

A porous tellurium interlayer for high-power and long-cycling garnet-based quasi-solid-state lithium-metal batteries

Corresponding Author: Dr Ju-Sik Kim

This manuscript has been previously reviewed at another journal. This document only contains information relating to versions considered at Nature Communications.

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The manuscript, "High-power and ultra-long-cycling quasi-all-solid-state lithium Li-metal batteries using a garnet-type solid electrolyte" by Kim et al., presents a novel approach where a 40-nm-thick porous Te layer is fabricated on the surface of LLZTO by selectively etching Ge from a sputtered GeTe film, followed by the infiltration of an Ag-C layer onto the porous Te layer.

Using this anode interlayer, the authors demonstrate a quasi-all-solid-state Li-metal battery cell containing a 20- μ m-thick Li-metal anode and a high-loading ionic liquid-based NCA811 cathode. The battery achieves over 4000 cycles at 25 °C under a current density of 2.2 mA/cm². Furthermore, a ~30-cm² pouch cell operates for over 400 cycles at 25 °C with a 0.5 C-rate. Impressively, the concept is demonstrated in a smartphone, highlighting its practical applicability.

I find the approach innovative and highly effective in addressing the issue of low lithium diffusivity in Te by utilizing its surface to transport charge carriers. The selective etching of Ge to create a porous Te layer is particularly clever, taking advantage of Ge's higher solubility in acids. The functionality of this porous layer is convincingly validated using XPS on the electrode surface by applying a virtual electrode.

Only minor comments needs to be addressed:

I have the following concerns and suggestions for improvement:

1. CCD Values:

* I question the stated polarization values. How do you achieve a polarization of <50 mV when applying 3 mA/cm², given a total resistance of <50 Ω ($50 \times 0.003 = 0.15$ V)?

* Please clarify this discrepancy.

2. Cycling Data:

* The cycling data related to the CCD test seems to be cute. At what point does the cell short-circuit? Is it at 4,5,6 mA/cm²?

* This is an important detail, and I suggest including this data, at least in the supplementary information (SI).

3. Page 10, Line 248:

* The conclusion regarding the partial fragmentation of Cu and its role in Li plating at the Ag-C/Cu interface versus the Ag-C/solid electrolyte interface is unclear.

* Please provide a more detailed explanation of this mechanism.

4. many experimental results are shown to support the claims but those are only little discussed. Although I appreciate to include only the main findings into the manuscript I think a more extensive elaboration should be provided in the SI.

Overall, this is a well-written and impactful manuscript presenting an innovative approach to quasi-all-solid-state Li-metal batteries. After addressing the above minor concerns, I believe this work is well-suited for publication.

Reviewer #2

(Remarks to the Author)

The paper describes results on quasi-solid-state cells using Ta-substituted LLZO separators and interlayers consisting of

porous Te with or without Ag/C, and ionic liquid catholytes. The results seem impressive and the paper is clearly written, but some critical information is missing as noted below:

- 1) Please give the density that was achieved for the LLZTO separators as a % of theoretical.
- 2) Some details on cathode fabrication need to be included. Was a binder like PVdF used? Was carbon added?
- 3) How many cells of each type were tested?
- 4) In Figure 3a, Ag should be included in the cell schematic.
- 5) Comparing the results of Figure 3 and Figure S4 suggests that the presence of Ag in the interlayer is still important for performance. Can the authors speculate as to why? Early in the paper, the authors mention that Ag is “lost” during cycling (i.e., it diffuses deep into the lithium). How many cycles does this take? Does it depend on how much excess lithium is present? Did the cell in Figure S4 fail before this would be expected to happen, or is the difference due to amount of excess lithium in the cells described in the literature? If only one cell of each type was tested, can we be sure that the results are representative?
- 6) Could the authors give some information about practical specific energy/energy density for the tested cells? They indicate that the separators were 140 μm thick. In ACS Energy Lett. 2021, 6, 1399–1404, a goal of 20 μm or less for the separator is cited. This is particularly important for LLZTO, since it is so heavy. Likewise, the Li anode will need to be scaled down from 20 μm to 5 μm or less. It would be useful to calculate where the authors are now in terms of specific energy and energy density for these cells, and what it would be in the future, if authors are able to achieve goals in the ACS Energy Letters paper. Then, mention what challenges that entails (for example, mechanical robustness of very thin separators, difficulties in obtaining very thin lithium-although some companies like Applied Materials are working on this).
- 7) The authors state that 2M LiFSI in EMISF was used as the catholyte, but 2M LiFSI in Pyr13FSI is also mentioned in the paper. Which catholyte was used for each cell? Recommend putting this in the Figure captions for each cell that was tested.
- 8) In some cases, LCO was used as the cathode material, in other cases NCA was. Flammability and nail penetration tests appear to have been done on cells with LCO. High nickel content electrode materials are notorious for oxygen release at high states-of-charge and may be more problematic in this regard. The authors should include a caveat here that the results may depend on choice of cathode material.
- 9) The authors note that compositional heterogeneity may be responsible for the lower capacity retention of the larger cell compared to the smaller ones. Is this the reason that this cell was tested at 45 degrees rather than 25 degrees? Larger separators may also suffer from more defects such as pores or microcracks.

Reviewer #3

(Remarks to the Author)

The manuscript submitted by Kim et al. investigates the impacts of a porous Te and carbon interlayer to improve the cycling stability of a quasi-solid state battery. The manuscript seeks to build upon an earlier paper from Samsung (Lee et al., Nature Energy 2020) which first demonstrated the impacts of a Ag-C interlayer on solid-state battery performance. The team reported on a pouch cell SSB exhibiting unprecedented rates, stack pressures, and stability during extended cycling. This work generated significant interest within the SSB community although the mechanistic reasons for these drastic improvements are still not well understood even to this day.

The manuscript submitted by Kim et al. demonstrates very impressive cycling results which would be of interest to the community. While the results are impressive, there are some inconsistencies and lack of explanation which leads to a disconnect between the authors' hypothesis and data. For this reason, I recommend publication of this manuscript only if major revisions can be made. Please find my detailed comments below:

1. The authors' proposed hypothesis is that Te is a more suitable interlayer metal than Ag because of its lower mobility in Li (as demonstrated by DFT). The authors proceed to show cycling of a quasi-all-solid-state Te/Ag-C/Li cell which demonstrates incredible cycling performance. However, when the Ag is removed, the performance of the cell drops significantly, and the observed 83% capacity retention after 500 cyclers is worse than even the Ag-C/Li cell that was published by Lee et al. in Nature Energy 2020. This leads the reader to believe that the real enabler of the high performance is the Ag, not the Te. This is directly opposed to the hypothesis proposed by the authors at the start of the manuscript and is not adequately explained. Understandably, the systems between the two manuscripts are different, with Lee et al.'s paper using a sulfide electrolyte and this paper using an oxide electrolyte. However, the authors should cycle a similar Ag-C cell with their electrolyte as a control or provide suitable explanation.
2. While the DFT results are convincing to show that the degree of mixing between Li and Te is much less than Li and Ag, it is not clear if the authors have considered the impacts of volume expansion. The authors demonstrate that the Li uptake is 2 Li per Te atom. This would lead to large volume expansion upon the original formation of a Li_2Te phase that would lead to large first-cycle capacity losses. This is the case with Sn, which the authors also suggest would be a good candidate of material. Understandably, the volume expansion would be less for Te than Sn, but still significant enough to lead to self-pulverization, delamination, and capacity loss. Presumably this is mitigated by the porous structure of the Te layer used by the authors but cannot be confirmed without microstructural images of the porous Te layer. It is also not clear if the porous Te layer remains porous after CIP at 250MPa.
3. The authors show Li-metal symmetric cells for the porous and dense Te layers in Figure S3. However, the Ohmic drops observed in Figure S3d is not consistent with the EIS shown in Figure S3b. Take the voltage response at 1 mA/cm² as an example. The observed potential is ~10 mV. This corresponds to an area specific resistance of $(10\text{mV})/(1\text{mA}/\text{cm}^2) = 10\text{ Ohm cm}^2$, while the measured area specific resistance is ~46 Ohm cm² in Fig S3b. Meanwhile, the observed potentials in Fig S3c are consistent – $(50\text{mV})/(1\text{mA}/\text{cm}^2) = 50\text{ Ohm cm}^2$, which is what is observed in Fig S3b. This leads me to believe that the Faradaic efficiency is not 100% in the porous Te cell, and that some soft-short or electronic shunt exists in the cell.
4. The authors show a cross section of the cell in Fig 3e-h. How was the cross section prepared? Li metal is notorious for being susceptible to beam damage under FIB. Are the features observed in Fig 3e,f real or artifacts from preparation?

5. Fig 3c also shows cycling behavior with an NCA cathode of reported 4.4 mAh/cm² areal capacity. However, the authors also report that the Li metal foil has a thickness of 20 μm. A 20 μm thick foil corresponds to a capacity of ~4.1 mAh/cm², which would make the Li metal the limiting electrode. It has been widely observed throughout academic literature and industry that cycling 100% of the lithium capacity dramatically worsens cell performance by accelerating current focusing, delamination, and dendrite formation (see papers by many in the field including Motoyama, Sakamoto, Janek, etc). Furthermore, the XPS results in Fig 2, demonstrate that there is some irreversibility when forming the Li-Te alloy that would lead to some irreversible loss of the Li capacity which would make it impossible to cycle above 4 mAh/cm². Given this, how do the authors reconcile these observations and differences with others in the field?

6. The ability to fabricate a 100 mAh cell is incredibly impressive and is a good example to the broader community. However, it is unclear why the large-area cell exhibits a low area specific resistance. The area specific resistance is a value used to scale resistances between different areas and thus should be independent of area. Please explain why the area specific resistances are so different between the small and large-format cells.

7. Please provide more information on how the cells are constructed. Are they coin cells? How much stack pressure is applied? What temperatures are they formed and cycled at? How have the authors ensured that ionic liquid is confined to the cathode side and is not serving as an alternate ionic pathway around the sides or through cracks in the solid electrolyte?

Reviewer #4

(Remarks to the Author)

This study details a novel cell architecture that demonstrates great cyclability with lithium metal. Because of the cycle life this study may warrant publication in nature communications. However to validate the author's claims a few questions that should be addressed.

