Expansion-tolerant architectures for stable cycling of ultrahigh-loading sulfur cathodes in lithium-sulfur batteries

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Lithium-sulfur batteries can displace lithium-ion by delivering higher specific energy. Presently, however, the superior energy performance fades rapidly when the sulfur electrode is loaded to the required levels—5 to 10 mg cm⁻²—due to substantial volume change of lithiation/delithiation and the resultant stresses. Inspired by the classical approaches in particle agglomeration theories, we found an approach that places minimum amounts of a high-modulus binder between neighboring particles, leaving increased space for material expansion and ion diffusion. These expansion-tolerant electrodes with loadings up to 15 mg cm⁻² yield high gravimetric (>1200 mA-hour g⁻¹) and areal (19 mA-hour cm⁻²) capacities. The cells are stable for more than 200 cycles, unprecedented in such thick cathodes, with Coulombic efficiency above 99%.

INTRODUCTION
The use of sulfur cathodes in lithium-sulfur (Li-S) batteries and silicon anodes in lithium-ion batteries (LIBs) is the most attractive example of inexpensive electrodes with excellent ability to store lithium, hence the potential for outperforming today’s LIBs. An inherent problem of these electrodes, regardless of the battery chemistry, is the structural fragmentation associated with the inevitable volume change during the absorption and release of large quantities of lithium (1, 2). The high-capacity sulfur cathode (1670 mA-hour g⁻¹) in the Li-S system suffers from a severe volume change (around 78%) upon cycling—typically around eight times higher than that of the electrodes in LIBs. These changes lead to a progressive loss of cohesion of particles and permanent distortion of the polymer binder and carbon matrix, both of which contribute to loss of capacity (3). The adverse effect of electrode disintegration becomes markedly more pronounced with any increase in the thickness of the cathode—the key parameter for achieving practical areal capacities (>6 mA-hour cm⁻²). The internal stress of cycling is more difficult to manage in the thick electrode, resulting in severe stress accumulation and impedance growth, hence rapid capacity loss (2, 4–8).

While substantial progress has been made in addressing the highly investigated issue of “polysulfide shuttle” in Li-S batteries very little attention has been devoted to the mechanical failure of thick cathodes in cycling duty. It might be argued that the first component to consider in dealing with this issue is the polymer binder. Binders, as essential ingredients in the electrode composition to glue the fillers (active material and conductive agent) together and also to the current collector, are mostly evaluated on the basis of their ability to make crack-free cathodes. Very little experimental work has been undertaken to understand the effects of the binder-filler interactions on the cycle-life performance (i.e., durability) of thick sulfur cathodes (9). While some binder systems have shown superiority over the traditional polyvinylidene difluoride (PVDF)–based sulfur cathodes in terms of reducing cracking, they only demonstrated good stability in low- to medium-loading cathodes (1 to 3.5 mg cm⁻²)—far from the >5 mg cm⁻² (and preferably >7 mg cm⁻²) targets of the Li-S battery to rival or outperform LIB (10). Examples include but are not limited to Gum Arabic in H₂O (11), Carboxymethylcellulose (CMC)/citric acid in H₂O/NN'-dimethylformamide (9), and CMC/Styrene-Butadiene Rubber (SBR) in ethanol/H₂O (12). Thick cathodes with practical sulfur loadings, if started at high capacities, showed rapid degradation due to the mechanical failure or, in most cases, did not deliver high capacities, and stability was achieved at a cost of limited capacity, i.e., low internal stress. To the best of our knowledge, no report of what might be called an “expansion-tolerant” (ET) architecture for thick battery electrodes that require improved binder characteristics has been proposed.

The initial discharge capacity of sulfur cathodes, which already suffer from the poor electronic conductivity of sulfur, is also critically dependent on the binder system (4). When a binder is used in the conventional way (i.e., added as a solution), it tends to create a continuous network across the bulk of the electrode and filling the voids of the carbon, markedly reducing a large fraction of the active surfaces and severely limiting the diffusion of the electrolyte to the full depth of the thick electrode (8). On this evidence, we argue that to achieve optimum electronic and electrochemical performance in thick sulfur cathodes, there needs to be a rethink of the design rules for their fabrication. The new approach must maximize the number of electrochemically available reaction sites while also providing a stronger physical support with which to manage the greater net forces within thick electrodes. Both goals must be met without sacrificing the electrical connections within the cathode that must be maintained throughout cycle life.

