Supplementary Information

$Li_{1.6}AlCl_{3.4}S_{0.6}$: A Low-Cost and High-Performance Solid Electrolyte for Solid-State Batteries

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Keywords: solid electrolytes; chalcohalide; local disorder; solid-state NMR; energy storage; batteries

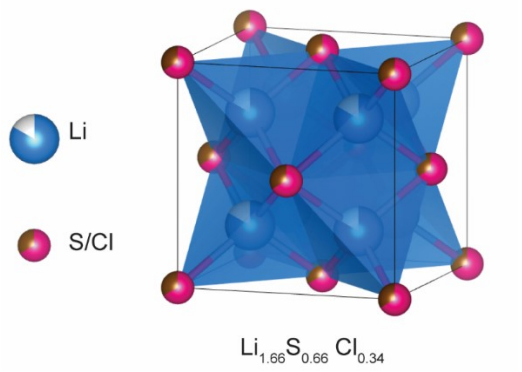

Figure S1. The structure of $Li_{1.66}S_{0.66}Cl_{0.34}$, a minor component observed from high-resolution X-ray diffraction and ^{6}Li MAS NMR in the $Li_{1.6}AlCl_{3.4}S_{0.6}$ sample.

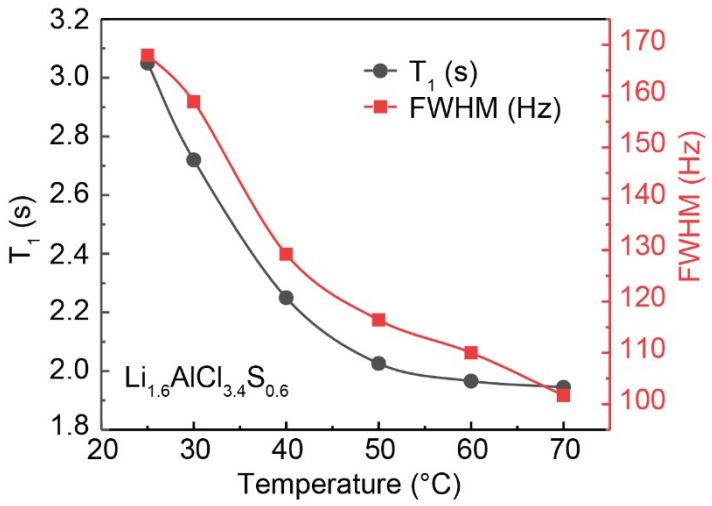

Figure S2. Variable-temperature ^{7}Li T_1 NMR relaxation time measurements for $Li_{1.6}AlCl_{3.4}S_{0.6}$ to probe Li^+ dynamics.

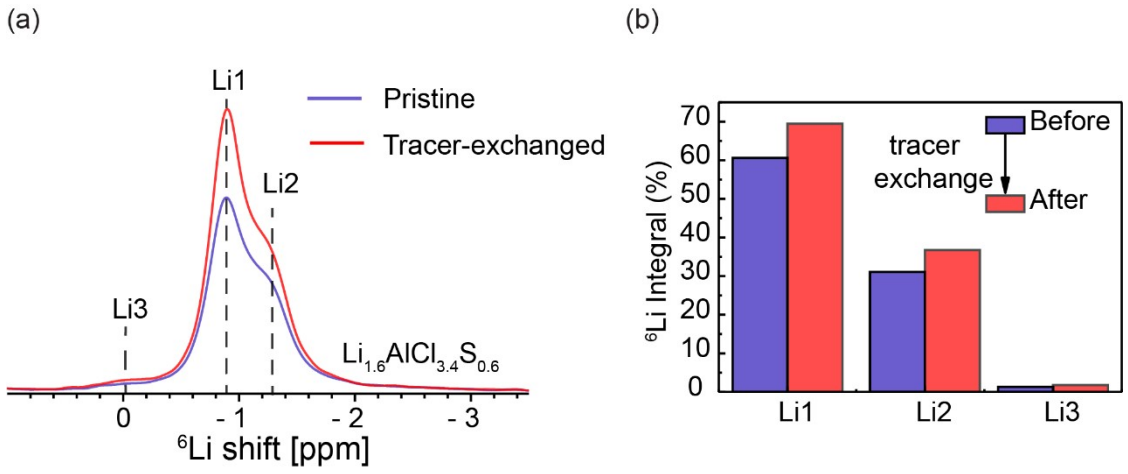

Figure S3. ^{6}Li→^{7}Li tracer-exchange NMR confirms the active role of the Li sites in $Li_{1.6}AlCl_{3.4}S_{0.6}$ (a) The comparison of the ^{6}Li MAS NMR spectra of pristine and tracer-exchanged (driven via electrochemical cycling) $Li_{1.6}AlCl_{3.4}S_{0.6}$; and (b) quantification of Li sites in $Li_{1.6}AlCl_{3.4}S_{0.6}$ before and after ^{6}Li→^{7}Li tracer-exchange.

