Electronic Supplementary Information (ESI)

Direct visualization of sulfur cathodes: new insights into Li-S batteries via *operando* X-ray based methods

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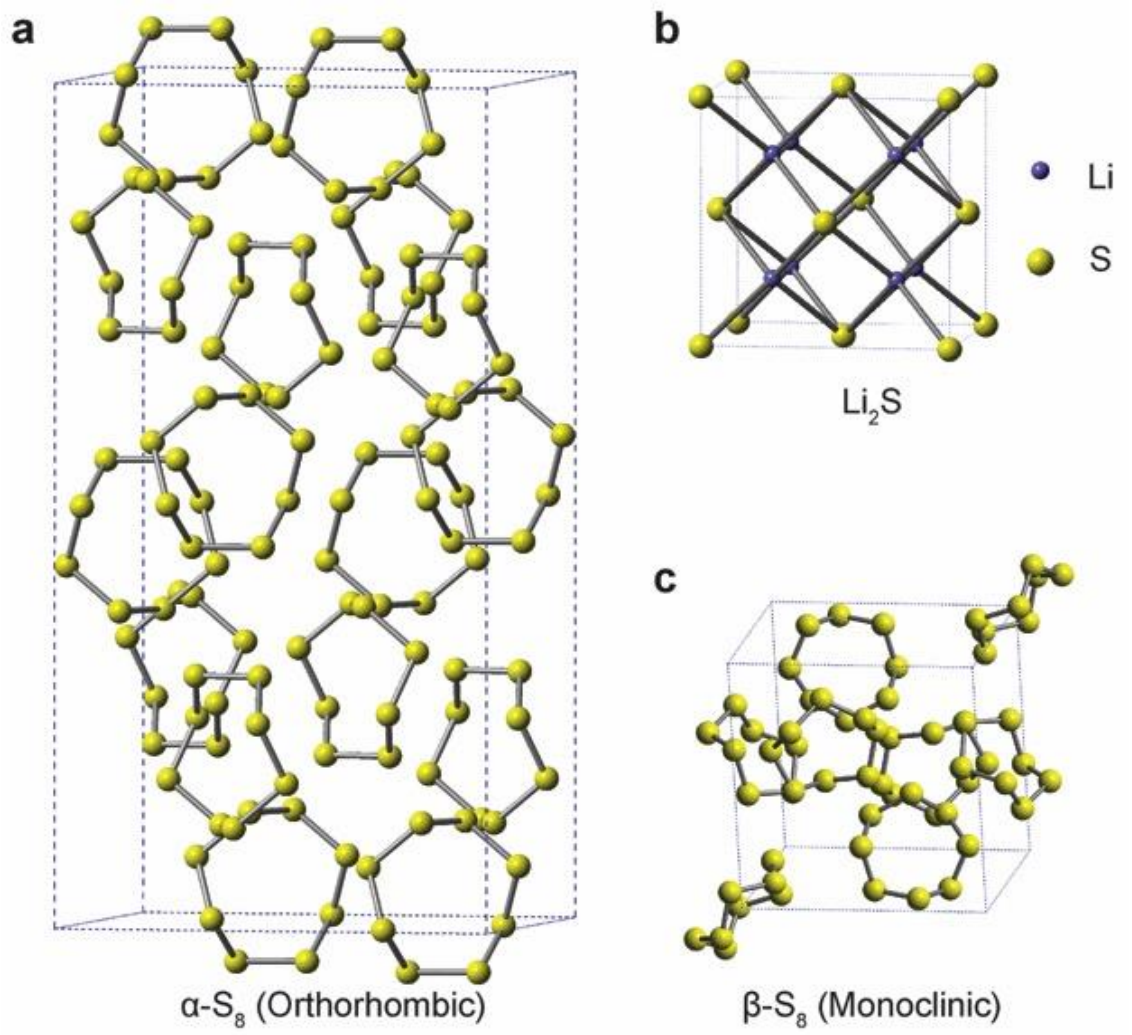

Fig. S1 Unit cell structure of (a) α-S_8, (b) Li_2S and (c) β-S_8.

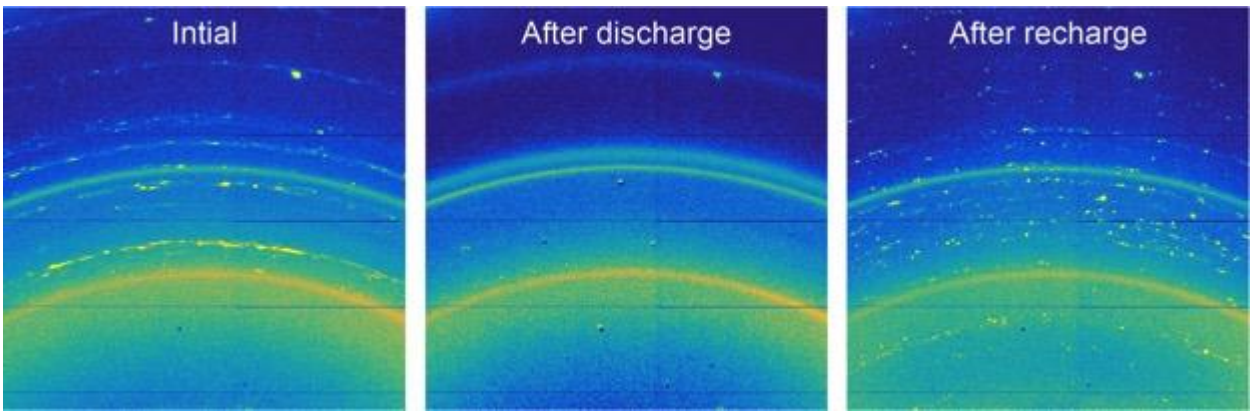

Fig. S2 Diffraction patterns of Li-S battery (a) before discharge, (b) when fully discharged and (c) when fully recharged.

