nature portfolio

Peer Review File

Maximizing interface stability in all-solid-state lithium batteries through entropy stabilization and fast kinetics

Reviewer #1 (Remarks to the Author):

The authors present a strategy to improve the performance of a solid-state battery constructed with LLZTO by the use of a 'high entropy' disordered rock salt oxyfluoride electrolyte. They claim that the use of mixed cations in the cathode, enables higher sintering temperatures needed to create interfaces with a lower resistance as well as prevents the migration of cations thereby ensuring chemical stability.

The first issue I have with this article is while the data is interesting, there is no explanation at all as to why having several cations in the cathode allows higher sintering temperatures or more stable cycling. The literature presented in the introduction is very sparse. Yes having many cations allows the space for a higher configurational entropy and in some cases can form stable structures. But in this specific case, why was this configuration selected. What role do the various components of this cathode composition play? What was the selection criteria: both for the cations selected as well as the stoichiometry. Its very non-specific and unclear.

Another issue I have with this article, is everywhere the authors refer to high entropy disordered rock salt cathodes which they call HE-DRXs, while the whole paper is in fact the study done on a single composition. Thus the term DRXs is misleading. The results are presented as a very general finding that would be applicable to more than one composition of this HE-DRX like material, but have only studied one single material composition. This makes the scope of the findings less widespread than the authors have presented them now.

I am not convinced that this article is suitable in its current form for publication in nature communications. I think the authors need to make their conclusions more general, by looking at more than one material. At the very least it needs to be written in a way that its clear that the conclusions apply only to the single cathode composition in combination with LLZTO. I leave this to the discretion of the editor.

I have several other concerns/comments which have been listed below

1. How was the chemical composition of the cathode, which is presented only once on page 5 of the manuscript determined? Was an ICP analysis or a similar method used to determine the stoichiometry of this material? If not the authors should be clear that this is the expected composition not the actual one.
2. On page 3 the sentence 'High-entropy materials composed …' ends abruptly
3. On the same page 3 it says 'high-entropy materials maximize configurational entropy and form highly stable structures. Consequently they exhibit high thermal stability and low sintering temperatures. ' I think this part needs more information. It forms the main pillar of the manuscript, but there is no detailed description as to why this would be the case, to what extent others have found these temperatures to be reduced? Whether or not this has to do with the chemical make-up of the material? What is the mechanism behind this?
4. On page 4, the authors state 'Due to the unique entropy effects, high-entropy materials have the potential to …' What entropy effects? The lack of any information in the previous section makes this even more unclear.
5. On page 6 of the manuscript the authors state that impurity phases are formed at 1400C as they see with XRD. What can this be indexed to?
6. On page 8 the authors use the EDX maps from SEM (Fig 3c) to prove the LLZTO and the HE-DRX do not react, but they only show the maps of La and Mn. What do the EDX maps of the other elements look like, both from the solid-electrolyte and the cathode. I think that all the cations need to be mapped and shown, at the very least in the supporting information. Plus the XPS data shown in the SI on the related dataset says XPS maps, but this is just a single

spectrum. There is no statistical information provided, also not in the methods. Were the XPS measurements done at multiple points? How can the authors base conclusions on a single measurement done for a presumably very small spot size.

7. Again on page 12, Fig 4e where the interface is examined between the cathode and solid electrolyte layers, only the EDS maps of La and Mn are shown. What about the other elements in LLZTO and the high entropy cathode? Unless all of these are also visualized, how can you confirm that there is no cross diffusion of ions? Plus in this situation there is no XPS now done, even from the cathode side to ensure that the desired elements are present and in the desired oxidation state.
8. In Figures 4d,e please add the circuit used to fit the impedance data. Its not clear how the authors got the values presented
9. In the section on electrochemical performance, the authors add LLZTO to the cathode to form the cathode layer, but no conductive carbon or any other electron conductor. What is the electronic conductivity of the HE cathode? Was this determined and is it sufficient to run a battery? What is the ionic conductivity of the HE cathode in the absence of the LLZTO?
10. Again in Figs 4c and 4d where they show a section of the battery, before and after cycling, only the EDS maps of La and Mn are seen. What about the other elements? How can they be sure that there is no cation migration? Some XPS may also be helpful here.
11. It also looks like the porosity of the cathode decreases on cycling from the SEM images. Could the authors comment on this?
12. The batteries were run at 150C, but could the authors also perhaps show the performance of the battery at temperatures more standard for LLZTO like 50-70C?
13. In the conclusions, the authors have a sentence ‘ The stable HE-DRX/LLZTO solid-state interface also mitigates the issue of transition metal migration and interfacial side reaction for the HE-DRX cathodes in liquid electrolyte’. I’m not sure what they mean by liquid electrolytes here, or whether this is just a typo..?

REVIEWER COMMENTS

Reviewer #2 (Remarks to the Author):

In introduction, some of the statements are not reasonably supported. For example, why does the author believe that HE materials have better chemical compatibility with LLZO electrolyte?

What is the difference in synthesis process for achieving HE-DRXs phase between ref.26 and this work? And why do you state HE-DRXs by RHS shows excellent thermal stability? What impurities phase forms when UHS took place at 1400oC?

There is mistake in explaining your observation in Figure 3a. The author stated no reaction above 800oC, which is wrong. Reaction started from 800oC according to in situ XRD. Another mistake is in the next sentences that stated the impurity phase appears up to 800oC. 'up to' should change to 'from' or similar.

SEM/EDS of Figure 3c do not clearly show inter diffusion across HE-DRXs and LLZO. EDS Line profiles at the DRX/LLZO interface between the sample for 3s vs. 30s, sintered at 1100oC might be more precise methods and samples for the proper comparison.

Interpretation of Raman spectra at around 600 wave number in Fig 3d is missing.

In Fig.3f, literature information on LCO needs to be revised. Chemical stability of LCO/LLZO is reported up to 1050oC in the following refs.

Sustainable Energy Fuels, 2019, 3,280

J Electroceram (2017) 38:197–206

J. Mater. Chem. A, 2022, 10, 2320-2326

What is the difference in experimental setting between Figure 3b and Supp. Figure 17? It is not clear.

In EIS measurement of symmetrical cells in Figure 4g,h, there is no explanation of how the interfacial resistance is defined. The author stated semicircle in the frequency range of 32kHz-2.5MHz without evidence. It can be clearer if the authors provide resistance values for all the possible components in your system including, cathode/LLZO interface, LLZO, Au/cathode interface with proper equivalent circuit model. It will add much clarity than current description.

Active material loading in this work is quite low, like other literature compared in Supp. Table 2. Then please do not point out other works and say 'loading is low' in the introduction.

What is the reason for measuring a full cell at 150oC? It is very close to the Li melting temperature. Does the author have some comment on any safety issue? Performance at different temperatures will be useful to compare with other literature in supp. table 2. Could you also provide what is limiting at lower temperature operation such as room temperature?

Point-by-Point Responses to Reviewers' Comments and Suggestions

We express our gratitude for the time and effort the reviewers dedicated to evaluating our manuscript. We highly value their thoughtful comments and suggestions, which have notably enhanced the quality and clarity of our work. In response, we performed additional experiments and thoroughly revised the manuscript to address all raised comments and concerns. The changes are highlighted in yellow within the revised manuscript. Our point-by-point responses are presented below.

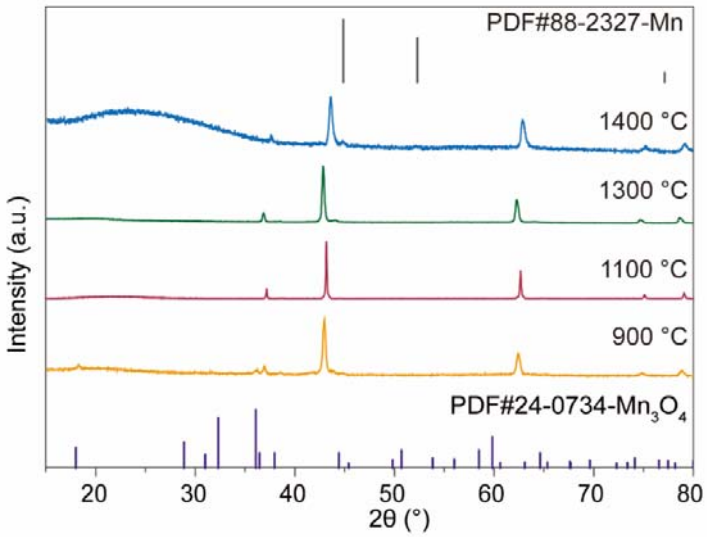
(**Note.** Fig. Number: Figures in the Manuscript; Fig. S Number: Figures in the Supporting Information; Fig. R Number: Figures in the Response letter; [Number]: References in the Response letter)

Reviewer #1's Comments:

The authors present a strategy to improve the performance of a solid-state battery constructed with LLZTO by the use of a "high entropy' disordered rock salt oxyfluoride electrolyte. They claim that the use of mixed cations in the cathode enables higher sintering temperatures needed to create interfaces with a lower resistance as well as prevents the migration of cations thereby ensuring chemical stability.
The first issue I have with this article is while ***the data is interesting****, there is no explanation at all as to why having several cations in the cathode allows higher sintering temperatures or more stable cycling. The literature presented in the introduction is very sparse.*

Response: We thank the reviewer for recognizing the interest in our data.

Regarding higher sintering temperatures. As the number of cations increases, the entropy-stabilizing effect not only contributes to high phase stability but also promotes synergistic interactions among the elements, resulting in intriguing properties such as sluggish diffusion[1]. HE-DRXs exhibit a single-phase structure even at temperature ranging from 1200 to 1300 °C, indicating their exceptional phase stability (**Supplementary Fig. 2**). This slow diffusion effect allows for the co-sintering of HE-DRX and LLZTO at 1100 °C for 3 s without experiencing mutual diffusion of elements (Fig.3f). The combined high phase stability and sluggish diffusion effects contribute to the elevated chemical stabilization temperatures observed in HE-DRX with LLZTO.
Furthermore, our experimental data show that the chemical stability of the DRX cathode and LLZTO gradually increases with an increasing number of cations (**Fig. 3b**).



Updated Supplementary Figure 2. XRD patterns of HE-DRXs synthesized at different temperatures by UHS.

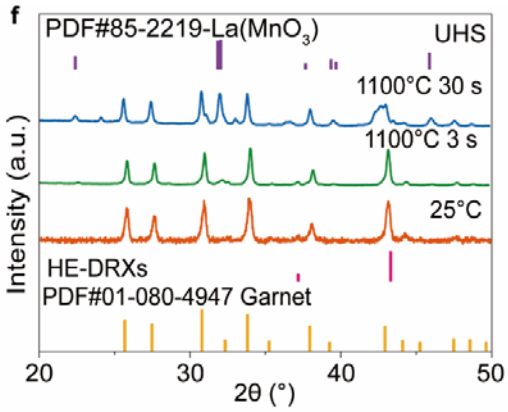
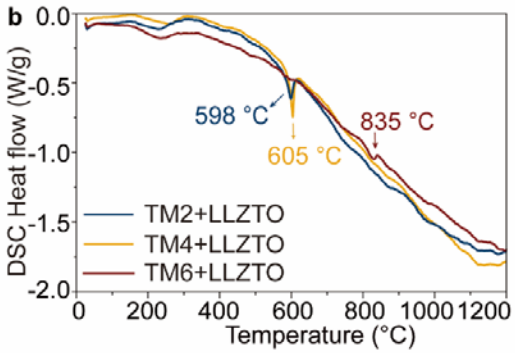


Figure 3. (f) XRD patterns of LLZTO and TM6 heated by UHS.



Update Figure 3. (b) DSC of a mixture of TM2 and LLZTO, TM4 and LLZTO, and TM6 and LLZTO.

[1] Oses, C., Toher, C. & Curtarolo, S. High-entropy ceramics. *Nature Reviews Materials* **5**, 295–309 (2020).

Regarding more stable cycling. The utilization of Mn-based DRX cathodes[2] (including HE-DRX) in liquid batteries often results in inadequate cycle stability due to side reactions between the cathode and electrolyte. However, the construction of a highly stable HE-DRX|LLZTO interface effectively addresses these issues, leading to improved cycle performance in all-solid-state batteries.

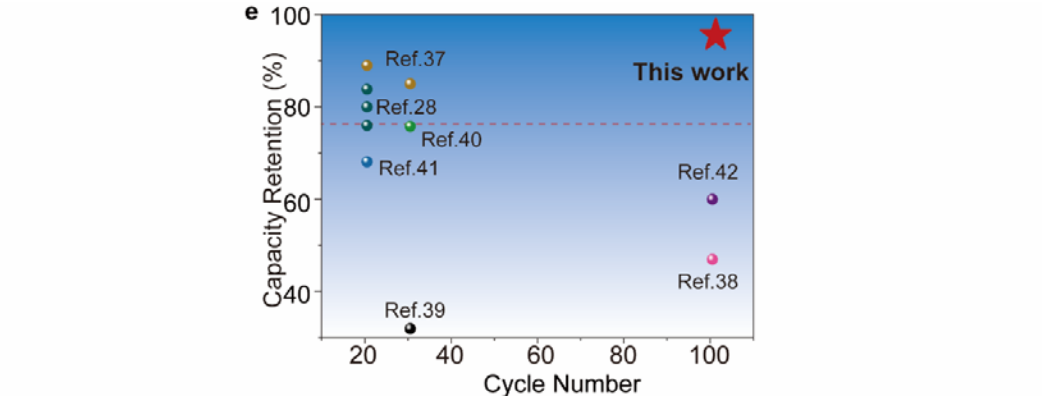


Figure 5. (e) Comparison of the capacity retention of DRXs in the literature.

[2] Clément, R. J., Lun, Z. & Ceder, G. Cation-disordered rocksalt transition metal oxides and oxyfluorides for high energy lithium-ion cathodes. *Energy and Environmental Science* **13**, 345–373 (2020).

