

Peer Review File

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



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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The manuscript by Hong et al. reports exceptional rate-performance of an ASSB cycled at very low temperature and employing an amorphous $\text{Li}_3\text{N}-\text{TaCl}_5$ solid electrolyte. The authors have used electrochemical characterization, structural & spectroscopic techniques, and ab-initio molecular dynamics simulations to rationalize the unprecedented capacity performance of the assembled composite $\text{LCO}|\text{L1.25NTCl-LGPS}|\text{Li-In}$ battery. Given the increasing focus on ASSB as alternatives to conventional Li-ion batteries and the need of better performances at very low T, improving the rate-performance & cyclability of ASSB is crucial as ionic transport at the interfaces is traditionally seen as the stumbling block to their commercialization. In this regard, the results presented in this manuscript are a timely and essential addition to the research on solid state batteries. However, the following points must be addressed in the revised manuscript before being accepted for publication in Nature Communications.

- The authors studied experimentally the local structure of the amorphous SSE by Raman spectroscopy and atomic pair distribution function (PDF). The discussion concerning the local Ta-Cl and Ta-N arrangement is not well presented and lacks clarity. The authors attributed the observed changes in interatomic distances to “stronger electronegativity of N compared to Cl”. In the Pauling scale these atoms have similar electronegativity so the authors should better support their statement or reconsider it. The PDF analysis has been used just for a qualitative assessment of possible structural characteristics of the amorphous L1.25NTCl SSE, however data fitting might give more details concerning the local structure.
- Did the author have any cycling results of cells containing just the amorphous L1.25NTCl without the addition of LGPS to better clarify the beneficial role of this second electrolyte which was at the interface with the anode?
- Please add the ball milling time in the caption of Fig 2(a) because it is unclear.
- Caption of Fig 4, please specify (c) at different rates at -30°C and similarly in the text when talking about this Fig 4c, “switching the rate from 1C to 0.2C” at -30°C .
- Can the authors make some additional comments about the death of the cell? How many cycles could it sustain before failing?

Reviewer #2 (Remarks to the Author):

The research topic is attractive and important to the field of electrochemical energy storage, especially the electric vehicle industry since charging/discharging safely at extremely low temperatures remains a formidable challenge up till now. In this report authors synthesized amorphous solid-state electrolyte, LNTCl under various conditions to maximize its ionic conductivity even at very low temperatures. Electrochemical properties of the ASSB are impressive, although they are not ideal and significant advancement is still needed. However, there are quite a few concerns required to be addressed as follows:

1. Double solid electrolytes in series were used to build solid state batteries, aiming to relieve the interface barrier with the anode. But the ionic conductivity of LGPS/LNTCL composite is not measured and shall be shared with the audience.
2. In addition, the electrochemical performance of solid-state batteries assembled using pure LGPS and LNTCL must be provided for comparison since there is a significant amount of LGPS used in the composite whose ionic conductivity is comparable to LNTCL.
3. As hypothesized by authors, amorphization benefits the enhancement of ionic conductivity. When $x=1.1$ and 1 , the ionic conductivity is more than ten times smaller than the ionic conductivity when $x=1.2$ and 1.25 . PXRD data clearly indicates LNTCL is amorphous when $x=1.0$ and 1.1 , while the x difference is less than 10%. Reasonable explanation is necessary to clarify the puzzle.
4. The impurity peaks in PXRD patterns shall be identified (Fig. 2).
5. There are multiple questions regarding the electrochemical data. Why don't authors add the $0.1C$ data at $-60\text{ }^{\circ}\text{C}$ in Fig. 4 instead of $0.04C$? Being consistent is necessary for comparison and drawing solid conclusions. Also, the voltage plateau is reduced from 4.1 V to 3.7 V when the temperature is decreased from -30 to $-60\text{ }^{\circ}\text{C}$, implying that there is a significant increase in overpotential and internal resistance, thus further lowering the energy density. Furthermore, the cyclability at $-60\text{ }^{\circ}\text{C}$ is much worse than at $-30\text{ }^{\circ}\text{C}$, although the low capacity is understandable (25%). Is there any tentative explanation?
6. The manuscript is generally well written with a few typos such as 'donated'.

Reviewer #3 (Remarks to the Author):

The authors designed an all-solid-state battery which can be operated under extreme cold conditions. The authors presented that the designed ASSB battery, containing LiCoO_2 cathode and Li-In anode, shows great electrochemical performance at $-60\text{ }^{\circ}\text{C}$ for over 200 h. The experimental analyses and cycling performance results in the manuscript are promising for future applications, which can open new doors for low-temperature battery technology. Therefore, I do recommend the publication of this manuscript in "Nature Communications", but several issues must be corrected before publishing. Some comments are provided below for further improvement:

1. Please refine the entire manuscript and avoid duplicate sentences. (The first and second sentences in the abstract and the introduction part are the same).
2. The authors briefly mentioned the higher activation energy of grain boundary for polycrystalline SSE and the decrease in ionic conductivity at the grain boundaries of SSEs in the Introduction part. Can authors go into detail about the relationship between the activation energy of grain boundary and ionic conductivity?
3. Please correct the spelling mistake in the labelling of results in Fig. 2c. ("rmp" to "rpm")
4. Please present the full version of the Nyquist plot of L1.25NTCl with different ball milling durations, which is partially inserted into Fig. 3b.
5. In Fig. 3c, typical impedance plots of L1.25NTCl measured at various temperatures are presented with the temperature range from -60 to $70\text{ }^{\circ}\text{C}$. On the other hand, Supplementary Fig. 3 shows the impedance of L1.25NTCl with the temperature range from -30 to $70\text{ }^{\circ}\text{C}$. Please include the overall results for L1.25NTCl with the temperature range from -60 to $70\text{ }^{\circ}\text{C}$ in the manuscript.

6. Can authors discuss the relation between ion conductivities and activation energies for $x\text{Li}_3\text{N-TaCl}_5$?
7. Recent articles reported that LGPS shows poor stability with Li anode (Energy Storage Materials, 63, 2023, 103038 / Nature, 593, 2021). In the meantime, the authors mentioned that $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) has interface stability with the Li-In alloy anode in the study. Can authors explain and discuss more about the interface stability of LGPS and Li-In anode?
8. In some of the ASSB performance results, 1C is 140 mAh g⁻¹. On the other hand, some graphs show that 1C is 180 mAh g⁻¹. Please explain the difference between 1C values.
9. Can authors give details about EIS measurements of $x\text{Li}_3\text{N-TaCl}_5$, such as electrode type and configuration.

Responses to reviewer's comments

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

Bolong Hong^{1,2,11}, Lei Gao^{3,4,11*}, Changping Li⁵, Genming Lai⁴, Jinlong Zhu^{1*}, Dubin Huang⁶, Yunxing Zuo⁷, Wen Yin⁸, Mengyu Sun⁹, Shusen Zhao⁹, Jiaxin Zheng⁴, Songbai Han^{2,9,10*}, Ruqiang Zou^{3,4*}

We would like to express our gratitude to the reviewers for their time and effort in reviewing our manuscript. This document serves to list the comments made by the reviewers and to describe the changes that have been made to the manuscript and the Supplementary information in response to those comments. For the sake of clarity, the reviewer's comments are presented in black text, while our responses are in blue text. In addition, copies of the manuscript and Supplementary information in which the changes are highlighted have been included with this submission.

Responses comments

Reviewer #1 (Remarks to the Author):

The manuscript by Hong et al. reports exceptional rate-performance of an ASSB cycled at very low temperature and employing an amorphous $\text{Li}_3\text{N-TaCl}_5$ solid electrolyte. The authors have used electrochemical characterization, structural & spectroscopic techniques, and ab-initio molecular dynamics simulations to rationalize the unprecedented capacity performance of the assembled composite $\text{LCO}|\text{L}_{1.25}\text{NTCl-LGPS}|\text{Li-In}$ battery. Given the increasing focus on ASSB as alternatives to conventional Li-ion batteries and the need of better performances at very low T, improving the rate-performance & cyclability of ASSB is crucial as ionic transport at the interfaces is traditionally seen as the stumbling block to their commercialization. In this regard, the results presented in this manuscript are a timely and essential addition to the research on solid state batteries. However, the following points must be addressed in the revised manuscript before being accepted for publication in Nature Communications.

Reply:

We appreciate for your positive comments on our studies and giving us a valuable opportunity to make the manuscript improved. We have revised the manuscript according to your suggestion.