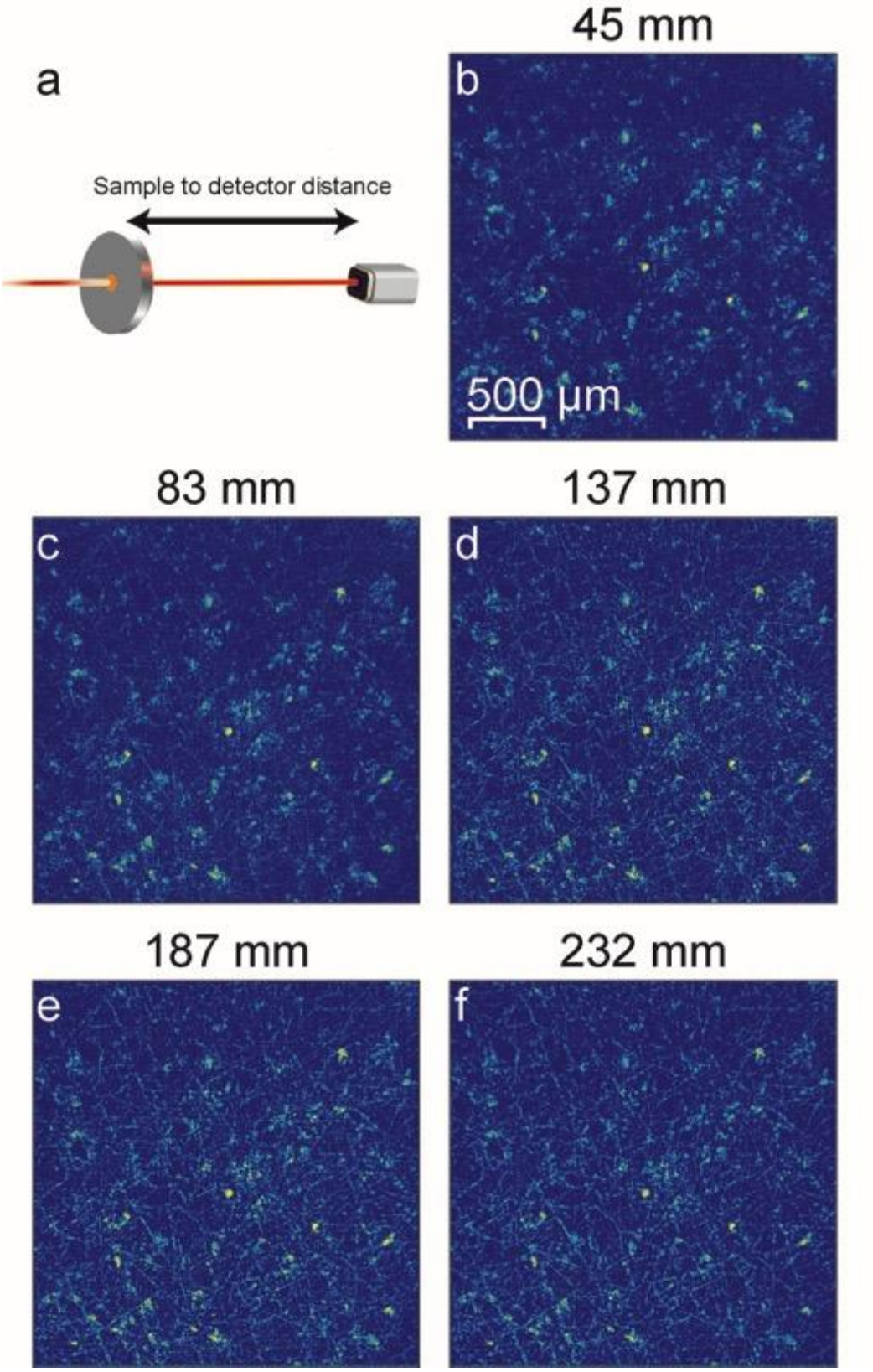

Fig. S3 X-ray microscopy of sulfur electrode at different distances between the sample and detector.

