Failure analysis of the Ge-substituted Li_6PS_5I with bare $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ and performance improvement via Li_2ZrO_3 coating

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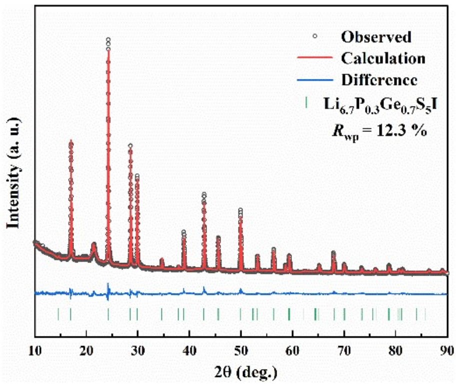

Figure S1. Rietveld refinement of $Li_{6.7}P_{0.3}Ge_{0.7}S_5I$ electrolytes.

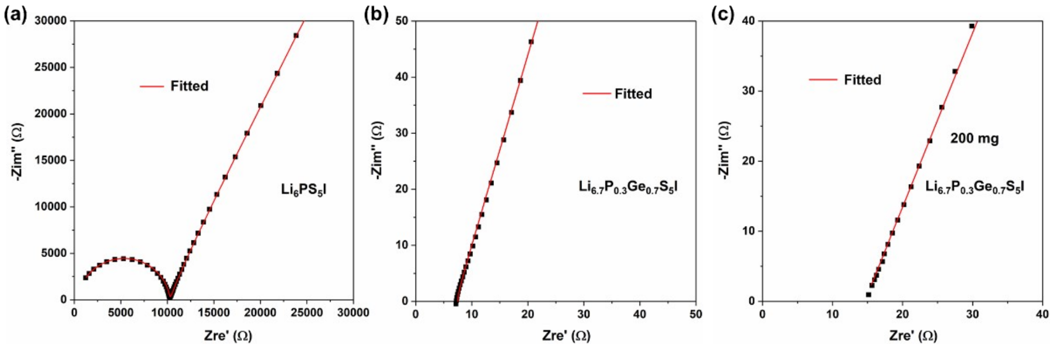

Figure S2. The EIS of **(a)** Li_6PS_5I with a mass loading 100 mg at room temperature. The EIS of $Li_{6.7}P_{0.3}Ge_{0.7}S_5I$ electrolytes with mass loading of **(b)** 100 mg and **(c)** 200 mg at room temperature.

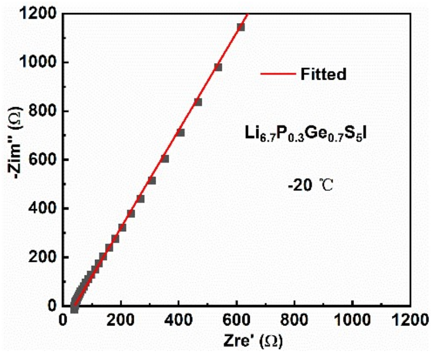

Figure S3. The EIS and fitted curse of $Li_{6.7}P_{0.3}Ge_{0.7}S_5I$ electrolyte at -20 ^{o}C.

