Mechanism of Li2S formation and dissolution in Lithium-Sulphur batteries

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Article  

Keywords: Li2S, Lithium Sulphur Batteries, SAXS, WAXS  

DOI: https://doi.org/10.21203/rs.3.rs-818607/v1  

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Mechanism of Li$_2$S formation and dissolution in Lithium-Sulphur batteries

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Abstract

Insufficient understanding of the mechanism that reversibly converts sulphur into lithium sulphide (Li$_2$S) via soluble polysulphides (PS) hampers the realization of high performance lithium-sulphur cells. Typically Li$_2$S formation is explained by direct electroreduction of a PS to Li$_2$S; however, this is not consistent with the size of the insulating Li$_2$S deposits. Here, we use in situ small and wide angle X-ray scattering (SAXS/WAXS) to track the growth and dissolution of crystalline and amorphous deposits from atomic to sub-micron scales during charge and discharge. Stochastic modelling based on the SAXS data allows quantification of the chemical phase evolution during discharge and charge. We show that Li$_2$S deposits predominantly via disproportionation of transient, solid Li$_2$S$_2$ to form primary Li$_2$S crystallites and solid Li$_2$S$_4$ particles. We further demonstrate that this process happens in reverse during charge. These findings show that the discharge capacity and rate capability in Li-S battery cathodes are therefore limited by mass transport through the increasingly tortuous network of Li$_2$S / Li$_2$S$_4$ / carbon pores rather than electron transport through a passivating surface film.
Main

Lithium-sulphur (Li-S) batteries are considered strategic candidates to reduce the environmental impact of current Li-ion batteries. The high expectations arise from the large theoretical capacities, abundance, and low cost of sulphur. Li-S batteries reversibly cycle sulfur to lithium sulfide (S / Li$_2$S), typically in a highly porous carbon cathode soaked with a liquid, non-aqueous electrolyte and using a lithium metal anode. Discharge converts S to Li$_2$S stepwise via polysulfides (PSs) Li$_2$S$_x$ ($2 < x < 8$). Practical realization of Li-S cells is hindered by incomplete S utilization, poor S/Li$_2$S mass loadings, rapid capacity fading, low rate capabilities, and irreversible reactions of PSs at the anode. These issues all trace back to insufficient understanding of S-to-Li$_2$S conversion.

The physical-chemical mechanism to reversibly form and dissolve solid Li$_2$S remains controversial. Many studies consider Li$_2$S to form via direct electroreduction of Li$_2$S$_2$ or higher-order PSs at the carbon-electrolyte interface. However, as electrodeposition of an insulator is in principle self-limited, the fact that Li$_2$S deposits are beyond tens and hundreds of nm in size suggest that they form via a solution-mediated process. This is supported by the finding that capacity is limited by mass transport in the tortuous Li$_2$S–carbon network. Such a solution-mediated processes could be the direct electroreduction of molecular Li$_2$S$_2$ to dissolved Li$_2$S (2 Li$^+ + S^2–$), which then precipitates solid Li$_2$S crystallites, similar to the electrodeposition of NaO$_2$ or KO$_2$ in Na-O$_2$ and K-O$_2$ batteries. However, large deposits beyond tens or hundreds of nanometers would require a solubility of Li$_2$S beyond the reported 10$^{-6}$ M. Disproportionation of PSs is widely accepted, and some studies consider Li$_2$S to form via disproportionation of dissolved Li$_2$S$_{13,16,20}$.

While operando x-ray diffraction and spectroscopy provide insights into the chemistries occurring during (de)lithiation, a complete understanding of the mechanisms of Li$_2$S formation requires a detailed chemical as well as structural picture. While the structures within Li-S has been studied using electron and X-ray microscopy, these techniques are limited by impractical cell designs, the Li$_2$S stability, the resolution, field of view, and the challenges of 3D imaging. Small angle scattering can provide complementary structural sensitivity from sub-nm to 100 nm, regardless of whether the probed phases are crystalline, amorphous or liquid. A recent operando small angle neutron scattering study confirmed the ability to follow the evolution of Li$_2$S particles not much larger than a few nm. Neutron and x-ray scattering are complementary methods since the phases are probed with different scattering contrasts.

Here, we perform in situ small and wide-angle X-ray scattering (SAXS/WAXS) to gain simultaneous structural and chemical insights from atomic to sub-micrometer scales with time resolutions of several seconds. Stochastic modelling enables quantitative interpretation of the SAXS results. During lithiation, we observe the formation of a hierarchical structure, consisting of aggregates of Li$_2$S crystallites and a second solid phase, which we identify to be Li$_2$S$_4$, both of which formed by disproportionation of the short chain PS Li$_2$S$_x$. During delithiation, the reverse occurs with the dissolution of the Li$_2$S / Li$_2$S$_4$ composite nanostructure via comproportionation to a Li$_2$S$_2$ polysulfide in solution. Complementary information from x-ray diffraction, electron microscopy, and electrochemical measurements allows us to validate this model for (de)lithiation. These findings show that discharge capacities and rates in Li-S batteries are limited by mass transport of PSs through the tortuous solid deposits and give insights into how cells design, electrolyte selection, and cycling proposals that control the Li$_2$S morphology can be used to optimize performance.

In situ small and wide angle X-ray scattering

In situ SAXS/WAXS experiments are carried out with a commercial electrochemical in situ scattering cell holding a high surface area carbon black cathode, a Li metal anode and a catholyte comprising 0.5 M Li$_2$S$_x$, 1 M LiTFSI, and 0.4 M LiNO$_3$ in diethylene glycol dimethyl ether (2G). To verify that our findings hold more generally, we also perform in situ SAXS/WAXS experiments on another common system with a carbon black / sulphur composite cathode and 1 M LiTFSI in tetraethylene glycol dimethyl ether:dioxolane (TEGDMEDOL, 1:1) without PSs as the electrolyte (Supplementary Fig. 1). SAXS and WAXS intensities are recorded on separate areal detectors (Fig. 1a) with a time resolution of 1 min during potentiostatic discharge/charge. The
x-ray beam hit the Li metal anode, the catholyte soaked separator and the carbon black cathode. All reversible structural changes seen by in situ SAXS/WAXS stem from the reversible deposition / dissolution of active material in the carbon black cathode only (Supplementary Fig. 2). More details are given in the Methods.

