 25 °C (Fig. 5c, and Supplementary Fig. 25). This good cycling stability is attributed to the well-maintained charge transfer across the indigo-LPSC interface and the progressive activation of S²⁺ redox through the outer-sphere pathway, as demonstrated by XPS and EIS analyses of the indigo|SP|LPSC electrode before and after cycling (Supplementary Fig. 26). To evaluate their practical viability, ASSBs incorporating bifunctional indigo are further evaluated at high active material loading and low temperature. Given the good redox kinetics in positive electrode composites facilitated by the indigo molecular catalyst, high-loading ASSBs (>10 mg cm⁻²) could deliver a high areal capacity of 3.8 mAh cm⁻² with no capacity degradation over 100 cycles under 0.2 C at 25 °C (Fig. 5d, e). Moreover, under a low operating temperature (-10 °C), ASSBs deliver the capacity of 290 mAh g⁻¹ and maintain 92% capacity after 200 cycles (0.09% per

cycle) (Fig. 5f, g). ASSBs incorporating bifunctional indigo tested under low stack pressures and higher positive electrode mass ratio were also carried out (Supplementary Fig. 27). Notably, while halide SEs exhibit a wider electrochemical window than sulfide SEs, their electrochemical performance is significantly inferior to the indigo|SP|LPSC electrode demonstrated here, underscoring the effectiveness of leveraging beneficial chemical reactions between indigo and LPSC SE to catalyze S^2 redox (Supplementary Fig. 28). The electrochemical performance of sulfide-based ASSBs incorporating bifunctional indigo was compared with that of other OEMs in ASSBs using both polymer and sulfide SEs (Fig. 5h, and Supplementary Table 5, Supplementary Table 6)^{38,55–63}. The comparison shows that most reported ASSBs operate at high temperatures whether they use polymer or sulfide SEs. Among them, ASSBs with bifunctional indigo exhibit the good cycling stability and the high areal capacity at 25 °C. Moreover, ASSBs incorporating bifunctional indigo represent the report of ASSBs using OEMs that can operate at low temperatures. In summary, the good integrated electrochemical performance highlights the potential of incorporating bifunctional indigo natural dye into ASSBs as a strategic solution to overcome the bottlenecks faced by OEMs in practical applications.

In this study, we report a bifunctional indigo natural dye that enhances the highly reversible synergistic redox between indigo and LPSC SE in sulfide-based ASSBs, achieving good electrochemical performance at both 25 °C and low temperatures (−10 °C). Contrary to the belief that limited performance of ASSBs using OEMs stems from the chemical incompatibility, our findings unveil a beneficial chemical reaction between indigo and LPSC SE catalyzing the rapid outer-sphere redox of LPSC SE. This conclusion is supported by multiple characterizations, including XAS, FT-IR, EIS, and solid-state NMR. This synergistic redox results in a reversible capacity of 583 mAh g^{−1} (LPSC contribution: 379 mAh g^{−1}) at a 0.1 C rate (1 C = 204 mA g^{−1}) and a high areal capacity of 3.8 mAh cm^{−2} at 25 °C, representing the good electrochemical performance among reported ASSBs using OEMs. Moreover, we demonstrate that microstructure engineering of positive electrode composites to achieve intimate tri-phase contact is crucial for realizing the rapid synergistic redox. The bifunctionality, cost-effectiveness, and enhanced synergistic redox of indigo in ASSBs underscore its promise for high-energy-density applications. This study highlights the promise of OEMs as solid molecular catalysts in sulfide-based ASSBs, offering a strategic pathway to address practical challenges in energy storage applications. Future research will focus on optimizing catalytic reactions for stable cycling at areal capacities exceeding 10 mAh cm^{−2}, thereby advancing the practical application of ASSBs using OEMs as active materials.

Methods

Chemicals

All reagents commercially available were used as received without further purification. Indigo (95%), bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 99.95%), 1,3-dioxolane (DOL, 99%), and 1,2-dimethoxyethane (DME, 99.5%) were purchased from Sigma-Aldrich. Carbon additives (AB, CNTs, KB and SP) and LPSC (99.9%) solid electrolyte were obtained from MSE supplies.