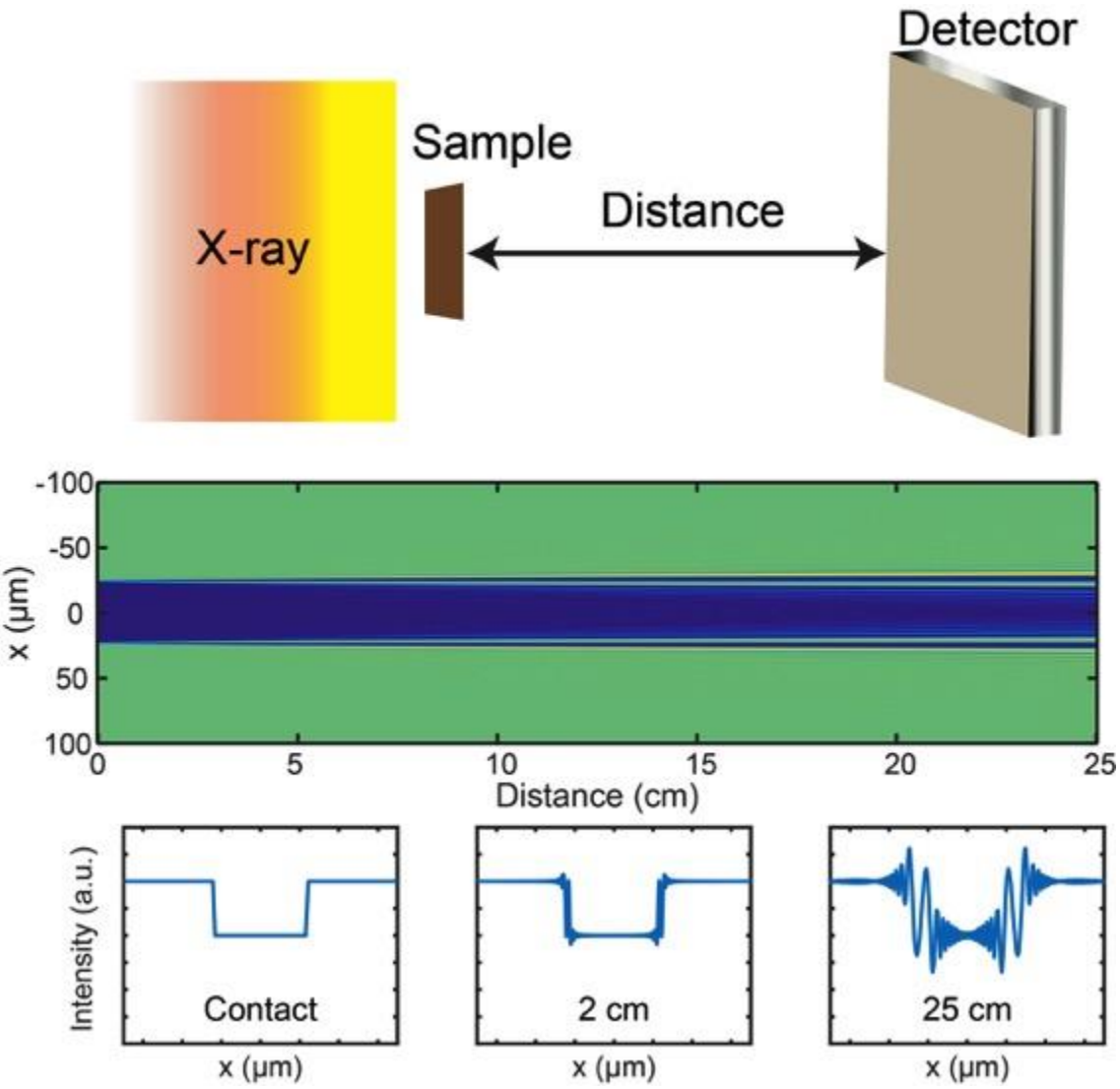

Fig. S4 Scheme for the phase enhancement in XRM and simulated X-ray intensity changing with the distance between sample and detector.

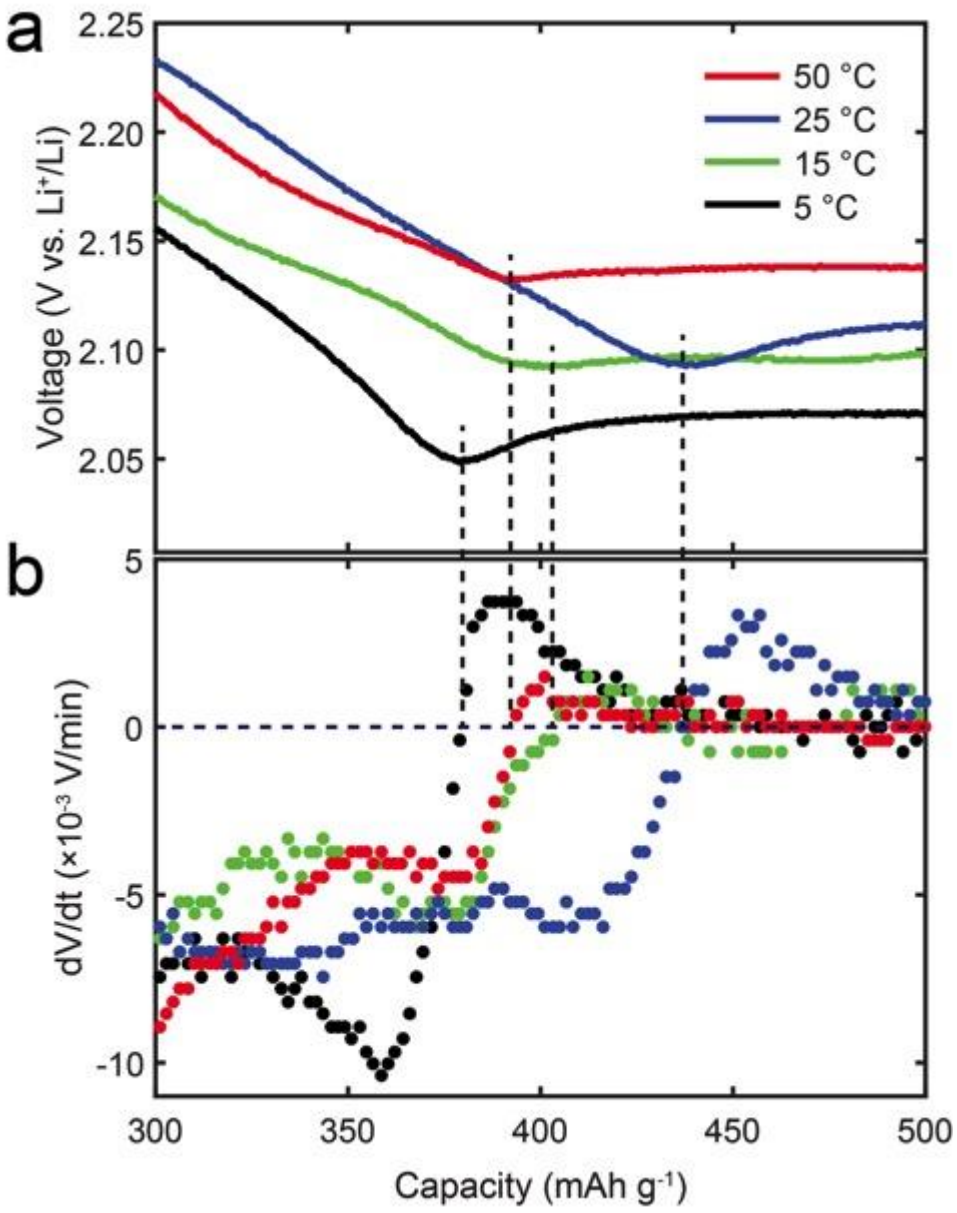

Fig. S5 (a) Voltage profiles around the end of the upper plateau and (b) their first derivatives at different temperatures.