Inspired by the classical mechanisms and bridging architectures recorded in particle agglomeration theories (13–15), here, we report

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that controlling the dispersion of Na-CMC, a commonly used high-modulus binder with rich carboxylic groups, enables the formation of mechanically strong bridging bonds between the fillers (in our case, colloidal sulfur and conductive carbon) to produce cathodes with a unique architecture. These cathodes have very large reaction surfaces, can efficiently accommodate cycling stresses, and have high ion accessibility and electrical conductivity. We believe that such a shift from the commonly observed networking mechanism (16, 17), where the binder forms a dense continuous network in the bulk of the electrode, to a bridging mechanism (17, 18), where the stiff binder links the neighboring particles without covering them, i.e., by connecting a fraction of the particle’s surface area to other neighboring particles, can be a straightforward solution for the successful fabrication and cycling of ultrathick sulfur cathodes. We demonstrate that this new approach, while apparently subtle, generates radically improved gravimetric capacities in high-loading ET cathodes (as high as 15 mg cm\(^{-2}\) and above) and brings excellent cyclability and Coulombic efficiency (CE) to high areal capacity Li-S batteries (6 to 19 mA cm\(^{-2}\)) fabricated from commonly sourced materials.

RESULTS AND DISCUSSION

Fabrication and characterization of thick sulfur cathodes

Inspired by the classical approaches in particle agglomeration processes, we report a critically adapted slurry and electrode fabrication approach, which is still in-line with conventional electrode-making processes. We fabricated four types of thick sulfur cathodes with identical compositions [70% colloidal sulfur (Sigma-Aldrich), 20% C, and 10% CMC] yet using different slurry preparation methods as explained in Table 1. For cathodes A and B, we mixed all the ingredients at once for 48 hours, followed by addition of deionized (DI) water to make the slurry. In cathode A, we added water to the mixture in a controlled manner to moderately wet the CMC particles and obtain a castable paste. The required amount of water for this cathode was found to be one-third of the amount required for full solubility of CMC in water at room temperature. For cathode B, we set the amount of water added to the dry mixture of S/C/CMC to be equal to the amount that satisfies the solubility limit of CMC (20 mg ml\(^{-1}\)). On the other hand, we prepared cathodes C and D based on the most common mixing method for fabrication of LIB electrodes, which is also adapted in the literature for Li-S cathodes: mixing of active material and conductive agent, both in powder form, to establish a homogeneous distribution of the conductive agent, followed by blending in the predissolved binder solution to provide the required adhesion between particle/particle and particle/current collector. In cathodes C and D, the predissolved binders are solutions of 20 mg CMC ml\(^{-1}\) water and 20 mg CMC ml\(^{-1}\) cross-linking solution, respectively. The mixtures are continuously mixed for 48 hours to ensure good dispersion.

We conducted detailed scanning electron microscopy (SEM) studies at a wide range of magnifications to investigate the effect of slurry preparation on the morphology of these cathodes. The high-resolution SEM micrographs revealed the nature of the interparticle links in the fabricated cathodes. We observed evenly distributed web-like bridging bonds across cathode A (Fig. 1, A and B), which is formed of discrete fine particles (fig. S1A). In cathode B, which is composed of segregated clusters (fig. S1B), with an increase in water content and a subsequent increased amount of the dissolved binder, we replaced the web-like bridging bonds with ribbon-like bridging bonds holding together the clusters (Fig. 1, D and E). In contrast, cathodes C (Fig. 1, G and H) and D (Fig. 1, J and K) show very compact microstructures where most of the filler particles were covered by a cohesive network of polymeric binder and there seemed to be very little room to buffer the volume change in these dense cathodes (fig. S1, C and D). Hence, the method we used for fabricating cathode A efficiently converted the compact microstructure, commonly observed in the literature, into a unique architecture with an increase in free space to potentially accommodate the cycling stresses—we term this ET architecture. Schematic illustration of the observed architectures is also shown in Fig. 1.

Cross-sectional SEM images of the four cathodes agree with the surface observations and provide more insight (Fig. 2). It is seen that the microstructures are most uniform in our unique dry mixing approach and the conventional wet mixing approach, although very different from one another. On the other hand, in cathodes B and D, there are areas where the binder presence is extremely localized, and this is most severe in the case of cathode D where cross-linking of the CMC binder could effectively limit the diffusion of the electrolyte throughout the thick cathode. The presence of these areas in cathode B highlights the necessity of using the small solvent amounts to limit the dissolution of binder, if our dry mixing approach is to be adopted for electrode making (Fig. 2, F and I). Otherwise, this inhomogeneity in the microstructure could result in nonuniform utilization of active material across the electrode.