1. The authors studied experimentally the local structure of the amorphous SSE by Raman spectroscopy and atomic pair distribution function (PDF). The discussion concerning the local Ta-Cl and Ta-N arrangement is not well presented and lacks clarity. The authors attributed the observed changes in interatomic distances to "stronger electronegativity of N compared to Cl". In the Pauling scale these atoms have similar electronegativity so the authors should better support their statement or reconsider it. The PDF analysis has been used just for a qualitative assessment of possible structural characteristics of the amorphous $\text{L}_{1.25}\text{NTCl}$ SSE, however data fitting might give more details concerning the local structure.

Reply:

Thank you for your question. We apologize for the lack of rigor in our initial discussion regarding the local Ta–Cl and Ta–N arrangements. Your kind suggestion has helped us refine and enhance the content of this discussion. We have now further fitted the PDF data of L_{1.25}NTCl to obtain a quantitative evaluation of the local structure. As shown in **Fig. 1**, the PDF data can be well fitted using the amorphous model constructed from AIMD simulations through small-box least square refinement ($R_w = 10.9\%$). Furthermore, partial PDF from Ta–Cl, Ta–N, Li–Cl, and Li–N pairs were extracted from the total PDF data of L_{1.25}NTCl. Due to the retention of local coordination relationships between Ta and Cl in the original structure of TaCl₅, partial PDF from Ta–Cl pairs accounts for the major contribution in the total PDF data of L_{1.25}NTCl, and the interatomic distance of Ta–Cl is mainly distributed at 2.40363 Å. In addition, due to the introduction of N atoms in L_{1.25}NTCl, the peaks corresponding to the interatomic distances of Ta–N and Li–N at 1.92291 Å and 2.04309 Å appeared in the partial PDF data 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 Li⁺ in the amorphous matrix of L_{1.25}NTCl.

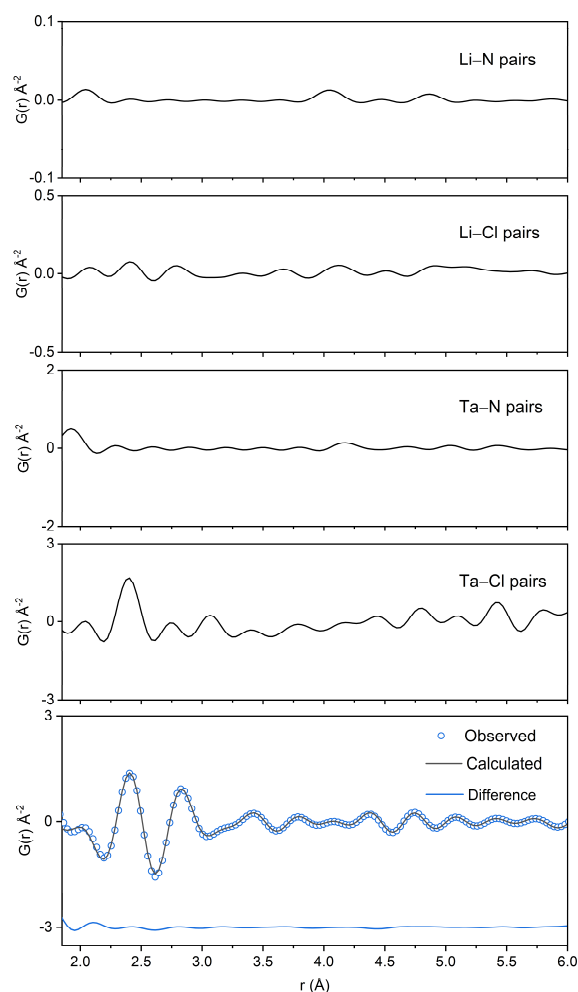


Fig. 1 | The small-box least-square refinement of PDF data of amorphous L_{1.25}NTCl, and the partial PDF from Ta–Cl, Ta–N, Li–Cl, and Li–N pairs extracted from the total PDF data.

Now we have provided the fitted PDF data in Results and Discussion of the manuscript, and revised the relevant content as follows:

“Also, the PDF data of amorphous $L_{1.25}NTCl$ 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 $L_{1.25}NTCl$. Due to the retention of local coordination relationships between Ta and Cl in the original structure of $TaCl_5$, partial PDF from Ta–Cl pairs accounts for the major contribution in the total PDF data of $L_{1.25}NTCl$, and the interatomic distance of Ta–Cl is mainly distributed at 2.40363 Å. In addition, by incorporating N atoms into $L_{1.25}NTCl$, the peaks corresponding to the interatomic distances of Ta–N and Li–N at 1.92291 Å and 2.04309 Å 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 Li^+ in the amorphous matrix of $L_{1.25}NTCl$.”

2. Did the author have any cycling results of cells containing just the amorphous $L_{1.25}NTCl$ without the addition of LGPS to better clarify the beneficial role of this second electrolyte which was at the interface with the anode?

Reply:

Thank you for your question. According to your suggestion, we have conducted charge and discharge cycles on the $LCO|L_{1.25}NTCl|Li-In$ battery at 0.1 C and $-30\text{ }^{\circ}C$. As shown in **Fig. 2**, the $LCO|L_{1.25}NTCl|Li-In$ cell exhibits a negligible capacity (approximately 0 mAh g^{-1}) after 100 cycles at $-30\text{ }^{\circ}C$. In contrast, the $LCO|L_{1.25}NTCl-LGPS|Li-In$ cell maintains a capacity of 121 mAh g^{-1} after 100 cycles (**Fig. 3a** in the manuscript and **Supplementary Fig. 13**). Additionally, we have appropriately integrated **Fig. 2** into **Supplementary Fig. 14a** in the **Supplementary Information** to clarify the beneficial role of the LGPS layer at the interface with the Li-In anode.

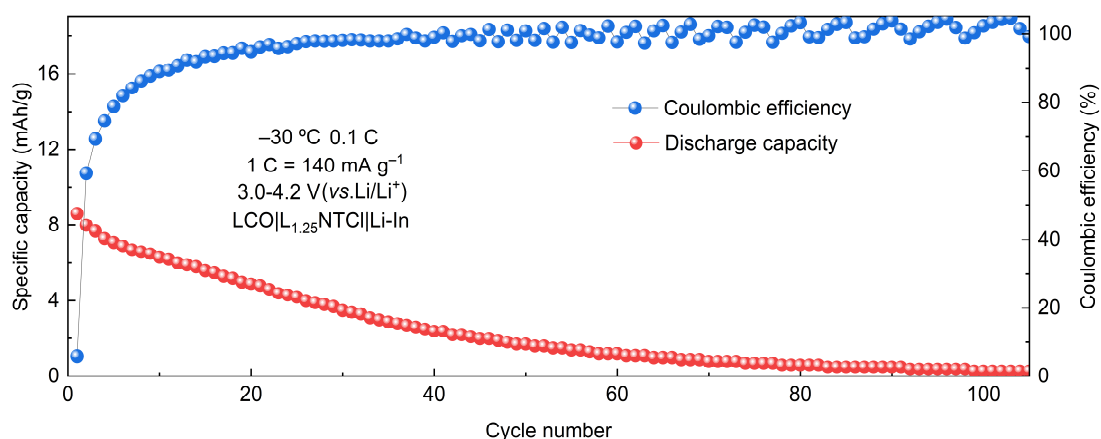


Fig. 2 | The electrochemical performance of $LCO|L_{1.25}NTCl|Li-In$ battery at $-30\text{ }^{\circ}C$ with voltage range of 3.0–4.2 V vs. Li/Li^+ .

3. Please add the ball milling time in the caption of Fig 2(a) because is unclear.

Reply:

Thank you for pointing it out. We apologize for the omission of related information in the manuscript. Based on your suggestion, we have included the ball-milling time in the caption of **Fig. 2a** in our manuscript. The revised caption of **Fig. 2a** is as follows:

“XRD patterns of the amorphous $x\text{Li}_3\text{N-TaCl}_5$ ($1 \leq 3x \leq 2$) ball-milled at 30 h.”

4. Caption of Fig 4, please specify (c) at different rates at -30 °C and similarly in the text when talking about this fig 4c, “switching the rate from 1C to 0.2 C” at -30 °C.

Reply:

Thank you for your suggestion. We have incorporated the following content into the caption of **Fig. 4c** in the manuscript:

“(b) The discharge profiles of ASSBs at 0.1 C and different temperatures (−10, −30, and −40 °C). (c) The cycling performance of ASSBs at −30 °C and different rates (0.1, 0.2, 0.33, 0.5, and 1 C) with voltage range of 3.0–4.5 V vs. Li/Li⁺. (d) The cycling performance of ASSBs at −30 °C with charge/discharge voltage range of 3.0–4.5 V vs. Li/Li⁺ at 0.1 C. (e) The charge/discharge profiles of ASSBs at −30 °C with cutoff voltages set at 3.0 V and 4.5 V vs. Li/Li⁺ at 0.1 C. (f–h) The charge/discharge profiles of ASSBs at −60 °C with cutoff voltages set at 3.0 V and 4.5 V vs. Li/Li⁺ at 0.04 C (f) and 0.1 C (g, h).”

