

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

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A pressing need for enhancing lithium-ion battery (LIB) performance exists, particularly in ensuring reliable operation under extreme cold conditions. All-solid-state batteries (ASSBs) offer a promising solution to the challenges posed by conventional LIBs with liquid electrolytes in low-temperature environments. In this study, leveraging the benefits of amorphous solid-state electrolytes (SSEs)  $x\text{Li}_3\text{N-TaCl}_5$  ( $1 \leq x \leq 2$ ), we develop ASSBs capable of functioning effectively under extreme cold conditions. The designed ASSBs, employing  $\text{LiCoO}_2$  positive electrode with a mass loading of  $4.46 \text{ mg cm}^{-2}$  and a Li-In negative electrode, demonstrate initial discharge capacities of 183.19, 164.8 and  $143.78 \text{ mAh g}^{-1}$  under  $18 \text{ mA g}^{-1}$  at  $-10$ ,  $-30$ , and  $-40^\circ\text{C}$ , respectively, and exhibit a final discharge capacity of  $137.6 \text{ mAh g}^{-1}$  at  $18 \text{ mA g}^{-1}$  and  $-30^\circ\text{C}$  in the 100th cycle. Moreover, the ASSBs demonstrate an initial discharge capacity of  $51.94 \text{ mAh g}^{-1}$  at  $18 \text{ mA g}^{-1}$  and  $-60^\circ\text{C}$  with cycling over 200 h.

Li-ion batteries (LIBs) have garnered widespread adoption across various sectors, including consumer electronics, electric vehicles, and stationary energy storage systems, owing to their remarkable attributes such as high energy density, extended cycle life, and electrochemical stability<sup>1–4</sup>. Nevertheless, amidst the escalating global demand for electrochemical energy storage, there is a pressing need to push the performance boundaries of LIBs even further. A significant demand for improvement of LIBs lies in reliably functioning under extreme temperature conditions<sup>5–7</sup>, such as polar expeditions and high-altitude stations, while maintaining a favorable capacity.

However, the attainment of stable operation at extreme temperatures remains a significant challenge in LIBs. Representatively,

under extreme cold conditions, LIBs experience pronounced reductions in capacity and power output<sup>8–10</sup>. A typical Panasonic 18650 Li-ion cell exhibits substantial reductions in energy density, retaining only 66% and 5% at slow charge-discharge rates ( $<0.1 \text{ C}$ ) when subjected to temperatures of  $-20^\circ\text{C}$  and  $-40^\circ\text{C}$ , respectively<sup>6</sup>. Besides, recharging under low-temperature conditions presents notable safety risks due to the increased likelihood of Li dendrite formation on the anode, especially with higher charging rates<sup>11</sup>. These challenges stem from heightened viscosity, which increases the interface impedance, and diminished ionic conductivity within the liquid electrolyte (LE)<sup>12,13</sup>. Additionally, the sluggish mass transport and limited Li solvation/desolvation capability at low temperatures impede reaction kinetics in LIBs<sup>10</sup>.

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All-solid-state batteries (ASSBs), employing solid-state electrolytes (SSEs), offer a promising solution for overcoming the challenges of conventional LIBs under extreme cold conditions. Generally, SSEs are insensitive to temperature fluctuations, which can avoid issues of LEs such as significant reductions in solubility/desorption capability or increased viscosity at low temperatures<sup>10,12</sup>. Moreover, the desolvation process occurring at the liquid/solid interface in traditional LIBs does not occur at the solid/solid interface in ASSB systems. This highlights the benefits of low charge transfer resistance and rapid electrochemical reactions at subzero temperatures in ASSBs compared to traditional LIBs<sup>14–16</sup>. Therefore, considering the potential benefits of ASSBs at low temperature, it becomes imperative to develop innovative SSEs and battery systems to surmount the limitations encountered by current LIBs.

Nonetheless, ASSBs encounter hurdles when operating under extreme cold conditions<sup>17</sup>. Typically, the activation energy associated with the grain boundaries of polycrystalline SSEs is higher than that of the bulk phase, which implies that ionic transport at the grain boundaries becomes more temperature-sensitive compared to the bulk phase<sup>18–21</sup>. Therefore, when considering SSEs as a whole, integrating both bulk of grain and grain boundary components, the higher activation energy and lower conductivity at grain boundaries lead to a decrease in the overall ionic conductivity. Under ultralow temperature conditions, this decrease in ionic conductivity at grain boundaries is substantially more pronounced than in the bulk of grains, which further exacerbates the reduction in overall ionic conductivity of SSEs and results in discontinuous ionic transport within the battery, adversely affecting the performance of ASSBs. This phenomenon also impedes ionic transport at the cathode/SSE interface<sup>22</sup>, resulting in severe polarization of the battery and preventing the cathode from fully exerting its capacity<sup>15</sup>. Moreover, the unresolved solid-solid interfacial contact issues may exacerbate the degradation of performance in ASSBs at low temperatures<sup>17</sup>.

In theory, amorphous SSEs, often referred to as the glassy form, offer a potential solution to the challenges faced by ASSBs at low temperatures. Amorphous SSEs are homogeneous non-crystalline solids characterized by the absence of resistive grain boundaries, maintaining isotropic conduction pathways within the SSEs<sup>23–27</sup>. This implies that, under extreme cold conditions, amorphous SSEs can