1) The study mentions the use of an ionic liquid in the full cell cycling data. Is there any data that can be shared to help demonstrate that lithium ions are not going "around" the solid electrolyte?

2) can the authors speak to the commercializability of this technique? What is the strategy for mass production?

3) for the operando XPS data to make conclusions about a Li-Te alloy or TeO₂ the O 1s spectra and the Li 1s spectra should be fit (and shown at least in the SI) so that the authors can demonstrate the appropriate relative intensities for the matching core shells in each phase (i.e. 2x more relative oxygen intensity for a TeO₂ phase).

4) capacity retention is not the whole story especially at high current densities. Therefore the authors need to show more electrochemical data. For example the constant voltage capacities per cycle, some of the time series data seems to suggest these values are very high. Also was "Constant voltage discharge" really the only type of discharge step as the methods section suggests? If so why? What is the cycle life for these cells under normal CC discharge conditions?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

I read through all responses and consider everything addressed well.
The manuscript can be published as it is.

Reviewer #2

(Remarks to the Author)

The authors have made a good faith effort to address reviewers' concerns in this revision, including additional experimentation and information. The paper is now ready for publication.

Reviewer #3

(Remarks to the Author)

Overall, the revisions to the manuscript by Kim et al. provide improvements to the clarity and consistency of the analysis. I particularly appreciate the level of detail to which comments were addressed, and the motivation to conduct additional experimentation as needed. I have one remaining comment but otherwise recommend publication:

1. I appreciate the authors' added detail about the role of Ag and the explanation about prior work and findings. I find that the authors' brief summary of past work very insightful to explaining the results in this work and would suggest adding this extra detail into the manuscript text. Particularly surrounding the following:

"In our previous study, when we adopted Li/Aginterlayer-C/Agbind/LLZTO configuration as an anode, we could cycle the cell for 800 cycles at the current density of 1.6 mA/cm². By contrast, when we replace Agbind with Tebind, such that the anode configuration is Li/Aginterlayer-C/Tebind/LLZTO, the cycling stability is highly improved (4000 cycles at the current density of 2.2 mA/cm²), clearly indicating that Tebind is considerably better than Agbind as a binding layer. We would like to additionally note that binding layers at the interface between solid electrolyte and the interlayer are only required for oxide solid electrolytes, as explained in the introduction of this manuscript. In Figure 5c of our previous paper [Nat. Commun. 14,

782 (2023)], the cell using LLZTO and Ag-C interlayer without the binding layer shorted after 2 cycles, whereas the sulfide cell showed high stability without the binding layer [Nat. Energy 5, 299 (2020)].”

The direct reference to the previous papers, the specific cycle numbers, and current densities are particularly helpful to clearly illustrate the difference in observed performance.

Reviewer #4

(Remarks to the Author)

Thank you for addressing the comments. I encourage the publication of this manuscript.

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Response Letter

Reviewer #1

Comments:

Reviewer #1 (Remarks to the Author):

The manuscript, "High-power and ultra-long-cycling quasi-all-solid-state lithium Li-metal batteries using a garnet-type solid electrolyte" by Kim et al., presents a novel approach where a 40-nm-thick porous Te layer is fabricated on the surface of LLZTO by selectively etching Ge from a sputtered GeTe film, followed by the infiltration of an Ag-C layer onto the porous Te layer.

Using this anode interlayer, the authors demonstrate a quasi-all-solid-state Li-metal battery cell containing a 20- μm -thick Li-metal anode and a high-loading ionic liquid-based NCA811 cathode. The battery achieves over 4000 cycles at 25 °C under a current density of 2.2 mA/cm². Furthermore, a ~30-cm² pouch cell operates for over 400 cycles at 25 °C with a 0.5 C-rate. Impressively, the concept is demonstrated in a smartphone, highlighting its practical applicability.

I find the approach innovative and highly effective in addressing the issue of low lithium diffusivity in Te by utilizing its surface to transport charge carriers. The selective etching of Ge to create a porous Te layer is particularly clever, taking advantage of Ge's higher solubility in acids. The functionality of this porous layer is convincingly validated using XPS on the electrode surface by applying a virtual electrode.

Only minor comments needs to be addressed:

I have the following concerns and suggestions for improvement:

Authors' response:

Thank you for carefully reviewing our manuscript and for your positive feedback. Your comments, followed by our point-by-point responses, are shown below.

1) CCD Values:

** I question the stated polarization values. How do you achieve a polarization of <50 mV when applying 3 mA/cm², given a total resistance of <50 Ω ($50 \times 0.003 = 0.15 \text{ V}$)?*

** Please clarify this discrepancy.*

Authors' Response:

We are most grateful for your insightful comments. As you pointed out, the extremely low overpotential observed under galvanostatic conditions in Supplementary Figure 4b clearly indicates the occurrence of a micro-short circuit. It appears that the electronically conductive metal interlayer (Te) formed a subtle connection at the edge of the LLZTO solid-state electrolyte pellet during the sputtering process when fabricating the symmetric cell.

To address this, we fabricated new symmetric cells using a thinner LLZTO pellet (~250 μm) than before. During the sputtering process, we applied tape to the edge of the pellet to prevent the metal from connecting to both electrodes. The newly measured symmetric cell results, shown in the figures below, now exhibit reasonable overpotentials corresponding to the applied current density and resistance.

Thank you once again for your astute insights. We have revised Supplementary Figure 4 with these newly measured results for the symmetric cell.

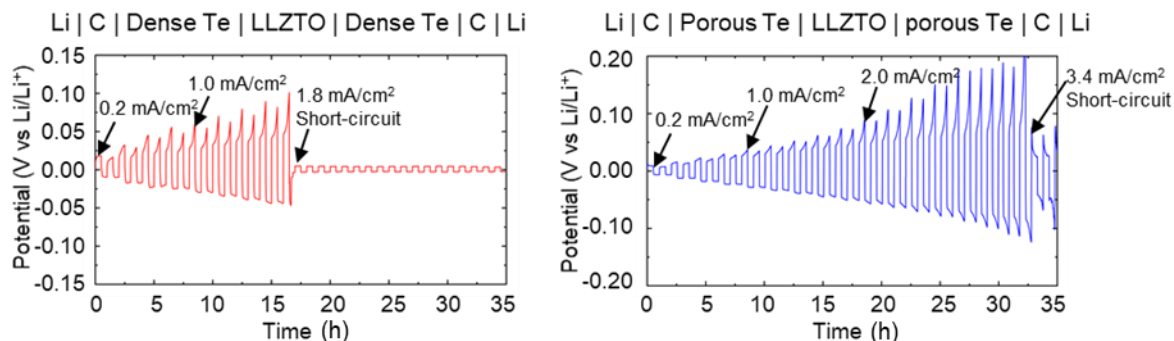


Figure S4. Galvanostatic cycling tests recorded with an increasing current density using (c) dense Te and (d) porous Te

2) Cycling Data:

* The cycling data related to the CCD test seems to be cute. At what point does the cell short-circuit? Is it at 4,5,6 mA/cm²?

* This is an important detail, and I suggest including this data, at least in the supplementary information (SI).

Authors' Response:

Following your suggestion, we increased the current density until failure occurred as a result of short-circuiting and measured the critical current density (CCD). The newly measured symmetric cell results in Supplementary Figure 4c,d show that cells with a dense Te/C and porous Te/C anode interlayer, respectively, experienced short circuits at 1.8 mA/cm² and 3.4 mA/cm².

3) Page 10, Line 248:

* The conclusion regarding the partial fragmentation of Cu and its role in Li plating at the Ag-C/Cu interface versus the Ag-C/solid electrolyte interface is unclear.

* Please provide a more detailed explanation of this mechanism.

Authors' Response:

We are grateful to you for pointing out the unclearness in the interpretation of the partial fragmentation of Cu. We believe that the partial fragmentation of Cu could have been mechanically induced, implying that Cu could have been continuously exposed to the mechanical damage that could have come from stress/strain from Li plating/stripping near the Cu. Therefore, we believe that the partial fragmentation of Cu could be evidence in support of Li plating at the Ag-C/Cu interface, rather than at the Ag-C/solid electrolyte interface, which is a key factor for the long-term cycling stability of

solid-state Li metal batteries. These are the messages we originally aimed to convey from the observation.

In addition, we expect that the degradation of Cu could possibly affect further Li plating behavior, as you suggested. For instance, the uniformity of Li plating and stripping could be undermined due to the irregular morphology of Cu, which could be one of the reasons for the slow capacity fade after 2000 cycles, as shown in Figure 3d. However, we believe that the partial fragmentation of Cu is not likely to change the preferential site of Li plating/stripping (Ag-C/Cu interface) as long as the Ag-C/solid electrolyte interface is tightly bonded. As demonstrated in previous studies [*Nat. Commun.* **14**, 782 (2023), *J. Mater. Chem. A* **10**, 21995 (2022)], Li tends to be plated at the Ag-C/Cu interface when the bonding between Ag-C/solid electrolyte is stronger than that between Ag-C/Cu. The degradation of Cu could only weaken the bonding between Ag-C/Cu; therefore, Li would still prefer to be plated at the Ag-C/Cu interface.

In response to your comment, we revised the manuscript as follows:

Revised text:

Interestingly, the partial fragmentation and agglomeration of the Cu particles near the interface of the Cu current collector with the Li-metal were observed (Fig. 3g), presumably attributable to the strain/stress induced by volume changes during repetitive Li plating/stripping. These results suggest that Li plating occurs primarily at the Ag-C/Cu interface rather than at the Ag-C/solid electrolyte interface, a key requirement for the long-term cycling stability of solid-state Li-metal batteries⁵. The degradation of Cu could possibly affect further Li plating behaviour; for instance, the uniformity of Li plating and stripping could be undermined due to the irregular morphology of Cu, a possible reason for the slow capacity fade after 2000 cycles (Fig. 3d). However, the partial fragmentation of Cu could be considered unlikely to change the preferred site of Li plating/stripping (Ag-C/Cu interface) as long as the Ag-C/solid electrolyte interface is tightly bonded. As demonstrated in previous studies^{5,35}, Li tends to be plated at the Ag-C/Cu interface when the Ag-C/solid electrolyte bonding is stronger than that at the Ag-C/Cu interface. The degradation of Cu could only weaken the bonding between Ag-C/Cu; therefore, Li would still prefer plating at the Ag-C/Cu interface.