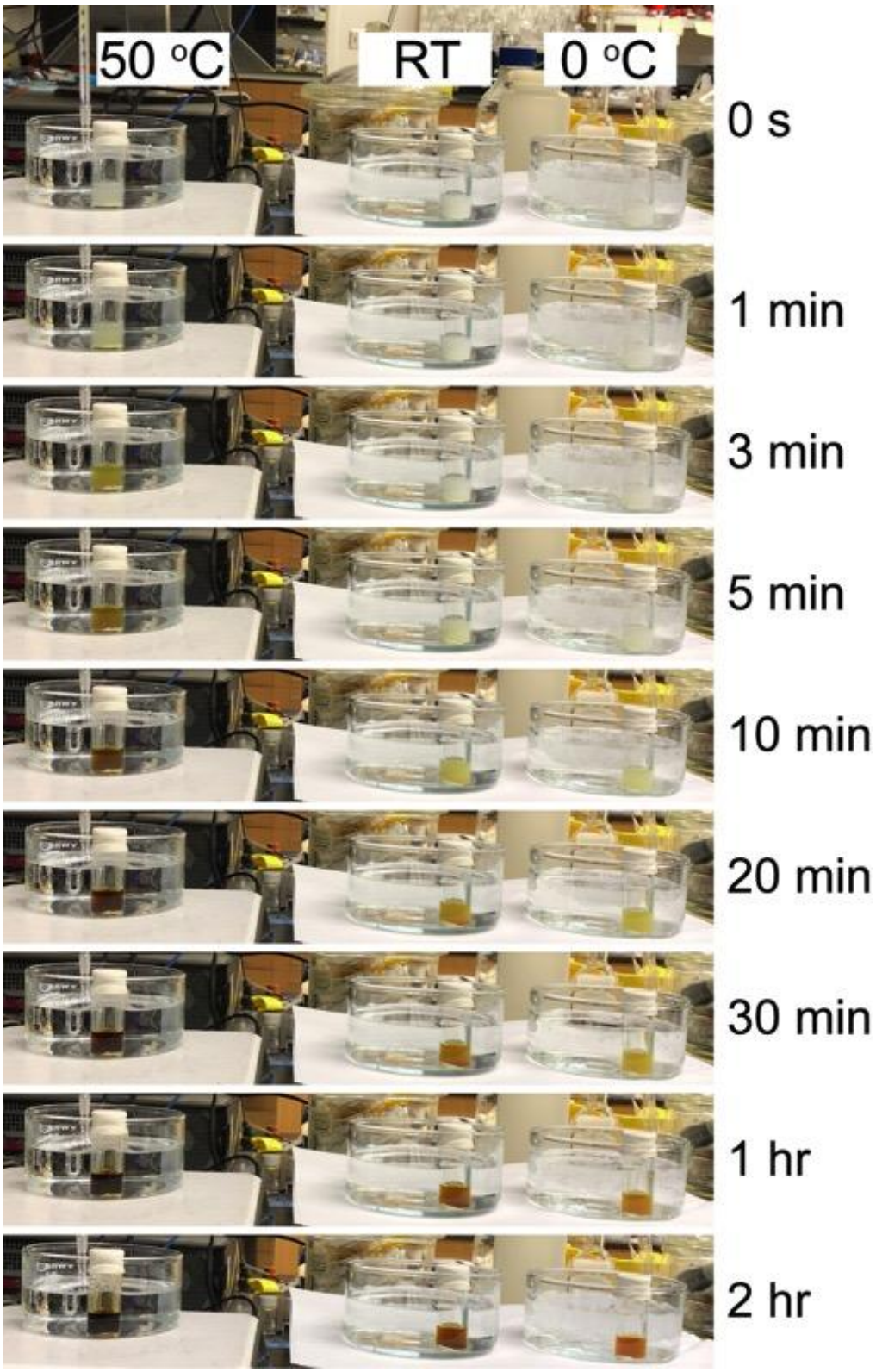

Fig. S6 Photographs of dissolution of polysulfide at different temperatures (50 °C, RT and 0 °C).

As shown in the enclosed photos (Fig. S6), we prepared three vials at different temperatures (50 °C, RT~25 °C, and 0 °C), having the same amount of homogeneously mixed S and Li_2S (7:1 in molar ratio). We then injected the same amount of electrolyte (which corresponded to 2 M if all of the material were completely dissolved) into the vials. When the electrolyte was injected into the S and Li_2S mixtures, the initial color was white (slightly yellowish) at all temperatures. The sample at 50 °C quickly changed in color, initially turning yellow (after 1 min), and then completely to red (after 10 min). Meanwhile, the other two samples (at RT and 0 °C) just turned yellow after 10 min. These experiments indicate that polysulfides dissolve faster at higher temperatures. In addition, considering that the temperature gaps between samples were equal (25°), but the color difference between 50 °C and RT was much more dramatic than that between RT and 0 °C, suggests that the effects of temperature on the dissolution of polysulfides is not linear; becoming much stronger at 50 °C. This, at least in part, explains why only the α-S_8 XRD peak at 50 °C decreased much faster than at the other temperatures.

