

Electronic Supplementary Information

New insight into working mechanism of Lithium/Sulfur batteries: *in situ* and *operando* X-ray diffraction characterization

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Experimental details

Positive electrode preparation

Bare sulfur (refined, -100 mesh, Aldrich) and carbon black (SuperP[®], Timcal) were manually grinded together in the mortar, with small volume of cyclohexane. After solvent evaporation, the resulting composite material was mixed with poly(vinylidene fluoride) (PVdF 6020, Solvay) solution in *N*-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%, Aldrich). The S/C/binder ratio was 80/10/10 wt%. Additional NMP was added to obtain homogenous mixture. Such prepared slurry was coated onto current collector (210 μm thick, porous nonwoven carbon sheet H2315, Freudenberg FCCT KG) by doctor blade technique. The choice of this collector was followed by two reasons: (i) due to high conductive surface area available for deposition of Li₂S – end of discharge can be prolonged which results in higher discharge capacity, (ii) signal of carbon does not contribute that much to the XRD pattern as in case of Al foil collector. The resulting electrode was dried at 55°C in air atmosphere during 48h. Rectangular cathodes of 35 × 18 mm were cut and dried under vacuum at room temperature. Aluminum stripe (60 × 5 mm) was stuck as current collector tab. The coated cathode active layer thickness was about 70 μm. However, due to the three-dimensional structure and high thickness of NwC sheet, some electrode slurry could have been deposited inside the porous collector layer, resulting in rather high sulfur loading of ~ 4.66 mg cm⁻².

Parallel to that, another electrode was made on Al current collector (the same way of slurry preparation) with lower sulfur loading (~ 1.7 mg cm⁻²). After drying at 55°C in air atmosphere for 48h, the electrode was cut into Ø14 mm disks and dried under vacuum for 24h at room temperature.

Pouch cell preparation

The pouch cell was composed of sulfur positive electrode casted on NwC, lithium foil as negative electrode, two layers of porous separator (Celgard[®] 2400 and Viledon[®]) soaked in liquid organic electrolyte: 1 mol L⁻¹ lithium bis(trifluoromethane) sulfonimide (LiTFSI, Rhodia) in a 1:1 volume mixture of tetraethylene glycol dimethylether (TEGDME, 99%, Aldrich) and 1,3-dioxolane (DIOX, anhydrous, 99.8%, Aldrich), with addition of 0.1 mol L⁻¹ lithium nitrate (LiNO₃, 99.99%, Aldrich). In order to eliminate the signal from aluminum-laminated pouches, three holes were cut (Ø 3 mm) and

Kapton[®] tape was stuck from both sides. To avoid any air penetration through Kapton[®] layer, the cell was tightly sealed in polyethylene bag. Each electrode had hole (Ø 3 mm), so that we could have the response from both positive and negative electrodes separately (Fig. 1). Viledon[®] was used as an additional layer of separator, which served as reservoir for sufficient amount of electrolyte in the cell. Due to the broad and strong XRD signal of Viledon[®], it had holes in exact positions as packaging foil, not to shield the eventual peaks of crystalline Li₂S and sulfur appearing during cycling. To maintain good electrical contact inside the prototype, a moderate pressure was applied by two parallel plastic plates (with three holes, Ø 3 mm) pinned to the cell with metal clips. The pouch cells were assembled in dry room (-40° dew point) and activated with electrolyte in argon-filled glove box (H₂O, O₂ < 0.1 ppm). During *in situ* XRD measurements the pouch cell was mounted on movable sample holder which allowed us to change the position of the prototype and scan it in three desired points.

Ex situ samples preparation

Sulfur electrodes (Ø 14 mm disks) casted on two different current collectors (Al and NwC) were assembled in argon-filled glove box into CR 2032 coin cells. Lithium metal foil (Ø 16 mm) was used as negative electrode. Celgard[®] 2400 and Viledon[®] separators (Ø 16.5 mm) were soaked in liquid organic electrolyte (the same electrolyte as in pouch cell). Galvanostatic cycling tests (1.5 V – 3.0V at C/20) were carried out on Arbin battery cycler. Only one cycle was performed and charged sulfur electrodes were recuperated inside the glove box. To minimize the effect of artifacts, the electrodes were gently rinsed with 1,3-dioxolane without further drying. Such prepared samples were placed on XRD sample holder and thin Kapton[®] foil was used to avoid any contact with air during data recording.

