Supporting Information

Silicon-Doped Argyrodite Solid Electrolyte Li_6PS_5I with Improved Ionic Conductivity and Interfacial Compatibility for High-Performance All-Solid-State Lithium Batteries

*Jun Zhang,‡ Lujie Li,‡ Chao Zheng, Yang Xia, Yongping Gan, Hui Huang, Chu Liang, Xinping He, Xinyong Tao and Wenkui Zhang**

College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou 310014, P.R. China.

‡J. Zhang and L. Li contributed equally to this work.

*Corresponding author. E-mail: msechem@zjut.edu.cn

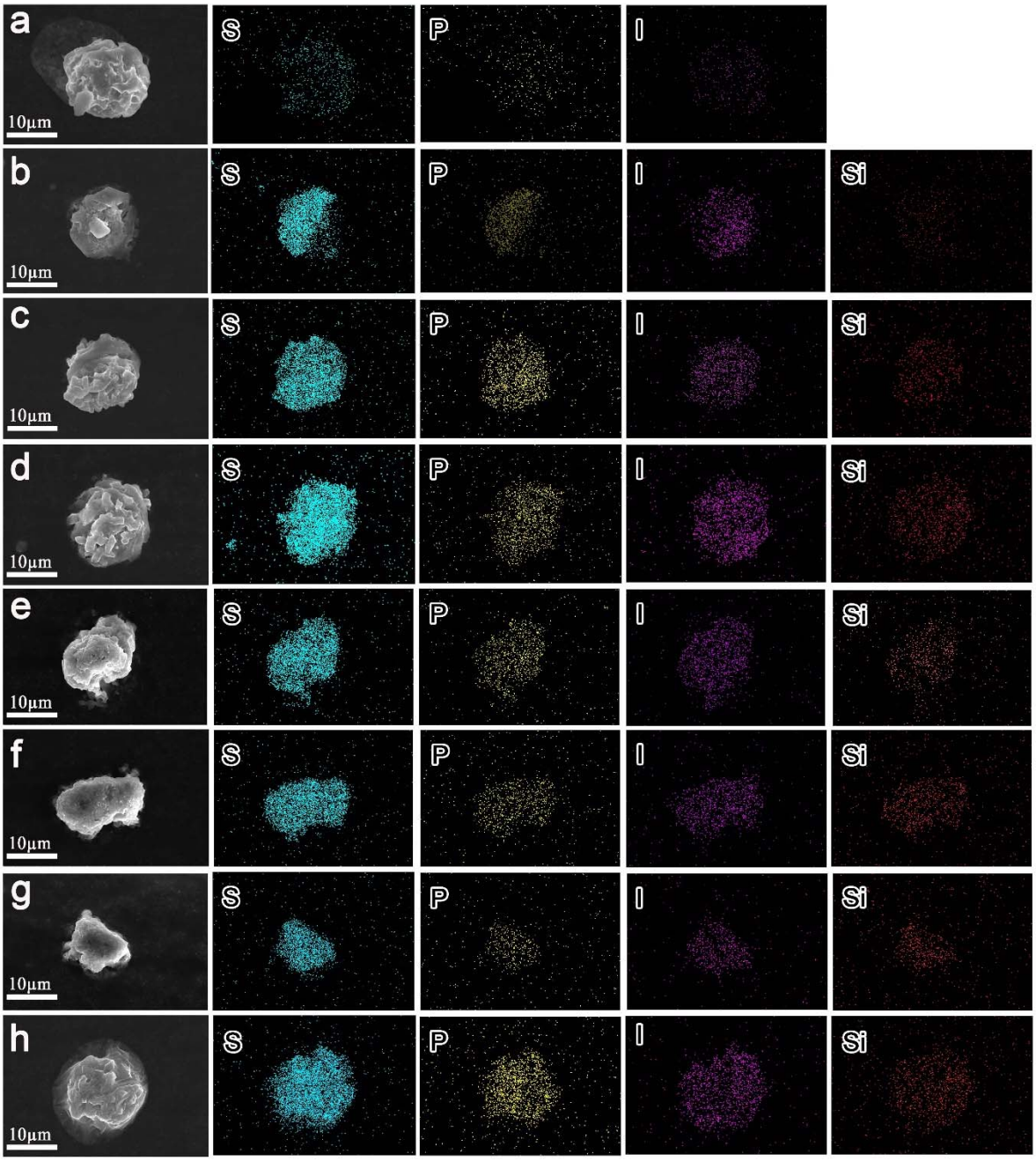

Figure S1. SEM images of (a) Li_6PS_5I, (b-h) $Li_{6+x}P_{1-x}Si_xS_5I$ ($0.1 \leq x \leq 0.6$) powders and the corresponding element mapping.