Regarding "The literature presented in the introduction is very sparse." We have added relevant references in the Revised manuscript (**pages 5-6, 144-147**), as follows:

Consequently, they exhibit high thermal stability[26,27] and low sintering temperature[28,29]. As cathode materials, high-entropy cationic disordered rock salt cathodes (HE-DRXs), have shown excellent lithium storage properties[28]. Due to the unique entropy effects[30–32], high-entropy materials have the potential to achieve a balance between chemical stability (high T_{stable}) and wettability (low $T_{wetting}$).

26. Sarkar, A. et al. High-Entropy Oxides: Fundamental Aspects and Electrochemical Properties. Advanced Materials 31, (2019).

29. Kuo, C. H. et al. A novel garnet-type high-entropy oxide as air-stable solid electrolyte for Li-ion batteries. APL Materials 10, (2022).

30. Bérardan, D., Franger, S., Meena, A. K. & Dragoe, N. Room temperature lithium superionic conductivity in high entropy oxides. Journal of Materials Chemistry A 4, 9536–9541 (2016).

31. Duan, C. Q. et al. New spinel high-entropy oxides $(FeCoNiCrMnXLi)_3O_4$ (X = Cu, Mg, Zn) as the anode material for lithium-ion batteries. Ceramics International 47, 32025–32032 (2021).

32. Ma, Y. et al. High-entropy energy materials: Challenges and new opportunities. Energy and Environmental Science 14, 2883–2905 (2021).

Yes, having many cations allows the space for a higher configurational entropy and in some cases can form stable structures. But in this specific case, why was this

configuration selected, what role do the various components of this cathode composition play? What was the selection criteria: both for the cations selected as well as the stoichiometry? It's very non-specific and unclear.

Response: We thank the reviewer for the concerns.

Regarding the reason for this configuration selected. Firstly, the rock salt structured cathode exhibits higher chemical stability when in contact with LLZTO[3]. Secondly, HE-DRX has been demonstrated to possess a remarkable capability to achieve high energy density in battery systems[4]. In combination with LLZTO, which offers a wide electrochemical window spanning from 0 to 5 V[5], the high energy density of HE-DRX can be fully utilized. Thirdly, Ceder et al[4]. have successfully used density functional theory (DFT) to estimate the mixing temperatures and HE-DRX (TM6, $Li_{1.3}Mn^{2+}_{0.1}Co^{2+}_{0.1}Mn^{3+}_{0.1}Cr^{3+}_{0.1}Ti_{0.1}Nb_{0.2}O_{1.7}F_{0.3}$) demonstrate good chemical compatibility and redox compatibility.

Regarding the role of the various components of this cathode composition. The cathode compositions include 30% Li excess ($Li_{1.3}$ per formula unit) to facilitate efficient Li^+ transport while minimizing any detrimental effects on the transition metal (TM) redox capacity. Additionally, 15% of the oxygen atoms are substituted with fluorine to enhance the TM redox reservoir. During cathode charging and discharging, the redox reactions of Co^{2+}/Co^{3+}, Cr^{3+}/Cr^{6+}, and Mn^{2+}/Mn^{4+} play a pivotal role, serving as the primary capacity source. These elements undergo reversible redox reactions, enabling charge storage and release during battery operation. Ti^{4+} and Nb^{5+} crystal stabilizing structures, do not contribute to the overall cathode capacity.

Regarding the selection criteria. The Mn^{3+}–Ti^{4+} combination was used as a baseline. Mn^{2+}, Nb^{5+}, $Co^{2+,}$ and Cr^{3+} were sequentially incorporated to form $Li_{1.3}Mn^{2+}_{0.1}Co^{2+}_{0.1}Mn^{3+}_{0.1}Cr^{3+}_{0.1}Ti_{0.1}Nb_{0.2}O_{1.7}F_{0.3}$. The assessment of redox compatibility and chemical compatibility among the transition metal (TM) ion pairs was conducted using the DFT. Chemical compatibility was quantified using the median mixing temperature of compounds containing the respective TM elements. The mixing temperature scale was derived from $(T-T_{min})/(T_{max}-T_{min})$, where T_{max} and T_{min} represent the highest and lowest mixing temperatures observed among all TM pairs[4].

[3] Ren, Y., Liu, T., Shen, Y., Lin, Y. & Nan, C. W. Chemical compatibility between garnet-like solid state electrolyte $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ and major commercial lithium battery cathode materials. *Journal of Materiomics* **2**, 256–264 (2016).

[4] Lun, Z. *et al.* Cation-disordered rocksalt-type high-entropy cathodes for Li-ion batteries. *Nature Materials* **20**, 214–221 (2021).

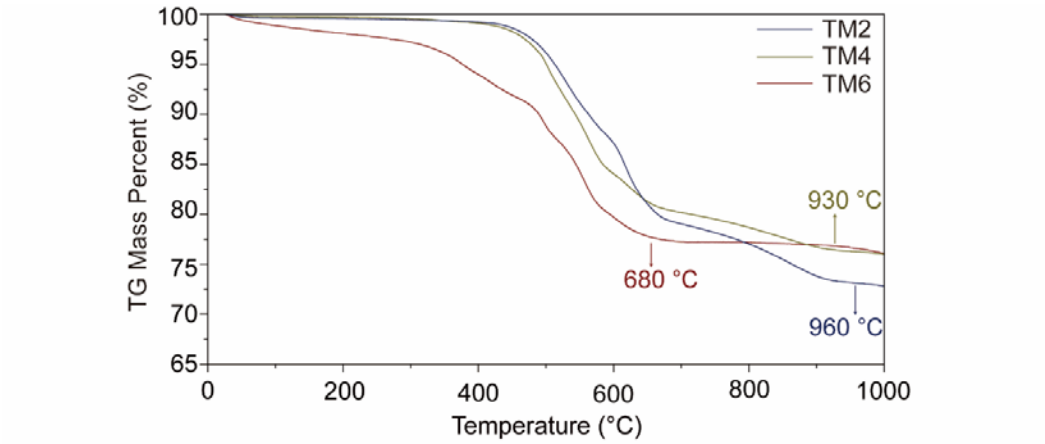
[5] Wang, C. *et al.* Garnet-Type Solid-State Electrolytes: Materials, Interfaces, and Batteries. *Chemical Reviews* **120**, 4257–4300 (2020).

Another issue I have with this article, is everywhere the authors refer to high entropy disordered rock salt cathodes which they call HE-DRXs, while the whole paper is in fact the study done on a single composition, Thus the term DRXs is misleading. The results are presented as a very general finding that would be applicable to more than one composition of this HE-DRX like material, but have only studied one single material composition, this makes the scope of the findings less widespread than the authors have presented them now.
I am not convinced that this article is suitable in its current form for publication in nature communications. I think the authors need to make their conclusions more general, by looking at more than one material. At the very least it needs to be written in a way that its clear that the conclusions apply only to the single cathode composition in combination with LLZTO. I leave this to the discretion of the editor.

Response: We appreciate the reviewer for their constructive comments. In response to your inquiry, we have conducted tests and comparative experiments to validate the uniqueness and advantages of HE-DRX.

We have incorporated a series of comparative tests and analysis of the physical and chemical properties of cationic disordered rock salt cathode materials (DRXs) with varying numbers of cations (TM2, TM4, TM6). These analyses revealed that high-entropy DRXs (HE-DRX, TM6) are better suited to address cathode|electrolyte interface challenges in all solid-state batteries.

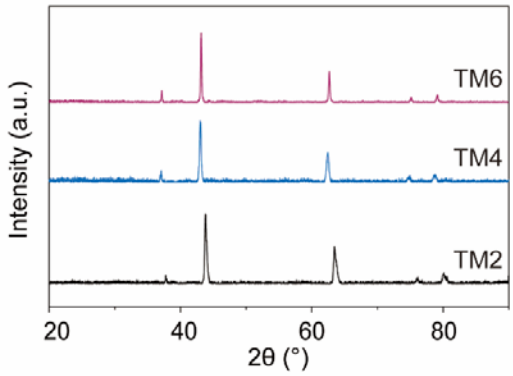
Supplementary experiments have been conducted:
1) Thermogravimetric Analysis (TGA) demonstrates that the synthesis temperature of cathode materials with cationic disorder decreases as the number of cations increases. Specifically, the synthesis temperature of TM6 is 250 °C and 280 °C lower than those of TM4 ($Li_{1.3}Mn^{2+}_{0.2}Mn^{3+}_{0.2}Ti_{0.1}Nb_{0.2}O_{1.7}F_{0.3}$) and TM2 ($Li_{1.3}Mn^{3+}_{0.4}Ti_{0.3}O_{1.7}F_{0.3}$).
The results and discussion have been added in the revised manuscript and supporting information (**page 9, 205-211**).
To verify the impact of the increasing number of cations on the synthesis and sintering temperature of rock salt cathode (DRXs), cathode precursors containing different numbers of cations (TM2, TM4, TM6) underwent thermogravimetric analysis (TGA). The precursor mass of TM6 stabilized at 680 °C, whereas the precursor masses of TM4 ($Li_{1.3}Mn^{2+}_{0.2}Mn^{3+}_{0.2}Ti_{0.1}Nb_{0.2}O_{1.7}F_{0.3}$) and TM2 ($Li_{1.3}Mn^{3+}_{0.4}Ti_{0.3}O_{1.7}F_{0.3}$) reached stability only at 930 °C and 960 °C, respectively. This indicates that the synthesis temperatures of TM6 were 250 °C and 280 °C lower than those of TM4 and TM2 (**Supplementary Fig. 5**).



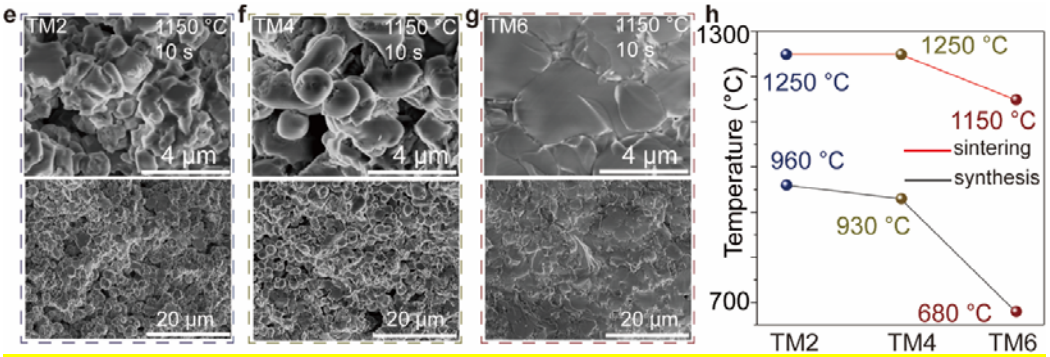
Supplementary Figure 5. TG curves for the precursor mass of TM2, TM4, and TM6.

2) We utilized the ultrafast high-temperature sintering (UHS) technique and SEM imaging to observed that the sintering temperature of TM6 is 100 °C lower than TM2 and TM4. The detailed results and discussion have been added in the revised manuscript and supporting information (**page 9, 211-220**).

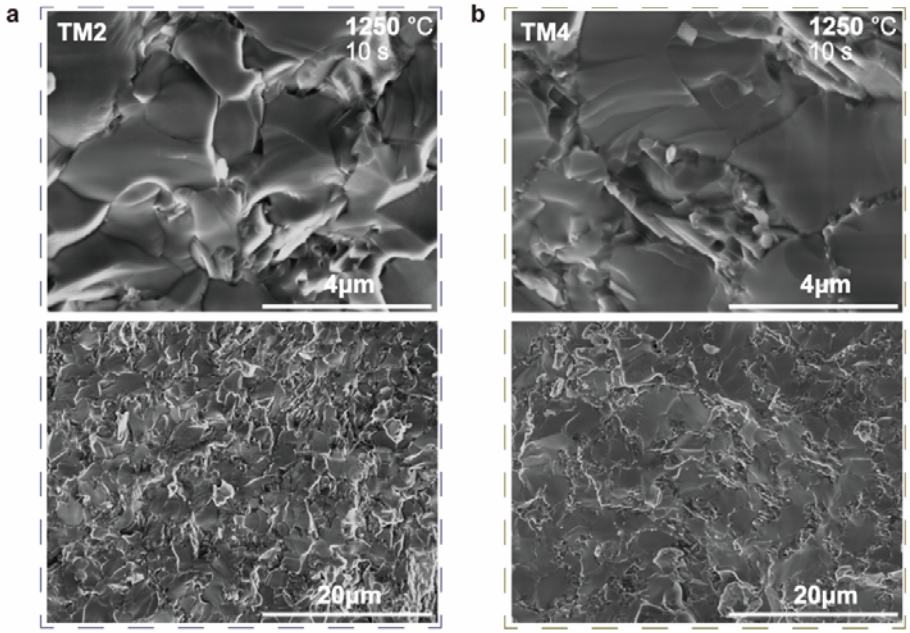
we investigated the sintering behavior of cathode materials with varying numbers of cations using UHS technology. TM2, TM4, and TM6 were subjected to one-step reaction sintering at 1150 °C for 10 s, resulting in successful phase formation (**Supplementary Fig. 6**). Scanning Electron Microscopy (SEM) analysis indicated that the grain size increased with an increasing number of cations during sintering at 1150 °C for 10 s. Specifically, TM6 exhibited a densification phenomenon in grain size, while the grain size of TM2 and TM4 appeared more dispersed (**Fig. 2e-g**). The densification of TM2 and TM4 occurred only when the temperature was raised to 1250 °C for 10 s (**Supplementary Fig. 7**), suggesting that the densification temperature of TM6 is 100 °C lower than that of TM4 and TM2 (**Fig. 2h**).



Supplementary Figure 6. XRD patterns of TM2, TM4, and TM6 were synthesized by UHS at 1150 °C for 10 s.