**Figure 1 | In situ SAXS / WAXS experimental set-up and potentiostatic discharge / charge.** a, Sketch of the experimental set-up for in situ SAXS / WAXS experiments at ELETTRA showing the separate detectors. b, Absolute specific current (blue) and absolute specific capacity (grey) versus time during potentiostatic discharge / charge of the in situ SAXS cell at 2.0 V / 2.45 V vs. Li/Li⁺. Both current and capacity are normalized by the bare carbon black electrode mass. c, Scanning electron microscopy images at different magnification show the hierarchical structure of Li₂S deposits on the carbon black electrode after potentiostatic discharge at 2.0 V vs. Li/Li⁺ to a capacity of 1520 mAh g⁻¹.

The (dis)charge profile in the in situ cell shows the expected behavior of a Li-S system (Fig. 1b). The absolute current during potentiostatic discharge at 2.0 V vs. Li/Li⁺ exhibits a distinct minimum indicating the onset of Li₂S nucleation. After nucleation, the current (i.e., the Li₂S formation rate) increases, since growth of Li₂S on existing Li₂S nuclei occurs at a lower activation energy than initial nucleation. The reduction in current after ~4500 s indicates the onset of capacity-limiting processes. The discharge is stopped after 2.5 h at a capacity of 1520 mAh g⁻¹ (normalized by the carbon mass, as there is no defined amount of sulphur present at the cathode). The maximum theoretical capacity of Li₂S in the 60 µl catholyte corresponds to ca. 2000 mAh g⁻¹, which is larger than the maximum values in Fig. 1b. Consistent with literature, SEM images of electrodes after full potentiostatic discharge show large structures with particle sizes beyond 100 nm (Fig. 1c) Due to the poor electronic conductivity of Li₂S, the resolution of SEM is not sufficient to resolve the nanostructure below 100 nm properly; however, these insights can be obtained by SAXS. During charge at 2.45 V vs. Li/Li⁺ for the same time, initially high currents fade quickly after ~2/3 of the capacity.

The initial SAXS intensity prior to discharge shows a roughly linear decay in the double-logarithmic plot (Fig. 2a). Such power law behavior is typical for the fractal-like structure of carbon black electrodes. During discharge, the SAXS intensity generally increases, with a larger increase at high q around 1.5 nm⁻¹ and at
low $q$ around 0.2 nm$^{-1}$. The background-corrected WAXS intensities indicate the formation of Li$_2$S crystallites during discharge (Fig. 2b).

To visualize the subtle SAXS intensity changes during the full potentiostatic discharge / charge cycle, we plot the relative SAXS intensity change with respect to the initial SAXS intensity prior to discharge as a function of time and scattering vector length $q$ (Fig. 2c, d). The WAXS intensity is also plotted as a function of time and scattering angle in Fig. 2e. As solid Li$_2$S starts to form (as evidenced by the decreasing current at ~5000 s in Fig. 2c and the emergence of the Li$_2$S crystallites in Fig. 2e), two distinct SAXS intensity maxima appear at low $q$ (regime $q_A$) and at high $q$ (regime $q_B$). In line with the high currents during charge (Fig. 1b, 2c), these features disappear quickly during charge compared to their emergence during discharge.

Comparing the changes in intensities of the SAXS and WAXS features (Fig. 2f) shows similarities in emergence of the WAXS and the high $q$ SAXS feature during discharge. Meanwhile the low $q$ SAXS feature decreases at the end of discharge. During charge, the low $q$ SAXS feature decreases quickest. The WAXS signal from the Li$_2$S crystallites decreases slower, with the high $q$ feature decreasing even slower. These observations suggest that the SAXS intensity maxima, while related to Li$_2$S deposition and dissolution, do not correlate directly to the Li$_2$S crystallites probed by WAXS.

This suggestion is further supported when considering the sizes of the features. From WAXS, we use the Scherrer equation to estimate that the Li$_2$S crystallite size (i.e., mean diameter) increases and plateaus at about ~7 nm (Fig. 2g). Spherical 7 nm single crystal particles should in a first approximation cause a broad SAXS intensity peak around 0.6 nm$^{-1}$ (Supplementary Fig. 3). However, neither the high-$q$ (1.5 nm$^{-1}$) nor the low-$q$ (0.2 nm$^{-1}$) SAXS intensity maximum relates to this primary Li$_2$S crystallite size, instead indicating features of approximately 2.5 nm and 24 nm, respectively.

To verify whether the features seen in the SAXS / WAXS data are specific to our selected materials and operating conditions, we galvanostatically discharge a sulphur / carbon black electrode (ENSACO 350G, Imerys) in a 1 M LiTFSI / TEGDME:DOL (1:1 vol.%) electrolyte at three different currents (Supplementary Fig. 1). For all currents, we find a 6 – 7 nm Li$_2$S crystallite size from the WAXS diffraction peak fitting and a high $q$ SAXS intensity maximum between 1 – 2 nm$^{-1}$. Primary Li$_2$S crystallite formation can therefore not be explained by classical nucleation and continuous growth, which would result in a crystallite size that strongly depends on current.

On the other hand, the low $q$ intensity maximum depends on the applied current (Supplementary Fig. 1). With increasing current, the intensity shifts to higher $q$-values (from ~0.1 nm$^{-1}$ at C/3 to <0.08 nm$^{-1}$ at C/30). We therefore attribute our low $q$ feature to aggregates comprised of the smaller primary Li$_2$S crystallites. At higher current, we have more, smaller aggregates which is in principle consistent with heterogenous nucleation and growth.

These SAXS/WAXS findings are in line with previous experimental data. Independently of the used materials or applied current, the Li$_2$S primary crystallite size has been shown to remain around 10 nm. Size and shape of the super-structures on the other hand, are very sensitive to the used materials and conditions such as current density. A feature similar to our signal at low-$q$ was observed using small angle neutron scattering. Finally, the Li$_2$S deposits observed with SEM are known to be larger than the primary crystallite size estimated by XRD via the Scherrer equation.