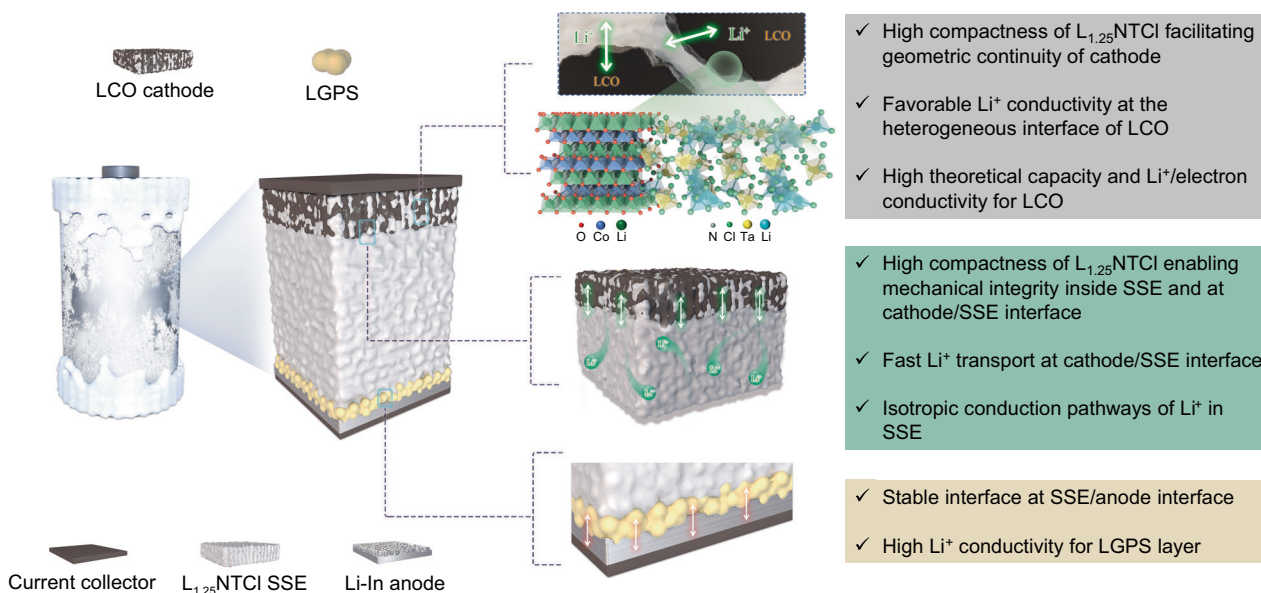
mitigate the discontinuous ionic transport observed in SSE and at the electrode/SSE interface in ASSBs. Consequently, the ASSBs utilizing amorphous SSEs may facilitate the achievement of higher capacities compared to ASSBs assembled using polycrystalline SSEs at low temperature.

In this work, we present a new category of ASSBs employing amorphous SSEs  $x\text{Li}_3\text{N-TaCl}_5$  ( $1 \leq 3x \leq 2$ ) for operation under extreme cold conditions. These amorphous SSEs achieve a significant ionic conductivity of  $5.91 \text{ mS cm}^{-1}$  at  $3x = 1.25$  (labeled as  $\text{L}_{1.25}\text{NTCl}$ ) at  $25^\circ\text{C}$ , which supports favorable ionic transport within the bulk phase of the battery and at the cathode/SSE interface. Specifically, the ASSBs are tailored for low-temperature operation by integrating  $\text{LiCoO}_2$  (LCO) cathode,  $\text{L}_{1.25}\text{NTCl}$  SSE,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  (LGPS) interface layer, and  $\text{Li-In}$  anode (Fig. 1). The designed  $\text{Li-In}|\text{LGPS-L}_{1.25}\text{NTCl}|\text{LCO}$  batteries exhibit unexpectedly high discharge capacities of 183.19, 164.8 and  $143.78 \text{ mAh g}^{-1}$  at  $-10$ ,  $-30$ , and  $-40^\circ\text{C}$ , respectively, and demonstrate a discharge capacity of  $137.6 \text{ mAh g}^{-1}$  at  $18 \text{ mA g}^{-1}$  and  $-30^\circ\text{C}$  in the 100th cycle with a capacity retention of 83.50%. Moreover, the ASSB has shown the capability to maintain stable charge/discharge cycles for over 200 hours at  $-60^\circ\text{C}$ , demonstrating its effectiveness in extreme cold conditions.

## Results and discussion

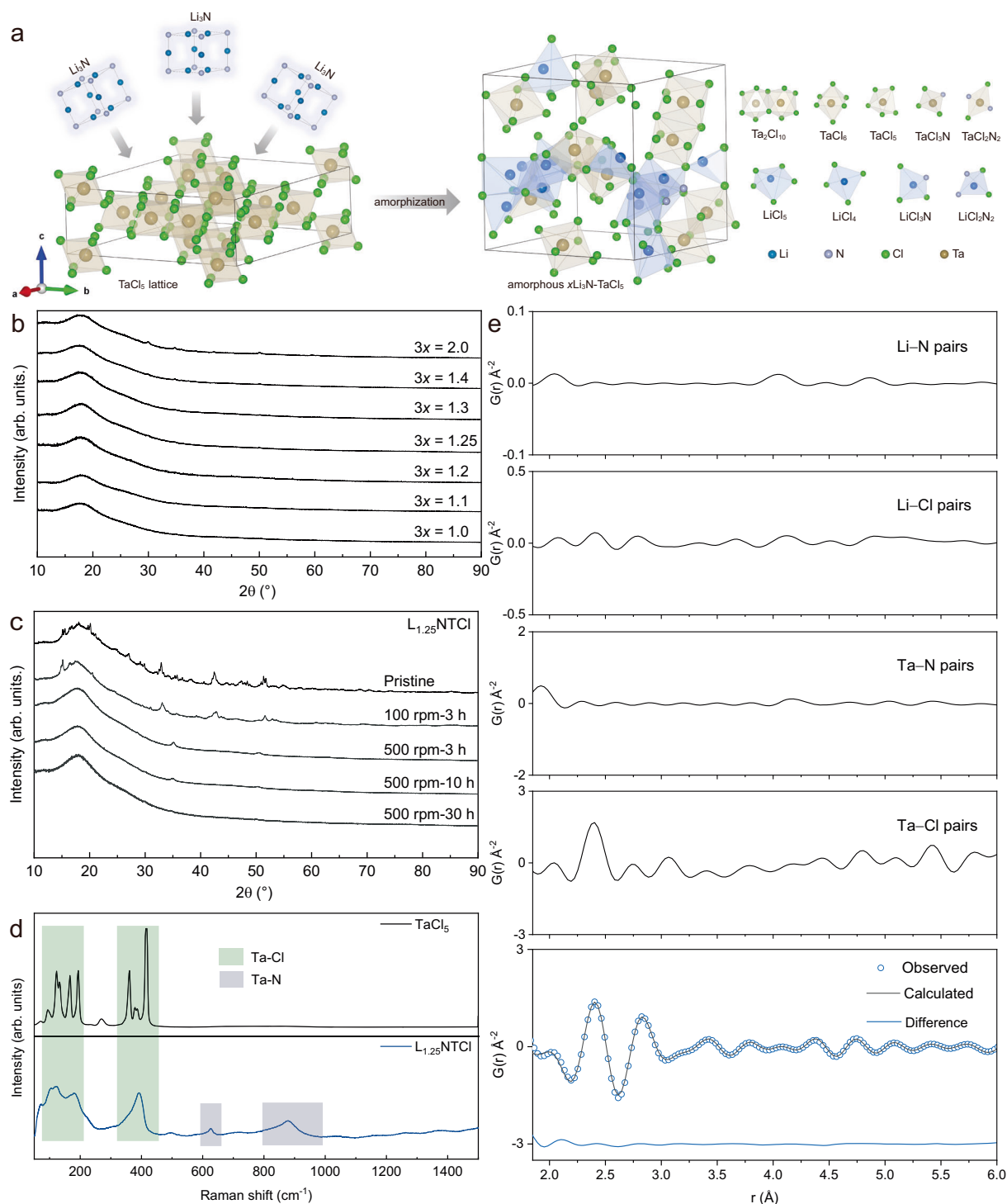
### Exploring amorphous $x\text{Li}_3\text{N-TaCl}_5$ for low-temperature ASSBs