Via the practice of dry mixing, a homogeneous mixture of binder/filler is achieved (fig. S6). With the addition of a moderate amount of water to the mixture, the particles become sticky. The process of moisture migration into both the powder bed and the dry interior parts of the particles is controllable by managing the amount of water. The particles stay sticky, while the central parts (pore interiors and

Table 1. Description of cathodes with identical compositions but different slurry preparation protocols.

| Cathode | Mixing method | Solvent | Solvent content per gram of electrode ingredients (ml) | Viscosity (Pa·s) at 0.01 s\(^{-1}\) shear rate |
|---------|---------------|---------|------------------------------------------------|---------------------------------------------|
| A (our work) | Dry mixing of all ingredients | DI water | 1.5 | 45,100.0 |
| B (our work) | Dry mixing of all ingredients | DI water | 5.0 | 379.0 |
| C (common practice) | Wet mixing of S/C mixture in a predissolved CMC solution | DI water | 5.0 | 0.8 |
| D (cross-linking) | Wet mixing of S/C mixture in a predissolved CMC solution | Cross-linking solution | 5.0 | 117.0 |
the interparticle spacing) are still dry. The localized wet surfaces containing a saturated solution of the binder can form bridges, thus attracting the particles together, while the formation of the viscous liquid bridges is sufficient to obstruct flow, a phenomenon that has been recorded in the processing of food and detergent powders (14, 15, 19). Such a mechanism of binding the particles can be observed in powder mixtures that are water soluble or contain water-soluble materials (14, 20) and are demonstrated here through

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**Fig. 1. Morphological study, tomographic reconstruction, and schematic illustration of cathodes with identical composition and different slurry preparation methods.** Top-view SEM images and schematic illustration of the architecture in (A to C) cathode A, demonstrating evenly distributed web-like bridging bonds holding the fine particles together. The arrows in (C) illustrate the high degree of freedom for expansion and the easily accessible surfaces in ET cathode. (D to F) Cathode B demonstrating ribbon-like bridging bonds holding large clusters together. (G to I) Cathode C demonstrating a cohesive network of agglomerated particles, heavily coated by the binder. (J to L) Cathode D demonstrating a very compact microstructure with particles being tapped in the network of the binder. More images can be found in figs. S1 and S2. (M and N) X-ray tomography. Grayscale 2D view and 3D rendering of a portion of the (M) ET cathode and (N) cathode C, demonstrating the noticeably finer morphology of the ET cathode. 3D gray shape visualizes all phases in the specimen. Pink shape enables the visualization of weakly absorbing features such as the polymeric binder and binder-coated fillers, the fraction of which is larger in cathode C in agreement with SEM observations. Yellow shape represents more strongly absorbing sample components such as exposed sulfur, the fraction of which is larger in ET cathode. Scale bars, 50 µm (2D image) and 10 µm (3D image).
extensive microscopy observations. Tomographic imaging using x-ray offers further insight into the electrode architectures at the three-dimensional (3D) level (Fig. 1, M and N).

Note that dry mixing approach (cathode A) enables the increase in the areal loading of the cathode to values as high as 20 mg cm⁻² and above, whereas the use of predissolved binder solutions (cathodes C and D) results in coating delamination from the aluminum current collector at these high loadings (fig. S4). This is an obstacle, which other groups have tried to address by replacing 2D metallic foils, on which mature industrial-scale processes for large-scale fabrication have been developed, with 3D hosts such as porous carbon papers (9, 21, 22). The adhesive strength of the four cathodes was also characterized

via 3M peeling test to give a qualitative comparison with each other and the commonly used PVDF- and Gum Arabic–based cathodes. As shown in fig. S5, the ET cathode remains intact after the peeling process, whereas some to almost all of the electrode material were peeled off in other cathodes.

To help place the notion of ET electrode processing into context, we conducted an extensive characterization of all of the slurries and electrode mixtures. Figure 3A shows a comparison of the shear viscosity of four cathode slurries prepared via different slurry preparation protocols. The viscosity, at very low shear rates (0.01 s⁻¹), showed pronounced differences for various slurries: a more than 50,000-fold and a nearly 500-fold for the slurries in our work (ET cathode and cathode B, respectively) compared to that of the typical practice in the literature (cathode C). The marked difference between viscosities of slurries B and C, given their similar solid content, directly demonstrates the substantial influence of slurry preparation on the rheological behavior of electrode slurries and, consequently, the resultant microstructures with different binder–filler interactions.

