

Constructing an anion-capturing interface to achieve Li⁺ cross phase transport in composite solid electrolytes

Corresponding Author: Professor Ling Huang

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

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors modified LLZTO with FeF₃ and used a stepwise mixing method to improve the compatibility of the filler with PVDF-HFP and the ionic conductivity, which is an interesting research work. However, many statements in the manuscript lack strong evidence. For example, the article is titled "Constructing an anion capture interface to achieve Li⁺ cross phase transport in composite solid electrolytes", but there is a lack of solid evidence of Li⁺ cross-phase transport in the article. In addition, the achieved electrochemical performance is not significantly better than the research results in existing literature. The maximum current density of lithium dendrite formation in the work is 2.5 mA/cm², but the test current of the Li symmetric battery is only 0.1 mA/cm², and the cycle time is only 600 hours. The electrode loading of LFP and NCM as the positive electrode is only about 2.0 mg/cm², which is far from practical application.

1. The author promotes the cross phase transport of Li⁺ in composite solid electrolytes by constructing an anion capture interface. However, the article lacks direct evidence of Li⁺ cross phase transport. Suggest conducting additional experiments, such as using the ⁶Li → ⁷Li tracer exchange technique in SSNMR, to quantitatively analyze the specific roles of different phases in Li⁺ transport in L-FL35PH and L@FL35PH samples.
2. What specifically does SCL refer to in the author's article? Does it refer to the interface between polymer and filler? If not, what is the relationship between SCL and the interface? What role does it play in the conduction of the interface? In addition, in the schematic diagram of Figure 2e, the author did not clearly label the interface inside the composite electrolyte.
3. The FTIR spectrum in Figure 1c lacks the comparative spectra of samples prepared by one-pot mixing method using LiTFSI, FeF₃, and LLZTO. For L-FL35PH and L@FL35PH membranes, the signal peak at 771 cm⁻¹ is significantly weakened compared to LiTFSI. What does this indicate? What could be the possible cause of this phenomenon? In addition, the author studied the interaction between TFSI⁻ and FeF₃ layers through peak shift, and concluded that this interaction weakens the binding force of S-N bonds. Is this explanation reasonable?
4. The authors mentioned TFSI⁻ gathering on FeF₃@LLZTO surface in L@FL35PH electrolyte, while TFSI⁻ in L-FL35PH electrolyte is predominantly dispersed within PVDF-HFP matrix, why N 1s and S 2p peaks intensity in L@FL35PH electrolyte increase along with measuring depth?
5. In the Figure 2e, L-FL35PH exhibits minimal Coulomb interaction on the equilibrium electric field, resulting in thick SCL that impedes Li⁺ transport. How thick is SCL? How is the thickness of SCL quantified? What is the role of SCL in ion conduction in composite electrolytes? Is thicker more unfavorable for ion conduction? As is well known, the interface between LLZTO and polymers plays an important role in ion conduction. Here, what is the relationship between SCL and the interface?
6. The cycle performance of Li|L-FL35PH|Li battery at 0.1 mA/cm² is only 600h, providing longer symmetric cell performance to evaluate the compatibility between the solid-state electrolyte and Li foil. In addition, the L@FL35PH electrolyte has a high CCD value of 2.5 mA/cm², and the current density of the symmetrical battery (0.1 mA/cm²) is relatively small. The authors should provide the cycling performance of symmetric cells measured at higher current densities (at least 1 mA/cm²-1 mAh/cm²).
7. In the Figure3f, the initial resistance of L-FL35PH and L @ FL35PH is the same, but the initial polarization current is significantly different, which is obviously contradictory. Moreover, after a testing time of 600s, the polarization current cannot reach steady state at all. It is recommended to retest tLi⁺ and extend the testing time (10000s).
8. Given that the loading of LPF is only about 2.0 mg/cm², please measure the cells with higher commercial loading

performances (>2.0 mAh/cm²) for a more comprehensive understanding of their performance.

9. Why choose 35% FeF₃@LLZTO in L@FL35PH sample as a proportion of composition? The relevant optimization and characterization data seem to lack specific explanations. In addition, the L@FL20PH and L@FL50PH samples mentioned in the experimental section have no relevant data in the entire text, and the purpose and significance of their settings are not reflected.

10. There are multiple writing errors in the article, such as “CCD test” being replaced by “GCD test” and confusion in the annotations in Figure 3d. The article uses “EDS”, while the supplementary materials (SI) use “EDX”. It is recommended that the article and supplementary materials remain consistent and provide the full name when the abbreviation first appears.

Reviewer #2

(Remarks to the Author)

See attached

Reviewer #3

(Remarks to the Author)

This study addresses the limited ionic conductivity of solid electrolytes in solid-state lithium batteries, focusing on mitigating the space charge layer and enhancing lithium-ion mobility. The authors developed a composite solid electrolyte (CSE) by creating an anion-trapping interface using FeF₃ on the LLZTO surface. This interface promotes LiTFSI dissociation and forms a TFSI⁻ aggregation layer, improving ionic transport. This is an intriguing study that explores the modification of the solid electrolyte interface. However, some ideas are unclear and require further explanation.

The following are comments and suggestions for improving the manuscript:

I. To ensure readers can clearly and accurately understand the article, please address the following issues:

(a) In Fig. S1d, kindly label the names of the XRD curves clearly.

(b) Specify the sample names for L-L35PH, L-FL35PH, and L@FL35PH.

(c) The location of the 'f' figure is not indicated in Fig. 1.

(d) The figures in Fig. 2e and 2f are unclear. Please revise them to align with the corresponding sections in the text.

(e) Carefully verify the sample names in Fig. 3d.

(f) Confirm whether the charge-discharge curves in Figs. S27 and S28 correspond to the correct cycle numbers.

II. In Fig. 4a, the LiF peak for L-FL35PH is significantly higher than that for L@FL35PH. The authors state in the article, 'It was evident that lower LiF content was detected for the L@FL35PH electrolyte, mainly due to the fact that most of the immobilized TFSI⁻ could not approach the electrode for decomposition.' However, in other references, such as Adv. Funct. Mater. 34 (2024) 2311848, it is stated that 'the in situ organic-inorganic LiF-rich dielectric layer effectively improves the stability and compatibility of the electrode/electrolyte interface, ensuring interfacial lithium conduction while facilitating stable Li⁺ plating/stripping.' These seem to present conflicting views. How do the authors reconcile these differences?

III. The author mentions, 'L-FL35PH exhibits minimal Coulomb interaction on the equilibrium electric field (Fig. 2e), leading to a thick SCL that hinders Li⁺ transport.' What are the criteria for defining a 'thick SCL'? How does the SCL relate to the formation of the LiF layer?

IV. The selection of FeF₃ is based on its electronic defect characteristics, but has it been evaluated against other materials with similar properties? For example, could MgF₂ or AlF₃ serve as potential alternatives.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

All issues have been properly resolved, and I am satisfied with the revised manuscript.

Reviewer #2

(Remarks to the Author)

The authors have added many important explanations to the revised manuscript, however, several points listed below should be supplemented to understand the work more clearly :

① Whether an electrolyte with FEC and LiTFSI (1 M LiTFSI in FEC) was added as the interface infiltration agent on both sides of the CSEs in all tested cells? If it is, the discussion should be supplemented for the explanation of EIS in the Fig.3 ;

② If possible, the cross-sectional images of the electrolyte membrane should be added to illustrate the distribution of LLZTO particles.

③ Line 581 in the text, it should be added the dry conditions for the electrolyte film.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

The authors have added some important explanations, and I am satisfied with the revised manuscript.

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RESPONSE TO REVIEWERS' COMMENTS

We thank all the reviewers for their valuable comments on our manuscript. Their constructive suggestions for improvement have certainly raised the quality of our manuscript. In order to address the reviewers' concerns, we have addressed their comments point by point below.

For Reviewer #1:

The authors modified LLZTO with FeF₃ and used a stepwise mixing method to improve the compatibility of the filler with PVDF-HFP and the ionic conductivity, which is an interesting research work. However, many statements in the manuscript lack strong evidence. For example, the article is titled "Constructing an anion capture interface to achieve Li⁺ cross phase transport in composite solid electrolytes", but there is a lack of solid evidence of Li⁺ cross-phase transport in the article. In addition, the achieved electrochemical performance is not significantly better than the research results in existing literature. The maximum current density of lithium dendrite formation in the work is 2.5 mA/cm², but the test current of the Li symmetric battery is only 0.1 mA/cm², and the cycle time is only 600 hours. The electrode loading of LFP and NCM as the positive electrode is only about 2.0 mg/cm², which is far from practical application.

Comment 1. *The author promotes the cross phase transport of Li⁺ in composite solid electrolytes by constructing an anion capture interface. However, the article lacks direct evidence of Li⁺ cross phase transport. Suggest conducting additional experiments, such as using the ⁶Li → ⁷Li tracer exchange technique in SSNMR, to quantitatively analyze the specific roles of different phases in Li⁺ transport in L-FL₃₅PH and L@FL₃₅PH samples.*

Response:

Following your suggestion, ⁶Li SSNMR spectra were collected to demonstrate Li⁺ cross-phase transport as shown in **Fig.3**, and the corresponding discussion has added into the revised manuscript as below:

“In order to reveal Li^+ cross-phase transport mechanism, $^6\text{Li}/\text{CSE}/^6\text{Li}$ symmetric batteries with L-FL₃₅PH and L@FL₃₅PH electrolytes were cycled for 60 h at 0.1 mA/cm². Partial $^7\text{Li}^+$ in CSE is substituted by $^6\text{Li}^+$ during cycling, and then Li^+ transport channels are identified using high-resolution ^6Li isotope SSNMR.^[14] The fitting result in **Fig.3e, f** indicate three types of Li^+ environments, i.e., Li^+ transport within LLZTO (light red peak), interface of FeF₃@LLZTO and PVDF-HFP (blue peak), and PVDF-HFP chains (orange peak).^[45] The fitting results of the ^6Li NMR spectra before cycling illustrate that the relative content difference of $^6\text{Li}^+$ between the interface and PVDF-HFP in L@FL₃₅PH electrolyte is 1%, which is much smaller than that of L-FL₃₅PH electrolyte (9%), demonstrating the influence of the charge gradient layers on anchoring TFSI⁻ distribution (**Fig.3g**). When cycling with ^6Li anode, $^6\text{Li}^+$ content within LLZTO for L@FL₃₅PH electrolyte increases from 73% to 87%, while its interfacial feature decreases from 13% to 3%, reflecting Li^+ transport within LLZTO as the primary mechanism. In comparison, $^6\text{Li}^+$ content within LLZTO changes from 67% to 26% for L-FL₃₅PH electrolyte. Therefore, due to the alleviated CGL effects, the concentrated TFSI⁻ in FeF₃ layer promotes Li^+ migration through LLZTO particles. Such Li^+ transport mechanism is further confirmed by the exchange current density of Li|L@FL₃₅PH|Li battery (0.41 mA/cm²) that is two-fold of the Li|L-FL₃₅PH|Li and Li|L-L₃₅PH|Li batteries (**Supplementary Fig.33**).”