New in this work is the high-$q$ SAXS intensity maximum corresponding to a feature with ~2.5 nm diameter. Understanding the origin of this feature can provide the missing piece of the puzzle in quantifying Li$_2$S formation and dissolution.
Figure 2 | In situ SAXS/WAXS experimental data. a, SAXS intensities versus scattering vector length \( q \) during potentiostatic discharge at 2.0 V vs. Li/Li\(^+\) up to a capacity of 1520 mAh g\(^{-1}\). b, The respective background corrected WAXS intensities versus scattering angle during potentiostatic discharge. The (111) and (200) Li\(_2\)S diffraction peaks are fitted using a Lorentz function. c, Specific current versus time during potentiostatic discharge / charge at 2.0 V / 2.45 V vs. Li/Li\(^+\). d, The relative SAXS intensity change as a function time and the scattering vector length \( q \). The SAXS intensities were normalized by the SAXS intensity prior to discharge at OCV. The \( q \)-regions \( q_A \) and \( q_B \) embrace intensity maxima that appear upon Li\(_2\)S formation at low and high \( q \), respectively. e, The WAXS intensities as a function of time and scattering angle. The dash-dotted lines indicate the (111) and (200) Li\(_2\)S diffraction peaks. f, Normalized, mean SAXS intensity of the low-\( q \) (\( q_A \)) and high-\( q \) (\( q_B \)) regimes during potentiostatic discharge / charge (black and grey) and (111) diffraction peak height \( A \) in blue (obtained from Lorentzian peak fit). g, Shift of the SAXS intensity maximum in \( q_B \), obtained by calculating the “center of mass” in the \( q_B \) regime (black) and Li\(_2\)S crystallite size in blue (obtained from the (111) peak width and the Scherrer equation) during potentiostatic discharge / charge.

Li\(_2\)S formation via polysulfide disproportionation

To develop a model for the chemical phase evolution and observed hierarchical structures that can be validated with the SAXS data, we consider potential scenarios for Li\(_2\)S formation. The observed aggregate sizes of more than 100 nm combined with the insulating nature of Li\(_2\)S mean that it is highly improbable that Li\(_2\)S forms via direct electroreduction and growth at the carbon/electrolyte interface or Li\(_2\)S/electrolyte interface\(^3\). Instead, the structural features point to species in the electrolyte supporting growth. This could be Li\(_2\)S if it redissolves (Li\(^+\), S\(^{2-}\)) and precipitates after having formed by direct reduction at the carbon; however,
the extremely low solubility of Li$_2$S suggests that dissolved Li$^+$ and S$_2^-$ could only form small Li$_2$S crystallites on or in close proximity to the carbon surface. Alternatively, it could be solution transport of PSs, which after diffusing in solution to a nucleation site disproportionate to form Li$_2$S (for example, Li$_2$S$_2$ $\rightarrow$ 2/3 Li$_2$S + 1/3 Li$_2$S$_4$) (Fig. 3a).

If Li$_2$S forms via disproportionation of PSs, we also expect PSs synthesized via chemical routes to disproportionate to Li$_2$S and a higher-order PS. To test this, we prepare solid PSs from their solutions and investigate whether Li$_2$S forms. We mix sulphur and Li metal in a solution of tetrahydrofuran (THF) at 50 °C to obtain nominal stoichiometries of Li$_2$S$_2$, Li$_2$S$_3$, Li$_2$S$_5$ and Li$_2$S$_7$. The stirring time to completely dissolve all S and Li varies between 1 day for nominally Li$_2$S$_7$ to 2 weeks for Li$_2$S$_5$. The solutions are dried under vacuum to obtain solid PS powders (details in the Methods).

X-ray diffraction patterns of the resulting solid PSs (Fig. 3b) show that the low-order PSs (nominal stoichiometry Li$_2$S$_2$ and Li$_2$S$_3$) contain crystalline Li$_2$S. Sharp diffraction peaks in the higher-order PSs indicate larger sulphur (α-S) crystallites. Ex situ nuclear magnetic resonance (NMR) spectra of PS powders confirm the coexistence of Li$_2$S and other higher order PS (or S). Interestingly, SAXS intensities of the nominally Li$_2$S$_2$ and Li$_2$S$_3$ solids (Supplementary Fig. 4) reveal a high-q SAXS intensity shoulder as observed for the electrochemically discharged electrode (Fig. 2d and Fig. 4a). The Li$_2$S diffraction peak width of the Li$_2$S$_2$ powder is nearly identical to the peak width of Li$_2$S obtained from electrochemical discharge, resulting in crystallite size of 5–7 nm. This indicates that Li$_2$S forms both in the electrochemical cell and upon drying PS solutions via disproportionation from solution species.

The fact that only low order PSs show crystalline Li$_2$S implies that the disproportionation educt is either Li$_2$S$_2$ or Li$_2$S$_3$. Since the latter is typically absent in glyme-based electrolytes, we hypothesize that Li$_2$S forms and dissolves predominantly via

$$3 \text{Li}_2\text{S}_2 \rightleftharpoons 2 \text{Li}_2\text{S} + \text{Li}_2\text{S}_4$$

(1)

and that the high-q SAXS intensity maximum therefore stems from solid Li$_2$S$_4$ particles.

**Figure 3 | Polysulfide disproportionation from solution.** a, Scheme of proposed reaction pathway during Li-S battery discharge. Solution-mediated disproportionation forms a solid Li$_2$S / Li$_2$S$_4$ composite. b, X-ray diffraction patterns (intensity vs. scattering angle Two Theta) of different solid polysulfides (nominally Li$_2$S$_2$ to Li$_2$S$_7$) as well as of the discharged electrode shown in Fig. 2b (Li$_2$S e-chem). The $(111)$, $(200)$, and $(220)$ Li$_2$S diffraction peaks indicate Li$_2$S crystallites of similar size to form in Li$_2$S$_2$, Li$_2$S$_3$ and Li$_2$S as well in upon electrochemical reduction (crystallite sizes: Li$_2$S$_2$ = 5.7 nm; Li$_2$S$_3$ = 3.4 nm; obtained from the $(111)$ diffraction peak and the Scherrer formula).

Formation of Li$_2$S via disproportionation of Li$_2$S$_2$ is consistent with a number of recent investigations, which predict the instability of Li$_2$S$_2$ further. Furthermore, as a sanity check that Li$_2$S$_2$ disproportionates to Li$_2$S and Li$_2$S$_3$, we perform a simple experiment. Higher order polysulfides are soluble in glymes so washing a dried, discharged electrode with fresh 2G should dissolve most Li$_2$S$_4$. Indeed, ex-situ SAXS of the dried electrode
shows a pronounced high-q SAXS intensity shoulder that disappears after washing (Supplementary Fig. 2). Alternative but unlikely SAXS data interpretations are discussed in Supplementary Note 1.