Characterizations

X-ray photoelectron spectroscopy (XPS) was performed on Thermo Scientific K-Alpha with Al K α X-ray radiation of 1486.6 eV. X-ray diffraction (XRD) measurements were performed on a Rigaku SmartLab SE X-ray diffractometer equipped with Cu K α radiation (λ = 1.5406 Å). XRD measurements were performed with a scan rate was 2° per minute and a step size of 0.02°. To protect air-sensitive samples, the sample holder was covered with Kapton tape during XRD measurements. Scanning electron microscope (SEM) images were obtained using a Hitachi S-4800 field-emission scanning electron microscope (FE-SEM) operating at an acceleration voltage of 1 kV. SEM images of indigo|KB|LPSC at

pristine state (after ball milled) and after 1st charged (1st 100% SOC, achieved capacity -360 mAh g^{−1} at 0.1 C in an average temperature of 25 °C) were analyzed. And SEM images of Indigo|SP|LPSC at pristine state (after ball milled) and after 1st charged (1st 100% SOC, achieved capacity -759 mAh g^{−1} at 0.1 C at average temperature of 25 °C) were also discussed. An ION-TOF GmbH (Germany) time-of-flight secondary ion mass spectrometry (TOF-SIMS) was used to investigate the samples using a pulsed 25 keV Bi₃⁺ primary cluster ion beam. By repeating the process of alternatively sputtering the surface in an area of 300 μ m $\times$ 300 μ m with a 3 keV Cs⁺ sputter ion beam for 1 s and collecting negative ion mass spectra using the Bi₃⁺ primary ion beam at 128 $\times$ 128 pixels over an area of 128 μ m $\times$ 128 μ m within the sputtered area, a layer of -10 nm was probed. By plotting the intensities of ions P₂S₂H[−] and S₂[−] against the rastered pixels, their images were obtained and presented in false color scales. Fourier-transform infrared spectroscopy (FT-IR) spectra were obtained using a Thermo Scientific Nicolet 6700 Analytical FTIR spectrometer equipped with an attenuated total reflection (ATR) apparatus. Surface area and pore size distribution were determined by N₂ adsorption-desorption isotherms at 80 °C using the Micromeritics TriStar II PLUS. X-ray absorption spectroscopy (XAS) data were acquired at the Soft X-ray Microcharacterization Beamline (SXRMB) at the Canadian Light Source. Samples were mounted onto double-sided, conductive carbon tape and loaded into the vacuum chamber with a 10^{−7} torr vacuum. A sulfur piece powder (Alfa Aesar) was used as a reference for energy calibration. A 7-element SDD detector was used to record the fluorescence yield (FLY). For ex situ experiments, ASSBs at various SOC and DOD were disassembled in an argon-filled glovebox (H₂O < 0.1 ppm, O₂ < 0.1 ppm) and then transferred to the sample chamber without exposure to air. Ex situ XRD patterns of indigo|SP|LPSC positive electrode composite were collected at 1st 100% DOD (achieved capacity -210 mAh g^{−1}), 1st 100% SOC (achieved capacity -759 mAh g^{−1}), and 2nd 100% DOD (achieved capacity -583 mAh g^{−1}) states at 0.1 C. Ex situ S K-edge XAS and FTIR of indigo|KB|LPSC positive electrode composite were collected at 1st 50% DOD (achieved capacity -159 mAh g^{−1}), 1st 100% DOD (achieved capacity -407 mAh g^{−1}), 1st 50% SOC (achieved capacity -167 mAh g^{−1}), 1st 100% SOC (achieved capacity -360 mAh g^{−1}), 2nd 50% DOD (achieved capacity -199 mAh g^{−1}), and 2nd 100% DOD (achieved capacity -330 mAh g^{−1}) states at 0.1 C. Ex situ S K-edge XAS and FTIR of indigo|SP|LPSC positive electrode composite were collected at 1st 50% DOD (achieved capacity -130 mAh g^{−1}), 1st 100% DOD (achieved capacity -210 mAh g^{−1}), 1st 50% SOC (achieved capacity -330 mAh g^{−1}), 1st 100% SOC (achieved capacity -759 mAh g^{−1}), 2nd 50% DOD (achieved capacity -300 mAh g^{−1}), and 2nd 100% DOD (achieved capacity -583 mAh g^{−1}) states at 0.1 C. All crystal structures shown in Fig. 1a and Supplementary Fig 1 were generated using the VESTA software⁶⁴.

