Supporting Information

$Li_{3.6}In_7S_{11.8}Cl$: An Air- and Moisture-Stable Superionic Conductor

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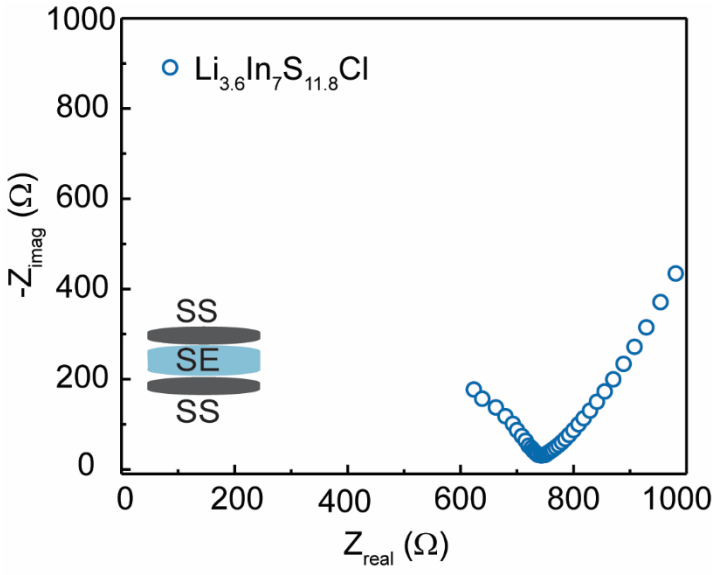
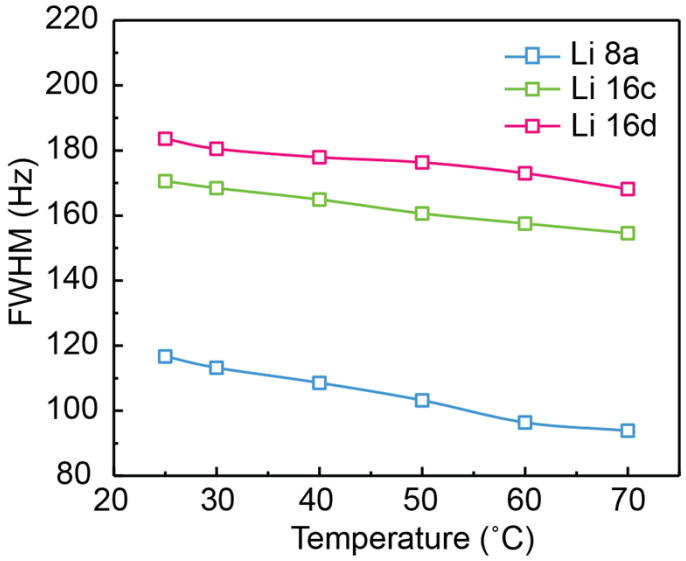
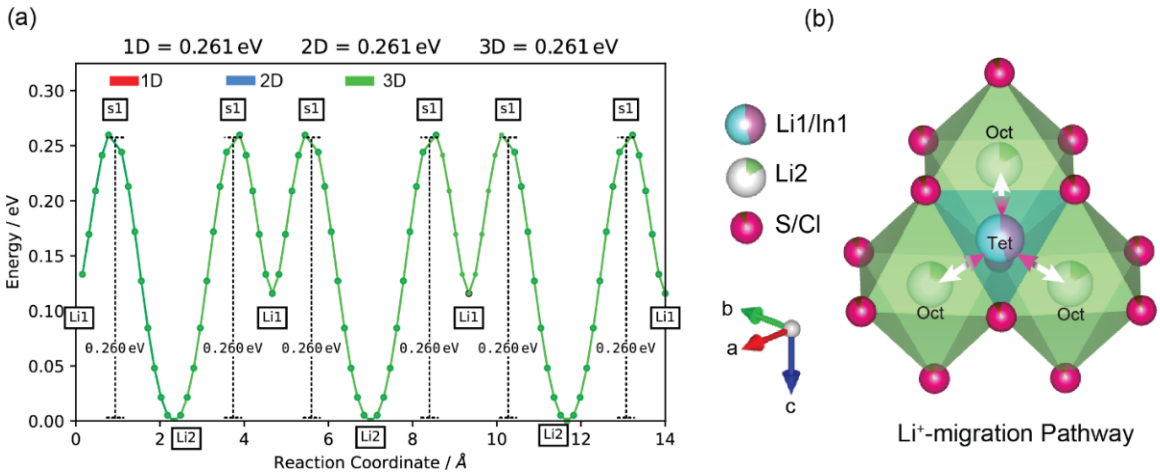