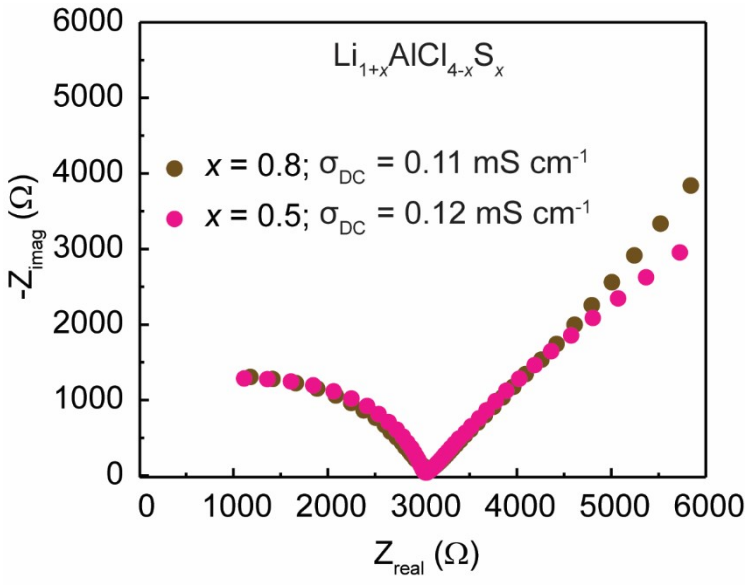

Figure S4. Nyquist plots of $Li_{1.5}AlCl_{3.5}S_{0.5}$ and $Li_{1.8}AlCl_{3.2}S_{0.8}$

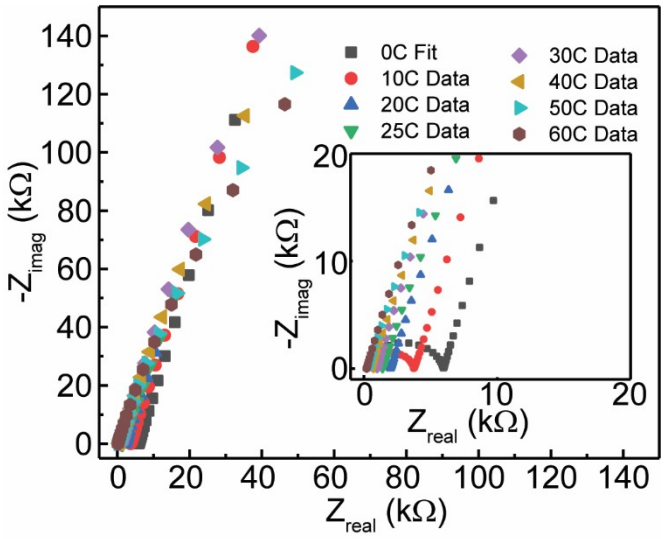

Figure S5. Representative Nyquist plots from variable-temperature electrochemical impedance spectroscopy of $Li_{1.6}AlCl_{3.4}S_{0.6}$.

