

Supplementary Information for

All-solid-state batteries designed for operation under extreme cold conditions

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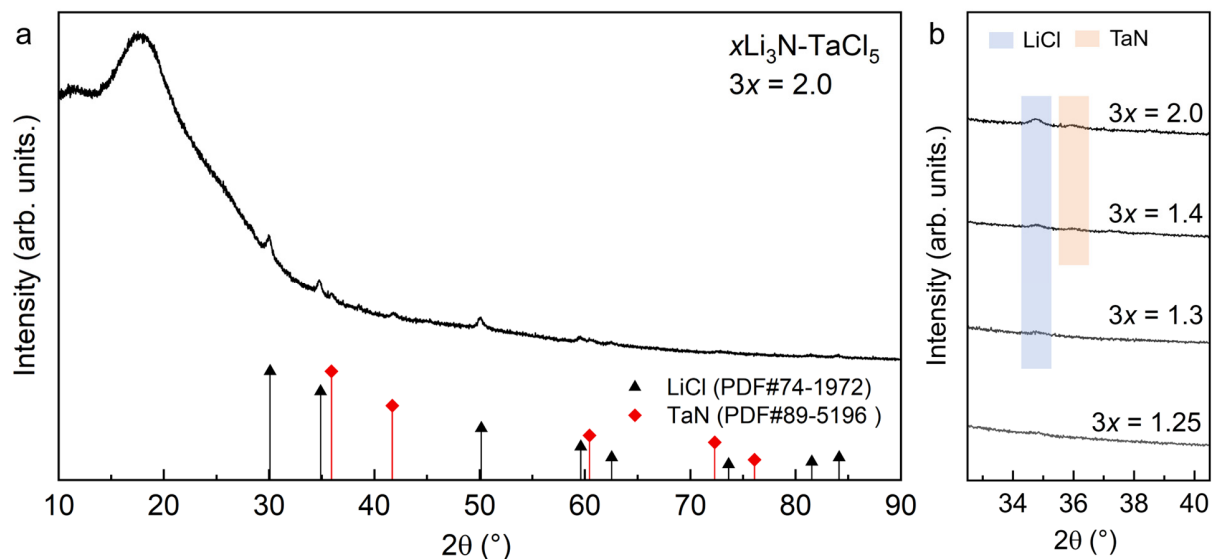
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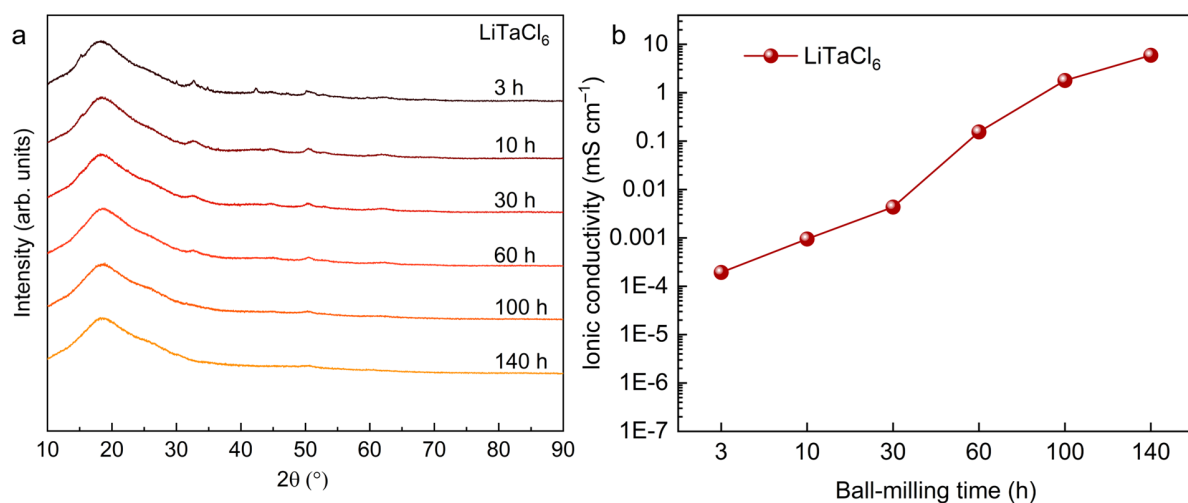
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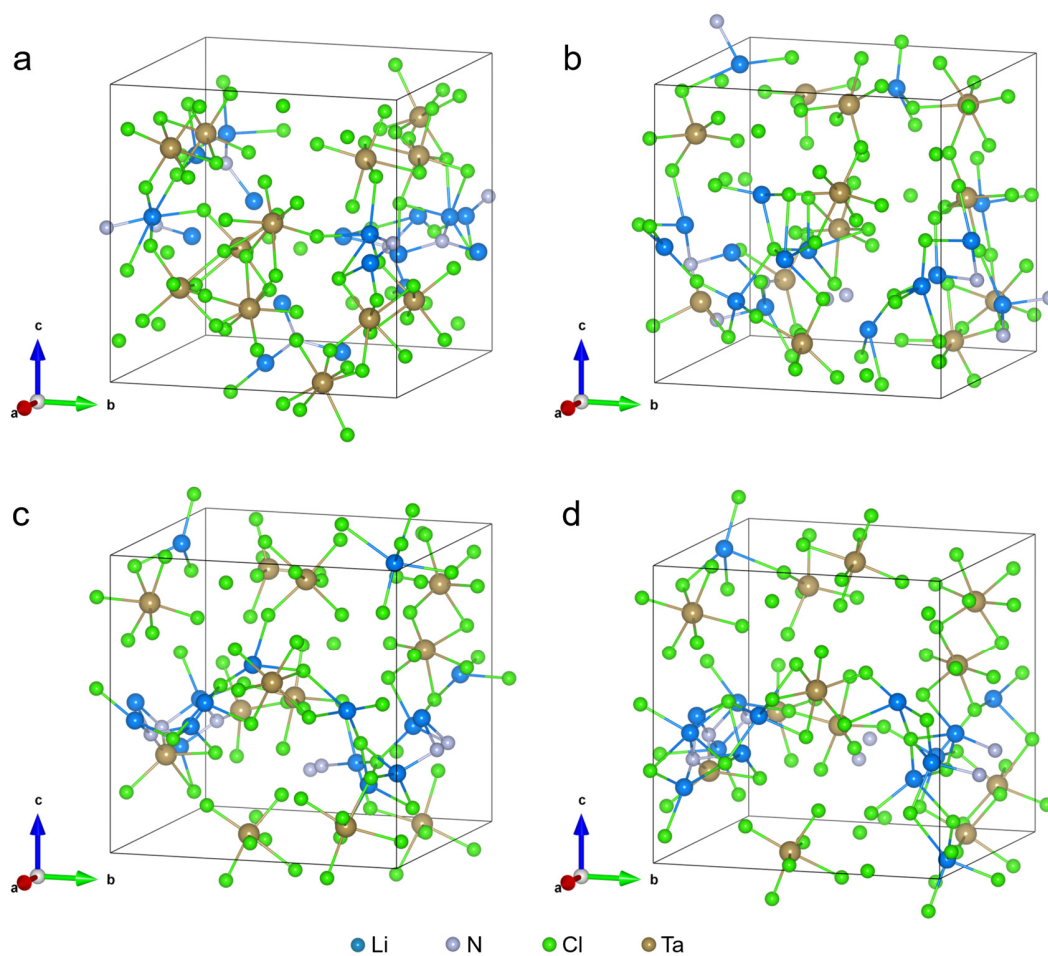
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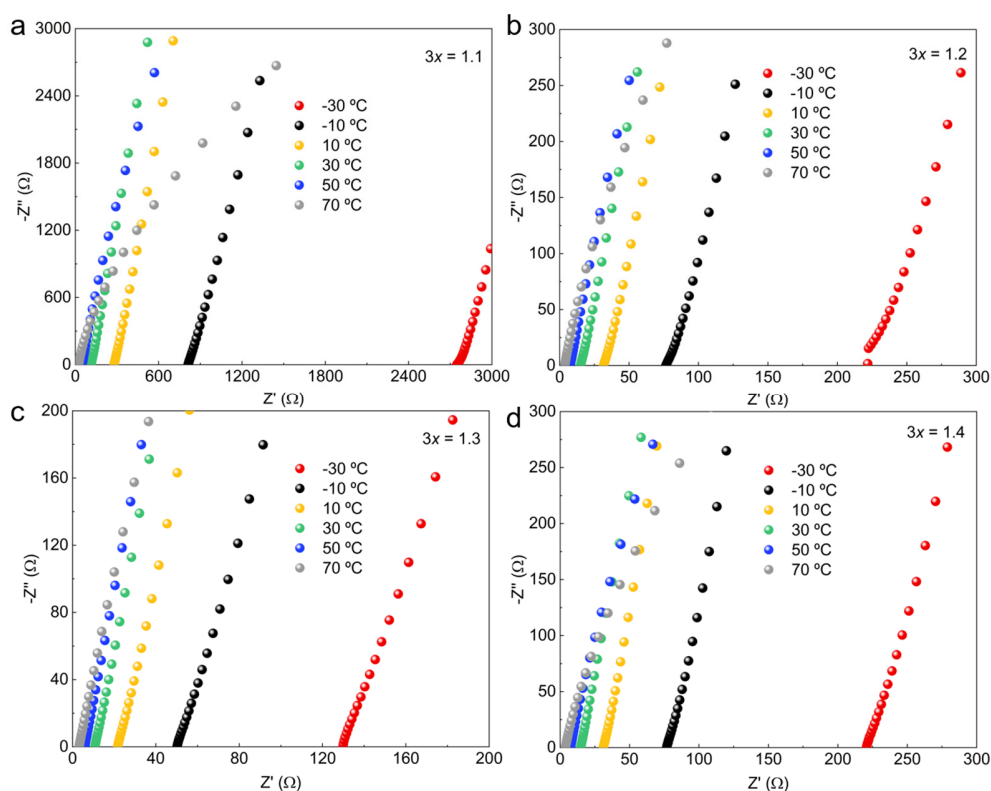
Supplementary Fig. 1 | XRD patterns of the amorphous $x\text{Li}_3\text{N-TaCl}_5$. (a) XRD patterns of the amorphous $x\text{Li}_3\text{N-TaCl}_5$ ($3x = 2$) at 30 hours of ball-milling. (b) XRD patterns of $x\text{Li}_3\text{N-TaCl}_5$ magnified within the 2θ range of 32.5° – 40.5° to show the impurities of LiCl and TaN.