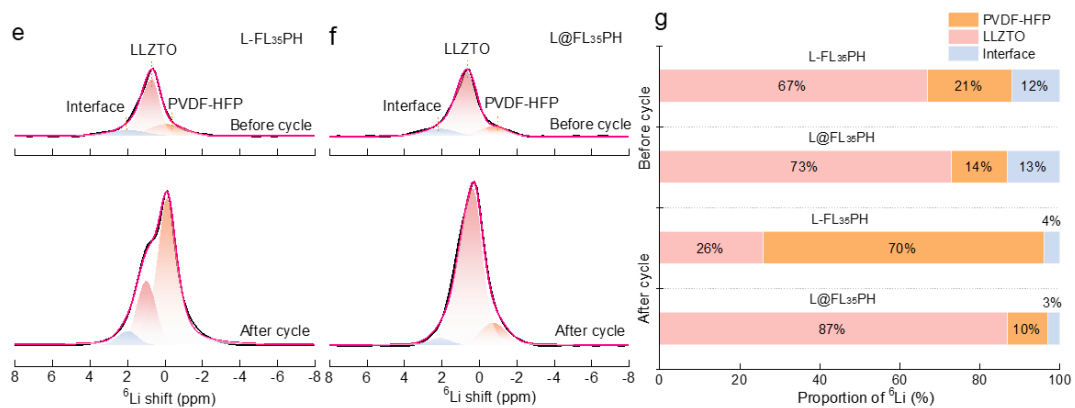
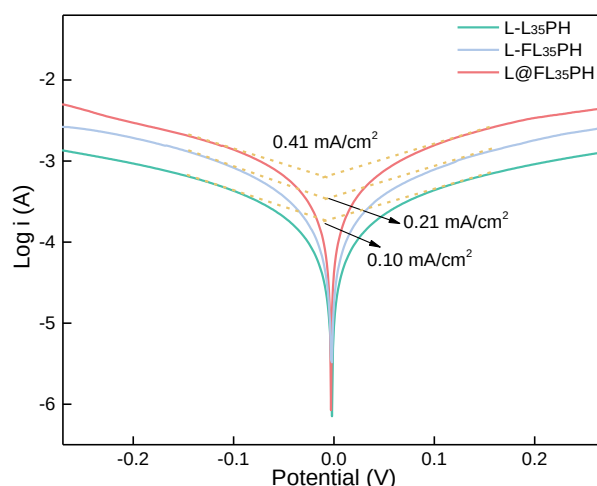


Fig. 3 (e-f) The ^6Li high-resolution Li isotope SSNMR spectra of the L-FL₃₅PH and L@FL₃₅PH electrolytes before and after ^6Li symmetric cell cycling, and (g) corresponding peak proportions of $^6\text{Li}^+$ with different transport paths.



Supplementary Fig.33 | The Tafel curves of Li|L-L₃₅PH|Li, Li|L-FL₃₅PH|Li and Li|L@FL₃₅PH|Li symmetric batteries

Comment 2. What specifically does SCL refer to in the author's article? Does it refer to the interface between polymer and filler? If not, what is the relationship between SCL and the interface? What role does it play in the conduction of the interface? In addition, in the schematic diagram of Figure 2e, the author did not clearly label the interface inside the composite electrolyte.

Response:

We would apologize for the vague clarification on the SCL concept. To address the reviewer's concern, it has been revised as the "charge gradient layer (CGL)" that describes Li⁺ or anions gradient distribution on the fillers interface within polymer matrix. It is established based on FeF₃ coating as the charge carriers, inducing a concentrated TFSI⁻ layer neutralized by another Li⁺ layer with increasing distribution outwards. The charge-carrying feature of FeF₃@LLZTO particles surface is reflected by the surface zeta potential of 441 mV (**Supplementary Fig.14c**). As the reference, it is measured as 59 mV on LLZTO particles, isolating FeF₃ coating with the charge aggregated surface. The CGL thickness is identified until reaching the charge equilibrium. It is distinguished with the physical interface between fillers and polymer, considering its charge-gradient feature. This CGL concept is analogous to the electric

double layer in aqueous electrolyte, *i.e.* the separation of positive and negative ions creates a built-in electric field preventing carriers migration at interface.^[R1] As widely reported in literatures, CGL is considered as the origin for the low interfacial Li^+ conduction within solid-state LMBs.^[R2] Specifically, its formation at solid-solid interfaces results in local depletion or enrichment of charge carriers, increasing the interfacial barrier for Li^+ transport as the repelling effect.^[R3-R5] Therefore, the interfacial charge density on fillers increases along with TFSI^- concentration, followed by the decreased CGL thickness (**Supplementary Fig.17**), the alleviated repelling effect (**Supplementary Fig.16**) and the promoted Li^+ conduction in solid-state LMBs (**Fig.3 and Supplementary Fig.20, 30**).

Following the reviewer suggestion, the schematic diagram in **Fig. 2e, f** has been revised to reflect the gradient distribution of Li^+ and TFSI^- within CGL, and the interface within composite electrolyte has been labeled carefully as below.

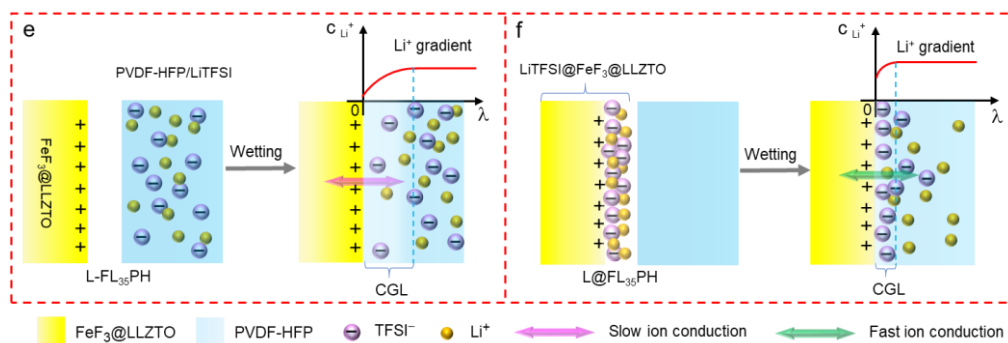
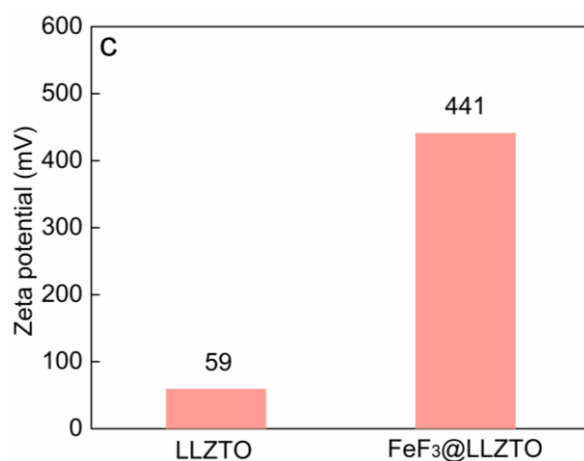
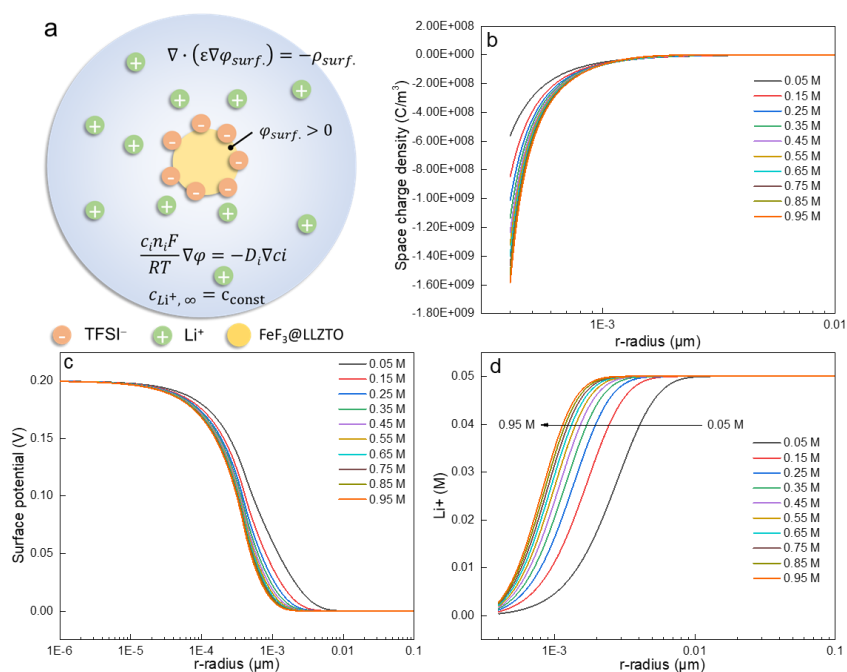


