Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

A facile synthetic approach to nanostructured Li_2S cathodes for rechargeable solid-state Li-S batteries

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Methods

Synthesis of Li_2S. Sulfur and lithium tert-butoxide were purchased from Sigma-Aldrich and used as-received as starting materials. The two materials are mixed in 1:2 mole ratio in Tetraglyme (Aldrich) in an argon filled glovebox. Solutions containing 0.075, 0.15 and 0.3 M sulfur were prepared. The mixtures were heated up to 100 °C for few minutes until a clear green solutions were obtained. 5 ml of a fresh solution was then heated in a sealed 10 mL microwave tube to 200 °C for 20 min using a CEM Discover SP microwave synthesizer (2.45 GHz, an upper power limit of 200W was applied). The resulting product was washed thoroughly with THF (3 × 3 ml of THF) and finally dried at 150 °C for 2h. The washing and drying steps were performed under an argon atmosphere. This procedure gave a product yield of 83%.

Synthesis of $Li_3PS_4/Li_2S/C$ nanocomposites. P_2S_5/C composites were first prepared by a melt diffusion technique. P_2S_5 (Sigma Aldrich) and carbon black (KETJENBACK EC-600JD, AkzoNobel) were mixed using a mortar and pestle in an argon filled glovebox and then heated at 290 °C for 2h in a sealed tube under an argon atmosphere to prepare composites that are 30 and 60 wt% in P_2S_5 (0.6 g each). $Li_3PS_4/Li_2S/C$ nanocomposites were prepared by mixing equal amounts (50 mg) of the produced P_2S_5/C composites and nanostructured Li_2S in THF (3 ml) and stirring overnight. The products were finally dried at 150 °C for 2h in an argon atmosphere.

Material characterization. XRD analysis was performed using a PANalytical X'Pert PRO diffractometer in reflection mode using Cu-Kα radiation. The powder materials were sealed in an airtight XRD sample holder in an argon filled glovebox to prevent reaction with moisture and oxygen. All presented patterns are overnight runs with data collection times exceeding 12h. SEM and EDX studies were performed using Zeiss Sigma field emission scanning electron microscope. EDX was collected using an Oxford Instruments Aztec Energy EDS Analysis System (80mm detector). Acceleration voltage of the SEM is 10kV. The machine is equipped with an angle selective backscattered electron detector (AsB), to obtain materials contrast images. Samples for SEM/EDX analyses were prepared in an argon filled glovebox, with air exposure time not exceeding 10 s during the introduction of the samples into the microscope.

Electrochemical characterization. For electrochemical characterization of $Li_3PS_4/Li_2S/C$ nanocomposites, laboratory-scale solid-state batteries were fabricated using Li, Li_3PS_4, and

$Li_3PS_4/Li_2S/C$ nanocomposites as anode, solid-electrolyte and cathode, respectively. Li_3PS_4 solid-electrolyte was prepared according to the procedure described in ref 34, using commercial Li_2S (Sigma Aldrich). Li foil (Sigma Aldrich) was thinned to ~ 0.3 mm before use. A three-layer pellet, 8 mm in diameter, consisting of Li, 110 mg Li_3PS_4 and 0.5-1 mg $Li_3PS_4/Li_2S/C$ composite, was obtained by pressing the three components at 2 tons for 30 s. Thin Ni-foil and Al-foil discs were used to support and collect the current from the anode and the cathode, respectively. In order to obtain a homogenous dispersion of $Li_3PS_4/Li_2S/C$ on the solid-electrolyte surface, the composite was dispersed on the surface of the Al-foil disc before pressing (the composite was re-dispersed in THF, dropped onto the Al-foil disc then dried at 150 °C for few minutes). A typical three-layer pellet is shown in Figure S4. The electrochemical performance of the assembled cells was evaluated in Swagelok cells using a BioLogic VSP potentiostat. The cells were charged and discharged by applying current densities 20-100 $\mu A/cm^2$ between 1.4 and 2.8 V vs Li/Li^+. The charge potential was held at a constant voltage of 2.8 V at the end of each charging cycle, while the current was dropped to 10% of the charging current. The obtained capacity was normalized by the weight of Li_2S in the cathode electrode. Electrochemical impedance spectroscopy measurements were performed before and after the electrochemical cycling process in the frequency range of 1 Hz and 1 MHz with an applied voltage of 0.07 V.

