

Anatomy of a SPAN Particle: A Four-Level Structural Framework for Lithium–Sulfur Batteries

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ABSTRACT

Sulfurized polyacrylonitrile (SPAN) has re-emerged as one of the most promising organosulfur cathodes for lithium–sulfur batteries, delivering substantial reversible capacity while largely suppressing the classical dissolved-polysulfide shuttle. Yet after more than two decades of study, the field still needs consensus on a deceptively basic question: what, structurally, is SPAN? Existing descriptions routinely conflate molecular bonding, mesoscale organization, and particle architecture; we argue that the central obstacle is not a shortage of high-quality studies but the absence of a shared structural language connecting observations across length scales. To close this gap, we propose a four-level hierarchical framework for dissecting a single SPAN particle: Primary Structure (Level I), the conjugated carbon–nitrogen backbone setting the electronic and insolubility foundation; Secondary Structure (Level II), sulfur-bearing covalent groups governing reversible and irreversible capacity; Tertiary Structure (Level III), noncovalent interchain organization defining a mesoscale reaction field; and Quaternary Structure (Level IV), particle-level hierarchy and intraparticle porosity. Rather than advocating a single “correct” structural formula, we frame SPAN as a coupled, thermal-history-dependent ensemble whose electrochemistry emerges from the interplay among levels. We further argue that the underdeveloped mesoscale (the interchain organization and soft confinement of Level III, and the intraparticle porosity of Level IV) may supply the missing structural basis for short-chain sulfur retention, partial sulfur dissolution–recovery, and capacities beyond classical stoichiometric expectations, all without conventional long-chain polysulfide signatures. By organizing the field around level-specific descriptors and explicit cross-level coupling, this perspective aims to provide an organizing, forward-looking basis for reproducible, high-loading, and scalable SPAN design.

1 | Introduction

Sulfurized polyacrylonitrile (SPAN) has been cycled thousands of times, scaled toward production, and studied by dozens of groups. Yet the community still cannot agree on what it is. This is not a failure of individual investigations; it is a failure of shared structural language [1–6].

More than two decades have passed since SPAN was first reported as a battery cathode [7]. Over this period, its

electrochemical performance has been steadily refined: reversible capacity normalized to SPAN mass has risen from roughly ~480 mAh g^{−1} in early studies to values exceeding 700 mAh g^{−1} in many recent reports [8, 9], while several industrial efforts have moved toward scaled production [10]. Yet the same period has not produced a comparably unified structural picture. Fundamental questions remain unsettled. What, precisely, is the dominant structural identity of SPAN? Why can it cycle stably in sulfur-based systems with little or no conventional shuttle? To

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what extent is its structure dynamically evolving during electrochemistry, rather than acting as a static host? And how can additional capacity be introduced without sacrificing the very cycle stability that makes SPAN attractive in the first place? These questions all converge on a single scientific bottleneck: the field still lacks a sufficiently integrated framework for discussing SPAN structure across scales.

As shown in Figure 1a, ideally, SPAN synthesis appears simple: polyacrylonitrile (PAN) and elemental sulfur are thermally treated under an inert atmosphere. But this apparent simplicity is misleading. In practice, PAN itself commonly exhibits broad molecular-weight distributions and may contain comonomer units or precursor-dependent heterogeneity [11, 12]. During thermal treatment, cyclization, dehydrogenation, sulfur radical reactions, and evolving local packing all occur under strongly

non-equilibrium conditions. As a result, upstream variations are effectively baked into the final material, shaping local chemistry, mesoscopic organization, and particle-level architecture in ways that are difficult to reconstruct a posteriori. Under such circumstances, the idea of a single uniquely defined repeat unit is less useful than the idea of a distributed structural ensemble.

In this sense, SPAN is better viewed not as a conventional polymer product converging toward one idealized structure or repeating unit, but as a glassy, thermal-history-dependent energy material. Its macroscopic electrochemical behavior is not owned by one structural motif alone; rather, it emerges from multiple kinetically trapped local minima, metastable sulfur environments, and processing-dependent organizational states. This view helps explain why seemingly similar synthesis

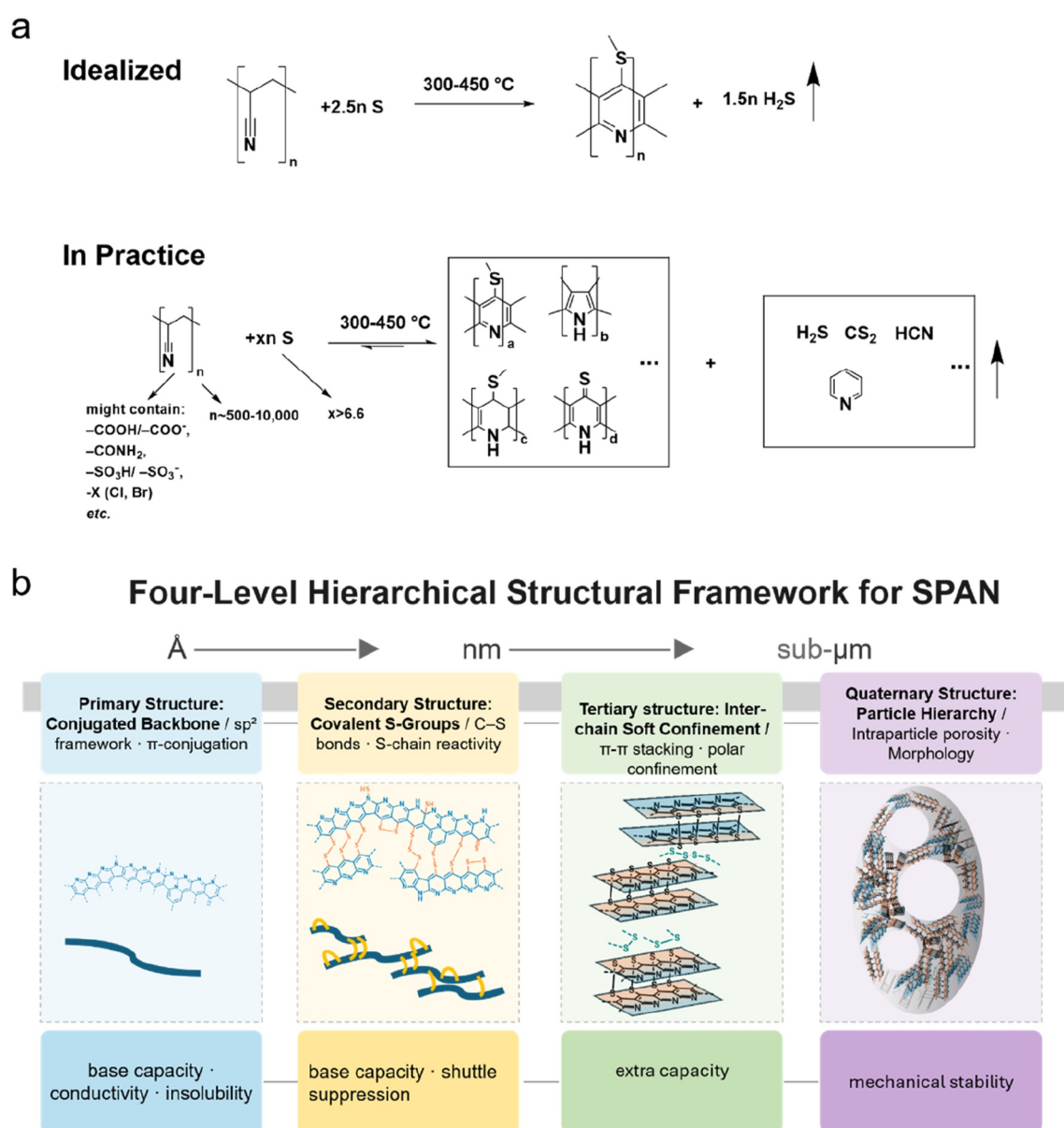


FIGURE 1 | Idealized versus real SPAN and its structural hierarchy. (a) Synthesis of SPAN. The idealized route (top) versus the reaction in practice (bottom). (b) A proposed four-level hierarchical framework for a single SPAN particle.

routes can produce materials with meaningfully different electrochemical behavior, and why mechanistic conclusions drawn from one observational window often fail to transfer cleanly into another.

Indeed, the current SPAN literature still resembles the classic parable of blind men describing an elephant [1–3, 13, 14]. Individual studies can be rigorous within their own measurement domain, yet insights obtained at one length scale do not automatically resolve questions at another. Some reports emphasize bonding motifs and sulfur functional groups, attempting to rationalize performance through local chemical structure [1, 2, 5, 14, 15]. Others focus on morphology, porosity, particle size, or electrode architecture, highlighting ion transport and mechanical stabilization [16–18]. Still others probe sulfur signatures during soaking or cycling and infer dynamic sulfur exchange processes [8, 19]. Each of these directions is valuable. The difficulty is that they are too often discussed in isolation, or with multiple variables changing simultaneously, preventing cumulative comparison and obscuring which structural level is being tuned.

This perspective therefore does not seek to identify a single “correct” structural model for SPAN, nor does it aim merely to catalog the existing interpretations. Instead, we argue that the field now needs a shared structural language: one hierarchical enough to respect SPAN’s complexity, yet practical enough to guide experimental design, cross-study comparison, and ultimately scalable materials engineering. To this end, as shown in Figure 1b, we organize SPAN into four interconnected structural levels: (1) the *primary structure* (Level I), the conjugated backbone; (2) the *secondary structure* (Level II), Level I backbones cross-linked by sulfur-containing covalent functional groups; (3) the *tertiary structure* (Level III), Level II units assembled through interchain interactions that softly confine sulfur; and (4) the *quaternary structure* (Level IV), the particle-scale morphologies built from Level III domains, including intraparticle porosity. Crucially, this framework is not meant simply to classify SPAN neatly. It identifies the key constraints and measurable parameters that define each level, and makes clear that battery performance comes from how the levels interact, not from any single level on its own.

