Supplementary

Materials synthesis:

Li_6OSI_2 solid electrolyte was prepared by high-energy ball milling and subsequent pressing without heating. Li_2O (99.9% metals basis), Li_2S (99.9%), and LiI (99.9% metals basis) powders were used as starting materials, which were mixed in the molar ratio Li_2O:Li_2S:LiI = 1:1:2 in an argon-filled glovebox (O_2<0.1ppm, H_2O<0.1ppm). The mixed powder was then transferred into an argon-filled zirconia milling container (100ml in volume), with the weight ratio of zirconia balls to powder being 8:1. Milling was carried out using a high-energy planetary ball mill at 280 rpm for 10h at room temperature. Crystalline powder of Li_6OSI_2 was obtained directly through cold pressing up to a pressure of 10 Mpa in the glovebox.

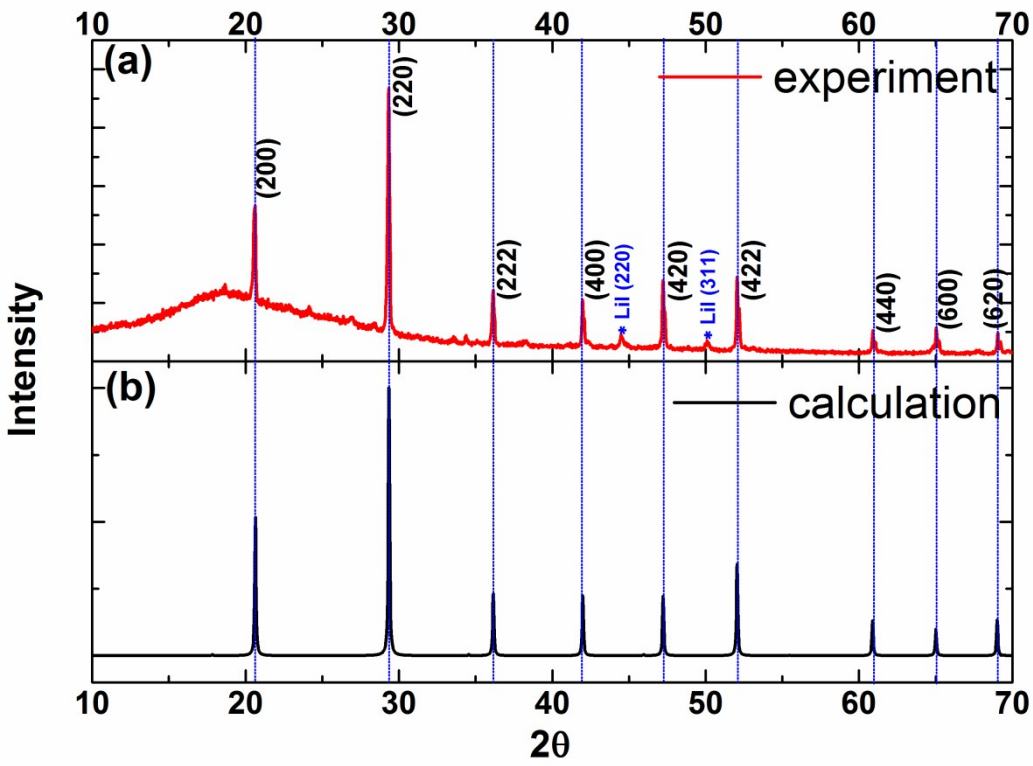

Fig. s1 Powder XRD pattern for the cold-pressed Li_6OSI_2 sample with double-anti-perovskite structure (a), in comparison to calculated pattern from simulated structure (b). Trivial remnant LiI peaks are present, with peak intensities for the major phase being in excellent agreement with the theoretical pattern. Background hillock at lower angle range was from the encapsulating polymer for sample protection from the atmosphere.

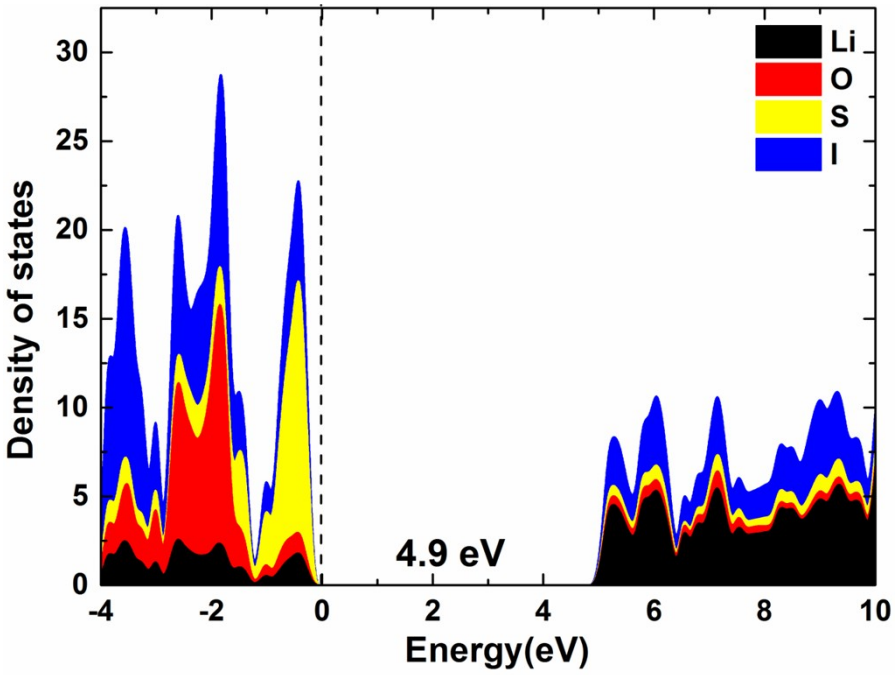

Fig. s2 Projected density of states calculated using the HSE06 functional for $Li_{25}O_4S_5I_7$.