Supplementary Information

Cl- and Al-Doped Argyrodite Solid Electrolyte Li₆PS₅Cl for All-Solid-State Lithium Batteries with Improved Ionic Conductivity

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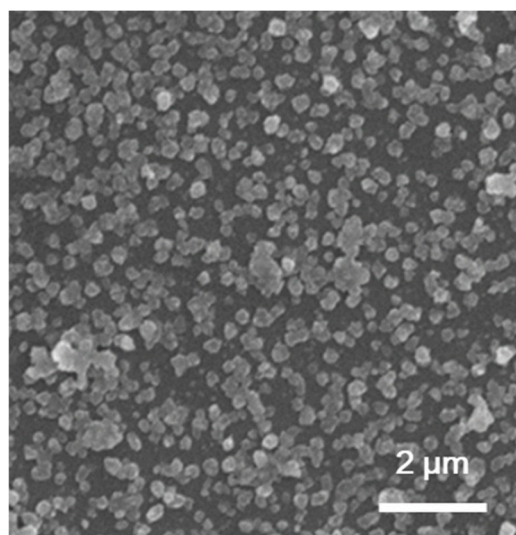[*] Correspondence: jungwoolee@pusan.ac.kr (J.W.L.); dulee@kitech.re.kr (D.H.L.)

