Experimental Section

To prepare the Li_6PS_5Br solid electrolyte, stoichiometric mixtures of Li_2S (Alfa Aesar, 99.9%), P_2S_5 (Loba Chemie, 98%) and LiBr (Sigma-Aldrich, 99.9%) were mechanically milled using high-energy planetary ball mill (Fritsch Pulverisette 7) at a rotating speed of 500 rpm for 20h. The amorphous ball-milled precursor was then pelletized and annealed at 300°C for 5h, leading to crystalline argyrodite-type Li_6PS_5Br. For the composite cathode powder, commercial MoS_2 (Sigma-Aldrich, 99%), Li_6PS_5Br, and super P carbon were mixed in a weight ratio of 40: 56: 4 and ball milled at 500 rpm for 30 min. All-solid-state MoS_2/Li_6PS_5Br/In-Li cell was assembled as follows. 100 mg of Li_6PS_5Br solid electrolyte powder, together with15 mg of the composite cathode powder, were put into a 13 mm die sequentially, and pelletized at a pressure of 6000 kg/cm^2. A foil of indium-lithium alloy as anode was attached to the electrolyte side of the pellet. Thereafter, the stack was mounted and sealed in a Swagelok-type cell. For comparison, MoS_2 cell using liquid electrolyte was also prepared. The same commercial MoS_2 was mixed with super P carbon and poly(vinylidene fluoride) (PVDF) in a weight ratio of 70:15:15 and dissolved in N-methylpyrrolidone (NMP). The obtained slurry was then pasted onto Cu current collector. Coin cell was assembled with Li foil as counter electrode, 1 M $LiPF_6$ in 1:1 EC/DEC as electrolyte and glass fiber (Whatman) as separator. The complete process was performed in a glove box under argon atmosphere.

The morphologies of the pristine MoS_2 powder and the composite cathode powder was investigated by Scanning Electron Microscopy (SEM, Zeiss Supra 40 VP). To understand the electrode reaction of the all-solid-state MoS_2 batteries, cyclic voltammetry (CV) was performed at a scanning rate of 0.02 mV/s between 0.1 V and 3.0 V (vs Li/Li^+) using a potentiostat/galvonostat (Arbin BT2000). Existence of Mo metal nanoparticles in MoS_2 cathodes after cycling was confirmed using Transmission Electron Microscopy (TEM, JEOL 2010F). The MoS_2 composite cathode powder at charged state was placed into deionized water (DI water) and sonicated for 1 min. By this treatment, the water-soluble lithium compounds in the composite cathode powder, such as solid electrolyte Li_6PS_5Br and Li_2S, will be dissolved, leaving behind the components insoluble in water (e.g. Mo, S, C, MoS_2, if they exist). The resulting solution was centrifuged and the insoluble black residue was used for TEM measurement. Room temperature electrochemical tests were conducted at a C rate of C/10 (i.e. a current density of 67 mA per gram of MoS_2). The voltage range was restricted to 0.1 – 3.0 V in the first 5 cycles and 1.0 V – 3.0 V in the subsequent cycles. High temperature rate performance was studied at 70 ºC up to 700 cycles. The charge/discharge current changed every 200 cycles from C/5, C/2 to 1C, and then back to C/5 for the last 100 cycles. In this case the voltage range was set to 0.1 – 3.1 V (vs. Li/Li^+) in the first cycle and 0.6 – 3.1 V (vs. Li/Li^+) in the following cycles. The cell using liquid electrolyte was tested at C/5 with the same voltage range up to 100 cycles. All voltages discussed in this manuscript are to be understood with respect to Li/Li^+, unless pointed out specially. The potential of indium vs. Li/Li^+ is 0.6 V.