The amorphous  $x\text{Li}_3\text{N-TaCl}_5$  were synthesized through straightforward ball-milling of  $\text{Li}_3\text{N}$  and  $\text{TaCl}_5$  at different stoichiometric ratios (Fig. 2a).  $\text{TaCl}_5$  serves as the fundamental structural framework, chosen for its capability to undergo amorphization upon the integration of foreign atoms, which is corroborated by multiple experiments<sup>28–33</sup>. For instant, by introducing Li (or Na) and O atoms into the  $\text{TaCl}_5$  matrix, the amorphous  $x\text{Li}_2\text{O-TaCl}_5$  ( $x\text{Na}_2\text{O}_2\text{-TaCl}_5$ ) SSEs can be achieved<sup>31,33</sup>, boasting remarkable ionic conductivity ( $> 1 \text{ mS cm}^{-1}$ ). Besides,  $\text{Li}_3\text{N}$  emerges as a lithium-rich material, furnishing abundant charge carriers (i.e., lithium ions) for the as-prepared SSEs, thereby contributing to the ionic conductivity. Figure 2b presents the X-ray diffraction (XRD) patterns of the resulting  $x\text{Li}_3\text{N-TaCl}_5$  samples ( $1 \leq 3x \leq 2$ ). When  $3x = 2$ , the XRD pattern primarily exhibits amorphous characteristics with trace impurities of  $\text{LiCl}$  and  $\text{TaN}$  (Supplementary Fig. 1a). As the molar ratio of  $\text{Li}_3\text{N}$  to  $\text{TaCl}_5$  decreases, impurity peaks gradually diminish and



**Fig. 1 | Schematic of tailored ASSB for operating under extreme cold conditions.** The ASSB consists of  $\text{LiCoO}_2$  (LCO) cathode, amorphous  $\text{Li}_{1.25}\text{N}_{0.417}\text{-TaCl}_5$  ( $\text{L}_{1.25}\text{NTCl}$ ) SSE,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  (LGPS) interface layer, and  $\text{Li-In}$  anode. This structural

configuration ensures both the mechanical and chemical stability of the battery, as well as favorable ionic transport in the SSE and at the electrode/SSE interface, even under extreme cold conditions.



**Fig. 2 | Structure analysis of amorphous  $x\text{Li}_3\text{N-TaCl}_5$ .** **a** Schematic of the incorporation of  $\text{Li}_3\text{N}$  into  $\text{TaCl}_5$  for the formation of amorphous  $x\text{Li}_3\text{N-TaCl}_5$  (left), structure and coordination polyhedra of amorphous  $x\text{Li}_3\text{N-TaCl}_5$  obtained from ab-initio molecular dynamics simulations (right). **b** XRD patterns of the amorphous  $x\text{Li}_3\text{N-TaCl}_5$  ( $1 \leq x \leq 2$ ) ball-milled at 30 h. **c** XRD patterns of the as-prepared

$\text{L}_{1.25}\text{NTCl}$  under different ball-milling conditions. **d** Raman spectra of  $\text{TaCl}_5$  and amorphous  $\text{L}_{1.25}\text{NTCl}$ . **e** The small-box least-square refinement of PDF data of amorphous  $\text{L}_{1.25}\text{NTCl}$ , and the partial PDF from Ta-Cl, Ta-N, Li-Cl, and Li-N pairs extracted from the total PDF data.

become nearly undetectable at  $3x=1.25$  (Supplementary Fig. 1b). Additionally, as a representative case, we investigated the synthesis process of  $\text{L}_{1.25}\text{NTCl}$  concerning ball-milling conditions. Figure 2c illustrates that when the ball-milling preparation time reaches 30 h (at 500 rpm), the  $\text{L}_{1.25}\text{NTCl}$  SSE achieves complete amorphization. It is interesting to note that the introduction of nitrogen element considerably reduced the preparation time to achieve complete

amorphization in  $\text{L}_{1.25}\text{NTCl}$  compared to the recently reported amorphous  $\text{LiTaCl}_6$  (Supplementary Fig. 2)<sup>28,29</sup>.

To delve into the intricate local coordination details of  $x\text{Li}_3\text{N-TaCl}_5$ , we employed ab-initio molecular dynamics (AIMD) simulations to reveal the formation process of its amorphous structure (Supplementary Fig. 3, Supplementary data 1 and 2). In the fundamental  $\text{TaCl}_5$  lattice, it comprises regularly arranged  $\text{Ta}_2\text{Cl}_{10}$  bi-

octahedra and  $\text{TaCl}_6$  octahedra (Fig. 2a, left panel). Upon introducing Li and N atoms, diverse anion-cation coordination relationships emerge in the resulting amorphous  $x\text{Li}_3\text{N-TaCl}_5$  matrix. These coordination relationships involve  $\text{Ta}_2\text{Cl}_{10}$ ,  $\text{TaCl}_6$ ,  $\text{TaCl}_5$ ,  $\text{TaCl}_3\text{N}$ ,  $\text{TaCl}_2\text{N}_2$ ,  $\text{LiCl}_5$ ,  $\text{LiCl}_4$ ,  $\text{LiCl}_3\text{N}$ , and  $\text{LiCl}_2\text{N}_2$  polyhedra interconnected through shared edges or corners (Fig. 2a, right panel), with all Ta (Li) atoms residing within the voids of polyhedra. Remarkably, in amorphous  $\text{LiTaCl}_6$ <sup>29</sup>, the coordination configurations (including  $\text{TaCl}_6$ ,  $\text{LiCl}_6$ ,  $\text{LiCl}_5$ ,  $\text{LiCl}_4$ ) are significantly fewer than those found in amorphous  $x\text{Li}_3\text{N-TaCl}_5$  matrix in this study. This disparity can be attributed to the increased complexity of the coordination mode between Ta and anions induced by the introduction of N in  $x\text{Li}_3\text{N-TaCl}_5$ , potentially rendering it more favorable for the formation of amorphous phase. Besides, the transport of interstitial  $\text{Li}^+$  in  $\text{LiCl}_x$  ( $\text{LiCl}_x\text{N}_y$ ) polyhedra may occur through the dynamic breaking and reforming of Li–Cl or Li–N bonds across the space among the  $\text{TaCl}_x$  ( $\text{TaCl}_x\text{N}_y$ ) polyhedra by stretching Ta–Cl or Ta–N, which has been demonstrated by Jiang et al. through machine-learning force field molecular dynamics simulations<sup>34</sup>.