Additionally, in the main text, we have revised the text as follows:

“Upon extending the charging/discharging voltage range to 3.0–4.5 V vs. Li/Li⁺, the ASSB demonstrates unexpectedly high discharge capacities of 183.19, 164.8 and 143.78 mAh g^{−1} at −10, −30, and −40 °C, respectively (**Fig. 4b**), as well as 139.1 mAh g^{−1} after switching the rate from 1 C to 0.2 C at −30 °C.”

5. Can the authors make some additional comments about the death of the cell? How many cycles could it sustain before failing?

Reply:

Thank you for your question. **Fig. 3** demonstrates the performance of LCO|L_{1.25}NTCl-LGPS|Li-In battery at −30 °C with voltage range of 3.0–4.2 V vs. Li/Li⁺ over an extended cycle period (Note: The battery is currently in operation). The ASSB 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. Despite the ASSB charging and discharging over 360 cycles at −30 °C, capacity degradation gradually appears after approximately 200 cycles. We have now made the additional comments about the capacity degradation of the cell in the caption of **Supplementary Fig. 13** in the **Supplementary Information** as follows:

“Supplementary Fig. 13 | Charge/discharge voltage profiles of LCO|L_{1.25}NTCl-LGPS|Li-In battery at −30 °C. 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.”

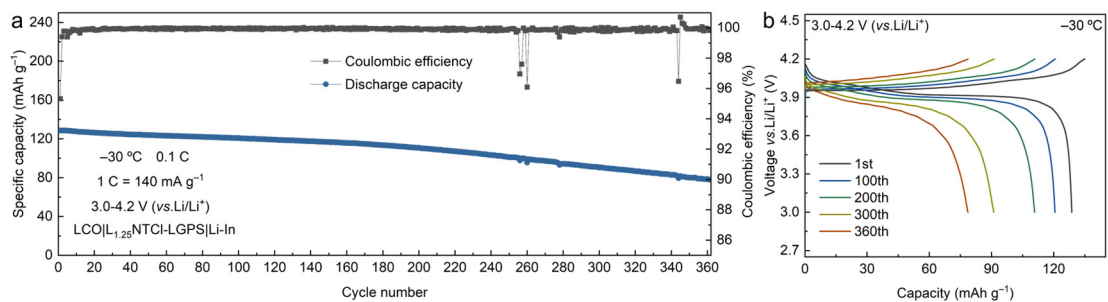


Fig. 3 | The cycling performance (a) and charge/discharge voltage profiles (b) of LCO|L_{1.25}NTCl-LGPS|Li-In battery at -30 °C with voltage range of 3.0–4.2 V vs. Li/Li⁺.

Reviewer #2 (Remarks to the Author):

The research topic is attractive and important to the field of electrochemical energy storage, especially the electric vehicle industry since charging/discharging safely at extremely low temperatures remains a formidable challenge up till now. In this report authors synthesized amorphous solid-state electrolyte, LNTCl under various conditions to maximize its ionic conductivity even at very low temperatures. Electrochemical properties of the ASSB are impressive, although they are not ideal and significant advancement is still needed. However, there are quite a few concerns required to be addressed as follows:

Reply:

Thank you very much for your comment and giving us a valuable opportunity to make the manuscript improved. We have revised the manuscript according to your suggestion.

1. Double solid electrolytes in series were used to build solid state batteries, aiming to relieve the interface barrier with the anode. But the ionic conductivity of LGPS/LNTCL composite is not measured and shall be shared with the audience.

Reply:

Thank you for pointing it out. We apologize for the omission of related information in the manuscript. Now, we have measured the electrochemical impedance spectroscopy (EIS) and obtained the ionic conductivity of the $\text{L}_{1.25}\text{NTCl-LGPS}$ composite SSE. **Fig. 1a** illustrates the EIS curves of $\text{L}_{1.25}\text{NTCl-LGPS}$ SSE across a temperature range from 70 °C to -60 °C. The ionic conductivities of $\text{L}_{1.25}\text{NTCl-LGPS}$ SSE are 0.388 mS cm^{-1} at -30 °C, 0.227 mS cm^{-1} at -40 °C, and 0.044 mS cm^{-1} at -60 °C, respectively. Furthermore, the fitting of Arrhenius plots reveals that the activation energy (E_a) for $\text{L}_{1.25}\text{NTCl-LGPS}$ SSE is 0.299 eV. Now, **Fig. 1** has also been incorporated into **Supplementary Information** as **Supplementary Fig. 8**.

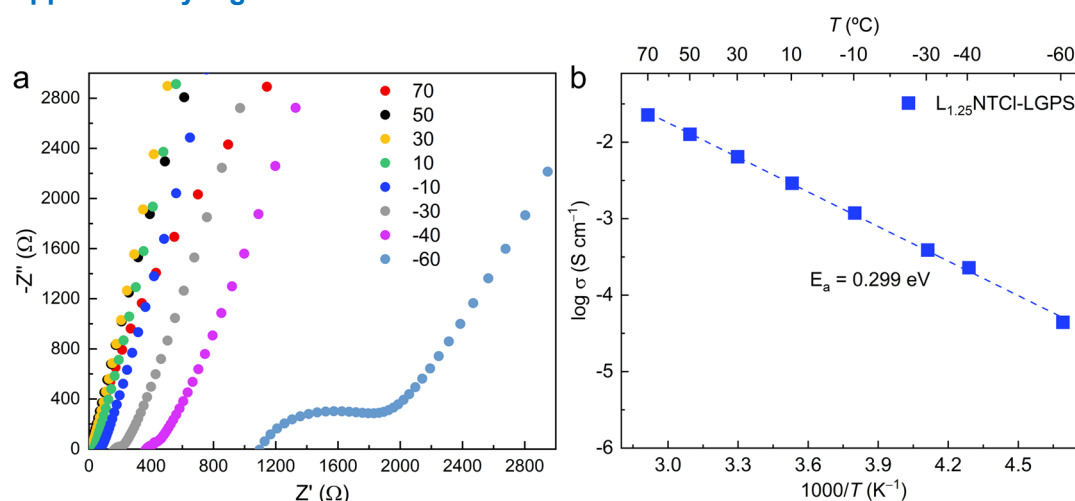


Fig. 1 | Li^+ conductivity of $\text{L}_{1.25}\text{NTCl-LGPS}$ SSE. (a) The electrochemical impedance spectroscopy of $\text{L}_{1.25}\text{NTCl-LGPS}$ SSE measured at various temperatures. (b) Arrhenius plots of $\text{L}_{1.25}\text{NTCl-LGPS}$ SSE in the temperature range from -60 to 70 °C.

2. In addition, the electrochemical performance of solid-state batteries assembled using pure LGPS and LNTCL must be provided for comparison since there is a significant amount

of LGPS used in the composite whose ionic conductivity is comparable to LNTCL.

Reply:

Thank you for your suggestion. We have conducted cycling performance tests on LCO|LGPS|Li-In and LCO|L_{1.25}NTCl|Li-In cells at 0.1 C and –30 °C for comparison with the LCO|L_{1.25}NTCl-LGPS|Li-In. As presented in **Fig. 2**, the LCO|LGPS|Li-In cell exhibits an approximate capacity of 0 mAh g^{–1} from the 1st cycle to 100th cycle. This unfavorable cycling performance may be attributed to the incompatibility of LGPS with the LCO cathode and the significantly elevated grain boundary resistance of LGPS at –30 °C. On the other hand, the LCO|L_{1.25}NTCl|Li-In cell exhibits an initial discharge capacity of 8.6 mAh g^{–1}, as depicted in **Fig. 3**. Then the capacity gradually declines to 0 mAh g^{–1} after 100 cycles, which can be attributed to the potential chemical reaction between L_{1.25}NTCl and Li-In anode. Also, the Li-In|L_{1.25}NTCl|Li-In symmetric cell demonstrates sharply increased polarization voltage (**Fig. 4a**) and impedance (**Fig. 4b**) at a current density of 0.2 mA cm^{–2}. This highlights the interfacial instability between L_{1.25}NTCl and Li-In, which is the primary reason for the low discharge capacity and poor cycling performance observed in the LCO|L_{1.25}NTCl|Li-In cell.