4) many experimental results are shown to support the claims but those are only little discussed. Although I appreciate to include only the main findings into the manuscript I think a more extensive elaboration should be provided in the SI.

Authors' Response:

In response to your insightful comments, we have added XPS data, constant voltage capacity per cycle and information regarding the cathode, the catholyte infiltration method, and the energy density for the quasi-solid-state battery. Please refer to the revised manuscript and the supplementary information.

Reviewer #2

Comments:

Reviewer #2 (Remarks to the Author):

The paper describes results on quasi-solid-state cells using Ta-substituted LLZO separators and interlayers consisting of porous Te with or without Ag/C, and ionic liquid catholytes. The results seem impressive and the paper is clearly written, but some critical information is missing as noted below:

Authors' Response:

Thank you for carefully reviewing our manuscript and for the encouraging feedback. Your comments, followed by our point-by-point responses, are shown below.

1) Please give the density that was achieved for the LLZTO separators as a % of theoretical.

Authors' Response:

We have added the relevant information regarding the relative density of the solid electrolyte to the Methods section of the main text.

Specifically, the LLZTO pellet has a measured density of 5.12 g/cm³, which corresponds to a relative density of 97.5% compared to its theoretical density (5.25 g/cm³). In the case of the tape, the measured density is 4.81 g/cm³, which represents a relative density of 91.65%.

In response to your comment, we revised the manuscript as follows:

Revised text:

A dense pellet (5.12 g/cm³, 97.5% relative density with respect to the theoretical density of LLZTO) was prepared by hot-pressing the LLZTO powder (100 g) in a graphite die at 3 kpsi, followed by sintering at 1100 °C for 2 h under an Ar atmosphere following heating at a rate of 300 °C/h. Subsequently, under air, a laser cutter was used to cut the pellet to a diameter of 14 mm and a thickness of 360 μm. This pellet was subjected to ultrasonic cleaning in hexane for 10 min and heat-treated at 800 °C for 1 h in dry air. Finally, the pellet surface was polished to a thickness of ~250 μm using a polishing machine (LaboForce-3, Struers).

A large-area (36 cm²) electrolyte film with a thickness of 110 μm was prepared via tape casting. For this purpose, LLZTO and Li₂CO₃ powders (9:1 LLZTO/Li₂CO₃ mass ratio) were added in the same mass to a mixed solvent of propyl propionate and butyl propionate (1:1 volume ratio) with a pre-dissolved Dispersbyk 2155 dispersant (BYK) and stirred at 25 °C for 24 h. Elvacite 2046 binder (ChemPoint, USA) and PL029 plasticiser (Polymer Innovations, USA) were then added to the slurry as the binder and the dispersant, respectively, and mixed for 24 h. The resulting slurry was cast into a thin film on a Mylar® sheet, and then dried at 60 °C. Subsequently, the resulting solid electrolyte tape was sintered at 1100 °C for 1 h. XRD analysis revealed that the 36-cm² LLZTO tape possessed a cubic garnet structure. The density of the solid electrolyte tape was measured to be 4.81 g/cm³, which corresponds to a relative density of 91.65% compared to its theoretical density (5.25 g/cm³).

2) Some details on cathode fabrication need to be included. Was a binder like PVdF used? Was carbon added?

Authors' Response:

Instead of fabricating the cathode directly, commercial cathodes (NCA, LCO) were utilized. These commercial cathodes contained 1.0 wt% poly(vinylidene fluoride) (PVDF) as a binder and 1.3 wt% carbon black as a conductive additive. We added this information to the Methods session of the revised manuscript.

Revised text:

Commercially available $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Al}_{0.1}\text{O}_2$ (NCA811, loading capacity: 5.1, 4.4 mAh/cm² with a specific capacity of ~200 mAh g⁻¹; active material: 97 wt%; polyvinylidene fluoride (PVDF): 1.0 wt%, carbon black: 1.3 wt%; Samsung SDI) and LiCoO_2 (LCO, loading capacity: 3.2 mAh/cm² with a specific capacity of ~170 mAh g⁻¹; active material: 97 wt%; polyvinylidene fluoride (PVDF): 1.0 wt%, carbon black: 1.3 wt%; Samsung SDI) were employed as the cathode active materials. As a current collector, Al foil (9- μm foil, Nippon Foil Mfg. Co., Ltd.) was used as received. 1-Ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMIFSI, 99.9%, water content <20 ppm, Kanto Chemical Co. Inc.) mixed with 2 M lithium bis(fluorosulfonyl)imide (LiFSI, 99.9%, water content <10 ppm) salt was used as the catholyte. The catholyte solution (20 wt% relative to the cathode) was infiltrated into the cathode in a dry room (dew point, -60 °C), and the cathode was placed under vacuum for 2 h. Following removal of the residual solution on the cathode surface using disposable wipers (Kimwipes, Kimberly-Clark Co. Inc.), the solution uptake by the cathode was ~10 wt%. The cathode infiltrated with the ionic liquid was then placed on the cathode side of the LLZTO in a single-layer pouch cell, and the cell was sealed under vacuum (750 Torr).

3) How many cells of each type were tested?

Authors' Response:

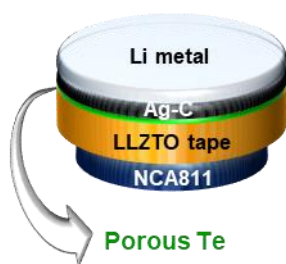
As described in the *Methods* section of the manuscript, at least five cells were evaluated to ensure reproducibility. Please refer to page 21 of the revised manuscript.

4) In Figure 3a, Ag should be included in the cell schematic.

Authors' Response:

We greatly appreciate your indication for the cell schematic of Figure 3a. We modified the cell schematic in Figure 3a as follows.

a



5) Comparing the results of Figure 3 and Figure S4 suggests that the presence of Ag in the interlayer is still important for performance. Can the authors speculate as to why? Early in the paper, the authors mention that Ag is “lost” during cycling (i.e., it diffuses deep into the lithium). How many cycles does this take? Does it depend on how much excess lithium is present? Did the cell in Figure S4 fail before this would be expected to happen, or is the difference due to amount of excess lithium in the cells described in the literature? If only one cell of each type was tested, can we be sure that the results are representative?

Authors’ Response:

Thank you for raising an important point regarding the role of Ag in the interlayer, which we also believe to have a large impact on the cell performance. First, we would like to clarify that Ag could be incorporated in two different parts in the anode; i) in the Ag-C interlayer ($\text{Ag}_{\text{interlayer}}$), ii) at the interface between the interlayer and the solid electrolyte as a binding element (Ag_{bind}).

The results in Figure 3 and Figure S4 suggest that the presence of $\text{Ag}_{\text{interlayer}}$ could be important, as you pointed out. Having conducted a series of experiments using the Ag-C interlayer over the years, we also had a question about the role of $\text{Ag}_{\text{interlayer}}$ and C. In our previous studies [*Nat. Commun.* **14**, 782 (2023), *ACS Energy Lett.* **8**, 9 (2023)], we demonstrated that the role of C is to guide the Li plating at the interlayer/current collector interface, thereby enhancing the cycle stability. Still, we observed results where $\text{Ag}_{\text{interlayer}}$ helps regardless of the electrolyte chemistry [this work and *Adv. Energy Sustainability Res.* **2**, 2100066 (2021)], as you pointed out. Currently, our understanding is that $\text{Ag}_{\text{interlayer}}$ facilitates the redox reaction of Li plating, which we presume to be attributable to its low Li nucleation barrier and high Li diffusivity in alloys [*Adv. Energy Mater.* **10**, 1903993 (2020), *J. Am. Chem. Soc.* **142**, 8818 (2020)].

The Ag that we described as “lost” in the introduction is Ag_{bind} , which was applied at the interface of solid electrolyte and interlayer as a binding material [*Nat. Commun.* **14**, 782 (2023)]. In our previous work, we designed a cell in which the anode comprises the Li/ $\text{Ag}_{\text{interlayer}}$ -C/ Ag_{bind} /LLZTO configuration. As described in the introduction of this manuscript, we discovered by cross-sectional SEM/EDS that Ag_{bind} was lost after 100 cycles, which motivated us to search for new binding materials that could replace Ag_{bind} . However, it is true that $\text{Ag}_{\text{interlayer}}$ also shows a high tendency of moving along with Li during alloying/dealloying. Considering that the phenomenon was also observed in a Li-less anode system [*Nat. Energy* **5**, 299 (2020)], we speculate that both $\text{Ag}_{\text{interlayer}}$ and Ag_{bind} move regardless of the excess Li in the cell. Finally, we believe that the abovementioned observations (Ag diffusion, beneficial role of $\text{Ag}_{\text{interlayer}}$) are representative and reliable, as they have been repeatedly reported in the literature [*Nat. Commun.* **14**, 782 (2023), *Nat. Energy* **5**, 299 (2020), *Adv. Energy Sustainability Res.* **2**, 2100066 (2021)].

In response to your comment, we revised the manuscript as follows:

Revised text:

Subsequently, a quasi-all-solid-state cell containing a porous Te/C interlayer was fabricated and evaluated to determine the effect of Ag on the performance of the carbon-based interlayer (Supplementary Fig. 6a). The interfacial resistance was calculated to be $23 \Omega \text{ cm}^2$ from the EIS measurements presented in Supplementary Fig. 6b, which is a slightly higher value than that of the cell containing the Te/Ag-C interlayer. The capacity retention of ~83% after 500 cycles (Supplementary Fig. 6c,d) is relatively inferior to that of the porous Te/Ag-C cell; however, stable operation was achieved up to a maximum of 500 cycles without any significant capacity drop. This indicates that the carbon interlayer can effectively bind to the porous Te metal layer, and that Li dendrite formation is suppressed up to a current density of 2.2 mA/cm^2 . Nevertheless, Ag in the interlayer certainly plays an important role, as the capacity retention of the Te/C cell (Supplementary Fig. 6d) is inferior to that of Te/Ag-C cell (Fig. 3d). The identical tendency was also reported for the sulphide electrolyte system, where the incorporation of Ag in the C interlayer resulted in improved cycling stability¹⁷. Considering that the critical current density is not highly dependent on the presence of Ag in the anode interlayer, Ag is expected to have a greater impact on the kinetics of Li plating/stripping than on the suppression of Li dendrite formation. The low Li nucleation barrier and high Li diffusivity in Li-Ag alloys^{18,28} presumably indicate that Ag in the C interlayer facilitates Li reduction and enhances the Li transport inside the interlayer. However, carbon was considered to play a pivotal role in preventing the formation of Li dendrites¹⁶.