Moreover, the local structure of amorphous  $\text{Li}_{1.25}\text{NTCl}$  was investigated by Raman spectroscopy and X-ray atomic pair distribution function (PDF) analysis. As presented in Fig. 2d, the peaks around  $180\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$  in the Raman spectra of  $\text{Li}_{1.25}\text{NTCl}$  correspond to Ta–Cl vibrations<sup>35,36</sup>, aligning with observations in  $\text{TaCl}_5$ . Moreover, distinct Ta–N fingerprints<sup>37–39</sup> appear in the Raman spectra of  $\text{Li}_{1.25}\text{NTCl}$  at the frequencies around  $600\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$ . Evidently, the amorphous  $\text{Li}_{1.25}\text{NTCl}$  not only preserves the original Ta–Cl bonds from  $\text{TaCl}_5$ , but also incorporates the binding with N in the local coordination environment of Ta under high-energy ball-milling conditions. Similar observations have been reported in amorphous oxychloride SSEs<sup>31</sup>, where O has a significant impact on amorphous formation, preferring to act as bridging atoms to connect Ta-centered trigonal bipyramids in  $x\text{Li}_2\text{O-TaCl}_5$  structure. Also, the PDF data of amorphous  $\text{Li}_{1.25}\text{NTCl}$  was fitted to obtain a quantitative evaluation of the local structure. As shown in Fig. 2e, the PDF data can be well fitted using the amorphous model constructed from AIMD simulations (Fig. 2a, right panel) through small-box least square refinement ( $R_w = 10.9\%$ ). The partial PDF from Ta–Cl, Ta–N, Li–Cl, and Li–N pairs were extracted from the total PDF of  $\text{Li}_{1.25}\text{NTCl}$ . Due to the retention of local coordination relationships between Ta and Cl in the original structure of  $\text{TaCl}_5$ , partial PDF from Ta–Cl pairs accounts for the major contribution in the total PDF data of  $\text{Li}_{1.25}\text{NTCl}$ , and the interatomic distance of Ta–Cl is mainly distributed at  $2.40363\text{ \AA}$ . In addition, by incorporating N atoms into  $\text{Li}_{1.25}\text{NTCl}$ , the peaks corresponding to the interatomic distances of Ta–N and Li–N at  $1.92291\text{ \AA}$  and  $2.04309\text{ \AA}$  appeared in the partial PDF from Ta–N and Li–N pairs, respectively. Interestingly, the interatomic distances of Li–Cl are variable and exhibit diffuse characteristics, which may be attributed to the diverse coordination relationships between Li and Cl, as well as the transport behavior of  $\text{Li}^+$  in the amorphous matrix of  $\text{Li}_{1.25}\text{NTCl}$ .

### Low-temperature-applicable amorphous $\text{Li}_{1.25}\text{NTCl}$

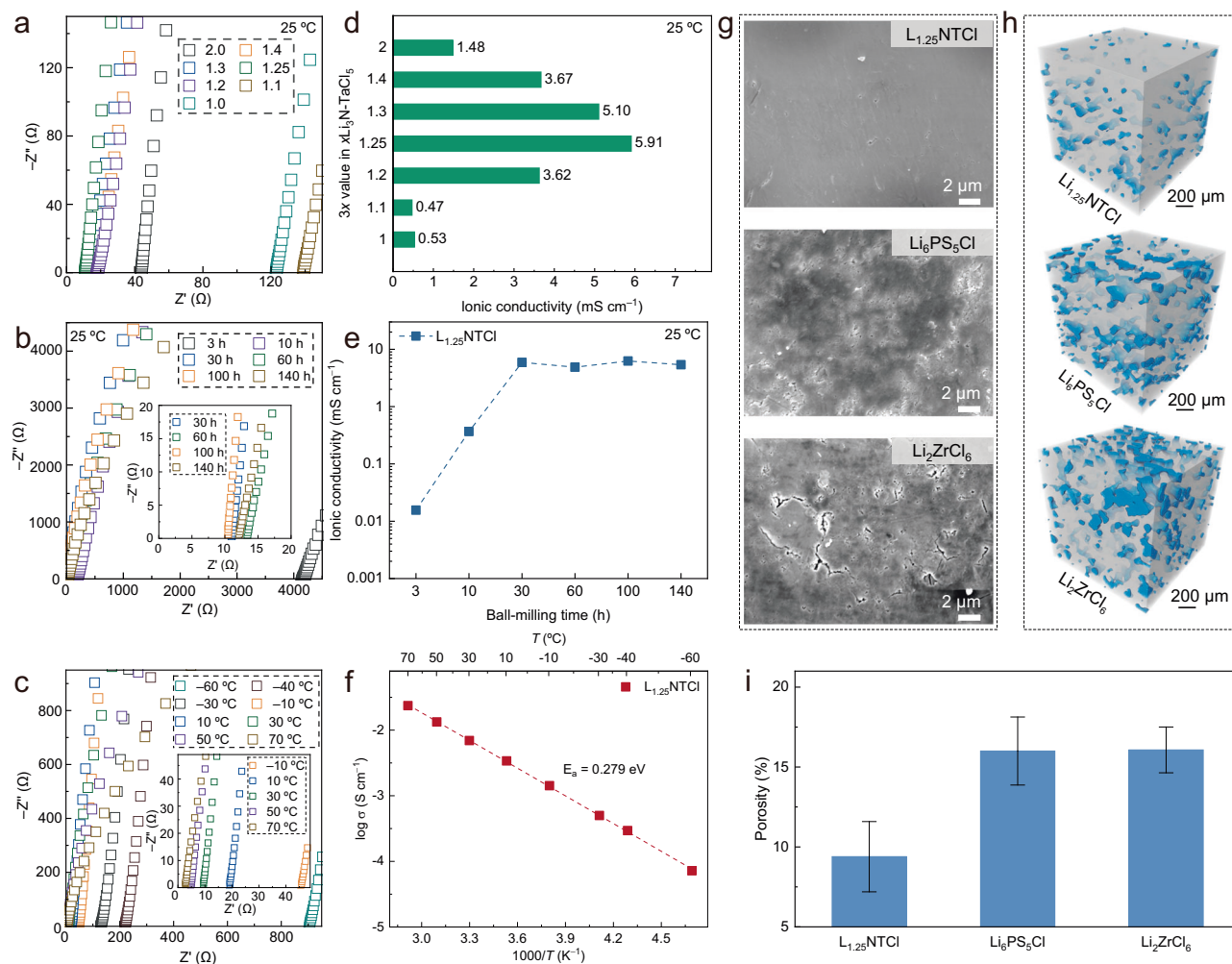
The ionic conductivities were analyzed by electrochemical impedance spectroscopy (EIS), and the Nyquist plots (Fig. 3a–c and Supplementary Fig. 4) reflect the impedance response of  $x\text{Li}_3\text{N-TaCl}_5$  SSEs in various  $x$  values, under different ball-milling conditions, and at different temperature. As illustrated in Fig. 3d, there is a non-monotonic trend observed in the ionic conductivities of  $x\text{Li}_3\text{N-TaCl}_5$  as the  $3x$  value gradually increases from 1 to 2. Notably, the ionic conductivity of  $x\text{Li}_3\text{N-TaCl}_5$  SSEs achieve a significant ionic conductivity of  $5.91\text{ mS cm}^{-1}$  at  $3x = 1.25$  (i.e.,  $\text{Li}_{1.25}\text{NTCl}$ ) at  $25\text{ }^\circ\text{C}$ . The non-monotonic trend in the ionic conductivities of  $x\text{Li}_3\text{N-TaCl}_5$ , as a function of  $x$  values, can be attributed to both the presence of impurities and the  $\text{Li}^+$  concentration within its amorphous matrix. On one hand, the peak intensities of LiCl and TaN impurities gradually diminish and become almost undetectable at