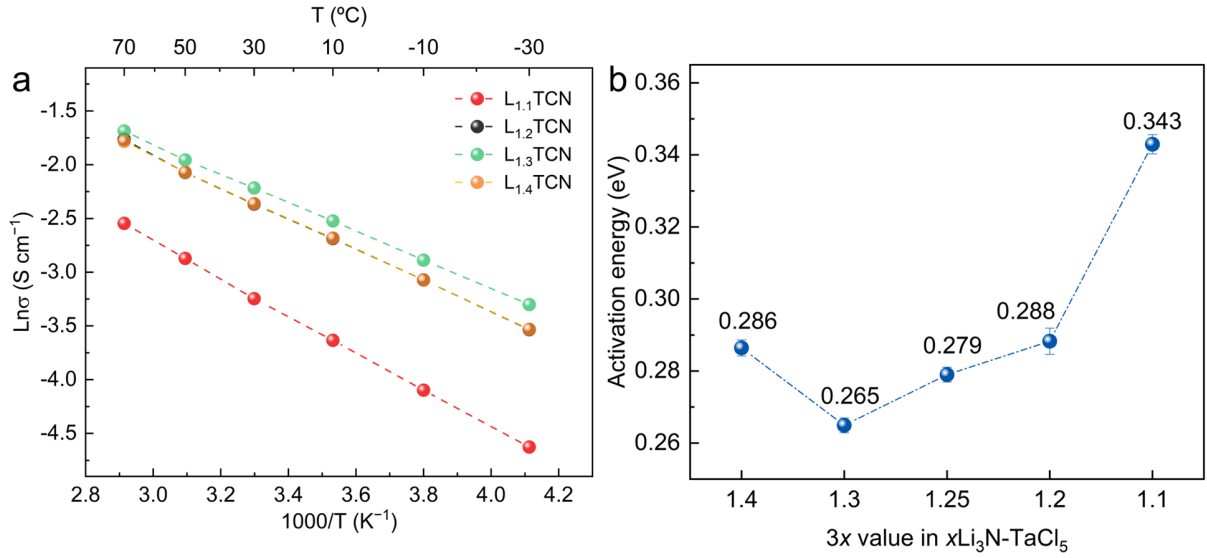
Supplementary Fig. 2 | XRD patterns and ionic conductivity of the as-prepared LiTaCl_6 under different ball-milling conditions. (a) XRD patterns of the as-prepared LiTaCl_6 at different ball-milling times with a constant rotation speed of 500 rpm. (b) Ionic conductivities of the as-prepared LiTaCl_6 at different ball-milling times with a constant rotation speed of 500 rpm at 25 °C. The amorphization degree of the sample increased with longer ball milling times, resulting in a corresponding increase in ionic conductivity. The ionic conductivity of LiTaCl_6 SSE increases from 0.19 to 5.96 mS cm^{-1} at RT, as the ball-milling time ranges from 3 to 140 h.