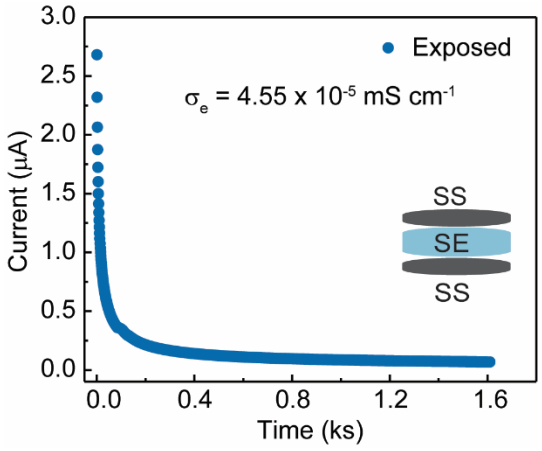
Supplementary Figure 1*:* The Nyquist plot of nominal $Li_{3.6}In_7S_{11.8}Cl$, yielding an ionic conductivity of 0.8 mS cm^{-1} at 25 ºC.



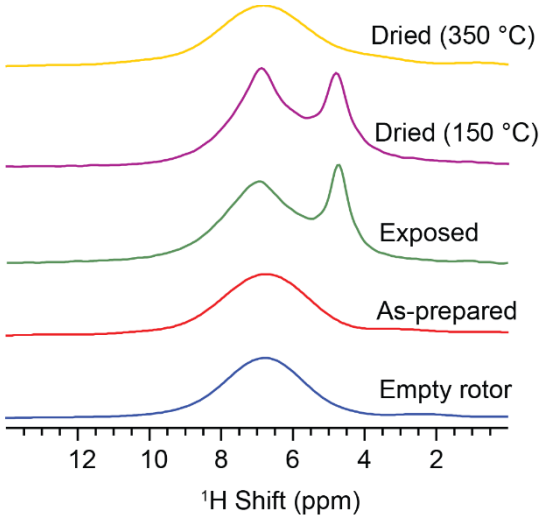
Supplementary Figure 2. ^{7}Li NMR peak line-width of $Li_{3.6}In_7S_{11.8}Cl$ as a function of temperature.



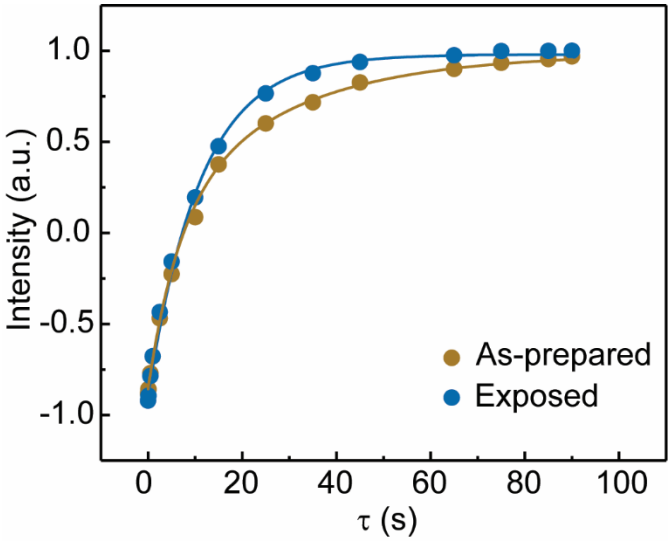
Supplementary Figure 3. Lithium-ion migration pathway analysis of $Li_{3.6}In_7S_{11.8}Cl$ using bond valance site energy (BVSE). (a) Migration barrier energy as a function of reaction coordinates obtained from BVSE calculation. (b) Lithium migration pathway illustration, oct-tet-oct, using the structure obtained from refining the high-resolution XRD pattern.