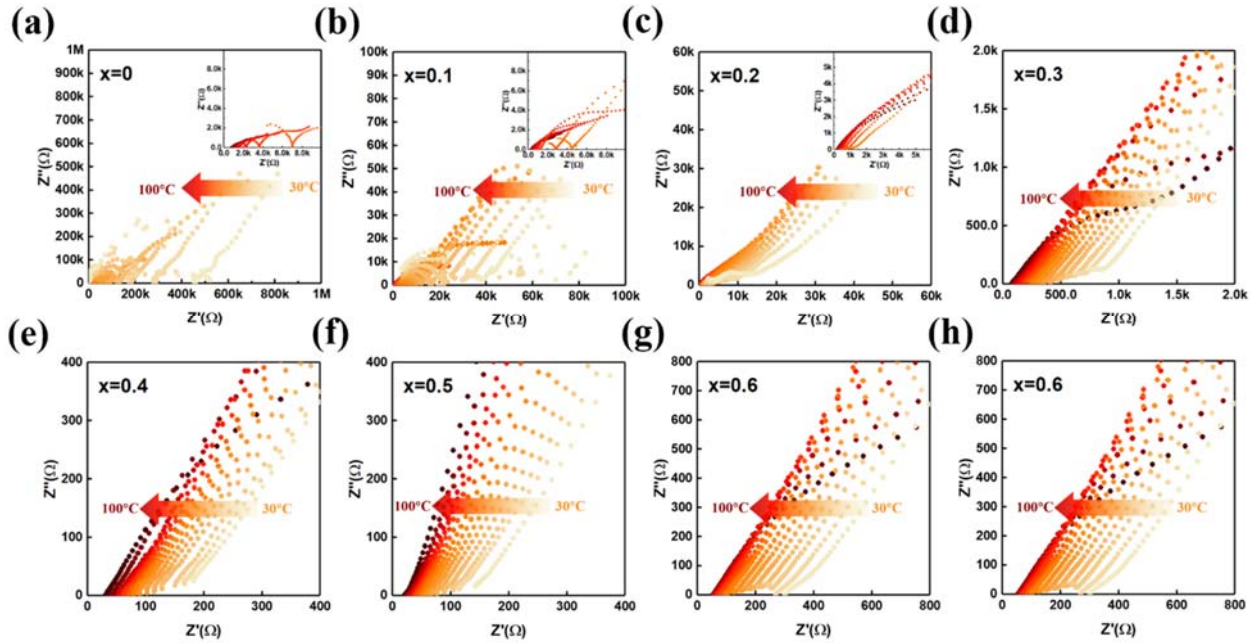

Figure S2. Nyquist plots of the (a) Li_6PS_5I (x = 0), (b-h) $Li_{6+x}P_{1-x}Si_xS_5I$ ($0.1 \leq x \leq 0.6$) samples measured from 30 ºC to 100 ºC, respectively.

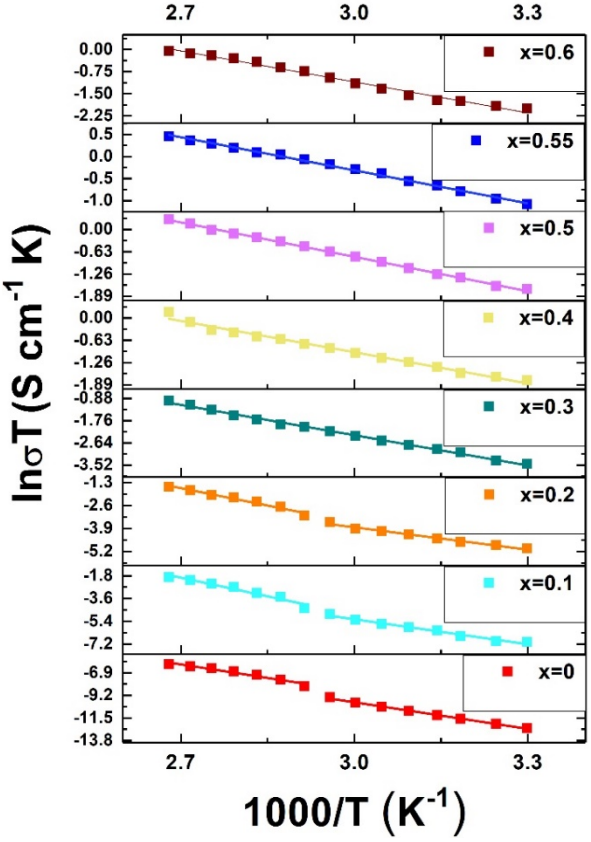

Figure S3. Arrhenius curves for activation energy of $Li_{6+x}P_{1-x}Si_xS_5I$ ($0 \leq x \leq 0.6$) samples.