6) Could the authors give some information about practical specific energy/energy density for the tested cells? They indicate that the separators were 140 μm thick. In ACS Energy Lett. 2021, 6, 1399–1404, a goal of 20 μm or less for the separator is cited. This is particularly important for LLZTO, since it is so heavy. Likewise, the Li anode will need to be scaled down from 20 μm to 5 μm or less. It would be useful to calculate where the authors are now in terms of specific energy and energy density for these cells, and what it would be in the future, if authors are able to achieve goals in the ACS Energy Letters paper. Then, mention what challenges that entails (for example, mechanical robustness of very thin separators, difficulties in obtaining very thin lithium-although some companies like Applied Materials are working on this).

Authors' Response:

As you suggested, the energy density is a critical performance metric for solid-state lithium metal batteries. Following this recommendation, we calculated the volumetric energy density of a single cell, including the packaging films. For the cell using a 140 μm -thick solid electrolyte shown in Figure 3e, the volumetric energy density was calculated to be 519 Wh L^{-1} , which is lower than that of current commercial lithium-ion batteries ($600\text{--}750 \text{ Wh L}^{-1}$). To surpass the energy density of conventional LIBs, the thickness of the solid electrolyte must be reduced to below 60 μm . To address this, we have been adopting Corning's ribbon ceramic processing technology. As shown in the figure below, we recently succeeded in fabricating solid electrolytes with a thickness of 30 μm . When combined with lithium metal, such thin solid electrolytes enable volumetric energy densities exceeding 880 Wh L^{-1} , thereby overcoming the energy density limitations of conventional LIBs. However, as pointed out by the reviewer, thinner solid electrolytes are inherently brittle and require improvements in their mechanical strength. Our group is actively pursuing this challenge as a key area of future research and development.

In addition, lithium metal can be fabricated to a thickness below 5 μm using electrodeposition or sputtering techniques. As you noted, Applied Materials' roll-to-roll sputtering technology enables the reduction of lithium metal thickness to below 5 μm . Employing such ultrathin lithium metal anodes can further enhance the volumetric energy density by over 10%. Information on energy density has been added to Supplementary Table 1, and we have incorporated a discussion in the main text on the importance of minimizing both the solid electrolyte and lithium metal thicknesses to achieve energy densities exceeding those of LIBs. The details on energy density calculations have been summarized in Supplementary Table S1.

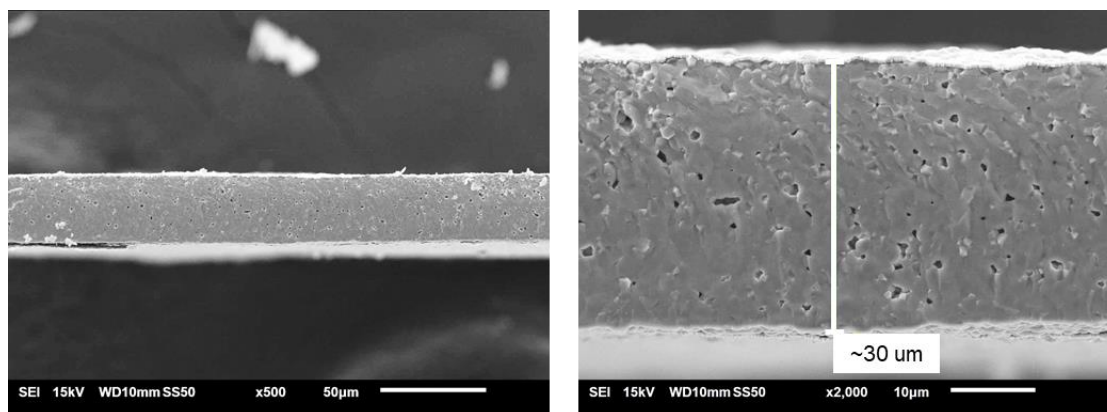


Figure S7. SEM images of the thin LLZTO solid electrolyte ($\sim 30 \mu\text{m}$).

Supplementary Table S1.

Cathode	Composition	NCM811
	Areal capacity (mAh/cm^2)	4.4
	Thickness (μm)	62
Solid electrolyte	Initial thickness (μm)	140
Anode	Te/AgC interlayer (μm)	6
	Li thickness (μm)	20
	Increased thickness after charging	22
Current collector	Al for cathode (μm)	9
	Cu for anode (μm)	9
Total thickness (μm)		246
Cell area (cm^2)		30.2
Cell volume including package film (L)		0.880
Discharge V_{ave} (V)		3.75

Energy density (Wh/L)	519
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Revised text:

Considering that the critical current density is not highly dependent on the presence of Ag in the anode interlayer, Ag is expected to have a greater impact on the kinetics of Li plating/stripping than on the suppression of Li dendrite formation. The low Li nucleation barrier and high Li diffusivity in Li-Ag alloys^{18,28} presumably indicate that Ag in the C interlayer facilitates Li reduction and enhances the Li transport inside the interlayer. However, carbon was considered to play a pivotal role in preventing the formation of Li dendrites¹⁶.

Assuming the cell configuration shown in Fig. 3a as a representative unit cell for battery pack integration, the calculated volumetric energy density is 519 Wh L⁻¹ (Supplementary Table 1). To achieve an energy density exceeding 700 Wh L⁻¹ (comparable to that of state-of-the-art commercial LIBs), both the thickness of the solid electrolyte and the lithium metal anode must be reduced from their current levels. Utilising Corning's fast-firing roll-to-roll ribbon ceramic processing⁴⁰, the thickness of the LLZTO solid electrolyte can be reduced to below 60 µm, while Applied Materials' sputtering technology allows the lithium metal thickness to be decreased to below 5 µm⁴¹. In fact, Corning's ribbon ceramic process enabled us to successfully fabricate a 30 µm-thick solid electrolyte (Supplementary Fig. 7). However, such thin solid electrolytes tend to be brittle, and therefore, mechanical reinforcement is necessary for practical application. Addressing this issue remains a critical focus of our ongoing and future research efforts.

7) The authors state that 2M LiFSI in EMISFI was used as the catholyte, but 2M LiFSI in Pyr13FSI is also mentioned in the paper. Which catholyte was used for each cell? Recommend putting this in the Figure captions for each cell that was tested.

Authors' Response:

In this study, EMISFI was used exclusively as the catholyte. The mention of Pyr13FSI was a typographical error. We greatly appreciate your careful observation. Accordingly, we modified the manuscript and added the catholyte information to the figure caption of Figures 3 and 4.

Revised text:

Commercially available LiNi_{0.8}Co_{0.1}Al_{0.1}O₂ (NCA811, loading capacity: 5.1, 4.4 mAh/cm² with a specific capacity of ~200 mAh g⁻¹; active material: 97 wt%; poly(vinylidene fluoride) (PVDF): 1.0 wt%, carbon black:1.3 wt%; Samsung SDI) and LiCoO₂ (LCO, loading capacity: 3.2 mAh/cm² with a specific capacity of ~170 mA g⁻¹; active material: 97 wt%; poly(vinylidene fluoride) (PVDF): 1.0 wt%, carbon black:1.3 wt%; Samsung SDI) were employed as the cathode active materials. As a current collector, Al foil (9-µm foil, Nippon Foil Mfg. Co., Ltd.) was used as received. 1-Ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMISFI, 99.9%, water content <20 ppm, Kanto Chemical Co. Inc.) mixed with 2 M lithium bis(fluorosulfonyl)imide (LiFSI, 99.9%, water content <10 ppm) salt was used as the catholyte. The catholyte solution (25 wt% relative to the cathode) was infiltrated into the cathode in a dry room (dew point, -60 °C), and the cathode was placed under vacuum for 2 h. Following removal of the residual solution on the cathode surface using disposable wipers (Kimwipes, Kimberly-Clark Co. Inc.), the solution uptake

by the cathode was ~10 wt%. The cathode infiltrated with the ionic liquid was then placed on the cathode side of the LLZTO in a single-layer pouch cell, and the cell was sealed under vacuum (750 Torr).

Fig. 3 | Fabrication and electrochemical performance of the quasi-all-solid-state Li-metal battery. (a) Schematic of the assembled Li/Ag-C/Te/LLZTO/NCA811-EMIFSI(2M LiFSI) cell. (b) Nyquist plots of the AC-impedance spectra obtained from the cell. (c) Galvanostatic voltage profiles recorded for the prepared cell. (d) Cycling performance of the quasi-all-solid-state Li-metal battery. (e) Cross-sectional SEM image of the cell after 4000 cycles. (f) SEM/EDS image of the cell at the LLZTO/Te interface after 4000 cycles. (g) Cross-sectional SEM image of the cell at the Li/Cu interface after 4000 cycles. (h) SEM image and (i) EDS mapping images of the NCA cathode after 4000 cycles.

Fig. 4 | Electrochemical performance of the Li/C/Te/LLZTO/LCO-EMIFSI(2M LiFSI) single cell. (a) The LLZTO tape and the LCO cathode used to fabricate the 100 mAh Li/C/Te/LLZTO/LCO single cell. (b) Nyquist plots of the AC-impedance spectra obtained from the prepared cell. (c) Galvanostatic voltage profiles recorded for the cell. (d) Cycling performance of the quasi-all-solid-state Li-metal battery.

8) In some cases, LCO was used as the cathode material, in other cases NCA was. Flammability and nail penetration tests appear to have been done on cells with LCO. High nickel content electrode materials are notorious for oxygen release at high states-of-charge and may be more problematic in this regard. The authors should include a caveat here that the results may depend on choice of cathode material.