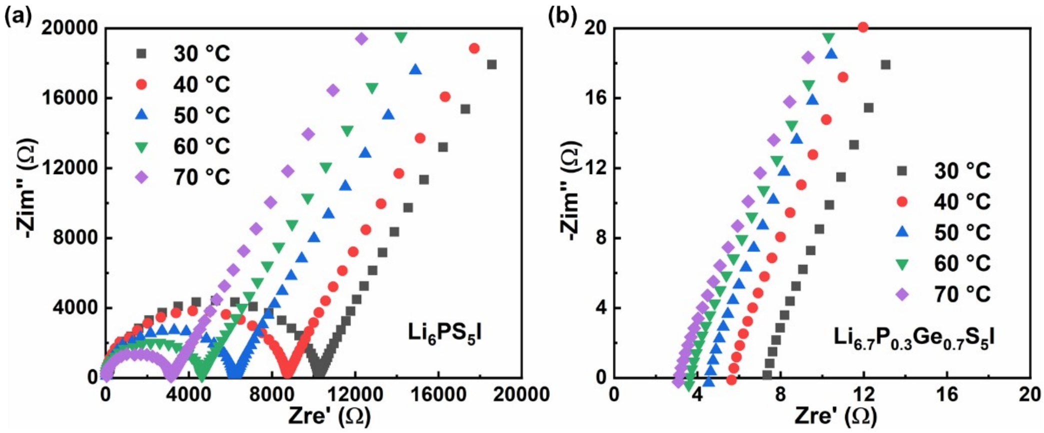

Figure S4. Complex EIS of **(a)** Li_6PS_5I and **(b)** $Li_{6.7}P_{0.3}Ge_{0.7}S_5I$ electrolytes at different temperatures.

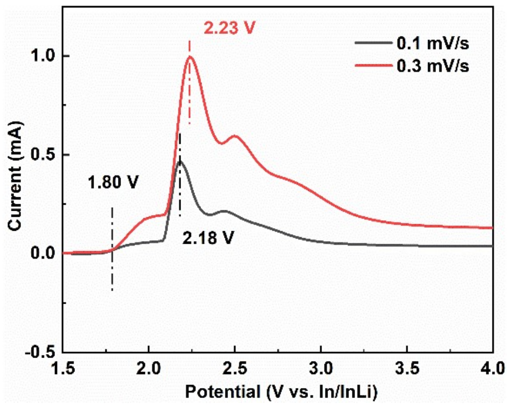

Figure S5. Comparison of $Li_{6.7}P_{0.3}Ge_{0.7}S_5I$@C/$Li_{6.7}P_{0.3}Ge_{0.7}S_5I$/In cells for CV tests with different scanning rates.

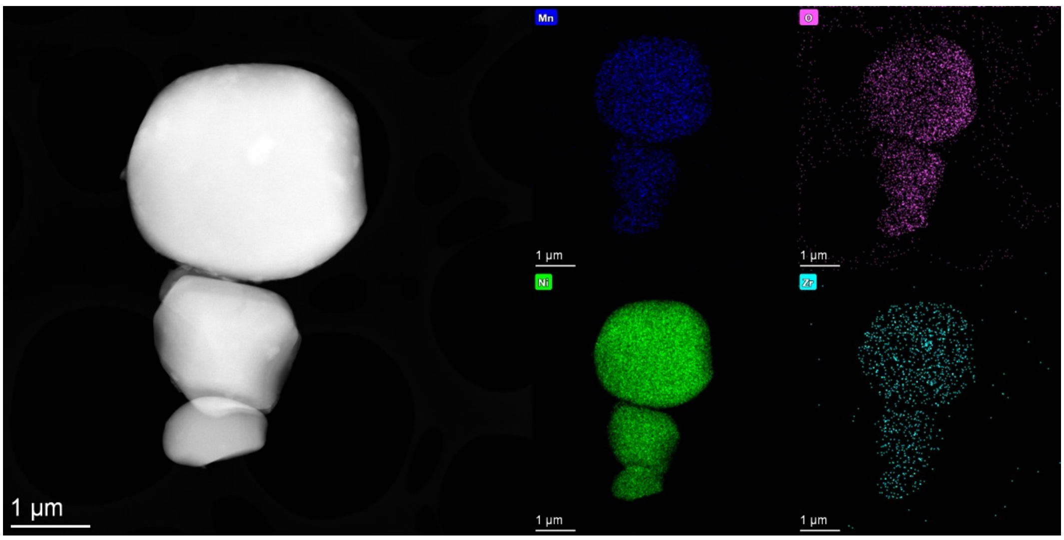

Figure S6. TEM and elemental mapping results for the LZO@NCM811particles.

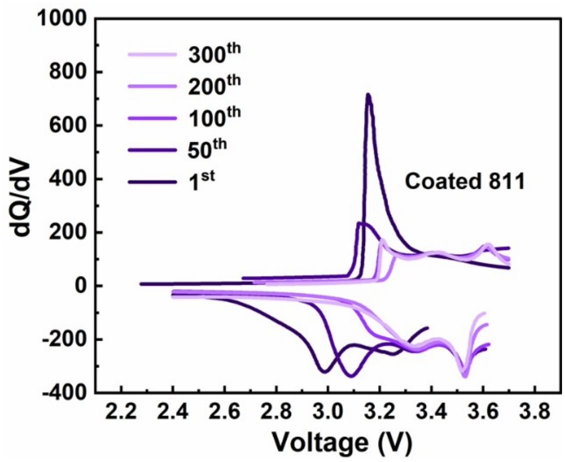

Figure S7. dQ/dV curses of the assembled LZO@NCM811/$Li_{6.7}P_{0.3}Ge_{0.7}S_5I$/In-Li battery at different cycles at room temperature.