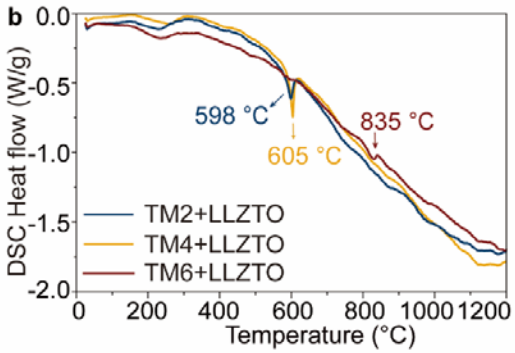
Updated Figure 2. SEM images of TM2(e), TM4(f) andTM6(g) sintered at 1150 °C for 10 s. (h) Comparison of synthesis temperature and sintering temperature of TM2, TM4 and TM6.



Supplementary Figure 7. SEM images of TM2 (a) and TM4 (b) reacted and sintered at 1250 °C for 10 s.

3) DSC analysis further confirmed that TM6 and LLZTO exhibit a higher chemical stabilization temperature, being 230 °C higher than TM4 and 237 °C higher than TM2. The detailed results and discussion regarding these findings have been added in the revised manuscript and supporting information (**page 11, 238-248**).

The differential scanning calorimetry (DSC) data revealed that as the temperature increased, TM2 reacted with LLZTO first at 598 °C, followed by TM4 at 605 °C (**Fig. 3b**). In contrast, a small peak only appeared at 835 °C for the TM6 and LLZTO system, indicating that the chemical stability of the DRX cathode and LLZTO gradually increases with an increasing number of cations.



Update Figure 3. (b) DSC of a mixture of TM2 and LLZTO, TM4 and LLZTO, and TM6 and LLZTO.

*How was **the chemical composition of the cathode**, which is presented only once on page 5 of the manuscript determined? Was an ICP analysis or a similar method used to determine the stoichiometry of this material? If not the authors should be clear that this is the expected composition not the actual one.*

Response: We thank the reviewer for this comment.
To determine the chemical composition, we performed ICP analysis on the samples. The result revealed that 1 mol of the synthesized TM6 contains 1.3 mol of Li, 0.1 mol of Ti, 0.11 mol of Cr, 0.21 mol of Mn, 0.11 mol of Co, and 0.2 mol of Nb (**Table S1**). The theoretical molar ratio of each cation in the cathode material is Li： Ti： Cr： Mn： Co： Nb =1.3： 0.1： 0.1： 0.2： 0.1： 0.2. Consequently, the experimental values of our synthesized cathode materials align well with the theoretical ones.
The detailed results and discussion have been added in the revised manuscript and supporting information (**page 9, 200-202**).
Elemental analysis confirms that the metal ratios in the as-synthesized materials closely align with the target compositions (**Supplementary Table 1**).

Table S1. Target versus measured atomic ratios of the as-synthesized materials.

Element	Measured	Measured ratio	Target atomic ratio
Li	9.04%	1.30	1.30
Ti	4.60%	0.10	0.10
Cr	5.81%	0.11	0.10
Mn	11.72%	0.21	0.20
Co	6.28%	0.11	0.10
Nb	18.66%	0.20	0.20

Comment #2 of Reviewer 1

On page 3 the sentence High-entropy materials composed ...' ends abruptly.
Response: We apologized for the oversight and appreciate your reminder.
We have revised the sentence "High-entropy materials composed of multiple components have received significant attention as an emerging class of" to " High-entropy materials, comprised of multiple components, have received significant attention as an emerging class of materials ". (**page 5, 141-142**)

Comment #3 of Reviewer 1

On the same page 3 it says high-entropy materials maximize configurational entropy and form highly stable structures. Consequently, they exhibit high thermal stability and low sintering temperatures. " think this part needs more information. It forms the main pillar of the manuscript, but there is no detailed description as to why this would be the case, to what extent others have found these temperatures to be reduced? Whether or not this has to do with the chemical make-up of the material? What is the mechanism behind this?

Response: We sincerely thank the reviewer for the valuable suggestion. We have done corresponding literature research and experiments to verify our views.

Regarding *"why this would be the case" and "What is the mechanism behind this".*

Firstly, the stability of a solid solution composed of elemental mixtures is closely associated with changes in Gibbs free energy (ΔG_{mix}), which can be be described by the equation:

$$\Delta G_{mix} = \Delta H_{mix} - T_{mix}\Delta S_{mix} \quad (1)$$

where ΔH_{mix} represents the enthalpy of the mixture, T_{mix} denotes the absolute temperature, and ΔS_{mix} corresponds to the entropy of mixing. As the mixing entropy increases, ΔG_{mix} decrease, thereby enhancing the stability of the solid solution[6].

Secondly, Ceder et al. have demonstrated, through density functional theory (DFT)[4], that the mixing temperatures of HE-DRX compounds are generally more than 500 K lower than those of LE-DRX (Low-entropy DRXs) compounds.

As a result, HE-DRX exhibits lower sintering temperatures.

Regarding *"what extent others have found these temperatures to be reduced".*

Ceder et al[4] found that the sintering temperature of TM6 (HE DRX) is 50 °C lower compared to TM2 and TM4 when using the furnace. In addition, Kuo et al[7] confrimed that the high entropy of the material helps to reduce the sintering temperature, showing that the sintering temperature of high entropy LLZO ($Li_{6.4}La_3Zr_{0.4}Ta_{0.4}Nb_{0.4}Y_{0.6}W_{0.2}O_{12}$) is 100 °C lower than that of mono-doped LLZO ($Li_{6.6}La_3Zr_{1.6}Ta_{0.4}O_{12}$).

We have also done corresponding experiments to support our view that HE-DRX materials have lower synthesis and sintering temperatures. Our result indicates that the

synthesis temperatures of TM6 were 250 °C and 280 °C lower than those of TM4 and TM2 and the sintering temperature of TM6 is 100 °C lower than that of TM4 and TM2. The results and discussion have been discussed in **Reviewer #1's Comments** (**pages 5-7**).

Regarding *"Whether or not this has to do with the chemical make-up of the material".* The chemical make-up of the material indeed plays a crucial role.

Firstly, the stability of HE-DRX is intricately linked to the redox compatibility and chemical compatibility of transition metal (TM) ion pairs. A notable example involves the coexistence of Mn^{3+} and V^{3+} in a DRX compound, where charge transfer reactions transpire[8].

Secondly, the mixing temperature of high entropy materials is influenced by the number and type of transition metals present. As indicated by the equation (1), an increase in mixing entropy leads to a decrease in T_{mix} (when $\Delta G_{mix} = 0$), thereby bolstering the stability of the solid solution. Additionally, according to our understanding of phase diagrams, T_{mix} is also associated with the melting point of the components.

[4] Lun, Z. *et al.* Cation-disordered rocksalt-type high-entropy cathodes for Li-ion batteries. *Nature Materials* **20**, 214–221 (2021).

[6] Akrami, S., Edalati, P., Fuji, M. & Edalati, K. High-entropy ceramics: Review of principles, production and applications. *Materials Science and Engineering R: Reports* **146**, 100644 (2021).

[7] Kuo, C. H. *et al.* A novel garnet-type high-entropy oxide as air-stable solid electrolyte for Li-ion batteries. *APL Materials* **10**, (2022).

[8] Kitchaev, D. A. *et al.* Design principles for high transition metal capacity in disordered rocksalt Li-ion cathodes. *Energy and Environmental Science* **11**, 2159–2171 (2018).

Comment #4 of Reviewer 1

On page 4, the authors state "Due to the unique entropy effects, high-entropy materials have the potential to ... What entropy effects? The lack of any information in the previous section makes this even more unclear.

Response: We thank the reviewer for this comment, and we have supplemented the information by reviewing the literature and supplementing the experimental data.

The entropy-stabilizing effect of high-entropy materials not only contributes to high phase stability but also enables the elements to interact synergistically, resulting in intriguing properties such as the cocktail effect, lattice distortion, and sluggish diffusion.

To verify the correlation of the high entropy effect, we conducted corresponding experiments.

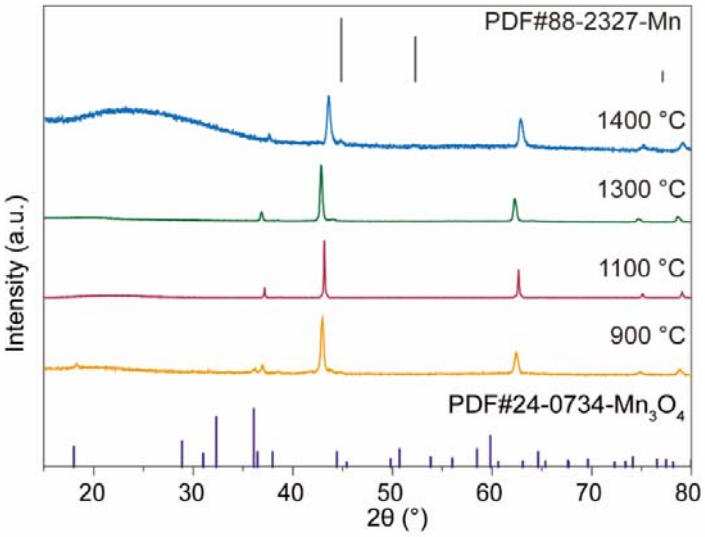
Firstly, we observed that HE-DRX has lower synthesis and sintering temperatures,

as discussed in **Reviewer #1's Comments** (**pages 5-7**). Secondly, HE-DRX and LLZTO have higher chemically stable temperatures due to entropy stability and sluggish diffusion, as elaborated in **Reviewer #1's Comments** (**pages 7-8**). *In situ* XRD also depicted that TM6 reacts with LLZTO above 800 °C before any side reactions occur, providing further support for the enhanced chemical stability of TM6 and LLZTO. This improvement in stability can be attributed to the sluggish diffusion of elements facilitated by the entropic stabilization effect present in high-entropy materials.

Comment #5 of Reviewer 1

On page 6 of the manuscript the authors state that impurity phases are formed at 1400 °C as they see with XRD. What can this be indexed to?

Response: We thank the reviewer very much for the valuable suggestion.
The identification of impurity phases formed at 1400 °C is indeed crucial. The impurity phase has been attributed to transition metal Mn monomers, as observed in **Supplementary Fig. 2**. Upon heating to 1400 °C, the high-valence transition metal elements undergo reduction to their metallic form due to the presence of a reducing atmosphere.
The results and discussion have been added in the revised manuscript and supporting information (**page 8, 187-190**).
As the temperature rises to 1400 °C, the transition metal elements in the high oxidation states undergo reduction to the metallic elements due to the influence of the reducing atmosphere (**Supplementary Fig. 2, 3**).



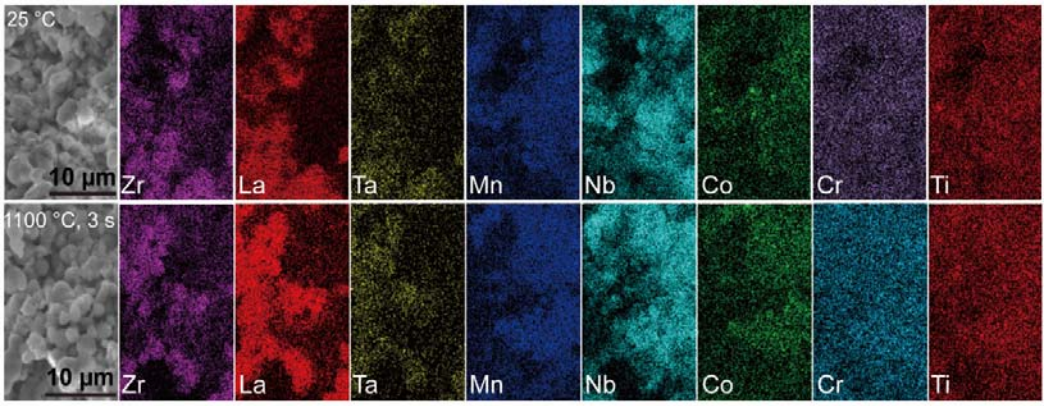
Updated Supplementary Figure 2. XRD patterns of HE-DRXs synthesized at different temperatures by UHS.

Comment #6 of Reviewer 1

On page 8 the authors use the EDX maps from SEM (Fig 3c) to prove the LLZTO and the HE-DRX do not react, but they only show the maps of La and Mn. What do the EDX maps of the other elements look like, both from the solid-electrolyte and the cathode. I think that all the cations need to be mapped and shown, at the very least in the supporting information. Plus, the XPS data shown in the SI on the related dataset says XPS maps, but this is just a single spectrum. There is no statistical information provided, also not in the methods. Were the XPS measurements done at multiple points? How can the authors base conclusions on a single measurement done for a presumably very small spot size?

Response: We appreciate the reviewer for the constructive comments.

Regarding *"all the cations need to be mapped and shown".*
We have incorporated EDS for other elements in Fig. 3c and Supplementary Fig. 8. This shows that all transition metal elements of HE-DRX and LLZTO have no detectable side reaction or cross-diffusion during UHS at 1100 °C for 3 s. Detailed results and discussion have been added in the supporting information.



Supplementary Figure 10. EDS diagrams of the HE-DRXs and LLZTO before and after heat treatment.