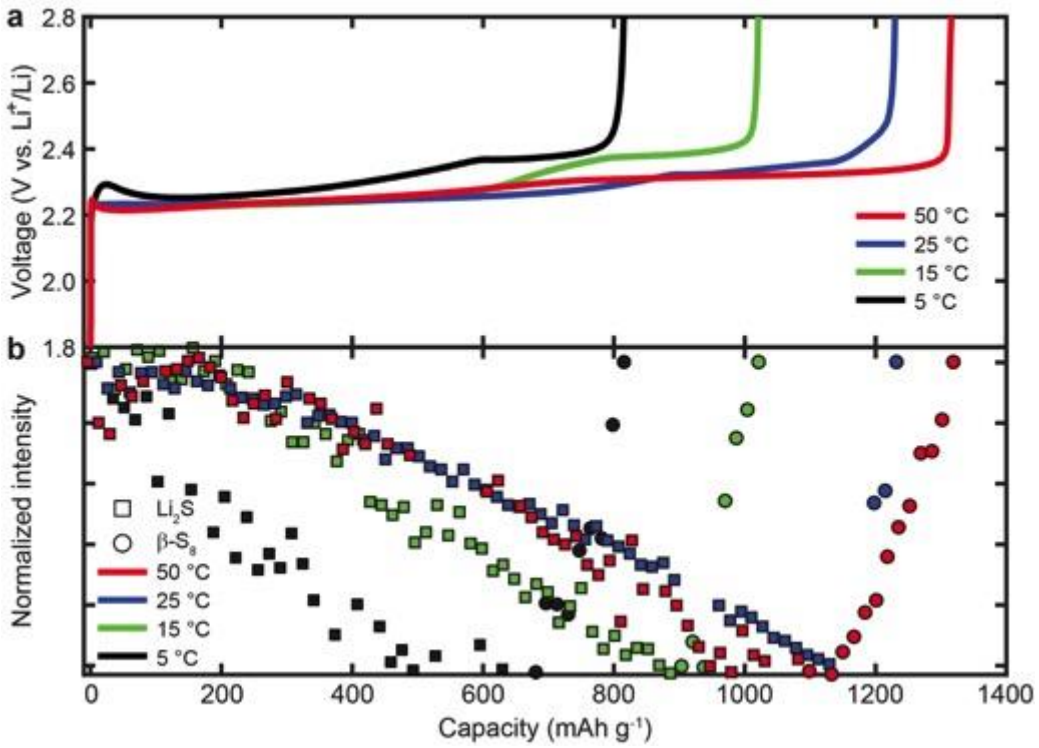

Fig. S7 Voltage profile and normalized intensity of X-ray diffraction from Li_2S and β-S_8 of sulfur electrodes at a rate of 0.2 C during charge at different temperatures.

Fig. S7 shows the voltage profile and the integrated intensity of X-ray diffraction of Li_2S and β-S_8 during the (re)charge. Independent of temperature, the β-S_8 is all formed around the end of the charge, even at 50 °C, and the intensity of β-S_8 increased linearly. Similar to the discharging process, the overpotential increased as the temperature decreased.

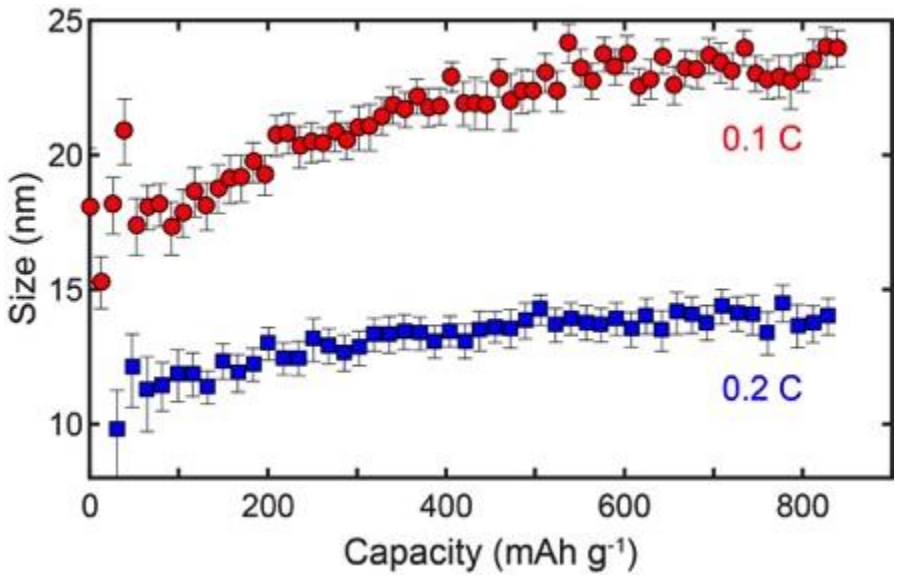

Fig. S8 Particle size of Li_2S calculated from the Li_2S (111) Bragg peak at 0.1 C and 0.2 C at 25 °C.