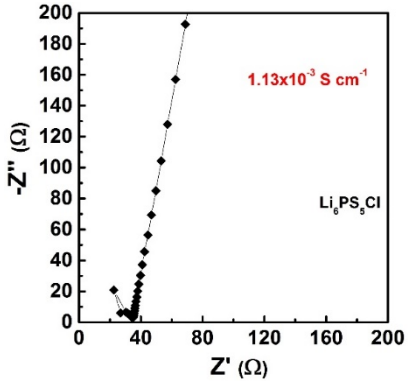

Figure S4. Nyquist plots of Li_6PS_5Cl sample measured at 30 °C.

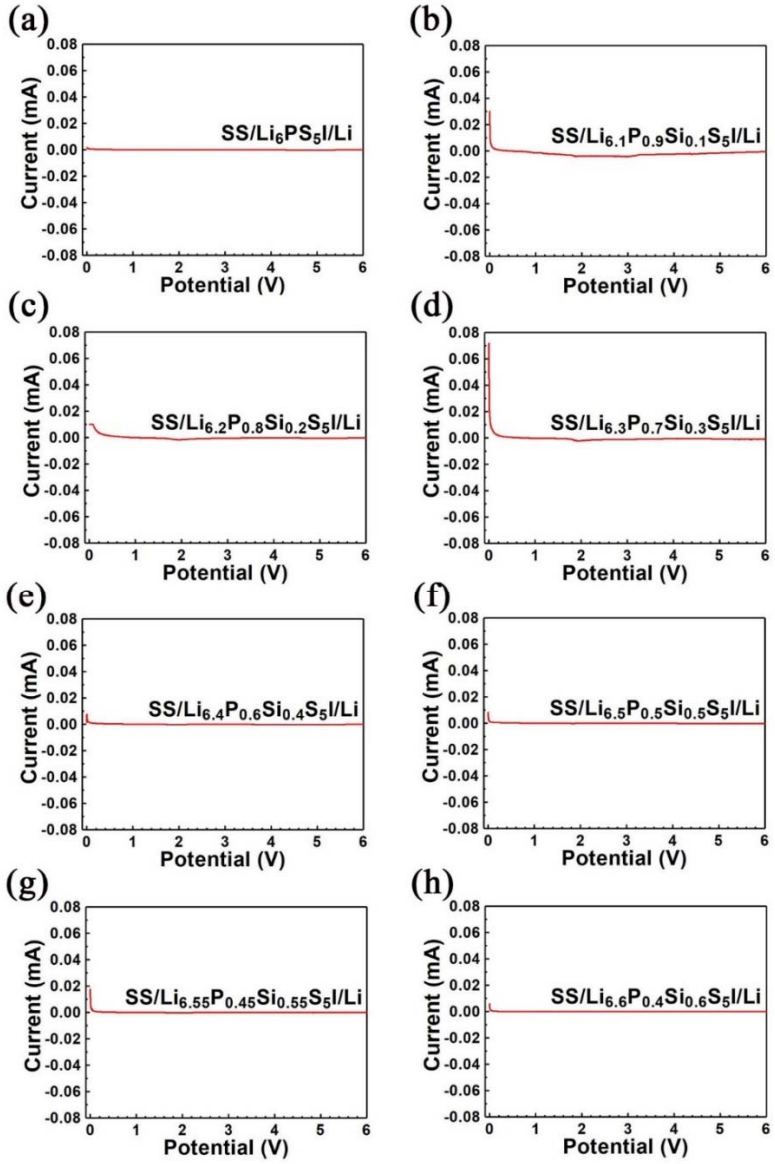

Figure S5. Linear sweep voltammogram (LSV) profile of (a) Li_6PS_5I, (b-h) $Li_{6+x}P_{1-x}Si_xS_5I$ ($0.1 \leq x \leq 0.6$) samples at a scan rate of 0.1mV s^{-1}, respectively.