We have included TEM images of the TM6|LLZTO interface to provide further verification that there was no mutual diffusion between TM6 and LLZTO elements. Additionally, the elemental distribution analysis of the TEM images clearly shows that TM6 and LLZTO do not undergo elemental diffusion (**Fig. R1**)

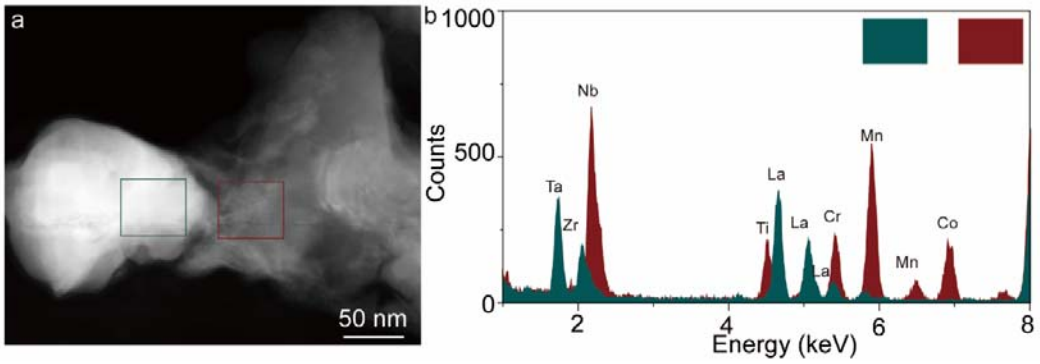
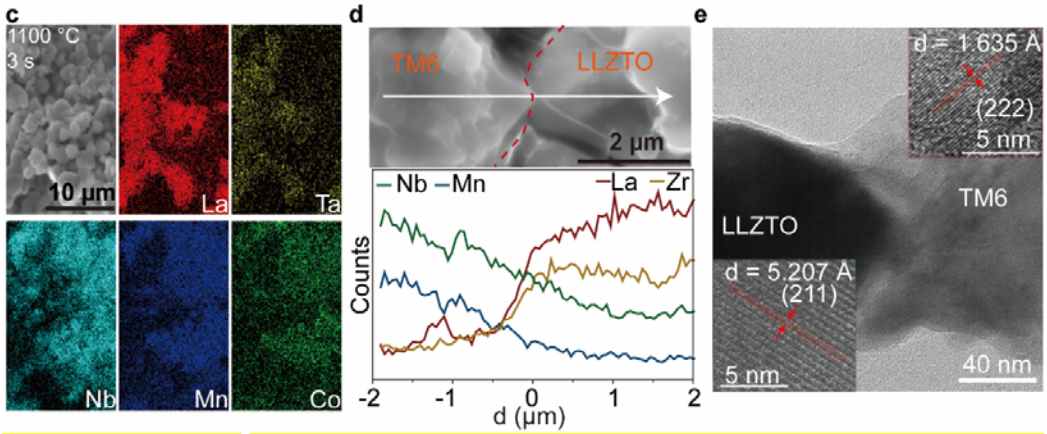


Figure R1. TEM of TM6 and LLZTO particles after heating treatment by UHS at 1100 °C for 3 s.

The results and discussion have been added in the Revised manuscript and Supporting information (**page 11, 248-251**).

The TEM image (Fig. 3e) reveals that the TM6|LLZTO interface exhibits a robust binding at the nanometer scale. On the right side, the lattice spacing measures 0.1635 nm, corresponding to the (222) plane of TM6 crystallization, while on the left side, the lattice spacing measures 0.5207 nm, consistent with the (211) plane of LLZTO crystallization.



Updated Figure 3. EDS mapping (c)and EDS Line profiles (d) of the TM6|LLZTO interface. (e) TEM images of TM6|LLZTO interface.

Regarding *"the XPS data shown in the SI on the related dataset says XPS maps".*

We apologized for our oversight and thank you for bringing it to our attention. We have rectified the error by replacing "XPS maps" with" XPS spectra". In this context, we utilized the XPS method to detect the changes in the valence states of LLZTO and HE-DRX.

The results and discussion have been added in the supporting information (**page 36, 620**).

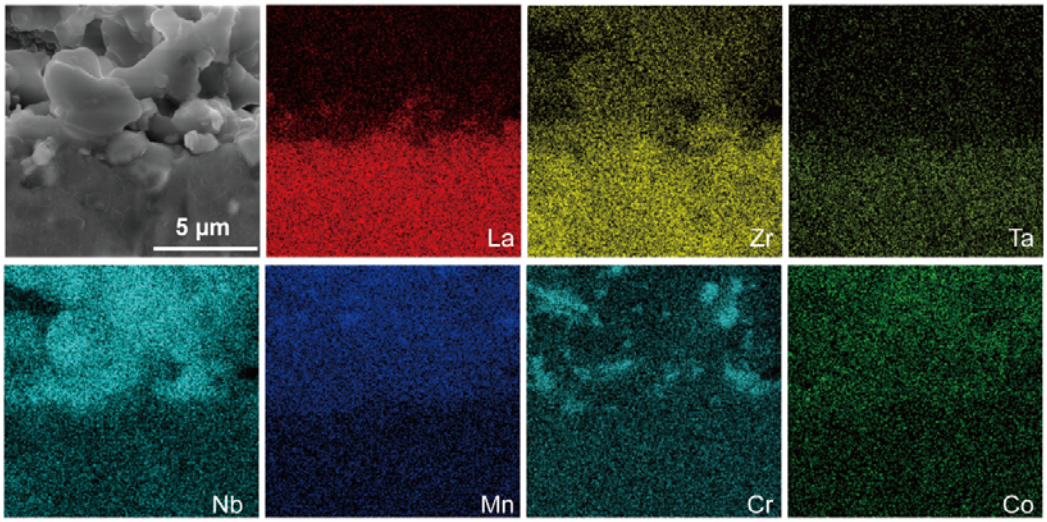
XPS spectra of after heating between the TM6 and LLZTO after heat treatment at 1100 °C for 3 s by UHS.

Comment #7 of Reviewer 1

Again on page 12, Fig 4e where the interface is examined between the cathode and solid electrolyte layers, only the EDS maps of La and Mn are shown. What about the other elements in LLZTO and the high entropy cathode? Unless all of these are also visualized, how can you confirm that there is no cross diffusion of ions? plus in this situation there is no XPS now done, even from the cathode side to ensure that the desired elements are present Andin the desired oxidation state.

Response: We appreciate your considerations and feedback.

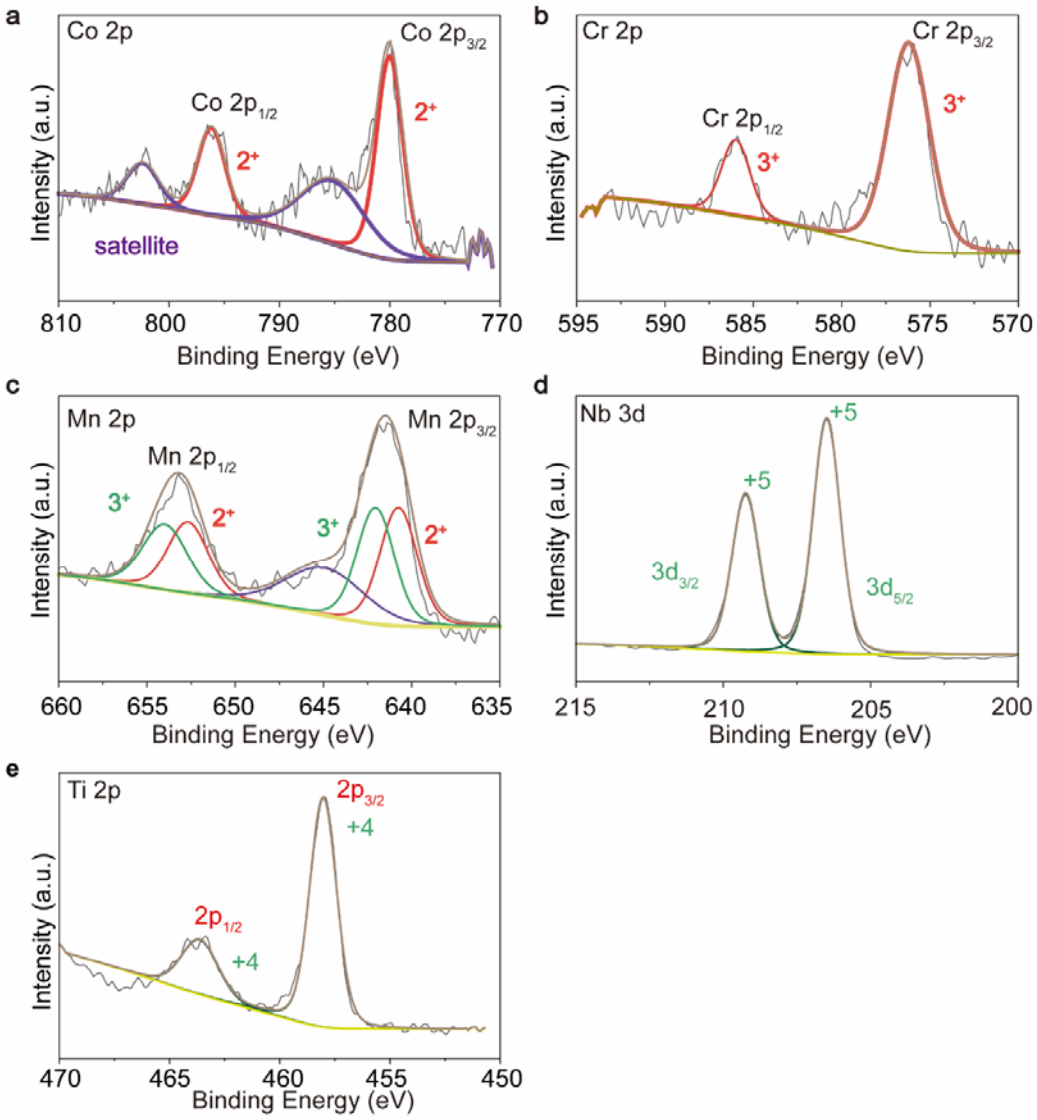
Regarding *"only the EDS maps of La and Mn are shown".* We have expanded the elemental mapping analysis to include additional elements in both LLZTO and high entropy cathodes, except for Ti. However, accurate characterization of the Ti and Cr spectra was challenging due to characteristic X-ray energy overlap between Ti (4.51) and La (4.65), as well as the relatively small Ti content. Additionally, some overlap observed between Zr (2.04) and Nb (2.17) due to the proximity of their elemental energies.
We have demonstrated in **Comment #6 of Reviewer 1 (page 12-13)** that TM6 and LLZTO do not interdiffuse after heating treatment by UHS at 1100 ℃ for 3 s.
The detailed results and discussion have been added in the supporting information.



Supplementary Figure 21. SEM–EDS images of the TM6|LLZTO interface.

Regarding *"in this situation, there is no XPS now done".* We have added XPS analysis in this section. The desired elements are present and in the desired oxidation state.
The detailed results and discussion have been added in the rvised manuscript and supporting information (**page 14, 291-293**).
XPS analysis provides additional confirmation that the transition metal elements remain unaltered during the rapid synthesis process, forming a stable high-entropy rock salt

structure (**Supplementary Fig. 24**).



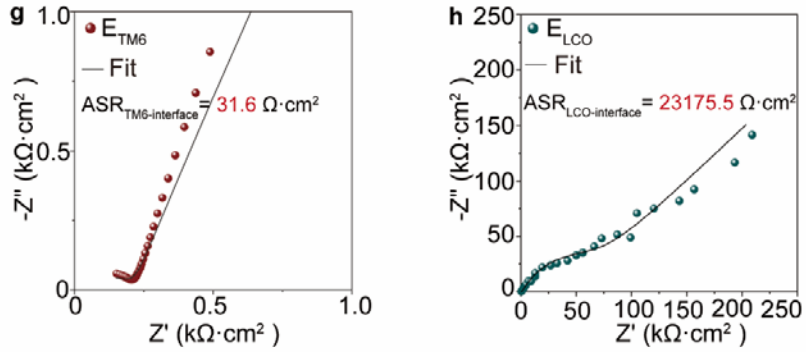
Supplementary Figure 24. XPS spectra of the in situ synthesized TM6 by UHS.

Comment #8 of Reviewer 1

In Figures 4d, e please add the circuit used to fit the impedance data. It is not clear how the authors got the values presented.

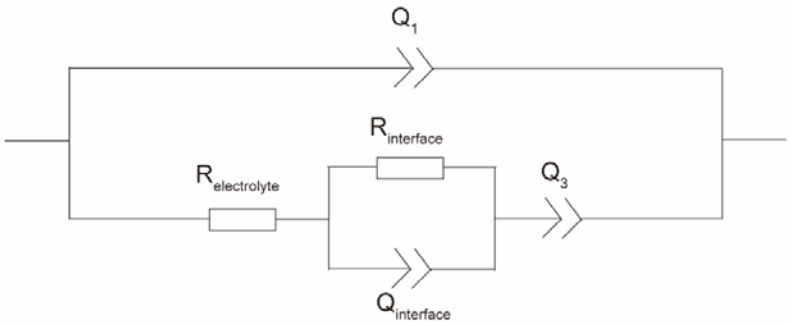
Response: We greatly appreciate this excellent suggestion. To determine the resistance of individual components, the curves were fitted to an equivalent circuit.
The results and discussion have been added in the revised manuscript and supporting information (**page 14-15, 297-303**).
By analyzing the EIS fitting curves of symmetric cells (**Supplementary Fig. 25**), we calculated that the area-specific resistance (ASR) at the interface of TM6|LLZTO is 31.6 $\Omega \cdot cm^2$ (**Fig. 4g**, **Supplementary Fig. 26 and Table S3**), whereas that of the

$LiCoO_2$|LLZTO interface is 23175.5 Ω·cm^2 (**Fig. 5b, Table S4**). Notably, the ASR of the TM6|LLZTO interface is approximately 700 times lower than that of the $LiCoO_2$|LLZTO interface, indicating a substantial reduction in resistance at the TM6|LLZTO interface compared to the $LiCoO_2$|LLZTO interface.