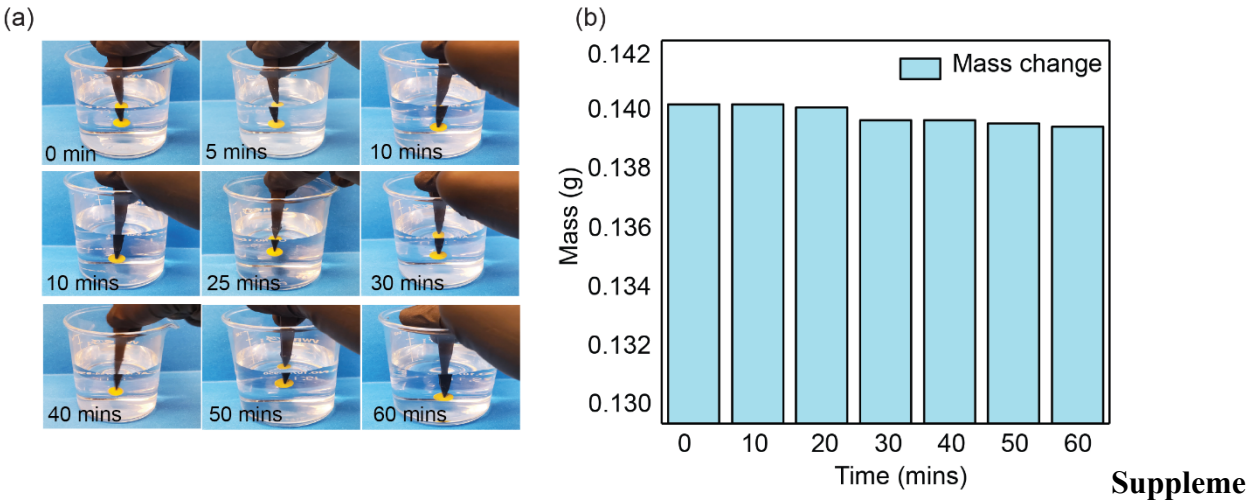
Supplementary Figure 4. DC polarization curve of the moisture-exposed $Li_{3.6}In_7S_{11.8}Cl$ for the cell set up SS|SE|SS for determining the electronic conductivity.



Supplementary Figure 5. ^{1}H NMR of the as-prepared, air/moisture-exposed, and dried $Li_{3.6}In_7S_{11.8}Cl$.



Supplementary Figure 6. ^{7}Li NMR T_1 inversion-recovery curve for the as-prepared and moisture-exposed $Li_{3.6}In_7S_{11.8}Cl$



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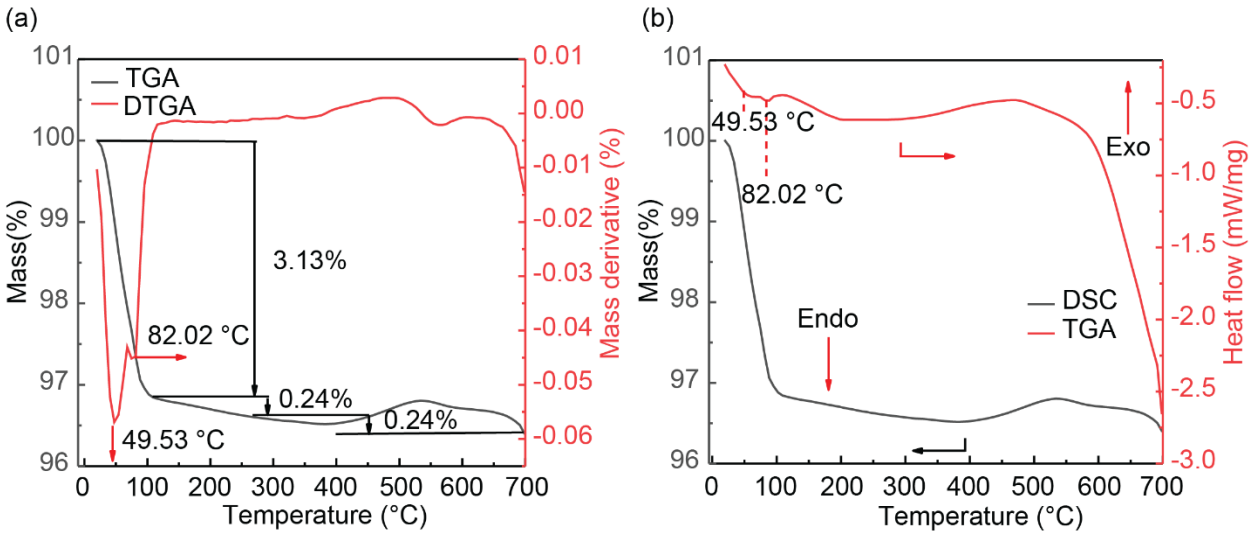
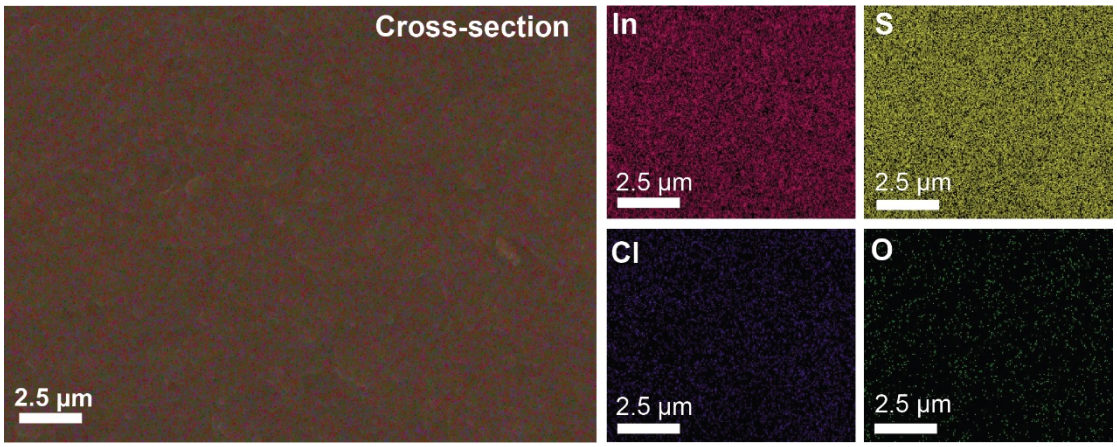
ntary Figure 7. Stability test of a $Li_{3.6}In_7S_{11.8}Cl$ pellet against water.