Solid-state nuclear magnetic resonance (NMR) measurements were performed on a Varian INOVA 600 (I600) spectrometer operating at a magnetic field strength of 14.1 T, using a 2.5 mm double resonance (H/X) Phoenix MAS probe. Samples were packed inside an argon-filled glovebox, and all measurements were conducted at an average temperature of 25 °C. Single pulse ⁷Li (232.25 MHz) MAS (20 kHz) spectra were acquired using a 45° pulse length of 1.3 μ s, a pulse delay of 1 s, and 4 scans. The ⁷Li NMR chemical shifts were referenced to a 1 M aqueous solution of LiCl at 0 ppm. Single pulse ³¹P (241.93 MHz) MAS (20 kHz) spectra were acquired using a 90° pulse length of 3.1 μ s, a pulse delay of 30 s, and 16 scans. The ³¹P chemical shifts were referenced to ammonium dihydrogen phosphate at 1.6 ppm. ³¹P cross-polarization magic angle spinning (CP-MAS) NMR was carried out with contact times of 2, 4 and 6 ms, and the Hartmann-Hahn matching condition was set up based on the compound of ammonium dihydrogen phosphate. ³¹P MAS NMR spectra of indigo|SP|LPSC positive electrode composite were collected at 1st 50% DOD (achieved capacity -130 mAh g^{−1}), 1st 100% DOD (achieved capacity -210 mAh g^{−1}), 1st 30% SOC (achieved capacity -131 mAh g^{−1}), 1st 60% SOC (achieved capacity -450 mAh g^{−1}), 1st 100% SOC (achieved capacity

-759 mAh g⁻¹, 2nd 30% DOD (achieved capacity -150 mAh g⁻¹), 2nd 60% DOD (achieved capacity -350 mAh g⁻¹), and 2nd 100% DOD (achieved capacity -583 mAh g⁻¹) states at 0.1 C.

All ex situ characterizations were carried out by disassembling the batteries inside an argon-filled glove box (O₂ and H₂O < 0.1 ppm). The electrodes were then sealed in bags before being removed and transferred for characterization. The ambient temperature within the glove box was maintained at -25 °C.

Battery fabrication

Fabrication of liquid cells. The homogeneous positive electrode slurries, comprising 50 wt% indigo, 40 wt% Super P, and 10 wt% polyacrylonitrile copolymer (La133, binder), were cast a single layer onto Al foil (113 μm thick) with an average loading of 2 mg cm⁻² and dried at 80 °C overnight. 2 M LiTFSI in DOL/DME (v:v = 1:1) was utilized as the electrolyte (20 μL) in Li-ion half cells (CR2032, stainless steel casing), with poly(propylene) (PP, Celgard 2400) serving as the separator, lithium anode (1 mm thick). All half cells were assembled within an argon-filled glovebox (H₂O < 0.1 ppm, O₂ < 0.1 ppm).

Preparation of positive electrode composites in ASSBs: Indigo powder, LPSC SE and various carbon additives were initially weighted at a mass ratio of 2:6:2. For higher positive electrode mass ratios, the components were weighed at different ratios: 3:2:5 and 5:2:3. The measured mixture, totaling ~500 mg, was then placed in a zirconia jar (100 ml) with 30 g zirconia balls in an argon-filled glovebox (H₂O < 0.1 ppm, O₂ < 0.1 ppm). The mixture was ball-milled for 4 h at 200 rpm and the resulting positive electrode composite was subsequently transferred back to the glovebox for further use.