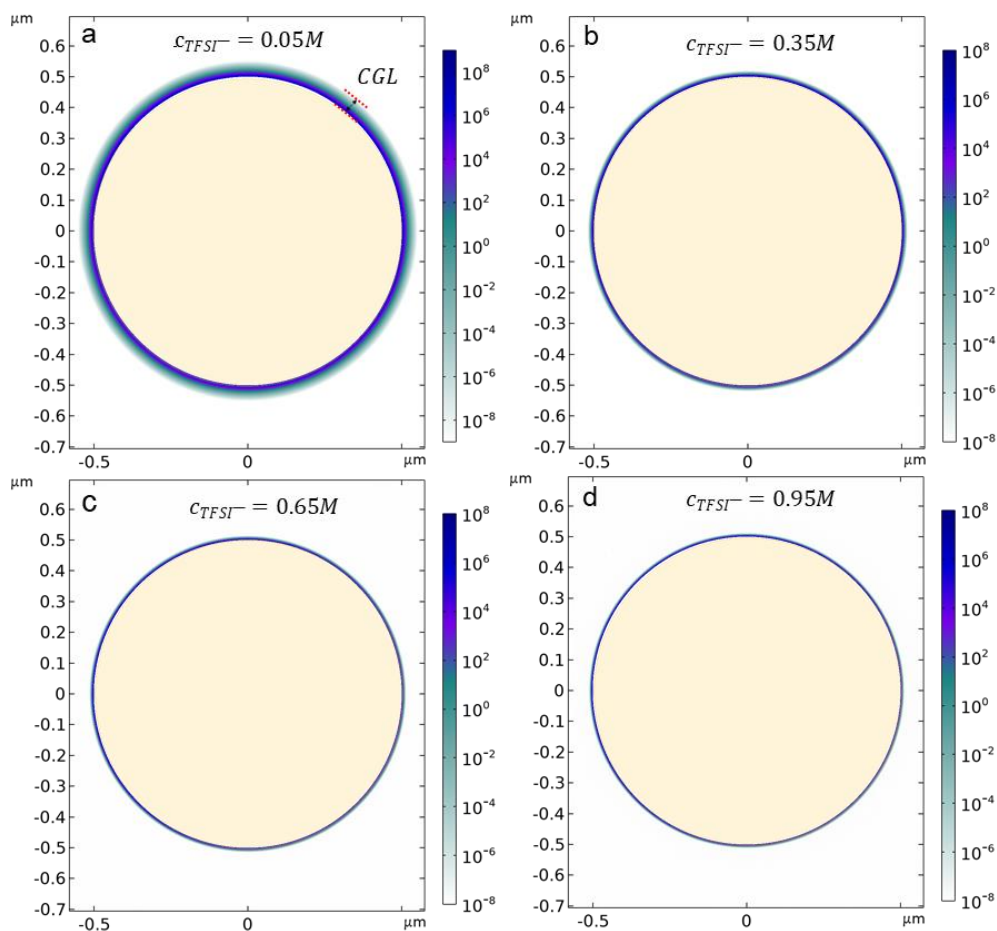
Fig.2 (e, f) The schematic diagram of the effect of CGL thickness on lithium ion transport channels.



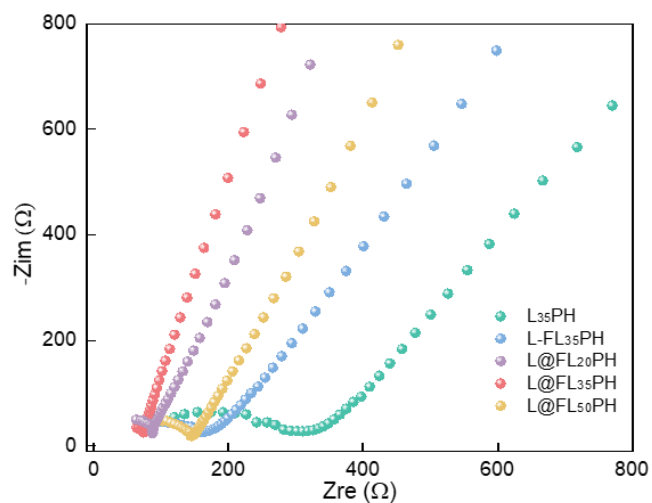
Supplementary Fig.14 (c) the surface Zeta potential of LLZTO and FeF₃@LLZTO particles.



Supplementary Fig.16 (a) FeF₃@LLZTO simulation models with surface TFSI⁻ aggregation, (b-c) the change of charge density, surface potential and Li⁺ concentration around FeF₃@LLZTO particles through altering TFSI⁻ concentration from 0.05 to 0.95 M.



Supplementary Fig.17 | The relationship between CGL thickness and TFSI⁻ concentration on the FeF₃@LLZTO particle surface.



Supplementary Fig.20 | Nyquist plots of SS|CSEs|SS batteries at room temperature.

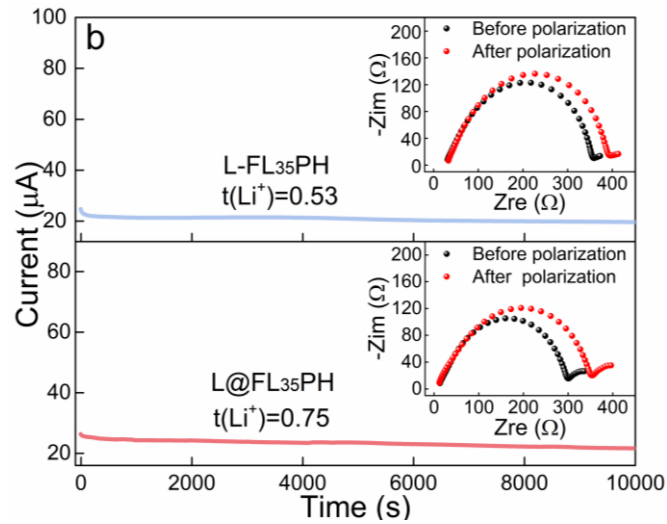
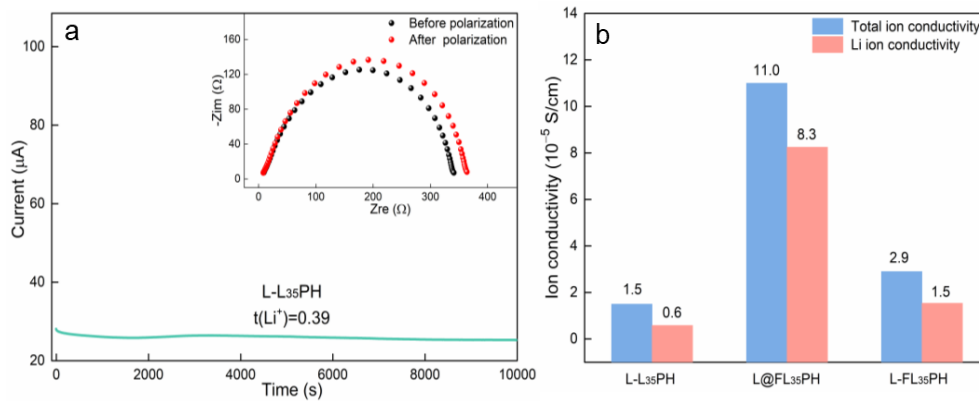


Fig.3 (b) Variation of current with time during polarization of Li|CSEs|Li symmetric batteries configuration; the inset figure shows the Nyquist plots before and after polarization.



Supplementary Fig.30| (a) Variation of current with time during polarization of a Li|L-L35PH|Li symmetric battery configuration; the inset figure shows the Nyquist plots before and after polarization. (b) Total ion conductivity and Li ion conductivity of three electrolytes

References

- [R1] Hui Shao, Yih-Chyng Wu, Zifeng Lin, et al. Nanoporous carbon for electrochemical capacitive energy storage, Cite this: Chem. Soc. Rev. 49, 3005 (2020).
- [R2] Wang, L., et al. In-situ visualization of the space-charge-layer effect on interfacial lithium-ion transport in all-solid-state batteries. Nat. Commun. 11(1):1-9

(2020).

[R3] Zhang, D.F., et al. A dielectric electrolyte composite with high lithium-ion conductivity for high-voltage solid-state lithium metal batteries. *Nat. Nanotechnol.* 18(6), 602 (2023).

[R4] Zhu Cheng,¹ Ming Liu,² Swapna Ganapathy, et al. Revealing the impact of space-charge layers on the Li-ion transport in all-solid-state batteries, *Joule* 4, 1311–1323 (2020).

[R5] Wu, J. F. & Guo, X. Origin of the low grain boundary conductivity in lithium ion conducting perovskites: $\text{Li}_{3-x}\text{La}_{0.67-x}\text{TiO}_3$. *Phys. Chem. Chem. Phys.* 19, 5880–5887 (2017).

Comment 3. The FTIR spectrum in Figure 1c lacks the comparative spectra of samples prepared by one-pot mixing method using LiTFSI, FeF_3 , and LLZTO. For L-FL₃₅PH and L@FL₃₅PH membranes, the signal peak at 771 cm^{-1} is significantly weakened compared to LiTFSI. What does this indicate? What could be the possible cause of this phenomenon? In addition, the author studied the interaction between TFSI⁻ and FeF_3 layers through peak shift, and concluded that this interaction weakens the binding force of S-N bonds. Is this explanation reasonable?