$3x = 1.25$  (Supplementary Fig. 1b), suggesting a corresponding reduction in their adverse impact on the ionic conductivity of  $x\text{Li}_3\text{N-TaCl}_5$ . On the other hand, the insufficient  $\text{Li}^+$  concentrations (such as  $3x = 1.0$  and  $1.1$ ) may limit  $\text{Li}^+$  transport within the polygonal coordination structures of the amorphous matrix, resulting in a decrease in ionic conductivity. Therefore, considering both the  $\text{Li}^+$  concentration and the impurities of LiCl and TaN, the ionic conductivity of  $x\text{Li}_3\text{N-TaCl}_5$  exhibits a non-monotonic trend as the  $3x$  value increases from 1 to 2. Moreover, the duration of ball-milling significantly influences the ionic conductivity of  $\text{Li}_{1.25}\text{NTCl}$ . As presented in Fig. 3e, the ball-milling conditions of 500 rpm for 30 h mark a pivotal point for a sudden increase in ionic conductivity, and extending the preparation time from 10 to 30 h results in the ionic conductivity of  $\text{Li}_{1.25}\text{NTCl}$  rising from  $0.368$  to  $5.91\text{ mS cm}^{-1}$  at  $25\text{ }^\circ\text{C}$ . Whereas, with further extension of the ball-milling time, minor fluctuations in its ionic conductivity are observed. Interestingly, the complete amorphization of  $\text{Li}_{1.25}\text{NTCl}$  also has been achieved under the ball-milling conditions of 500 rpm for 30 h (Fig. 2c), which suggests a close association between its ionic conductivity and the degree of amorphization. Figure 3f and Supplementary Fig. 5a display the Arrhenius plots for  $x\text{Li}_3\text{N-TaCl}_5$  SSE, demonstrating the relationship between ionic conductivity and temperature. The activation energies of amorphous  $x\text{Li}_3\text{N-TaCl}_5$  (Supplementary Fig. 5b) are obtained from the slope in the Arrhenius plots base on the formula:  $\sigma = A \exp(-E_a/k_B T)$ , where  $\sigma$  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. With a low activation energy of  $0.279\text{ eV}$ , the  $\text{Li}_{1.25}\text{NTCl}$  SSE exhibits high ionic conductivities of  $0.5$ ,  $0.29$  and  $0.07\text{ mS cm}^{-1}$  even at the low temperatures of  $-30\text{ }^\circ\text{C}$ ,  $-40\text{ }^\circ\text{C}$ , and  $-60\text{ }^\circ\text{C}$ , respectively.

In addition, the amorphous  $\text{Li}_{1.25}\text{NTCl}$  exhibits a favorable processability and high compactness. The scanning electron microscope (SEM) images (Fig. 3g and Supplementary Fig. 6) highlight the better compactness of  $\text{Li}_{1.25}\text{NTCl}$  compared to argyrodite-type  $\text{Li}_6\text{PS}_5\text{Cl}$  and halide  $\text{Li}_2\text{ZrCl}_6$  under identical pressing conditions of  $500\text{ MPa}$ , obviously demonstrating that  $\text{Li}_{1.25}\text{NTCl}$  features a smoother surface and lower porosity. To further illustrate the advantages of  $\text{Li}_{1.25}\text{NTCl}$  in compactness, computed tomography (CT) was employed to quantitatively analyze the porosity of these SSEs. As shown in Fig. 3h and i, the three-dimensional distribution of  $\text{Li}_{1.25}\text{NTCl}$  shows a significantly lower porosity ( $9.39\%$ ) compared to  $\text{Li}_6\text{PS}_5\text{Cl}$  ( $16\%$ ) and  $\text{Li}_2\text{ZrCl}_6$  ( $16.07\%$ ). This advantage implies that ASSBs based on amorphous  $\text{Li}_{1.25}\text{NTCl}$  can streamline the process flow when forming large dimensions, as there is no need for special densification treatments. Moreover, this high compactness characteristic facilitates intimate contact both within the bulk and at the interfaces inside the ASSB utilizing  $\text{Li}_{1.25}\text{NTCl}$  SSE, ensuring geometric continuity of the battery and uninterrupted  $\text{Li}^+$  conduction on a macroscopic scale at low temperatures.

### ASSBs tailored for operation under extreme cold conditions

As demonstrated in the schematic (Fig. 1), according to the respective properties of the materials utilized for the different components in battery, we intentionally designed the ASSB for operation under extreme cold conditions. The amorphous  $\text{Li}_{1.25}\text{NTCl}$  is selected as the electrolyte component, which stems from its impressive ionic conductivities of  $0.5$ ,  $0.29$ , and  $0.07\text{ mS cm}^{-1}$  at the low temperatures of  $-30\text{ }^\circ\text{C}$ ,  $-40\text{ }^\circ\text{C}$ , and  $-60\text{ }^\circ\text{C}$ , respectively. More importantly, the fully amorphous nature of  $\text{Li}_{1.25}\text{NTCl}$  eliminates resistive grain boundaries<sup>23–27</sup>, allowing it to sustain isotropic and continuous  $\text{Li}^+$  transport pathways within the SSE under extreme cold conditions. This continuous ionic transport characteristic also facilitates  $\text{Li}^+$  diffusion at the cathode/SSE interface<sup>22</sup>, enhancing the exertion of the capacity of the cathode. In addition, the high processability and compactness of  $\text{Li}_{1.25}\text{NTCl}$  SSE enable close contact between particle-particle and solid-solid interfaces, maintaining the geometric continuity within the batteries. Apart from electrolyte,  $\text{LiCoO}_2$  (LCO) is selected as the cathode