Fabrication of ASSBs. 80 mg of LPSC (size: < 10 μm) was placed into a PEEK die with an inner diameter of 10 mm and cold-pressed under 2 tons for 3 minutes to form a central solid electrolyte layer (thickness: ~0.8 mm). Subsequently, 10 mg of the positive electrode composite was evenly distributed over the LPSC central layer and compressed at 3.5 tons for another 3 minutes. For high-loading cells, the positive electrode composite mass can vary up to 50 mg. On the negative electrode side, the home-made Li-In alloy pieces were attached to LPSC central layer and pressed together at 2 tons to ensure intimate contact. To prepare the homemade Li-In alloy, lithium and indium foils were stacked at a weight ratio of 1:40. The stacked layers were repeatedly folded to enhance compositional uniformity, and subsequently punched into pieces with a diameter of 1 cm. Assembled ASSBs were tested on Neware test system (BTS4000, China) with the potential range of 0.6–2.4 V vs. In/In-Li under a stack pressure of 250 MPa or 10 MPa.

Electrochemical characterizations

Each electrochemical experiment was conducted with more than three test batteries to ensure reproducibility. The Coulombic efficiency (CE) for each cycle was determined by dividing the charge capacity by the corresponding discharge capacity.

EIS measurements were performed using the German VMP3 multichannel potentiostat 3/Z, covering a frequency range from 7 MHz to 100 mHz during charge-discharge process. Before the EIS test, the cells always have a 0.5-h rest to achieve equilibrium. All the measurements were performed in potentiostatic mode with an AC amplitude of 10.0 mV and 50 data points per frequency decade.

In situ EIS and CV tests. The testing procedure for in situ EIS measurements was similar to that described above. The cells underwent charging/discharging at a 0.2 C rate (1 C = 204 mA g⁻¹) for 1 h, followed by a 0.5-h rest to achieve equilibrium. The distribution of specialized relaxation times in the obtained EIS spectra was analyzed using the DRT technique implemented in the MATLAB GUI toolbox developed by Ciucci's research team⁶⁵. CV analyses of assembled ASSBs and liquid half-cells were conducted employing the versatile multichannel

potentiostat 3/Z (VMP3) at a scan rate of 0.1 mV s⁻¹. Additionally, linear sweep voltammetry (LSV) measurements of the LPSC SE were carried out using the same equipment, with a positive scan range from the open-circuit voltage (OCV) to 6 V and a negative scan range from OCV to 0 V, also at a scan rate of 0.1 mV s⁻¹.

DC polarization. To assess the electronic conductivities of the positive electrode composites, 50 mg of the composites were cold-pressed into pellets at 3 tons for 3 minutes. These pellets were then subjected to a voltage range of 0.1 V to 0.4 V in 0.1 V increments, with each voltage step maintained for 60 minutes to measure the current response. For testing the ionic conductivities, 50 mg of the positive electrode composite was initially cold-pressed into pellets at 3 tons for 3 minutes. 50 mg of the LPSC SEs was then evenly spread over both sides of the central layer and pressed together at 3 tons for an additional 3 minutes. Homemade Li-In alloy pieces (1:40 weight ratio) were attached to the opposite sides of the LPSC central layer and pressed together at 2 tons to ensure intimate contact. The resulting pellets were subjected to a voltage range of 0.01 V to 0.025 V in 0.005 V increments, with each voltage step maintained for 60 minutes to measure the current response.

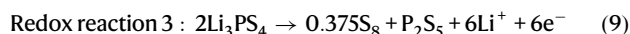
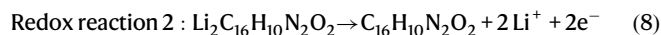
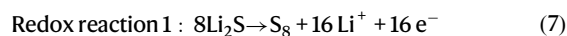
GITT measurement. GITT tests were conducted on a Neware BTS4000 test system (China). The ASSBs were tested within a potential range of 0.6–2.4 V vs. In/In-Li at 25 °C. A constant specific current of 0.2 C (1 C = 204 mA g⁻¹) was applied for 10 minutes, followed by a relaxation period of 2 h at open circuit. A constant specific current of 0.5 C for 3 min and then relaxing for 30 min at open circuit (1 C corresponds to the specific current of 204 mA g⁻¹) was exploited. During the measurements, data was collected every 28.8 seconds. Afterwards, the Li-ion diffusion coefficients were calculated using the following equation:

$$D_{\text{Li}^+} = \frac{4}{\pi} \left(\frac{n_m V_m}{S} \right)^2 \left(\frac{\Delta E_s}{\tau(dE_t/d\sqrt{\tau})} \right)^2 = \frac{4}{\pi} \left(\frac{V}{S} \right)^2 \left(\frac{\Delta E_s}{\tau(dE_t/d\sqrt{\tau})} \right)^2 \approx \frac{4}{\pi^2} (L)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (6)$$

In this equation, n_m is the mole number of the active materials; V_m is the molar volume of active materials; S is the effective area of the electrode; τ is the relaxation time; L is the average thickness of the electrode; ΔE_s is the potential change between neighboring relaxation end times; ΔE_t is the potential change caused by every constant current charge/discharge process.