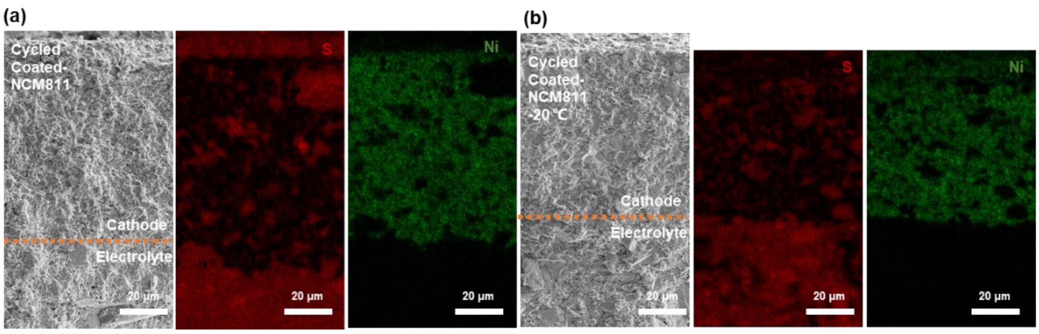

Figure S8. SEM images and the corresponding EDS mapping of the cross-section of the cycled LZO@NCM811/$Li_{6.7}P_{0.3}Ge_{0.7}S_5I$/In-Li batteries **(a)** at room temperature and **(b)** at -20 ^oC.

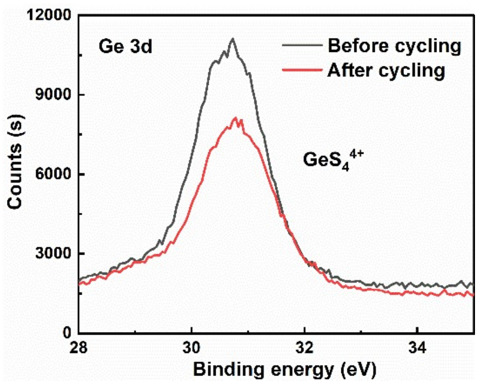

Figure S9. XPS results of the LZO@NCM811cathode for Ge 3d (e) before and (f) after cycling at -20 ^oC

Table S1. Crystallographic information of fitted $Li_{6.7}P_{0.3}Ge_{0.7}S_5I$ electrolytes.

λ1(Cu) = 1.54056, λ2(Cu) = 1.54439

a = 10.28625 Å, R_{wp} = 12.3 %

Atom	Wyckoff Site	x	y	z	Occ
Li0		0.02329	0.25	0.25	0.25
P1	4b	0	0	0.5	0.0125
Ge1	4b	0	0	0.5	0.0292
S1	16e	0.11784	0.11784	0.61784	0.16667
S2	4d	0.25	0.25	0.25	0.03957
S3	4a	0	0	0	0.00208
I1	4a	0	0	0	0.03957
I2	4d	0.25	0.25	0.25	0.00208

Table S2. The relevant parameters of different samples for the ionic conductivity calculation.

Samples	Thickness (cm)	Area (cm^2)	Resistance (Ω)	Ionic conductivity (mS/cm)
$Li_{6.7}P_{0.3}Ge_{0.7}S_5I$ (RT, 100mg)	0.0713	0.785	6.94	13.09
Li_6PS_5I (RT, 100mg)	0.073	0.785	9946	0.0093
$Li_{6.7}P_{0.3}Ge_{0.7}S_5I$ (RT, 200mg)	0.1481	0.785	14.56	12.96
$Li_{6.7}P_{0.3}Ge_{0.7}S_5I$ (-20℃, 100 mg)	0.0713	0.785	41.24	2.2