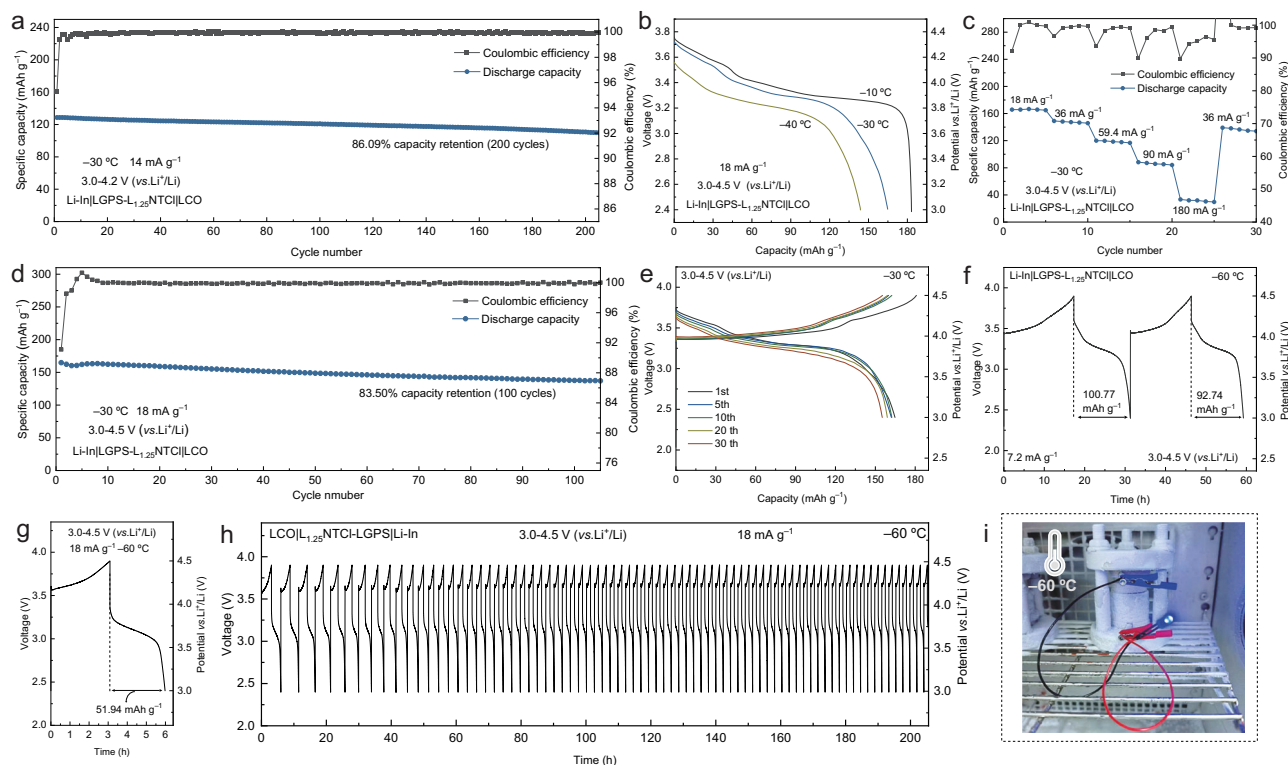
**Fig. 3 | Properties of amorphous  $x\text{Li}_3\text{N-TaCl}_5$ .** **a–c** Nyquist plots reflect the impedance response of  $x\text{Li}_3\text{N-TaCl}_5$  SSEs in various  $3x$  values (**a**), under different ball-milling conditions (**b**), and at different temperature (**c**). **(d)** Ionic conductivities of amorphous  $x\text{Li}_3\text{N-TaCl}_5$  ( $1 \leq 3x \leq 2$ ) at 25 °C. **e** Ionic conductivities of the as-prepared  $\text{L}_{1.25}\text{NTCl}$  under different ball-milling conditions at 25 °C. **f** Arrhenius ionic

conductivity plots of amorphous  $\text{L}_{1.25}\text{NTCl}$  in the temperature range from –60 to 70 °C. **g** SEM images of  $\text{L}_{1.25}\text{NTCl}$ ,  $\text{Li}_6\text{PS}_5\text{Cl}$ , and  $\text{Li}_2\text{ZrCl}_6$  SSEs. **h** 3D volume rendered images from CT scan, where the blue regions represent the voids within SSEs. **i** Porosity analyzed by CT for  $\text{L}_{1.25}\text{NTCl}$ ,  $\text{Li}_6\text{PS}_5\text{Cl}$ , and  $\text{Li}_2\text{ZrCl}_6$  SSEs.

due to its high theoretical capacity and charging cutoff voltage, as well as good  $\text{Li}^+$ /electron conductivity, enabling it to deliver a high specific capacity at low temperature<sup>40,41</sup>. The anode segment features a Li-In alloy, chosen for its compatibility with SSEs, absence of sluggish diffusion kinetics, and capacity to ensure uniform lithium deposition<sup>42,43</sup>. Besides, we incorporate  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  (LGPS) superionic conductor as the interface layer on the anode side, leveraging its excellent ionic conductivity ( $10^{-2} \text{ S cm}^{-1}$ , close to liquid electrolytes) and interface stability with Li-In alloy anode (Supplementary Fig. 7)<sup>44,45</sup>. Overall, the tailored ASSB, in principle, not only ensures the mechanical and chemical stability of the bulk phase and interface inside the battery, but also facilitates favorable ionic transport in the electrolyte (Supplementary Fig. 8) and at the electrode/SSE interface, even under low-temperature operating conditions.