We used the elemental energy-dispersive x-ray mapping analysis to study the homogeneity of the ET cathode. The elemental mapping images in Fig. 3B revealed a homogeneous distribution of sulfur, carbon, and CMC across the cathode, ruling out the necessity of wet mixing of active material–carbon mixture in a predissolved binder solution to achieve homogeneity, as suggested by the rich literature of LIB electrodes. Raman spectroscopy further supports this observation (fig. S6). Achieving a homogeneous distribution of the fillers in a sulfur cathode is known to be more crucial than for the electrodes

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**Fig. 2. Cross-sectional SEM images and elemental mapping of cathodes with identical composition and different slurry preparation methods.** Providing further insight to top-view SEM images: (A and B) Cathode A demonstrates a segregated structure and the presence of bridging bonds across the thickness of the cathode. (D and E) Cathode B demonstrates large clusters in an open structure. (G and H) Cathode C demonstrates compactness throughout the thickness. (J and K) Cathode D demonstrates areas where cross-linking has resulted in the formation of binder films. More images can be found in fig. S3. Elemental mapping images demonstrate (C) excellent sulfur exposure in cathode A, as opposed to (F) nonuniformity in cathode B, and (I and L) heavy coverage with binder in cathodes C and D, respectively.
This is mainly due to the higher fractions of conductive agent and binder in a sulfur cathode and the fact that they are required to provide functionality in excess of simply bringing conductivity and cohesion to the electrode. No vibration modes could be assigned to sulfur or CMC in Raman curves of the electrode mixture of the cathodes prepared via dry mixing, supporting homogeneity.

The ratio of $I_D/I_G$ was used to compare the degree of the presence of surface functional groups in the carbon of the cathodes and as additional evidence to microscopy (23, 24). It was noted that the $I_D/I_G$ of cathodes, prepared via the dry mixing approach, was lower compared to that of cathodes prepared via the commonly used method of wet mixing in predissolved binder solutions (fig. S6). This suggests that carbon in the latter cases is more sp$^3$, originating from a large number of surface functional groups of dissolved CMC.

This observation was further confirmed with x-ray photoelectron spectroscopy (XPS) analysis conducted on substantially purified filler powders recovered from the electrodes fabricated via dissolved binder solution, according to the procedure in (25). The comparison of the C 1s and O 1s spectra of the purified and original powders showed the retention of significant content of cellulose residue on the surface of the fillers (Fig. 3C, fig. S8, and table S1). This indicates that predissolved binder coats a large proportion of the available filler surface, which reduces the active surface area of the electrode. This is also evident in the cross-sectional elemental mapping of the four cathodes where the sulfur exposure is dominant in the case of the ET cathode as opposed to the extensive binder coverage in cathodes prepared via wet mixing (Fig. 2, C, F, I, and L). We also observed a correlation between the bulk electrical conductivity of cathodes and peak ratios ($I_D/I_G$); higher conductivity was measured when a lower $I_D/I_G$ value was observed, as can be seen in fig. S9.

### Cycling performance and structural evolution of thick cathodes

We tested high-loading sulfur cathodes under different discharge rates to evaluate the cycle life, CE, and rate dependence (Fig. 4A and fig. S10). After 100 cycles and as compared with the other cathodes, the ET cathode showed excellent rate capability and cyclability performance, along with well-developed voltage-time profiles and exceptional CE. Such a high level of sustained capacity performance is unprecedented at these very high sulfur loadings. We attribute this performance directly to the uniquely developed microstructure, which not only ensures the availability of a majority of surfaces sites for redox reactions, resulting in high levels of sulfur utilization, but also provides active material particles with enough space to accommodate
the increased volume required by the products of discharge (Fig. 2). This feature effectively removes much of the cycling stress and, at the same time, minimizes the limitations that conventionally deployed binders place on electronic conductivity and ion transport. Namely, the partial/full particle coverage with binder is minimized, and carbon pore filling with the binder solution is prevented.

We conducted electrochemical impedance spectroscopy (EIS) to further understand the advantages of the ET architecture before and after cycling (Fig. 4, B and C). Impedance curves are composed of one depressed semicircle in high-frequency regions, followed by an inclined line in low-frequency regions. The intersection of the semicircles with the real part of impedance at higher frequency represents the interphase contact resistance, which simulates the electron conduction process from the current collector to the reaction sites. The diameter of the semicircles corresponds to the charge transfer resistance at the interface of cathode/electrolyte (26). It is evident from the EIS data that cathode D exhibits significantly larger contact resistance compared to that of cathodes A, B, and C. The larger contact resistance of cathode D can be attributed to the poor adhesion of the cathode to the current collector, as found by the peeling test (fig. S5). Among all cathodes, cathode A has the smallest charge transfer resistance due to the minimized binder coverage across the cathode.