### A model for Li$_2$S Deposition and Dissolution

Our experiments point to the following process for the formation and dissolution of Li$_2$S: during discharge, solid Li$_2$S$_2$ precipitates and disproportionates, forming a composite structure consisting of solid Li$_2$S and Li$_2$S$_4$ particles (Fig. 3a). The solid Li$_2$S$_4$ particles are responsible for the SAXS feature in region $q_B$ in Fig. 2d and have a mean size around 2.5 nm. The 7 nm Li$_2$S crystallites (WAXS) and these Li$_2$S$_4$ particles aggregate to form features with a mean size (diameter) around 24 nm (region $q_A$ SAXS). These polycrystalline aggregates arrange into the larger structures >100 nm seen by SEM (Fig. 1c). During charge, the aggregates first dissolve into primary Li$_2$S and Li$_2$S$_4$ particles. Li$_2$S$_4$ dissolution lagging behind Li$_2$S dissolution during the entire charge (in Fig 2f, the low-q maximum disappears faster than WAXS diffraction peaks and high-q shoulder).

To validate this and gain further insights into the structural evolution of the Li$_2$S/Li$_2$S$_4$ nanostructure, we use the concept of plurigaussian random fields to create the three-phase Li$_2$S / Li$_2$S$_4$ / electrolyte structure (Methods). With this structure, we then model the expected time-dependent SAXS intensity change during discharge and charge based on our proposed mechanism and compare it to the measured SAXS data.

To remove the scattering contribution of carbon black and electrolyte structure factor from the evolving Li$_2$S / Li$_2$S$_4$ composite structure, we subtract the SAXS intensity prior to discharge as well as a constant background from all in situ SAXS intensities (Methods). The remaining, reduced SAXS intensities correspond to the Li$_2$S / Li$_2$S$_4$ scattering contribution, assuming negligible correlations between Li$_2$S / Li$_2$S$_4$ and carbon black structures (Fig. 4a).

By fitting the SAXS intensity of the fully discharged electrode (Fig. 4a), we extract parameters for (i) the feature sizes of Li$_2$S and Li$_2$S$_4$, (ii) the respective volume fractions of Li$_2$S and Li$_2$S$_4$, and (iii) a parameter accounting for the spatial correlation between the Li$_2$S and Li$_2$S$_4$ structures (Table S1). The latter parameter ($\delta$, see Methods) defines whether Li$_2$S$_4$ particles are preferably located close to the Li$_2$S surface ($\delta \rightarrow 0^\circ$) or randomly distributed across cavities that form amongst the Li$_2$S particles ($\delta \rightarrow 90^\circ$). The value of $\delta = 45^\circ$ shows that Li$_2$S$_4$ particles are growing in close proximity to the Li$_2$S crystallites. This is in line with the disproportionation reaction in Equation 1 and Fig. 3a. With these parameters, we generate a 3D representation of the Li$_2$S/Li$_2$S$_4$ nanostructure on a 3D lattice shown in Fig. 4b (cross section) and Fig. 4c (3D visualization). This visualization highlights the smaller size of Li$_2$S$_4$ particles compared to Li$_2$S particles, the Li$_2$S$_4$ growth in close proximity to the solid Li$_2$S, and the mean aggregate size around 24 nm.

With the time-dependent input parameters described in Supplementary Note 2, we model the SAXS intensity during discharge and charge. The salient features of the experimental in situ data (Fig. 4d) are reproduced by the model (Fig. 4e) for the full discharge/charge cycle. Deviations between the model and experiment can be explained by carbon-Li$_2$S/Li$_2$S$_4$ correlations, which were not considered here. The comparatively better model fit for Li$_2$S/Li$_2$S$_4$ deposited on glassy carbon beads confirm this (Supplementary Fig. 5).

Fig. 4f shows the Li$_2$S and Li$_2$S$_4$ volumes as used in the time-dependent PGRF model. They are calculated by multiplying the Li$_2$S and Li$_2$S$_4$ volume fractions $\phi_{Li_2S}$ and $\phi_{Li_2S_4}$ with the relative volume change of the Li$_2$S / Li$_2$S$_4$ deposits $V/V_{max}$ (both model inputs, see Supplementary Fig. 10). We see that the Li$_2$S$_4$ volume grows at initial stages of charge, and so do the Li$_2$S$_4$ particles (high-q maximum shifting to smaller $q$ as shown in Fig. 4d). Li$_2$S$_4$ dissolution lags behind Li$_2$S dissolution during the entire charge, shifting relative volume fractions towards Li$_2$S$_4$, and suggesting that Li$_2$S$_4$ is the driver for Li$_2$S dissolution.

The Li$_2$S and Li$_2$S$_4$ pair distance distribution functions (Fig. 4g-h) quantify the time evolution of the Li$_2$S and Li$_2$S$_4$ structures in real-space. Note that the maxima for Li$_2$S$_4$ (white to red shading) do not track the mean particle radius of around 1.25 nm (black dash-dotted line). This can be explained by the significant correlations between the Li$_2$S$_4$ and Li$_2$S structure (quantified by the parameter $\delta = 45^\circ$). Hence Li$_2$S$_4$ particles preferably grow next to the Li$_2$S crystallites, which is consistent with a disproportionation reaction (Equation 1).
Figure 4 | A stochastic SAXS model to describe the nanoscale phase evolution of Li$_2$S / Li$_2$S$_4$ deposits. 

A, reduced SAXS intensities versus scattering vector length $q$ during potentiostatic discharge at 2.0 V vs. Li/Li$^+$. The SAXS intensity prior to discharge (at OCV) and hence the carbon scattering contribution was subtracted from the SAXS intensities shown in Fig. 2a. The plurigaussian random field (PGRF) model fit is given in blue. 

B-C, The corresponding representative real space model generated via PGRFs and the input parameters obtained from the model fit in A. B shows a 100 nm$^2$ cross section, C a 3D visualization of a 30 nm$^3$ cut-out. White dashed lines indicate schematically that Li$_2$S aggregates consist of individual Li$_2$S grains. 