Now, **Fig. 2**, **Fig. 3** and **Fig. 4a** have been appropriately included in the **Supplementary Information**, and the relevant content has been incorporated into the **Results and discussion** section as follows:

“Besides, both the LCO|L_{1.25}NTCl|Li-In battery and the LCO|LGPS|Li-In battery exhibit capacities approaching 0 mAh g^{–1} after 100 cycles, highlighting the necessity of the bilayer L_{1.25}NTCl-LGPS SSE design for enhancing the performance of ASSB”.

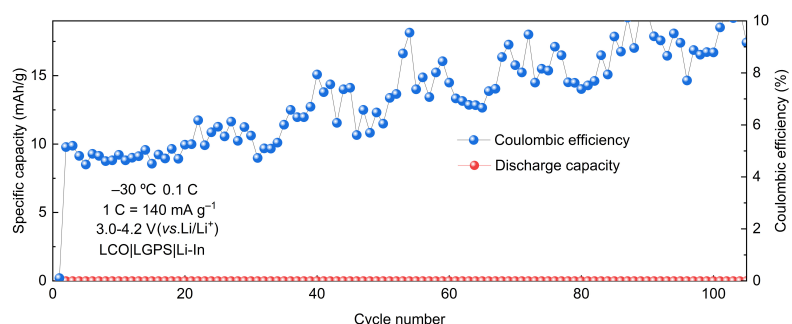


Fig. 2 | The electrochemical performance of LCO|LGPS|Li-In battery at –30 °C with voltage range of 3.0–4.2 V vs. Li/Li⁺.

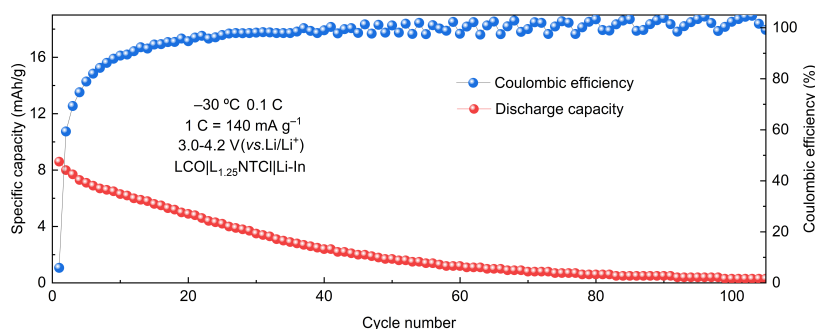


Fig. 3 | The electrochemical performance of LCO|L_{1.25}NTCl|Li-In battery at –30 °C with voltage range of 3.0–4.2 V vs. Li/Li⁺.

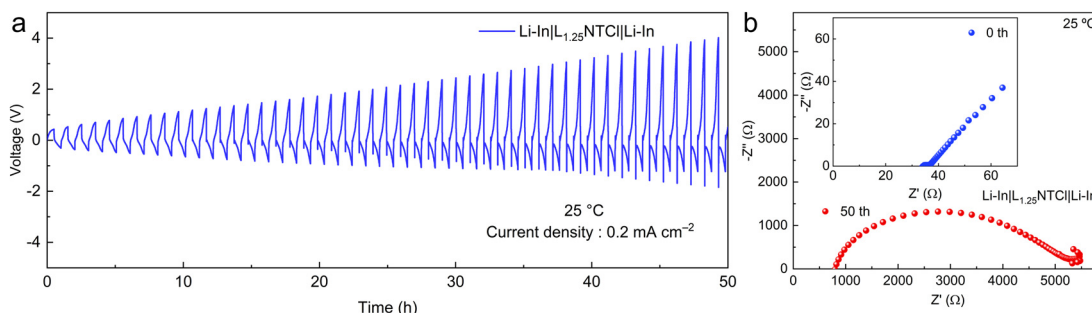


Fig. 4 | The electrochemical performance of Li-In symmetric cell based on $L_{1.25}NTCl$ SSEs. (a) The galvanostatic cycling of Li-In symmetric cell at 25 °C. (b) The EIS results for the Li-In symmetric cell at its initial state and after 50th cycle.

Reference

1. Zhang, M. et al. Self-sacrificing reductive interphase for robust and high-performance sulfide-based all-solid-state lithium batteries. *Adv. Energy Mater.* 14, (2024).
2. Wang, C.-W. et al. Engineering the interface between $LiCoO_2$ and $Li_{10}GeP_2S_{12}$ solid electrolytes with an ultrathin $Li_2CoT_{13}O_8$ interlayer to boost the performance of all-solid-state batteries. *Energy Environ. Sci.* 14, 437–450 (2021).
3. Wang, C.-W. et al. Mechanochemical reactions between polyanionic borate and residue Li_2CO_3 on $LiCoO_2$ to stabilize cathode/electrolyte interface in sulfide-based all-solid-state batteries. *Nano Energy* 108, 108192 (2023).

3. As hypothesized by authors, amorphization benefits the enhancement of ionic conductivity. When $x=1.1$ and 1, the ionic conductivity is more than ten times smaller than the ionic conductivity when $x=1.2$ and 1.25. PXRD data clearly indicates LNTCL is amorphous when $x=1.0$ and 1.1, while the x difference is less than 10%. Reasonable explanation is necessary to clarify the puzzle.

Reply:

Thank you for your question. For the $xLi_3N-TaCl_5$ SSEs system, both the x values in $xLi_3N-TaCl_5$ (i.e., Li^+ concentration) and the amorphization degree play importance roles in influencing their ionic conductivities. When x in a specific value, such as $3x = 1.25$ (as shown in **Fig. 2c** in our manuscript), the ball-milling process (ranging from 3 to 30 hours at 500 rpm) exhibits a discernible trend: increased amorphization correlates with enhanced conductivity. On the other hand, when keeping the same ball-milling conditions of 30 hours at 500 rpm, although the PXRD data indicate $xLi_3N-TaCl_5$ SSEs are amorphous when $3x = 1.0$ and 1.1, the insufficient Li^+ concentrations (i.e., carriers) may limit the Li^+ transport between the polyhedral coordination structure within the amorphous matrix. Besides, similar phenomena have been reported for $xLi_2O-TaCl_5$ and $NaTaCl_6$ systems^{1,2}.

We have now incorporated this relevant content into the **Results and discussion** section as follows:

“It is worth noting that although the $xLi_3N-TaCl_5$ SSEs are completely amorphous (as observed with $3x = 1.0$ and 1.1), the insufficient Li^+ concentrations may limit Li^+ transport within the polyhedral coordination structures of the amorphous matrix.”

Reference

1. Zhang, S. et al. A family of oxychloride amorphous solid electrolytes for long-cycling all-solid-state lithium batteries. *Nat. Commun.* 14, (2023).
2. Hu, Y. et al. Superionic amorphous NaTaCl_6 halide electrolyte for highly reversible all-solid-state Na-ion batteries. *Matter* 7, 1018–1034 (2024).

4. The impurity peaks in PXRD patterns shall be identified (Fig. 2).

Reply:

Thank you for pointing it out. The impurity peaks can be identified in the PXRD pattern of $x\text{Li}_3\text{N-TaCl}_5$ with $3x = 2$. As depicted in **Fig. 5**, trace amounts of LiCl and TaN impurities are observed. This finding implies that there is a limiting value for Li_3N that can be incorporated in TaCl_5 , and exceeding this limit leads to the formation of impurities, which could potentially affect the ionic conductivity of the $x\text{Li}_3\text{N-TaCl}_5$ SSEs. Additionally, **Fig. 5** have been appropriately included in the **Supplementary Information** as **Supplementary Fig. 1**.

We have now added this relevant content into the **Results and discussion** section as follows:

“When $3x = 2$, the XRD pattern primarily exhibits amorphous characteristics with trace impurities of LiCl and TaN.”

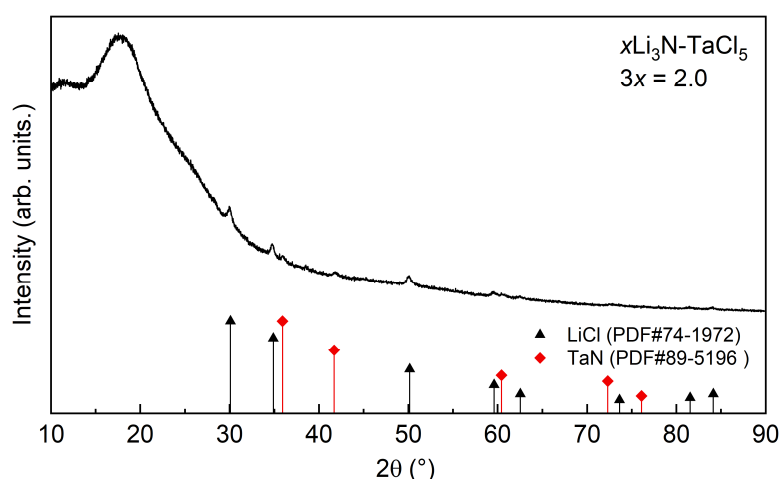


Fig. 5 | XRD patterns of the amorphous $x\text{Li}_3\text{N-TaCl}_5$ ($3x = 2$) at 30 hours of ball-milling.