A central claim of this perspective is that the mesoscale of SPAN (Level III, the interchain noncovalent organization, together with the intraparticle porosity that develops within Level IV) has been underrecognized. Level I and Level II are routinely interrogated through spectroscopy and local-bonding arguments, and the external morphology of Level IV is now commonly tuned through deliberate morphology control; by comparison, this mesoscale layer has remained conceptually acknowledged yet methodologically underdeveloped. We suggest that these missing mesoscale layers may be central to interpreting one of the field’s most important unresolved observations, the persistence of “extra” reversible capacity beyond what classical sulfur stoichiometry alone would predict, and may hold the key to long-term cycling stability. If this hypothesis holds, the next stage of SPAN research should not be framed simply as better synthesis or higher capacity, but as a transition from empirical optimization to an organizing, cross-scale structural logic.

In the sections that follow, we examine each structural level in turn, then discuss how the levels constrain one another and how the community might translate this framework into level-specific descriptors, closed-loop experiments, and more reproducible design rules. Our broader aim, however, is not only to clarify SPAN but to demonstrate a way of reasoning about it. Indeed, this approach need not stop here: we return at the end to its transferability to other complex polymer and organic cathodes.

2 | The Four-Level Framework

The framework proposed here is not intended as a rigid ontology, nor as a claim that every SPAN material can be reduced to a single universal structural map. Rather, it is a pragmatic way to separate scales of structural control that are too often conflated. In many SPAN studies, molecular bonding arguments, mesoscale packing effects, and particle-level transport limitations are run together in a single line of reasoning, which makes causal attribution difficult. By distinguishing four structural levels, we aim to clarify which observables belong to which scale, what kind of experiment is needed to probe each level, and how cross-level coupling should be interpreted.

2.1 | Primary Structure (Level I): The Conjugated Backbone as Electronic Foundation

Level I refers to the conjugated carbon–nitrogen backbone formed as PAN undergoes concurrent cyclization, dehydrogenation, aromatization, and partial degradation during sulfuration [20, 21]. This level provides the most basic structural continuity of SPAN: it is the electronic scaffold, the insoluble framework, and the anchoring environment within which sulfur functionalities are generated and subsequently evolve under electrochemical cycling. In most mechanistic discussions, Level I is treated as background. Yet without specifying its chemical and topological character, higher-level interpretations remain under-constrained.

Prior studies broadly converge on several features. First, the sulfuration of PAN does not simply yield a sulfur-decorated linear polymer; rather, the nitrile-rich precursor chain undergoes extensive cyclization and unsaturation, producing a largely sp^2 -rich, nitrogen-containing conjugated framework with varying degrees of local graphitic character. Second, pyridinic or pyridine-like nitrogen environments are commonly invoked and are consistent with a backbone electronically distinct from pristine PAN. Third, the backbone is not a passive matrix: its conjugation length, defect density, nitrogen distribution, and local rigidity all influence electron transport, sulfur-binding environments, and mechanical evolution during cycling [2, 4, 22].

From a design perspective, Level I sets at least three boundary conditions. The first is electronic continuity: if the conjugated backbone is too poorly developed, sulfur redox cannot be efficiently accessed throughout the particle bulk. The second is structural insolubility: SPAN’s defining advantage over classical sulfur cathodes depends fundamentally on a backbone capable of retaining sulfur-bearing motifs under electrochemical perturbation. The third is chemical preconditioning: the local

electronic environment created by the backbone governs which sulfur functionalities are stabilized in the first place. Beyond these constraints, several studies indicate that the conjugated backbone is not merely an inert host but itself contributes part of the reversible capacity [2, 6, 23]. Preserving a well-developed, low-defect sp^2 framework is therefore foundational: It underpins the stable, long-term cycling on which SPAN's overall performance ultimately depends. We therefore see a clear direction for Level I: A longer conjugation length with fewer defects gives more efficient electron transport along the backbone, makes sulfur redox more accessible throughout the particle, and thereby raises the cathode's redox activity and rate capability. Synthesis routes that improve conjugation continuity while suppressing defect formation are thus a concrete lever for SPAN performance.

Importantly, the primary structure (Level I) should not be represented by an idealized repeat unit alone. Even when a clean schematic is useful for communication, the real SPAN backbone is more likely a statistical ensemble shaped by precursor molecular weight, copolymer content, sulfur/PAN ratio, heating rate, dwell time, and local thermal gradients. Because cyclization, dehydrogenation, degradation, and sulfurization all proceed concurrently during the conversion of PAN to SPAN, the functional groups that constitute Level I are inherently heterogeneous, coexisting as a population rather than as a single species. This is the situation depicted in Figure 2: Although the 4-sulfurized pyridinic motif, which combines redox activity and aromaticity, is commonly regarded as the dominant and relatively ideal structure, a substantial fraction of “defect” configurations coexists alongside it. Recent work has drawn particular attention to non-aromatic units arising from incomplete dehydrogenation, five-membered pyrrolic rings formed through

degradation, and redox-inert aromatic structures of similarly degradative origin [2, 15].

Where do these degradative motifs come from? The volatile byproducts of synthesis (Figures 1a and 2) offer a mechanistic window. Thermogravimetry–mass spectrometry shows that the gases evolved during sulfurization fall into two temperature regimes: H_2S dominates below $\sim 400^\circ C$, whereas CS_2 dominates above it [24, 25]. The two gases report on chemically opposite channels. H_2S is the productive one: sulfur abstracts backbone hydrogen, and the resulting dehydrogenation drives the cyclization and aromatization that build the conjugated framework itself (Figure 1a) [7]. CS_2 , by contrast, is a parasitic channel that consumes backbone carbon. Its formation ($C + 2S \rightarrow CS_2$) is endergonic at room temperature ($\Delta fG^\circ_{298} \approx +67 \text{ kJ mol}^{-1}$) but strongly entropy-driven, becoming favorable only at elevated temperature; for the same reason, industrial CS_2 is manufactured from carbon or methane and sulfur at $600^\circ C$ – $1000^\circ C$ [26]. Because the standard synthesis window ($300^\circ C$ – $450^\circ C$, Figure 1a) straddles the $\sim 400^\circ C$ crossover, where a given protocol sits within this window largely sets its exposure to carbon loss. In this sense, we propose that CS_2 can be regarded as the terminal product of complete sulfurization, much as CO_2 is the terminal product of complete oxidation when a polymer reacts with O_2 : it marks the point at which sulfur stops functionalizing carbon and begins consuming it.

The structural consequences follow directly. Each CS_2 event removes a ring carbon, and with it a prospective sulfur-anchoring site, but leaves nitrogen in place. We therefore propose that CS_2 evolution is one plausible origin of the appreciable pyrrolic population in SPAN: when a carbon destined for a six-membered pyridinic ring escapes as CS_2 , ring closure around

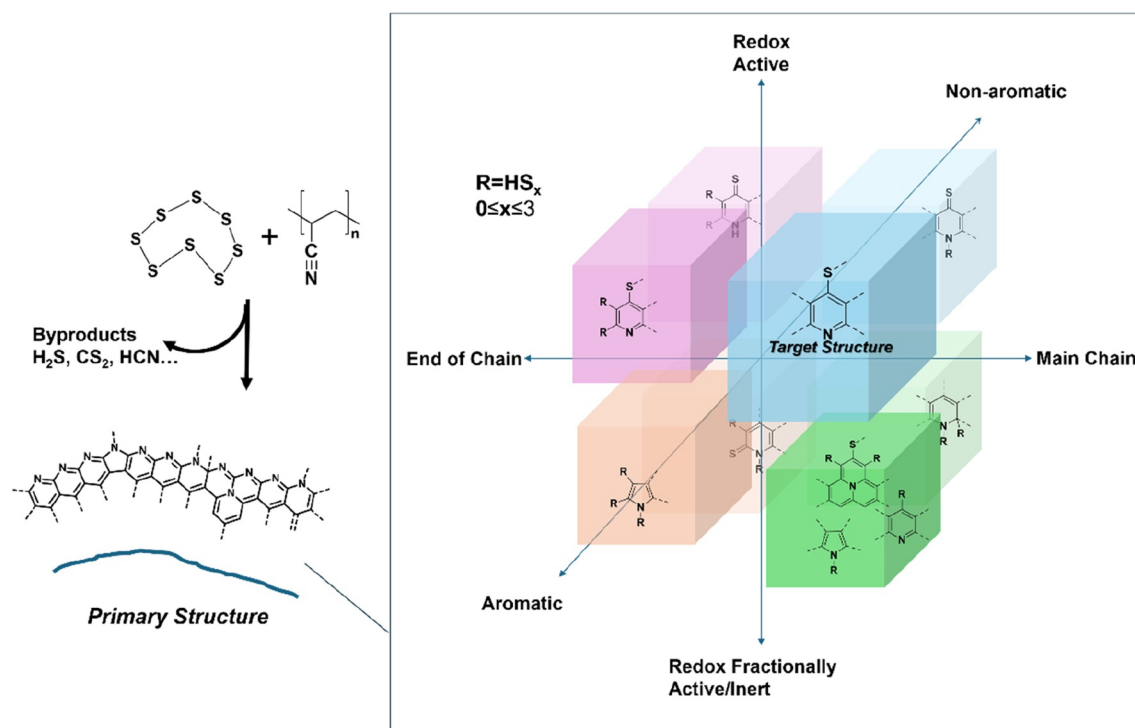


FIGURE 2 | Primary structure (Level I): The conjugated C–N backbone as a synthesis-defined structural ensemble.

the remaining atoms yields a five-membered, nitrogen-retaining ring instead. This hypothesis is consistent with X-ray absorption evidence that pyrrolic and other degradative structures emerge above $\sim 250^\circ\text{C}$ [15], and it parallels reactive-force-field simulations of sulfur-free PAN carbonization, in which gas evolution is likewise coupled to the interconversion of five- and six-membered rings [27, 28]. It also bears on nitrogen retention: CS_2 evolution alone would drive C/N below the ideal value of 3, so the observation that measured ratios sit slightly above 3 implies only a mild parallel loss of nitrogen-bearing volatiles such as HCN (Figure 1a) [25]. Finally, the two channels frame an inherent synthetic trade-off. Sufficient sulfur and temperature are required to complete dehydrogenation; the idealized stoichiometry of Figure 1a already demands 1.5 equivalents of H_2S per repeat unit. By simple equilibrium reasoning, however, the same sulfur excess at elevated temperature also shifts the $\text{C} + 2\text{S} \rightarrow \text{CS}_2$ balance toward carbon loss and erosion of pyridinic rings. Designing sulfur donors and reaction schemes that drive dehydrogenation to completion while suppressing CS_2 , for example by decoupling backbone cyclization from sulfur incorporation through pre-cyclized precursors or low-temperature routes, is therefore, in our view, a key step toward the “ideal” region of Figure 2 [20].