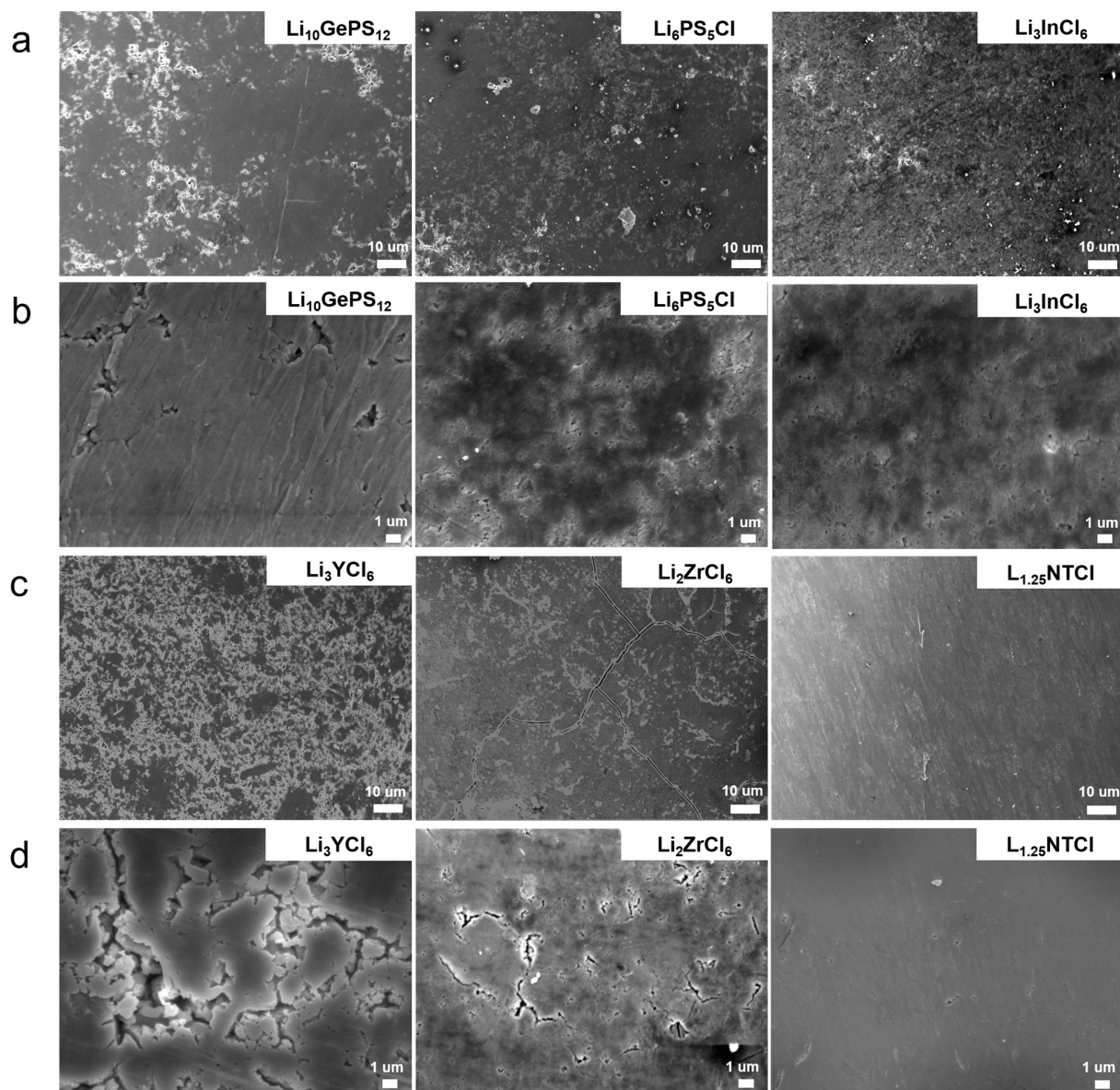
Supplementary Fig. 3 | Structure and coordination of as-prepared $x\text{Li}_3\text{N-TaCl}_5$ obtained from ab-initio molecular dynamics simulations. (a) The original structure before melting by heating. (b) The structure after melting by heating to 1200 K using the NVT ensemble for 4 ps. (c) The structure after quenching from 1200 K to 300 K. (d) The structure after using the NVT ensemble at 300 K for 4 ps.