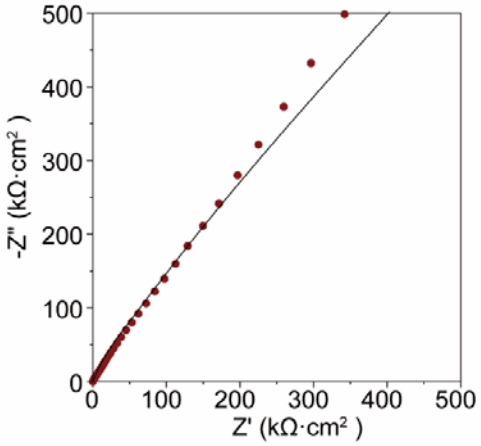


Updated Figure 4 (g-h). (g)Zoomed in EISs of TM6 symmetric cells. (h) EISs of $LiCoO_2$ (LCO) symmetric cells.

By analyzing the EIS fitting curves of symmetric cells, the conductivity of LLZTO was determined to be 4.08 × 10^{-4} S/cm for Au|TM6|LLZTO|TM6|Au and 2.77 × 10^{-4} S/cm for Au|$LiCoO_2$|LLZTO|$LiCoO_2$|Au, which aligns well with the reported conductivity values for LLZTO in the literature. This consistency further confirms the accuracy of the employed equivalent circuit **(Supplementary Fig. 25)**. Based on the fitting data presented in **Supplementary Table 3** and **Supplementary Table 4**, the calculated area-specific resistance (ASR) at the interface of TM6|LLZTO is 31.6 Ω·cm^2, while that of the $LiCoO_2$|LLZTO interface is 23175.5 Ω·cm^2. The ASR of the TM6|LLZTO interface is approximately 700 times lower than that of the $LiCoO_2$|LLZTO interface. This significant difference indicates a substantially reduced resistance at the TM6|LLZTO interface compared to the $LiCoO_2$|LLZTO interface.



Supplementary Figure 25. Equivalent circuit for determining ionic conductivity of symmetric cells using the Li$^+$ blocking configuration (Au|Cathode|LLZTO|Cathode|Au).



Supplementary Figure 26. EIS of the TM6|LLZTO symmetric cell after rapid annealing by the UHS method, tested at 25 °C.

Supplementary Table 3. Fit values for EIS spectra using the equivalent circuits (Au|TM6|LLZTO|TM6|Au).

$Q_1/(R_{LLZTO} + R_{interface}/Q_{interface} + Q_3)$	Value	Unit
Q_1	0.5162×10^{-6}	F.s^(a-1)
a_1	0.4651	
R_{LLZTO}	319.6	Ohm
$R_{interface}$	85.87	Ohm
$Q_{interface}$	3.676×10^{9}	F.s^(a-1)
$a_{interface}$	0.4922	
Q_3	0.2135×10^{-6}	F.s^(a-1)
a_3	0.766	

Supplementary Table 4. Fit values for EIS spectra using the equivalent circuits (Au|LCO|LLZTO|LCO|Au).

$Q_1/(R_{LLZTO} + R_{interface}/Q_{interface} + Q_3)$	Value	Unit
Q_1	9.277×10^{-15}	F.s^(a-1)
a_1	0.3556	
R_{LLZTO}	534.7	Ohm
$R_{interface}$	68668	Ohm
$Q_{interface}$	0.4494×10^{-6}	F.s^(a-1)
$a_{interface}$	0.7997	
Q_3	3.905×10^{-6}	F.s^(a-1)
a_3	0.4851	

Comment #9 of Reviewer 1

In the section on electrochemical performance, the authors add LLZTO to the cathode form the cathode layer, but no conductive carbon or any other electron conductor. What is the electronic conductivity of the HE cathode? Was this determined and is it sufficient to run a battery? What is the ionic conductivity of the HE cathode in the absence of the LLZTO?

Response: We appreciate the reviewer for this question.

The electronic conductivity is calculated to be 2.0×10^{-8} S/cm, while the Li^+ conductivity value for the bulk phase is determined to be 1.59×10^{-7} S/cm. The low conductivity of electrons and ions makes it difficult for the overall operation of the battery at room temperature.

To assess the electronic and Li^+ conductivity of TM6, we fabricated Ag|TM6|Ag symmetric cells with sputtered Ag electrodes and conducted EIS tests. The presence of Warburg elements in the EIS spectra suggests that the primary physical processes occurring at low frequencies involve charge transfer and semi-infinite diffusion of Li^+ in the Ag electrode. We employed an equivalent circuit with R_b to representing bulk phase resistance and R_{gb} representing grain boundary resistance (**Fig. R2**)[9]. Analysis of the calculated capacitance reveals two semicircles representing bulk and grain boundary conduction, respectively (**Fig. 3**). The fitting results of the equivalent circuit yield a Li^+ conductivity value of 1.59×10^{-7} S/cm for the bulk phase (**Table R1**).

Additionally, we monitored the current evolution over time at a constant voltage of 1V using the Hebb-Wagner DC polarization measurement with blocked cells to clarify the contribution of electronic conductivity. The data indicate that the initial current (I_0) is 0.5 μA, resulting in an overall conductivity of 1.5×10^{-7} S/cm. The current stabilizes over time to a value of I_e = 66.4 nA, from which the electronic conductivity is calculated to be 2.0×10^{-8} S/cm (**Fig. R4**). The overall conductivity is primarily

influenced by ionic conduction due to the lower electronic conductivity compared to the ionic conductivity,. The results from the DC polarisation measurements align well with those derived from electrochemical impedance spectroscopy, demonstrating good agreement between the two methods.

Consistently, the outcomes of the DC polarization measurement and EIS indicate remarkably low electron and ion conductivity in TM6, presenting obstacles to the transfer of lithium ions and electrons within the cathode region of the all-solid-state battery.

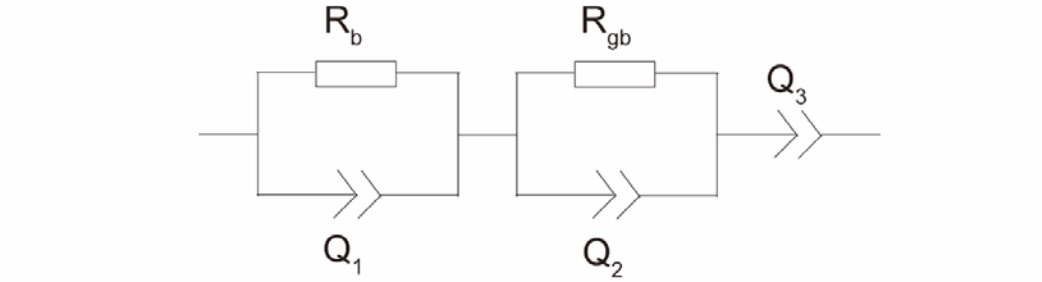


Figure R2. Equivalent circuit for determining ionic conductivity of symmetric cells using the Li^+ blocking configuration (Ag|TM6|Ag).

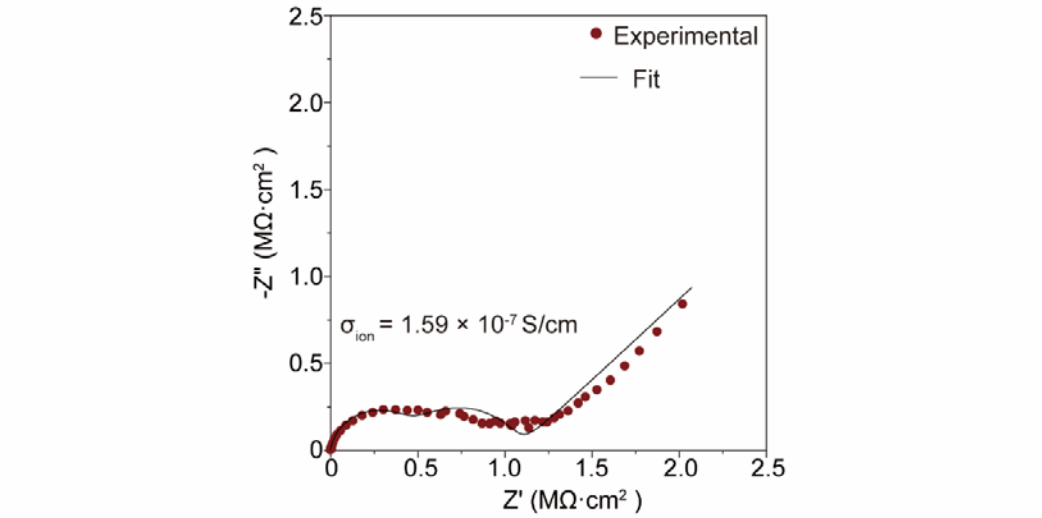


Figure R3. Schematic of EIS with Ag Li-ion blocking electrodes and corresponding EIS for HE-DEXs at room temperature.

Table R1. Fit values for EIS spectra are shown in Figure R3 using the equivalent circuits.

$R_b/Q_b + R_{gb}/Q_{gb} + Q_3$	Value	Unit
R_b	1.898×10^{6}	Ohm
Q_b	2.903×10^{-9}	F.s^(a-1)
a_b	0.7736	
R_{gb}	1.317×10^{6}	Ohm
Q_{gb}	60.75×10^{-12}	F.s^(a-1)
a_{gb}	0.9149	
Q_3	0.9037×10^{-6}	F.s^(a-1)
a_3	0.4768	

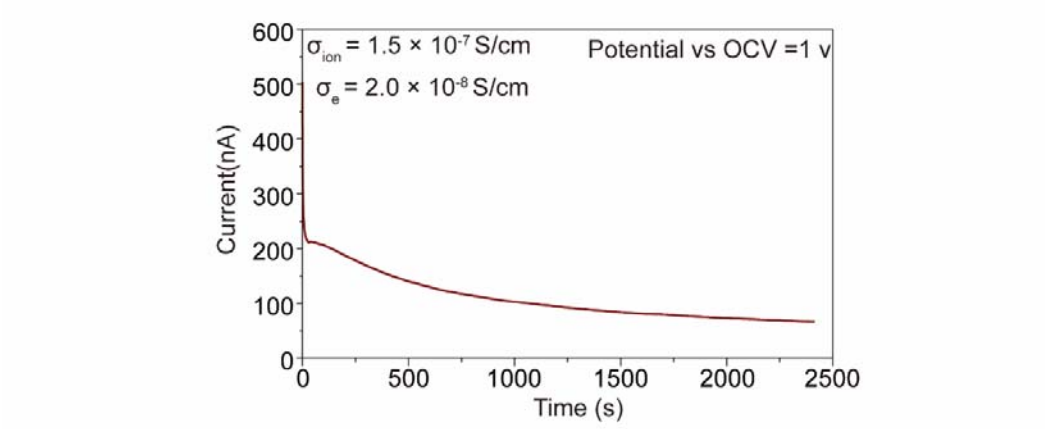


Figure R4. DC polarization measurements for electronic and ionic conductivity of TM6.

[9] Wang, M. J., Wolfenstine, J. B. & Sakamoto, J. Mixed Electronic and Ionic Conduction Properties of Lithium Lanthanum Titanate. *Advanced Functional Materials* **30**, 1–9 (2020).

Comment #10 of Reviewer 1

Again in Figs 4c and 4d where they show a section of the battery, before and after cycling, only the EDS maps of La and Mn are seen. What about the other elements? How can they be sure that there is no cation migration? Some XPS may also be helpful here.

Response: We appreciate your considerations and feedback.

We have now completed the EDS spectra for the other elements except Ti and Zr. The accurate characterization of the Ti spectra was challenging due to characteristic X-ray energy overlap between Ti (4.51) and La (4.65), as well as the relatively small Ti content. Additionally, some overlap was observed between Zr (2.04) and Nb (2.17) due to the close proximity of their elemental energies.

As demonstrated in **Comment #6 of Reviewer 1 (page 12-13)**, TM6 and LLZTO do not exhibit interdiffusion after heating treatment by UHS at 1100 °C for 3 s. Nevertheless, the comprehensive data collectively indicate the absence of elemental inter-diffusion at the highly stable interface of TM6|LLZTO, which has been successfully constructed.

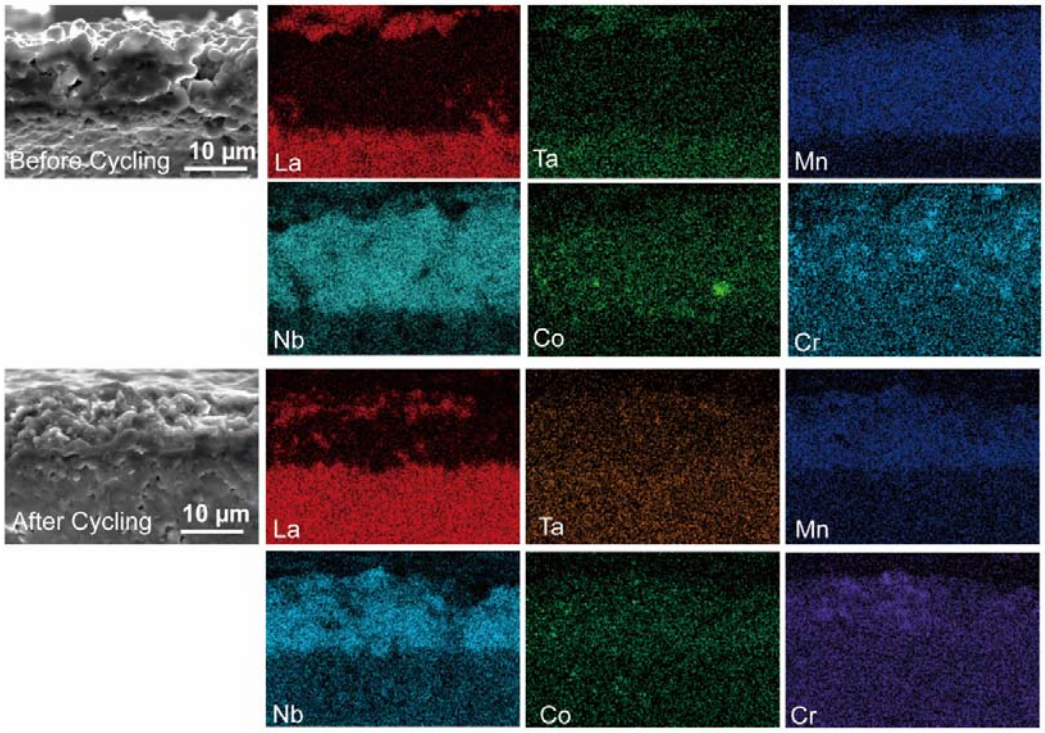


Figure R5. SEM and EDS images (above) before and (below) after cycling.