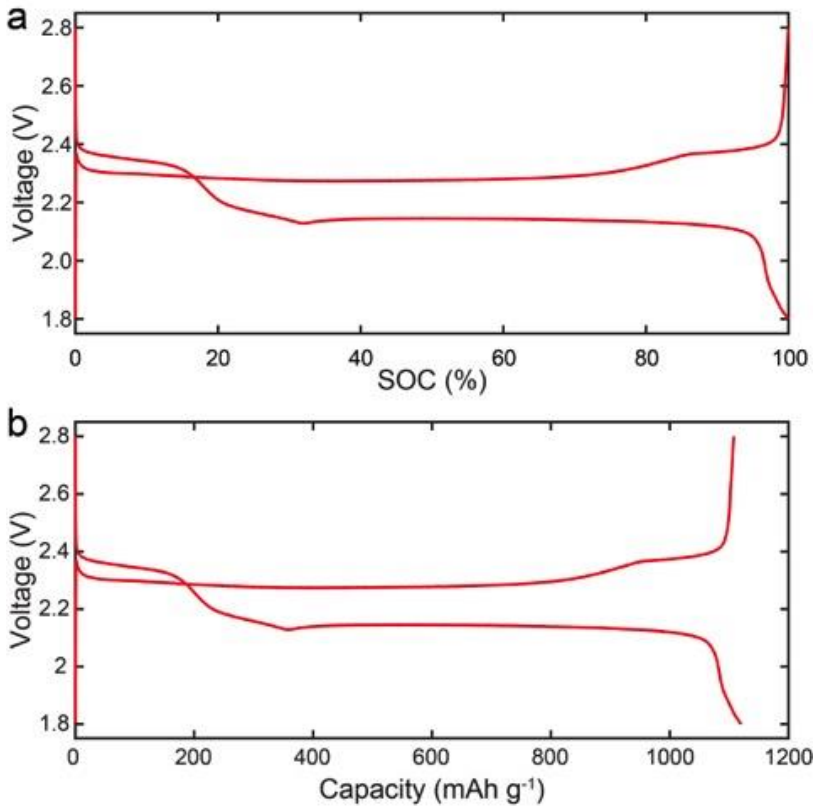

Fig. S9 Voltage profile of the sulfur cathode at the second cycle, as a function of (a) state of charge and (b) specific capacity.

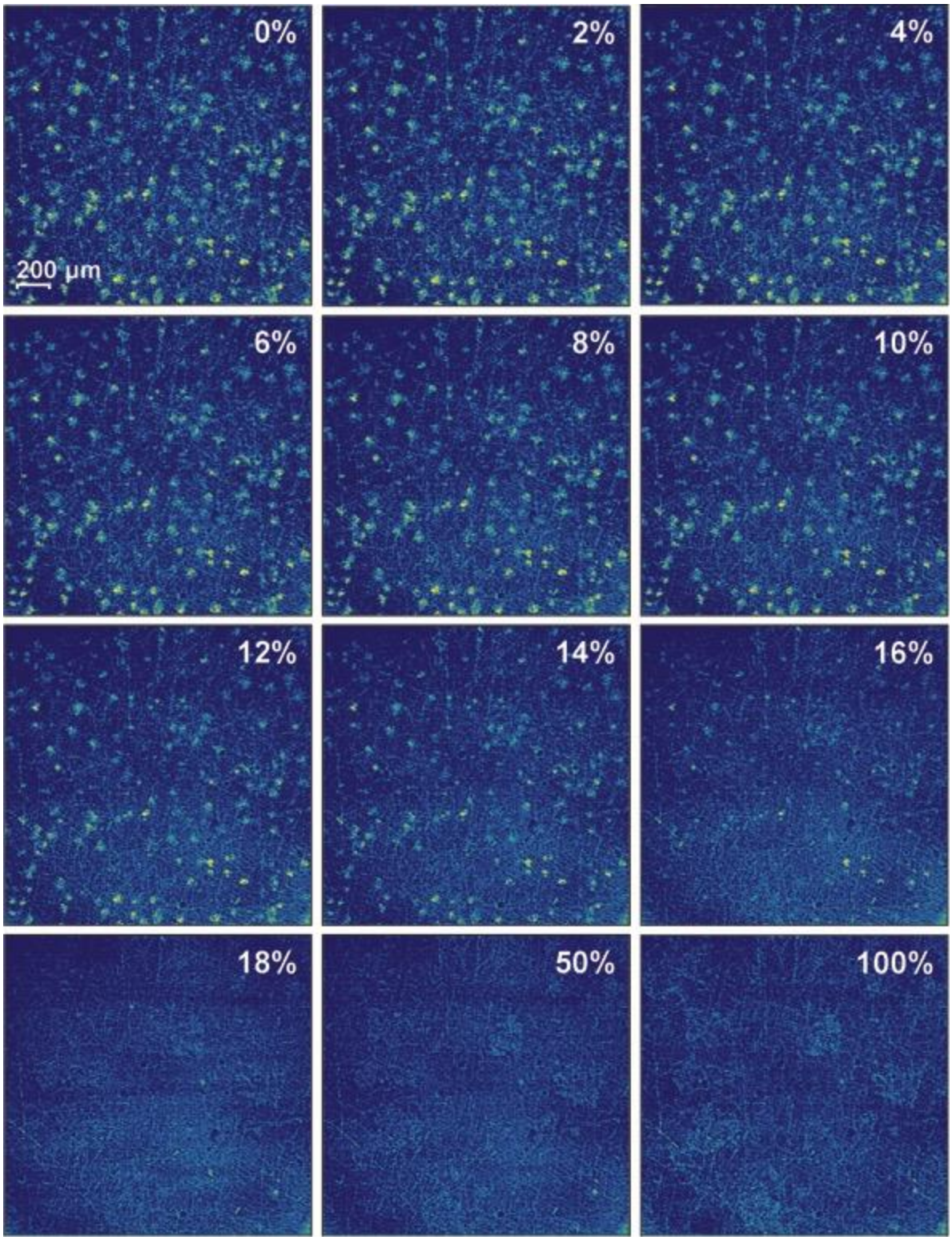

Fig. S10 *Operando* X-ray microscopy images of sulfur electrode at different DODs during the second discharge.