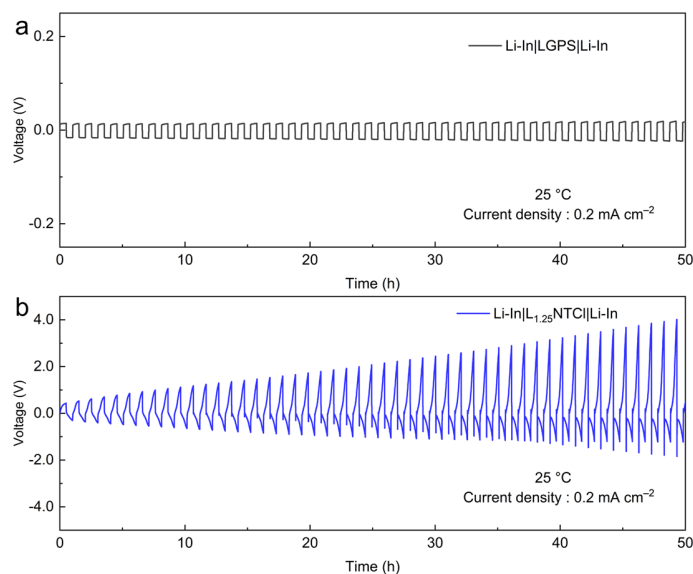
Supplementary Fig. 4 | Nyquist plots of amorphous $x\text{Li}_3\text{N}-\text{TaCl}_5$. (a-d) Nyquist plots of $x\text{Li}_3\text{N}-\text{TaCl}_5$ at different temperatures with various x values: (a) $3x = 1.1$, (b) $3x = 1.2$, (c) $3x = 1.3$, and (d) $3x = 1.4$.



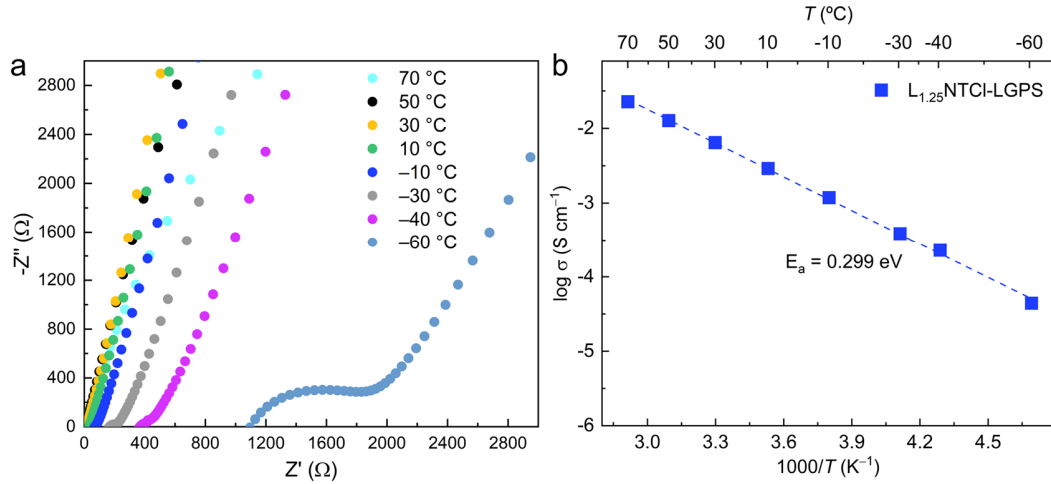
Supplementary Fig. 5 | Arrhenius plots and activation energy values for $x\text{Li}_3\text{N-TaCl}_5$. (a) Arrhenius plots of amorphous $x\text{Li}_3\text{N-TaCl}_5$ ($3x = 1.1, 1.2, 1.3$ and 1.4) in the temperature range from -30 to 70 °C. (b) The activation energies of amorphous $x\text{Li}_3\text{N-TaCl}_5$ and the error bars represent the standard deviation calculated by linearly fitting the Arrhenius ionic conductivity plots in Supplementary Fig. 6a and Fig. 3f of main text. It is important to note that the discrepancy between the ionic conductivities and activation energies of amorphous $x\text{Li}_3\text{N-TaCl}_5$ may be ascribed to the influence of the preexponential parameter A , as described in the Arrhenius formula: $\sigma = A \exp(-E_a/k_B T)$, where σ is the ionic conductivity, A represents the preexponential parameter, E_a signifies the activation energy, T stands for absolute temperature, and k_B is the Boltzmann constant.