Response:

Following suggestion of the reviewer, FTIR spectra of LiTFSI/ FeF_3 /LLZTO obtained through one-pot mixing method has been added in **Fig.1c** as shown below. The S-N peak at 771 cm^{-1} of LiTFSI/ FeF_3 /LLZTO remains at its position, representing the low dissociation degree of LiTFSI. While its blueshift in L-FL₃₅PH and L@FL₃₅PH electrolytes indicates S-N bond relaxation under the presence of FeF_3 . As for its relative intensity, the change is ascribed to electrolytes variation in thickness and composition. This is also validated by integrating Raman spectra showing TFSI⁻ concentration of 71% in L@FL₃₅PH and 59% in L-FL₃₅PH (**Supplementary Fig.19**). Meanwhile, TGA analysis indicates lower DMF content in L@FL₃₅PH electrolyte

(1.4wt.%) than that in L-FL₃₅PH (1.8wt.%) electrolyte (**Supplementary Fig.11**). The FTIR results illustrate that the presence of DMF-related free -N-C=O bonds is not detected in the L@FL₃₅PH and L-FL₃₅PH electrolytes, indicating that the residual DMF is all bound to Li⁺ and there is no free DMF molecules (**Supplementary Fig.13**). Therefore, LiTFSI dissociation is promoted by Li⁺-DMF solvation and the FeF₃/TFSI⁻ interaction. However, combining the results of TGA, Raman and FTIR, it indicates that the interaction of FeF₃/TFSI⁻ is more favorable for the dissociation of LiTFSI. Therefore, the interaction between TFSI⁻ and FeF₃ layers promote the dissociation of LiTFSI, reducing the interaction between Li⁺ and TFSI⁻, thus weakens the binding force of S-N bonds. The corresponding results and discussion have been added into the revised manuscript.

“The synthetic impacts on TFSI⁻ adsorption behaviors have been revealed through FTIR spectroscopy (**Supplementary Fig.6**). To alleviate the internal integration of CSEs components, L-FL₃₅PH and L@FL₃₅PH electrolytes are fragmented as shown in the insert to **Supplementary Fig.6**. **Fig.1c**, it exhibits a signal peak of LiTFSI at 771 cm⁻¹ corresponding to its S-N bond, which blueshifts to 766 cm⁻¹ after being adsorbed within LiTFSI@FeF₃@LLZTO particles.^[22] Such S-N bond relaxation is attributed to LiTFSI dissociation with presence of FeF₃, which is also appropriate for L@FL₃₅PH electrolyte.^[23-24] While its position of L-FL₃₅PH electrolyte maintains at 770 cm⁻¹, indicating the weak interactions between TFSI⁻ and FeF₃. In addition, the S-N peak at 771 cm⁻¹ of LiTFSI/FeF₃/LLZTO remains at its position, representing the low dissociation degree of LiTFSI. In order to gather insights into such interaction, the adsorption energy has been calculated using density functional theory (DFT) as shown in **Fig.1d**. It exhibits an adsorption energy of 10.24 kcal/mol between TFSI⁻ and Li⁺, which elevated towards 29.78 kcal/mol on FeF₃. The electrostatic interaction between Fe and N leads to FeF₃ with preference for capturing TFSI⁻ and promoting LiTFSI dissociation.”

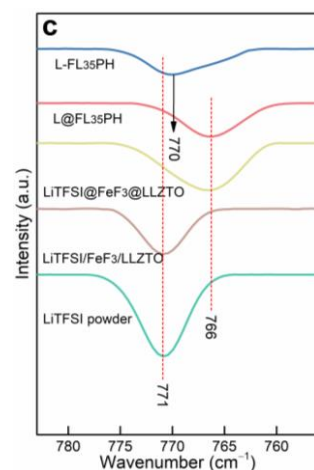
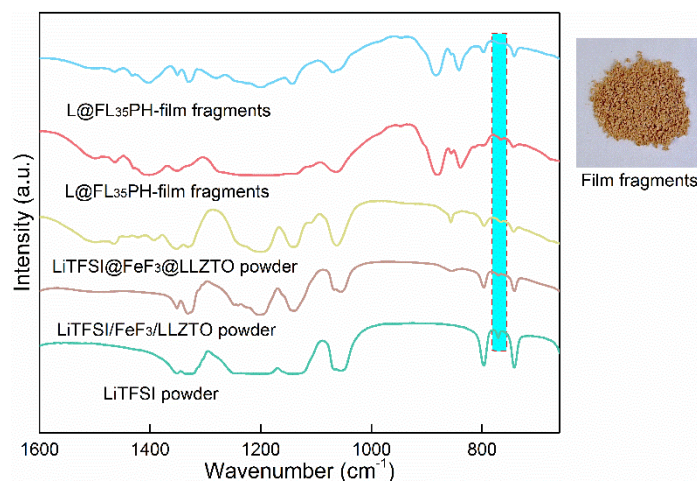
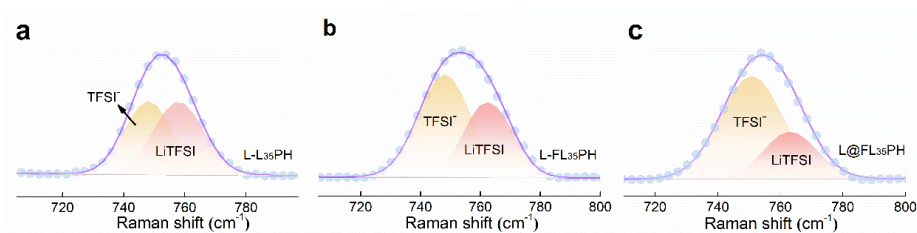


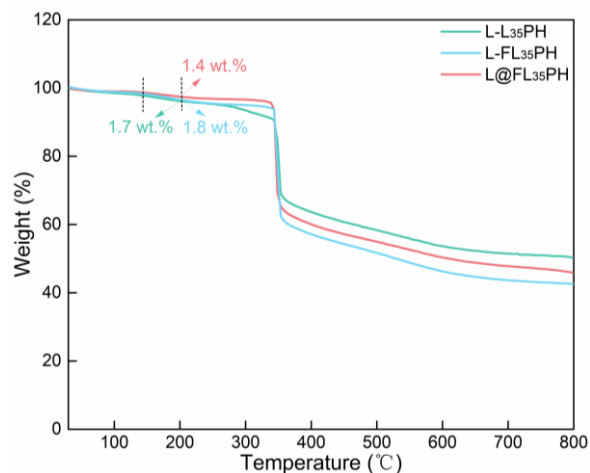
Fig.1 (c) FTIR spectra of various samples.



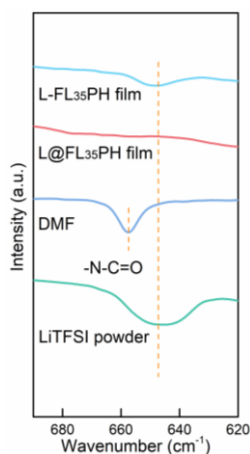
Supplementary Fig.7| FTIR spectra of different samples. The inset figure shows the film being ground into fragments by placing it in liquid nitrogen.



Supplementary Fig.19| (a-c) Raman spectra of L-L₃₅PH、L-FL₃₅PH and L@FL₃₅PH fitted with TFSI⁻ and LiTFSI groups at 710-800 cm^{-1} .



Supplementary Fig.11| TGA curves of L-L₃₅PH, L-FL₃₅PH and L@FL₃₅PH electrolytes.



Supplementary Fig.13| FTIR spectra of different samples

Comment 4. The authors mentioned TFSI⁻ gathering on FeF₃@LLZTO surface in L@FL₃₅PH electrolyte, while TFSI⁻ in L-FL₃₅PH electrolyte is predominantly dispersed within PVDF-HFP matrix, why N 1s and S 2p peaks intensity in L@FL₃₅PH electrolyte increase along with measuring depth?

Response:

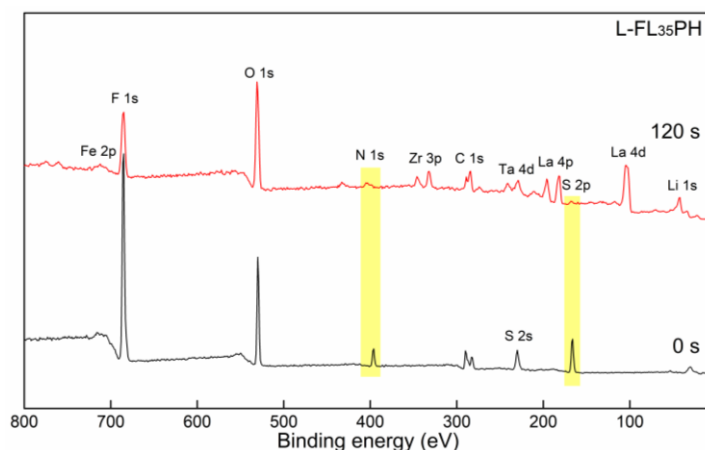
Thank you very much for your comments. The variation in elements distribution between L@FL₃₅PH and L-FL₃₅PH is validated by XPS spectra as the result of TFSI⁻ adsorption on FeF₃@LLZTO. L-FL₃₅PH surface that yields S 2p and N 1s signals,

while they are absent in L@FL₃₅PH. Meanwhile, neither of them captures LLZTO features. At bulk region, S and N peaks are collected in L@FL₃₅PH electrolyte, while they weaken in L-FL₃₅PH electrolyte. In the meantime, the presence of LLZTO is detected in both electrolytes. The reason for this phenomenon is attributed to the differences in the processes of L-FL₃₅PH and L@FL₃₅PH electrolytes, leading to variations in the distribution of TFSI⁻. L@FL₃₅PH exerted the adsorption effect of FeF₃ to TFSI⁻ through the distribution mixing method, resulting in the enrichment of TFSI⁻ on the surface of FeF₃@LLZTO. The L-FL₃₅PH electrolyte prepared by the one-pot mixing method causes TFSI⁻ to be uniformly dispersed in PVDF-HFP matrix due to its weak interaction with FeF₃. Before etching, XPS detection depth is insufficient to reach FeF₃@LLZTO particles, the elemental composition of PVDF-HFP is detected in both L@FL₃₅PH and L-FL₃₅PH. Unlike L-FL₃₅PH, while TFSI⁻ in L@FL₃₅PH mainly accumulates on FeF₃@LLZTO surface, almost no N and S elements were detected in PVDF-HFP. As the etching depth increases, the peak intensities of N 1s and S 2p in L@FL₃₅PH increase due to the fact that N and S elements of TFSI⁻, and a large amount of TFSI⁻ is adsorbed in the surface of FeF₃@LLZTO, only a small amount of TFSI⁻ is dispersed in the PVDF-HFP matrix (**Supplementary Fig.8-9**). Therefore, the peak intensities of N 1s and S 2p in L@FL₃₅PH electrolyte increase following depth.