Authors' Response:

Thank you for the thoughtful comment. We agree that the cathode chemistry, particularly high-nickel materials such as NCA, can significantly influence the thermal and safety characteristics of a cell. In this work, however, our primary goal was to evaluate the flammability characteristics of a hybrid cell structure composed of a cathode infiltrated with an ionic liquid electrolyte and combined with an LLZTO solid-state electrolyte. To this end, we selected LCO as the cathode material to minimize additional thermal contributions from the cathode itself, allowing us to focus more clearly on the flammability behavior of the overall hybrid electrolyte structure. Additionally, this choice aligns with our target application of small-scale mobile batteries, where LCO remains a widely used and practical cathode material.

9) The authors note that compositional heterogeneity may be responsible for the lower capacity retention of the larger cell compared to the smaller ones. Is this the reason that this cell was tested at 45 degrees rather than 25 degrees? Larger separators may also suffer from more defects such as pores or microcracks.

Authors' Response:

As you pointed out, in large-area cells, the volatile nature of lithium during the high-temperature sintering process probably increases surface defects such as impurities, pores, and microcracks. These defects can reduce the number of electrochemically active sites and lead to non-uniform lithium plating and stripping, ultimately degrading cell performance. In particular, localized current concentrations caused by such inhomogeneities can trigger micro-short circuits, making large-area cells more prone to shorting than small-area cells. At relatively elevated temperatures, faster lithium diffusion can alleviate issues related to non-uniform plating/stripping. For this reason, we evaluated the large-area cells at 45 °C. To improve the clarity, a description regarding the evaluation temperature for large-area cells has been added to the manuscript.

Revised text:

To further examine the applicability of the cell for use in commercial devices, such as smartphones, a 100-mAh-capacity cell was fabricated and evaluated using a large-area tape solid electrolyte (36 cm²), a Te/C interlayer, and a 3.2 mAh/cm²-LCO cathode (Fig. 4a). The impedance spectrum (Fig. 4b) indicates that the large-area cell exhibits a low initial interfacial resistance of <10 Ω cm². The lower interfacial resistance of the large-area cell compared to that of the small-area cell shown in Fig. 3b is likely due to the increased surface area of the large-area solid electrolyte resulting from inhomogeneous distribution of Li on the surface and subsequent increased porosity during acid treatment. Because large-area cells are more susceptible to micro-short circuits due to the increased formation of surface defects and localised current densities as compared to small-area cells, the long-term cycling performance was evaluated at 45 °C, at which the enhanced lithium mobility can mitigate failure due to micro-short circuits. The charge/discharge curves and capacity retention after cycling this cell at the 0.5 C rate for up to 400 cycles (Fig. 4c,d) demonstrate successful operation without short circuits and that the capacity was maintained at ~95 mAh.

Reviewer #3

Comments:

Reviewer #3 (Remarks to the Author):

The manuscript submitted by Kim et al. investigates the impacts of a porous Te and carbon interlayer to improve the cycling stability of a quasi-solid state battery. The manuscript seeks to build upon an earlier paper from Samsung (Lee et al., Nature Energy 2020) which first demonstrated the impacts of a Ag-C interlayer on solid-state battery performance. The team reported on a pouch cell SSB exhibiting unprecedented rates, stack pressures, and stability during extended cycling. This work generated significant interest within the SSB community although the mechanistic reasons for these drastic improvements are still not well understood even to this day.

The manuscript submitted by Kim et al. demonstrates very impressive cycling results which would be of interest to the community. While the results are impressive, there are some inconsistencies and lack of explanation which leads to a disconnect between the authors' hypothesis and data. For this reason, I recommend publication of this manuscript only if major revisions can be made. Please find my detailed comments below:

Authors' Response:

We appreciate your careful review of our manuscript and for your helpful comments. Your comments, followed by our point-by-point responses, are shown below.

1. The authors' proposed hypothesis is that Te is a more suitable interlayer metal than Ag because of its lower mobility in Li (as demonstrated by DFT). The authors proceed to show cycling of a quasi-all-solid-state Te/Ag-C/Li cell which demonstrates incredible cycling performance. However, when the Ag is removed, the performance of the cell drops significantly, and the observed 83% capacity retention after 500 cyclers is worse than even the Ag-C/Li cell that was published by Lee et al. in *Nature Energy* 2020. This leads the reader to believe that the real enabler of the high performance is the Ag, not the Te. This is directly opposed to the hypothesis proposed by the authors at the start of the manuscript and is not adequately explained. Understandably, the systems between the two manuscripts are different, with Lee et al.'s paper using a sulfide electrolyte and this paper using an oxide electrolyte. However, the authors should cycle a similar Ag-C cell with their electrolyte as a control or provide suitable explanation.

Authors' Response:

We are grateful to you for pointing out an important aspect of the role of Ag in our anode design. We also believe that Ag in the interlayer has an important effect on the long-term cycle stability. Before we address your concern, we would like to note that a similar point was raised by one of the other reviewers; thus, part of this response could be found in our response to reviewer #2's comment #5.

First, we would like to clarify that Ag could be incorporated in two different parts in the anode; i) in Ag-C interlayer ($\text{Ag}_{\text{interlayer}}$), ii) at the interface between interlayer and the solid electrolyte as a binding element (Ag_{bind}). As we described in the introduction of the manuscript, we previously discovered via cross-sectional SEM/EDS that a major part of the Ag_{bind} seemed to be lost after 100 cycles [*Nat. Commun.* **14**, 782 (2023)]. This finding motivated us to search for new binding materials that could replace Ag_{bind} . Throughout this work, we demonstrated that Te_{bind} is more suitable as an interface binding layer by theoretical prediction and experimental validation. In our previous study, when we adopted Li/ $\text{Ag}_{\text{interlayer}}$ -C/ Ag_{bind} /LLZTO configuration as an anode, we could cycle the cell for 800 cycles at the current density of 1.6 mA/cm². By contrast, when we replace Ag_{bind} with Te_{bind} , such that the anode configuration is Li/ $\text{Ag}_{\text{interlayer}}$ -C/ Te_{bind} /LLZTO, the cycling stability is highly improved (4000 cycles at the current density of 2.2 mA/cm²), clearly indicating that Te_{bind} is considerably better than Ag_{bind} as a binding layer. We would like to additionally note that binding layers at the interface between solid electrolyte and the interlayer are only required for oxide solid electrolytes, as explained in the introduction of this manuscript. In Figure 5c of our previous paper [*Nat. Commun.* **14**, 782 (2023)], the cell using LLZTO and Ag-C interlayer without the binding layer shorted after 2 cycles, whereas the sulfide cell showed high stability without the binding layer [*Nat. Energy* **5**, 299 (2020)].

Nevertheless, it is true that $\text{Ag}_{\text{interlayer}}$ also has a large impact on the cycle stability, as you pointed out. Having conducted a series of experiments using this Ag-C interlayer over the years, we also had a question about the independent role of $\text{Ag}_{\text{interlayer}}$ and C. In our previous studies [*Nat. Commun.* **14**, 782 (2023), *ACS Energy Lett.* **8**, 9 (2023)], we demonstrated that the role of C is to guide the Li plating at the interlayer/current collector interface, thereby enhancing the cycle stability. However, as you pointed out, we have also observed results where $\text{Ag}_{\text{interlayer}}$ helps regardless of the electrolyte chemistry [this work and *Adv. Energy Sustainability Res.* **2**, 2100066 (2021)]. Currently, our understanding is that $\text{Ag}_{\text{interlayer}}$ facilitates the redox reaction of Li plating, which we can presume by its low Li nucleation barrier and high Li diffusivity in alloys [*Adv. Energy Mater.* **10**, 1903993 (2020), *J. Am. Chem. Soc.* **142**, 8818 (2020)].

In response to the reviewer's comment, we revised the manuscript as follows:

Revised text:

Subsequently, a quasi-all-solid-state cell containing a porous Te/C interlayer was fabricated and evaluated to determine the effect of Ag on the performance of the carbon-based interlayer (Supplementary Fig. 6a). The interfacial resistance was calculated to be $23 \Omega \text{ cm}^2$ from the EIS measurements presented in Supplementary Fig. 6b, which is a slightly higher value than that of the cell containing the Te/Ag-C interlayer. The capacity retention of ~83% after 500 cycles (Supplementary Fig. 6c,d) is relatively inferior to that of the porous Te/Ag-C cell; however, stable operation was achieved up to a maximum of 500 cycles without any significant capacity drop. This indicates that the carbon interlayer can effectively bind to the porous Te metal layer, and that Li dendrite formation is suppressed up to a current density of 2.2 mA/cm^2 . Nevertheless, Ag in the interlayer certainly plays an important role, as the capacity retention of the Te/C cell (Supplementary Fig. 6d) is inferior to that of Te/Ag-C cell (Fig. 3d). The identical tendency was also reported for the sulphide electrolyte system, where the incorporation of Ag in the C interlayer resulted in improved cycling stability¹⁷. Considering that the critical current density is not highly dependent on the presence of Ag in the anode interlayer, Ag is expected to have a greater impact on the kinetics of Li plating/stripping than on the suppression of Li dendrite formation. The low Li nucleation barrier and high Li diffusivity in Li-Ag alloys^{18,28} presumably indicate that Ag in the C interlayer facilitates Li reduction and enhances the Li transport inside the interlayer. However, carbon was considered to play a pivotal role in preventing the formation of Li dendrites¹⁶.

2. While the DFT results are convincing to show that the degree of mixing between Li and Te is much less than Li and Ag, it is not clear if the authors have considered the impacts of volume expansion. The authors demonstrate that the Li uptake is 2 Li per Te atom. This would lead to large volume expansion upon the original formation of a Li_2Te phase that would lead to large first-cycle capacity losses. This is the case with Sn, which the authors also suggest would be a good candidate of material. Understandably, the volume expansion would be less for Te than Sn, but still significant enough to lead to self-pulverization, delamination, and capacity loss. Presumably this is mitigated by the porous structure of the Te layer used by the authors but cannot be confirmed without microstructural images of the porous Te layer. It is also not clear if the porous Te layer remains porous after CIP at 250MPa.