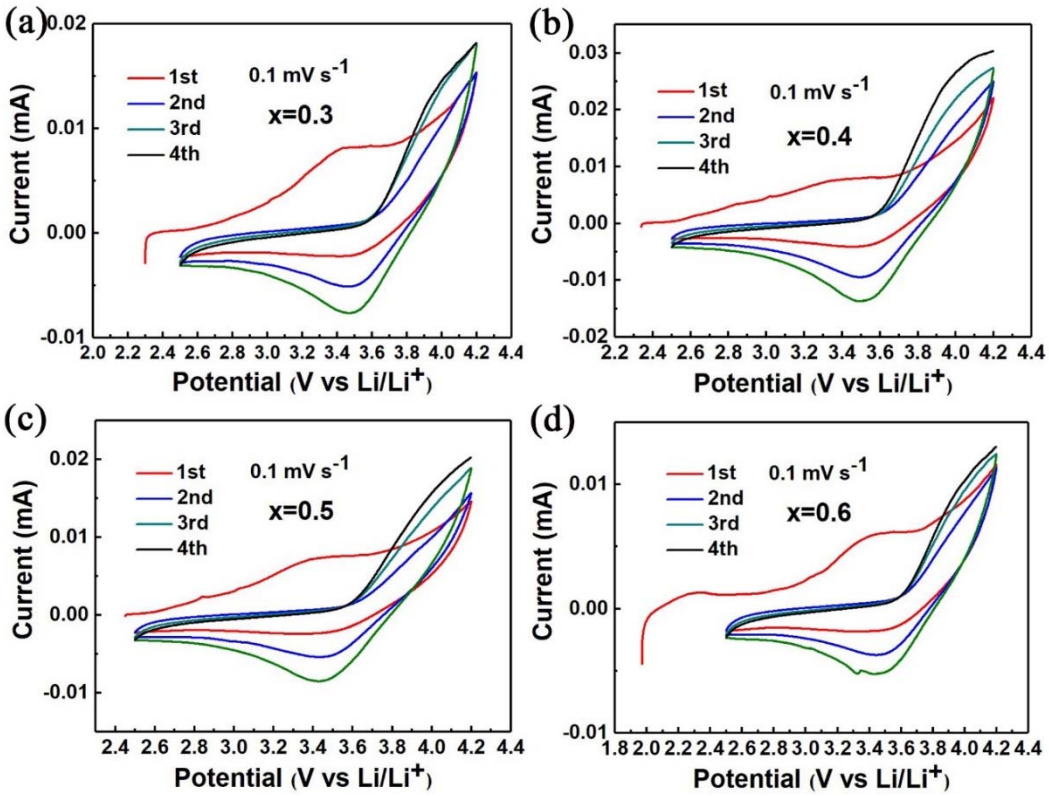

Figure S6. CV curves of the (a-d) $Li_{6+x}P_{1-x}Si_xS_5I$ ($0.3 \leq x \leq 0.6$) of NCM-Li_6PS_5Cl/ $Li_{6+x}P_{1-x}Si_xS_5I$/ Li ASSLBs at a scan rate of 0.1 mV s^{-1}.

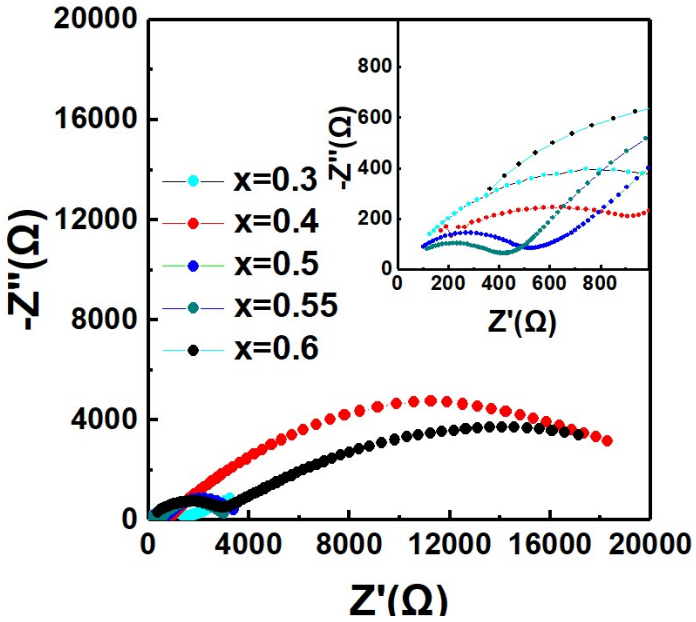

Figure S7. Impedance spectra of NCM-Li_6PS_5Cl/ $Li_{6+x}P_{1-x}Si_xS_5I$ (x = 0.3, 0.4, 0.5 and 0.6)/ Li ASSLBs after 300 cycles.