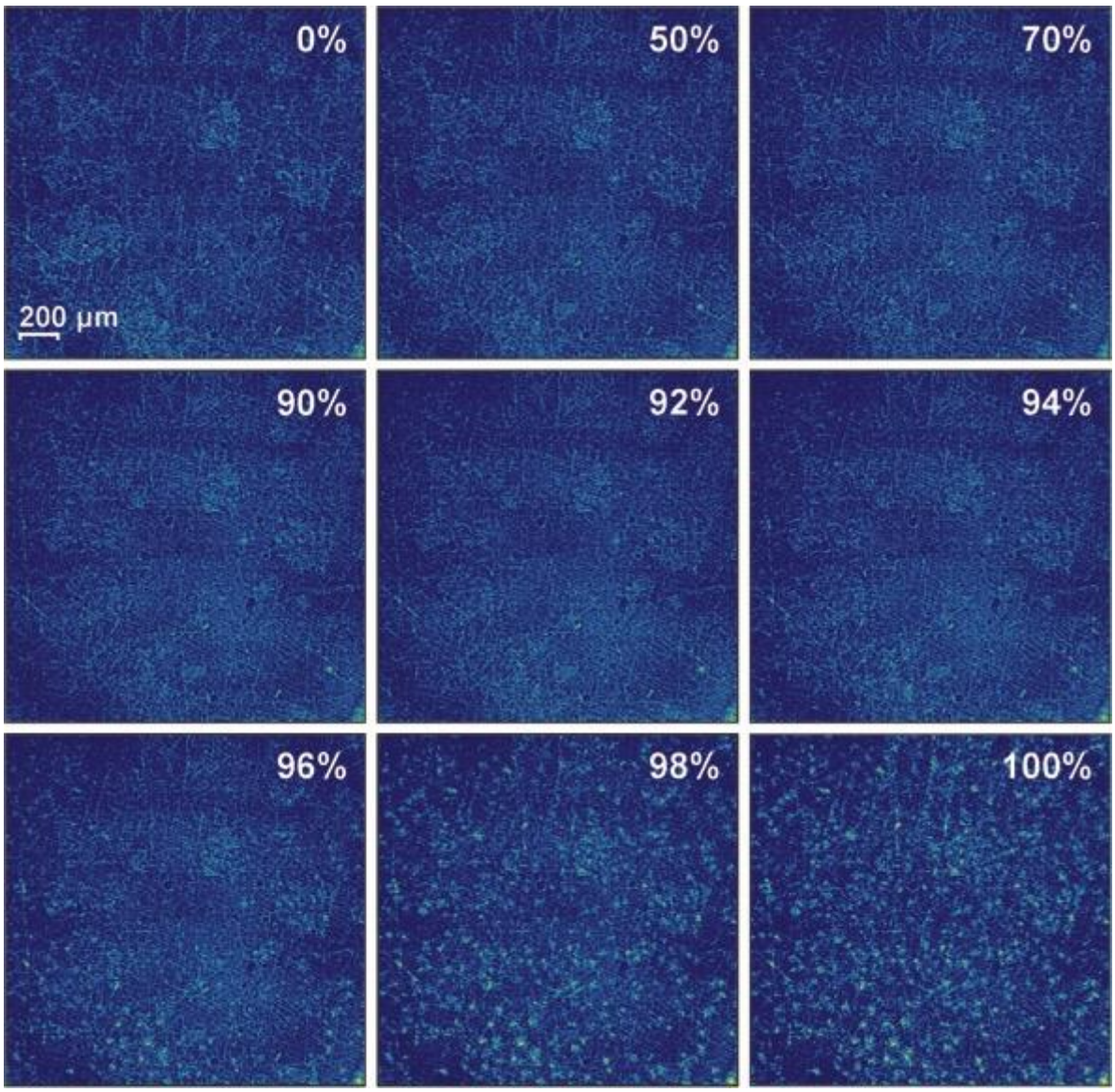

Fig. S11 *Operando* X-ray microscopy images of sulfur electrode at different DODs during the second charge.