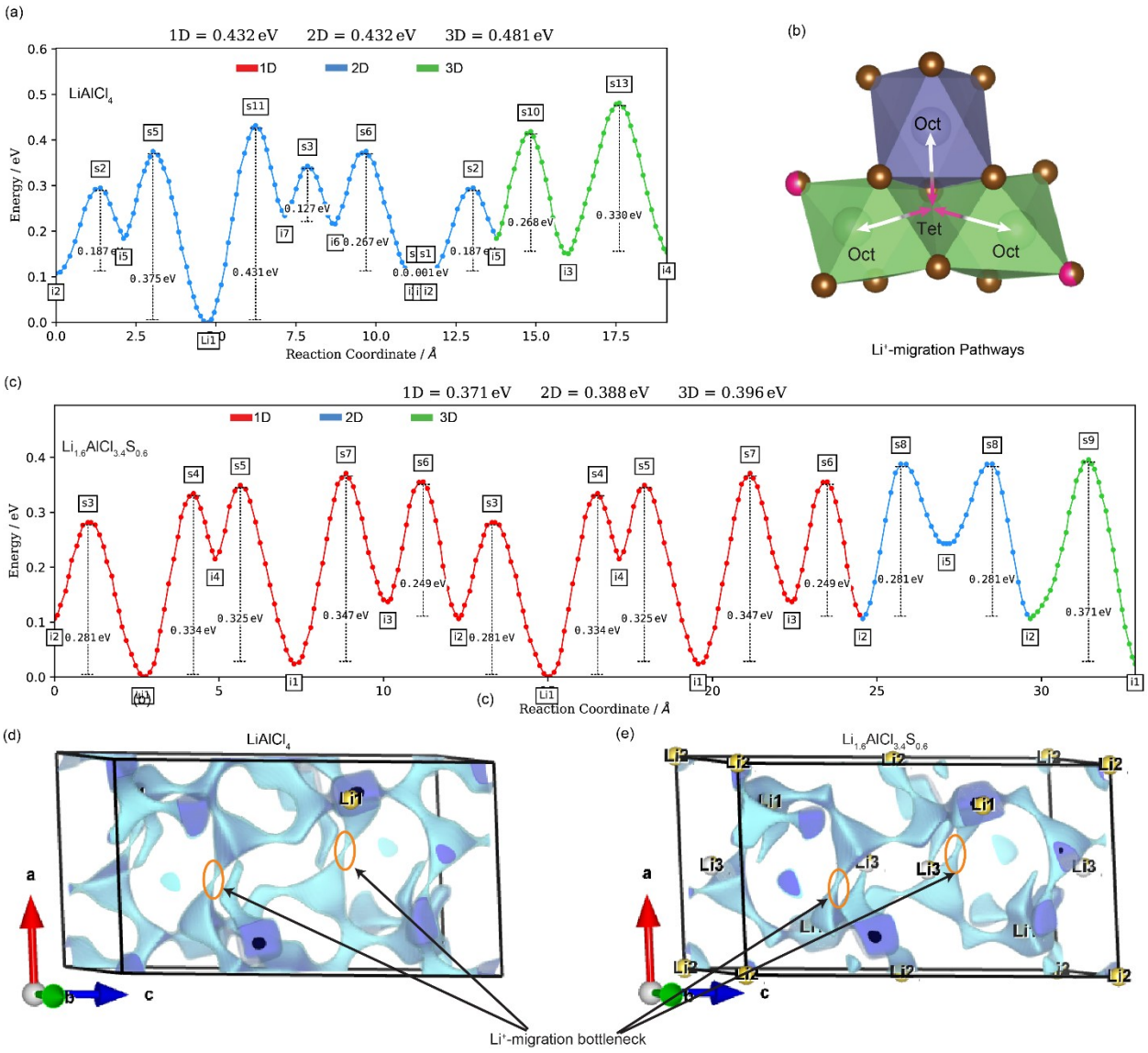

Figure S6. BVSE calculation and its energy landscape of (a) $LiAlCl_4$ (c) $Li_{1.6}AlCl_{3.4}S_{0.6}$. (b) Possible Li-ion migration pathways in $Li_{1.6}AlCl_{3.4}S_{0.6}$. The Li-isosurfaces of (d) $LiAlCl_4$ (e) $Li_{1.6}AlCl_{3.4}S_{0.6}$ structures.

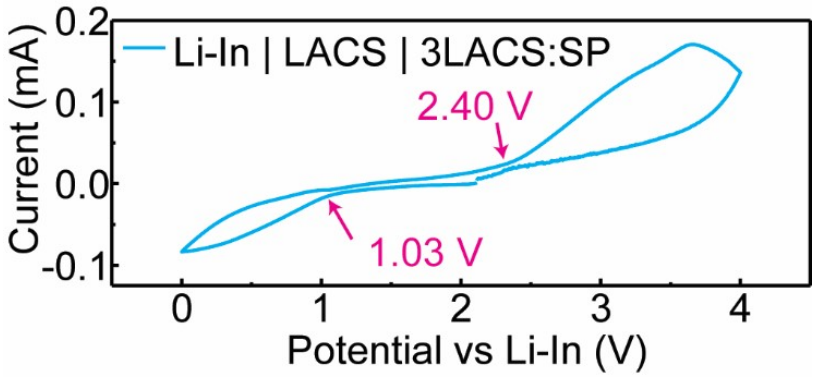

Figure S7. Cyclic voltammogram of $Li_{1.6}AlCl_{3.4}S_{0.6}$ using carbon black (Super P) as the electronic conductive medium in $3Li_{1.6}AlCl_{3.4}S_{0.6}$:SP. An electrochemical stability window of 1.03 V to 2.40 V is obtained for $Li_{1.6}AlCl_{3.4}S_{0.6}$.