D, Experimental relative SAXS intensity change as a function of time and scattering vector $q$ during potentiostatic discharge / charge. The data is equivalent to the data shown in Fig. 2d. E, Modelled relative SAXS intensity change using the PGRF model and the time-dependent input parameters shown in Supplementary Note 2. 

F, Li$_2$S and Li$_2$S$_4$ volume fractions as used in the time-dependent PGRF model multiplied by the relative volume change of Li$_2$S / Li$_2$S$_4$ deposits V/V$_{max}$ (see Supplementary Fig. 10). G, Li$_2$S – Li$_2$S pair distance distribution function (PDDF) as a function of time and distance $r$, corresponding to the time-dependent PGRF model shown in E. H, Li$_2$S$_{2r}$–Li$_2$S$_4$ PDDF as a function of time and distance $r$, corresponding to the time-dependent PGRF model shown in E. The dashed and dashed-dotted black curves in G-H correspond to a Li$_2$S and Li$_2$S$_4$ particle correlation length, respectively, and serves as a guide for the eye for the time-dependency of particle sizes. The correlation length is arbitrarily defined as the distance where the correlation function equals 0.2 (Supplementary Fig. 6). Details are given in the methods section.

Solid-state disproportionation

We next investigate whether the dis- and com-proportionation reactions can in principle occur in the solid state. The relatively constant Li$_2$S crystallite sizes independent of the used electrolytes and experimental
conditions suggest diffusion-limitation dictated by the solid phase rather than by the electrolyte, and hence a solid-state process to be involved. We rolled crystalline sulphur onto a piece of Li metal in a molar ratio of 2:1 under Ar atmosphere and recorded the XRD pattern of the resulting mixture from 3 to 20 hours after mixing (Fig. 5, details see Methods). The crystallite size obtained from the diffraction peak widths remained constant for the different resting times and similar to the Li$_2$S size obtained from electrochemical discharge (Fig. 5). This suggests that Li$_2$S during Li-S battery discharge is formed by solid-state disproportionation.

This can be explained by expanding Equation 1 by the electron transfer process between Li$_2$S$_4$ and Li$_2$S$_2$, from which we obtain

$$1.5 \text{Li}_2\text{S}_4(\text{sol}) + 3\text{Li}^+ + 3\text{e}^- \rightleftharpoons 3\text{Li}_2\text{S}_2(\text{sol}) \overset{\text{DISP}}{\rightleftharpoons} 2\text{Li}_2\text{S}_2(\text{s}) + \text{Li}_2\text{S}_2(\text{s/sol})$$

(2)

$3\text{Li}_2\text{S}_2(\text{s})$ denotes transient solid Li$_2$S$_2$ crystallites.

The processes in Equation 2 are illustrated in Fig. 6. Prior to disproportionation, the precipitation step forms transient solid Li$_2$S$_2$ crystallites, which determine the number density, size and shape of the final Li$_2$S/Li$_2$S$_4$ aggregates. We hypothesize that the crystalline Li$_2$S$_2$ is not detectable with WAXS/XRD as the Li$_2$S$_2$ are transient. Only under specific conditions transient, crystalline Li$_2$S$_2$ has been observed experimentally.

Disproportionation via transient solid Li$_2$S$_2$ explains why Li$_2$S deposits in Li-S batteries can form distinct single crystal-like shapes (e.g. platelets) of sizes beyond several 100 nm, where the primary Li$_2$S crystal size (as observed by XRD) is constantly around 10 nm. Further, it explains why Li$_2$S aggregate size and shape depend strongly on current and solvent, while the Li$_2$S primary crystallite size does not.

Alternative routes such as disproportionation in solution followed by precipitation ($3\text{Li}_2\text{S}_2(\text{sol}) \rightleftharpoons 2\text{Li}_2\text{S}_2(\text{sol}) + \text{Li}_2\text{S}_4(\text{sol})$) appear unlikely given the unfavorable solvation of Li$_2$S. Upon discharge, Li$_2$S$\delta$ is both the educt to form Li$_2$S$_2$ via electron transfer and the product of disproportionation. Upon charge, Li$_2$S$\delta$ is both the product of Li$_2$S oxidation and the educt of comproportionation. Hence, the very right hand side of Equation 2 feeds back to the very left. Except for the electron transfer step, all steps are equilibria. The direction of electron transfer will, therefore, create a net flow with the same direction in these equilibria; disproportionation (DISP) following reduction and comproportionation (COMP) following oxidation. Spatially,
electron transfer at the carbon surface and DISP/COMP at Li$_2$S surfaces (mostly inside porous deposits) are separated, requiring diffusive transport in between.

**Figure 6 | The reversible DISP/COMPproportionation process during discharge/charge.** a,b. Processes and equilibria upon discharge (a) and charge (b). The mechanism centers around the DISP/COMP equilibrium \( \text{Li}_2\text{S}_{2(\text{sol})} \leftrightarrow (\text{Li}_2\text{S})_{2(\text{g})} + \text{Li}_2\text{S}_{4(\text{sol})}) \). The net direction (red arrows) is set by the electron transfer step. Dashed arrows indicate diffusion. Solid Li$_2$S, Li$_2$S$_2$, and Li$_2$S$_4$ are illustrated according to their Wulff shapes$^{47}$. According to Equation 2, some Li$_2$S$_2$ and Li$_2$S$_4$ will remain dissolved at the end of discharge. This is because neither is directly electrochemically converted to Li$_2$S. This is in accord with a relative Li$_2$S-to-Li$_2$S$_4$ volume fraction of 2:1 (Fig. 4f). The 2:1 Li$_2$S:Li$_2$S$_4$ molar ratio from disproportionation in Equation 1 would result in a Li$_2$S:Li$_2$S$_4$ volume ratio of 0.7:1. During charge, dissolved Li$_2$S$_2$ is electrochemically oxidized to Li$_2$S$_4$(sol). Hence, solid Li$_2$S$_4$(s) can still grow (as seen in Fig. 4d). Li$_2$S$_4$(sol) thus acts as mediator to oxidize and dissolve Li$_2$S without any electronic conduction through Li$_2$S deposits. Galvanostatic charging of a discharged electrode after washing and drying confirms this (Supplementary Fig. 7). Since washing removes part of the dissolved Li$_2$S$_2$ and Li$_2$S$_4$, charging after washing leads to higher overpotentials at initial stages of charge.$^{48}$ Without the dissolved PSs serving as mediators, initial charging requires the direct oxidation of Li$_2$S, likely at Li$_2$S/C/electrolyte three-phase boundaries.