Fig. 4. Cycling performance of high-loading sulfur cathodes. (A) Comparing the discharge profile of different cathodes demonstrates the superiority of cathode A over other cathodes; long-term cycling, CE, and 0.5 C discharge profile comparison is available in fig. S10. (B and C) Electrochemical impedance spectroscopy: the evolution of cell impedance for the four cathodes, demonstrating the importance of the ET architecture in maintaining good contact with the current collector and excellent electron/ion conductivity upon cycling. (D) Excellent cyclability of ultrahigh-loading cathodes prepared via the undissolved binder approach in terms of gravimetric capacity, areal capacity, and CE at 0.1 C rates. (E) Excellent long-term cycling performance of a sulfur cathode prepared via undissolved CMC binder and expanded graphite as the conductive agent at 0.2 C; CE remains close to 100% after 200 cycles. (F) The plot of areal and gravimetric capacity as a function of sulfur loading demonstrates that the optimum performance happens at 13 mg cm⁻². (G) Performance of cathode A in a pouch cell configuration demonstrates excellent correlation with coin cell data; energy metrics are calculated on the basis of the whole package and are shown in fig. S13. (H) Comparing the areal capacity and total gravimetric capacity of the cathodes after 50 cycles (calculated on the basis of the mass of S/binder/carbon) in various references demonstrates unique metrics for our cathodes.
Figure 4D and fig. S11 show the long-term cycling performance of the ET cathode at different high and ultrahigh loadings of sulfur (6 to 15 mg cm$^{-2}$). In addition to cycling stability, impressive CEs (≥99%) were achieved, where the influence of sulfur loading appears minimal. To the best of our knowledge, this combination of excellent cyclability and CE is unique in the literature of high-loading sulfur cathodes, where reporting of CE is often disregarded (Fig. 4H) (4, 9, 21, 27–31). In addition, as shown in Fig. 4F, with the increase in sulfur loading, the gravimetric capacity demonstrates an excellent retention such that at 5 mg cm$^{-2}$, the cathode delivers the theoretical capacity of 1670 mA·hour g$^{-1}$ and, at 13 mg cm$^{-2}$, it still delivers a gravimetric capacity as high as 1440 mA·hour g$^{-1}$. Benefiting from an unprecedented sulfur utilization in thick cathodes, the areal capacity shows almost a linear increase with sulfur loading, up to 18.7 mA-hour cm$^{-2}$ (equivalent to only 215% lithium excess in the case of using a 200-μm Li anode) (fig. S12), which is delivered at a sulfur loading of 13 mg cm$^{-2}$.

We fabricated eight-layered pouch cells with the standard pouch cell dimension of ~80 mm by 50 mm at sulfur loadings up to 12 mg cm$^{-2}$ (Fig. 4G and figs. S13 and S14). We obtain levels of sulfur utilization in pouch cells that are essentially the same as those obtained for corresponding coin cells data, e.g., delivering a gravimetric capacity of 1490 mA·hour g$^{-1}$ (6.5 mA-hour cm$^{-2}$) at 4.5 mg cm$^{-2}$. This part of the scale-up process of battery technology development, so far a major challenge in work to date on the Li-S system, is effectively resolved via our ET cathode fabrication approach. The superior behavior of these cathodes is emphasized by postmortem analysis of cycled pouch cells, which shows that other aspects of Li-S technology must now be improved. In particular, we find signs of inhomogeneity on the surface of the lithium anode, indicative of nonuniform utilization of the negative electrode, and swelling of pouch cells due to gas formation (fig. S15). These observations demonstrate the importance of assembling test cells with high areal capacity cathodes that are present. Ultimately, to ensure a rapid transition to commercial-level designs, prototypes must embody realistic proportions of component materials (fig. S12) (32, 33). To this end, our results show that ET cathodes provide a powerful tool.

To exclude the stress absorbing effect of the conductive agent, we replaced the porous activated carbon with expanded graphite with near zero porosity (fig. S16). SEM analysis demonstrated a similar bridging mechanism, as shown in the inset of Fig. 4E. The cycling performance was also comparable, and it can be inferred that the use of a highly porous carbon is not required for absorbing the cycling stress of an ET electrode. It is also noteworthy that the use of colloidal sulfur is crucial to our approach and to the success of establishing bridging bonds. Replacing submicron-sized colloidal sulfur particles with several micrometer-sized crystalline sulfur particles in the formulation of the cathode resulted in a nonhomogeneous microstructure and poor performance metrics due to the often disregarded coarsening effect of crystalline sulfur and the strong tendency of S atoms to catenate (34). More information can be found in fig. S17. Another important factor related to aggregate behavior of the ET cathode is
that while cellulose maintains its adhesive properties in dry mixing method (despite being incompletely dissolved), other conventional binders such as PVDF lose their adhesive power under such conditions. In addition, as far as we can ascertain, there is no report on the formation of bridging bonds in the presence of solvents other than water (20). More information and comparison with traditionally made electrodes are provided in figs. S18 to S20.