DFT calculations

The molecular orbital energies of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of indigo, along with the calculation of the Gibbs reaction free energy for three redox reactions of Li₂S, Indigo, and Li₃PS₄ were based on the density functional theory (DFT) via the Gaussian 16 package⁶⁶. The molecular geometries for the ground states were optimized by density functional theory at the B3LYP/6-31 G level. The energy of molecules was evaluated at the B3LYP/6-31 G level as well.



Data availability

The data generated in this study are provided in the Source Data file. Source data are provided as a Source Data file. Source data are provided with this paper.

References

- Lu, Y. & Chen, J. Prospects of organic electrode materials for practical lithium batteries. *Nat. Rev. Chem.* **4**, 127–142 (2020).
- Poizot, P. et al. Opportunities and challenges for organic electrodes in electrochemical energy storage. *Chem. Rev.* **120**, 6490–6557 (2020).
- Lee, S., Hong, J. & Kang, K. Redox-active organic compounds for future sustainable energy storage system. *Adv. Energy Mater.* **10**, 2001445 (2020).
- Williams, D., Byrne, J. & Driscoll, J. A high energy density lithium/dichloroisocyanuric acid battery system. *J. Electrochem. Soc.* **116**, 2 (1969).
- Han, X. Y., Chang, C. X., Yuan, L. J., Sun, T. L. & Sun, J. T. Aromatic carbonyl derivative polymers as high-performance Li-ion storage materials. *Adv. Mater.* **19**, 1616–1621 (2007).
- Armand, M. et al. Conjugated dicarboxylate anodes for Li-ion batteries. *Nat. Mater.* **8**, 120–125 (2009).
- Zhao, L. et al. Disodium terephthalate ($\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$) as high performance anode material for low-cost room-temperature sodium-ion battery. *Adv. Energy Mater.* **2**, 962–965 (2012).
- Tobishima, S. I., Yamaki, J. I. & Yamaji, A. Cathode characteristics of organic electron acceptors for lithium batteries. *J. Electrochem. Soc.* **131**, 57 (1984).
- Shi, R. et al. Nitrogen-rich covalent organic frameworks with multiple carbonyls for high-performance sodium batteries. *Nat. Commun.* **11**, 178 (2020).
- Peng, C. et al. Reversible multi-electron redox chemistry of π -conjugated N-containing heteroaromatic molecule-based organic cathodes. *Nat. Energy* **2**, 17074 (2017).
- Visco, S. J. & DeJonghe, L. C. Ionic conductivity of organosulfur melts for advanced storage electrodes. *J. Electrochem. Soc.* **135**, 2905 (1988).
- Pan, Z., Brett, D. J., He, G. & Parkin, I. P. Progress and perspectives of organosulfur for lithium–sulfur batteries. *Adv. Energy Mater.* **12**, 2103483 (2022).
- Nakahara, K. et al. Rechargeable batteries with organic radical cathodes. *Chem. Phys. Lett.* **359**, 351–354 (2002).
- Wu, S. F. et al. Highly durable organic electrode for sodium-ion batteries via a stabilized α -C radical intermediate. *Nat. Commun.* **7**, 13318 (2016).
- Mao, M. et al. A pyrazine-based polymer for fast-charge batteries. *Angew. Chem. Int. Ed.* **58**, 17820–17826 (2019).
- Zhang, C. et al. Toward high performance thiophene-containing conjugated microporous polymer anodes for lithium-ion batteries through structure design. *Adv. Funct. Mater.* **28**, 1705432 (2018).
- Lu, Y., Zhang, Q., Li, L., Niu, Z. Q. & Chen, J. Design strategies toward enhancing the performance of organic electrode materials in metal-ion batteries. *Chem* **4**, 2786–2813 (2018).
- Bhosale, M. E., Chae, S., Kim, J. M. & Choi, J. Y. Organic small molecules and polymers as an electrode material for rechargeable lithium ion batteries. *J. Mater. Chem. A* **6**, 19885–19911 (2018).
- Hu, J. et al. Emerging organic electrodes for Na-ion and K-ion batteries. *Energy Storage Mater.* **56**, 267–299 (2023).
- Muench, S. et al. Polymer-based organic batteries. *Chem. Rev.* **116**, 9438–9484 (2016).
- Deng, W. W., Shen, Y. F., Liang, X. M., Feng, J. W. & Yang, H. X. Redox-active organics/polypyrrole composite as a cycle-stable cathode for Li ion batteries. *Electrochim. Acta* **147**, 426–431 (2014).
