Designing solution chemistries for low-temperature synthesis of sulfidebased solid electrolytes

*Hee-Dae Lim, Xiujun Yue, Xing Xing, Victoria Petrova, Matthew Gonzalez, Haodong Liu and Ping Liu**

Department of Nanoengineering, University of California, San Diego, La Jolla, CA 92093, USA

* Corresponding author: piliu@eng.ucsd.edu

Experimental

Synthesis procedure of reference Li₃PS₄ and LiSEt@Li₃PS₄ solid electrolytes

High purity precursors of Li₂S (99.98%) and P_2S_5 (99%) (Aldrich) were used as received, and anhydrous THF solvent (99.9%) was pre-treated with molecular sieves to completely remove residual water before use. The reference Li₃PS₄ powder was purchased from the NEI corporation. All the experiments have been conducted in Ar glove box without exposure to air. A 3:1 molar ratio of Li₂S and P_2S_5 was added into THF solvent and the solution was stirred for 12 h to make a reference Li₃PS₄ solid electrolyte. Then, the prepared solutions were stirred overnight and centrifuged to collect precipitated powders, which were heat treated at 140 °C for 10 h at a heating rate of 2 °C min⁻¹. To prepare the LiSEt@Li₃PS₄ solid electrolyte, LiSC₂H₅ was added into the solution (3:1:1 molar ratio of Li₂S:P₂S₅:LiSC₂H₅), and the same procedures were followed with the reference Li₃PS₄.

Characterization and electrochemical analyses

To analyze the synthesized solid electrolytes, all the measurements have been carefully conducted without exposure to air. X-ray diffractometry (XRD, Bruker, D2 Phaser) with Cu-K α radiation was conducted to analyze crystal structure of solid electrolytes and images of solid electrolytes were collected using focused ion beam-scanning electron microscopy (FIB-SEM, FEI Scios, Scios DualBeam). Bonding environments of solid electrolytes were investigated using Raman spectroscopy (Raman, Perkin Elmer, Raman Station 400F) and Fourier transform-infrared spectroscopy (FT-IR, Perkin Elmer, Spectrum 100 FT-IR). Impedance spectra were measured using electrochemical impedance spectroscopy (EIS, BioLogic, VMP-300t) in a frequency range from 7 MHz to 1 mHz. Chemical structures and possible reaction mechanism were investigated via Nuclear magnetic resonance (NMR, Jeol ECA 500) with air-tight sample tubes. 85% phosphoric acid was used as external

standard. Solid electrolyte powders were pelletized using a hydraulic press at 300 MPa and the blocking electrode was prepared by placing solid electrolytes between two pieces of carbon coated Al foils.



Figure S1. Schematic illustrations showing the differences between (a) the conventional and (b) modified solution-based synthesis methods.

Conventionally, insoluble precursors of P_2S_5 and Li_2S are dispersed and reacted in various solvents. In this process, the final products such as Li_3PS_4 and $Li_7P_3S_{11}$ are insoluble, therefore, by-products or residuals are inevitably incorporated with the final products. Solvents just help to disperse the precursors particles. On the other hand, the modified solution-based synthesis methods utilize the soluble precursor of $LiSEt \cdot P_2S_5$. The reaction between liquid and solid reactants would be kinetically favorable condition compared to the conventional method. Also,

even if there are residuals or by-products, they can be easily washed out, therefore high quality solid electrolytes can be obtained.



Figure S2. P-NMR analyses of the THF solutions dissolving P_2S_5 and $LiSC_2H_5$ with different molar ratios of 1:0.75, 1:1, 1:3, and 1:6, which corresponds to samples [4.5], [5], [6], and [7], respectively.

When increasing the relative molar ratio of LiSEt from samples [4.5] to [7], the two dominant peaks at 118 and 88 ppm (P(SR)₃ and PS₄³⁻, respectively) show different tendencies. The peaks of P(SR)₃ and unknown peak 2 (UN2) decrease while the signals of PS₄³⁻ and UN1 gradually

increase. The dissolved neutral $P(SR)_3$ changes to an ionic compound by adding more LiSEt, and it reaches PS_4^{3-} , the highest ionic state in solution [7]. The peaks of UN1 and UN2 are expected to be intermediate compounds with one or two ionic state such as $P(SR)_x^{-}$ and $P(SR)_x^{2-}$, which needs to be further investigated. Consequently, it is clear that the addition of LiSEt can break the mother structure of P_2S_5 into various small units of ionic compound, which is an origin of the enhanced solubility.



Figure S3. (a) SEM image (inset table: elemental atomic ratio of S and P) and (b-d) the corresponding EDS elemental mapping results of the synthesized $LiSEt@Li_3PS_4$ solid electrolyte. The elemental ratio of P and S in the particle is 3.73, which provides a clue for the formation of Li_3PS_4 .



Figure S4. (a) SEM image and (b-d) the corresponding EDS elemental mapping results of the synthesized $LiSEt@Li_3PS_4$ solid electrolyte at a low magnification. It demonstrates that all the particles are composed of sulfur and phosphor without carbon.



Figure S5. XRD patterns spectra from (a) 10° to 80° and (b) 15° to 35° of the synthesized LiSEt@Li₃PS₄ solid electrolyte. The crystallinity of LiSEt@Li₃PS₄ is better than that of reference Li₃PS₄ and even comparable to the reference β -Li₃PS₄ powder.



Figure S6. Arrhenius plots of LiSEt@Li₃PS₄, reference Li₃PS₄, and reference β -Li₃PS₄ powder. To measure conductivity, a test cell was fabricated by placing solid electrolytes between two pieces of carbon coated Al foils which serve as blocking electrodes. Reference Li₃PS₄ was prepared by using the conventional solution-based synthesis method without the addition of LiSEt, and reference β -Li₃PS₄ powder was purchased from the NEI corporation.



Figure S7. (a) Cyclic voltammetry of the Li/LiSEt@Li₃PS₄/SUS cell for 10 cycles at a constant scan rate of 10 mV s⁻¹ from -0.5 to 6.0 V (*vs.* Li/Li⁺). (b) Cycling test of a Li symmetric cell (Li/LiSEt@Li₃PS₄/Li) at a constant current density of 0.1 mA cm⁻² with a 1 h time interval at room temperature.

As shown in Figure S7a, the LiSEt@Li₃PS₄ solid electrolyte shows a stable electrochemical window between -0.5 and 6.0 V, and stable, reversible lithium plating and stripping was obtained. In addition, a galvanostatic cycling test was carried out using a Li symmetric cell with a configuration of Li/LiSEt@Li₃PS₄/Li at a current density of 0.1 mA cm⁻² with 1 h time interval (Figure S7b). Stable cell voltages were maintained. The cyclic voltammetry and galvanostatic cycling performance demonstrate the electrochemical stability and reversibility of LiSEt@Li₃PS₄ as a solid electrolyte for Li batteries.