In other words, the backbone is already history-dependent before any sulfur redox takes place. The notion that one can define “the” SPAN structure without specifying its synthesis trajectory is therefore conceptually misleading. A more productive approach is to treat Level I in terms of descriptor distributions: Average aromaticity, nitrogen speciation, conjugation continuity, and defect topology.

This distinction matters because many disagreements in the literature may reflect not analytical error but genuine differences in backbone ensemble [29]. A highly cyclized, more rigid, and more conjugated SPAN need not respond electrochemically in the same way as a looser, more defect-rich framework, even when both are labeled simply as “SPAN.” When the field compares performance across synthesis routes without adequately characterizing Level I, it is effectively comparing different reaction scaffolds [30].

In summary, Level I should be regarded as the electronic and insoluble foundation of SPAN, but also as a distributed synthetic outcome rather than a unique formula. It does not by itself explain SPAN’s most intriguing electrochemical behaviors, yet it defines the space within which all higher-level sulfur chemistry can exist. More critically, the central challenge at this level is synthetic control: learning how to deliberately steer the reaction toward the ideal region of Figure 2 (the redox-active, aromatic, and sulfur-bearing motif), rather than accepting whatever ensemble a given synthesis happens to yield.

2.2 | Secondary Structure (Level II): The Covalent Sulfur Network

The secondary structure (Level II) consists of a series of primary structures together with the sulfur that covalently links them, as shown in Figure 3a. If Level I is pictured as a line, then Level II turns SPAN into a network through covalent sulfur held in place by C–S and C = S bonds. Geometrically, the progression

from Level I to Level II therefore corresponds to a transition from a one-dimensional chain to a two-dimensional connected framework. This level comprises the sulfur-containing covalent motifs attached to, or bridging, portions of the conjugated backbone. It is here that the field most often seeks a mechanistic explanation for SPAN’s reversible capacity, its first-cycle irreversible loss, its voltage profile, and its suppression of the classical dissolved-polysulfide signatures.

Level II has naturally received substantial attention, since it is the most intuitive place to look for a molecular explanation of sulfur electrochemistry [6, 7, 16, 29–32]. Researchers ask what sulfur species are present after synthesis, how many sulfur atoms can be accounted for by covalent attachment, whether sulfur occurs as short chains or isolated motifs, and how these structures transform upon lithiation and delithiation. These questions are necessary, but they have often been posed within an overly simplified frame: The assumption that identifying the dominant bonding motif is equivalent to identifying the dominant electrochemical mechanism.

One further reported motif deserves explicit placement in this taxonomy: the N–S bond. The proposal has accumulated across several independent studies, each resting on a different combination of evidence. Combined CP-MAS $^{15}\text{N}/^{13}\text{C}$ solid-state NMR, FTIR, and XPS first led to the assignment of N–S alongside NC–S linkages in as-synthesized SPAN [4]. A subsequent XPS/solid-state NMR/DFT study proposed a molecular structure in which vicinal pyridinic and pyrrolic nitrogen pairs attract S_2 and thereby template N–S formation, offering this as the feature that distinguishes SPAN from other nitrogen-containing sulfurized polymers [22]. In situ Raman and X-ray absorption spectroscopy, supported by DFT, were then read as evidence for $-\text{N}-\text{S}_x-\text{N}-$ ($x < 4$) bridges coexisting with C–S and S–S [33]. Most recently, a formation-mechanism study has depicted SPAN as alternating C–S and N–S layers twisted by $\sim 30^\circ$ – 40° and interconnected through C– S_x –N linkages [3]. Against these stands the one study to have applied fragment-specific analysis, which detected no NS-indicative fragment by either ToF-SIMS or high-resolution XPS, while intense NCS and NC_3S fragments pointed instead to thioamidic nitrogen (nitrogen adjacent to a C–S/C = S unit rather than bonded to sulfur) [34]. The assignment is therefore better described as proposed than as established, not least because the spectral windows on which it rests are congested: C–S, S–S, thiophenic, and polysulfide sulfur all crowd into ~ 162 – 165 eV in S 2p, an S–N nitrogen component would overlap pyrrolic nitrogen near ~ 400 eV in N 1s, and the $\sim 900\text{ cm}^{-1}$ Raman feature has been variously assigned to C–S, S–S, and N–S [35].

What this literature does not address is whether the proposed bond is electrochemically reversible. The claims are, without exception, structural: They concern what forms during synthesis rather than what happens across a cycle. Only one of them extends to electrochemistry at all, reporting that N–S and S–S are cleaved during the first discharge and that the resulting Li–N and Li–C bonds raise the electron density of the conjugated framework, reducing voltage hysteresis from the second cycle onward [4]. Few studies have reported an N–S bond re-forming on charge. If N–S exists, is it cleaved once in the first cycle, electrochemically inert, or reversibly cycled? The field has not yet posed this question, let alone answered it.

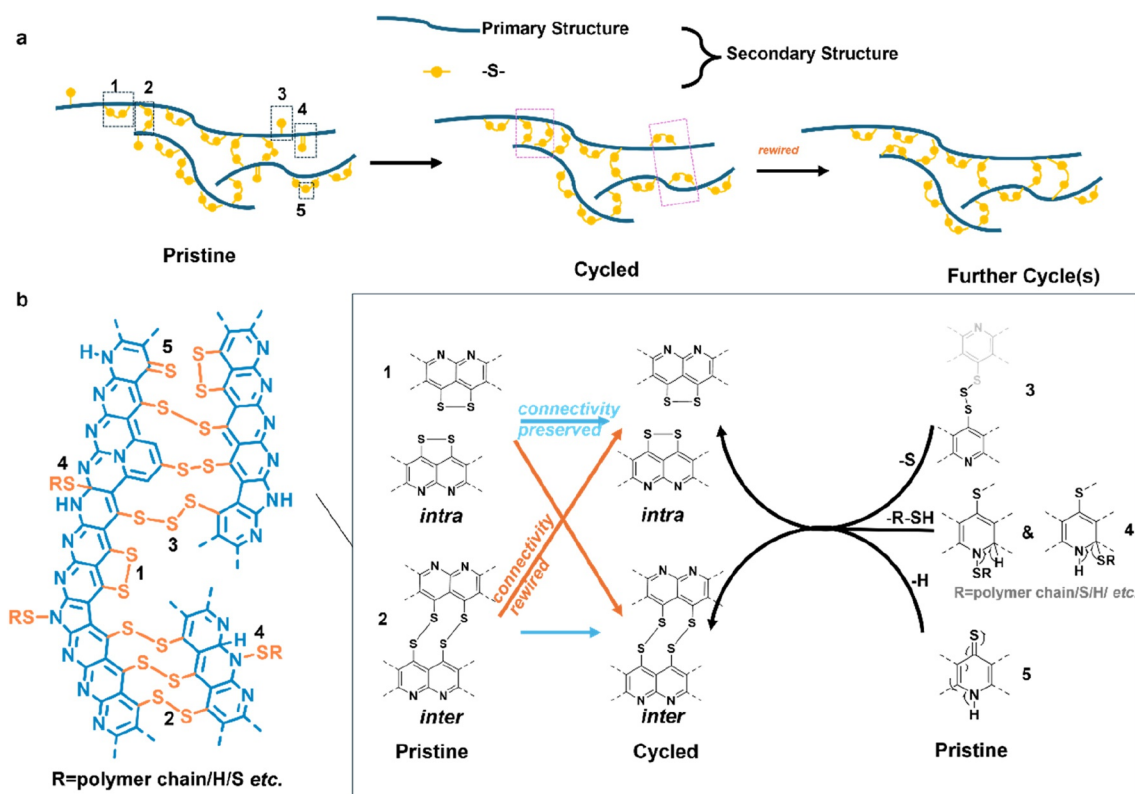


FIGURE 3 | Secondary structure (Level II): The covalent sulfur network. (a) At the chain scale, covalent sulfur groups ($-S-$) tie the primary backbone into a secondary structure; across repeated cycling, this network reorganizes (“rewires”) while retaining overall connectivity. (b) Left: a representative assembled secondary structure locating the five motif classes (1–5) within one covalent network (R = polymer chain, H, S, etc.). Right: the fate of each motif’s sulfur after cycling. Motifs 1 (intra-chain) and 2 (inter-chain) S–S bridges either retain their connectivity (intra $\rightarrow$ intra, inter $\rightarrow$ inter; blue) or rewire (intra $\leftrightarrow$ inter; orange); motifs 3–5 instead lose sulfur or hydrogen, released as S, R–SH, and H.

We suggest that the answer, if the bond is covalent, should depend on which nitrogen carries it, and that the two cases point in opposite directions (Figure 3). On a six-membered azacycle, an N–S bond should be cleaved irreversibly. A nitrogen inside such a ring can carry an exocyclic sulfur only while the ring is still non-aromatic; once the ring closes to pyridine, the nitrogen lone pair lies in the ring plane and is no longer available to sulfur without acquiring a formal positive charge. Scission of the N–S bond is therefore thermodynamically favored, because it is the step that lets the ring aromatize. This is the same driving force that governs the first-cycle structural transformation of SPAN, in which intramolecular dehydrogenation together with sulfur loss raises the aromaticity of the backbone and increases its electronic conductivity by more than two orders of magnitude [2]. A six-membered-ring N–S would sit on that same trajectory: Consumed once, in the direction of the more aromatic structure, with no return path on charge. It would belong with motifs 3–5 of Figure 3b rather than alongside the reversible 4-position C–S, and it is drawn as such: The nitrogen-bound variant of motif 4, whose sulfur departs as R–SH as the ring aromatizes over the first cycles.