Authors' Response:

Thank you for raising an important point about the volume expansion of binding layer metals. We totally agree with your concern that the complete lithiation of Te would result in a large volume expansion, and we certainly considered its impact before we decided to apply porous Te as a binding layer.

One of the reasons why we thought Te could work well is because of its porous structure, as you pointed out. It could certainly relieve the problem related to volume expansion by offering some free space. More importantly, we believe that the sluggish Li diffusion in bulk Te could have helped considerably in terms of avoiding the volume expansion. As described in the manuscript, the diffusion coefficient of Li in Te was reported to be 10^{-14} – $10^{-15} \text{ cm}^2/\text{s}$ [*Adv. Energy Mater.* **11**, 2003248 (2021)], whereas in Ag and Sn, it is $\sim 10^{-8} \text{ cm}^2/\text{s}$ and $\sim 10^{-9} \text{ cm}^2/\text{s}$, respectively [*J. Am. Chem. Soc.* **142**, 8818 (2020), *J. Electrochem. Soc.* **134**, 3098 (1987)]. This value is a few orders of magnitude lower than the self-diffusion coefficient of Li ($\sim 10^{-11} \text{ cm}^2/\text{s}$) [*J. Electrochem. Soc.* **130**, 737 (1983)]. Moreover, the electrochemical active area of Te/solid electrolyte interface is small because Te was simply coated as a layer on the solid electrolyte surface.

Based on these reasons, we expect that the complete lithiation of Te might not take place under our charge/discharge rate condition (0.5 C), similar to the recent report where the lithiation of Si in solid-solid interface is limited to the surface [*Nat. Mater.* **23**, 244 (2024)]. This could have led to the small volume change of the Te layer. Ideally, the interlayer material should not react with Li to avoid all potential issues; however, our results demonstrate that Te can serve as an excellent binding layer for ~4000 cycles, suggesting that volume expansion and related issues, including self-pulverization and delamination, were well mitigated in our design. We tried to validate our theory by taking a microstructural image (SEM) with high magnification to observe the nanoscale porosity; however, unfortunately, increasing the beam energy resulted in side effects such as beam-induced Li precipitation at the surface.

In response to your comment, we revised the manuscript as follows:

Revised text:

Among the two, Te was ultimately selected because of its lesser degree of Li uptake (2 Li per Te) compared to Sn (4.4 Li per Sn) during alloying, which could help minimise morphological and volumetric changes during charge/discharge cycling. The sluggish Li diffusion in Te (diffusion coefficient of 10^{-14} – 10^{-15} cm²/s)²⁵ could be also beneficial for alleviating the volume change, as it could limit the rate of Li-Te alloying reaction and possibly restrict the alloying region to the surface of Te, similar to what was recently reported for the lithiation of Si at the solid-solid interface²⁶.

3. The authors show Li-metal symmetric cells for the porous and dense Te layers in Figure S3. However, the Ohmic drops observed in Figure S3d is not consistent with the EIS shown in Figure S3b. Take the voltage response at 1 mA/cm² as an example. The observed potential is ~10 mV. This corresponds to an area specific resistance of (10mV)/(1mA/cm²) = 10 Ohm cm², while the measured area specific resistance is ~46 Ohm cm² in Fig S3b. Meanwhile, the observed potentials in Fig S3c are consistent – (50mV)/(1mA/cm²) = 50 Ohm cm², which is what is observed in Fig S3b. This leads me to believe that the Faradaic efficiency is not 100% in the porous Te cell, and that some soft-short or electronic shunt exists in the cell.

Authors' Response:

We greatly appreciate your insightful comment regarding the potential occurrence of a micro-short in the symmetric cell of Supplementary Figure S3. One of the other reviewers also raised the same concern. Please refer to our response to reviewer #1's comment #1.

As you pointed out, the extremely low overpotential observed under galvanostatic conditions in Supplementary Figure S3b clearly indicates the occurrence of a micro-short. It appears that the electronically conductive metal interlayer (Te) formed a subtle connection at the edge of the LLZTO solid-state electrolyte pellet during the sputtering process when fabricating the symmetric cell.

To address this, we fabricated new symmetric cells using a thinner LLZTO pellet (~250 μm) than before. During the sputtering process, we applied tape to the edge of the pellet to prevent the metal from connecting to both electrodes. The newly measured symmetric cell results, shown in the figures below, now exhibit reasonable overpotentials corresponding to the applied current density and resistance.

We thank you once again for your sharp insights. We have revised Supplementary Figure S3 with these newly measured symmetric cell results.

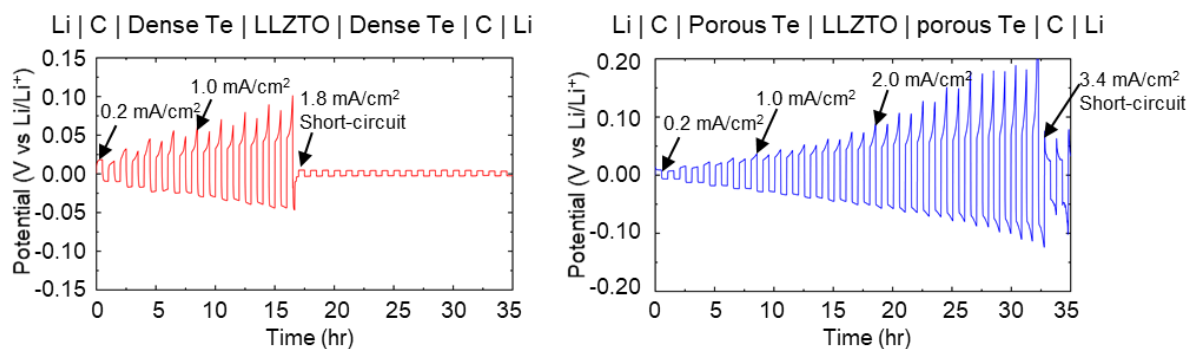


Figure S4. Galvanostatic cycling tests recorded with an increasing current density using (c) dense Te and (d) porous Te.

4. The authors show a cross section of the cell in Fig 3e-h. How was the cross section prepared? Li metal is notorious for being susceptible to beam damage under FIB. Are the features observed in Fig 3e,f real or artifacts from preparation?

Authors' Response:

As you pointed out, Li metal is highly sensitive to beam damage. Thus, we prepared the sample using a cooling cross-sectional polisher with an Ar-ion beam. The specific details are provided below, and we have now revised the Methods section in the manuscript.

Cross-sectional SEM samples were prepared using a cooling cross-sectional polisher (IB-19520ccp JEOL). The samples were handled in an Ar-filled glove box and transferred to the analysis instruments via a sealed-transfer vessel to prevent air exposure. To mitigate potential thermal and structure damage, the samples were etched with a 5 kV Ar-ion beam for 8 h while maintaining the temperature below -140°C . The optimized cross-sectional polishing procedure was established through trial-and-error iteration.

Revised text:

The cross-sectional microstructure of the interface between the anode and LLZTO electrolyte was examined using field-emission SEM (FE-SEM; Hitachi SU-8030) coupled with EDS at an accelerating voltage of 5 kV and a working distance of 8 mm. For sample preparation, the cycled cells were disassembled in an Ar-filled glove box, and after the removal of the cathode, the cross-sections of LLZTO in contact with the Te/Ag-C/Li anode were mounted on the sample holder using a load-lock chamber to avoid exposure to air. To mitigate potential thermal and structure damage, the samples were etched with a 5 kV Ar-ion beam for 8 hours while the temperature was maintained below -140°C . The cross-sectional polishing procedure was optimised using trial-and-error iteration.

5. Fig 3c also shows cycling behavior with an NCA cathode of reported 4.4 mAh/cm^2 areal capacity. However, the authors also report that the Li metal foil has a thickness of $20\mu\text{m}$. A $20\mu\text{m}$ thick foil

corresponds to a capacity of ~ 4.1 mAh/cm², which would make the Li metal the limiting electrode. It has been widely observed throughout academic literature and industry that cycling 100% of the lithium capacity dramatically worsens cell performance by accelerating current focusing, delamination, and dendrite formation (see papers by many in the field including Motoyama, Sakamoto, Janek, etc). Furthermore, the XPS results in Fig 2, demonstrate that there is some irreversibility when forming the Li-Te alloy that would lead to some irreversible loss of the Li capacity which would make it impossible to cycle above 4 mAh/cm². Given this, how do the authors reconcile these observations and differences with others in the field?

Authors' Response:

Thank you for your helpful suggestions. In lithium metal batteries, the lithium metal anode serves to provide a reversible electrochemical reaction site for Li plating/stripping reactions and is not limited by the cathode capacity. Generally, in lithium metal batteries, the charging process occurs first, and lithium from the cathode plates onto the lithium metal anode, increasing the thickness of the lithium metal anode. In the cell described in Figure 3 of this paper, the charging process was also performed first, and after charging, an increase in lithium metal thickness of ~ 21.5 μ m, corresponding to the cathode capacity of 4.4 mAh/cm², was observed.

Solid-state batteries composed of ~ 6 mAh/cm² capacity NCA cathodes and AgC-based Li-free anodes reported in the literature [Nat. Energy 5, 299–308 (2020)] are also lithium metal batteries of the same type. In our study, the 20 μ m-thick lithium metal was introduced solely for the purpose of pre-lithiation to compensate for the initial irreversible capacity of the Te/AgC interlayer, rather than being fully utilized as active lithium.

In response to your comment, we revised the manuscript as follows:

Revised text:

The Ag-C layer was attached as an anode interlayer to the acid-treated LLZTO surface via cold isostatic pressing (CIP) at 250 MPa. Subsequently, Li-metal foil (99.99%, thickness = 20 μ m, Honjo Metal Co., Ltd.) was attached to the Ag-C surface via CIP, again at 250 MPa. The 20 μ m-thick lithium metal was used for pre-lithiation to improve the initial irreversibility of the Te/Ag-C interlayer.

6. The ability to fabricate a 100 mAh cell is incredibly impressive and is a good example to the broader community. However, it is unclear why the large-area cell exhibits a low area specific resistance. The area specific resistance is a value used to scale resistances between different areas and thus should be independent of area. Please explain why the area specific resistances are so different between the small and large-format cells.