Supplementary Figure 8. (a) TGA–DTGA curve for moisture-exposed $Li_{3.6}In_7S_{11.8}Cl$ (b) TGA–DSC curve for moisture-exposed $Li_{3.6}In_7S_{11.8}Cl$.



Supplementary Figure 9. SEM image and EDS elemental mapping of In, S, Cl, and O for the cross-section of $Li_{3.6}In_7S_{11.8}Cl$ pellet dried at 350 ºC.

Table S1. Rietveld-refinement results of high-resolution X-ray diffraction data for $Li_4In_7S_{12}Cl$.

Refined composition: $Li_{3.6}In_7S_{11.8}Cl$

Lattice parameter: a = b = c = 10.78014(5), α = β = γ = 90.000,

Unit-cell volume = 1252.776(7) $Å^3$

Density of $Li_{3.6}In_7S_{11.8}Cl$ = 4.127 g/cm^3

R_{wp} = 7.675 %, Space group *Fd-3m*, Impurity phase: 6.6 wt% of $LiInS_2$

Name	Atom	Wycoff position	Atomic coordinates			Occupancy	U_{iso}
			x	y	z		
Li1	Li	8a	0.125	0.125	0.125	0.540(3)	0.017(4)
Li2	Li	16c	0	0	0	0.161(5)	0.016(3)
Li3	Li	16d	0.5	0.5	0.5	0.132(4)	0.016(4)
In1	In	8a	0.125	0.125	0.125	0.460(3)	0.017(4)
In2	In	16d	0.5	0.5	0.5	0.868(4)	0.016(4)
S1	S	32e	0.258(3)	0.258(3)	0.258(4)	0.926(3)	0.022(2)
Cl1	Cl	32e	0.258(3)	0.258(3)	0.258(4)	0.074(3)	0.022(2)

Table S2. SEM-EDX elemental analysis of $Li_{3.6}In_7S_{11.8}Cl$ pellet.

Element	Mole ratio (SXRD)	Mole ratio (SEM-EDX)
In	7.00	6.80
S	11.80	11.87
Cl	1.00	1.00

Table S3. ^{6}Li NMR shift, calculated using CASTEP.

Sample	Chemical Shift [ppm]	η	C_q (MHz)
$LiInS_2$	-0.8	0.58	-0.05

Table S4. Li (%) distribution in various components in $Li_{3.6}In_7S_{11.8}Cl$ from ^{6}Li NMR analysis.

Sample	^{6}Li (%)			
	Li8a	Li16c	Li16d	Impurity
$Li_{3.6}In_7S_{11.8}Cl$ (AP)	37.4	29.1	24.5	9.00
$Li_{3.6}In_7S_{11.8}Cl$ (E)	31.9	32.0	22.3	13.8

Table S5. ^{6}Li line width of as-prepared-, exposed-, and dried- $Li_{3.6}In_7S_{11.8}Cl$.

Sample	^{6}Li, Line width [Hz]		
	Li8a	Li16c	Li16d
$Li_{3.6}In_7S_{11.8}Cl$ (As-prepared)	55.7	56.5	51.7
$Li_{3.6}In_7S_{11.8}Cl$ (Exposed)	45.3	43.8	30.8
$Li_{3.6}In_7S_{11.8}Cl$ (Dried)	59.4	64.6	52.4

Table S6. The resistance and fitted capacitance values from the EIS analysis on as-prepared (AP) and moisture-exposed (E) $Li_{3.6}In_7S_{11.8}Cl_{.5}$at 25 ºC. The fitted capacitances agree with the bulk and grain boundary contribution (GB) capacitance range.

Sample	R_1 (Bulk) [Ω]	C_1 (Bulk) [pF]	R_2 (GB) [Ω]	C_2 (GB) [nF]
$Li_{3.6}In_7S_{11.8}Cl$ (AP)	780.2	0.89	171.7	0.56
$Li_{3.6}In_7S_{11.8}Cl$ (E)	197.8	0.31	46.6	0.67