The pyrrolic case is genuinely open, and we do not think it can be settled from the data now available. A five-membered ring is already aromatic, so cleavage buys no aromatization, and an N–S bond there is unobjectionable on bonding grounds: The exocyclic position at nitrogen accommodates sulfur as readily as hydrogen. The same equivalence, however, also allows the

opposite outcome. If the bond cleaves and the nitrogen captures hydrogen from the electrolyte, the result is the N–H pyrrole, plausibly the more stable terminus and reached irreversibly. A pyrrolic N–S is thus either the one persistent, load-bearing sulfur–nitrogen motif in SPAN or a slower version of the six-membered-ring case, and the two possibilities are not currently distinguishable. Resolving them will require synthesis control precise enough to enrich one nitrogen environment relative to the other, combined with element-selective spectroscopy. N K-edge and S K-edge XAS, probes of the kind recently applied to SPAN formation, can distinguish pyridinic from pyrrolic nitrogen and identify the bonding partner of sulfur; applied *operando*, they would show directly whether any nitrogen-bound sulfur survives a cycle [15].

Level II is better understood statistically than categorically. The key issue is not whether a particular motif can be drawn, but what distribution of sulfur-containing motifs exists across the material, how these motifs are embedded within the Level I backbone environment, and how their populations evolve during synthesis and cycling.

At this level, SPAN’s classical advantages begin to make chemical sense. Covalently embedded sulfur is less likely to behave like freely dissolved long-chain polysulfides; it can suppress shuttle, alter reaction thermodynamics, and narrow the population of mobile sulfur intermediates. Yet this stabilization carries trade-offs. Stronger immobilization can improve cycle stability but

tends to lower the total sulfur content the framework can hold, and with it the attainable capacity. More weakly constrained sulfur may raise capacity but at the cost of leakage, parasitic reactions, and poor long-term retention. As illustrated in Figure 3b, the carbon-bound sulfur at the 4-position of the pyridine ring (the C–S motif) is generally regarded as the principal source of reversible sulfur in SPAN [2, 5, 6]. The remaining species are thought to undergo irreversible transformation during discharge, either detaching from the polymeric backbone or ultimately converting into the reversible C–S form: thioketones, thiols (–SH), vicinal sulfur on non-aromatic rings, N–S, and bridging long-chain sulfur (the population near ~164 eV in X-ray photoelectron spectroscopy (XPS) S 2p spectra) [1, 2].

Notably, these non-ideal motifs are the molecular residue of the competing synthesis channels discussed under Level I: Incomplete dehydrogenation leaves behind –SH groups and vicinal sulfur on non-aromatic rings, and the same dehydrosulfurization chemistry that evolves H₂S during synthesis persists into the first electrochemical cycles, where motifs 3–5 complete their transformation by shedding S, RSH (R = SPAN polymer, H or S), and H (Figure 3b). The Level II sulfur speciation is thus not an independent inventory but a fingerprint of the synthesis conditions: The temperature and sulfur budget that set the H₂S/CS₂ balance at Level I.

How this 4-position C–S is reversible, however, remains contested. One view holds that the C–S bond does not cleave during cycling and that the sulfur simply accommodates a single lithium per site on discharge [2, 6]. The rationale is mechanistic: were the C–S to break, the exposed 4-position pyridine carbons would likely crosslink into a highly stable fused-ring structure that could no longer reopen to re-bond reversibly with sulfur. A competing viewpoint points to spectroscopic evidence—infrared (IR) and Raman C–S signatures that fade on discharge and reappear on charge [22, 23].

These two readings can be weighed rather than merely listed. The spectroscopic case is weaker than it first appears. The relevant bands sit in the congested windows discussed above, where C–S, S–S, and proposed N–S assignments overlap, and converting C–S–S–C into C–S[–]Li⁺ on discharge alters the force constant, conjugation, and polarizability of a surviving C–S oscillator while removing the adjacent S–S modes [35]. Fading and reappearing intensity is therefore expected even if no carbon–sulfur bond ever breaks: Band intensity in an electronically evolving solid is not a count of bonds. The stability argument is stronger. A scission–reformation mechanism must restore the correct C–S linkage with near-perfect fidelity every cycle to sustain thousands of stable cycles, and any per-cycle loss (thiolate lost as Li₂S, or carbons lost to the fused-ring dead end noted above) accumulates. An intact anchor requires no such fidelity. The one exception is geminate re-formation enforced by confinement; in that case even a scission mechanism would be a cross-level property, sustained by Level III rather than intrinsic to the bond. On this weighing we take a position: The 4-position C–S anchor survives steady-state cycling, and the reversible event at this site is interconversion between the disulfide/short-chain state and the lithium thiolate on an intact C–S, one lithium per sulfur, as the non-cleavage view proposes [2, 6]. Genuine C–S scission, where it occurs,

contributes instead to the first-cycle irreversible capacity, alongside dehydrogenation and edge-site proton–lithium exchange, and to the slow fade thereafter [36]. The position is falsifiable, and the discriminating experiments are within reach. The sharpest is an isotope-scrambling test of dynamic covalency: Cycle SPAN against a ³⁴S-labeled external sulfur reservoir and ask, by fragment-specific mass spectrometry, whether ³⁴S ever becomes carbon-bound. A static anchor stays ³²S; a scission–reformation mechanism scrambles. State-of-charge-resolved ¹³C solid-state NMR of the sulfur-bearing carbon offers a second, direct probe, and operando S K-edge XAS, already demonstrated across SPAN formation [15] and cycling [36], can quantify the carbon-bound sulfur fraction at each potential. Together with the nitrogen-edge measurements proposed above, these define a single campaign that would settle the covalent dynamics of Level II.

A second open question concerns connectivity: Whether the C–S–S–C linkage between 4-position pyridines forms within a single primary chain (intrachain, motif 1 in Figure 3b) or bridges two chains (interchain, motif 2 in Figure 3b). An intrachain C–S–S–C must accommodate appreciable five-membered-ring strain, although two neighboring C–S groups can more readily find each other; an interchain linkage relieves that ring strain, but forming it continuously is nearly impossible: Pairing all the 4-position sulfurs across chains would require two chains to stay parallel and in register over a long range, which a defective Level I backbone cannot sustain. The most plausible picture is therefore the one sketched in Figure 3: These reversible C–S–S–C linkages interconvert dynamically between intra- and interchain configurations, so that with each cycle their attachment to the primary structure is partially rewired. Whether this rewiring can be reliably characterized, let alone quantified, remains an open experimental question. What it ultimately means for SPAN's cycling stability is likewise unresolved and warrants dedicated study.

This is why Level II should be framed not as a static inventory of bonds but as a functional network that balances retention against reactivity. Different synthetic routes move the material along this balance in different ways: Higher sulfurization temperatures may favor one motif distribution over another, changes in precursor composition may alter the ratio of sulfur sites to conjugated carbon–nitrogen domains, and additional heteroatoms or post-treatments may selectively stabilize sulfur environments. Such interventions do not simply “add sulfur”; they reshape the topology of the sulfur functional network.

A major need for the field is therefore descriptor-based reporting at Level II. Rather than broad statements such as “C–S bonds were formed” or “sulfur was chemically anchored,” studies should increasingly aim to quantify sulfur-motif fractions, apparent sulfur-chain-length distributions, reversible versus irreversible sulfur-site populations, and the evolution of these descriptors across electrochemical history.

Accordingly, we regard Level II as the primary chemical reservoir of SPAN and the first-order determinant of its core redox chemistry. Yet the most important question is no longer simply which motif exists, but how the Level II sulfur network interacts with the organizational field above it.

2.3 | Tertiary Structure (Level III): Interchain Organization as the Missing Mesoscale Field

Where Level II describes the covalent connectivity, the tertiary structure (Level III) is where noncovalent interactions become important. It has two coupled features: The organization between Level II planes, and the additional sulfur that can be held in the space these interactions create (Figure 4a). If Level II is a two-dimensional covalent network, Level III is a short-range-ordered three-dimensional structure. This step from 2D to 3D has two consequences that we discuss below: It provides some spatial and mechanical stabilization of the particle, and it contributes capacity that the covalent framework alone cannot explain.

Level III has only recently begun to receive attention, a shift driven largely by the plateauing of Level II's covalent capacity: As that reservoir approached its ceiling, the field was forced to look beyond it. There is also a methodological reason. Covalent

motifs are easier to identify than an evolving mesoscale reaction field; particles are easier to image than soft confinement is to quantify; and electrochemical performance is easier to correlate with synthesis temperature than with the distribution of inter-chain organization. As a result, this region between bond-level chemistry and particle morphology has often been treated as a background variable rather than studied directly.

Consider the capacity ceiling of an idealized Level II structure. If the secondary structure consisted entirely of the 4-position-substituted, fused-pyridine ring-belt repeat unit (Motifs 1 and 2 in Figure 3b), its formula would be $(C_3NS)_n$, in which sulfur accounts for only ~ 39 wt%. Such a unit can host at most Li_2C_3NS , giving a theoretical ceiling near 650 mAh g^{-1} . However, many laboratory and commercial SPAN materials already deliver reversible capacities above 700 mAh g^{-1} [3, 9, 10, 13]. This excess cannot come from a “perfect” secondary structure, so some electrochemically active sulfur must be held outside the covalent ribbon.