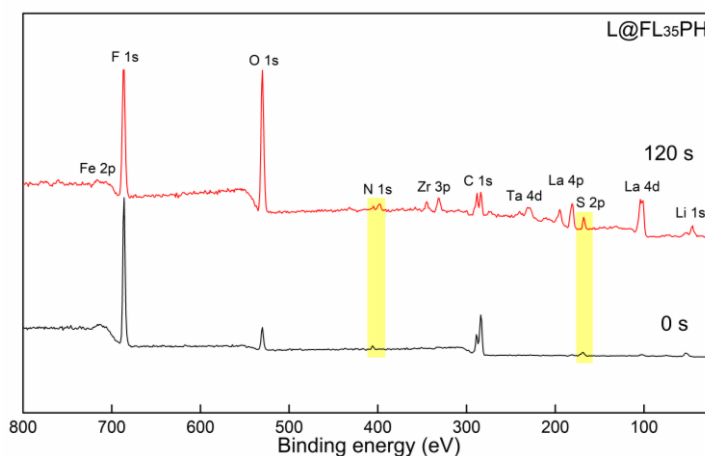
The corresponding description on depth analysis of XPS spectra has been provided in the revised manuscript as following.

“XPS full spectra of two electrolytes are shown in **Supplementary Figs.8-9**. L-FL₃₅PH surface that yields S 2p and N 1s signals, while they are absent in L@FL₃₅PH. Meanwhile, neither of them captures LLZTO features. The intensity of N 1s and S 2p peaks in L@FL₃₅PH electrolyte increases along with measuring depth, whereas L-FL₃₅PH peaks appear reversing trend. In the meantime, the presence of LLZTO is detect in both electrolytes after etching. The origin for this phenomenon is due to the that the L@FL₃₅PH exerted the adsorption effect of FeF₃ to TFSI⁻ through the distribution mixing method, resulting in enrichment of TFSI⁻ on the surface of

FeF₃@LLZTO. While the L-FL₃₅PH electrolyte prepared by the one-pot mixing method causes TFSI⁻ to be uniformly dispersed in PVDF-HFP matrix for its weak interaction with FeF₃. Such result aligns with the anticipated outcomes in **Figs.1a, b**. The variation in TFSI⁻ concentration gradient from surface to bulk between L-FL₃₅PH and L@FL₃₅PH could be further reflected in high-resolution C 1s spectra (**Figs.1e, f**), covering C-F species at 291.8 eV attributed to LiTFSI and PVDF-HFP, C-C/C-H peak at 284.8 eV of PVDF-HFP, and C-S peak at 289.7 eV of TFSI⁻.^[26] At the bulk region, O=C-N species appears at 286.4 eV, as evident for residual DMF solvent in L@FL₃₅PH.^[27] Comparing to L-FL₃₅PH, the intensity ratio of C-F/C-C in L@FL₃₅PH increases from surface to bulk, and the increase in C-S/C-C ratio is much larger than that of the L-FL₃₅PH electrolyte. The result validates that the TFSI⁻ is immobilized on FeF₃@LLZTO particles surface via the stepwise mixing method.”



Supplementary Fig.8| XPS spectra of L-FL₃₅PH electrolyte before and after etching.



Supplementary Fig.9| XPS spectra of L@FL₃₅PH electrolyte before and after etching.

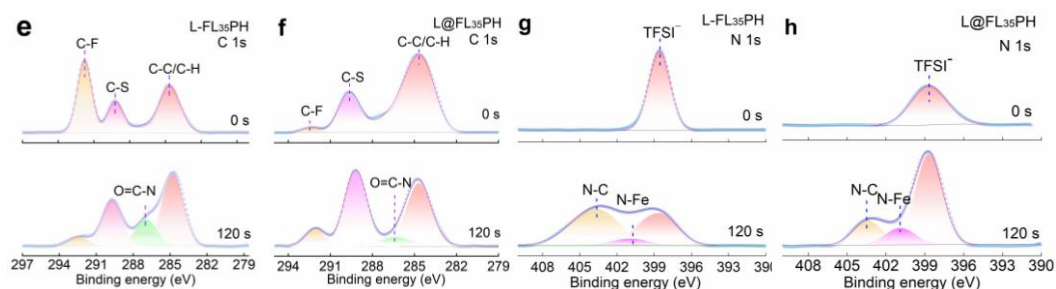


Fig.1 (e-f) C 1s and (g-h) N 1s spectra of L-FL₃₅PH and L@FL₃₅PH before and after etching.

***Comment 5.** In the Figure 2e, L-FL₃₅PH exhibits minimal Coulomb interaction on the equilibrium electric field, resulting in thick SCL that impedes Li⁺ transport. How thick is SCL? How is the thickness of SCL quantified? What is the role of SCL in ion conduction in composite electrolytes? Is thicker more unfavorable for ion conduction? As is well known, the interface between LLZTO and polymers plays an important role in ion conduction. Here, what is the relationship between SCL and the interface?*

Response:

We thank the reviewer for constructive suggestion. As explained in comment 2, the concept of SCL has been replaced by charge gradient layers (CGLs) that epitomize heterogeneous ion-distribution phenomena at filler/polymer interfaces, characterized by Li⁺ or anion concentration gradients. Specifically, FeF₃ coatings act as charge carriers, inducing a TFSI⁻ interfacial layer electrically neutralized by an outward-diffusing Li⁺ layer, establishing an ion concentration gradient. The equilibrium width reached by the resulting charge concentration from non-uniform to homogeneous distribution is defined as the CGL thickness. However, the contact interface between polymer and inorganic filler in composite solid-state electrolytes is complex, making it difficult to quantify CGL thickness within the interface region. Here, the Kelvin probe force microscope (KPFM), Zeta potential measurement, cyclic voltammetry (CV) and theoretical calculation are combined as the qualitative analysis of CGL thickness in **Supplementary Fig.14-17**. The charge-carrying feature of FeF₃@LLZTO particles surface is reflected by the surface zeta potential of 441 mV (**Supplementary Fig.14**). KPFM analysis in **Fig.2c, d** exhibit the surface potential of

L@FL₃₅PH electrolyte at -340 mV, which is lower than L-FL₃₅PH. It suggests that the enrichment of TFSI⁻ on FeF₃@LLZTO surface decreases the potential difference of organic-inorganic, thus weaken CGL effect.^[R6] Similarly, the double-layer capacitance of stainless steel (SS)/Celgard/L@FL₃₅PH is 9.4 μF/cm², which is higher than the 6.5 μF/cm² of SS/Celgard/L-FL₃₅PH (**Supplementary Fig.15b, 15d**). The result is due to the enrichment of TFSI⁻ that enhances the surface charge density of FeF₃, promoting its closer arrangement, thereby compressing the charge layer spacing and simultaneously increasing the capacitance of the double-layer.^[R7] Theoretical calculations also reveal that increasing the TFSI⁻ concentration (0.05 - 0.95 M) near the FeF₃@LLZTO interface induces an elevation in interfacial charge density, accompanied by a reduction in CGL thickness as the anion concentration rises (**Supplementary Fig.16-17**).

The role of CGL in ion conduction of composite electrolytes is mainly reflected in its hindering effect on Li⁺ transport.^[R8] CGL is an interface charge redistribution phenomenon driven by electrochemical potential differences, results in local charge carrier depletion or enrichment, thus prevents most charge carriers from further diffusing from one side to each other.^[R9] The low carrier concentration resulting in the presence of Li-deficient region, increasing the interfacial barrier for lithium-ion transport.^[R9-R10]

The width when the carrier concentration extends from the interface to the bulk phase and reaches the stable region is the thickness of CGL. That is, the thicker the CGL, the greater the concentration gradient of charge. The large concentration gradient means that Li⁺ need to pass through a longer non-equilibrium concentration region, resulting in an increase in the diffusion energy barrier and being unfavorable for Li⁺ migration, which reduces the overall ionic conductivity.^[R11]

The CGL is generated by the contact interface between LLZTO and PVDF-HFP through interfacial charge redistribution, which is driven by the electrochemical potential difference between both. The region formed by rearrangement will repel surrounding lithium ions/positive charges and prevent most charge carriers from

further diffusing, making this region a charge gradient layer.^[R9] Thereby the CGL as an intrinsic interfacial characteristic with a subordinate relationship to interface.