5. There are multiple questions regarding the electrochemical data. Why don't authors add the 0.1 C data at -60°C in Fig. 4 instead of 0.04 C? Being consistent is necessary for comparison and drawing solid conclusions. Also, the voltage plateau is reduced from 4.1 V to 3.7 V when the temperature is decreased from -30°C to -60°C , implying that there is a significant increase in overpotential and internal resistance, thus further lowering the energy density. Furthermore, the cyclability at -60°C is much worse than at -30°C , although the low capacity is understandable (25%). Is there any tentative explanation?

Reply:

Thank you for your question and suggestion.

According to your suggestion regarding the electrochemical data at -60°C , we have incorporated the charge/discharge voltage profiles of the $\text{LCO}|\text{Li}_{1.25}\text{NTCl-LGPS}|\text{Li-In}$

battery at the current density of 0.1 C and the temperature of $-60\text{ }^{\circ}\text{C}$ (as shown in **Fig. 6**). Also, for better comparison of ASSB performance, **Fig. 5** of our manuscript presents the specific capacities of the LCO|L_{1.25}NTCI-LGPS|Li-In batteries at different temperature ($-10\text{ }^{\circ}\text{C}$, $-30\text{ }^{\circ}\text{C}$, $-40\text{ }^{\circ}\text{C}$, and $-60\text{ }^{\circ}\text{C}$) and the same current density of 0.1 C.

Regarding the declining cyclability of battery at $-60\text{ }^{\circ}\text{C}$, we agree with you that the significant increase in overpotential and internal resistance led to the distinct decrease in capacity. The worse cycling performance of the LCO|L_{1.25}NTCI-LGPS|Li-In cell at $-60\text{ }^{\circ}\text{C}$ compared to $-30\text{ }^{\circ}\text{C}$ can be attributed to increased resistance and the decrease in ionic conductivity of the L_{1.25}NTCI-LGPS bilayer SSE at $-60\text{ }^{\circ}\text{C}$. Specifically, the L_{1.25}NTCI-LGPS SSE exhibits ionic conductivities of 0.388, 0.227, and 0.044 mS cm^{-1} at $-30\text{ }^{\circ}\text{C}$, $-40\text{ }^{\circ}\text{C}$, and $-60\text{ }^{\circ}\text{C}$ (as shown in **Fig. 1**), respectively. In addition, when the LCO|L_{1.25}NTCI-LGPS|Li-In ASSB is charged/discharged at $-60\text{ }^{\circ}\text{C}$, the decreased ionic conductivity of L_{1.25}NTCI-LGPS cannot sustain the fast Li⁺ transport between the cathode/SSE interface, which further influences the exertion of the cathode capacity.

We have now added this relevant content into the **Results and discussion** section as follows:

“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 L_{1.25}NTCI-LGPS bilayer SSE and at the cathode/SSE interface.”

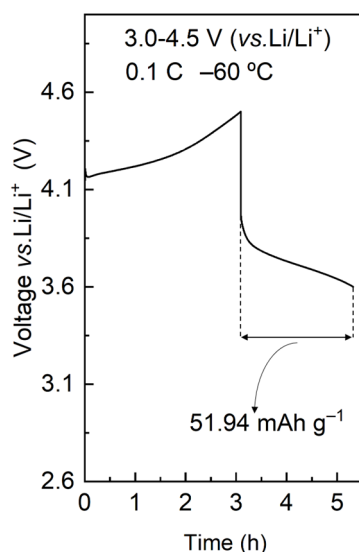


Fig. 6 | The charge/discharge voltage profiles of LCO|L_{1.25}NTCI-LGPS|Li-In battery within the range of 3.0–4.5 V vs. Li/Li⁺ at 0.1 C and $-60\text{ }^{\circ}\text{C}$.

6. The manuscript is generally well written with a few typos such as ‘donated’.

Reply:

Thank you for your suggestion.

We have replaced the term “donated” with “labeled” in the manuscript to enhance the clarity and precision.

Reviewer #3 (Remarks to the Author):

The authors designed an all-solid-state battery which can be operated under extreme cold conditions. The authors presented that the designed ASSB battery, containing LiCoO₂ cathode and Li-In anode, shows great electrochemical performance at –60 °C for over 200 h. The experimental analyses and cycling performance results in the manuscript are promising for future applications, which can open new doors for low-temperature battery technology. Therefore, I do recommend the publication of this manuscript in "Nature Communications", but several issues must be corrected before publishing. Some comments are provided below for further improvement:

Reply:

Reply:

Thank you very much for your comment and giving us a valuable opportunity to make the manuscript improved. We have revised the manuscript according to your suggestion.

1. Please refine the entire manuscript and avoid duplicate sentences. (The first and second sentences in the abstract and the introduction part are the same).

Reply:

Thank you for your pointing it out. Based on your suggestion, we have rechecked and adjusted the entire manuscript to avoid repetitive sentences.

2. The authors briefly mentioned the higher activation energy of grain boundary for polycrystalline SSE and the decrease in ionic conductivity at the grain boundaries of SSEs in the Introduction part. Can authors go into detail about the relationship between the activation energy of grain boundary and ionic conductivity.

Reply:

Thank you for your question.

In the context of Li⁺ conductivity in SSEs, the transport of Li⁺ occurs across multiple scales—the atomic, structural, and interfacial. Both the inherent crystal structures (i.e., bulk of grains) and grain boundaries significantly influence the ionic conductivity of SSEs. For Li⁺ transport within the structure of SSEs, the Li⁺ conduction behavior relies on the factors such as the concentration of mobile ions, energy barriers for hopping, and the attempt frequency, which can be described by the Arrhenius relationship¹. On the other hand, the Li⁺ transport barriers at grain boundaries are typically higher than those in the bulk of grains, which is evident in various types of SSEs, including halide³, sulphide⁴, and oxide⁵. Consequently, 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, further exacerbating the reduction in overall ionic conductivity of SSEs.

Now the relevant content has been added into the **Introduction** section as follows:

“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. 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.”

Reference

1. Bachman, J. C. et al. Inorganic solid-state electrolytes for lithium batteries: Mechanisms and properties governing ion conduction. *Chem. Rev.* 116, 140–162 (2016).
2. Sasano, S. et al. Grain boundary Li-ion conductivity in $(\text{Li}_{0.33}\text{La}_{0.56})\text{TiO}_3$ polycrystal. *Appl. Phys. Lett.* 116, (2020).
3. Li, W. et al. Precise tailoring of lithium-ion transport for ultralong-cycling dendrite-free all-solid-state lithium metal batteries. *Adv. Mater.* 36, (2024).
4. Hwang, T., Conlin, P., Cho, M. & Cho, K. Electrochemical stability and Li ion diffusion kinetics of grain boundaries in $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid electrolyte. *J. Phys. Chem. C Nanomater. Interfaces* 127, 7528–7535 (2023).
5. Yu, S. & Siegel, D. J. Grain boundary contributions to Li-ion transport in the solid electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO). *Chem. Mater.* 29, 9639–9647 (2017).

3. Please correct the spelling mistake in the labelling of results in Fig. 2c. (“rmp” to “rpm”)

Reply:

Thank you for pointing it out.

Now, we have changed the “rmp” in **Fig. 2c** of the manuscript to “rpm”.

4. Please present the full version of the Nyquist plot of $\text{L}_{1.25}\text{NTCl}$ with different ball milling durations, which is partially inserted into Fig. 3b.

Reply:

Thank you for your suggestion. We have presented the full version of the Nyquist plot of $\text{L}_{1.25}\text{NTCl}$ with different ball milling durations in **Fig. 3** of our manuscript, which also is shown in **Fig.1** as follows:

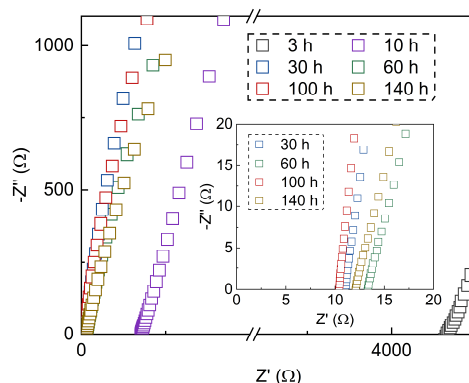


Fig. 1 | Nyquist plots of $\text{L}_{1.25}\text{NTCl}$ SSE with different ball milling durations at 25 °C.