Electrochemical tests and XRD analysis

Electrochemical charge-discharge test in voltage range 1.5V – 3.0V was carried out using VMP Biologic at the current rate C/20 (~ 85 mA g⁻¹). *In situ* XRD measurements were recorded at the CRISTAL beamline in French national synchrotron facility (SOLEIL) at a wavelength of 0.66785Å. Diffraction intensities were recorded every 3 min (recording time: 1 min, reading the image and changing the sample position: 2 min) by a MAR345 detector. 1D diffractograms were obtained by processing with fit2D software.

Ex situ diffraction patterns were recorded on a Brüker D8 advance in θ - θ configuration and with a Cu anticathode.

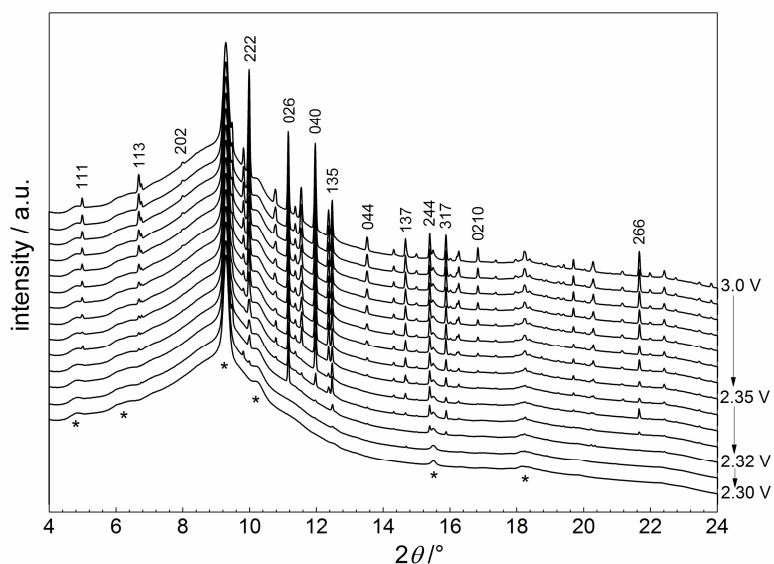


Fig. S1. *In situ* XRD patterns evolution (zoomed image) indicating disappearance of solid sulfur during initial discharge. Peaks attribution according to orthorhombic α -Sulfur, PDF-2 no. 00-008-0247. * marks peaks coming from packaging.

The moment of complete disappearance of sulfur was chosen when some peaks (for example: (222), (026), (040), (135), (317)) disappeared as the last ones. However, for few reflections (for example: (111), (202), (0210)) more abrupt decrease was observed. This is related with the fact that only small number of particles participates in the signal (limited by the beam size – 300 x 300 μm). Some particles, having the same orientation, might get reduced before the others thus accelerating the peaks disappearance.