The related discussion has been added in the revised manuscript as follows:

“The impact of TFSI⁻ adsorption on CSEs surface potential is reflected through KPFM tests as depicted in **Fig.2** and **Supplementary Fig.14a, b**. When comparing to L-L₃₅PH, uniform potential distribution on L@FL₃₅PH and L-FL₃₅PH electrolytes is revealed, illustrating FeF₃ encapsulation on LLZTO improves interface compatibility between organic and inorganic components. The charge-carrying feature of FeF₃@LLZTO particles surface could be recognized by the surface zeta potential that is measured at 441 mV (**Supplementary Fig.14c**). As a reference, the surface zeta potential of LLZTO particles is measured to be 59 mV, indication an isolated FeF₃ coating as the charge aggregated surface. However, the surface zeta potential of L@FL₃₅PH electrolyte is measured at -340 mV, which is much lower than those of L-FL₃₅PH and L-L₃₅PH. It is induced by its higher concentration of TFSI⁻, which decreases potential difference at the organic-inorganic interface, the reduced CGL thickness facilitates Li⁺ transport crossing phase boundaries.^[33] The L-FL₃₅PH exhibits minimal Coulomb interaction on the equilibrium electric field (**Fig.2e**), resulting in thick CGL that impedes Li⁺ transport. It hinders Li⁺ migration from PVDF-HFP matrix towards FeF₃@LLZTO particles within CSEs. While the stepwise mixing method endows L@FL₃₅PH with the concentrated TFSI⁻ on FeF₃@LLZTO surface (**Fig.2f**). The organic-inorganic interface Coulomb interactions is established to decrease CGL thickness. Then, slow unidirectional pathway for Li⁺ transport is transformed into fast bidirectional pathway, and ion transport efficiency is improved. CGL is the charge distribution caused by the electric field intensity at the interface and has an electric bilayer effect.^[34-35] The result indicated that the double-layer capacitance of stainless steel (SS)/celgard/L@FL₃₅PH is 9.4 μF/cm², which is bigger than that of SS/celgard/L-FL₃₅PH (6.5 μF/cm², **Supplementary Fig.15**). The result is ascribed to the enrichment of TFSI⁻ that enhances the surface charge density of FeF₃, promoting its closer arrangement, thereby compressing the charge layer spacing and

simultaneously increasing the capacitance of the double-layer capacitance.^[35] In order to further validate CGL thickness, DFT models with various TFSI⁻ concentrations from 0.05 to 0.95 M have been constructed to simulate Li⁺ concentration, surface potential and charge density on FeF₃@LLZTO surface. The interfacial charge density increases along with TFSI⁻ concentration, resulting in decreasing surface potential and repelling effect for Li⁺ (**Supplementary Fig.16**). Similarly, the introduction of anions leads to the redistribution of charge at the interface, resulting in a decrease in CGL thickness with increasing TFSI⁻ concentration (**Supplementary Fig.17**). This theoretical simulation result is consistent with the KPFM and electric double layer capacity analysis ”

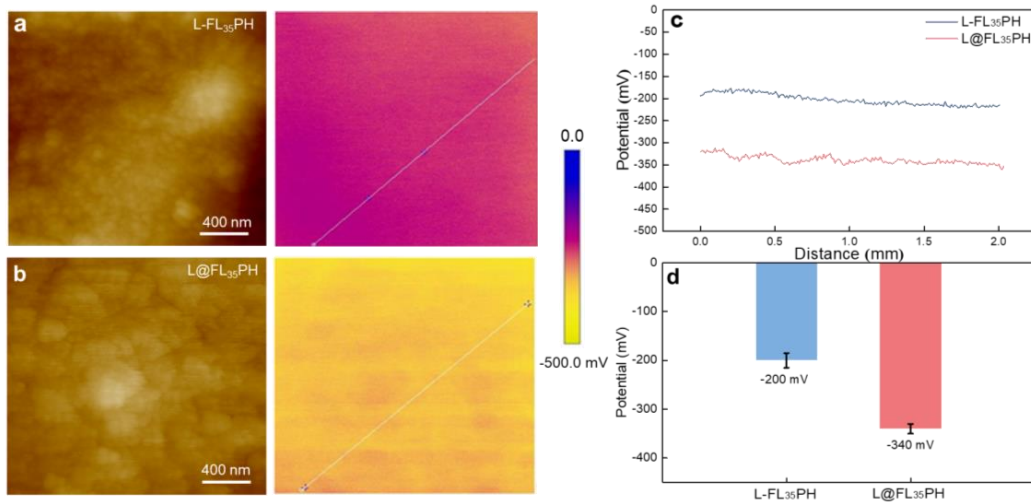
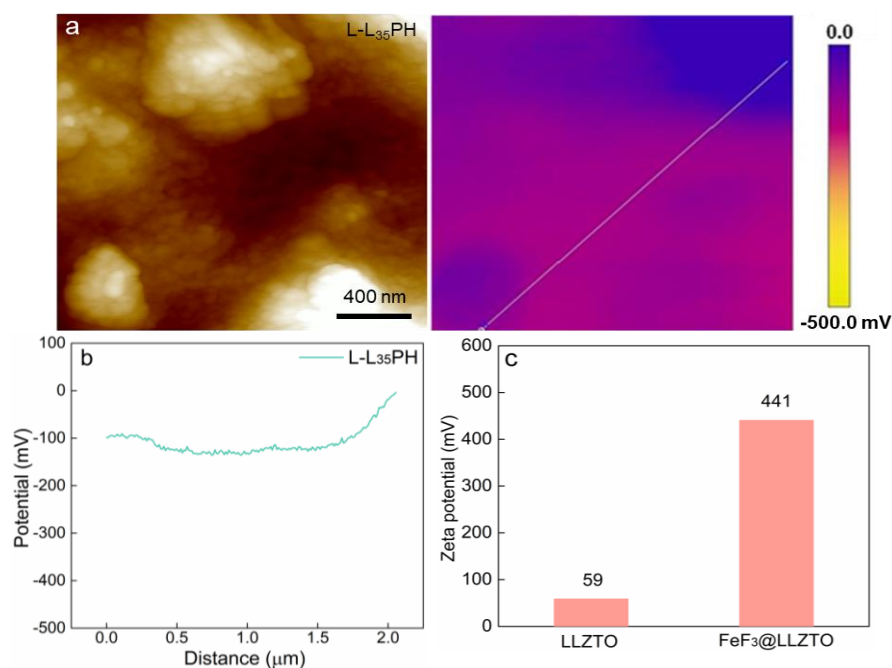
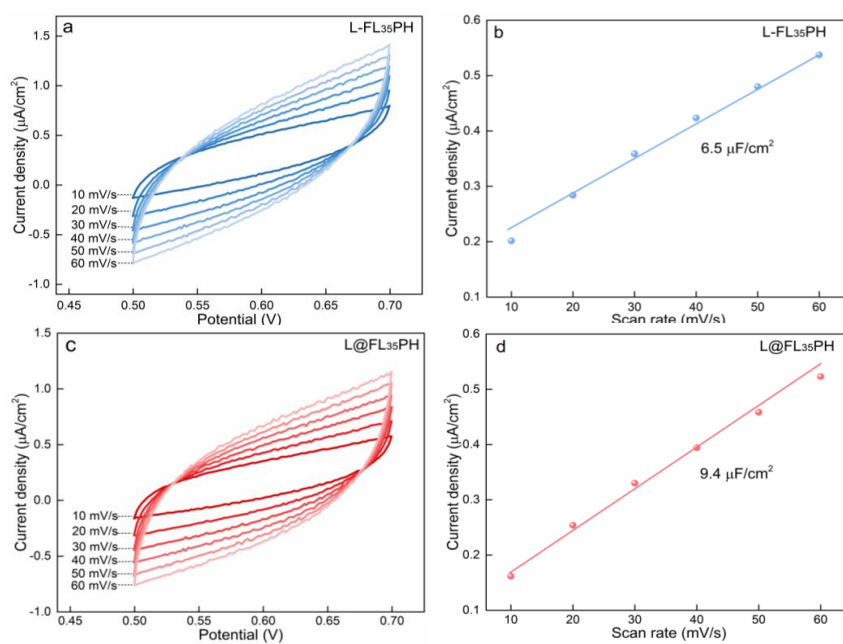


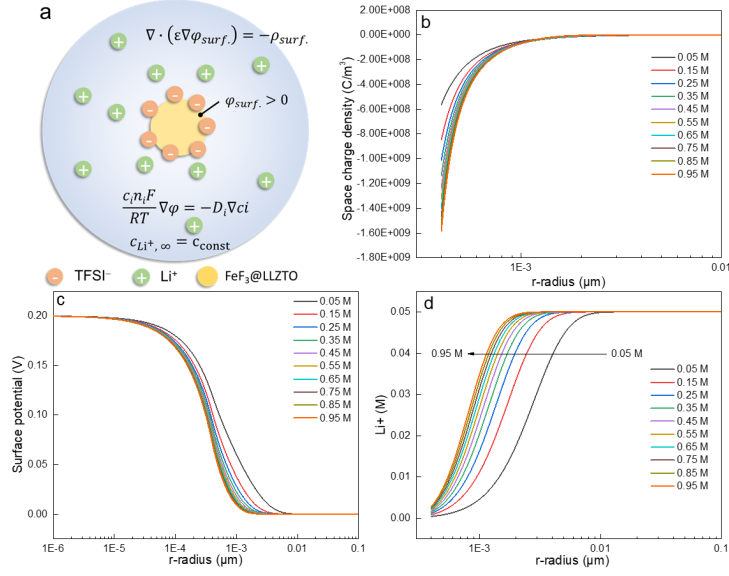
Fig.2 (a-d) Interface potential distribution images of L-FL₃₅PH and L@FL₃₅PH electrolytes.



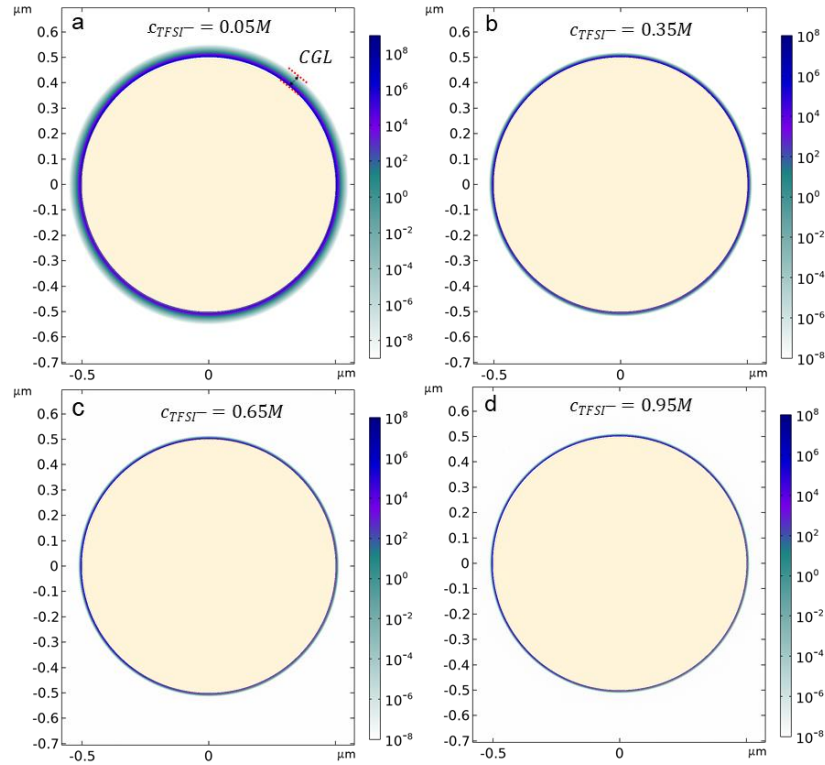
Supplementary Fig.14 (a-b) Interface potential distribution images of L-L₃₅PH electrolyte and (c) the surface Zeta potential of LLZTO and FeF₃@LLZTO particles.