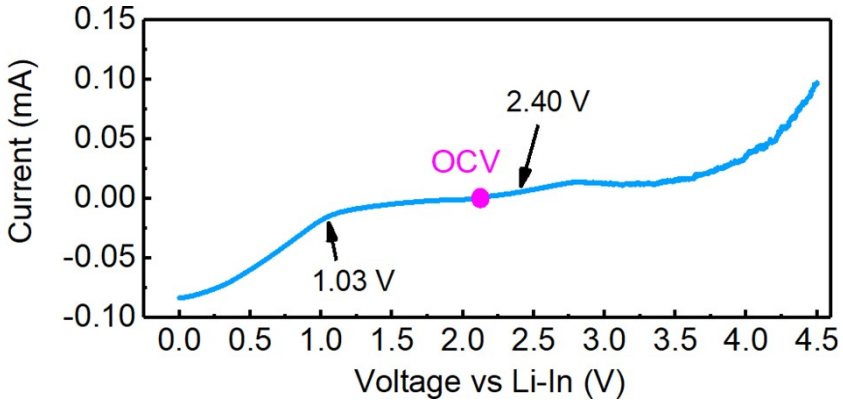

Figure S8. Linear Sweep voltammogram of $Li_{1.6}AlCl_{3.4}S_{0.6}$ using carbon black (Super P) as the electronic conductive medium in $3Li_{1.6}AlCl_{3.4}S_{0.6}$:SP. An electrochemical stability window of 1.03 V to 2.40 V is obtained for $Li_{1.6}AlCl_{3.4}S_{0.6}$.

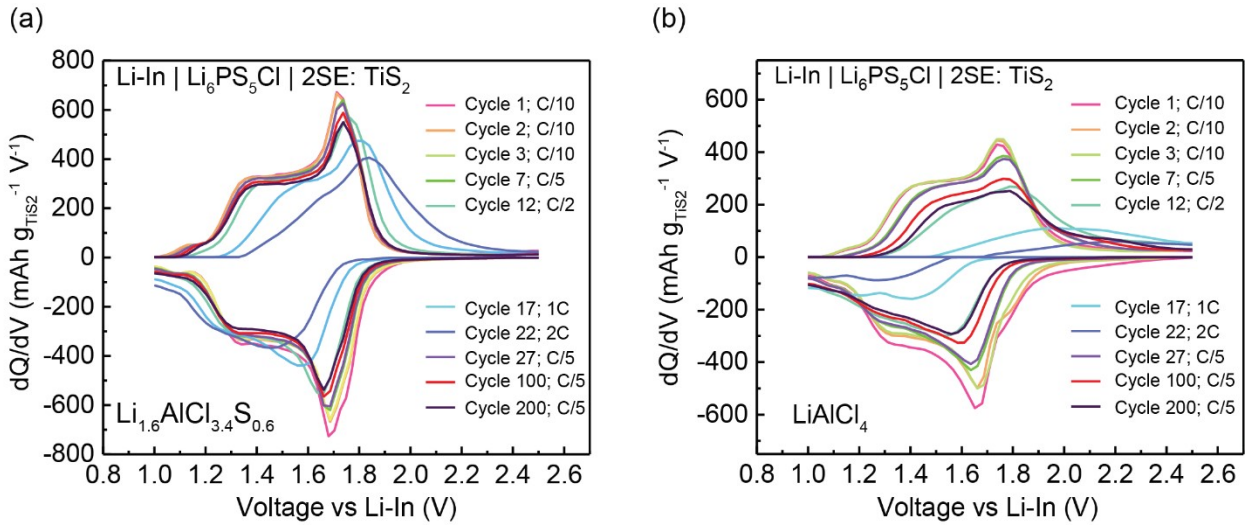

Figure S9. The differential capacity plots of Li-In | LPSCl | 2SE:TiS2 cells using (a) $Li_{1.6}AlCl_{3.4}S_{0.6}$ and (b) LiAlCl4 as the solid electrolyte (SE).

Table S1. Rietveld-refinement results of high-resolution X-ray diffraction data at room temperature for the mechanochemically synthesized $LiAlCl_4$.