As the SAXS data modelling may involve systematic errors, it is important to understand which outcomes are based on model-free experimental results. The fact that Li$_2$S forms via disproportionation is clear. It is verified by in situ WAXS, SEM and ex situ XRD of PS powders and Li metal mixed with solid sulphur. Details of the nanostructure quantified via the stochastic SAXS model on the other hand need further refinement. Instead of Li$_2$S$_4$, in principle, other solid higher-order PSs, i.e. other disproportionation reactions than Equation 1 may explain the high-q SAXS intensity shoulder. Given the consistency of the derived mechanism with all experimental data and the possible disproportionation reactions$^{20,41}$, alternative SAXS data interpretations remain highly unlikely (see Supplementary Note 1).

**Conclusions**

In conclusion, we provide direct experimental evidence that solid Li$_2$S in Li-S batteries forms via precipitation of short-chain polysulfides (such as Li$_2$S$_2$) and subsequent solid-sate disproportionation or phase separation. Besides solid Li$_2$S, the SAXS data indicate the formation of a second solid PS phase (such as Li$_2$S$_4$), with smaller particle size. During charge, the particles of this second phase initially grow while Li$_2$S already disappears. The behavior is consistent with a DISP/COMP equilibrium between the short-chain PS and Li$_2$S plus a longer-chain PS. Electron transfer interconverts the short- and longer-chain PSs and its direction determines the net flux through the equilibrium, giving rise to Li$_2$S formation/dissolution on discharge/charge without the need for electron transport across the insulating Li$_2$S.
Converting Li$_2$S$_2$ to Li$_2$S affords half of the theoretical capacity of Li-S cells and is – as we show – a chemical rather than electrochemical reaction. It means that discharge capacity of a Li-S battery cathode is limited by mass transport\textsuperscript{16,17} through the tortuous network of Li$_2$S / Li$_2$S$_4$ / carbon pores rather than electron transport through a passivating surface film\textsuperscript{11} (note that macroscopic PS transport through the separator and PS reactions at the anode might be limiting as well in practical systems). Knowing this, shifts paradigms of how to control the discharge capacity. The achievable Li$_2$S pore filling and hence the discharge capacity is not only limited by the electrolyte solvation strength, but equally by the applied current density and the mobility of the reactive species. Theoretical sulphur capacities may never be achieved as a certain amount of higher-order PSs remains in solution and/or as a second solid phase. Concerning the initial overpotential during charging, remaining PSs are beneficial as they mediate charge transfer via solution, bypassing the insulating Li$_2$S.

Given the known relation between electrolyte solvation and Li$_2$S morphology\textsuperscript{13,15} (i.e., Li$_2$S nucleation and growth), we believe that solvation energies influence on the one hand Li$_2$S$_2$ crystallization in terms of nucleation and size/shape, of which the Li$_2$S deposits form replicas. On the other hand, the electrolyte determines redissolution and diffusion of the longer-chain DISP product, which is critical for approaching theoretical capacities.

More broadly, the solid-state disproportionation mechanism indicates solid state DISP of precipitated Li$_2$S$_2$ to have similar kinetics to precipitation of Li$_2$S$_2$ and redissolution of Li$_2$S$_4$. Solid state DISP requires Li redistribution from the Li$_2$S$_2$ into the Li$_2$S and Li$_2$S$_4$ phases, which appears sufficiently facile on a scale of up to 10 nm, as indicated by the Li$_2$S crystallite sizes. This implies that solid-state S-to-Li$_2$S conversion (SSC) is possible at practical rates if S/Li$_2$S structures are properly engineered, which is a very important message for all Li-S design strategies that avoid the polysulfide shuttling problem by utilizing SSC, but so far struggled to convert practical S amounts.
Methods

Materials

As cathode material we used a high-surface area carbon black (Ketjenblack, EC-600JD, ANR Technologies) with a BET area of 1400 m$^2$g$^{-1}$. The free-standing film electrodes were prepared by mixing carbon with polytetrafluoroethylene (PTFE, 60 mass% suspension in water, Aldrich) at 90/10 mass ratio with isopropanol.

The resulting dough-like material was rolled to a 50-70 µm thick film, washed in acetone/H$_2$O mixture and finally dried at 120 °C under vacuum overnight. As catholyte we used a solution of 0.5 M Li$_2$S$_8$ + 1 M lithium bis(trifluoromethane)sulfonimide (LiTFSI) + 0.4 M lithium nitrate (LiNO$_3$) in diethylene glycol dimethyl ether (2G).

In Supplementary Fig. 1 we show in situ SAXS/WAXS data using a sulphur infiltrated carbon black cathode (ENSACO 350G/S) with a solution of 1 M LiTFSI + 0.1 M LiNO$_3$ in 1:1 (v:v) 1,3-dioxolan (DOL) + tetraethylene glycol dimethyl ether (TEGDME) as electrolyte. The ENSACO 350G carbon (Imerys) / sulphur composite was prepared in a C:S = 1:2 mass ratio by melt infiltration under Ar atmosphere at 155 °C. The electrode was prepared by adding Printex (Degussa) conductivity additive and PVdF binder to the C/S composite in a mass ratio of 1:1:8. All solvents were used as received and dried under freshly activated Molecular Sieves (type 4 Å). All salts were dried at elevated temperature (90 °C) and reduced pressure.

Lithium polysulfide powders were synthesized by mixing a stoichiometric amount of elemental sulphur (Sigma Aldrich) and lithium metal (FMC) in excess of dried THF (the THF was dried in a multistep process using Al$_2$O$_3$, molecular sieves, and distillation, after which the water content was measured by Karl Fischer titration (Mettler Toledo, C20) and kept below 2 ppm.). The synthesis procedure was conducted in an argon filled dry box with controlled levels of water and oxygen content (below 0.1 ppm). The mixture was stirred at slightly elevated temperatures (50 °C) until all the reactants dissolved. THF was then removed under reduced pressure to obtain dry polysulfide powders.

The solid 2 Li + S mixture was prepared by rolling fine sulphur powder (large S crystals crushed with mortar and pestle) onto a thin piece of Li metal on a glass plate in inert atmosphere. The Li and S mass correspond to a molar ratio of 2:1. After a short time of rolling the Li/S piece was turning brittle, indicating immediate Li$_2$S crystal formation.