Supplementary Fig.15 (a-d) CV Curve and (d) electric double layer capacitance of SS/Celgard/L-FL₃₅PH or SS/Celgard/L@FL₃₅PH cells at the various scan rates.



Supplementary Fig.16 (a) FeF₃@LLZTO simulation models with surface TFSI⁻ aggregation, (b-c) the change of charge density, surface potential and Li⁺ concentration around FeF₃@LLZTO particles through altering TFSI⁻ concentration from 0.05 to 0.95 M .



Supplementary Fig.17 The relationship between CGL thickness and TFSI⁻ concentration on the FeF₃@LLZTO particle surface.

References

- [R6] Zhao, L., et al. Rationally coordinating polymer enabling effective Li-ion percolation network in composite electrolyte for solid-state Li-metal batteries, *Energy Storage Mater.* 68, 103360 (2024).
- [R7] Hang Luo, et al. Interface design for high energy density polymer nanocomposites, *Chem. Soc. Rev.* 48, 4424 (2019).
- [R8] Jin Li, et al. Enhanced interphase ion transport via charge-rich space charge layers for ultra-stable solid-state lithium metal batteries, *Adv. Energy Mater.* 15, 2402746 (2025).
- [R9] Zhang, D.F., et al. A dielectric electrolyte composite with high lithium-ion conductivity for high-voltage solid-state lithium metal batteries. *Nat. Nanotechnol.* 18(6), 602 (2023).
- [R10] Zhu Cheng,¹ Ming Liu,² Swapna Ganapathy, et al. Revealing the impact of space-charge layers on the Li-ion transport in all-solid-state batteries, *Joule* 4, 1311–1323 (2020).
- [R11] Nie, K., et al. Interfaces between cathode and electrolyte in solid state lithium batteries: Challenges and perspectives, *Front. Chem.* 6, 616 (2018).

Comment 6. The cycle performance of Li|L-FL₃₅PH|Li battery at 0.1 mA/cm² is only 600h, providing longer symmetric cell performance to evaluate the compatibility between the solid-state electrolyte and Li foil. In addition, the L@FL₃₅PH electrolyte has a high CCD value of 2.5 mA/cm², and the current density of the symmetrical battery (0.1 mA/cm²) is relatively small. The authors should provide the cycling performance of symmetric cells measured at higher current densities (at least 1 mA/cm²-1 mAh/cm²).

Response:

Following suggestion of the reviewer, we have provided the symmetric Li|L-FL₃₅PH|Li and Li|L-FL₃₅PH|Li batteries with extended cycling time and elevated

current in **Fig.3** and **Supplementary Fig.31**, and the related description has also been revised as below.

“Li|CSEs|Li symmetrical batteries have been assembled to study compatibility between solid-state electrolyte and Li foil. As illustrated in **Fig. 3d**, Li|L-L₃₅PH|Li battery shows the highest overpotential of 114 mV and fails at 40 h. In comparison, Li|L@FL₃₅PH|Li and Li|L-FL₃₅PH|Li batteries both exhibit overpotentials of 28 mV. While Li|L-FL₃₅PH|Li battery gradually increases after 40 h, due to the increased interface resistance induced by side reactions of Li anode with TFSI⁻.^[44] While Li|L@FL₃₅PH|Li battery maintains its overpotential for above 1300 h cycling. Even elevating current density to 1.0 mA/cm² with an area capacitance of 1.0 mAh/cm², the Li|L@FL₃₅PH|Li battery still operates for over 600 h (**Supplementary Fig.31**). The post-cycling SEM images reveal obvious Li dendrites in Li|L-L₃₅PH|Li battery, while their growth is constrained in Li|L-FL₃₅PH|Li battery (**Supplementary Fig.32**).”

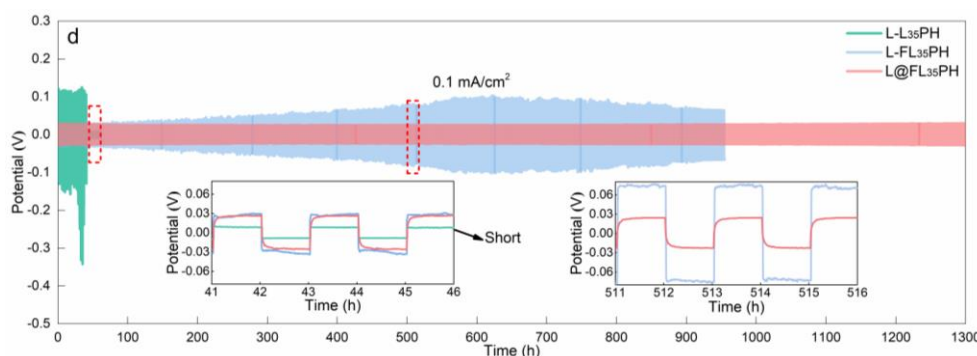
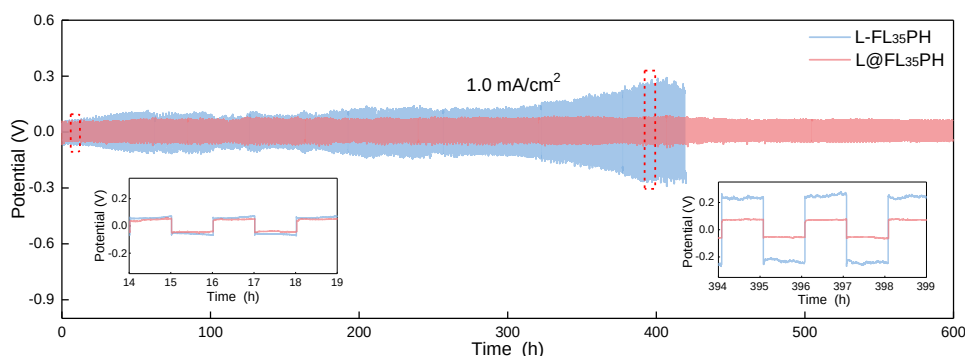
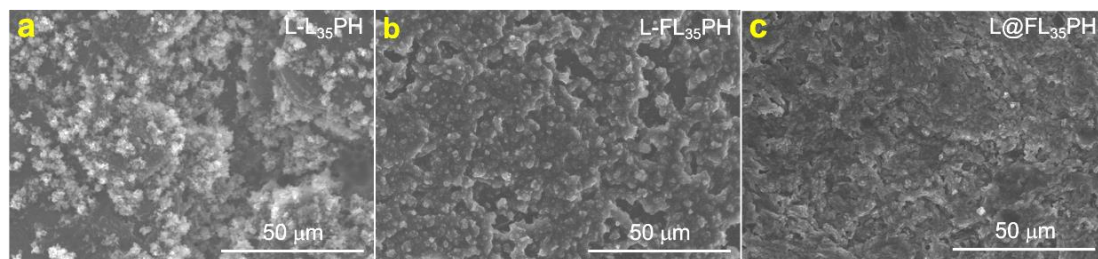


Fig.3 (d) Cycling performances of Li|CSEs|Li symmetric batteries with CSEs at 0.1 mA/cm².



Supplementary Fig.31 Cycling performances of Li|CSEs|Li symmetric batteries

with CSEs at 1.0 mA/cm².



Supplementary Fig.32 | Morphology of Li anode surface after 40 h of Li|CSEs|Li symmetrical batteries.

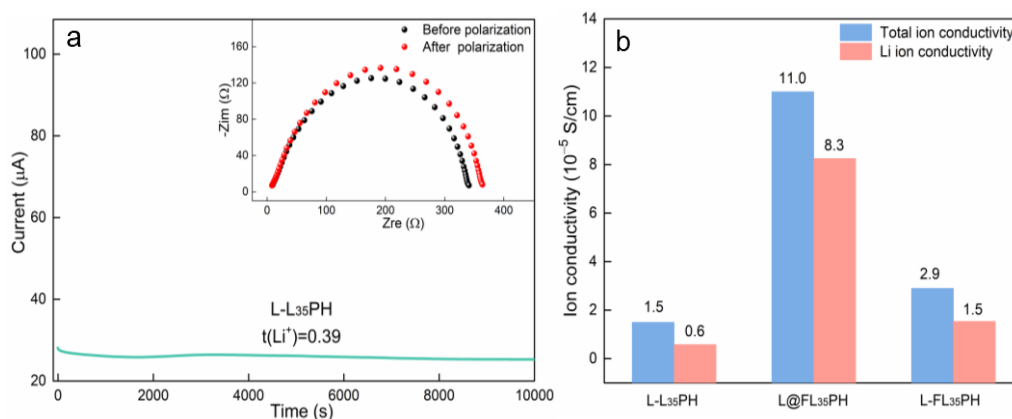
Comment 7. In the Figure 3f, the initial resistance of L-FL₃₅PH and L@FL₃₅PH is the same, but the initial polarization current is significantly different, which is obviously contradictory. Moreover, after a testing time of 600s, the polarization current cannot reach steady state at all. It is recommended to retest $t(\text{Li}^+)$ and extend the testing time (10000s).