Authors' Response:

During the fabrication of LLZTO solid electrolyte tapes, lithium content can become unevenly distributed on the surface due to Li volatilization during the high-temperature sintering process, depending on the specific processing conditions. Unless the process is optimized to ensure the perfect homogeneity, this inhomogeneity always appears regardless of the tape area. While it is true that the area of the tape does not affect the degree of the inhomogeneity, we expect that the chance for the occurrence of severe inhomogeneity is higher for large-area tapes assuming that inhomogeneity has a probability distribution. As a result, when the large solid electrolyte undergoes acid treatment, it can

lead to increased pore formation and surface roughness.

While this increased surface area in large-area solid electrolytes might expand the effective electrochemical reaction sites with the anode, potentially leading to a lower ASR (Area Specific Resistance) compared to smaller-area solid electrolytes, we anticipate that if the surface uniformity of the solid electrolyte is improved through better process control, this ASR difference would disappear, rendering the ASR consistent regardless of the area.

To aid understanding, we have added relevant content to the revised manuscript.

Revised text:

To further examine the applicability of the cell for use in commercial devices, such as smartphones, a 100-mAh-capacity cell was fabricated and evaluated using a large-area tape solid electrolyte (36 cm²), a Te/C interlayer, and a 3.2 mAh/cm²-LCO cathode (Fig. 4a). The impedance spectrum (Fig. 4b) indicates that the large-area cell exhibits a low initial interfacial resistance of <10 Ω cm². The lower interfacial resistance of the large-area cell compared to that of the small-area cell shown in Fig. 3b is likely due to the increased surface area of the large-area solid electrolyte resulting from inhomogeneous distribution of Li on the surface and subsequent increased porosity during acid treatment. Because large-area cells are more susceptible to micro-short circuits due to the increased formation of surface defects and localised current densities as compared to small-area cells, the long-term cycling performance was evaluated at 45 °C, at which the enhanced lithium mobility can mitigate failure due to micro-short circuits.

7. Please provide more information on how the cells are constructed. Are they coin cells? How much stack pressure is applied? What temperatures are they formed and cycled at? How have the authors ensured that ionic liquid is confined to the cathode side and is not serving as an alternate ionic pathway around the sides or through cracks in the solid electrolyte?

Authors' Response:

In this study, pouch cells were used for all electrochemical evaluations regardless of their electrode area. We applied an external pressure of 0.3 MPa, consistent with the typical pressure applied in coin cells. All cells, with the exception of the large-area cells, were evaluated for their cycling performance at 25 °C. For the large-area cells, charge-discharge cycling tests were conducted at 45 °C to mitigate short-circuiting issues arising from surface defects.

To ensure the ionic liquid remained localized at the cathode and did not migrate towards the Li metal anode, we infiltrated it into the cathode and subsequently removed any excess from the surface using disposable wipers. Gravimetric analysis after the removal process revealed that approximately ~10 wt% of the ionic liquid remained infiltrated within the cathode. The optical images presented below clearly show that no significant amount of excess ionic liquid was present. Thus, given the limited uptake of ionic liquid by the cathode, its migration to the lithium metal anode is considered unlikely.

For the sake of clarity, we modified Fig. 4a as follows:

Figure 4a

a

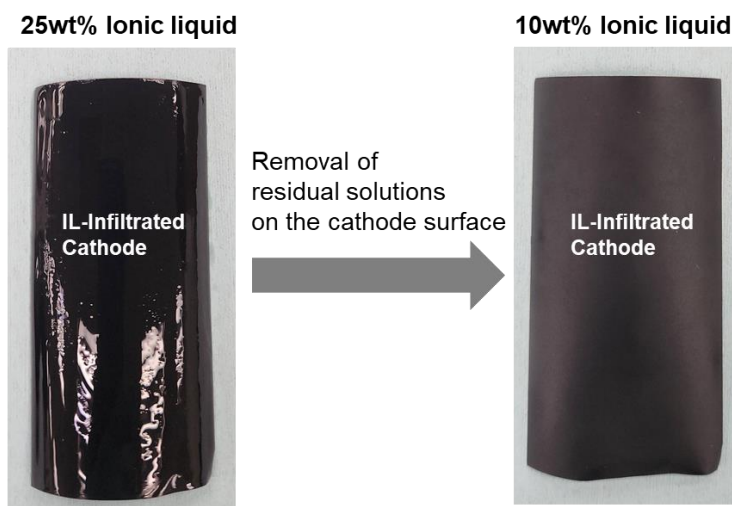


Fig. R1. Optical images of the ionic-liquid-infiltrated cathode before and after removing the residual solutions on its surface.

Reviewer #4

Comments:

Reviewer #4 (Remarks to the Author):

This study details a novel cell architecture that demonstrates great cyclability with lithium metal. Because of the cycle life this study may warrant publication in nature communications. However to validate the author's claims a few questions that should be addressed.

Authors' Response:

Thank you for carefully reviewing our manuscript and for your helpful comments. Your comments, followed by our point-by-point responses, are shown below.

1) The study mentions the use of an ionic liquid in the full cell cycling data. Is there any data that can be shared to help demonstrate that lithium ions are not going "around" the solid electrolyte?

Authors' Response:

Thank you for your insightful comment concerning the possibility of ionic liquid migration to the Li metal anode. We would like to note that a similar point was raised by one of the other reviewers, so some part of this response could be also found in our response to reviewer #3's comment #7.

To ensure the ionic liquid remained localized at the cathode and did not migrate towards the Li metal anode, we infiltrated it into the cathode and subsequently removed any excess from the surface using disposable wipers. Gravimetric analysis after the removal process revealed that approximately ~10 wt% of the ionic liquid remained infiltrated within the cathode. The optical images below clearly show that no significant amount of excess ionic liquid was present. Thus, given the limited uptake of ionic liquid by the cathode, its migration to the lithium metal anode is considered unlikely.

For improved clarity, we modified Figure 4a as follows:

Figure 4a

a



2) can the authors speak to the commercializability of this technique? What is the strategy for mass production?

Authors' Response:

Thank you for pointing out an important subject regarding the commercialization of the lithium metal batteries with a garnet oxide electrolyte. Because the quasi-solid-state batteries can employ commercial LIB cathodes, the most critical factor for their commercialization is the continuous fabrication of thin, uniform solid electrolytes. We anticipate that leveraging Corning's ribbon ceramic process

[https://www.corning.com/media/worldwide/Innovation/documents/ribbonceramics/1_CGMSeptember2020.pdf], which is based on fast-firing technology, will enable the mass production of thin solid electrolytes with uniform composition.

We have incorporated this information into the revised manuscript.

Revised text:

Considering that the critical current density is not highly dependent on the presence of Ag in the anode interlayer, Ag is expected to have a greater impact on the kinetics of Li plating/stripping than on the suppression of Li dendrite formation. The low Li nucleation barrier and high Li diffusivity in Li-Ag alloys^{18,28} presumably indicate that Ag in the C interlayer facilitates Li reduction and enhances the Li transport inside the interlayer. However, carbon was considered to play a pivotal role in preventing the formation of Li dendrites¹⁶.

Assuming the cell configuration shown in Fig. 3a as a representative unit cell for battery pack integration, the calculated volumetric energy density is 519 Wh L⁻¹ (Supplementary Table 1). To achieve an energy density exceeding 700 Wh L⁻¹ (comparable to that of state-of-the-art commercial LIBs), both the thickness of the solid electrolyte and the lithium metal anode must be reduced from their current levels. Utilising Corning's fast-firing roll-to-roll ribbon ceramic processing⁴⁰, the thickness of the LLZTO solid electrolyte can be reduced to below 60 μm, while Applied Materials' sputtering technology allows the lithium metal thickness to be decreased to below 5 μm⁴¹. In fact, Corning's ribbon ceramic process enabled us to successfully fabricate a 30 μm-thick solid electrolyte (Supplementary Fig. 7). However, such thin solid electrolytes tend to be brittle, and therefore, mechanical reinforcement is necessary for practical application. Addressing this issue remains a critical focus of our ongoing and future research efforts.

3) for the operando XPS data to make conclusions about a Li-Te alloy or TeO₂ the O 1s spectra and the Li 1s spectra should be fit (and shown at least in the SI) so that the authors can demonstrate the appropriate relative intensities for the matching core shells in each phase (I.e. 2x more relative oxygen intensity for a TeO₂ phase).

Authors' Response:

Thank you for pointing out the unclearness in the interpretation of the operando XPS data for Te layer. The O 1s spectrum contains contributions from oxygen bound to Te, oxygen in the solid electrolyte, and oxygen associated with surface contaminants such as carbon. However, the binding energies of these species are not sufficiently distinct to allow clear and precise peak separation. Consequently, peak fitting of the O 1s spectrum does not yield accurate results (please refer to Supplementary Figure 3). For the same reason, accurate deconvolution of the Li 1s spectrum through peak fitting is also challenging. Despite the challenges in peak fitting for O 1s and Li 1s, the spectral separation of Te-

metal, Li-Te alloy, and Te oxides (e.g., TeO_2) is relatively well-defined, allowing for a relatively precise analysis of changes in Li plating and stripping near the interface. Fig. 2d presents the variation in the relative percentage of individual components within the Te $3d_{5/2}$ spectrum over time under beam irradiation. Additionally, Fig. 2e presents the changes in Li and Te composition by representing their calculated atomic percent (at. %) as the Li/Te ratio.

Further explanations and revisions have been incorporated into the manuscript to enhance clarity and reduce potential ambiguities.

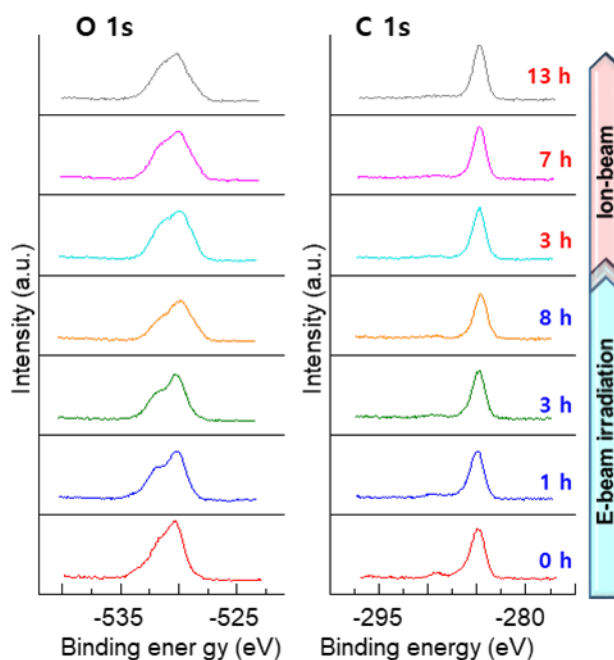


Fig. S3 | Change in the core level spectra of the LLZTO electrolyte during Li-ion migration.