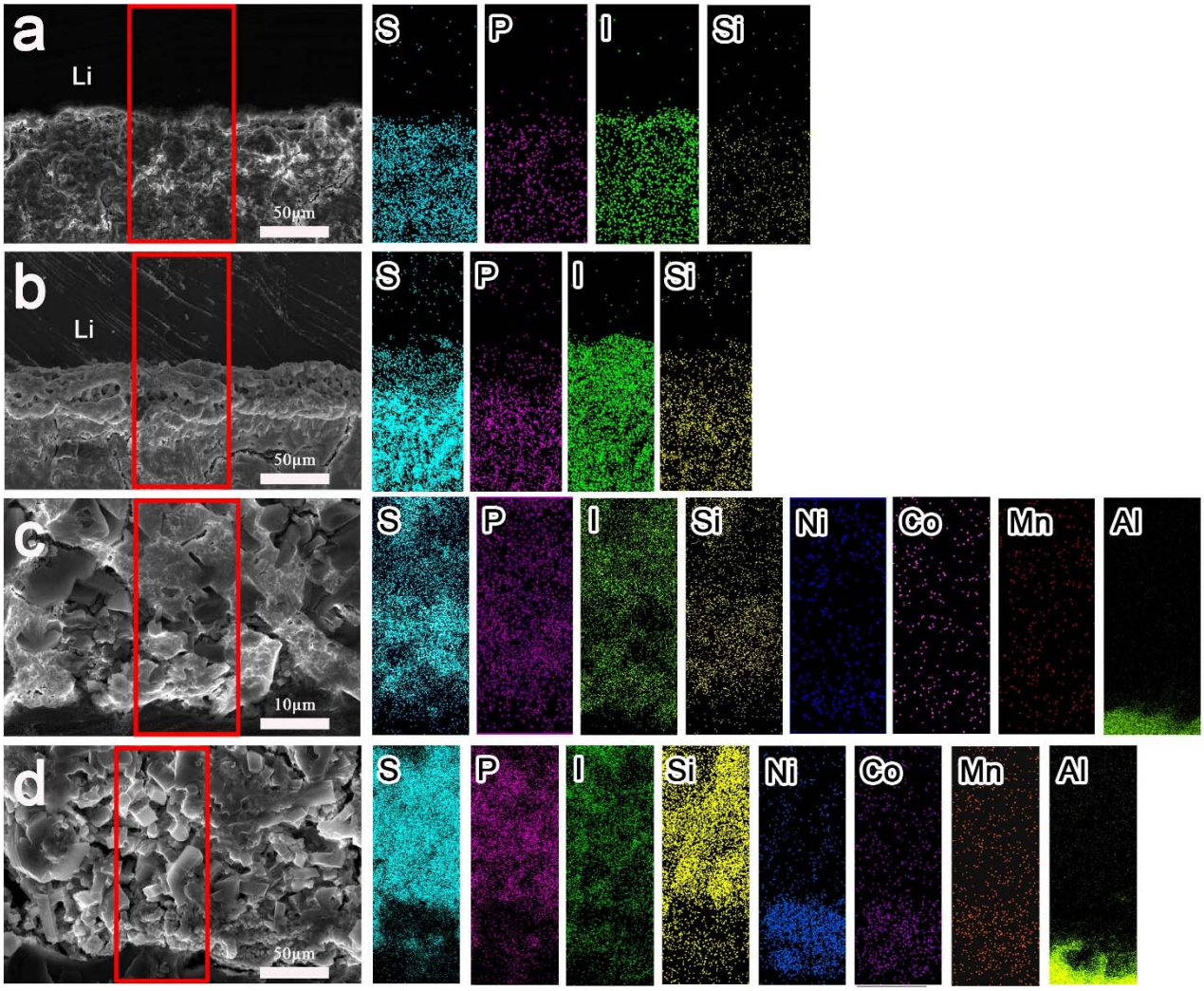

Figure S8. The cross-sectional SEM images and the corresponding elemental mappings of the interface of $Li_{6.55}P_{0.45}Si_{0.55}S_5I$ SE/Li before (a) and after cycling (b); $Li_{6.55}P_{0.45}Si_{0.55}S_5I$ SE/NCM before (c) and after cycling (d).