Comment #11 of Reviewer 1

It also looks like the porosity of the cathode decreases on cycling from the SEM images. Could the authors comment on this?

Response: We thank the reviewer very much for the valuable suggestion.

During the cycle process, the cathode undergoes a lithium removal reaction, leading to a certain extent of valume change and a decrease in porosity. Nevertheless, our test results show that this change did not significantly affect the performance of the battery. The TM6-ASSLBs deliver a remarkable capacity retention of 95% after 100 cycles. This outcome could be attribute to the fact that cathode materials did not experience cracking during the cycling despite undergoing volume changes (as shown in the SEM images after cycling), which resulted in good reversible lithiation/delithiation

performance. In addition, in the case of ASSLBs, the absence of liquid electrolyte means that changes in porosity do not affect the contact between the cathode and liquid electrolyte, as observed in liquid batteries.

Comment #12 of Reviewer 1

The batteries were run at 150 ℃ but could the authors also perhaps show the performance of other battery at temperatures more standard for LLZTO like 50-70 ℃?
Response: We are grateful to the reviewer for raising this question.
We assembled all-solid-state TM6|LLZTO|Li batteries (TM6-ASSLBs) with a highly stable TM6|LLZTO interface. Even at a reduced temperature of 70 ℃, TM6-ASSLBs still deliver a specific capacity of 130 mAh/g at a current density of 20 mA/g. Although the specific capacity is reduced due to the lower temperature causing insufficient electron and Li^+ transport, it is noteworthy that all-solid-state batteries maintain high stability with almost no capacity delay.

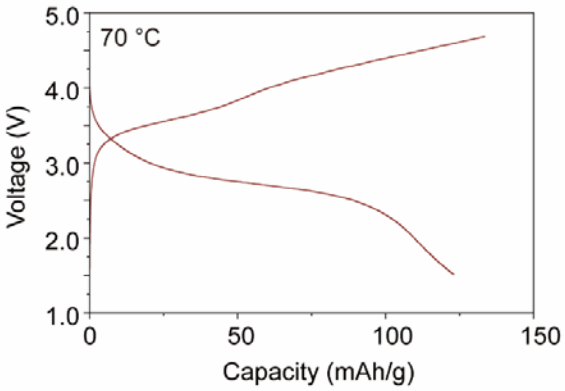


Figure R6. Charge/discharge profiles of the all-solid-state battery at 70 ℃.

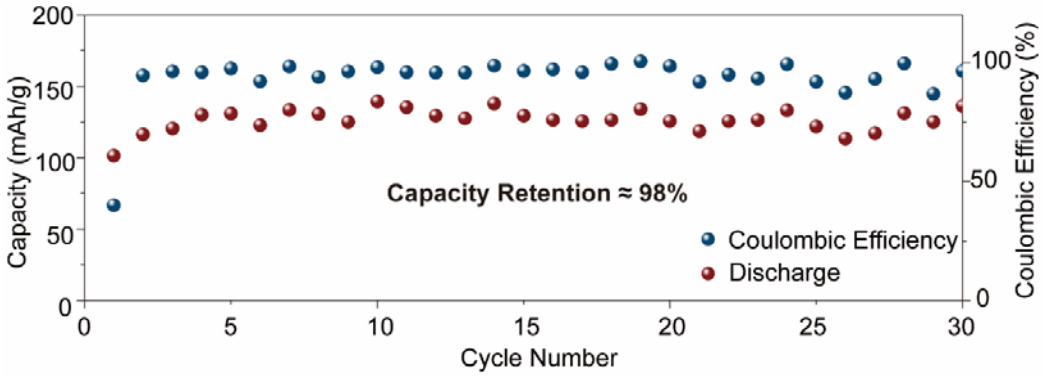


Figure R7. Cycling performance and Coulombic efficiency of the HE-DRX-ASSLBs at 70 ℃.

Comment #13 of Reviewer 1

In the conclusions, the authors have a sentence " The stable HE-DRX/LLZTO solid-state interface also mitigates the issue of transition metal migration and interfacial side reaction for the HE-DRX cathodes in liquid electrolyte'. I'm not sure what they mean by liquid electrolytes here, or whether this is just a typo..?

Response: We greatly appreciate your suggestion. This is not a typo.
The utilization of Mn-based DRX cathodes (including HE-DRX) in liquid batteries often results in poor cycle stability due to side reactions between the cathode and electrolyte, as well as migration of transition metal ions. However, the construction of a highly stable HE-DRX|LLZTO interface effectively addresses these issues, leading to improved cycle performance in all-solid-state batteries. As a result, the ASSLBs (HE-DRXs|LLZTO|Li) exhibit a remarkable capacity retention of 95% after 100 cycles, surpassing the performance of TM6 in liquid batteries (76% retention after 20 cycles)[4]. Furthermore, the cyclic stability demonstrated by HE-DRXs in all-solid-state batteries exceeds that shown by most DEXs cathode materials in liquid electrolytes, attributable to the excellent solid-state interface greatly enhancing the cyclic stability of HE-DRXs (Fig. 5e).

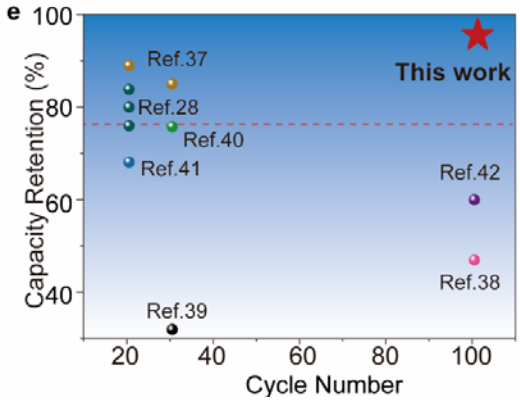


Figure 5. (e) Comparison of the capacity retention of DRXs in the literature.

[4] Lun, Z. *et al.* Cation-disordered rocksalt-type high-entropy cathodes for Li-ion batteries. *Nature Materials* **20**, 214–221 (2021)

Reviewer #2's Comments:

Comment #1 of Reviewer 2

1. *In introduction, some of the statements are not reasonably supported. For example, why does the author believe that HE materials have better chemical compatibility with LLZO electrolyte?*

Response: We thank the reviewer for this comment. We have conducted thorough literature research and experiments to validate our views.

The entropy-stabilizing effect of high-entropy materials not only enhances phase stability but also produces remarkable properties such as sluggish diffusion. These properties help to improve the chemical compatibility with LLZTO electrolyte.

To substantiate our claims, we conducted a series of comparative tests and analyses on the physical and chemical properties of cationic disordered rock salt cathode materials (DRXs) with varying numbers of cations (TM2, TM4, TM6). Our findings revealed that high-entropy DRXs (HE-DRX, TM6) exhibit superior capacities in addressing cathode|electrolyte interface challenges in all solid-state batteries. Detailed results and discussion have been discussed in **Reviewer #1's Comments (pages 5-8)**.

Regarding *"why does the author believe that HE materials have better chemical compatibility with LLZO electrolyte"*, The differential scanning calorimetry (DSC) data revealed that as the temperature increased, TM2 reacted with LLZTO first at 598 °C, followed by TM4 at 605 °C. In contrast, a small peak only appeared at 835 °C for the TM6 and LLZTO system, indicating that the chemical stability of DRX cathode materials gradually increases with an increasing number of cations in conjunction with LLZTO. Detailed results and discussion have been discussed in **Reviewer #1's Comments (pages 7-8)**.

Comment #2 of Reviewer 2

What is the difference in synthesis process for achieving the HE-DRXs phase between ref.26 and this work? And why do you state HE-DRXs by UHS shows excellent thermal stability? What impurities phase forms when UHS took place at 1400 ℃?

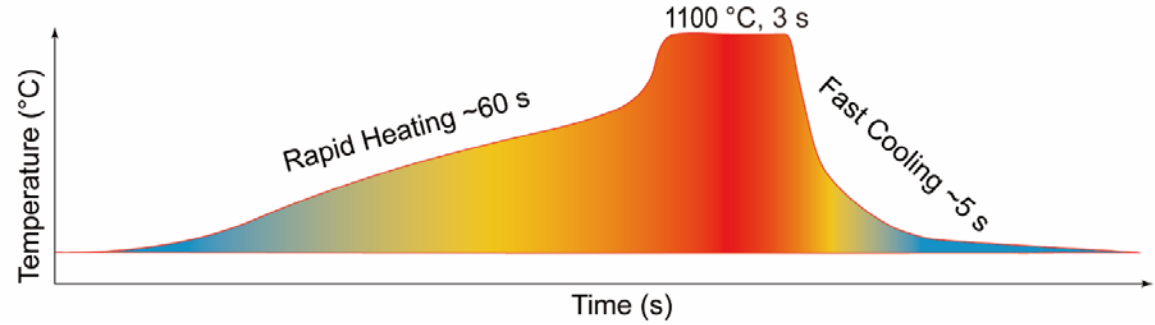
Response: We appreciate the reviewer for this question.

Regarding *"What is the difference in synthesis process for achieving HE-DRXs phase between ref.26 and this work"*, This work presents a distinct synthesis approach from that of ref.26. In our methodology, we utilized UHS technology to achieve a rapid one-step synthesis of the HE-DRXs. Specifically, a pressed green pellet of the HE-DRX precursor powders was placed between two Joule-heated carbon strips, serving as a high-temperature reactor. The reactor was heated from room temperature to the targeted temperature within ~ 60 s, followed by isothermal sintering for approximately 3 s, and

rapid cooling for 5 s (Supplementary Fig. 1). Importantly, our synthesis process, characterized by short duriation and high temperature, effectively inhibits the volatilization of lithium, thereby ensuring the measured composition remains consistent with the target atomic ratio of the synthesized material.

In contrast, the synthesized method described in ref.26 involved a two-part method using conventional furnace-heated synthesis. Precursor pellets were pre-heated at 600 °C for 3 h followed, followed by sintering at 1,000 °C for 6 h under an argon atmosphere[4].

Our approach significantly reduces the synthesis time compared to the previously reported literature, cutting it from 6 hours to just 3 s.



Supplementary Figure 1. The rise and fall curves of the HE-DRXs are synthesized in one step.

Table S1. Target versus measured atomic ratios of the as-synthesized materials.

Element	Measured	Measured ratio	Target atomic ratio
Li	9.04%	1.30	1.30
Ti	4.60%	0.10	0.10
Cr	5.81%	0.11	0.10
Mn	11.72%	0.21	0.20
Co	6.28%	0.11	0.10
Nb	18.66%	0.20	0.20

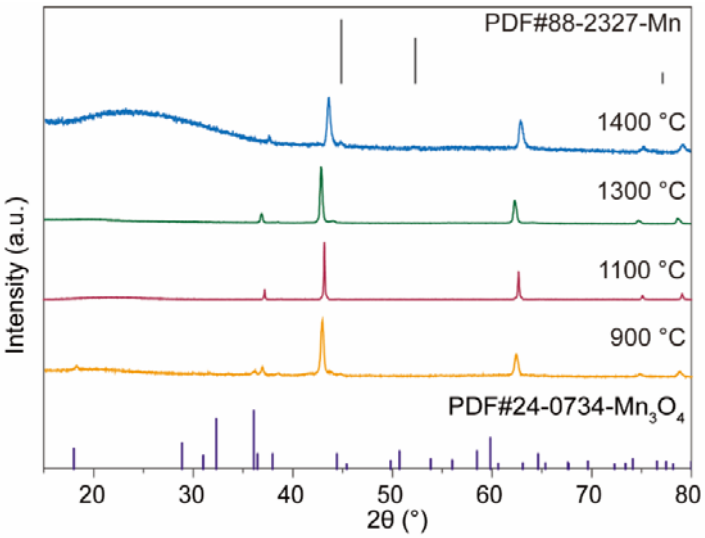
Regarding *"why do you state HE-DRXs by UHS shows excellent thermal stability".*

Our experimental data show that HE-DRXs synthesized via UHS remain intact below 1400 °C. This level of thermal stability surpasses that of other cathode materials such as $LiFePO_4$ and $LiMn_2O_4$. For example, $LiFePO_4$ and $LiMn_2O_4$ materials start decomposing and releasing oxygen at a much lower temperature of 700 °C[10].

Regarding *"What impurities phase forms when UHS took place at 1400 ℃".*

The impurity phase is indexed to transition metal Mn monomers (Supplementary Fig. 3). As the temperature rises to 1400 ℃, the high-valence transition metal elements undergo reduction to their metal elements due to the influence of the reducing

atmosphere.



Update Supplementary Figure. 3. XRD patterns of HE-DRXs synthesized at different temperatures by UHS.

[4] Lun, Z. *et al.* Cation-disordered rocksalt-type high-entropy cathodes for Li-ion batteries. *Nature Materials* **20**, 214–221 (2021).

[10] Du, Y. C. *et al.* Thermal stability of $LiFePO_4$/C-$LiMn_2O_4$ blended cathode materials. *Science China Technological Sciences* **60**, 58–64 (2017).