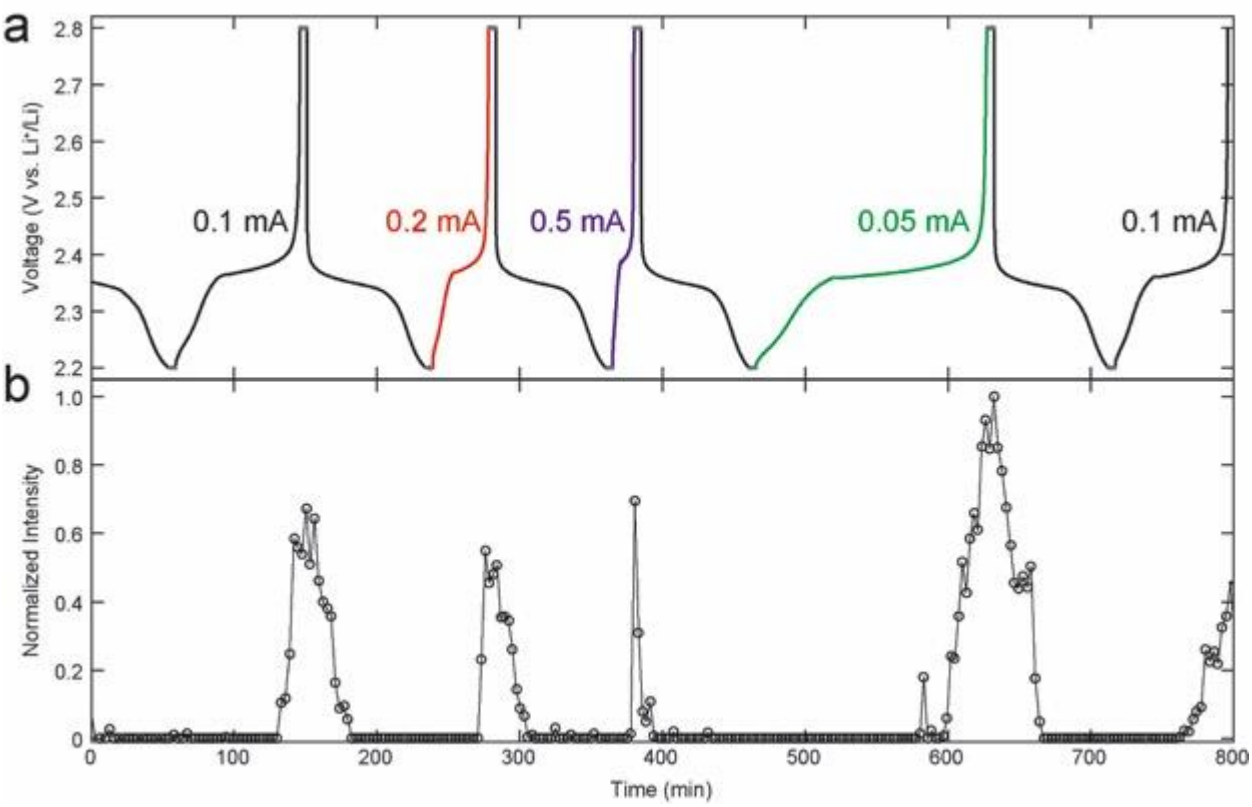

Fig. S12 (a) Voltage profile and (b) normalized intensity of X-ray diffraction of β-S_8 in a lithium/polysulfide battery. The discharge rate was fixed at 0.1 mA, and charging rates were varied from 0.05 to 0.5 mA.

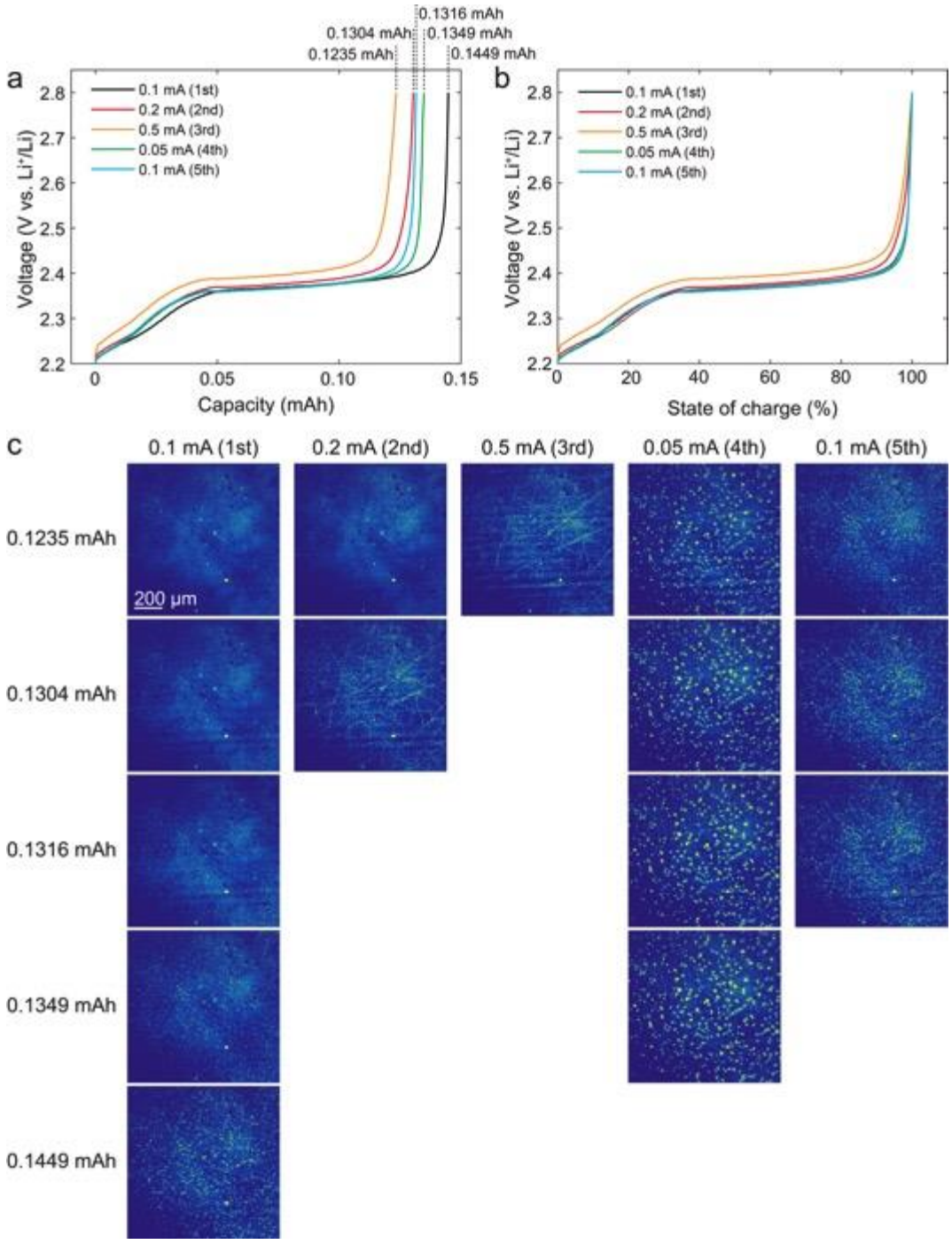

Fig. S13 (a) Voltage versus capacity, (b) voltage versus SOC and (c) the XRM images of cathode of a lithium/polysulfide battery at different capacity.

	Initial	After 1st cycle	After 2nd cycle
<100 μm²	42.3%	43.6%	62.2%
100 - 1000 μm²	49.5%	52.5%	37.4%
> 1000 μm²	8.2%	3.9%	0.4%

Table S1 Percentage of sulfur cluster area for the before cycle and after the 1st cycle and after 2nd cycle.