To characterize the integrity of the cathodes upon cycling, we disassembled all cycled cells and examined the components. Top-view and cross-sectional SEM studies on the cycled cathodes (Figs. 5 and 6) revealed no obvious microstructural changes for ET cathode and cathodes B and D, whereas clear structural disintegration was observed for cathode C. Figures 5B and 6C and fig. S21 provide clearer observations of the preserved bridging links between the neighboring particles in heavily cycled ET cathode. This observation confirms the strength of these ultrafine bridges, which have been exposed to large cycling stresses. In contrast, the structural disintegration in cathode C (Figs. 5, E and F, and 6, G to I) demonstrates the ineffectiveness of the networking mechanism for maintaining the electrode integrity of high-capacity materials, such as sulfur, which experience substantial volume changes upon cycling. The reason that cathode D, with a similar networking mechanism, develops no major cracks upon cycling (Fig. 5, G and H) is due to the fact that, at such low capacities, the volume expansion is minimal and the cathode is not greatly stressed. This situation arises, as described earlier, because this electrode-making methodology promotes (i) strong bonding of binder to particles; (ii) dense morphology, where particles are covered with the binder (leaving very little room to expand); and (iii) that dissolved binder permeates and fills voids in the electrode, severely limiting electrolyte movement. Achieving stable cycling performance from thick cathodes at very low specific capacities is, of course, hardly remarkable. It can detract from overall perceptions of the technology in question. A similar situation has arisen in the case of silicon anodes (theoretical volume change of 400%), where reasonably stable anode performance can be achieved using blends of carbon with silicon, which effectively dilute the expansion stresses but only deliver modest levels of specific capacity.

Cross section of the cycled ET cathodes was further studied and compared with that of cathode C, over a relatively large area of around 100 μm by 50 μm prepared via focused ion beam (FIB) milling to obtain a smooth and clean cleavage with minimum damage (Fig. 7 and figs. S22 and S23). The combination of FIB and freeze-fractured cross-sectional observations of the cycled electrodes allowed for unambiguous imaging of the structural integrity of the ET cathode in the presence of bridging bonds as opposed to the evolution of major cracks throughout the thickness of cathode C, prepared via the traditional wet mixing method.

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**Fig. 6. Detailed cross-sectional observation of the four cathodes after an intense cycling regime.** Cross-sectional SEM images of (A to C) cycled ET cathode demonstrating integrity. (D to F) Cathode B demonstrating areas with the strong presence of binder. (G to I) Cathode C demonstrating the evolution of large cracks. (J to L) Cathode D demonstrating binder films and torn binder nets.
CONCLUSION
To date, the polymeric binders used in the fabrication of sulfur cathodes have been evaluated simply on the basis of their ability to make crack-free dense microstructures. We have shown that smaller proportions of the same binders can be deployed, by means of a elegantly simple method, to produce a cathode architecture that offers minimum interference with electrochemical reactions and ion movement and accommodates natural volume expansion during discharging, thereby resulting in markedly higher performance metrics. Our thick, ET cathodes, with sulfur loadings as high as 13 mg cm\(^{-2}\), demonstrate very high sulfur utilization (≈85%), delivering unprecedentedly high areal capacities (≈19 mA·hour cm\(^{-2}\)). Complete cells exhibit very high CE (>99%) as well, a crucial performance index that is often absent in the literature of high-loading sulfur cathodes. In addition to improving the performance of sulfur cathodes, a shift from networking mechanism to bridging mechanism may provide advantages to other high-capacity electrode materials such as the highly investigated Si anode in Li-ion battery. All these attractive performance features, along with low cost, environmental friendliness, abundance of materials available, and ease of processing, make this new design of electrodes promising for large-scale real-world applications as demonstrated with our Li-S pouch cells.

MATERIALS AND METHODS
Sulfur cathodes
All sulfur cathode slurries described in Table 1 were coated by a lab-scale doctor blade on a battery-grade Al foil and dried at room temperature for 6 hours, followed by overnight drying at 70°C under vacuum to remove all traces of solvent.