Comment #3 of Reviewer 2

3. There is mistake in explaining your observation in Figure 3a. The author stated no reaction above 800 ℃, which is wrong. Reaction started from 800 ℃ according to in situ XRD. Another mistake is in the next sentences that stated the impurity phase appears up to 800 ℃. 'up to' should change to 'from' or similar.

Response: We think this is an excellent suggestion. As suggested by the reviewer, we have corrected the 'up to' into 'from'. We have made the necessary revisions to the original text (**page 11, 237**), as follows:

However, the impurity phase $LaMnO_3$ appears from 800 °C (**Supplementary Fig. 8**), which is unfavorable for interface stability and Li^+ transport.

Comment #4 of Reviewer 2

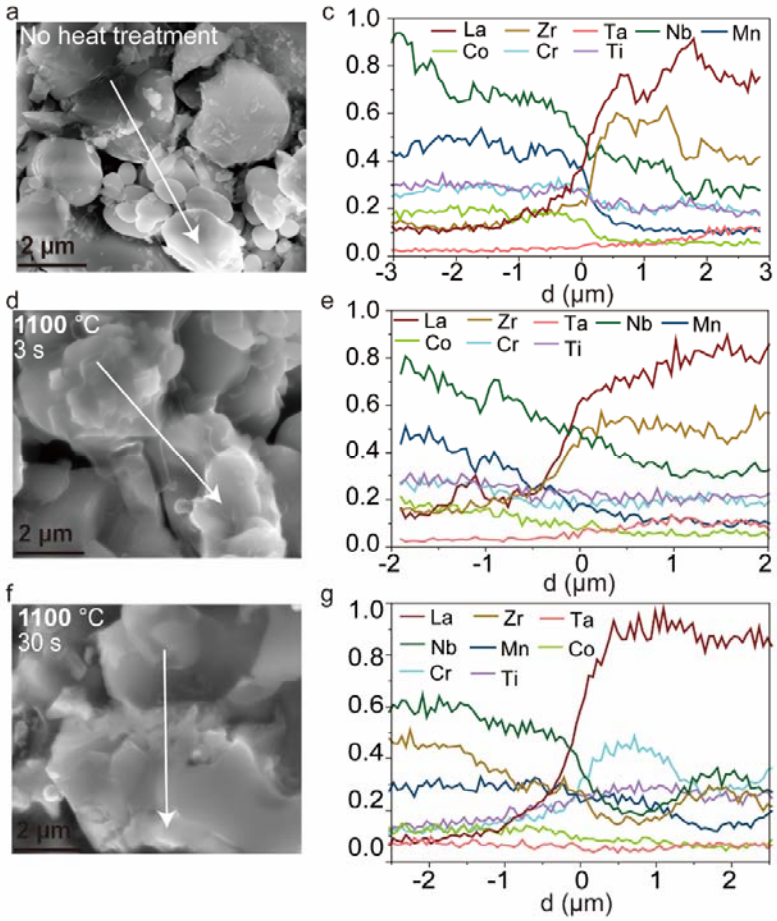
4. SEM/EDS of Figure 3c do not clearly show inter diffusion across HE-DRXs and LLZO. EDS Line profiles at the DRX/LLZO interface between the sample for 3 s vs. 30 s, sintered at 1100 ℃ might be more precise methods and samples for the proper comparison.

Response: We are very grateful to the reviewers for their suggestions.

EDS line profiles of the DRX/LLZO interface have been added between samples sintered at both 1100 °C for 3 s and 30 s. SEM/EDS Line profiles showed that the mixed powder of TM6 and LLZTO particles without heat treatment exhibited a dispersed distribution. Following heating treatment at 1100 °C for 3 s, a notable improvement in bonding between TM6 and LLZTO particles was observed, and EDS Line profiles further showed the absence of element diffusion between TM6 and LLZTO after heat treatment (Fig. 3d, e). However, after heat treatment at 1100 °C for 30 s, interdiffusion of elements between TM6 and LLZTO was observed (**Supplementary Fig. 9**).

The results and discussion have been added in the revised manuscript and supporting information (**page 34, 602-610**).

SEM/EDS Line profiles showed that the mixed powder of TM6 and LLZTO particles without heat treatment exhibited a dispersed distribution. After heating treatment at 1100 °C for 3 s, a notable improvement in bonding between TM6 and LLZTO particles was observed and EDS Line profiles further showed that there was no element diffusion between TM6 and LLZTO after heat treatment. After heating treatment at 1100 °C for 30 s, the elements of TM6 and LLZTO become interdiffusion.



Supplementary Figure 9. EDS Line profiles of the TM6 and LLZTO after heating treatment at 1100 °C for 3 s.

Comment #5 of Reviewer 2

5. Interpretation of Raman spectra at around 600 wave number in Fig 3d is missing.

Response: We appreciate the serious consideration given to your concerns.
Flores et al [11] compared the spectra of the lithiated $LiMO_2$ oxides, and found that all lithiated Mn-containing oxides show a band centered at 600 cm^{-1}, with the intensity of this band scaling with the Mn content. Therefore, we attribute the peak at 600 cm^{-1} to the modulated Mn-induced effect.

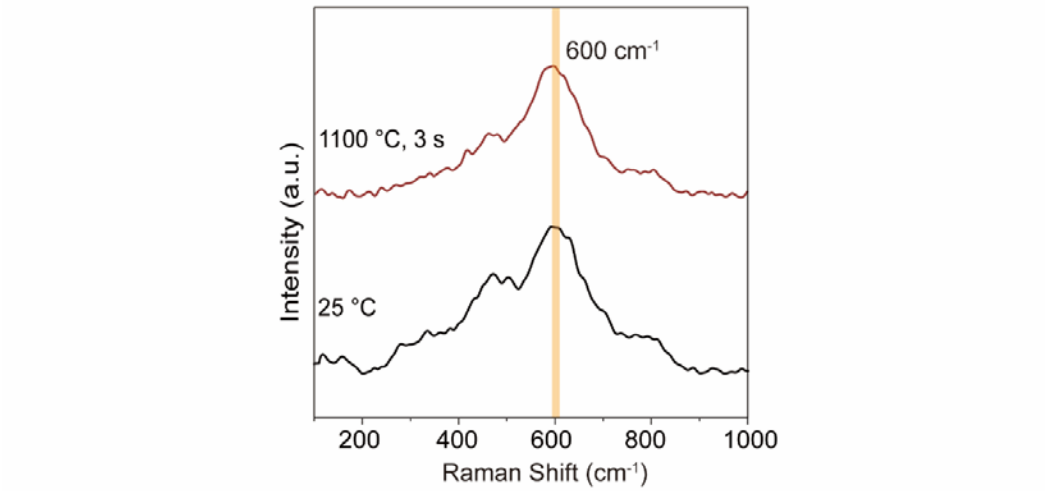


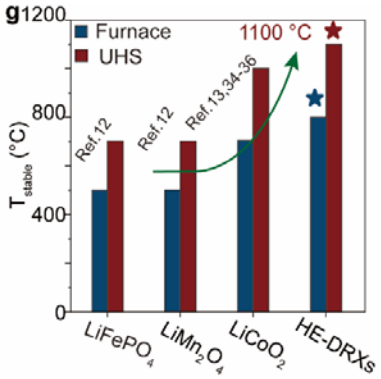
Figure R8. Raman spectra of the HE-DRXs and LLZTO before and after heat treatment.

[11] Flores, E., Novák, P., Aschauer, U. & Berg, E. J. Cation Ordering and Redox Chemistry of Layered Ni-Rich $Li_xNi_{1-2y}Co_yMn_yO_2$: An Operando Raman Spectroscopy Study. *Chemistry of Materials* **32**, 186–194 (2020).

Comment #6 of Reviewer 2

6. In Fig.3f, literature information on LCO needs to be revised. Chemical stability of LCO/LLZO is reported up to 1050 ℃ in the following refs.
Sustainable Energy Fuels, 2019, 3,280
J Electroceram (2017) 38:197–206
J. Mater. Chem. A, 2022, 10, 2320-2326.
Response: We deeply appreciate the professional evaluation of our article. We have meticulously reviewed the literature you recommended, which has provided us with a comprehensive understanding of the test methods for assessing the chemical stability of cathodes and LLZTO. We have diligently incorporated this knowledge into our study. However, we respectfully disagree with the proposal to modify the chemical stability temperatures of LCO and LLZTO to 1050 °C. The DSC data available in the literature clearly indicate that the reaction between LCO and LLZTO initiates at 700 °C, with a

violent reaction occurring at 1080 °C[12–14]. Finally, we have revised the original article, adjusting the stabilization temperatures of LCO and LLZTO to 700 °C, as supported by the cited literature you provided.



Update Figure 3. (g) Comparison of chemical stability between different cathodes and LLZTO.

[12] Tsai, C. L. *et al.* A garnet structure-based all-solid-state Li battery without interface modification: Resolving incompatibility issues on positive electrodes. *Sustainable Energy and Fuels* **3**, 280–291 (2019).

[13] Uhlenbruck, S. *et al.* Cathode-electrolyte material interactions during manufacturing of inorganic solid-state lithium batteries. *Journal of Electroceramics* **38**, 197–206 (2017).

[14] Rosen, M., Finsterbusch, M., Guillon, O. & Fattakhova-Rohlfing, D. Free standing dual phase cathode tapes-scalable fabrication and microstructure optimization of garnet-based ceramic cathodes. *Journal of Materials Chemistry A* **10**, 2320–2326 (2022).

Comment #7 of Reviewer 2

7. What is the difference in experimental setting between Figure 3b and Supp. Figure 17? It is not clear.

Response: We express our sincere gratitude to the reviewer for their meticulous reading and valuable insights. In the original Fig. 3b , we demonstrated that LLZTO and TM6 remain stable at 1100 °C for 3 s without any side reactions. However, as depicted in the original Supp. Fig. 17, after the precursor powder of HE-DRX was co-sintered with LLZTO, the in situ synthesis of HE-DRX occurred with no observable side reaction with LLZTO. Conversely, when the single-component HE-DRX was co-sintered with LLZTO, side reactions were observed, suggesting entropic stabilization.

Comment #8 of Reviewer 2

8. In EIS measurement of symmetrical cells in Figure 4g, h, there is no explanation of how the interfacial resistance is defined. The author stated semicircle in the frequency range of 32kHz-2.5MHz without evidence. It can be clearer if the authors provide resistance values for all the possible components in your system including, cathode/LLZO interface, LLZO, Au/cathode interface with proper equivalent circuit model. It will add much clarity than current description.

Response: We think this is an excellent suggestion. The results and discussion have been discussed in the last response to **Comment #8 of Reviewer 1 (page 15-18)**.
The calculated area-specific resistance (ASR) at the interface of HE-DRXs|LLZTO is 31.6 $\Omega \cdot cm^2$, while that of the $LiCoO_2$|LLZTO interface is 23175.5 $\Omega \cdot cm^2$ (Fig. R9,10). The ASR of the HE-DRXs|LLZTO interface is approximately 700 times lower than that of the $LiCoO_2$|LLZTO interface. This significant difference indicates a substantially reduced resistance at the HE-DRXs|LLZTO interface compared to the $LiCoO_2$|LLZTO interface.

Comment #9 of Reviewer 2

9. Active material loading in this work is quite low, like other literature compared in Supp. Table 2. Then please do not point out other works and say 'loading is low' in the introduction.

Response: We express our sincere gratitude to the reviewer for their meticulous reading and valuable insights. We deeply apologize for any confusion caused by our previous expression and have made the necessary revisions to the original text, as follows:
Although the use of low melting point solder as a buffer layer has been explored to improve cathode-electrolyte contact, it inevitably reduces the capacity due to the limited active material content in composite cathodes.

Comment #10 of Reviewer 2

10. What is the reason for measuring a full cell at 150 ℃? It is very close to the Li melting temperature. Does the author have some comment on any safety issue? Performance at different temperatures will be useful to compare with other literature in supp. table 2. Could you also provide what is limiting at lower temperature operation such as room temperature?

Response: We thank the reviewer very much for the good suggestion.

Regarding *"What is the reason for measuring a full cell at 150 ℃"*. The reason why

the whole battery works at 150 ℃ is due to the low ionic and electronic conductivity of TM6. The electronic conductivity is calculated to be 2.0 × 10^{-8} S/cm, and the Li^+ conductivity value is 1.59 × 10^{-7} S/cm for the bulk phase. These results were discussed in the last response to **Comment #9 of Reviewer 1 (page 18-20)**.

Regarding *"Does the author have some comment on any safety issue"*, Garnet-type solid-state electrolytes are inherently safe and possess an extended operating temperature range due to their non-flammablility. At temperatures nearing the melting point of lithium (150 ℃), the capacity retention rate of the all-solid-state battery remained remarkably high at 95% after 100 cycles . This demonstrates the exceptional stability of LLZTO to Li even at elevated temperatures such as 150 ℃.

Regarding *"Could you also provide what is limiting at lower temperature operation"*. Due to the low electron and ion conductivity of the cathode, all-solid-state TM6|LLZTO|Li batteries (TM6-ASSLBs) face challenges in operating at room temperature. Therefore, increasing the temperature becomes necessary to enhance electron and Li^+ transport. Even at a reduced temperature of 70 ℃, TM6-ASSLBs still exhibit a specific capacity of 130 mAh/g at a current density of 20 mA/g. The results and discussion have been discussed in the last response to **Comment #12 of Reviewer 1 (page 22)**, where we also provide a comparison of ASSLBs performance based on garnet with other literature (**Table R2**).

Table R2. Electrochemical performance of LLZO-based all-solid-state batteries.