Experimental

In situ SAXS/WAXS and XRD measurements were carried out with a commercial electrochemical in situ scattering cell (BatterycellSAXS, Anton Paar, Austria). We used polytetrafluoroethylene (PTFE) X-ray windows due to their chemical stability and relatively low background in the SAXS regime. The small diameter of the windows (2 mm) ensures a relatively equal pressure distribution across the cell assembly. It consisted of a Li metal anode, a Celgard separator, a Freudenberg (FS 2125) separator, a carbon black cathode, and an Aluminium grid current collector. The X-ray beam irradiates all cell materials; reversible and significant structural changes are only detected in the cathode. A Biologic SP240potentiostat/galvanostat was used for electrochemical cycling.

In situ SAXS/WAXS measurements were carried out on the Austrian SAXS beamline at the Synchrotron ELETTRA® (Trieste, Italy) using an X-ray wavelength of 0.154 nm and a Pilatus 1M SAXS and Pilatus 100K WAXS detector (Dectris, Switzerland). During potentiostatic discharge / charge measurements, SAXS and WAXS patterns were collected with 1 s exposure time (to avoid radiation damage) and 60 s period (to avoid huge amounts of data). We discharged the cell at 2.0 V vs. Li/Li$^+$ for 2.5 hours (giving a capacity of 1520 mAh g$^{-1}$) and charged it at 2.45 V vs. Li/Li$^+$ for maximum 2.5 hours (to reverse the capacity of 1520 mAh g$^{-1}$). In situ SAXS data shown in Supplementary Fig. 1 were recorded on a laboratory SAXS/WAXS instrument (SAXSpoint 2.0, Anton Paar, Austria) with an EIGER2 R 1M area detector (Dectris, Switzerland) and a time resolution of XX min. All recorded SAXS patterns were azimuthally averaged and normalized by transmission values. The SAXS background intensity was recorded separately for each cell after removing the cathode. The averaged and normalized background intensity was then subtracted from all recorded in situ SAXS
curves. The azimuthally averaged 2D in situ WAXS data were corrected by subtracting the WAXS intensity prior to discharge (at OCV).

Scanning Electron Microscopy (SEM) images were collected with a Hitachi SU-8200 at 5.0 kV acceleration voltage using a secondary electron detector. Ex situ XRD (and SAXS) measurements (Fig. 3b, Fig. 5, Supplementary Figs. 2, 4) were carried out on a Rigaku SmartLab 9 kW System, with rotating Cu anode and 2D solid state detector (HyPix-3000 SL).

In situ SAXS data modelling via plurigaussian random fields

The SAXS intensity of the discharged cathode can be split into three terms,

\[ I(q) = I_{Li_2S,Li_2S_4}(q) + I_c(q) + BG. \] (3)

The first term \( I_{Li_2S,Li_2S_4}(q) \) corresponds to the scattering contribution of the \( Li_2S / Li_2S_4 \) structure, the second term \( I_c(q) \) to the scattering contribution of the electrolyte-filled carbon structure and the third background term to the constant (low-\( q \)) intensity of electrolyte (and carbon) atomic structure factor. Correlations between carbon black and the \( Li_2S / Li_2S_4 \) structure are neglected (see discussion in Supplementary Note 1 and Supplementary Fig. 5).

To separate the SAXS intensity of the \( Li_2S / Li_2S_4 \) structure we subtract \( I_c(q) \), i.e., the SAXS intensity measured prior to discharge at OCV. Further, we subtract the electrolyte (and carbon) structure factor background \( BG \) by a Porod background subtraction in a \( q \)-range from 3–5 nm\(^{-1}\).

The SAXS intensity of the \( Li_2S / Li_2S_4 \) nanostructure (Fig. 4a) can be written as

\[ I_{Li_2S,Li_2S_4}(q) = K (V/V_{max}) [A q^{-4} + I_{PGRF}(q)] , \] (4)

with \( K \) being a constant that depends on instrumental parameters, such as detector efficiency and irradiated sample volume, and \( V/V_{max} \) the relative volume of the deposited \( Li_2S / Li_2S_4 \) nanostructure. The first power law term stems from the large \( Li_2S (Li_2S_4) \) agglomerates beyond 100 nm (see SEM images in Fig. 1c. Given their large expansion, the SAXS intensity in the measured \( q \) range is proportional to \( q^{-4} \) (Porod decay). The second term accounts for the \( Li_2S / Li_2S_4 \) nanostructure in the size regime between 1 to 50 nm and is modelled via plurigaussian random fields, as described further below. The least square error sum is minimized by particle swarm optimization with reasonable parameter constraints. Deviations between model fit (blue curve in Fig. 4a) and experimental data (black curve in Fig. 4a) can explained by carbon black – \( Li_2S/Li_2S_4 \) correlations. \( Li_2S / Li_2S_4 \) nanostructures deposited on a planar Glassy carbon substrate with negligible cross correlations show an improved fit quality (Supplementary Fig. 5).

Time-dependent SAXS intensity change during discharge and charge are modelled by using the fit parameters of the model fit to the fully discharged electrode in Fig. 4a (Table S1) as a starting point. All input parameters for the modelled in situ SAXS data are given in Supplementary Note 2.

We model the reduced in situ SAXS data \( I_{PGRF}(q) \) using the concept of plurigaussian random fields (PGRF). This allows retrieving 3D real space models of the solid \( Li_2S / Li_2S_4 \) nanostructure during discharge and charge (Fig. 4). A detailed theoretical description of the PGRF method is given by Gommes et al.

The SAXS intensity \( I_{PGRF}(q) \) is the Fourier transform of the electron density correlation function \( C(r) \)

\[ I_{PGRF}(q) = \int_0^\infty C(r) \frac{\sin(qr)}{qr} 4\pi r^2 dr . \] (5)

\( C(r) \) for our three-phase system consisting of phases \( Li_2S, Li_2S_4, \) Electrolyte (EL) can be written as
Here, $\rho_i$ is the electron density, $\phi_i$ the volume fraction and $P_i(r)$ the two-point correlation function of phase $i$. Using clipped Gaussian random fields, a 3D model of a two-phase nanopore structure can be generated from a fit to the structure’s experimental SAXS intensity. Plurigaussian random fields use a second Gaussian random field to model SAXS intensities and 3D real space structures of disordered three-phase systems. A Gaussian random field $P_i$ is the sum of cosine waves with wave vector lengths distributed according to their power spectral density $f_i(k)$ and phase factors $\varphi_i$ randomly distributed between 0 and $2\pi$.