5. In Fig. 3c, typical impedance plots of $L_{1.25}NTCl$ measured at various temperatures are presented with the temperature range from -60 to 70 °C. On the other hand, Supplementary Fig. 3 shows the impedance of $L_{1.25}NTCl$ with the temperature range from -30 to 70 °C. Please include the overall results for $L_{1.25}NTCl$ with the temperature range from -60 to 70 °C in the manuscript.

Reply:

Thank you for pointing it out.

We have incorporated the overall results of the Nyquist plot for $L_{1.25}NTCl$, obtained across various temperatures, into **Fig. 3** of our manuscript. Notably, in both the EIS (**Fig. 2a**) and the Arrhenius plot (**Fig. 2b**), the data recorded at each temperature point correspond directly and consistently.

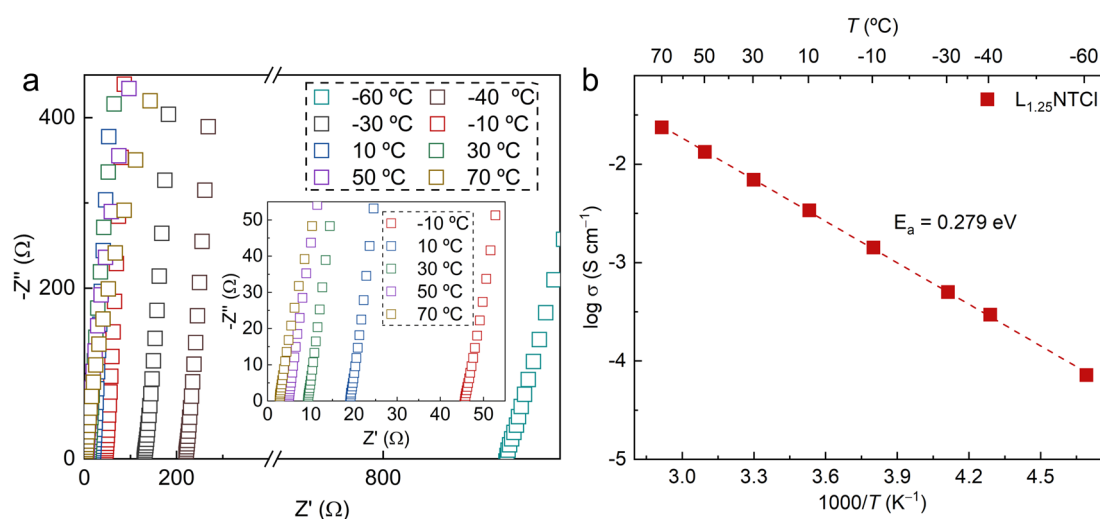


Fig. 2 | Li^+ conductivity of $L_{1.25}NTCl$ SSE. (a) The electrochemical impedance spectroscopy of $L_{1.25}NTCl$ SSE measured at various temperatures. (b) Arrhenius plots of $L_{1.25}NTCl$ SSE in the temperature range from -60 to 70 °C.

6. Can authors discuss the relation between ion conductivities and activation energies for $xLi_3N-TaCl_5$?

Reply:

Thank you for your question.

The ionic conductivity peaks at 5.91 mS cm^{-1} for $L_{1.25}NTCl$ ($xLi_3N-TaCl_5$, $3x = 1.25$) at 25 °C, while the activation energy reaches a minimum of 0.265 eV for $L_{1.3}NTCl$. Similarly, previous studies have highlighted the significant impact of oxygen content on the amorphization degree of oxychloride xLi_2O-MCl_y and $LiAlCl_{4-2x}O_x$ SSEs¹⁻³, as well as their respective ionic conductivities and activation energies. It is important to note that the discrepancy between the ionic conductivities and activation energies of amorphous $xLi_3N-TaCl_5$ 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.

Now the relevant content has been added beneath the caption of Supplementary Fig. 5 in **Supplementary Information** as follows:

“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.”

Reference

1. Zhang, S. et al. A family of oxychloride amorphous solid electrolytes for long-cycling all-solid-state lithium batteries. *Nat. Commun.* 14, 3780 (2023).
2. Tanaka, Y. et al. New oxyhalide solid electrolytes with high lithium ionic conductivity $>10 \text{ mS cm}^{-1}$ for all-solid-state batteries. *Angew. Chem. Int. Ed Engl.* 62, e202217581 (2023).
3. Dai, T. et al. Inorganic glass electrolytes with polymer-like viscoelasticity. *Nat. Energy* 8, 1221–1228 (2023).

7. Recent articles reported that LGPS shows poor stability with Li anode (Energy Storage Materials, 63, 2023, 103038 / Nature, 593, 2021). In the meantime, the authors mentioned that $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) has interface stability with the Li-In alloy anode in the study. Can authors explain and discuss more about the interface stability of LGPS and Li-In anode?

Reply:

Thank you for your suggestion.

As a widely adopted solid-state electrolyte, LGPS serves the crucial role in protecting the easily reducible cathode-side SSEs (e.g., Li_3InCl_6) from reacting with Li-In alloys¹⁻³. Its exceptional ionic conductivity positions LGPS as a promising candidate for all-solid-state batteries operating at low-temperature.

Moreover, to demonstrate the interface stability of LGPS and Li-In anode, we conducted a charge and discharge cycle on a Li-In|LGPS|Li-In symmetric battery at a current density of 0.2 mA cm^{-2} (as depicted in **Fig. 3a**). Remarkably, the Li-In|LGPS|Li-In symmetric cell exhibits stable cycling for over 50 hours. In contrast, the Li-In| $\text{L}_{1.25}\text{NTCl}$ |Li-In symmetric cell demonstrates a sharp increase in polarization voltage at the same current density of 0.2 mA cm^{-2} (**Fig. 3b**), highlighting the interfacial stability between LGPS and Li-In.

In our study, the $\text{LCO}|\text{L}_{1.25}\text{NTCl-LGPS}|\text{Li-In}$ battery demonstrates excellent electrochemical performance at extreme cold conditions. Specifically, we employ a novel $\text{L}_{1.25}\text{NTCl}$ solid electrolyte on the cathode side, which exhibits favorable compatibility with LCO cathodes. The amorphous nature of $\text{L}_{1.25}\text{NTCl}$ promotes close interfacial contact between the electrolyte and cathode particles, facilitating rapid Li^+ transport. On the anode side, we utilize an LGPS solid electrolyte, primarily aimed at preventing undesirable reactions between the $\text{L}_{1.25}\text{NTCl}$ and the Li-In alloy anode while maintaining high ionic conductivity.

Now, **Fig. 3a** and **Fig. 3b** have been appropriately included in the **Supplementary Information** as **Supplementary Fig. 7a** and **Supplementary Fig. 7b**.

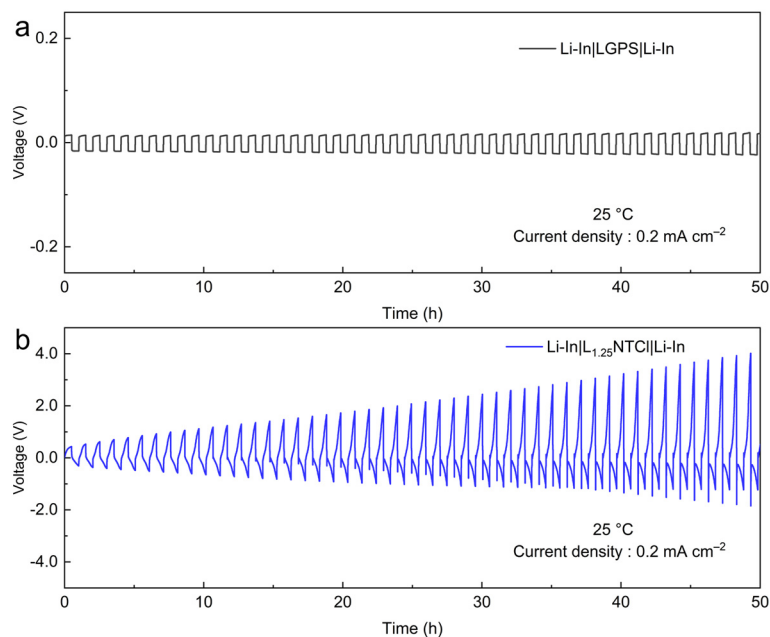


Fig. 3 | The electrochemical performance of Li-In symmetric cell based on LGPS and L_{1.25}NTCI SSEs. (a) The galvanostatic cycling of Li-In|LGPS|Li-In symmetric cell at 25 °C. (b) The galvanostatic cycling of Li-In|L_{1.25}NTCI|Li-In symmetric cell at 25 °C.