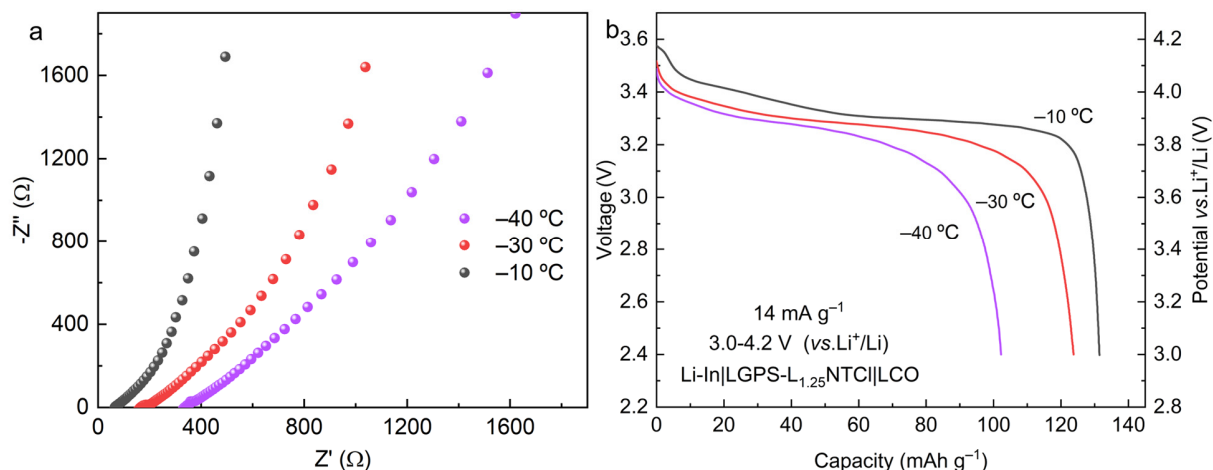
Supplementary Fig. 6 | SEM images of $\text{Li}_{10}\text{GePS}_{12}$, $\text{Li}_6\text{PS}_5\text{Cl}$, Li_3InCl_6 , Li_3YCl_6 , Li_2ZrCl_6 and $\text{L}_{1.25}\text{NTCl}$ SSEs. (a–d) SEM images with low (a, c) and high (b, d) magnifications for the cold-pressed pellets of $\text{Li}_{10}\text{GePS}_{12}$, $\text{Li}_6\text{PS}_5\text{Cl}$, Li_3InCl_6 , Li_3YCl_6 , Li_2ZrCl_6 , and $\text{L}_{1.25}\text{NTCl}$. $\text{Li}_{10}\text{GePS}_{12}$, $\text{Li}_6\text{PS}_5\text{Cl}$, and Li_3InCl_6 were purchased from MTI Corp., and Li_3YCl_6 and Li_2ZrCl_6 were obtained by ball-milling at a speed of 500 rpm for 45 h using a planetary mill (Pulverisette 7, FRITSCH). For SEM measurements, SSE pellets were fabricated by cold pressing 100 mg of SSE powder at a pressure of 2 tons for 30 seconds using a stainless-steel mold with an inner diameter of 7 mm. All processes were carried out in an Ar-filled glove box (H_2O , $\text{O}_2 < 0.1$ ppm).



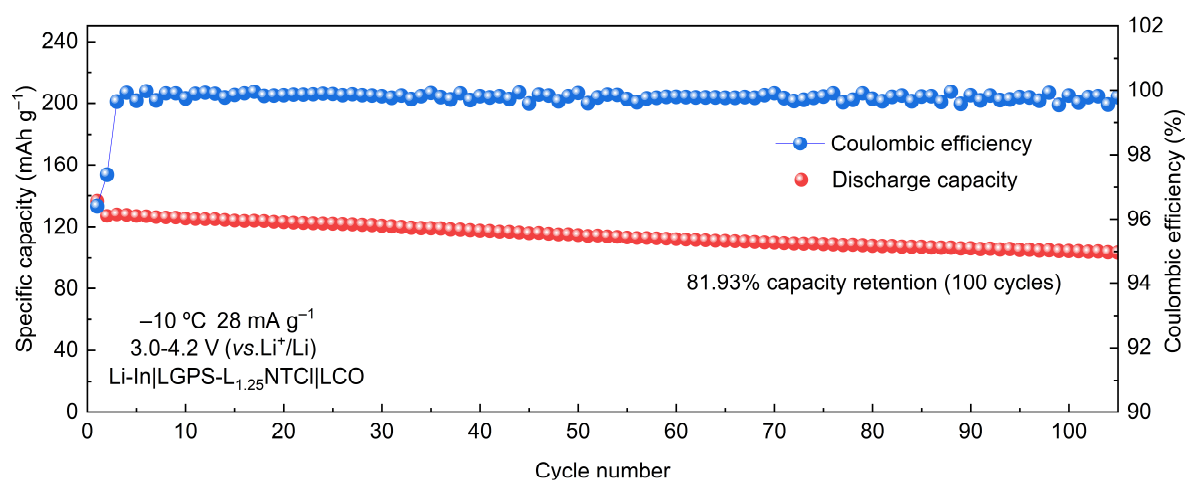
Supplementary Fig. 7 | The electrochemical performance of Li-In symmetric cell based on LGPS and L_{1.25}NTCl SSEs. (a) The galvanostatic cycling of Li-In|LGPS|Li-In symmetric cell at 25 °C. **(b)** The galvanostatic cycling of Li-In|L_{1.25}NTCl|Li-In symmetric cell at 25 °C. The assembly process involves several steps: Initially, approximately 100 mg of SSE powder was pressed into a pellet within a PEEK mold (ϕ 10 mm) at a pressure of 3 tons for 1 min. Subsequently, In foils (ϕ 10 mm) were applied to both sides of the SSE pellet, followed by Li foils (ϕ 10 mm) affixed to the In foils at a Li/In weight ratio of 1:40. Finally, the entire Li-In|SSE|Li-In cell assembly was pressed at 0.2 tons to prepare it for electrochemical tests.