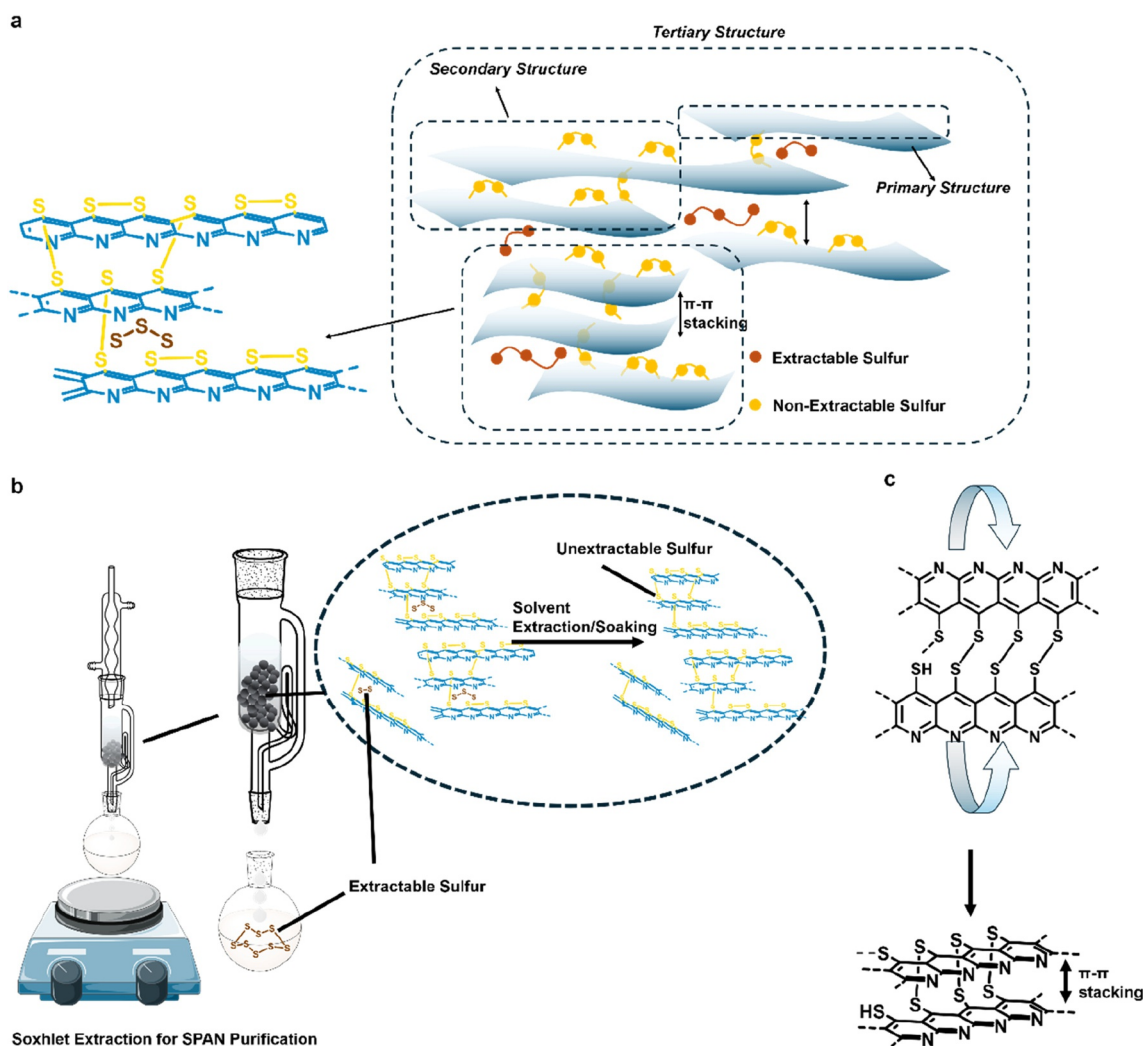


FIGURE 4 | Tertiary Structure (Level III): Noncovalent interchain organization and soft-confined sulfur. (a) Interchain π - π stacking organizes the secondary-structure ribbons into a short-range-ordered 3D host that accommodates two sulfur populations: covalently anchored, non-extractable sulfur (yellow) and soft-confined, extractable short-chain sulfur (red). (b) Soxhlet purification: Solvent extraction/soaking removes the soft-confined extractable sulfur while the covalently bound (unextractable) sulfur is retained. (c) Delocalized π electrons along the pyridinic ring belts drive the π - π stacking that converts the 2D cross-linked network into a stacked 3D arrangement.

The clearest experimental handle on this sulfur comes from attempts to remove it. To obtain a “pure” SPAN for mechanistic study, some studies use Soxhlet extraction with solvents such as toluene, in which elemental sulfur is sparingly soluble, assuming that what is removed is impurity elemental sulfur (Figure 4b) [4, 33]. This extraction is usually accompanied by a measurable loss of reversible capacity, which indicates that the removed sulfur is not inert. The data also show an apparent contradiction: time-of-flight secondary-ion mass spectrometry (ToF-SIMS) of pristine SPAN shows negligible S_x with $x > 3$ [14, 19], suggesting that the extra sulfur is fixed as short chains, whereas chromatography of electrolyte-soaked SPAN detects S_8 [19]. Together, these results suggest a sulfur population that exists as short chains within the host but can reorganize and leach as larger species when the solvent environment changes. Unlike the covalently anchored sulfur of Level II, this sulfur is partly responsive to its surroundings.

Controlled-extraction data now let the magnitude of this population's contribution be stated explicitly [8]. Toluene extraction that lowers the sulfur content from ~49.8 to ~43.1 wt% (removing ~7 wt% of weakly bound sulfur) reduces the equilibrium capacity from 772 to 536 mAh g⁻¹ in an ether electrolyte, with a comparable differential in carbonate. Two arithmetic anchors put this number in perspective. First, the removed sulfur's own stoichiometric share is at most ~115 mAh g⁻¹ even assuming full conversion to Li₂S, so the observed ~235 mAh g⁻¹ differential is roughly twice what the removed sulfur alone could supply: the soft-confined population not only contributes its own capacity but evidently raises the utilization of the covalent network around it. Second, measured against the ~650 mAh g⁻¹ ceiling derived above, the pristine material's 772 mAh g⁻¹ sits ~19% above the covalent limit (a model-independent lower bound on the non-covalent contribution), while the extracted material falls to ~82% of that ceiling, as expected for a real covalent network with sub-ideal utilization. In round numbers, soft confinement thus accounts for on the order of 15%–20% of the reversible capacity of present high-performing SPAN, with the exact share set by synthesis and electrolyte.

Our hypothesis is that, under appropriate structural conditions, SPAN can stabilize a population of short-chain or weakly associated sulfur species through noncovalent soft confinement. This does not mean free long-chain polysulfides dissolved in the bulk electrolyte, nor does it mean that covalent anchoring becomes irrelevant. Instead, it describes an intermediate regime: sulfur species that remain spatially restricted, repeatedly recruitable, and electrochemically coupled to the solid host because they are confined in a polar, conjugated, and topologically constrained mesoscale environment.

In our view, this soft-confined sulfur is the key to raising SPAN capacity beyond the Level II ceiling, but it has a cost. Recent work shows that while it increases capacity, it can also slow Li⁺ diffusion in the cathode, which is a kinetic drawback [8]. The experimental identity of this population is itself well defined. It can be removed by toluene extraction without perturbing the covalent network, leaving the C–S (314, 370 cm⁻¹) and S–S (473, 950 cm⁻¹) Raman signatures unchanged; it produces no crystalline S_8 reflections in X-ray diffraction; and it begins to leave the framework from as low as ~180°C in thermogravimetry. These are the

hallmarks of a mobile, non-crystalline sulfur population held by weak interactions rather than covalent bonds [8]. The same study finds that this extractable sulfur increasing solid-state diffusion resistance, consistent with weakly bound species partially obstructing Li⁺ pathways within the interchain space. Controlling its relative amount—enough to gain capacity without suppressing transport—will be an important optimization problem in the coming years. Because this confinement is noncovalent and solvent-sensitive, Level III is also closely related to the cathode–electrolyte interphase (CEI).

This relation deserves to be stated as a principle rather than an aside. Confinement at Level III is not an intrinsic property of the solid but the net of two opposing terms: A retention barrier set by the host (the polar, conjugated, topologically constrained interchain environment) and an extraction driving force set by whatever solvation environment reaches that interior through the open porosity of Level IV. The same solid therefore confines to different degrees in different electrolytes. In ether-rich environments that solvate short-chain sulfur species well, extraction can win, consistent with the chromatographic detection of S_8 from electrolyte-soaked SPAN noted above [19]. In carbonate electrolytes, where these species are poorly solvated and SPAN cycles shuttle-free [33], and in localized high-concentration formulations that suppress free-solvent activity further, the driving force falls and the same barrier holds. As for the literal question of infiltration, geometry constrains it: the coherent π -stacked galleries sit at spacings of ~3.5–3.7 Å [36], below the molecular dimensions of carbonate and ether solvents, and a cathode operating at 1–3 V offers no co-intercalation driving force of the kind that opens graphite. What the electrolyte reaches is the disordered remainder of the ensemble: domain boundaries, amorphous margins, and pore-facing surfaces. Infiltration therefore re-weights the distribution at its edges rather than flooding the stacks. The extraction kinetics discussed later in this section point the same way from the transport side: The diffusion penalty imposed by the soft-confined population is essentially independent of electrolyte, as expected if the galleries' interior is set by the solid [8], while the retention of that population is negotiated at the solid–electrolyte boundary. The CEI is in this sense not merely adjacent to Level III but part of its boundary condition. We return to this point under Level IV.