Reference

1. Yoon, K., Kim, J.-J., Seong, W. M., Lee, M. H. & Kang, K. Investigation on the interface between Li₁₀GeP₂S₁₂ electrolyte and carbon conductive agents in all-solid-state lithium battery. *Sci. Rep.* 8, (2018).
2. Wang, S. et al. Ultrathin all-inorganic Halide solid-state electrolyte membranes for all-solid-state Li-ion batteries. *Adv. Energy Mater.* 14, (2024).
3. Li, X. et al. Air-stable Li₃InCl₆ electrolyte with high voltage compatibility for all-solid-state batteries. *Energy Environ. Sci.* 12, 2665–2671 (2019).

8. In some of the ASSB performance results, 1 C is 140 mAh g⁻¹. On the other hand, some graphs show that 1 C is 180 mAh g⁻¹. Please explain the difference between 1 C values.

Reply:

Thank you for your question.

The theoretical capacity of 1 C for the LiCoO₂ (LCO) cathode varies depending on the charge cut-off voltage, and the higher cut-off voltage means the higher theoretical capacity. Typically, when the charge cut-off voltage is set at 4.2 V (vs. Li⁺/Li), the theoretical capacity is defined as 140 mAh g⁻¹. In addition, when at a higher cut-off voltage of 4.5 V (vs. Li⁺/Li), the theoretical capacity is defined as 180 mAh g⁻¹. The delithiation of LCO is limited to ≈ 0.5 Li per formula at around 4.2 V (vs. Li⁺/Li), yielding a capacity of ≈ 140 mAh g⁻¹, charging LCO to a higher voltage increases the deliverable capacity (e.g., ≈ 180 mAh g⁻¹ at 4.5 V)¹⁻³.

Reference

1. Liu, J. et al. Tuning interphase chemistry to stabilize high-voltage LiCoO₂ cathode material via spinel

coating. *Angew. Chem. Int. Ed Engl.* 61, (2022).

2. Wang, C.-W. et al. High-voltage LiCoO₂ material encapsulated in a Li₄Ti₅O₁₂ ultrathin layer by high-speed solid-phase coating process. *ACS Appl. Energy Mater.* 3, 2593–2603 (2020).

3. Zhang, H. et al. 1,3,5-Trifluorobenzene and fluorobenzene co-assisted electrolyte with thermodynamic and interfacial stabilities for high-voltage lithium metal battery. *Energy Storage Mater.* 48, 393–402 (2022).

9. Can authors give details about EIS measurements of xLi₃N-TaCl₅, such as electrode type and configuration.

Reply:

Thank you for your suggestion.

We have now provided the details about EIS measurements in **Methods** section as follows:

“The ionic conductivity of as-prepared xLi₃N-TaCl₅ was studied using electrochemical impedance spectroscopy (EIS). The EIS of xLi₃N-TaCl₅ was tested by pressing 130 mg of SSE powder into a pellet in a polyether-ether-ketone (PEEK) mold under a pressure of 3 tons, and two stainless-steel rods were clamped on both sides of the SSE as the blocking electrodes. 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. The ionic conductivities (σ) 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.”

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have replied point by point to the reviewers' comments, and have made the necessary changes to the main text. The manuscript can now be accepted for publication.

Reviewer #2 (Remarks to the Author):

There must be a magic effect from the combination of two badly-performing solid state electrolytes, resulting in much improved electrochemical performance. Also, authors argued that the low ionic conductivity when $3X = 1.0$ and 1.1 is due to insufficient amount of Li ions. Here is my question: when $3X = 1.3$ and 1.4 , there are sufficient amount of Li ions and they are amorphous as determined by PXRD data, why are their ionic conductivities lower than those of $3X = 1.2$ and 1.25 . The explanation seems to be self-conflicting. Overall, authors have input significant effort on the revision.

Reviewer #3 (Remarks to the Author):

Thank you to the authors for their corrections and additions. Before publication, I would like to suggest additional comment to the manuscript, which is mentioned below.

1. Can the authors add the explanation in the 'response to the letter' related to the theoretical capacity of 1 C for the LiCoO_2 (LCO) cathode depending on the charge cut-off voltage to the manuscript? It is believed that this explanation will help the possible reader better understand.

Responses to reviewer's comments

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

Bolong Hong^{1,2,11}, Lei Gao^{3,4,11*}, Changping Li⁵, Genming Lai⁴, Jinlong Zhu^{1*}, Dubin Huang⁶, Yunxing Zuo⁷, Wen Yin⁸, Mengyu Sun⁹, Shusen Zhao⁹, Jiaxin Zheng⁴, Songbai Han^{2,9,10*}, Ruqiang Zou^{3,4*}

We would like to express our gratitude to the reviewers for their time and effort in reviewing our manuscript. This document serves to list the comments made by the reviewers and to describe the changes that have been made to the manuscript and the Supplementary information in response to those comments. For the sake of clarity, the reviewer's comments are presented in black text, while our responses are in blue text. In addition, copies of the manuscript and Supplementary information in which the changes are highlighted have been included with this submission.

Responses comments

Reviewer #1 (Remarks to the Author):

The authors have replied point by point to the reviewers' comments, and have made the necessary changes to the main text. The manuscript can now be accepted for publication.

Reply:

Thank you for your positive comments on our studies and for giving us the valuable opportunity to publish in *Nature Communications*, and we believe our breakthrough findings will generate widespread interest in the field of all-solid-state batteries.

Reviewer #2 (Remarks to the Author):

There must be a magic effect from the combination of two badly-performing solid state electrolytes, resulting in much improved electrochemical performance. Also, authors argued that the low ionic conductivity when $3X = 1.0$ and 1.1 is due to insufficient amount of Li ions. Here is my question: when $3X = 1.3$ and 1.4 , there are sufficient amount of Li ions and they are amorphous as determined by PXRD data, why are their ionic conductivities lower than those of $3X = 1.2$ and 1.25 . The explanation seems to be self-conflicting. Overall, authors have input significant effort on the revision.

Reply:

Thank you for your insightful question, which has helped us enhance the rigor and quality of our manuscript.

Regarding your first question, we agree with you that the combination of two badly-performing solid-state-electrolytes results in much improved electrochemical performance of battery, which can be attributed to a magic effect exerted by $\text{L}_{1.25}\text{NTCl}$ and LGPS at the cathode and anode interfaces of the battery, respectively. Specifically, LGPS is stable with the Li-In anode, while $\text{L}_{1.25}\text{NTCl}$ is not (as shown in **Figure 1** below). On the other side, $\text{L}_{1.25}\text{NTCl}$ is stable with the LCO cathode and its continuous ionic transport characteristic facilitates the exertion of the capacity of the LCO cathode at low temperature (as presented in schematic Fig. 1 of our manuscript), while LGPS is incompatible to LCO cathode [1]. Therefore, the above factors have resulted in poor performance of both $\text{LCO}|\text{L}_{1.25}\text{NTCl}|\text{Li-In}$ and $\text{LCO}|\text{LGPS}|\text{Li-In}$ batteries. However, by combining $\text{L}_{1.25}\text{NTCl}$ and LGPS in the $\text{LCO}|\text{L}_{1.25}\text{NTCl-LGPS}|\text{Li-In}$ configuration, we can harness the strengths of both solid-state-electrolytes while mitigating their respective weaknesses, leading to a marked improvement in battery performance.

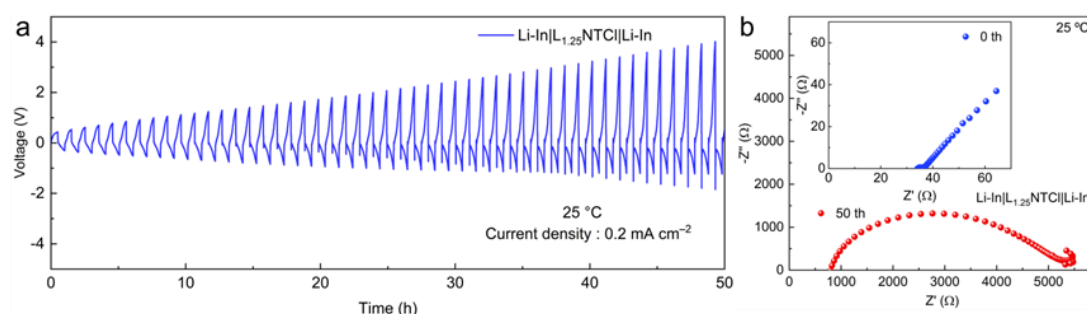


Figure 1. The electrochemical performance of Li-In symmetric cell based on $\text{L}_{1.25}\text{NTCl}$ SSEs. (a) The galvanostatic cycling of Li-In symmetric cell at 25 °C. (b) The EIS results for the Li-In symmetric cell at its initial state and after 50th cycle.