A suitable analytic two-point correlation function of the GRF is

$$g_\gamma(r) = \frac{1}{\cosh(r/l_\gamma)} \cdot \frac{\sin(2\pi r/d_\gamma)}{(2\pi r/d_\gamma)}, \quad (8)$$

where $l_\gamma$ is a correlation parameter related to the mean size of the structure and $d_\gamma$ a parameter accounting for ordering effects via the second oscillation term. Equation 7 translates into the following analytic expression for the power spectral density:

$$f_\gamma(k) = \frac{k}{\pi} l_\gamma d_\gamma \frac{\sinh(\pi kl_\gamma/2) \sinh(\pi^2 l_\gamma/d_\gamma)}{\cosh(\pi kl_\gamma) + \cosh(2\pi^2 l_\gamma/d_\gamma)}. \quad (9)$$

To generate a two-phase porous structure from the GRF, we define the threshold values $g$ for the Gaussian distributed $Y(x)$ values. All spatial coordinates $x$ with $\alpha < Y(x) \leq \infty$ are assigned to the pore space (i.e. phase Li$_2$S$_4$ + EL); all other coordinates to the Li$_2$S skeleton. The two threshold values are related to the Li$_2$S volume fraction $\phi_{Li_2S}$ via:

$$\phi_{Li_2S} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp \left( -\frac{t^2}{2} \right) dt. \quad (10)$$

To model SAXS intensities and real space structures of the three phase system, we generate a second independent GRF $Z(x)$ using the same correlation function (Equation 8-9) with different input parameters $l_z$ and $d_z$ (Supplementary Fig. 8c). The Li$_2$S$_4$ phase with the volume fraction $\phi_{Li_2S_4}$ is generated by cutting $Z(x)$ and $Y(x)$ according to Equation 11 and the cut-offs visualized in Supplementary Fig. 8.

$$\phi_{Li_2S_4} = \iint_{(Y,Z) \in \partial_{Li_2S_4}} \frac{1}{2\pi} \exp \left( -\frac{(Y^2 + Z^2)}{2} \right) dY \, dZ. \quad (11)$$

The two-point correlation functions of the phase Li$_2$S$_4$ (equivalent for Li$_2$S) are calculated via

$$P_{Li_2S_4Li_2S_4} = \int_{\partial_{Li_2S_4}} dY_1 dZ_1 \int_{\partial_{Li_2S_4}} dY_2 dZ_2 g_{\gamma(Y_1,Y_2)} g_{\beta(Z_1,Z_2)}. \quad (12)$$
with \( G_g(Y_1,Y_2) \) being the bivariate Gaussian distribution with mean 0, variance 1, and covariance \( G \). Their calculation via Hermite polynomials is described in Ref. 44. Depending on the angle \( \delta \) and the Li\( \text{S}/\text{EL} \) boundary line in Supplementary Fig. 8d-f, the morphology of the Li\( \text{S}_4 \) phase will be different. The Li\( \text{S}_4 \) phase will perfectly cover/wet the Li\( \text{S} \) phase in form of a thin film if \( \delta \to 0 \) (Supplementary Fig. 8d,g). In contrast, for an Li\( \text{S}/\text{EL} \) boundary parallel to the Y-axis (\( \delta \to \pi/2 \)) the Li\( \text{S}_4 \) (EL) structure inside the Li\( \text{S} \) cavities is statistically independent from the Li\( \text{S} \) structure (Supplementary Fig. 8f,i). Inserting Equation 12 into Equation 5-6 gives the corresponding scattering intensities (Fig. 4).

The modelled relative SAXS intensity change (Fig. 4e) is obtained by calculating \( l_{\text{Li2S,Li2S4}}(q) \) via Equation 4 using the fit parameters shown in Supplementary Fig. 10 and adding \( I_c(q) + BG \) (i.e. the experimental SAXS intensity at OCV). Finally, the generated SAXS intensities are normalized by the modeled SAXS intensity at \( t = 0 \), prior to discharge.

The pair distance distribution functions \( p_{XX}(r) \) of phase \( X \) in Fig. 4g, h are calculated by normalizing the two-point correlation function \( P_{XX}(r) \) (Equation 13).

\[
p_{XX}(r) = r^2 \frac{[P_{XX}(r) - P_{XX}(r \to \infty)]}{[P_{XX}(r = 0) - P_{XX}(r \to \infty)]}
\]

The correlation lengths of Li\( \text{S} \) and Li\( \text{S}_4 \) structures are arbitrarily taken as the distance where the normalized correlation function \( [P_{XX}(r) - P_{XX}(r \to \infty)]/[P_{XX}(r = 0) - P_{XX}(r \to \infty)] \) has decayed to a value of 0.2 (see Supplementary Fig. 6).
Data availability

The data that support the findings of this study are available from the corresponding authors on request.

Code availability

The codes used for in situ SAXS data analysis and stochastic modelling are available from the corresponding author C.P. on request.
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Acknowledgements

This project has received funding from the European Union’s Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant NanoEvolution, grant agreement No 894042. The authors acknowledge TU Graz for support through the Lead Project LP-03. Likewise, the use of SOMAPP Lab, a core facility supported by the Austrian Federal Ministry of Education, Science and Research, the Graz University of Technology, the University of Graz, and Anton Paar GmbH is acknowledged. S.D.T, A.V. and R.D. acknowledge the financial support by the Slovenian Research Agency (ARRS) research core funding P2-0393. Furthermore, A.V. acknowledge the funding from the Slovenian Research Agency, research project Z2-1863. S.A.F. is indebted to IST Austria for support.

Author Contributions

C.P. carried out in situ scattering, electrochemical and electron microscopy experiments, the corresponding data analysis and the stochastic modelling. S.D.T. and A.V. provided carbon/sulphur composites and polysulfide powders. C.P., S.A.F. and V.W. conceptualized the work. C.P. wrote the initial version of the manuscript. C.P., S.D.T., A.V., H.A., R.D, S.A.F. and V. W. contributed to results interpretation and revising the manuscript.

Competing Interests

The authors declare no competing interests.
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