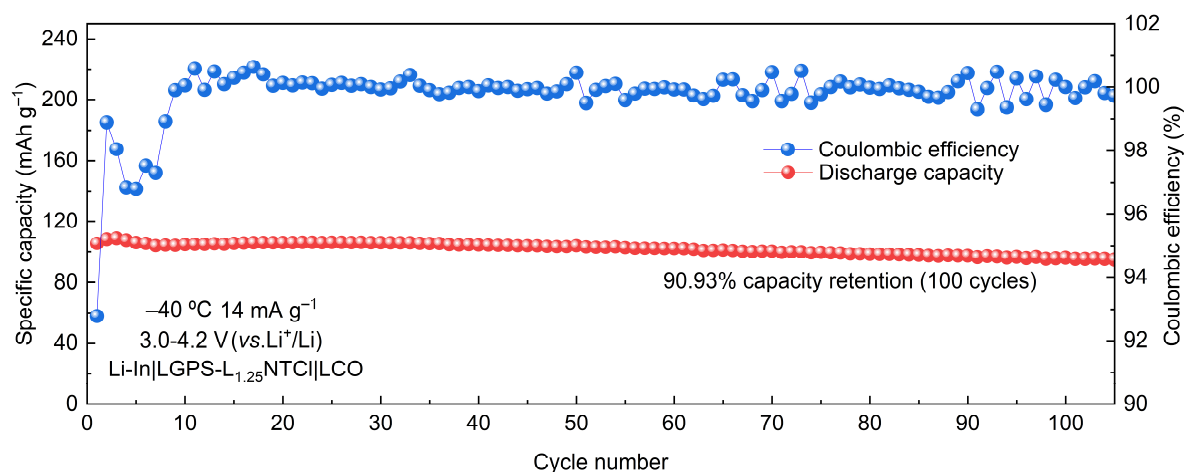
Supplementary Fig. 8 | Li^+ conductivity of $L_{1.25}NTCl-LGPS$ SSE. (a) The electrochemical impedance spectroscopy (EIS) of $L_{1.25}NTCl-LGPS$ SSE was measured at various temperatures. (b) Arrhenius plots of $L_{1.25}NTCl-LGPS$ SSE in the temperature range from -60 to $70\ ^\circ C$. To test the EIS of $L_{1.25}NTCl-LGPS$, 80 mg of $L_{1.25}NTCl$ powder and 40 mg of LGPS powder were sequentially layered into a PEEK mold and then pressed into a pellet at a pressure of 3 tons, and stack pressure of 3 tons was applied to the battery for EIS tests. The Arrhenius plots reveal the ionic conductivities of the $L_{1.25}NTCl-LGPS$ SSE at $-30\ ^\circ C$, $-40\ ^\circ C$, and $-60\ ^\circ C$, which are 0.388, 0.227, and $0.044\ mS\ cm^{-1}$, respectively.



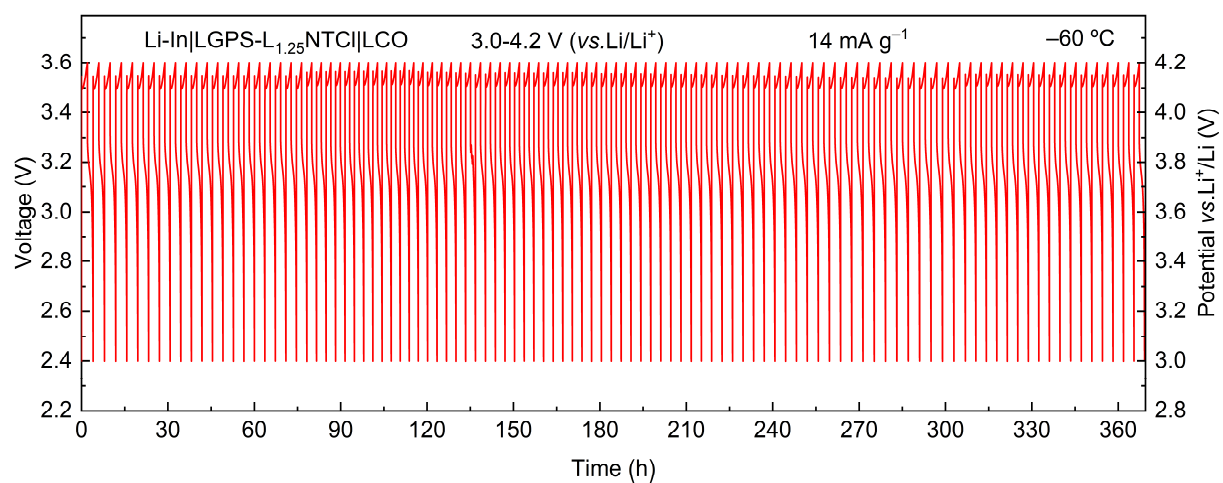
Supplementary Fig. 9 | The performance of Li-In|LGPS-L_{1.25}NTCl|LCO ASSBs operating at different temperatures. (a) Electrochemical impedance spectra of ASSBs at different temperatures. (b) The discharge profiles of ASSBs at different temperatures with charging/discharging potential range of 3.0–4.2 V vs. Li^+/Li at 14 mA g^{-1} . ASSBs are tested under a stack pressure of 0.5 ton. At temperatures of -10°C , -30°C , and -40°C , the ASSBs exhibit low resistances of 65Ω , 194Ω , and 337Ω , respectively, and show high discharge capacities of 131.4 mAh g^{-1} , 123.7 mAh g^{-1} , and 102.2 mAh g^{-1} .