Study	Cathode Composition	Proportion of active substance	Temperature	Current	Voltage Range (V)	Capacity (mAh/g)	No. of Cycles	Capacity retention
Ref.[15]	LCO-LLZTO	50%	80 °C	50 μA/cm^2	3.4-4.2	N/A	60	33.3%
Ref.[16]	Li_3BO_3@LCO+LLZO+ITO	60%	80 °C	0.1C (14 mA/g)	3.0-4.1	101	40	66%
Ref.[17]	LCO+Li_3BO_3 +LLZO (42:35:23)	42%	25 °C	0.01 C (1.4 mA/g)	3.0-4.2	78	1	N/A
Ref.[18]	$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$	100%	80 °C	0.5C (70 mA/g)	3.0-4.2	77	10	< 79%
Ref.[19]	LCO + porous LLZO (3:10)	23%	80 °C	0.05 C (7 mA/g)	3.0-4.05	118	14	97%
Ref.[20]	LCO@Li_2CO_3+ LLZO@Li_2CO_3+ $Li_{2.3}C_{0.7}B_{0.3}O_3$ (58:30:12)	58%	100 °C	0.05C (7 mA/g)	3.0-4.05	106	40	66%
Ref.[21]	V_2O_5+ CNT (9:1)	90%	100 °C	50 mA/g	1.2-4.5	150	27	83.3%
This work	HE-DRXs +LLZTO (5:1)	83.33%	150 °C	25 mA/g	1.7-4.7	**238**	**100**	**95%**
	HE-DRXs	100%	70 °C	20 mA/g	1.5-4.7	**130**	**30**	**98%**

[15] Kato, T. *et al.* In-situ $Li_7La_3Zr_2O_{12}$/$LiCoO_2$ interface modification for advanced all-solid-state battery. *Journal of Power Sources* **260**, 292–298 (2014).

[16] Ramkumar, B., So-young, K., Chan-woo, N., Aravindan, V. & Yun-Sung, L. $LiBO_2$-modified $LiCoO_2$ as an efficient cathode with garnet framework $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ electrolyte toward building all-solid-state lithium battery for high-temperature operation. *Electrochimica Acta* **359**, 136955 (2020).

[17] Ohta, S. *et al.* Co-sinterable lithium garnet-type oxide electrolyte with cathode for all-solid-state lithium ion battery. *Journal of Power Sources* **265**, 40–44 (2014).

[18] Kim, Y., Waluyo, I., Hunt, A. & Yildiz, B. Avoiding CO_2 Improves Thermal Stability at the Interface of $Li_7La_3Zr_2O_{12}$ Electrolyte with Layered Oxide Cathodes. *Advanced Energy Materials* **12**, 2102741 (2022).

[19] Kim, K. J. & Rupp, J. L. M. All ceramic cathode composite design and manufacturing towards low interfacial resistance for garnet-based solid-state lithium batteries. *Energy and Environmental Science* **13**, 4930–4945 (2020).

[20] Han, F. *et al.* Interphase Engineering Enabled All-Ceramic Lithium Battery. *Joule* **2**, 497–508 (2018).

[21] Liu, B. *et al.* Rapid thermal annealing of cathode-garnet interface toward higherature solid state batteries. *Nano Letters* **17**, 4917–4923 (2017).

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

Based on the revisions done by the authors I am happy to recommend this manuscript for publication. The have alleviated my concerns sufficiently. I do advise a full language sweep since it remains hard to read at places.

Reviewer #2 (Remarks to the Author):

Authors addressed all the points.

One last recommendation before publication is to revise and include the table summarizing 'Electrochemical performance of LLZO-based all-solid-state batteries' in the main figure 6. Here, cathode loading as mg/cm2 must be added. This work has demonstrated novel synthesis and advanced oxide battery performance but with relatively small cathode loading, which is not really visible throughout the script. So I think adding the table is necessary for the readers to compare overall performances from the literatures. Following literature should be added in LLZO-based ASSB with relatively high loading;

Journal of Power Sources 545 (2022) 231872 -> 2 mg/cm2

J. Power Sources 2021, 482, 228905. -> 16 mg/cm2

Sustain Energ Fuels 2019, 3 (1), 280–291 -> 12.6 mg/cm2

Point-by-Point Responses to Reviewers' Comments and Suggestions

We express our gratitude for the time and effort the reviewers dedicated to evaluating our manuscript. We highly value their thoughtful comments and suggestions, which have notably enhanced the quality and clarity of our work. In response, we performed additional experiments and thoroughly revised the manuscript to address all raised comments and concerns. The changes are highlighted in yellow within the revised manuscript. Our point-by-point responses are presented below.

(**Note.** Fig. Number: Figures in the Manuscript; Fig. S Number: Figures in the Supporting Information; Fig. R Number: Figures in the Response letter; [Number]: References in the Response letter)

Reviewer #1's Comments:

Based on the revisions done by the authors I am happy to recommend this manuscript for publication. The have alleviated my concerns sufficiently. I do advise a full language sweep since it remains hard to read at places.

Response: We thank the reviewer for feedback and recommendation. We appreciate your acknowledgment of the revisions we made.

Regarding full language sweep. We have done a thorough language check on the article to improve readability. For example, we have revised the sentence " ASSLBs featuring HE-DRXs exhibit a high specific capacity of 238 mAh/g with 95% capacity retention after 100 cycles, far beyond the cycling performance in liquid electrolytes, which retain only 76% capacity after 20 cycles." to " At 150 °C, HE-DRXs in ASSLBs (Li|LLZTO|HE-DRXs) exhibit an average specific capacity of 239.7 ± 2 mAh/g at 25 mA/g, with a capacity retention of 95% after 100 cycles relative to the initial cycle—a stark contrast to the 76% retention after 20 cycles at 25 °C in conventional liquid batteries. "

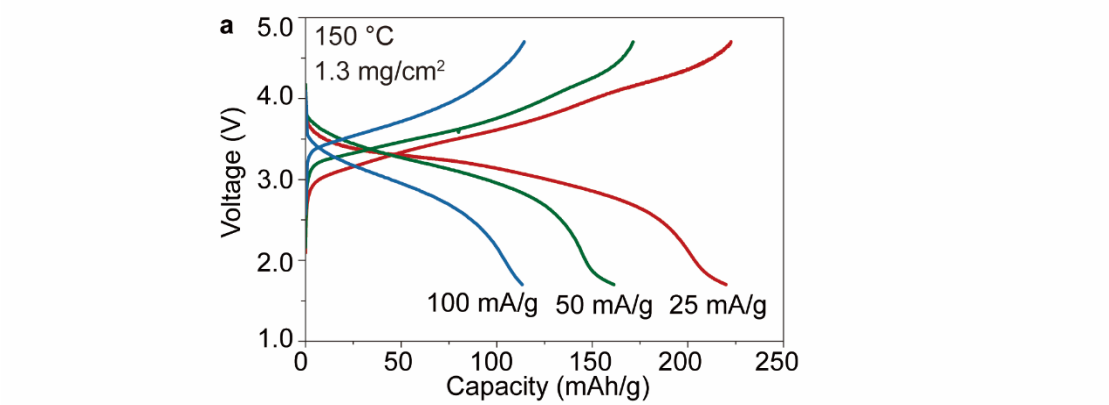
Reviewer #2's Comments:

Authors addressed all the points.

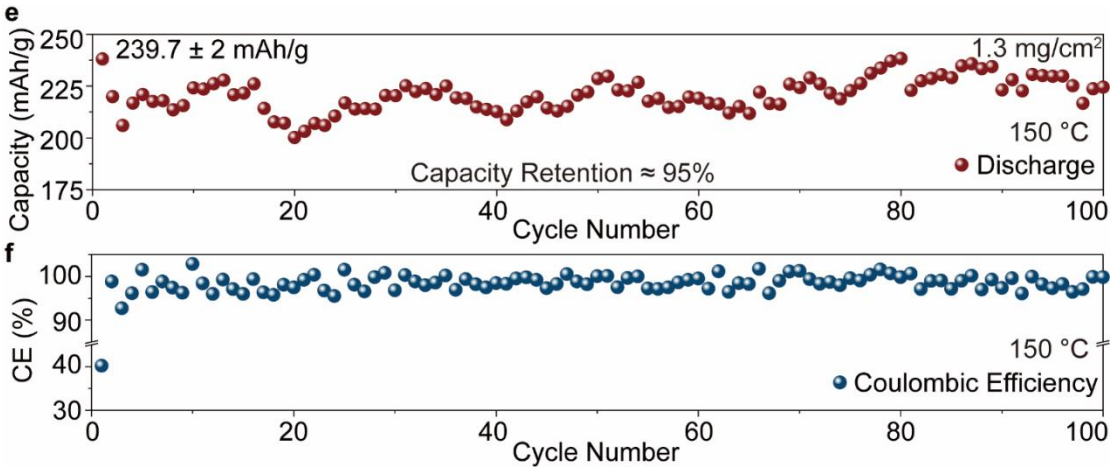
One last recommendation before publication is to revise and include the table summarizing 'Electrochemical performance of LLZO-based all-solid-state batteries' in the main figure 6. Here, cathode loading as mg/cm2 must be added. ***This work has demonstrated novel synthesis and advanced oxide battery performance*** *but with relatively small cathode loading, which is not really visible throughout the script. So I think adding the table is necessary for the readers to compare overall performances from the literatures. Following literature should be added in LLZO-based ASSB with relatively high loading;*

Journal of Power Sources 545 (2022) 231872 -> 2 mg/cm2
J. Power Sources 2021, 482, 228905. -> 16 mg/cm2
Sustain Energ Fuels 2019, 3 (1), 280−291 -> 12.6 mg/cm2

Response: We greatly appreciate the professional evaluation and innovative recognition of our articles.
Regarding" cathode loading as mg/cm2 must be added ". We have added load descriptions to Figures 5a and e.



Updated Figure 5a. Charge/Discharge profiles of the all-solid-state battery at different rates from 25 mA/g to 100 mA/g.



Updated Figure 5. (e) Cycling performance and (f) Coulombic efficiency of the HE-DRX-ASSLBs at 25 mA/g. All electrochemical measurements were performed at 150 °C without organic electrolyte and external pressure

Regarding *"adding the table is necessary for the readers to compare overall performances from the literatures"*.

We have carefully reviewed your recommended literature, and we have updated our comparison of Electrochemical performance of LLZO-based all-solid-state batteries (Update Supplementary Table 5), and we cite your recommended literature.

Update Supplementary Table 5. Electrochemical performance of LLZO-based all-solid-state batteries.

Study	Cathode Composition	Proportion of active substance	Temperature	Loading (mg/cm^2)	Current	Voltage Range (V)	Capacity (mAh/g)	No. of Cycles	Capacity retention
Ref.[1]	LCO-LLZTO	50%	80 °C	N/A	50 μA/cm^2	3.4-4.2	N/A	60	33.3%
Ref.[2]	Li_3BO_3@LCO +LLZO+ITO	60%	80 °C	1	0.1C (14 mA/g)	3.0-4.1	101	40	66%
Ref.[3]	LCO+Li_3BO_3 +LLZO (42:35:23)	42%	25 °C	N/A	0.01 C (1.4 mA/g)	3.0-4.2	78	1	N/A
Ref.[4]	$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$	100%	80 °C	N/A	0.5C (70 mA/g)	3.0-4.2	77	10	< 79%
Ref.[5]	LCO + porous LLZO scaffold (3:10)	23%	80 °C	0.73	0.05 C (7 mA/g)	3.0-4.05	118	14	97%

Ref.[6]	$LCO@Li_2CO_3$ + $LLZO@Li_2CO_3$+ $Li_{2.3}C_{0.7}B_{0.3}O_3$ (58:30:12)	58%	100 °C	1	0.05C (7 mA/g)	3.0-4.05	106	40	66%
Ref.[7]	V_2O_5+ CNT (9:1)	90%	100 °C	0.2	50 mA/g	1.2-4.5	150	27	83.3%
Ref.[8]	LCO+LLZO	60%	60 °C	2	25 mA/g	2.8-3.6	110	5	71%
Ref[9].	LCO+LLZO	N/A	80 °C	16	3 mA/g	2.8-3.4	75	5	66.7%
Ref.[10]	LCO+LLZTO	50%	50 °C	12.6	4 mA/g	2.4-3.6	110	100	27.6%
This work	HE-DRXs +LLZTO (5:1)	83.33%	150 °C	1.3	25 mA/g	1.7-4.7	**238**	**100**	**95%**

References

1. Kato, T. *et al.* In-situ Li7La3Zr2O12/LiCoO2 interface modification for advanced all-solid-state battery. *Journal of Power Sources* **260**, 292–298 (2014).
2. Ramkumar, B., So-young, K., Chan-woo, N., Aravindan, V. & Yun-Sung, L. LiBO2-modified LiCoO2 as an efficient cathode with garnet framework Li6.75La3Zr1.75Nb0.25O12 electrolyte toward building all-solid-state lithium battery for high-temperature operation. *Electrochimica Acta* **359**, 136955 (2020).
3. Ohta, S. *et al.* Co-sinterable lithium garnet-type oxide electrolyte with cathode for all-solid-state lithium ion battery. *Journal of Power Sources* **265**, 40–44 (2014).
4. Kim, Y., Waluyo, I., Hunt, A. & Yildiz, B. Avoiding CO2 Improves Thermal Stability at the Interface of Li7La3Zr2O12 Electrolyte with Layered Oxide Cathodes. *Advanced Energy Materials* **12**, 2102741 (2022).

5. Kim, K. J. & Rupp, J. L. M. All ceramic cathode composite design and manufacturing towards low interfacial resistance for garnet-based solid-state lithium batteries. *Energy and Environmental Science* **13**, 4930–4945 (2020).
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8. Scheld, W. S. *et al.* Rapid thermal processing of garnet-based composite cathodes. *Journal of Power Sources* **545**, (2022).
9. Ihrig, M. *et al.* Low temperature sintering of fully inorganic all-solid-state batteries – Impact of interfaces on full cell performance. *Journal of Power Sources* **482**, (2021).
10. Tsai, C. L. *et al.* A garnet structure-based all-solid-state Li battery without interface modification: Resolving incompatibility issues on positive electrodes. *Sustainable Energy and Fuels* **3**, 280–291 (2019).