An Iodide Based Li$_7$P$_2$S$_8$I Superionic Conductor

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Experimental Section

Materials Synthesis: Li$_3$PS$_4$ was synthesized using Li$_2$S (Alfa Aesar – 99.9%) and P$_2$S$_5$ (Sigma Aldrich – 99%) mixed stoichiometrically in a 2:1 ratio (excess P$_2$S$_5$ was used) in Acetonitrile (Sigma Aldrich – 99.8% anhydrous) for 24 hrs. The resulting powders are treated at 80$^\circ$C to remove excess acetonitrile (ACN) yielding Li$_3$PS$_4$·2ACN. The Li$_3$PS$_4$·2ACN is further dispersed in acetonitrile containing the requisite amount of LiI and mixed in a turbulent mixer for 15 minutes. The resulting slurry is dried ambiently for 12 hours and treated in vacuum at 200$^\circ$C to obtain the solid solution. On account of the sensitivity to O$_2$ and moisture for the system, all the experimental procedures are carried out in a glove box with <0.1 ppm of O$_2$ and H$_2$O.

Characterization: Crystallographic phase identification was conducted by using a PANalytical X’Pert Pro Powder Diffractometer with Cu Kα radiation. XRD samples were prepared in a glove box with Ar atmosphere. Kapton® films were used to seal quartz slides to exclude air contact. Qualitative analyses were conducted by the software of HighScore Plus, which is developed by PANalytical. Scanning Electron Microscopy (SEM) characterizations were conducted utilizing environment sensitive sample holders in a MERLIN Field Emission Scanning Electron Microscope (FE-SEM) from Carl Zeiss. Electrochemical Impedance Spectroscopy (EIS) measurements were conducted using a 1260 Solartron Frequency Response Analyzer between 1 MHz and 0.1 Hz at the amplitude of 100 mV. Carbon coated Al-foils were used as blocking electrodes. Pellets for the symmetric cells and cyclic voltammetry studies were cold pressed at 320 Mpa and Li foils (3/8“ dia and ≈100 µm thick) were attached to them after cold pressing. Cyclic voltammetry investigations were conducted using a Bio-logic VSP multi channel potnetiostat using a scan rate of 1 mV s$^{-1}$. Samples were packed in 3.2 mm MAS rotors in an Argon-filled glove box. MAS NMR experiments were performed with a 7.05 T Varian-S Direct Drive Wide Bore spectrometer and a 3.2 mm MAS probe operating at 122.0 MHz and 60.3 MHz to study $^{31}$P and $^{127}$I respectively. A 20 kHz MAS speed was used. $^{31}$P single-pulse experiments were run with a 3.1 µs π/2 pulse length, a 600 s recycle delay and 128 transients. $^{31}$P chemical shifts are referenced to 85% H$_3$PO$_4$ aqueous solution (δ = 0 ppm). $^{127}$I rotor-synchronized solid-echo experiments (π/2 pulse – τ – π/2 pulse – τ – acquire) were run with a 2 µs π/2 pulse length, a 0.5 s recycle delay and 130,000 transients.
Figure S1: Experimental (markers), Le Bail fitted (line), and difference (line below observed and calculated patterns) XRD profiles for 2Li₃PS₄-Lii (Cu Ka radiation), space group Pnma. Vertical bars indicate the calculated positions of Bragg peaks. Goodness of fit: $R_{wp}$=14.6%, $R_p$=10.2%, $\chi^2$=3.92. Regions with noticeable diffraction peaks from the precursor impurity phases were excluded in the data fit. The refined lattice parameters for space group Pnma are: $a$=12.703(1)Å, $b$=8.4458(9) Å, and $c$=5.9421(5) Å. Le Bail profile refinements were performed using the GSAS package
(1) on the XRD data. Excellent fits were obtained, proving that the new phase is indeed a single phase.

Figure S2: A 48 hour wash of the Li_7P_2S_8I in acetonitrile (ACN) clearly illustrates that the structural reversibility, with the reformation of Li_3PS_4·2ACN and Li_3PS_4 (crystalline). Due to its solubility, LiI is lost during the acetonitrile removal procedure prior to XRD analysis. ‘•’ indicates the presence of Li_3PS_4·2ACN phase and ‘*’, indicates the presence of an unknown phase.
Figure S3: Cyclic voltammogram for (a) 1:1 Li$_3$PS$_4$ : LiI mixture illustrating the oxidation of the excess LiI and also the lack of anodic stability (Onset of reduction prior to 0 V vs Li/Li$^+$) which is in stark contrast to the Li$_7$P$_2$S$_8$I phase that is stable at the anodic and cathodic cycles of CV. (b) The onset of reduction occurs only beyond 0 V vs Li/Li$^+$ illustrating the stability for the newly formed phase with Li anode. The included arrows illustrate the direction of the CV scan.

Figure S4: The excellent interfacial kinetics is manifested in the close proximity for the EIS measurements conducted in a blocking configuration and for the Li/Li$_7$P$_2$S$_8$I/Li symmetric cells.
The reduction of the cell resistance immediately before cycling and after the completion of 100 cycles is the resultant of a homogenous Li layer formed during the cycling process.

**Figure S5:** Individual cycle charge and discharge polarization curves for a Li/Li$_7$P$_2$S$_8$I/Li cell indicating the uniform polarization as a function of cycle number even after multiple hundreds of cycles. A minor reduction (≈ 5%) in polarization is observed between Cycles 1-5 and subsequent cycles. This can be attributed to the establishment of a homogenous Li layer at the Li-Li$_7$P$_2$S$_8$I interface.

**Figure S6:** SEM images of the cross section of an Li$_7$P$_2$S$_8$I membrane warm pressed at 270°C. The fracture morphology confirms the occurrence of densification occurring during the warm
press procedure. It also illustrates a lack of voids / pores and hence the effectiveness of the densification.