$LiAlCl_4$ – Ball milled for 20 h.

Composition: $LiAlCl_4$

Lattice parameter: a = 7.0035(7), b = 6.5088(6), c = 13.0008(8), $\alpha = \gamma = 90.000$, $\beta = 93.34(7)$,

Unit-cell volume = 591.62(8) $Å^3$

Density of $LiAlCl_4$ = 1.973 g/cm^3

R_{wp} = 5.482 %, Space group P21/c, Impurity phases: 2.8 wt% of LiCl

Name	Atom	Wycoff position	Atomic coordinates			Occupancy	U_{iso}
			x	y	z		
Li1	Li	4e	0.176(3)	1.009(4)	0.380(2)	1	0.038(6)
Al1	Al	4e	0.7098(8)	0.329(1)	0.9006(5)	1	0.039(2)
Cl1	Cl	4e	0.6944(8)	0.1834(8)	0.0459(5)	1	0.045(2)
Cl2	Cl	4e	0.8085(8)	0.6225(8)	0.9265(5)	1	0.036(2)
Cl3	Cl	4e	0.9232(8)	0.1819(9)	0.8136(5)	1	0.038(2)
Cl4	Cl	4e	0.4469(8)	0.3062(8)	0.8127(5)	1	0.035(2)

Table S2. Rietveld-refinement results of the high-resolution X-ray diffraction data for the mechanochemically synthesized Li_2AlCl_3S.

Refined composition : $Li_{1.6}AlCl_{3.4}S_{0.6}$

Lattice parameter: a = 7.0207(8), b = 6.5206(8), c = 13.004(2), a = g = 90.0000, b = 93.43(1),

Unit-cell volume = 594.26(8) $Å^3$;

Density of $Li_{1.6}AlCl_{3.4}S_{0.6}$= 1.984 g cm^{-3}

R_{wp} = 2.85 %, Space group *P2₁/c*

Impurity phases: 14 wt% of Li_2S and 10 wt% of $Li_{1.66}S_{0.66}Cl_{0.34}$

Name	Atom	Wycoff position	Atomic coordinates			Occupancy	U_{iso}
			x	y	z		
Li1	Li	4e	0.198(1)	0. 035(1)	0.349(6)	1	0.14(4)
Li2	Li	2a	0	0	0	1(4)	0.08(2)
Li3	Li	2a	0.5	0	0.5	0.17(3)	0.59(7)
Al2	Al	4e	0.728(2)	0.335(2)	0.898(1)	1	0.057(3)
Cl1	Cl	4e	0.685(2)	0.200(2)	0.043(1)	1	0.025(5)
Cl2	Cl	4e	0.955(2)	0.164(2)	0.809(1)	1	0.032(3)
Cl3	Cl	4e	0.812(2)	0.622(1)	0.925(1)	1	0.032(3)
Cl4	Cl	4e	0.464(2)	0.296(2)	0.806(1)	0.519(6)	0.065(6)
S4	S	4e	0.464(2)	0.296(2)	0.806(1)	0.481(6)	0.065(6)

Table S3. Rietveld-refinement results of the $Li_{1.66}S_{0.66}Cl_{0.34}$-phase present in Li_2AlCl_3S.

Refined composition: $Li_{1.66}S_{0.66}Cl_{0.34}$

Lattice parameter: a = 5.7138(7), a = b = g = 90.0000,

Unit-cell volume = 186.64(5) $Å^3$;

Density of $Li_{1.66}S_{0.66}Cl_{0.34}$ = 1.592 g/cm^3

Space group *Fm-3m*

Name	Atom	Wycoff position	Atomic coordinates			Occupancy	U_{iso}
			x	y	z		
Li	Li	8c	0.25	0.25	0.25	0.83(1)	0.015(5)

S	S	4a	0	0	0	0.66(1)	0.012(1)
Cl	Cl	4a	0	0	0	0.34(2)	0.012(2)

Table S4. Li (%) distribution in various components in $LiAlCl_4$ and $Li_{1.6}AlCl_{3.4}S_{0.6}$ from ^6Li NMR analysis.

Sample	^6Li (%)					
	Li1	Li2	Li3	Li_2S	LiCl	$Li_{1.66}S_{0.66}Cl_{0.34}$
$LiAlCl_4$	92.5	-	-	-	7.5	-
$Li_{1.6}AlCl_{3.4}S_{0.6}$	60.6	31.1	1.3	3.1	-	3.9