Figure S1. FE-SEM images of Li₅.₄Al₀.₁PS₄.₇Cl₁.₃ electrolytes.
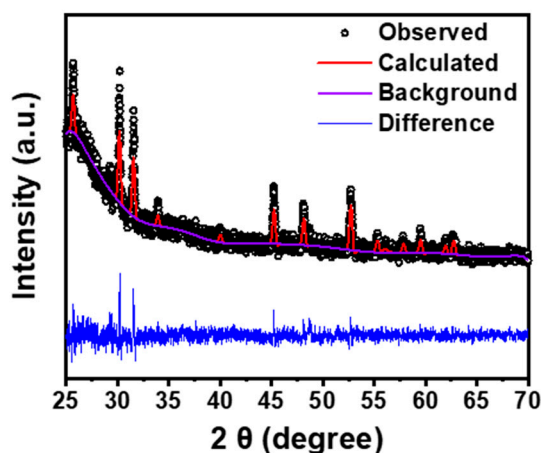
Figure S2. XRD pattern of and the corresponding Rietveld refinement of Li₅.₄Al₀.₁PS₄.₇Cl₁.₃ electrolyte.
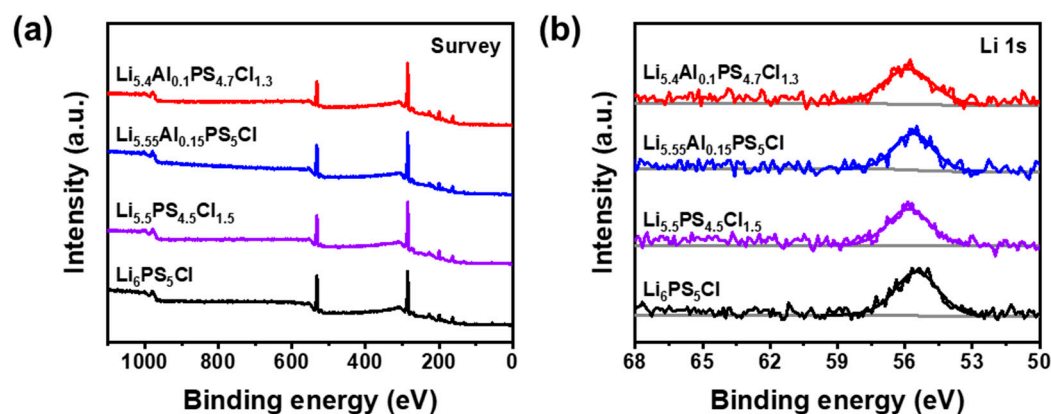
Figure S3. XPS spectra of Li_6PS_5Cl, $Li_{5.5}PS_{4.5}Cl_{1.5}$, $Li_{5.55}Al_{0.15}PS_5Cl$, and $Li_{5.4}Al_{0.1}PS_{4.7}Cl_{1.3}$ electrolytes for **(a)** Survey, and **(b)** Li 1s.
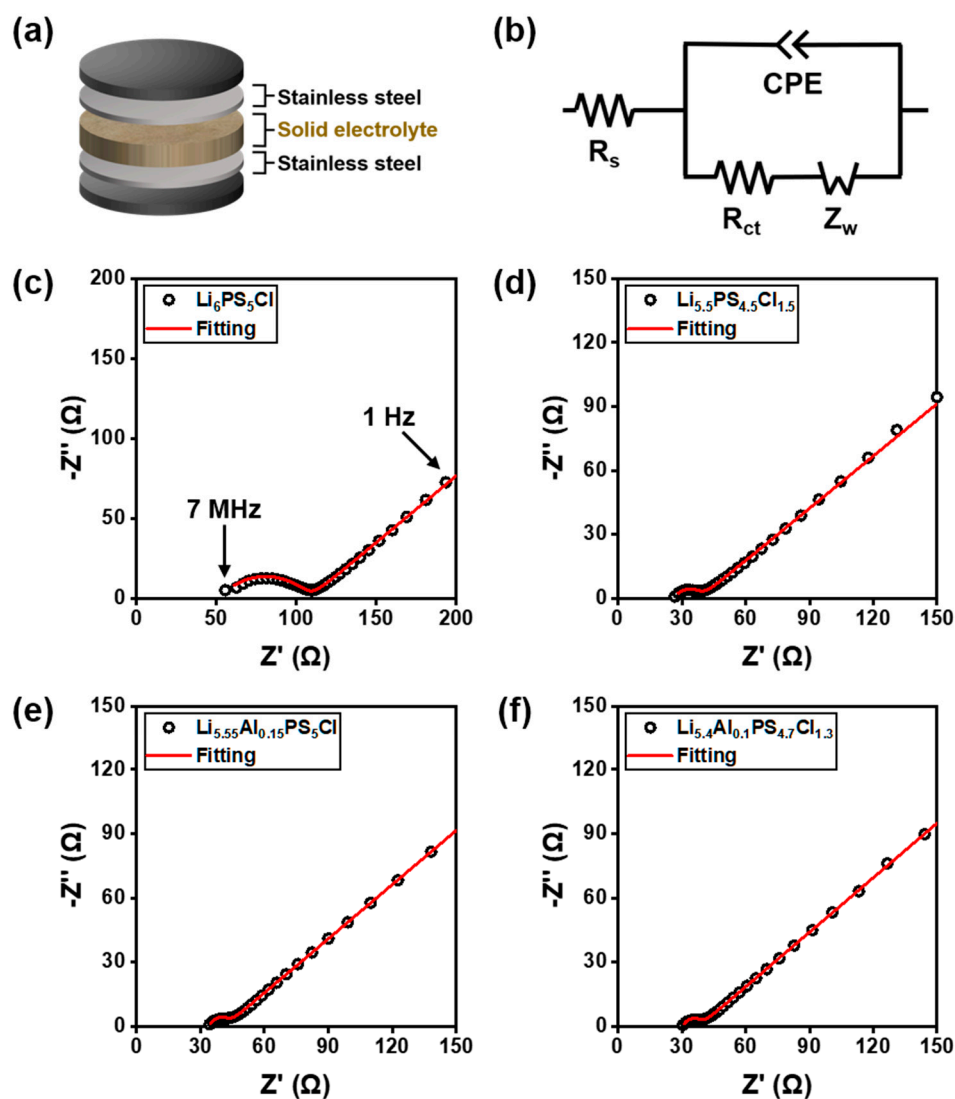