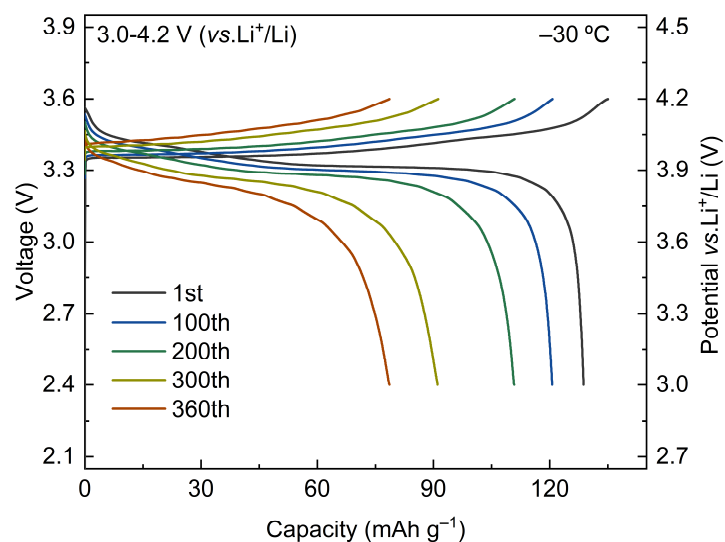
Supplementary Fig. 10 | The cycling performance of Li-In|LGPS-L_{1.25}NTCl|LCO ASSB at $-10\text{ }^{\circ}\text{C}$ and under a stack pressure of 0.5 ton. The ASSB exhibits a capacity retention of 81.93% after 100 cycles within the charge/discharge potential range of 3.0–4.2 V vs. Li^+/Li at 28 mA g^{-1} and $-10\text{ }^{\circ}\text{C}$.



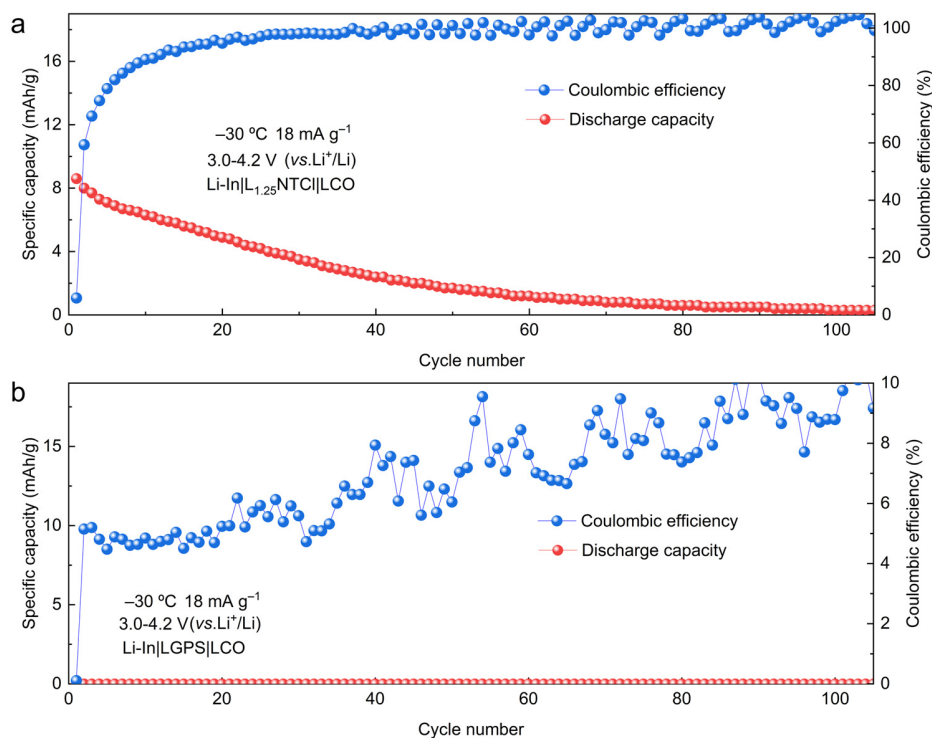
Supplementary Fig. 11 | The cycling performance of Li-In|LGPS-L_{1.25}NTCl|LCO ASSB at –40 °C under a stack pressure of 0.5 ton. The ASSB exhibits a capacity retention of 90.93% after 100 cycles within the charge/discharge potential range of 3.0–4.2 V vs. Li⁺/Li at 14 mA g^{–1} and –40 °C.