Electrochemical tests
All sulfur cathodes both in coin cell and pouch cell assembly were paired with carbon-coated glass fiber (1.0 to 1.3 mg cm\(^{-2}\)) to prevent the surface passivation and pore blocking of the thick cathode. The carbon-coated separators were prepared by rod coating of an aqueous slurry of activated carbon [80 weight % (wt %)] and Gum Arabic (20 wt %) on glass fiber, followed by overnight drying at 100°C under vacuum to remove all traces of water. The main electrolyte salt was 1 M LiTFSI, and 0.25 wt % LiNO\(_3\) was used as an additive in a mixed solvent of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, v/v). The electrolyte/sulfur ratio was ≈3:1 to 5:1 μl mg\(^{-1}\), depending on the cathode microstructure and sulfur loading. For example, for ET cathode at 6 and 13 mg cm\(^{-2}\), 30 and 40 μl of the electrolyte were used to wet the cathodes, respectively. For safety reasons, a Celgard separator was also used. The initial cycle of cycling tests was at 0.05 C rate.

SEM and FIB cross-sectional imaging
For SEM studies, to monitor the microstructural evolution of the sulfur cathodes after cycling, cycled electrodes were washed with 1 ml of DOL/DME (1:1, v/v) after disassembly in an Argon glove box. All cells were stopped at full charge before disassembly. The samples were mounted on an aluminum stub with double-sided conductive carbon tape and iridium coated using a Cressington 208HRD sputter coater. The thickness of the iridium coating was approximately 4 nm (60 mA for 30 s). Conductive coating is necessary to prevent charge accumulation in an electron microscope to obtain clear images, especially for insulating material. The samples were imaged using a ZEISS MERLIN FESEM (field-emission scanning electron microscope) operated in the secondary electron mode to observe the topographical features. Energy-dispersive spectroscopy (EDS) was used to identify elements present within the samples. The EDS system used was AZtec, manufactured by Oxford Instruments Pty Ltd. using their X-Max Extreme 100-mm\(^2\) windowless silicon drift detector. Magellan 400 FESEM and Nova 450 FESEM were also used for secondary electron imaging and energy-dispersive x-ray spectroscopy. Quanta 3D FESEM was used for ion beam milling.
X-ray computed tomography
An ultrahigh-resolution (spatial resolution, 0.7 μm) x-ray microscopy (XRM) system (XRM520Versa, Xradia, Pleasanton, CA, USA), available at the Department of Civil Engineering of Monash University [an Australian Research Council (ARC) Linkage Infrastructure, Equipment and Facilities–funded facility], was used for image acquisition in this study. Such an imaging technique allows for the visualization (or a better contrast) of weakly absorbing features, such as polymers, in low-density objects or in the presence of more strongly absorbing components of the specimen (34). Image projections were acquired by rotating the load-stage 360° around its vertical axis. The frame size of the projection was 1024 pixels by 1024 pixels. The scanning parameters used for all the scans are as follows: source voltage, 140 kV; power, 10 W; exposure time, 60 s. In this study, a total of 401 projections with a pixel size of 0.60 μm was taken. The 2D projections were reconstructed to 3D volumes using XRM Reconstructor software (Cone Beam-10, Xradia, Pleasanton, CA, USA). The reconstructed images were postprocessed using commercially available image processing software Avizo (FEI, Hillsboro, OR, USA). Further details on the experimental setup can be found elsewhere (35).

Raman spectroscopy
Raman spectroscopy was used to quantitatively compare the degree of the presence of surface functional groups in the carbon of the different cathodes. Raman spectroscopic measurements were undertaken using a Renishaw inVia Raman Microscope. An Innova Ar+ laser (emitting at 514 nm) was used as the light source operating at 10% power. Extended scans (10 s) were performed over the range of 3200 to 200 cm⁻¹. Data were collected from three to four different points for the same sample. Once the baseline was corrected, peak analysis was carried out using the GRAMS/AI software package, and the peak intensities were used to determine the I_D/I_G ratios.