Figure S4. (a) Schematic diagram of cell geometry for impedance measurement. **(b)** Equivalent circuit for modeling the EIS data. Nyquist plots of **(c)** Li_6PS_5Cl, **(d)** $Li_{5.5}PS_{4.5}Cl_{1.5}$, **(e)** $Li_{5.55}Al_{0.15}PS_5Cl$, and **(f)** $Li_{5.4}Al_{0.1}PS_{4.7}Cl_{1.3}$ electrolytes, respectively. Experimental data (circles) was fitted with the simulated data from equivalent circuit modeling (lines).
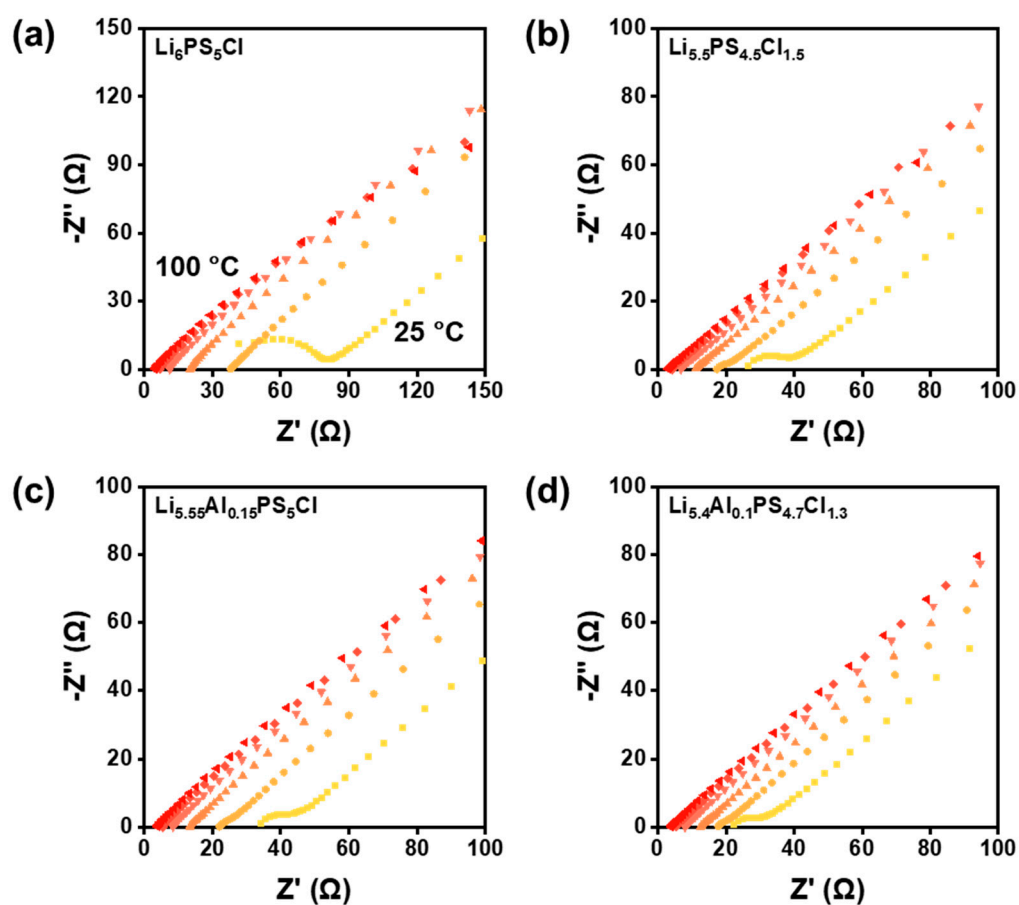
Figure S5. Nyquist plots of the **(a)** Li_6PS_5Cl, **(b)** $Li_{5.5}PS_{4.5}Cl_{1.5}$, **(c)** $Li_{5.55}Al_{0.15}PS_5Cl$, and **(d)** $Li_{5.4}Al_{0.1}PS_{4.7}Cl_{1.3}$ electrolytes measured from 25 to 100 °C, respectively.

Table S1. Rietveld refinements data of $Li_{5.4}Al_{0.1}PS_{4.7}Cl_{1.3}$ electrolyte.

space group $F\bar{4}3m$, a=10.28 Å, R_{wp}=19.51 %						
atom	site	x	y	z	OCC.	Uiso (Å²)
Li1	24g	0.25	0.25	0.36369	1	-2.62899
P1	4b	0.5	0	0	1	0.05134
S1	4a	0.25	0.25	0.25	1	-1.02402
S2	4c	0.12684	0.37316	0.87316	1	-0.05982
Cl1	4a	0	0	0	1	-0.11452