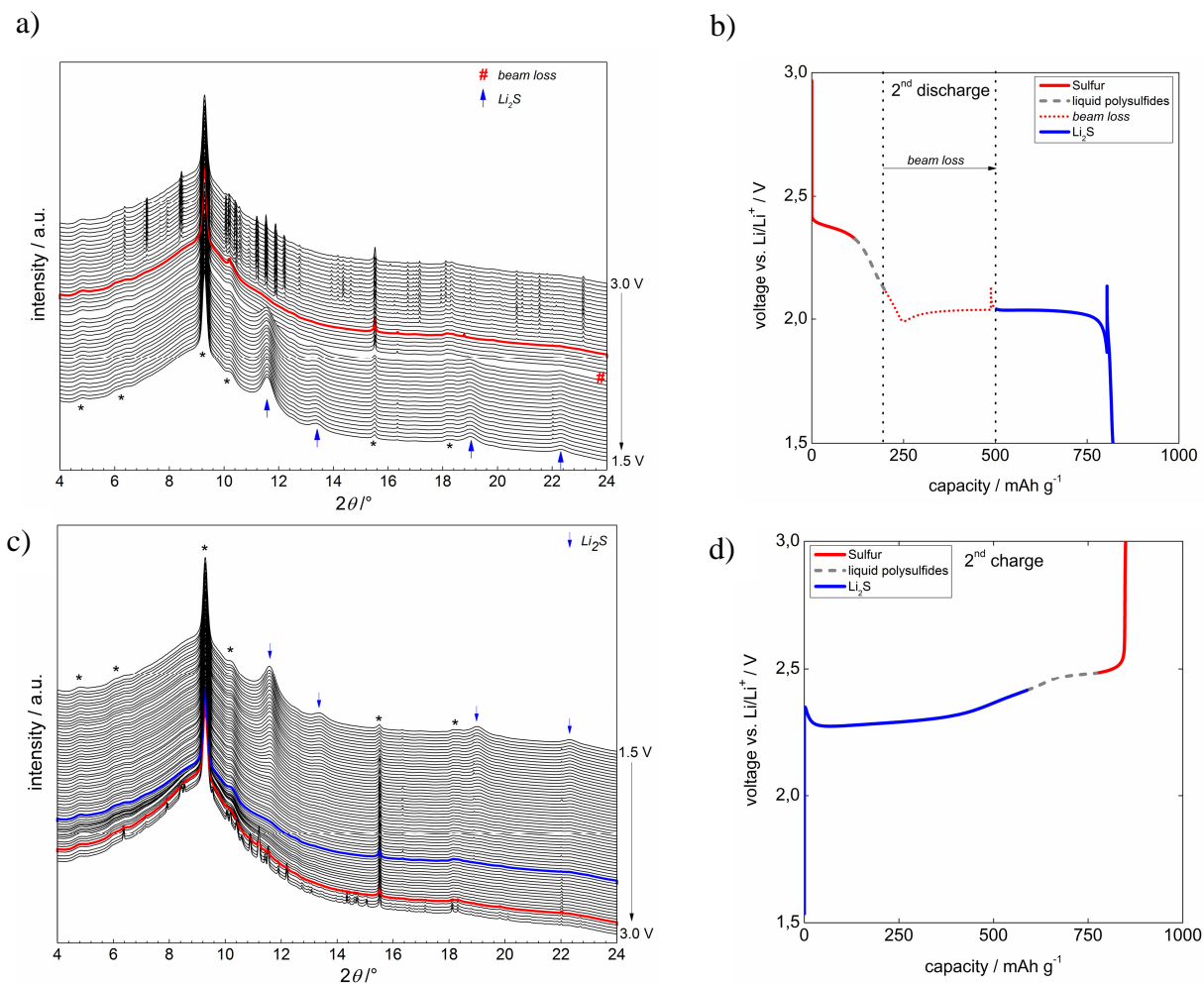


Fig. S2. *In situ* XRD peaks evolution and corresponding electrochemical curve recorded during 2nd cycle: discharge (a, b); charge (c, d). Peaks related with packaging are marked by *. Due to the beam loss, the moment of Li_2S phase appearance was missed.

Due to the beam loss we cannot observe directly when the nucleation of Li_2S begins. However, we can compare the intensity of Li_2S signal at the end of the beam loss and the intensity of the signal after the same amount of charge is passed on the lower plateau during first discharge. During second discharge, the 2V plateau starts at 245 mAh/g and the first diffractogram is taken when 487 mAh/g are passed. As this plateau begins at 318 mAh/g in the first discharge, we compare the first diffractogram after beam loss with the one obtained at 560 mAh/g (318+(487-245)) during first discharge. This is what is shown in the following figure (Fig. S3).