The second feature of Level III is the organization of the chains themselves. Compared with a flat picture of two pyridinic ring belts joined by sulfur cross-links, the large number of delocalized π electrons makes interchain π – π stacking essentially unavoidable (Figure 4c). This stacking is no longer merely inferred; it has been observed directly. Operando high-energy total scattering during synthesis reveals a low-Q peak at ~1.7 Å⁻¹ (a d-spacing of ~3.5–3.7 Å, matching the interlayer distance of π -stacked conjugated carbons) emerging after ~20 min at 320°C, concurrent with the growth of the 1.75 Å S–C correlation in the pair distribution function. Two control observations tie this order specifically to sulfur chemistry: Sulfur-free cyclized PAN heated identically develops no stacking peak at 320°C (one appears only near 500°C and is then disrupted as the chains fuse into two-dimensional networks), and PDF analysis indicates ordered pyridine domains of only ~20 Å (roughly eight rings): Short-range stacked order, not graphitic crystallinity [36]. The functional evidence is equally direct: A

molecular analogue (4,4'-dipyridyl disulfide) carrying the same S–C chemistry but lacking stacking order lithiates on the first discharge yet fades within a few cycles, whereas stacked SPAN cycles stably (89% retention over 1000 cycles for well-stacked, short-chain material), and density functional theory shows the stacked configuration possesses a higher density of states near the Fermi level than its unstacked analogue, providing continuous electronic pathways that stabilize sulfur-centered radicals. Computational models of the lithiation and dissolution behavior of SPAN likewise build on this stacked architecture [35, 36]. Note that the C–S–S–C cross-linking of Level II does not connect only two chains but bridges several, so the chains are drawn together and form multiple interchain stacking contacts. Figure 4a,c are therefore a simplified depiction; the real structure involves many chains.

The effects of this stacking are still largely speculative, but a consistent picture is forming. Most directly, stacking should stabilize the network: Without it, individual chains are more likely to detach into the electrolyte and reduce cathode capacity. The move from a 2D to a 3D arrangement also creates locally ordered interchain space, which may be where the soft-confined sulfur is held, connecting the two features of Level III. Operando scattering supports this connection directly: As synthesis proceeds, sequential S–S cleavage and re-anchoring draw neighboring backbones together in a “zipper-like” contraction, with short sulfur chains increasingly bridging the π – π -stacked network. This is direct evidence that the residual sulfur and the stacked architecture occupy the same interchain space and evolve together [36].

The same ordering acts on transport twice over. Electronically, stacked backbones provide interchain pathways (density functional calculations show a higher density of states near the Fermi level for the stacked configuration than for its unstacked analogue), so charge can delocalize across, not merely along, the chains [36]. Ionically, ordered interchain galleries should likewise form more continuous, less tortuous Li^+ pathways. The soft-confined sulfur held in those same galleries, however, acts in the opposite direction, partially obstructing the very channels the ordering creates. These two features of Level III therefore push Li^+ transport in opposite directions, and the net outcome is set by how much sulfur the galleries hold. Controlled-extraction kinetics make this competition concrete. Removing the extractable population lowers the solid-state diffusion resistance across nearly the full state-of-charge range (most sharply near full delithiation), yet leaves the diffusion activation energy unchanged (≈ 0.11 – 0.15 eV at intermediate states of charge for both materials). Occupancy thus limits how many pathways are available without altering the transport mechanism through them. The penalty is essentially independent of electrolyte, confirming that it is set inside the solid [8]. One further point is instructive: The same confined sulfur that impedes bulk diffusion lowers the charge-transfer barrier at the interface. “Transport” thus splits into an interfacial term it helps and a bulk term it hurts, which is why its presence degrades fast-charging capability far more than discharge [8]. The design variable, then, is not whether to order the chains but how much sulfur to load into the ordered space, and where. This raises a design question like the one for soft-confined sulfur: Can π – π stacking be tuned to strengthen or relax this organization to

improve performance? Because PAN is mainly used as the precursor for carbon fiber, the methods that industry uses to increase the structural order of carbon fibers may be useful here.

Progress at Level III will require three things. First, the field needs level-appropriate descriptors: interchain gap distributions, local coordination environments around polar nitrogen sites, bridging-motif probabilities, sulfur residence characteristics in confined domains, and signatures of reversible sulfur redistribution under electrochemical bias. Second, experimental design should shift from static structure assignment toward perturbation–response measurements. Third, theory should move beyond idealized repeat units toward ensemble-like local environments that can stabilize short sulfur fragments through combined electrostatic, dispersive, and π -mediated interactions.

Level III is what sets SPAN apart from a simple sulfurized polymer: its conjugated, polar, short-range-ordered host can confine sulfur selectively without giving up the stability of a solid-state cathode. It is also where the remaining capacity gains lie, because the covalent capacity of Levels I and II is close to its limit, so further improvement depends on understanding and controlling the soft-confined sulfur at this level. We therefore regard Level III as the least understood but most consequential part of the SPAN structure, and the main target for future work.

2.4 | Quaternary Structure (Level IV): Particle Morphology and Intraparticle Porosity

Quaternary Structure (Level IV) concerns the size, shape, and intraparticle porosity of SPAN particles and electrodes. At this level, the unit of description is a complete SPAN primary particle. Geometrically, Level IV closes the progression: Level III domains pack into a finite particle whose internal voids are themselves a structural feature. Relative to Level III, Level IV is defined not only by its larger scale and its external morphology, but also by an internal feature. A SPAN primary particle is built up from packed Level III domains, and the space left between them forms the intraparticle pores: some enclosed within the particle as closed pores, others connected to the surface as open pores. As shown in Figure 5a, the external morphology and the internal pores together define Level IV.

Most work on Level IV has so far focused on morphology (Figure 5b). Conventionally synthesized SPAN is usually close to spherical [7, 31]. Because PAN dissolves in some high-boiling-point organic solvents (such as DMF and DMSO), techniques such as electrospinning can produce fiber-shaped particles, which give SPAN better mechanical strength and maintain good charge transport at least along the fiber axis [37–39]. Using spin-coating followed by sulfur-vapor treatment, we have prepared thin-film SPAN with lateral dimensions on the order of cm^2 and a thickness of only a few hundred nanometers; this geometry ensures charge transport along the z -axis while providing a complete, cm^2 -scale interface, which makes it a useful platform for interfacial characterization of SPAN [2]. Hierarchical morphologies, such as nano-flower SPAN, have also been developed for gradient charge collection [40]. These studies remain within the scope of conventional nanomaterial design, and morphology control is necessary for improving the energy density of the cell.

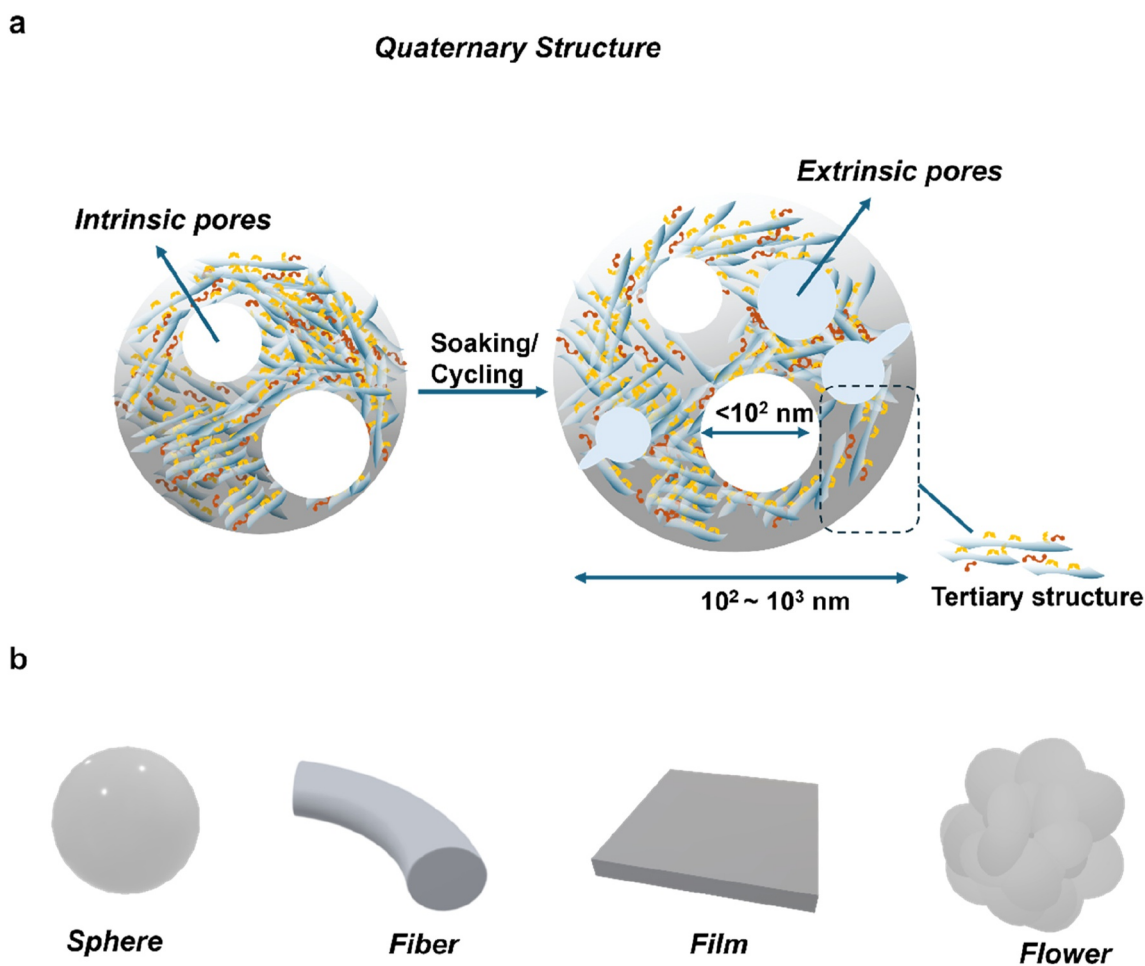


FIGURE 5 | Quaternary Structure (Level IV): primary-particle morphology and intraparticle porosity. (a) A SPAN primary particle is built from packed tertiary-structure (Level III) domains (dashed inset, with non-extractable (yellow) and extractable (red) sulfur). The pristine particle (left) contains intrinsic pores formed during synthesis; after soaking and cycling (right), additional extrinsic pores form and connect to the particle surface. (b) Representative SPAN particle morphologies enabled by the processability of PAN: sphere, fiber, film, and flower.