Remarkably, the engineered ASSBs exhibit stable cycling and high capacities under extreme cold conditions (Supplementary Figs. 9 to 12). As shown in Fig. 4a and Supplementary Fig. 13, after 200 cycles within the charging/discharging potential range of 3.0–4.2 V vs.  $\text{Li}^+/\text{Li}$  at 18  $\text{mA g}^{-1}$  and –30 °C, the  $\text{Li-In|LGPS-L}_{1.25}\text{NTCl|LCO}$  battery maintains a specific capacity of 110.8  $\text{mAh g}^{-1}$ . Besides, both the  $\text{Li-In|L}_{1.25}\text{NTCl|LCO}$  battery and the  $\text{Li-In|LGPS|LCO}$  battery exhibit capacities approaching 0  $\text{mAh g}^{-1}$  after 100 cycles, highlighting the

necessity of the bilayer  $\text{L}_{1.25}\text{NTCl-LGPS}$  SSE design for enhancing the performance of ASSB (Supplementary Fig. 14). Upon extending the charging/discharging potential range to 3.0–4.5 V vs.  $\text{Li}^+/\text{Li}$ , the ASSB demonstrates unexpectedly high discharge capacities of 183.19, 164.8 and 143.78  $\text{mAh g}^{-1}$  at –10, –30, and –40 °C, respectively (Fig. 4b), as well as 139.1  $\text{mAh g}^{-1}$  after switching the rate from 180  $\text{mA g}^{-1}$  to 36  $\text{mA g}^{-1}$  (Fig. 4c) at –30 °C. Also, the  $\text{Li-In|LGPS-L}_{1.25}\text{NTCl|LCO}$  battery exhibits discharge capacity of 137.6  $\text{mAh g}^{-1}$  at 18  $\text{mA g}^{-1}$  in the 100th cycle with a capacity retention of 83.50% (Fig. 4d and e). It should be noted that the enhanced capacities shown in Fig. 4d, compared to those in Fig. 4a, are attributed to the different charge cut-off potential, where the deliverable capacity increases from approximately 140  $\text{mAh g}^{-1}$  at a cut-off potential of 4.2 V (vs.  $\text{Li}^+/\text{Li}$ ) to 180  $\text{mAh g}^{-1}$  at a cut-off potential of 4.5 V (vs.  $\text{Li}^+/\text{Li}$ )<sup>46,47</sup>. Moreover, the  $\text{Li-In|LGPS-L}_{1.25}\text{NTCl|LCO}$  battery demonstrates stable charging and discharging at –60 °C, showcasing its effectiveness in extreme cold conditions and expanding the potential application of ASSBs on a global scale. As presented in Fig. 4f, the ASSB shows discharge capacities of 100.77  $\text{mAh g}^{-1}$  at 7.2  $\text{mA g}^{-1}$  and –60 °C. Furthermore, when the rate is increased to 18  $\text{mA g}^{-1}$ , it can exert discharge capacities of 51.94  $\text{mAh g}^{-1}$  in the first cycle (Fig. 4g) and maintain stable charging/discharging at –60 °C for more than 200 h (Fig. 4h, i and



**Fig. 4 | Design and performance of ASSBs tailored for operation under extreme cold conditions.** **a** The cycling performance of ASSBs at  $-30\text{ }^{\circ}\text{C}$  with charging/discharging potential range of 3.0–4.2 V vs.  $\text{Li}^+/\text{Li}$  at  $14\text{ mA g}^{-1}$ . **b** The discharge profiles of ASSBs at  $18\text{ mA g}^{-1}$  and different temperatures ( $-10$ ,  $-30$ , and  $-40\text{ }^{\circ}\text{C}$ ). **c** The cycling performance of ASSBs at  $-30\text{ }^{\circ}\text{C}$  and different rates ( $18$ ,  $36$ ,  $54$ ,  $90$ , and  $180\text{ mA g}^{-1}$ ) with potential range of 3.0–4.5 V vs.  $\text{Li}^+/\text{Li}$ . **d** The cycling performance of ASSBs at  $-30\text{ }^{\circ}\text{C}$  with charge/discharge potential range of 3.0–4.5 V vs.  $\text{Li}^+/\text{Li}$  at

$18\text{ mA g}^{-1}$ . **e** The charge/discharge profiles of ASSBs at  $-30\text{ }^{\circ}\text{C}$  with cutoff potential set at 3.0 V and 4.5 V vs.  $\text{Li}^+/\text{Li}$  at  $18\text{ mA g}^{-1}$ . **f–h** The charge/discharge profiles of ASSBs at  $-60\text{ }^{\circ}\text{C}$  with cutoff potentials set at 3.0 V and 4.5 V vs.  $\text{Li}^+/\text{Li}$  at  $7.2\text{ mA g}^{-1}$  (**f**) and  $18\text{ mA g}^{-1}$  (**g, h**). **i** The photo of ASSB operating at  $-60\text{ }^{\circ}\text{C}$ . All potentials vs.  $\text{Li}^+/\text{Li}$  are obtained by adding 0.6 V to the actual cell voltage, and all ASSBs were tested under a stack pressure of 0.5 ton.

Supplementary Movie 1), highlighting the potential of the  $\text{Li-In/LGPS-L}_{1.25}\text{NTCl/LCO}$  configuration for applications under extreme cold conditions. Notably, the distinct reduction in discharge capability of the ASSB at  $-60\text{ }^{\circ}\text{C}$  compared to  $-30\text{ }^{\circ}\text{C}$  can be attributed to the increased overpotential during cycling, stemming from the unfavorable ionic conductivity within the  $\text{L}_{1.25}\text{NTCl-LGPS}$  bilayer SSE (Supplementary Fig. 8) and at the cathode/SSE interface. Also, the designed ASSBs assembled with the amorphous  $\text{L}_{1.25}\text{NTCl}$  SSE has been evaluated alongside other solid-state batteries (SSBs) at low temperatures (Supplementary Fig. 15). Compared to previously reported SSBs<sup>15,29,31,48–54</sup>, this study reveals distinct advantages of  $\text{Li-In/LGPS-L}_{1.25}\text{NTCl/LCO}$  battery in terms of specific capacities different temperatures and the lowest rechargeable temperature ( $-60\text{ }^{\circ}\text{C}$ ). This battery design concept, integrating amorphous SSE tailored for extreme cold conditions, extends the performance capabilities of ASSB and offers significant inspiration for the future development of low-temperature battery technology.

## Methods

### Material synthesis

The amorphous  $x\text{Li}_3\text{N-TaCl}_5$  ( $1 \leq x \leq 2$ ) SSE powders were synthesized by Ar-protected ball-milling in sealed  $\text{ZrO}_2$  grinding jars with  $\text{ZrO}_2$  grinding balls. Stoichiometric amounts of  $\text{TaCl}_5$  (over 99.9% purity, Aladdin) and  $\text{Li}_3\text{N}$  (over 99.9% purity, Aladdin) were firstly mixed in an agate mortar for 10 min within an Ar-filled glovebox. The resulting mixture was then milled in Ar atmosphere in zirconia jars (45 ml) using zirconia balls (5 mm and 10 mm diameter) with a ball-to-powder mass ratio of 45:1 on a planetary mill (Pulverisette 7, FRITSCH) at 100 rpm for 3 h then at 500 rpm for 3–140 h. The ball-

milling program included repeated counterclockwise rotation for 15 min followed by a 5 min rest, then clockwise rotation for 15 min followed by a 5 min rest.