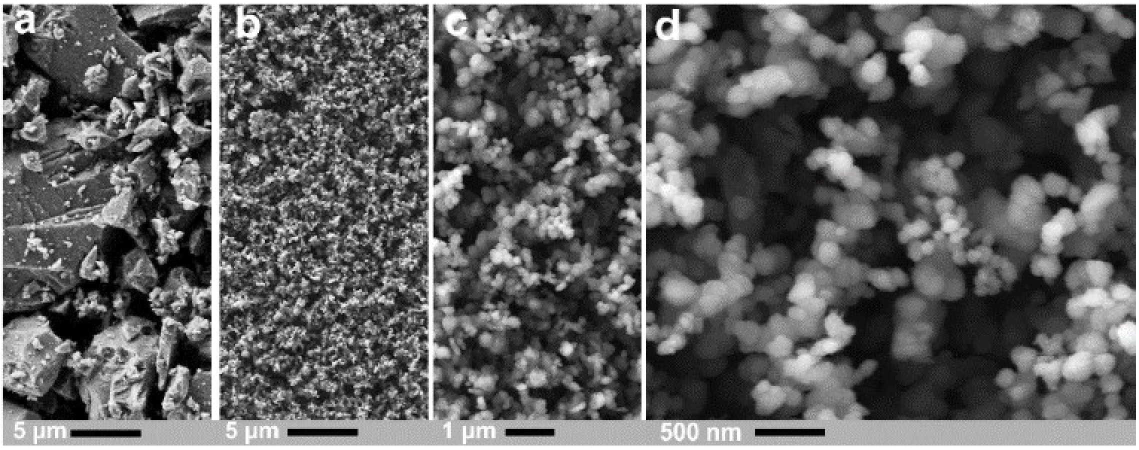

Figure S1 Morphology of (a) commercial Li_2S and (b-d) microwave-synthesised Li_2S using 0.15 M sulfur solution.