By comparison, the pores within the Level IV structure have received much less attention. As indicated in Figure 5a, the intraparticle pores can be classified by their origin into intrinsic and extrinsic pores.

Intrinsic pores form during SPAN synthesis. Because synthesis involves gas evolution (Figure 1a), a small number of pores form as the material is made. Recent work has shown that controlling the synthesis conditions can introduce a higher density of intrinsic pores, and that doing so improves both reactivity and particle stability [10, 41, 42]. The main reason intrinsic pores improve stability is that they buffer the volume change of SPAN during lithiation and delithiation [43]. This volume-expansion problem may deserve more attention for SPAN than for conventional sulfur cathodes, particularly in localized high-concentration electrolyte (LHCE) systems. In a conventional sulfur cathode, volume expansion can be partly relieved because polysulfides dissolve into the electrolyte [44]; in SPAN, especially given the additional soft-confined sulfur of Level III, the fully lithiated cathode cannot relieve expansion this way, since polysulfide dissolution is suppressed in a low-solubility LHCE. Intrinsic pores therefore become important: They are one of the

few routes by which SPAN can accommodate the volume change of cycling and avoid the resulting cathode failure.

Besides these intrinsic pores, a second population appears only after cycling: Absent in the pristine material, it emerges once the electrode has been charged and discharged [2]. Because these pores are absent in the pristine material and are produced by external factors such as charge–discharge, we can call them extrinsic pores. Many of them are connected to the external environment, which has two opposing consequences. On one hand, electrolyte can reach internal reaction sites through these pores, increasing the CEI contact area and raising cathode activity. On the other hand, the same pores can trap electrolyte and cause its irreversible consumption. The interphase that forms on these pore-facing surfaces adds a third, dynamic consequence: Because open pores are the channels through which the external solvation environment reaches the Level III interior, CEI growth at pore mouths can throttle or seal that exchange, functionally converting an open pore into a closed one and stranding part of the soft-confined population beyond electrochemical reach. The stable extended cycling of SPAN argues that wholesale self-sealing is not the norm, but partial

gating of this kind would be nearly invisible to standard metrics and could contribute both to first-cycle irreversibility and to rate dependence. It is also testable: Tracking open-versus closed-pore populations across interphase formation, and asking whether a CEI formed in a non-solvating carbonate electrolyte can subsequently hold the soft-confined sulfur in place in a solvating ether one, would show directly whether the interphase acts as the valve between Levels III and IV. In addition, an extrinsic pore can be viewed as the result of local tearing of the particle; as this tearing accumulates, long-term cycling may lead to structural collapse and a corresponding loss of cell life [45].

Importantly, the origin-based classification (intrinsic vs. extrinsic) is independent of pore topology (open vs. closed): Both intrinsic and extrinsic pores can each be open or closed. An intrinsic pore may be sealed inside the particle or may reach the surface, and an extrinsic pore may open to the electrolyte or remain internal. This distinction matters, because open and closed pores act differently: Open pores govern electrolyte access and loss, whereas closed pores govern mechanical buffering and internal damage. Yet at present there is little work that separates the two, and even less that quantifies how each population, defined by either origin or topology, affects capacity, kinetics, and degradation. Closing this quantitative gap will be necessary before the role of intraparticle porosity can be settled.

Morphology and porosity are not, however, independent attributes: The pore architecture of a SPAN particle is set at two distinct stages, and the external morphology participates in both. The first stage is shaping. The same processing step that fixes a particle's outer form also templates an internal pore structure in the PAN precursor. Uniaxial drawing during electrospinning aligns chains and elongates free volume, so fiber SPAN should inherit preferentially oriented, axis-parallel channels, the axial void anisotropy long documented in PAN-derived carbon fibers. Rapid nonsolvent exchange during precipitation forms a dense skin that seals solvent-rich domains before they drain, so fast-precipitated particles should carry a higher closed-pore fraction than slowly precipitated ones. A spin-cast film, thin and surface-dominated, should template little enclosed volume at all [2]. We state these as testable predictions: orientation-resolved small-angle scattering on aligned fiber mats, and helium-pycnometry–physisorption partitioning of closed versus open volume across a precipitation-rate series, would decide them. The second stage is sulfurization, whose gas evolution (the $\text{H}_2\text{S}/\text{CS}_2$ budget set at Level I) nucleates pores whose number density and size respond to temperature, ramp, and sulfur ratio [10, 41, 42]. Yet even these are not shape-independent. Whether an evolved gas pocket vents, leaving an open channel, or is sealed as a closed void is a race between two processes: Escape to the nearest free surface, a length set by particle size and shape, and the closing of the densifying matrix around it, set by the heating program. A few-hundred-nanometer film vents almost everywhere, whereas the interior of a micron-scale sphere is far likelier to seal. Both stages feed what we have called the intrinsic population: shaping supplies the template, sulfurization the gas-born additions. The division of labor is then clear. Pore number density and size distribution are chiefly sulfurization-kinetic quantities; orientation, skin structure, and the inherited template are chiefly shaping quantities; and the open-versus-closed balance, the characteristic that matters most for electrolyte access and loss,

belongs to neither alone, because it is the coupling term between the two. This coupling is also what makes Level IV functional rather than descriptive. With Levels I–III fixed, external shape leaves the redox thermodynamics untouched. What it sets are the boundary conditions (transport lengths, interfacial areas, gas-escape paths, and mechanical constraint) under which the chemistry of Levels I–III operates and, through the open-pore population, whether that chemistry remains reachable at all.

For Level IV, then, two coupled directions matter. The first is morphology, which is accessible because of the strong processability of PAN. The second, which we consider underdeveloped, is the intraparticle porosity: Its role needs to be evaluated systematically. Whether its overall effect is beneficial or detrimental, how these pores can be controlled, and how they evolve over cycling are all important questions for future work.

3 | Coupling and Characterization Across Levels

3.1 | How the Levels Couple

Much of the apparent disagreement in the SPAN literature arises because each structural level can, in isolation, look like a sufficient explanation. This is the “elephant” of the introduction seen one part at a time: Bond-focused studies emphasize sulfur-motif chemistry; morphology-focused studies highlight particle structure; and interfacial studies focus on sulfur dissolution. Each captures part of the picture. As we have argued, however, SPAN is a coupled system (Figure 6): Because the four levels are interdependent, its electrochemical behavior emerges only when the relevant levels are considered together.

Each level plays a defined role. Level I sets the baseline electronic continuity and the insoluble character of the host. Level II fixes the primary sulfur network and therefore the first-order distribution of reversible and irreversible sulfur sites. Level III determines whether interchain organization creates a mesoscale reaction field able to stabilize non-classical sulfur populations. Level IV determines whether that field remains accessible, recruitable, and mechanically stable at the particle and electrode scale. Structurally, each level is the substrate on which the next is built. Performance, however, does not map onto single levels: each property of interest draws on a specific combination of levels (Figure 6, top), and it is these combinations, not the levels in isolation, that the field must learn to control.

Controlling synthesis quality couples Levels I and II. The functional-group defects, meaning the gases evolved during synthesis (H_2S below $\sim 400^\circ\text{C}$, CS_2 above [24]) and the groups associated with irreversible structural change, arise where backbone formation and sulfur attachment compete.

Carrying out the deprotonation that accompanies sulfur attachment without thermally degrading the primary structure is therefore a Level I–II problem, as is precursor chemistry: the purity of the precursors and the way they are mixed strongly affect how cleanly the primary and secondary structures form and how much byproduct remains. The gas evolution that accompanies this conversion also sets the intrinsic porosity of Level IV, so synthesis quality reaches the particle scale as well.

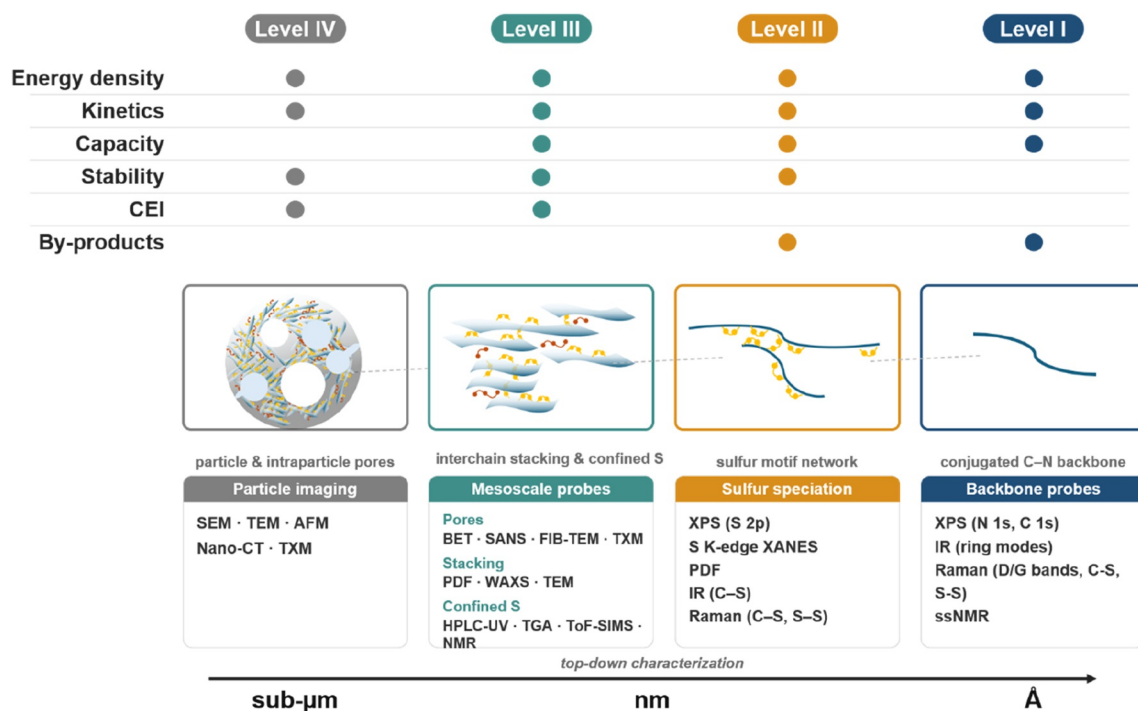


FIGURE 6 | Cross-level coupling and top-down characterization.