- Ma, T., Zhao, Q., Wang, J., Pan, Z. & Chen, J. A sulfur heterocyclic quinone cathode and a multifunctional binder for a high-performance rechargeable lithium-ion battery. *Angew. Chem. Int. Ed.* **55**, 6428–6432 (2016).
- Luo, C., Fan, X. L., Ma, Z. H., Gao, T. & Wang, C. S. Self-healing chemistry between organic material and binder for stable sodium-ion batteries. *Chem* **3**, 1050–1062 (2017).
- Bai, S. et al. Permselective metal–organic framework gel membrane enables long-life cycling of rechargeable organic batteries. *Nat. Nanotechnol.* **16**, 77–84 (2021).
- Lakrachi, A. E., Picton, E. S., Liang, Y., Shaffer, D. L. & Yao, Y. Suppressing shuttle effect with a size-selective covalent organic framework based bilayer membrane. *ACS Energy Lett.* **8**, 5032–5040 (2023).
- Guo, C., Zhang, K., Zhao, Q., Pei, L. & Chen, J. High-performance sodium batteries with the 9, 10-anthraquinone/CMK-3 cathode and an ether-based electrolyte. *Chem. Commun.* **51**, 10244–10247 (2015).
- Song, Z. & Zhou, H. Towards sustainable and versatile energy storage devices: an overview of organic electrode materials. *Energy Environ. Sci.* **6**, 2280–2301 (2013).
- Song, Z. et al. Polyanthraquinone as a reliable organic electrode for stable and fast lithium storage. *Angew. Chem. Int. Ed.* **127**, 14153–14157 (2015).
- Song, Z., Qian, Y., Zhang, T., Otani, M. & Zhou, H. Poly (benzoquinonyl sulfide) as a high-energy organic cathode for rechargeable Li and Na batteries. *Adv. Sci.* **2**, 1500124 (2015).
- Zhao, L., Lakrachi, A. E., Chen, Z., Liang, Y. & Yao, Y. Roadmap of solid-state lithium-organic batteries toward 500 Wh kg^{-1} . *ACS Energy Lett.* **6**, 3287–3306 (2021).
- Hao, F. et al. Taming active material–solid electrolyte interfaces with organic cathode for all-solid-state batteries. *Joule* **3**, 1349–1359 (2019).
- Zhao, Q., Stalin, S., Zhao, C.-Z. & Archer, L. A. Designing solid-state electrolytes for safe, energy-dense batteries. *Nat. Rev. Mater.* **5**, 229–252 (2020).
- Banerjee, A., Wang, X., Fang, C., Wu, E. A. & Meng, Y. S. Interfaces and Interphases in all-solid-state batteries with inorganic solid electrolytes. *Chem. Rev.* **120**, 6878–6933 (2020).
- Chi, X. et al. Tailored organic electrode material compatible with sulfide electrolyte for stable all-solid-state sodium batteries. *Angew. Chem. Int. Ed.* **57**, 2630–2634 (2018).
- Hao, F. et al. High-energy all-solid-state organic–lithium batteries based on ceramic electrolytes. *ACS Energy Lett.* **6**, 201–207 (2020).
- Yang, Z. et al. Room-temperature all-solid-state lithium-organic batteries based on sulfide electrolytes and organodisulfide cathodes. *Adv. Energy Mater.* **11**, 2102962 (2021).
- Ji, W. et al. Practically accessible all-solid-state batteries enabled by organosulfide cathodes and sulfide electrolytes. *Adv. Funct. Mater.* **32**, 2202919 (2022).
- Zhang, J. et al. Microstructure engineering of solid-state composite cathode via solvent-assisted processing. *Joule* **5**, 1845–1859 (2021).
- Ji, W. et al. A high-performance organic cathode customized for sulfide-based all-solid-state batteries. *Energy Storage Mater.* **45**, 680–686 (2022).
- Deiseroth, H. J. et al. $\text{Li}_6\text{PS}_5\text{X}$: a class of crystalline Li-rich solids with an unusually high Li^+ mobility. *Angew. Chem. Int. Ed.* **120**, 767–770 (2008).
- Han, F., Gao, T., Zhu, Y., Gaskell, K. J. & Wang, C. A battery made from a single material. *Adv. Mater.* **27**, 3473–3483 (2015).
- Ohno, S., Rosenbach, C., Dewald, G. F., Janek, J. & Zeier, W. G. Linking solid electrolyte degradation to charge carrier transport in the thiophosphate-based composite cathode toward solid-state lithium-sulfur batteries. *Adv. Funct. Mater.* **31**, 2010620 (2021).
- Tan, D. H. et al. Elucidating reversible electrochemical redox of $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte. *ACS Energy Lett.* **4**, 2418–2427 (2019).