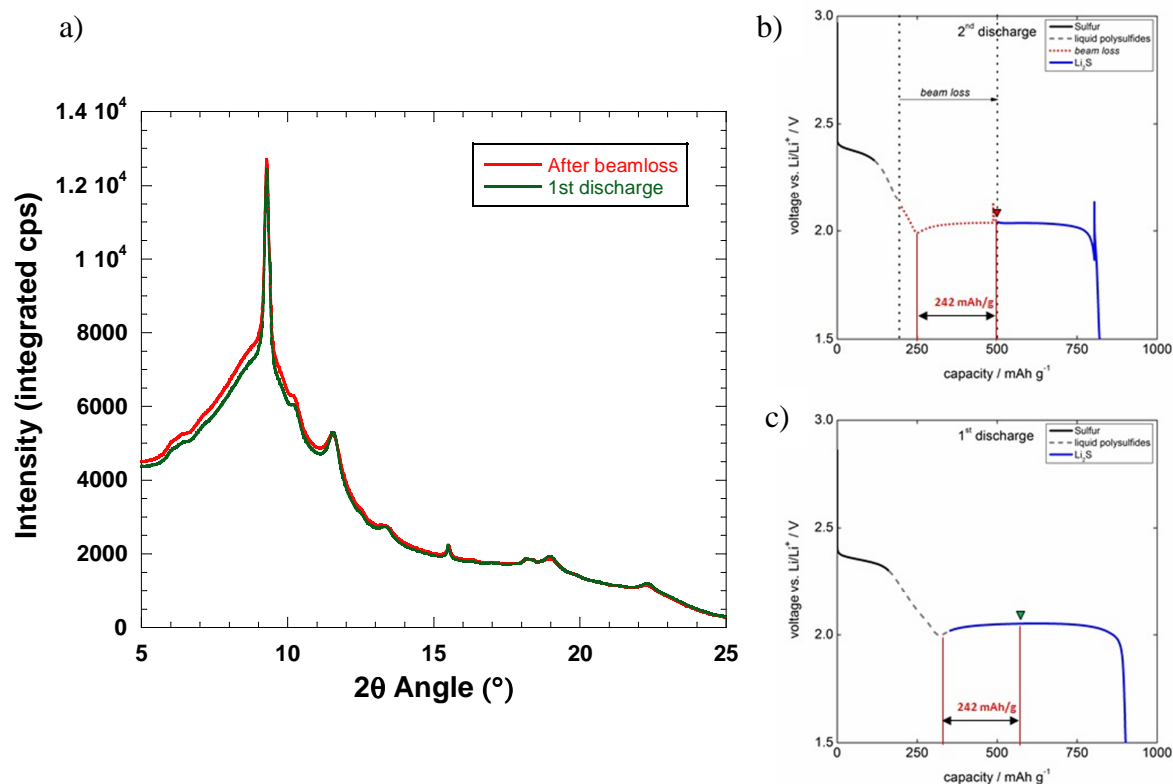


Fig. S3. Comparison of XRD patterns (a) obtained during 1st and 2nd discharge at the moment when the same amount of charge is passed, starting from the beginning of lower discharge plateau (b, c). Red and green triangles mark the points on discharge curves (b, c) at which recorded XRD patterns were compared.

The intensities of Li₂S signal (peaks at $2\theta = 11.6^\circ, 13.4^\circ, 19.0^\circ, 22.3^\circ$) in both diffractograms are very similar, meaning that the amounts of Li₂S formed at this point of the plateau are very close. This tends to indicate that the nucleation process should have started around the same time point, which is the beginning of lower discharge plateau.