### Material characterizations and analysis

X-ray diffraction (XRD) measurements were conducted on a diffractometer (Malvern Panalytical, Empyrean) with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406\text{ \AA}$ ). Before XRD measurements, the sample was sealed with Kapton film under an inert atmosphere to avoid air exposure. The morphology of samples was analyzed by the field emission scanning electron microscope (SEM, JEOL-JSM7610), and a liquid-nitrogen-cooled silicon detector was used for obtaining energy-dispersive spectroscopy (EDS). A high-resolution imaging system developed by the National Center for Applied Mathematics Shenzhen (NCAMS) was used to acquire the X-ray transmission computed tomography (XCT) images. The visualization and segmentation of XCT images were performed using Avizo software (Thermo Fisher Scientific, USA). Raman spectrometer (LabRAM Odyssey, Horiba) was used to monitor the Raman vibrational characteristics of  $x\text{Li}_3\text{N-TaCl}_5$  SSEs. The samples were tested in glass capillaries with a diameter of 1.0 mm filled in Ar. Pair distribution function (PDF) data were acquired at room temperature using a PANalytical Empyrean powder diffractometer equipped with  $\text{Ag K}\alpha$  radiation ( $0.559\text{ \AA}$ ) and a GaliPIX3D detector. The samples were encapsulated in 1.0 mm diameter glass capillaries. Total scattering data were collected over a  $2^\circ$ – $140^\circ$  range during a 17-hour measurement. The coherent X-ray scattering data,  $I_c(Q)$ , was processed to obtain the structure function,  $S(Q)$ , which was then Fourier transformed into PDF data and refined using PDFgui software<sup>55</sup>.

## Electrochemical measurements and fabrication of batteries

The ionic conductivity of as-prepared  $x\text{Li}_3\text{N-TaCl}_5$  was studied using electrochemical impedance spectroscopy (EIS). The EIS of  $x\text{Li}_3\text{N-TaCl}_5$  was tested by pressing 130 mg of SSE powder into a pellet in a polyether-ether-ketone (PEEK) mold with a 10 mm diameter under a pressure of 3 tons, and two stainless-steel rods were clamped on both sides of the SSE as the blocking electrodes. The thickness of the pellets was between 0.05 cm and 0.055 cm. EIS was measured on an electrochemical workstation (Solartron 1470E) in the frequency range of 0.1 Hz to 1 MHz with an amplitude voltage of 10 mV at different temperatures. In addition, the nature of the applied signal is potentiostatic, and the overall data points are 71. The ionic conductivities ( $\sigma$ ) of SSEs were detected by the EIS method and calculated according to the formula of  $\sigma = L / (R\pi r^2)$ , where  $L$ ,  $R$ ,  $r$  are the thickness, total resistance, and radius of SSEs, respectively.

The composite cathode for the all-solid-state batteries (ASSBs) was prepared by mixing  $\text{LiCoO}_2$  (LCO, from Guangdong Canrd New Energy Technology Co., Ltd), amorphous  $\text{Li}_{1.25}\text{NTCl}$ , and vapor grown carbon nanofibers (VGCF, also from Guangdong Canrd New Energy Technology Co., Ltd) in a weight ratio of 70: 25: 5. This mixture was ground in an agate mortar for 10 min to ensure uniformity. The ASSBs were assembled employing composite cathode combined with  $\text{Li}_{1.25}\text{NTCl} / \text{Li}_{10}\text{GeP}_2\text{S}_{12}$  (LGPS) bilayer electrolyte and Li-In alloy anode. Firstly,  $\text{Li}_{1.25}\text{NTCl}$  powder (~80 mg) was pressed at 1 ton in a PEEK mold. Then, 5 mg of the composite cathode was uniformly distributed on the  $\text{Li}_{1.25}\text{NTCl}$  layer and pressed at 2 tons, followed by the distribution of LGPS powder (~40 mg) on the other side of  $\text{Li}_{1.25}\text{NTCl}$  layer, pressing with a force of 3 tons. A piece of In foil (over 99.99% purity,  $\phi$  10 mm, thickness 0.19 mm) was attached to the surface of LGPS, and a Li foil (over 99.9% purity,  $\phi$  8 mm, thickness 0.12 mm) with a weight ratio of Li/In = 1:40 was attached to the In foil through pressing under 0.5 ton to assemble the integrated ASSB. Finally, a stack pressure of 0.5 ton was applied to the battery for electrochemical tests. It should be noted that the terms ‘anode’ and ‘cathode’ here refer to the negative and positive electrodes during discharge, respectively. All cell fabrication processes were carried out in an Ar-filled glove box ( $\text{H}_2\text{O}$ ,  $\text{O}_2 < 0.1$  ppm). All measurements were performed using the Wuhan Land battery test system at different temperatures within the low temperature test chambers, except for the  $-60^\circ\text{C}$  test, which utilized the Solartron 1470E electrochemical workstation.

## Ab-initio molecular dynamics (AIMD) simulations and the amorphous model construction

We used the Vienna ab initio simulation package (VASP)<sup>56,57</sup> based on density functional theory (DFT) to perform all the AIMD simulations. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) parametrized exchange-correlation functional was employed for the calculations<sup>58</sup>. Valence electron wave functions were represented using plane wave basis sets, while core-electron interactions were modelled with the projector augmented wave (PAW) method<sup>59</sup>. The Grimme’s DFT+D3 method<sup>60</sup> was used to account for van der Waals interactions. The plane-wave cut-off energy was set to be 520 eV for all calculations. The Brillouin zone integration was performed using only the gamma point<sup>61</sup>. The amorphous model was constructed by the following steps. Firstly, we randomly mixed the crystallographic structures of  $\text{TaCl}_5$  and  $\text{Li}_3\text{N}$  obtained from the Materials Project<sup>62</sup>. The mixing ratio was 12:5 and the density was set as  $3.13\text{ g/cm}^3$ , consistent with the experiments. Secondly, the structure was melted by heating it to 1200 K using the NVT ensemble for 4 ps. Then, the melted configuration was quenched to room temperature (300 K) at a rate of  $1.5 \times 10^{14}\text{ K/s}$ . Finally, AIMD simulations were conducted using the NVT ensemble at 300 K for 4 ps.

## Data availability

The data that support the findings of this study are available within the paper (and its Supplementary Information files) and from the corresponding authors upon request. Source data are provided in Figshare (<https://doi.org/10.6084/m9.figshare.26788072>).

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## Competing interests

The authors declare no competing interests.

## Additional information

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