44. Kim, J. T. et al. Manipulating $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ mixed discharge products of all-solid-state lithium sulfur batteries for improved cycle life. *Nat. Commun.* **14**, 6404 (2023).
45. Ong, S. P., Wang, L., Kang, B. & Ceder, G. Li-Fe-P- O_2 phase diagram from first principles calculations. *Chem. Mater.* **20**, 1798–1807 (2008).
46. Huang, W. et al. Synthesis and application of Calix[6] quinone as a high-capacity organic cathode for plastic crystal electrolyte-based lithium-ion batteries. *Energy Storage Mater.* **26**, 465–471 (2020).
47. Gao, X. et al. All-solid-state lithium-sulfur batteries enhanced by redox mediators. *J. Am. Chem. Soc.* **143**, 18188–18195 (2021).
48. Li, X. N. et al. Totally compatible $\text{P}_4\text{S}_{10+n}$ cathodes with self-generated Li^+ pathways for sulfide-based all-solid-state batteries. *Energy Storage Mater.* **28**, 325–333 (2020).
49. Ketenoglu, D. A general overview and comparative interpretation on element-specific X-ray spectroscopy techniques: XPS, XAS, and XRS. *X-Ray Spectrom.* **51**, 422–443 (2022).
50. Khimyak, Y. Z. & Klinowski, J. ^1H - ^{31}P C P/MAS NMR studies of mesostructured aluminophosphates. *Phys. Chem. Chem. Phys.* **3**, 2544–2551 (2001).
51. Metz, G., Ziliox, M. & Smith, S. O. Towards quantitative CP-MAS NMR. *Solid State Nucl. Magn. Reson.* **7**, 155–160 (1996).
52. Zhou, J. et al. Healable and conductive sulfur iodide for solid-state Li-S batteries. *Nature* **627**, 301–305 (2024).
53. Wang, D. et al. Realizing high-capacity all-solid-state lithium-sulfur batteries using a low-density inorganic solid-state electrolyte. *Nat. Commun.* **14**, 1895 (2023).
54. Lu, Y. et al. The carrier transition from Li atoms to Li vacancies in solid-state lithium alloy anodes. *Sci. Adv.* **7**, eabi5520 (2021).
55. Yang, X. Y. et al. A Truxenone-based Covalent Organic Framework as an All-Solid-State Lithium-Ion Battery Cathode with High Capacity. *Angew. Chem. Int. Ed.* **59**, 20385–20389 (2020).
56. Yang, Z. et al. Room-Temperature All-Solid-State Lithium–Organic Batteries Based on Sulfide Electrolytes and Organodisulfide Cathodes. *Adv. Energy Mater.* **11**, 2102962 (2021).
57. Wei, W., Li, L., Zhang, L., Hong, J. & He, G. An all-solid-state Li-organic battery with quinone-based polymer cathode and composite polymer electrolyte. *Electrochem. commun.* **90**, 21–25 (2018).
58. Lécuyer, M. et al. A rechargeable lithium/quinone battery using a commercial polymer electrolyte. *Electrochem. commun.* **55**, 22–25 (2015).
59. Lécuyer, M., Deschamps, M., Guyomard, D., Gaubicher, J. & Poizot, P. Electrochemical Assessment of Indigo Carmine Dye in Lithium Metal Polymer Technology. *Molecules* **26**, 3079 (2021).
60. Li, W. et al. All-solid-state secondary lithium battery using solid polymer electrolyte and anthraquinone cathode. *Solid State Ion.* **300**, 114–119 (2017).
61. Zhou, X. et al. A Highly Stable Li-Organic All-Solid-State Battery Based on Sulfide Electrolytes. *Adv. Energy Mater.* **12**, 2103932 (2022).
62. Hao, F. et al. High-energy all-solid-state organic-lithium batteries based on ceramic electrolytes. *ACS Energy Lett.* **6**, 201–207 (2021).
63. Luo, C. et al. Solid-state electrolyte anchored with a carboxylated azo compound for all-solid-state lithium batteries. *Angew. Chem. Int. Ed.* **57**, 8567–8571 (2018).
64. Momma, K. & Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **44**, 1272–1276 (2011).
65. Wan, T. H., Saccoccio, M., Chen, C. & Ciucci, F. Influence of the discretization methods on the distribution of relaxation times deconvolution: implementing radial basis functions with DRT tools. *Electrochim. Acta* **184**, 483–499 (2015).
66. Gaussian 16, Revision C.01, Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Petersson, G.A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A.V., Bloino, J., Janesko, B.G., Gomperts, R., Mennucci, B., Hratchian, H.P., Ortiz, J.V., Izmaylov, A.F., Sonnenberg, J.L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V.G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Montgomery, J.A. Jr, Peralta, J.E., Ogliaro, F., Bearpark, M.J., Heyd, J.J., Brothers, E.N., Kudin, K.N., Staroverov, V.N., Keith, T.A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A.P., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Millam, J.M., Klene, M., Adamo, C., Cammi, R., Ochterski, J.W., Martin, R.L., Morokuma, K., Farkas, O., Foresman, J.B., Fox, D.J. Gaussian, Inc., Wallingford CT. (2016).