In addition, we have added this relevant content into the **Results and discussion** section as follows:

“Besides, both the $\text{LCO}|\text{L}_{1.25}\text{NTCl}|\text{Li-In}$ battery and the $\text{LCO}|\text{LGPS}|\text{Li-In}$ battery exhibit capacities approaching 0 mAh g^{-1} after 100 cycles (Supplementary Fig. 14), demonstrating the positive effect of $\text{L}_{1.25}\text{NTCl}$ and LGPS at the cathode and anode interfaces, respectively, and highlighting the necessity of the bilayer $\text{L}_{1.25}\text{NTCl-LGPS}$ SSE design for enhancing the performance of ASSB.”

Reference

[1] Zhang, W.; Richter, F. H.; Culver, S. P.; Leichtweiss, T.; Lozano, J. G.; Dietrich, C.; Bruce, P. G.; Zeier, W. G.; Janek, J., Degradation Mechanisms at the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{LiCoO}_2$ Cathode Interface in an All-Solid-State Lithium-Ion Battery. *Appl. Mater. Interfaces* **2018**, *10* (26), 22226-22236.

Regarding your second question, we apologize for the insufficient rigor in our explanation of the variation trend of ionic conductivities with the x values in $x\text{Li}_3\text{N-TaCl}_5$ SSEs. In fact, the concentration of Li^+ and the presence of impurities like LiCl and TaN in the as-prepared $x\text{Li}_3\text{N-TaCl}_5$ ($1 \leq 3x \leq 2$) samples simultaneously influence ionic conductivity. When the XRD pattern of these samples is magnified within the 2θ range of 32.5° – 40.5° , trace amounts of LiCl and TaN impurities can be detected (as shown in **Figure 2** below), which are detrimental to the ionic conductivities of $x\text{Li}_3\text{N-TaCl}_5$. As the x value decreases, the peak intensities of these impurities gradually diminish and become almost undetectable at $3x = 1.25$, suggesting a corresponding reduction in their adverse impact on ionic conductivity. On the other hand, the Li^+ concentration within the amorphous $x\text{Li}_3\text{N-TaCl}_5$ matrix also plays an important role in determining ionic conductivity. The insufficient Li^+ concentrations (such as $3x = 1.0$ and 1.1) may limit Li^+ transport within the polygonal coordination structures of the amorphous matrix, resulting in a decrease in ionic conductivity. Therefore, considering both the 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.

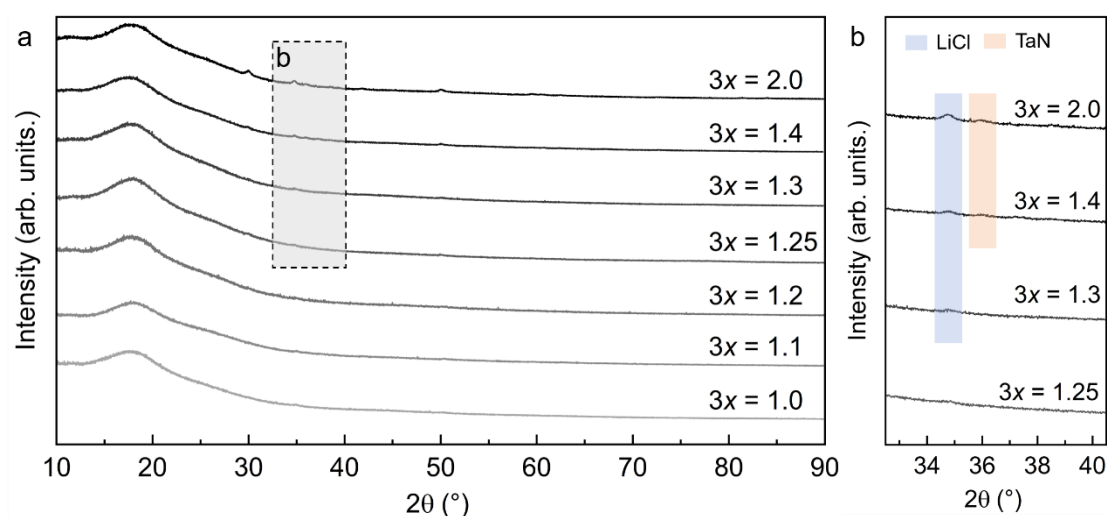


Figure 2. (a) XRD patterns of the amorphous $x\text{Li}_3\text{N-TaCl}_5$ ($1 \leq 3x \leq 2$) ball-milled at 30 h. (b) XRD patterns of $x\text{Li}_3\text{N-TaCl}_5$ magnified within the 2θ range of 32.5° – 40.5° to show the impurities of LiCl and TaN .

Now we have revised the relevant content in the **Results and discussion** section as follows:

“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 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. 1), 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 Li^+ concentrations (such as $3x = 1.0$ and 1.1) may limit Li^+ transport within the polygonal coordination structures of the amorphous matrix, resulting in a decrease in ionic conductivity. Therefore, considering both the 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.”

Reviewer #3 (Remarks to the Author):

Thank you to the authors for their corrections and additions. Before publication, I would like to suggest additional comment to the manuscript, which is mentioned below.

1. Can the authors add the explanation in the 'response to the letter' related to the theoretical capacity of 1 C for the LiCoO₂ (LCO) cathode depending on the charge cut-off voltage to the manuscript? It is believed that this explanation will help the possible reader better understand.

Reply:

Thank you for your kind suggestion, which has helped us enhance the rigor of our manuscript.

Now we have added the content related to theoretical capacity of 1 C for the LiCoO₂ (LCO) cathode depending on the charge cut-off voltage to the manuscript as follow:

"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 voltages, where the deliverable capacity increases from approximately 140 mAh g⁻¹ at a cut-off voltage of 4.2 V (vs. Li⁺/Li) to 180 mAh g⁻¹ at a cut-off voltage of 4.5 V (vs. Li⁺/Li) ^{46, 47}."

Reference

46. Qian J, *et al.* Electrochemical surface passivation of LiCoO₂ particles at ultrahigh voltage and its applications in lithium-based batteries. *Nat. Commun.* **9**, 4918 (2018).
47. Liu J, *et al.* Tuning Interphase Chemistry to Stabilize High-Voltage LiCoO₂ Cathode Material via Spinel Coating. *Angew. Chem. Int. Ed Engl* **61**, e202207000 (2022).

REVIEWER COMMENTS

Reviewer #2 (Remarks to the Author):

Authors added explanations for the magic effect of combining two kinds of electrolytes, which makes sense. As for the second question, they changed their original explanation by adding the effect of impurities. However, quantitative analyses of the effects of Li concentration and impurity are lacking. For example, maintaining the concentration of impurity constant, vary the concentration of Li. Then maintaining the concentration of Li constant, vary the concentration of impurity. Overall, the quality of the manuscript is decent.

Reviewer #3 (Remarks to the Author):

The authors made the requested change to the main text. I thank the authors for the corrections and additions. I would like to suggest that the manuscript can now be accepted for publication.

REVIEWER COMMENTS

Reviewer #2 (Remarks to the Author):

Authors added explanations for the magic effect of combining two kinds of electrolytes, which makes sense. As for the second question, they changed their original explanation by adding the effect of impurities. However, quantitative analyses of the effects of Li concentration and impurity are lacking. For example, maintaining the concentration of impurity constant, vary the concentration of Li. Then maintaining the concentration of Li constant, vary the concentration of impurity. Overall, the quality of the manuscript is decent.

Reply:

Thank you for your question and positive comments on our studies.

During the sample synthesis process, the molar ratio of the quantitative Li_3N and TaCl_5 precursors results in the formation of $x\text{Li}_3\text{N-TaCl}_5$ SSEs with a determined x value, corresponding to a specific Li^+ concentration and a specific impurity phase content (almost undetectable at $3x = 1.25$). In other words, for each synthesized $x\text{Li}_3\text{N-TaCl}_5$ with different x values, the included Li^+ concentration and impurity phase content (if any) are fixed. Therefore, it is not feasible to keep one constant while varying the other in this material, which is beyond the scope of this work. Overall, we greatly appreciate your insightful questions and perspectives.

Reviewer #3 (Remarks to the Author):

The authors made the requested change to the main text. I thank the authors for the corrections and additions. I would like to suggest that the manuscript can now be accepted for publication.

Reply:

Thank you for your positive comments on our studies and for giving us the valuable opportunity to publish in *Nature Communications*, and we believe our breakthrough findings will generate widespread interest in the field of all-solid-state batteries.