X-ray photoelectron spectroscopy
Substantial surface coverage of the fillers with the dissolved binder was further confirmed with XPS analysis according to the procedure in (25). For this study, a pure sulfur electrode (S-electrode) and a pure carbon electrode (AC-electrode) were fabricated using a pre-dissolved CMC solution. The dried electrodes were then immersed in DI water and stirred for several hours. Sulfur powders and carbon powders were collected after filtering. The dried powders were subjected to repetitive immersing in water and filtering. After substantial washing, the collected samples were vacuum-dried for 24 hours at 80°C before spectroscopy measurement. XPS analysis was performed using an AXIS Nova spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al Kα source at a power of 180 W (15 kV × 12 mA), a hemispherical analyzer operating in the fixed analyzer transmission mode and the standard aperture (analysis area, 0.3 mm by 0.7 mm). The total pressure in the main vacuum chamber during analysis was typically between 10⁻⁹ and 10⁻⁸ mbar. Survey spectra were acquired at a pass energy of 160 eV. To obtain more detailed information about chemical structure, oxidation states, etc., high-resolution spectra were recorded from individual peaks at 40-eV pass energy (yielding a typical peak width of 1.0 eV for polymers). Each specimen was analyzed at an emission angle of 0° as measured from the surface normal. Assuming typical values for the electron attenuation length of relevant photoelectrons, the XPS analysis depth (from which 95% of the detected signal originates) ranges between 5 and 10 nm for a flat surface. Since the actual emission angle is ill-defined in the case of particles and powders (ranging from 0° to 90°), the sampling depth may range from 0 nm to approximately 10 nm. Data processing was performed using CasaXPS processing software version 2.3.15 (Casa Software Ltd., Teignmouth, UK). All elements present were identified from survey spectra. The atomic concentrations of the detected elements were calculated using integral peak intensities and the sensitivity factors supplied by the manufacturer. Binding energies were referenced to the C 1s peak at 285 eV (aliphatic hydrocarbon) or 284.4 eV (graphitic carbon), where applicable. Component fits were performed using standard Gaussian-Lorentzian components (GL30) and model spectra derived from experimental data, a methodology detailed elsewhere (36). Tentative component assignments for the fits shown in Fig. 3 and fig. S8 are as follows (37):

- Sample “CMC” and “AC from the electrode (after purification)”:
  - C1, C─C and C─H; C2, C─O; C3, C═O and O─C─O; C4, O─C═O;
  - O1, C═O; O2, C═O; Na, Na KLL.
- Sample “S from the electrode (after purification)”:
  - CMC, experimental data obtained from pure Na-CMC sample; C1, C─C and C─H; C2, C─O; C3, C═O and O─C─O; C4, O─C═O;
  - C5, CF; O1, C═O; O2, C═O; Na, Na KLL.

The accuracy associated with quantitative XPS is ca. 10 to 15%. Precision (i.e., reproducibility) depends on the signal/noise ratio but is usually much better than 5%. The latter is relevant when comparing similar samples.

Determination of specific surface area
Surface area and pore textural characteristics of the conductive agents used in this work were obtained from the N2 adsorption isotherms for pressures up to 1 bar measured by a volumetric method using a Micromeritics ASAP 2420 instrument at 77 K (liquid nitrogen bath). Samples were evacuated and activated at 200°C under dynamic vacuum at 10⁻⁸ torr for 12 hours to remove any residual solvent and measure the sample mass precisely. Gas adsorption measurements were performed using ultrahigh-purity nitrogen. Brunauer-Emmett-Teller surface area and pore-size distribution data were calculated from the N2 adsorption isotherms based on the density functional theory model in the software provided within the Micromeritics ASAP 2420 instrument.

3M peeling test
A strong 3M bonding tape designed for mounting was used to test the coatings’ adhesion of different cathodes. The tape was applied by rolling a 1 kg steel roller on the tape and then peeled off after 2 min in 1 cycle. A new piece of tape was used for each cathode.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/ content/full/6/1/eay2757/DC1
Fig. S1. Microstructural study of different cathodes.
Fig. S2. High-resolution SEM images of the cross-linking cathode.
Fig. S3. Cross-sectional SEM images of cathodes.
Fig. S4. Images of ET cathode A and cross-linking cathode C.
Fig. S5. Peeling test on several different cathodes.
Fig. S6. Raman spectroscopy.
Fig. S7. Photographs of slurries of wet mixing and dry mixing cathodes.
Fig. S8. An XPS study: Evaluation of the binder-filler interactions.
Fig. S9. Electrical conductivity data of different cathodes.
Fig. S10. Cycling performance of different high-loading sulfur cathodes.
Fig. S11. Cycling performance of high- and ultrahigh-loading ET cathodes.
Fig. S12. Plot of lithium excess percentage versus areal capacity of sulfur cathode.
Fig. S13. Cell-level energy metrics in pouch cell configuration.
Fig. S14. Charge-discharge profile of the ET cathode in pouch cell configuration.
Fig. S15. Postmortem analysis of a cycled pouch cell.
Table S1. Elemental quantification derived from XPS survey spectra.

Fig. S19. Cycling performance of sulfur cathodes with minimally dissolved PVDF binder.

Fig. S20. SEM images of cathodes fabricated via traditional wet mixing method using PVDF and Gum Arabic binder.

Fig. S21. High-resolution SEM images of the cycled ET cathode.

Fig. S22. FIB cross-sectional SEM images of the cycled ET cathode.

Fig. S23. FIB cross-sectional SEM images of the cycled wet mixing cathode.

Table S1. Elemental quantification derived from XPS survey spectra.

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Expansion-tolerant architectures for stable cycling of ultrahigh-loading sulfur cathodes in lithium-sulfur batteries

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