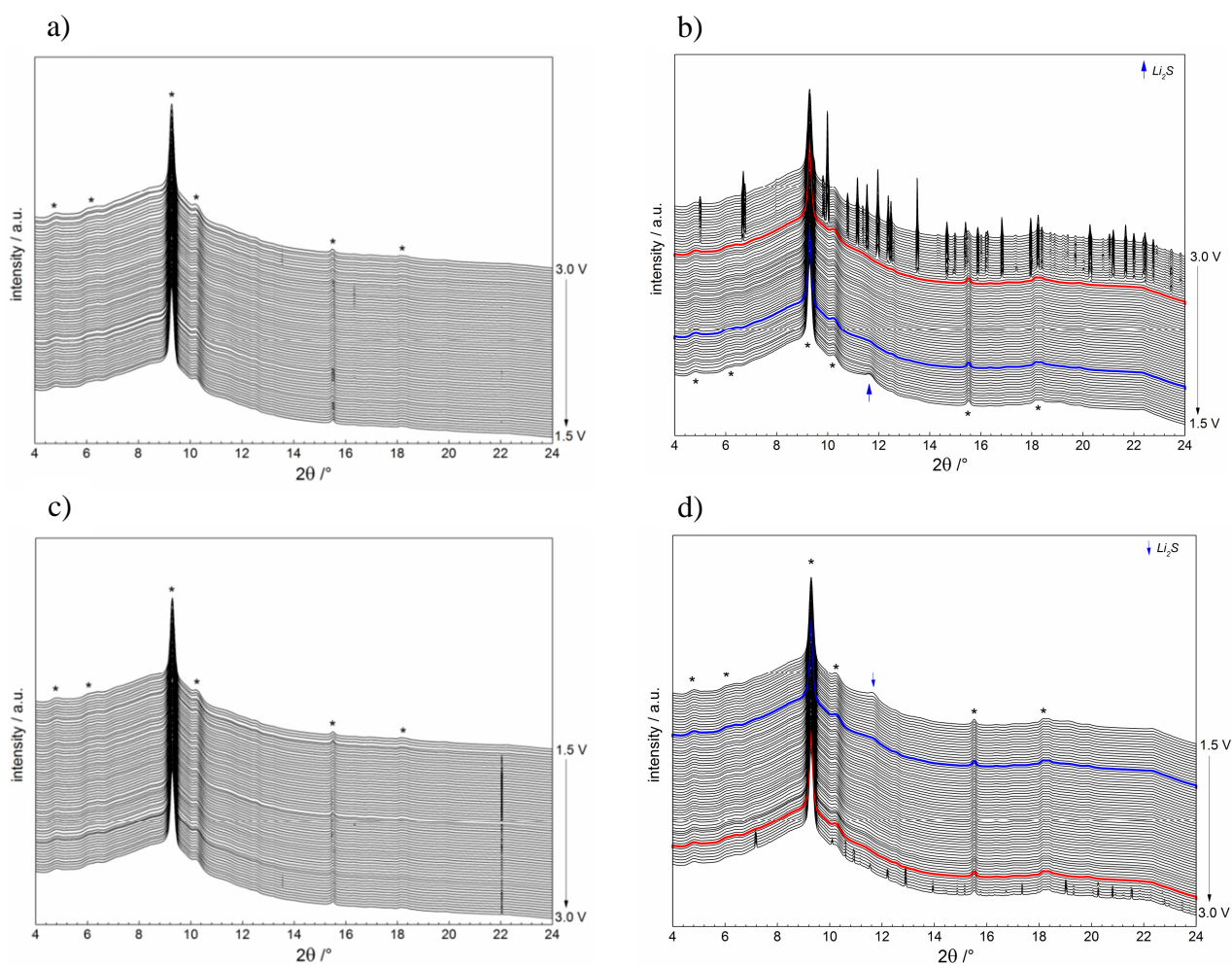


Fig. S4. *In situ* XRD peaks evolution recorded during 1st discharge and charge at each electrode separately: Li⁰ anode (a,c) – position [1], sulfur cathode (b,d) – position [3]. Peaks associated with packaging are marked by *. Bold lines indicate moments of solid phases appearance/disappearance.

It has been proven that the structural changes which occur in the complete cell take place on positive electrode, as expected (Fig. S4 b,d). Rather similar peak evolution is observed as compared with complete cell (Fig. 2). However, the signal intensities are lower as well as moments of Li₂S and S₈ appearance/disappearance are shifted. This is probably related with the fact that electrochemical reactions occurring at the position [3] (see Fig. 1) are slightly delayed due to the hole cut on the lithium electrode which results in disrupted current line. Presence of crystalline Li₂S is confirmed by the most intensive peak (111) at $2\theta = 11.6^\circ$.