Capacity spans Levels I to III. The continuous pyridinic backbone of Level I hosts some lithium; the covalently fixed sulfur sites of Level II provide the main reversible capacity; and the soft-confined sulfur of Level III adds further capacity beyond the covalent ceiling. A central design question is how to keep a high density of ideal 4-position fused-pyridine repeat units while also introducing soft-confined sulfur that survives long-term cycling.

A stable CEI, and with it efficient ion exchange between SPAN and the electrolyte, is set jointly by Levels III and IV. The π – π stacking of Level III may favor Li^+ transport through the bulk of SPAN, helping the capacity reach its working-condition value; and in an electrolyte with low polysulfide solubility, more of the Level III soft-confined sulfur is retained. The morphology and pores of Level IV then determine how readily electrons and ions reach these sites.

Stability is a Level II–IV concern. Some of the Level II sulfur detaches from the polymer chains during cycling; some of the Level III soft-confined sulfur can leave the particle; and changes in π – π stacking act together with the particle-volume changes of Level IV to determine whether the structure holds. The pores of Level IV cut both ways: Some buffer the volume change, while others mark the onset of structural collapse.

Kinetics couples Levels I, III, and IV. The conjugated, delocalized backbone of Level I carries electrons along the chain; the π – π stacking of Level III carries them between chains; and the amount of soft-confined sulfur sets whether ion transport is impeded [8]. At the particle scale, Level IV morphology orients the overall electron and ion pathways.

Energy density, finally, is the property of no single level but the integral of all four: Among the material-intrinsic factors, it

follows from how the levels are coupled and from the core property each contributes (Figure 6, top).

3.2 | Characterizing the Levels

How can the four levels be observed? Whereas the preceding sections built the particle bottom-up, characterization is most natural top-down: from particle to bond, following a descending length scale (Figure 6, bottom).

At Level IV, morphology techniques dominate. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) resolve the particle from the outside in, and focused ion beam (FIB) sectioning reaches the interior of a single particle [2]. What the field still lacks is a way to assess how stable SPAN itself is under these probes: For an amorphous material there is no crystallinity to track, so beam-induced change must be followed indirectly, through energy-dispersive X-ray spectroscopy (EDX) or electron energy-loss spectroscopy (EELS) measurements of composition. In practice, SPAN morphology appears stable under room-temperature TEM, but whether cryogenic(cryo) conditions are needed to preserve composition, or whether room-temperature imaging is already sufficient, remains open [46]. Pore characterization is harder, because two distinctions overlap here: Intrinsic versus extrinsic (origin) and open versus closed (connectivity). Brunauer–Emmett–Teller (BET) sees only open, gas-accessible pores, so closed pores, possibly a large fraction of both populations, escape it; electron microscopy reveals some internal pores but samples only small volumes and, under ultra-high vacuum, is not ideal for electrolyte-related extrinsic porosity. Open intrinsic and extrinsic pores can in principle be separated by comparing BET before and after cycling, since extrinsic pores appear only after cycling.

Resolving the closed pores instead requires probes whose signal does not depend on connectivity. Here the two leading candidates, small-angle neutron scattering (SANS) and transmission X-ray microscopy (TXM), answer complementary questions. SANS is an ensemble probe: the beam averages over macroscopic sample volumes containing many millions of particles, and the scattering contrast between the SPAN matrix and void space makes open and closed pores equally visible from roughly one nanometer to several hundred nanometers (ultra-small-angle instruments extend this toward micrometers). Its decisive capability is contrast variation. Filling the open porosity with an H/D-mixed solvent tuned to the scattering length density of the matrix extinguishes the open-pore signal, so the residual scattering quantifies the closed fraction; this is currently the most direct quantitative route to a closed-pore number, and comparison before and after cycling can further separate intrinsic from extrinsic contributions [47]. What SANS cannot do is say where any of these pores are: the measurement is reciprocal-space and model-dependent, with no spatial localization. TXM has the opposite profile. Operated tomographically, it delivers real-space, three-dimensional maps at resolutions down to a few tens of nanometers over fields of view of tens of micrometers, resolving the spatial arrangement of pores within an individual particle, their connectivity above the resolution limit, and their evolution during cycling [48]. Its blind spots mirror SANS's strengths. Pores below the resolution limit are invisible, and the gas-evolution-derived intrinsic pores may sit exactly there; the statistics are those of one particle at a time. Focused-ion-beam serial sectioning with SEM or TEM imaging bridges the two regimes, reconstructing interior volumes at higher resolution than TXM, though destructively and over still smaller volumes. A further caution is that these methods do not even share a definition of "closed". BET classifies by gas accessibility, SANS contrast matching by solvent accessibility, and TXM by geometric connectivity at finite resolution, so the same particle can legitimately return three different closed-pore fractions: Sub-resolution throats inflate TXM's closed count, whereas a poorly wetting solvent shifts SANS's. In short, SANS tells us how much pore volume exists and of what kind, averaged over the ensemble; TXM tells us where it is and how it connects, one particle at a time. A trustworthy Level IV pore picture will therefore come from correlative workflows that put both probes, ideally with FIB-based sectioning, on the same material [46].

At Level III, the short-range π - π stacking is accessible to the synchrotron methods now appearing in the literature: wide-angle X-ray scattering and pair-distribution-function analysis in Q-space [36]. Whether cryo-TEM can image this short-range order directly has not yet been reported, though the technique should be capable of it. The soft-confined sulfur is best approached through a combination of liquid chromatography [19], thermal analysis [2], and nuclear magnetic resonance (NMR) [22], which together can begin to identify and quantify it. Developing methods that can separate and quantify the pores of Level IV, the stacking of Level III, and the soft-confined sulfur will, in our view, be decisive for the next round of performance gains. The tools for Levels I and II are, by comparison, mature, and we will not rehearse them. The opportunity there is not new techniques but new conditions: Operando and in situ versions of these spectroscopies [23, 33], and above all methods

able to follow the SPAN synthesis itself as the primary and secondary structures form.

This coupling has two consequences for how the field should work. First, causal attribution must become more disciplined. A study that attributes a performance gain to changed sulfur bonding should also report whether backbone conjugation, interchain packing, or particle structure changed at the same time; the field needs to be explicit about what is being tuned and what is merely co-varying, a distinction that only level-resolved characterization can make. Second, cross-level incompatibility may explain many failures to translate promising chemistry into devices. A material with attractive local sulfur chemistry can still perform poorly if its Level IV architecture strands the active domains; another can begin with high sulfur accessibility yet fade quickly because its Level III confinement is too weak to hold transient sulfur. These are not contradictions but expressions of the same coupled design space.

4 | Conclusion and Outlook

We began with a question that should have a simple answer but does not: What, structurally, is SPAN? Our argument has been that the question has resisted resolution because it is usually asked one scale at a time. We have separated SPAN into four structural levels: the conjugated backbone (Level I), the covalent sulfur network (Level II), the interchain organization and soft-confined sulfur (Level III), and the particle morphology and intraparticle porosity (Level IV). In doing so, we have tried to replace the search for a single correct formula with a description that matches what SPAN actually is: A thermal-history-dependent ensemble whose electrochemistry comes from how these levels are coupled, not from any one of them alone.

Within this picture, the levels are not equally understood. The backbone and the covalent sulfur motifs of Levels I and II have been studied extensively and are, in our view, approaching the limit of what they can explain on their own. The open questions now sit at the mesoscale. The soft-confined sulfur of Level III offers the most credible account of the reversible capacity that exceeds the covalent stoichiometric ceiling, and the intraparticle porosity of Level IV governs whether that capacity stays accessible and whether the particle survives repeated cycling. The next major gains in SPAN capacity and stability will therefore come from learning to control Levels III and IV, still the least quantified parts of the material.

Acting on this will require three changes in practice. First, the field should adopt level-specific descriptors (sulfur-motif distributions, interchain organization, and pore populations resolved by origin and topology), so that materials are compared along the dimension actually being changed rather than under a single "SPAN" label. Second, characterization should become level-resolved and, where possible, top-down and operando, since only measurements that separate the levels can distinguish what a synthesis change tunes from what merely co-varies with it. Third, and most immediately, the community should build characterization aimed squarely at the two underdeveloped levels: Methods to quantify soft-confined sulfur and interchain stacking, and methods to separate intrinsic from extrinsic and open from closed porosity. Progress here would turn several of

the field's long-standing disagreements from apparent contradictions into measurable, coupled design variables.

Finally, we want to be clear about what kind of contribution this framework is. It is not a structural model to be defended against alternatives, and its value does not depend on every detail of the soft-confinement hypothesis proving correct. It is a way of reasoning about a material whose properties arise across length scales rather than from a single motif. Identify the levels, specify each as a distribution rather than an ideal unit, and treat performance as a function of how the levels couple. That logic is not specific to SPAN. Many other organosulfur, organic, and polymeric electrode materials share its defining difficulties: Poorly defined long-range order, history-dependent structure, and behavior that cannot be read from any single scale. We expect the same level-based, descriptor-driven reasoning to be more productive for them than a continued search for one "correct" structure. In this sense, the framework returns to the language it borrows from: Just as a protein is understood not as a single formula but through primary, secondary, tertiary, and quaternary structure, SPAN is best read as a hierarchy of coupled levels rather than one motif.

For SPAN itself, the practical payoff is a clearer target. Rather than optimizing synthesis empirically and hoping for higher capacity, the field can now ask, at each level, what is being controlled and what is merely changing alongside it. We hope that this framework, and the shared language it provides, helps move SPAN from a material that works for reasons still debated toward one that is designed on principles the field can agree on.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

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

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