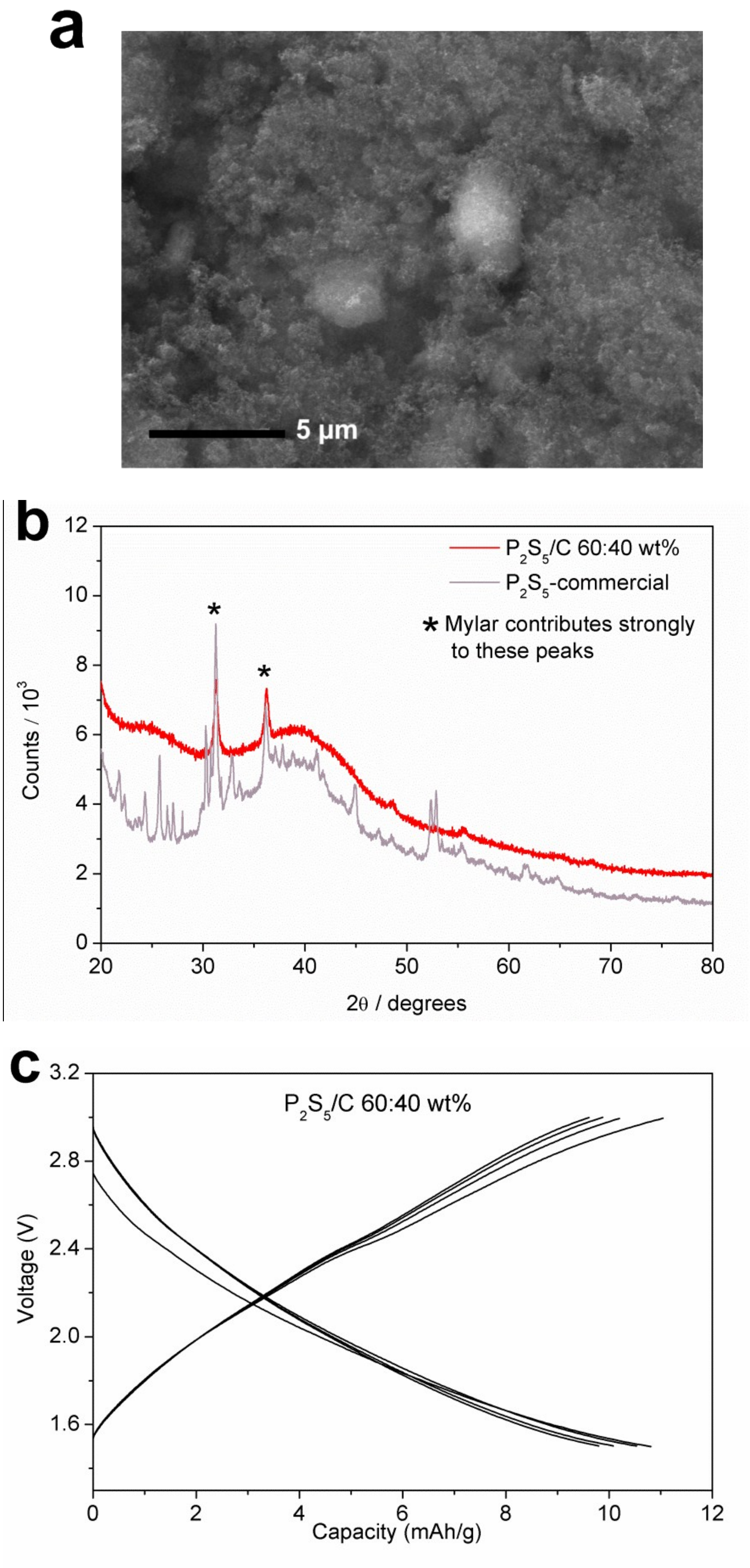

Figure S2 (a) SEM image of P_2S_5/C composite (30:70 wt%). b) XRD patterns of P_2S_5 and P_2S_5/C (60:40 wt%). c) First few cycles of a battery employing P_2S_5/C (60:40 wt%) as the cathode, Li as the anode, and 1 M LiTFSI in 1:1 DOL/DME as the electrolyte.

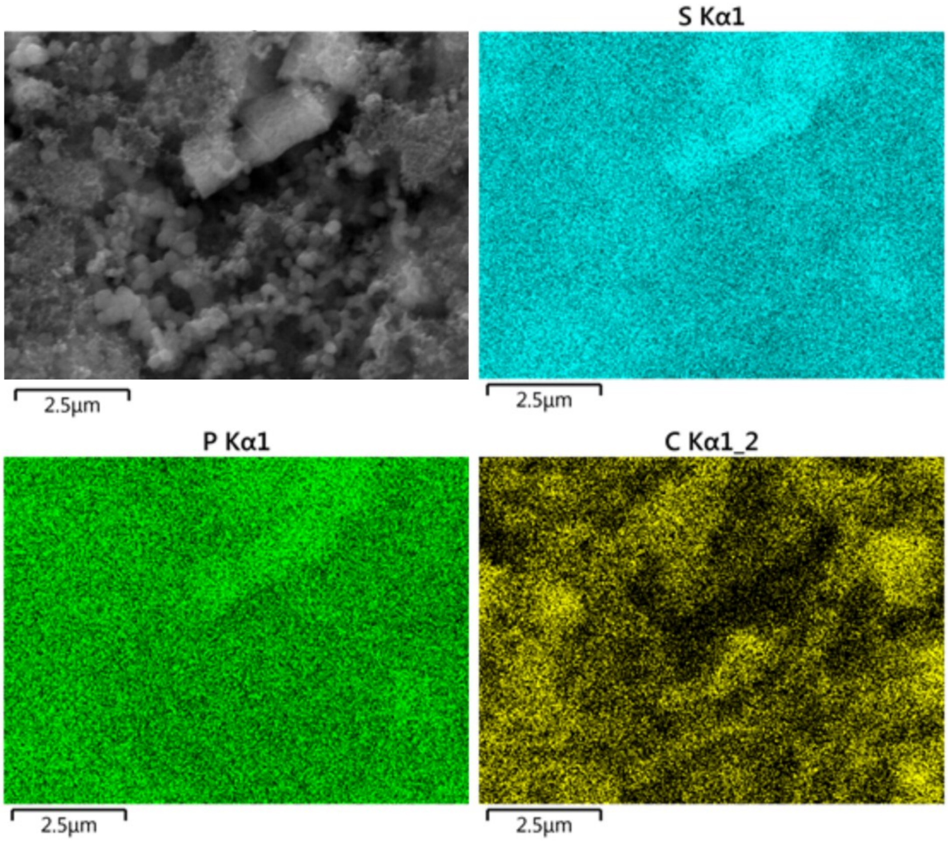

Figure S3 EDX elemental mapping of LS-PS60/C40.

