Chlorine-rich lithium argyrodite enables stable interfacial Li plating/stripping behavior in anodefree all-solid-state batteries

Donghee Gu^{a,b}, Hyoungchul Kim^a, Byung-Kook Kim^a, Jong-Ho Lee^{a,c*}, and Sangbaek Park^{d,*}

^aEnergy Materials Research Center, Korea Institute of Science and Technology (KIST), Seoul, 02792, Republic of Korea

^bSchool of Civil, Environmental and Architectural Engineering, Korea University, Seoul 02841, South Korea

^cDivision of Nanoscience and Technology, University of Science and Technology (UST), Seoul, 02792, Republic of Korea

^dDepartment of Materials Science and Engineering, Chungnam National University, Daejeon, 34134, Republic of Korea

*Corresponding author. Tel.: +82 2 958 5529; fax: +82 2 985 5544. *E-mail address:* jongho@kist.re.kr (J. Lee) Tel.: +82 42 821 6639; fax: +82 42 822 5850. *E-mail address:* sb.park@cnu.ac.kr (S. Park)



Fig. S1. Porosity analysis of SE pellets. (a) BSE images and (b) the corresponding porosity calculation of the surface for compressed SE pellets with Li_3YCl_6 , Li_3PS_4 , $(Li_3PS_4)_{0.7}(LiI)_{0.3}$, Li_6PS_5Cl , and $Li_{5.5}PS_{4.5}Cl_{1.5}$ in order from top to bottom.



Fig. S2. Morphology and composition characterization of Ag-C layer. (a) Plane and crosssectional view of SEM images, and (b) EDS mapping of Ag-C layer. (c) TEM image and HRTEM images of Ag-C composites.



Fig. S3. Electrochemical performance of a symmetric cell $(\text{Li}\|(\text{Li}_3\text{PS}_4)_{0.7}(\text{LiI})_{0.3}\|\text{Li})$. Voltagetime profiles of the Li plating/stripping process in Li symmetric cell with $(\text{Li}_3\text{PS}_4)_{0.7}(\text{LiI})_{0.3}$ SE at the current density of 0.5 mAcm⁻².



Fig. S4 Planar (a) SEM and (b) EDS images of Li plating with Ag-C layer. Cross-sectional (c) SEM and (d) EDS images of SE/Ag-C/Li/SS interfaces in the NCM||Ag-C full cell using Li_{5.5}PS_{4.5}Cl_{1.5} solid electrolyte after charging at 0.1 C for 10 h.