Acknowledgements

The authors thank the supports from the Natural Sciences and Engineering Research Council of Canada (NSERC RGPIN/04105-2021, RGPAS/00041-2021), Canada First Research Excellence Fund (Concordia Volt-Age Seed 10093), Fonds de recherche du Québec Nature et technologies (FRQNT 327052, FRQNT 203321), Concordia University Research Chair Program (CURC), and Western University. The synchrotron-related characterizations were completed at the SXMB beamlines in Canadian Light Source (CLS), a national research facility of the University of Saskatchewan, which is supported by the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council (NSERC), the National Research Council (NRC), Canadian Institutes of Health Research (CIHR), Government of Saskatchewan, and the University of Saskatchewan.

Author contributions

Q.Y. and Y.Hu. contributed equally to this work. Q.Y. and Y.Hu conceived the idea, collected the experimental data and drafted the raw manuscript; Q.Y. and Y.Hu created all the crystal structure and elements by VESTA software. Q.Y. and Y.Hu analyzed the data and discussed the project; Q.Y., Y.Hu, S.D., M.S., J.C., and T.K.S. collected and analyzed synchrotron data at CLS. Y.Hu and H.Y.N. collected the TOF-SIMS data at Surface Science Western. Y.Hu, V.M., Y.Huang and Y.Z. collected and analyzed the solid-state NMR data. Q.Y., Y.Hu, M.S., T.K.S., V.M., Y.Huang, K.Z. and X.L. participated in discussions and manuscript revision. X.L. supervised the project.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41467-025-62301-z>.

Correspondence and requests for materials should be addressed to Xia Li.

Peer review information *Nature Communications* thanks Bingwen Hu and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. A peer review file is available.

Reprints and permissions information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

© The Author(s) 2025