Revised text:

The variation in the relative percentage quantity of each chemical state within in the Te $3d_{5/2}$ spectra was determined using curve fitting as a function of the irradiation time. We note that the O 1s and Li 1s spectra could not be utilised to analyse the chemical state, as multiple contributions from various sources were included in the spectra (Fig. S3). The Li-Te alloy content increased to 90.8% after 8 h of e-beam irradiation and then decreased to 8.8% as a result of ion-beam irradiation (Fig. 2d), indicating that the Li-Te alloying reaction was almost reversible, although a small amount of Li-Te alloy remained at the surface. Furthermore, identical measurements were performed for the dense Te layer to determine whether the creation of a porous layer facilitates Li transport. The Li/Te atomic ratio—derived from the calculated atomic percentages (at. %) of Li and Te (Fig. 2e) to analyse the variation in the layer composition during irradiation—indicated that this ratio increases more rapidly in the porous than in the dense Te layer. After 8 h of e-beam irradiation, the Li/Te ratio of the porous Te layer increased to 10.3, whereas that of the dense Te layer was 3.4. An identical trend was observed during ion-beam irradiation, where the Li/Te ratio decreased more rapidly in the porous Te layer. These findings therefore indicate that the design strategy described herein for the preparation of a porous Te layer is effective for accelerating Li

transport, as corroborated by the theoretical investigation (Supplementary Fig. 2).

4) capacity retention is not the whole story especially at high current densities. Therefore the authors need to show more electrochemical data. For example the constant voltage capacities per cycle, some of the time series data seems to suggest these values are very high. Also was "Constant voltage discharge" really the only type of discharge step as the methods section suggests? If so why? What is the cycle life for these cells under normal CC discharge conditions?

Authors' Response:

As you suggested, we have plotted the constant voltage (CV) charging capacity per cycle. We observed that the rate at which the CV capacity increases accelerates after 2000 cycles. This indicates a decrease in the electrochemical reaction kinetics, which might be attributed to the micro-cracking degradation of the cathode, as shown in Fig. 3h,i. We have added this description to the manuscript and CV charging capacity per cycle as Supplementary Fig. 5.

For the discharge process, we conducted cycle tests under constant current (CC) discharge conditions, which are typical for commercial mobile battery testing, rather than CV. We appreciate your attention to detail, as there was a typo in the Methods section, which we have now corrected in the revised text.

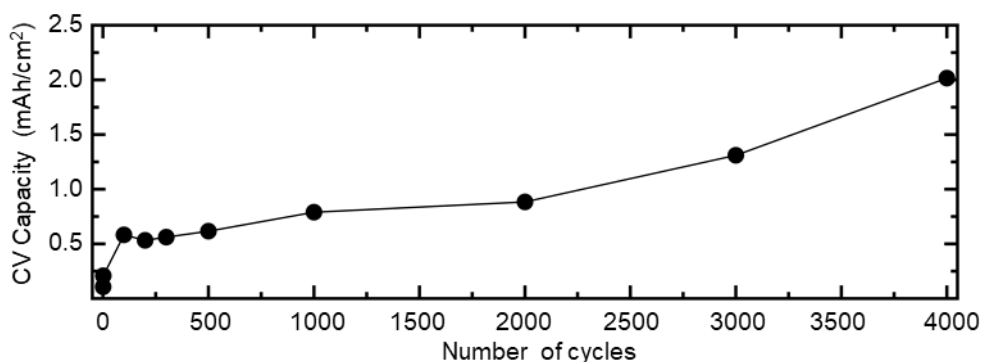


Fig. S5 | Constant voltage (CV) capacity of the Li/C/Te/LLZTO/LCO-EMIFSI (2M LiFSI) single cell per cycle.

Revised text

The excellent lifespan of the prepared cell provides meaningful insights not only into the durability of the anode interface, but also into the long-term stability of the NCA811 cathode material. The SEM/EDS cross-sectional images of the cathode (Fig. 3h,i) reveal the presence of microcracks and the partial infiltration of ionic liquids among the NCA811 particles after 4000 cycles. This phenomenon is commonly associated with the microcracking degradation behaviour observed in NCA and NCM ($\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$) electrodes, originating from transformation of the surface phases into spinel and rock salt phases. This micro-cracking degradation of the cathode can affect not only the capacity retention but also the electrochemical kinetics of the cell. Indeed, observation of the charging capacity in the CV region across cycles reveals an increase after 2000 cycles

(Supplementary Fig. 5). This signifies an increase in overpotential under constant current conditions and is presumably due to degradation caused by micro-crack formation in the cathode and/or degradation at the cathode-ionic liquid interface. Interestingly, the remarkable capacity retention of 80.1% after 4000 cycles for the prepared quasi-all-solid-state Li-metal battery surpasses the reported cycling performances of the high-Ni NCA or NCM electrodes in LIBs containing carbonate-based liquid electrolytes^{36–39}. This strongly suggests that the degradation behaviours at the cathode/liquid interfaces, including transition metal dissolution, surface reconstruction of the cathode, and electrolyte decomposition, occur much less frequently for ionic liquids (2 M LiFSI in EMIFSI) with high oxidation potentials than for carbonate-based liquid electrolytes.

Methods section

A battery cycler (Toscat-3100, Toyo System Co. LTD., Japan) was employed to measure the charge/discharge curves of the quasi-all-solid-state cells at 25 °C. The cells were cycled in constant current (CC)–constant voltage (CV) charging and CC discharging mode in the potential ranges of 2.8–4.4 and 2.8–4.5 V (vs. Li/Li⁺) for NCA811 and LCO, respectively. Five cells from each sample were evaluated to determine the data reliability.

Response Letter

Reviewer #1

Comments:

Reviewer #1 (Remarks to the Author):

*I read through all responses and consider everything addressed well.
The manuscript can be published as it is.*

Author reply:

We appreciate the reviewer for the positive assessment of our response. The reviewer's comments were truly helpful for us to improve the quality of the manuscript.

Reviewer #2

Comments:

Reviewer #2 (Remarks to the Author):

The authors have made a good faith effort to address reviewers' concerns in this revision, including additional experimentation and information. The paper is now ready for publication.

Author reply:

We are grateful to the reviewer for acknowledging our efforts. The reviewer's insightful comments helped us a lot to improve the clarity of the paper.

Reviewer #3

Comments:

Reviewer #3 (Remarks to the Author):

Overall, the revisions to the manuscript by Kim et al. provide improvements to the clarity and consistency of the analysis. I particularly appreciate the level of detail to which comments were addressed, and the motivation to conduct additional experimentation as needed. I have one remaining comment but otherwise recommend publication:

Author reply:

We appreciate the reviewer for recognizing our efforts. The reviewer's critical comments were greatly helpful for us to improve the quality of the manuscript.

1. I appreciate the authors' added detail about the role of Ag and the explanation about prior work and findings. I find that the authors' brief summary of past work very insightful to explaining the results in this work and would suggest adding this extra detail into the manuscript text. Particularly surrounding the following:

"In our previous study, when we adopted Li/Aginterlayer-C/Agbind/LLZTO configuration as an anode, we could cycle the cell for 800 cycles at the current density of 1.6 mA/cm². By contrast, when we replace Agbind with Tebind, such that the anode configuration is Li/Aginterlayer-C/Tebind/LLZTO, the cycling stability is highly improved (4000 cycles at the current density of 2.2 mA/cm²), clearly indicating that Tebind is considerably better than Agbind as a binding layer. We would like to additionally note that binding layers at the interface between solid electrolyte and the interlayer are only required for oxide solid electrolytes, as explained in the introduction of this manuscript. In Figure 5c of our previous paper [Nat. Commun. 14, 782 (2023)], the cell using LLZTO and Ag-C interlayer without the binding layer shorted after 2 cycles, whereas the sulfide cell showed high stability without the binding layer [Nat. Energy 5, 299 (2020)]."

The direct reference to the previous papers, the specific cycle numbers, and current densities are particularly helpful to clearly illustrate the difference in observed performance.

Author reply:

We are grateful to the reviewer for the positive assessment of our response. We agree that the incorporation of those details into the manuscript could improve the clarity, and revised the manuscript as follows:

Revised text:

Compared with state-of-the-art quasi-all-solid-state cells with a garnet-type solid electrolyte reported thus far^{5,6,16,29–34}, the performance of our cell in terms of areal capacity, current density, and long-term capacity retention is remarkable. In our previous study, when we adopted Li/Ag-C/Ag/LLZTO configuration as an anode⁵, we could cycle the cell for 800 cycles at the current density of 1.6 mA/cm². By contrast, when we replace interface-binding material from Ag to Te, such that the anode configuration is Li/Ag-C/Te/LLZTO, the cycling stability is highly improved (4000 cycles at the current density of 2.2 mA/cm²), clearly indicating that Te is considerably better than Ag as a binding layer. This clearly verifies the described design strategy for the exploration of interface-binding materials, namely to identify an element with a low mobility towards Li (Fig. 1). We would like to additionally note that binding layers at the interface between solid electrolyte and the interlayer are only required for oxide solid electrolytes, as explained in the introduction of this manuscript. In Figure 5c of our previous paper⁵, the cell using LLZTO and Ag-C interlayer without the binding layer shorted after 2 cycles, whereas the sulfide cell showed high stability without the binding layer¹⁵.

Reviewer #4

Comments:

Reviewer #4 (Remarks to the Author):

Thank you for addressing the comments. I encourage the publication of this manuscript.

Author reply:

We appreciate the reviewer for the positive comment. The reviewer's comments were definitely helpful for us to improve the quality of this paper.