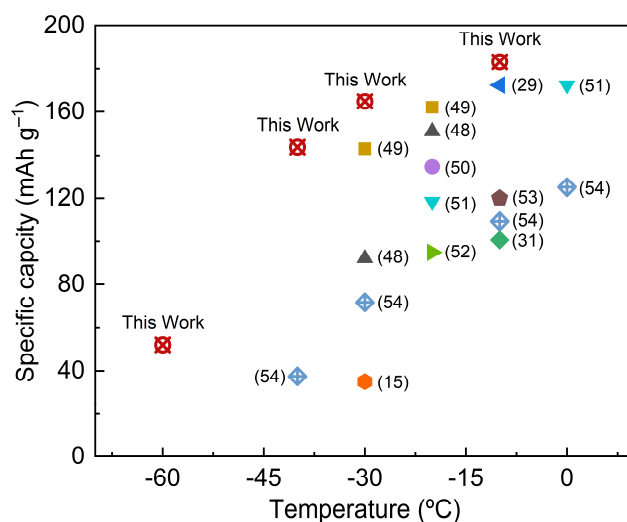
Supplementary Fig. 12 | The charge/discharge voltage profiles of Li-In|LGPS-L_{1.25}NTCl|LCO ASSB at -60 °C and under a stack pressure of 0.5 ton. The ASSB can maintain stable charging and discharging at 14 mA g⁻¹ and -60°C for more than 360 h.



Supplementary Fig. 13 | Charge/discharge voltage profiles of Li-In|LGPS-L_{1.25}NTCl|LCO battery at -30 °C and under a stack pressure of 0.5 ton. The battery exhibits discharge capacities of 128.7, 121, 110.8, 90.5, and 78.6 mAh g⁻¹ at 1st, 100th, 200th, 300th, and 360th cycle, respectively. The capacity degradation gradually appears after approximately 200 cycles, even though the ASSB can be charged and discharged over 360 cycles at -30 °C.



Supplementary Fig. 14 | The electrochemical performance of LCO|SSE|Li-In battery at –30 °C with potential range of 3.0–4.2 V vs. Li/Li⁺. (a) Cycling performance of LCO| L_{1.25}NTCl |Li-In battery. (b) Cycling performance of LCO|LGPS|Li-In battery. All batteries were tested under a stack pressure of 0.5 ton. The LCO|LGPS|Li-In cell exhibits an approximate capacity of 0 mAh g⁻¹ from the 1st cycle to 100th cycle. In comparison, the LCO|L_{1.25}NTCl|Li-In cell exhibits an initial discharge capacity of 8.6 mAh g⁻¹ and gradually declines to 0 mAh g⁻¹ after 100 cycles.



Supplementary Fig. 15 | Comparison for specific capacities of Li-In|LGPS-L_{1.25}NTCl|LCO ASSBs at 18 mA g⁻¹ in this study and recently reported SSBs at low temperatures. The corresponding literature is listed in Supplementary Table 1, and the numbering of the data points in the graph corresponds to the reference numbers in the main text.

Supplementary Table 1
Low-temperature performance comparison for SSBs.

References	Electrolyte	Cathode	Anode	Voltage range vs. Li/Li ⁺ (V)	Operating temperature (°C)	Rate (C)	Specific Capacity (mAh g ⁻¹)
This work	L_{1.25}NtCl	LiCoO₂	In-Li alloy	3.0~4.5	-10 -30 -40 -60	0.1	183.19 164.80 143.78 51.94
<i>Nat. Commun.</i> 14 , 482 (2023).	TXE-FDMA-LiDFOB	NCM 811	Li metal	2.6~4.5	-20 -30	0.1	151 92
<i>Energy Storage Mater.</i> 65 , 103179 (2024).	MPS-GPE	NCM 811	Li metal	2.8~4.3	-20 -30	0.1	162 143
<i>Nat. Commun.</i> 14 , 3780 (2023).	1.6Li ₂ O-TaCl ₅	LiCoO ₂	In-Li alloy	2.5~4.3	-10	0.2	100.6
<i>J. Am. Chem. Soc.</i> 145 , 27774-27787 (2023)	A-LTC-LiCl	S-NCM 88	In-Li alloy	2.8~4.3	-10	0.113	172.5
<i>Chem. Eng. J.</i> 430 , 132896 (2022)	Li _{5.5} PS _{4.5} Cl _{1.5}	NCM 622	In-Li alloy	3.0~4.3	-20	0.05	134.6
<i>Energy Environ. Sci.</i> 16 , 4453-4463 (2023).	Li ₆ PS ₅ Cl	NCM 9064	In-Li alloy	2.7~4.3	0 -20	0.1	172.5 118.4
<i>ACS Appl. Mater. Interfaces</i> 14 , 4179-4185 (2022).	Li _{5.5} PS _{4.425} O _{0.075} Cl _{1.5}	NCM 811	In-Li alloy	2.5~4.3	-20	0.02	94.8
<i>Chem. Commun.</i> 54 , 14116-14119 (2018).	Li ₆ PS ₅ Cl	NCM 622	In-Li alloy	2.6~4.2	-30	0.06	35.1
<i>Adv. Funct. Mater.</i> 32 , 2205594 (2022).	Li ₃ InCl ₆	LiCoO ₂	In-Li alloy	2.7~4.2	-10	0.1	~120
<i>Electrochemistry</i> 90 , 027001-027001 (2022).	Li ₆ PS ₅ Cl	NCM 532	In-Li alloy	3.0~4.25	0 -10 -30 -40	0.1	~125 ~109.4 ~71.8 ~37.5