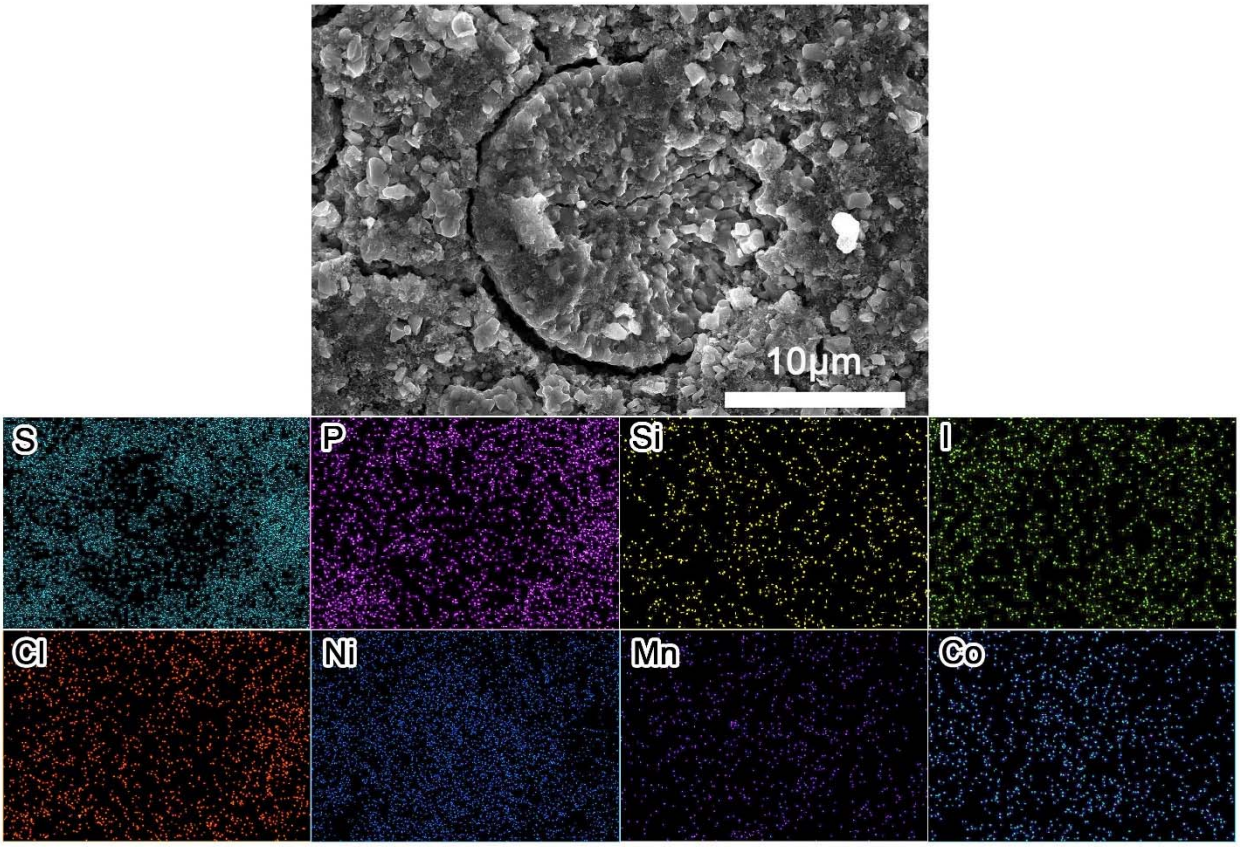

Figure S9. The SEM image and the corresponding elemental mappings of the cathode at the interface of $Li_{6.55}P_{0.45}Si_{0.55}S_5I$ SE/NCM.

Table S1. The extracted values of ionic conductivity and activation energy from Figure 3d.

x in $Li_{6+x}P_{1-x}Si_xS_5I$	Ionic conductivity (mS cm^{-1})	Activation energy (eV)
0	0.00023	0.73 / 0.76
0.1	0.0028	0.62 / 0.63
0.2	0.021	0.38 / 0.46
0.3	0.12	0.32
0.4	0.53	0.24
0.5	0.66	0.26
0.55	1.1	0.19
0.6	0.48	0.27