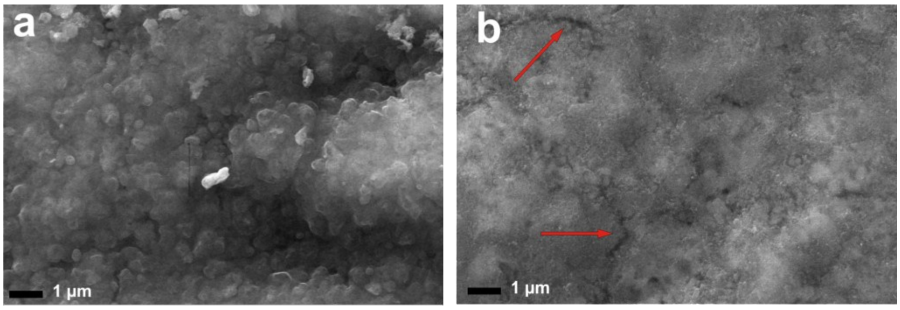

Figure S4 Morphology of LS-PS30/C70 electrode before (a), and after 410 cycles (b), at 100 µA/cm^2 current density. The arrows point to observed cracks.

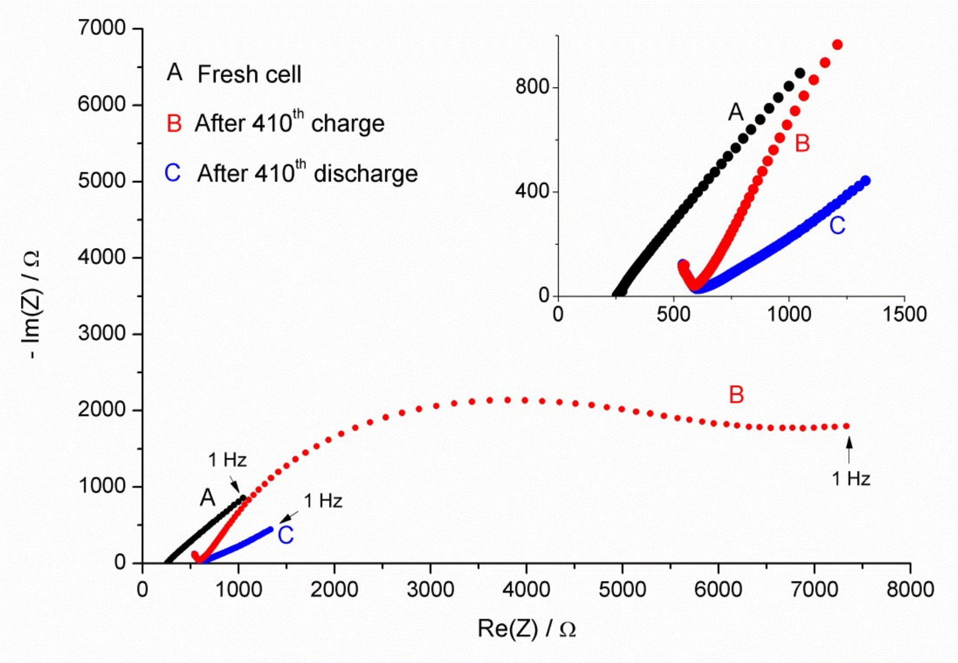

Figure S5 Impedance spectra collected from fresh LS-PS30/C70 battery and after final (410th) charge/discharge. The Nyquist plot of a fresh battery only shows a line starting from about 250 Ω (curve A). The Nyquist plot of the battery after charging (410th charge; curve B) shows an undefined high frequency semicircle and low-frequency semicircle corresponding to charge-transfer resistances associated with the solid-electrolyte/cathode and solid-electrolyte/Li-anode interfaces, respectively [1-5]. In the very low frequency region a noticeable Warburg impedance may be assigned to the chemical diffusion of Li in the cathode particles [1,4]. Since the impedance at high frequency is not well-defined, due to the limited frequency range of our equipment, the resistance at the solid-electrolyte/cathode interface can be estimated from the difference between the intercepts of curves A and B with the real z axis [1]. Interestingly, after discharge (410th discharge), the semicircle corresponding to solid-electrolyte/Li-anode interface greatly diminishes, which corresponds to a great drop of the resistance at the Li/solid-electrolyte interface in the discharged state. Similar dramatic changes of the interfacial resistances upon charge/discharge is observed for In anodes in similar solid-state cells, however, higher resistances are observed in the discharged state [1]. Further understanding of this effect requires a detailed study of Li/Li_3PS_4 interface which is beyond the scope of this report. In a possible interpretation, the intercept of the two curves B and C with the real z axis may correspond to an increased resistance of the solid-electrolyte, however, we could not observe a change in the morphology/sinterability of the solid-electrolyte, e.g. pulverization, and it is also unlikely that (repetitive) charge/discharge and associated interface formation do not lead to respective impedances in the studies frequency range. In related solid-state cells, including cells showed a similar initial impedance to our system, the impedance corresponding to interfaces were retained after cycling [1-3].

References

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