Response:

Following the reviewer suggestion, we have retested $t(\text{Li}^+)$ and extended to 10000s as described in **Fig.3** and **Supplementary Fig.30**. The initial resistance of L-FL₃₅PH and L@FL₃₅PH is different. Here, in order to compare the charge transfer resistance before and after cycling, the impedance profiles are normalized using their initial resistance, and the corresponding discussion has also been revised as following.

“According to ion migration pathway, the sum of t_a and $t(\text{Li}^+)$ is a constant parameter equaling to 1. It is determined through Eq.2 that limiting anion movement and increasing $t(\text{Li}^+)$ prolong τ_{Sand} , thereby delaying the formation of Li dendrites. To verify this rule, the t_{Li^+} of L@FL₃₅PH, L-FL₃₅PH and L-L₃₅PH electrolytes are tested in Li|CSEs|Li symmetric batteries, as shown in **Fig.3b**. It is obvious that t_{Li^+} of L-L₃₅PH electrolyte is calculated as 0.39, shortening the time τ_{Sand} and making it difficult to inhibit the Li dendrites growth (**Supplementary Fig.30**). With FeF₃ coating on LLZTO, the migration number in L-FL₃₅PH electrolyte increases to 0.53 (**Fig.3b**), but it is still struggling to suppress Li dendrite growth at high current densities, such as 1.3 mA/cm². Through increasing the fixed TFSI⁻ on FeF₃ surface in

L@FL₃₅PH electrolyte, it promotes LiTFSI dissociation and establishes the cross-phase ion transfer channels, and thus a high Li migration number of 0.75 is obtained to extends time τ_{Sand} . This result is also in line with the corresponding trend of Li ion conductivity (Supplementary Fig.30b)”



Supplementary Fig.30 (a) Variation of current with time during polarization of a Li|L-L₃₅PH|Li symmetric battery configuration; the inset figure shows the Nyquist plots before and after polarization. (b) Total ion conductivity and Li ion conductivity of three electrolytes.

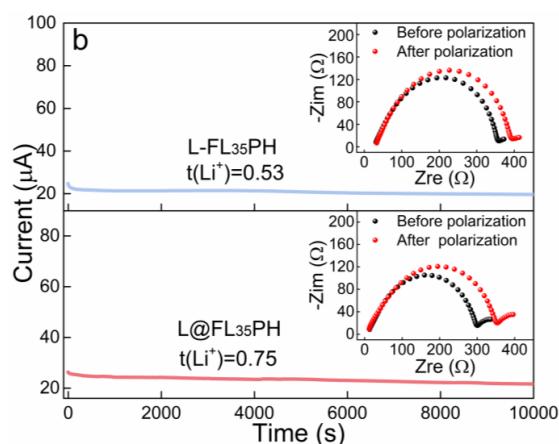


Fig.3 (b) Variation of current with time during polarization of Li|CSEs|Li symmetric batteries configuration; the inset figure shows the Nyquist plots before and after polarization.

Comment 8. Given that the loading of LFP is only about 2.0 mg/cm², please measure the cells with higher commercial loading performances (>2.0 mAh/cm²) for a more

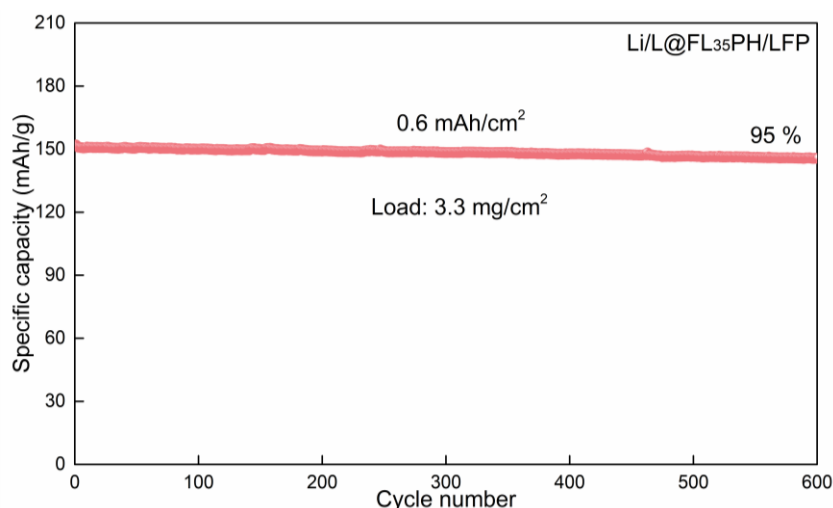
comprehensive understanding of their performance.

Response:

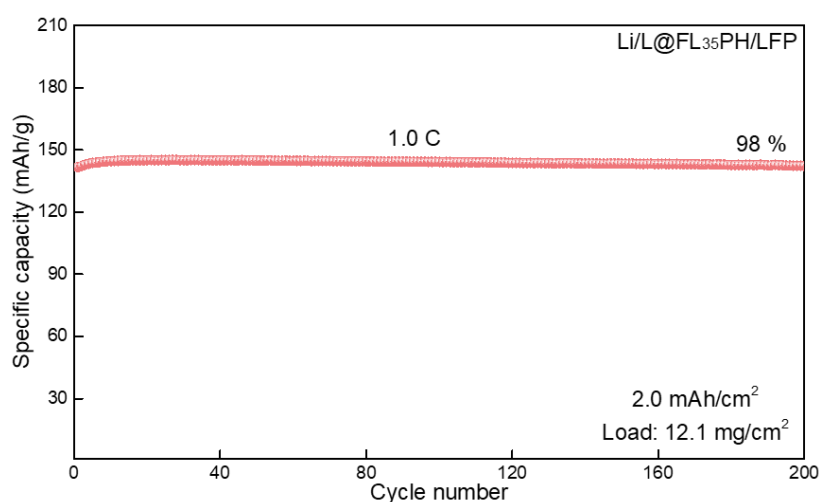
Based on the reviewer comments, the battery performance with high LFP loading has been provided in the revised manuscript, and the related discussion is also added as below.

“The electrochemical performance of Li|CSEs|LFP solid-state batteries is collected. The charge-discharge curves of three solid-state Li metal batteries at 0.5 C, as illustrated in **Fig.5a**. The discharge specific capacity of Li|L@FL₃₅PH|LFP battery reaches 159.4 mAh/g, closed to the theoretical specific capacity of LiFePO₄, and higher than the value 147.3 mAh/g of Li|L-FL₃₅PH|LFP battery and the 139.5 mAh/g of Li|L-L₃₅PH|LFP battery. As demonstrated in **Fig.5b**, the Li|L-L₃₅PH|LFP battery exhibited a larger polarization voltage, attributing to the presence of Li₂CO₃ on the LLZTO surface, which is in consistent with lithium deposition/stripping results. **Figs.5c, d** displayed the rate charge-discharge curves and rate performance of Li|CSEs|LFP batteries. At 0.5, 1.0, 1.5, 2.0 and 3.0 C rates, the reversible capacity values of Li|L@FL₃₅PH|LFP battery were 159.4 mAh/g, 152.8 mAh/g, 140.3 mAh/g, 133.5 mAh/g and 121.4 mAh/g, respectively, significantly higher than Li|L-FL₃₅PH|LFP and Li|L-L₃₅PH|LFP batteries. With increasing rates, the discharge specific capacity of Li|L@FL₃₅PH|LFP and Li|L-FL₃₅PH|LFP batteries exhibited similar attenuation amplitudes. But when the rate was decreased back to 0.5 C, the discharge specific capacity of Li|L-FL₃₅PH|LFP battery could not recover its initial level. This result indicated that the Li|L@FL₃₅PH|LFP battery possesses better rate performance. After 600 cycles, compared to the initial capacity of 152.8 mAh/g, the Li|L@FL₃₅PH|LFP battery retains 96% capacity, much higher than 71% of the Li|L-FL₃₅PH|LFP battery. To further validate the feasibility of practical application of L@FL₃₅PH electrolyte, we increased the loading of LFP to 3.3 mg/cm² (0.6 mAh/cm²), and the initial capacity of Li|L@FL₃₅PH|LFP battery is 152.0 mAh/g at 1.0 C. After 600 cycles, compared to the initial capacity, retains 95% capacity (**Supplementary Fig.36**). When the LFP loading is further increased up to 12.1

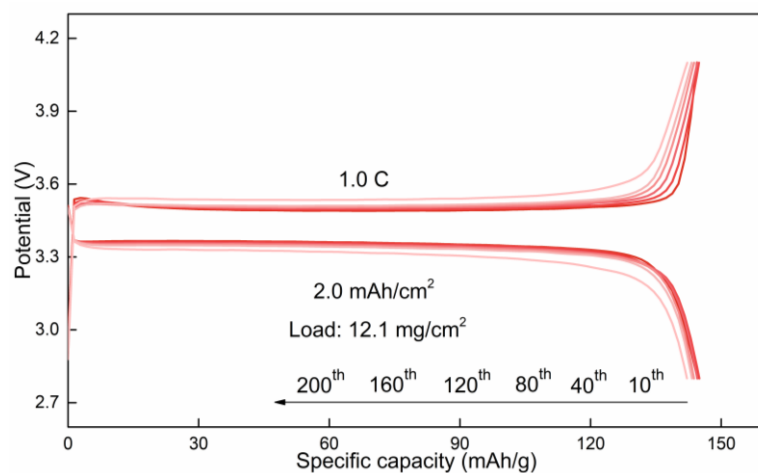
mg/cm² (2.0 mAh/cm²), the Li|L@FL₃₅PH|LFP battery still gives a specific capacity of 144.6 mAh/g at 1.0 C, and the capacity retention rate maintains 98% after 200 cycles (**Supplementary Figs.37-38**). At the same time, after subjected to high rate (3.0 C) charging and discharging, it exhibits still a good rate recovery performance (**Supplementary Figs.39-40**). Due to uneven particle dispersion and poor interface compatibility, the Li|L-L₃₅PH|LFP battery quickly experiences a short circuit.”



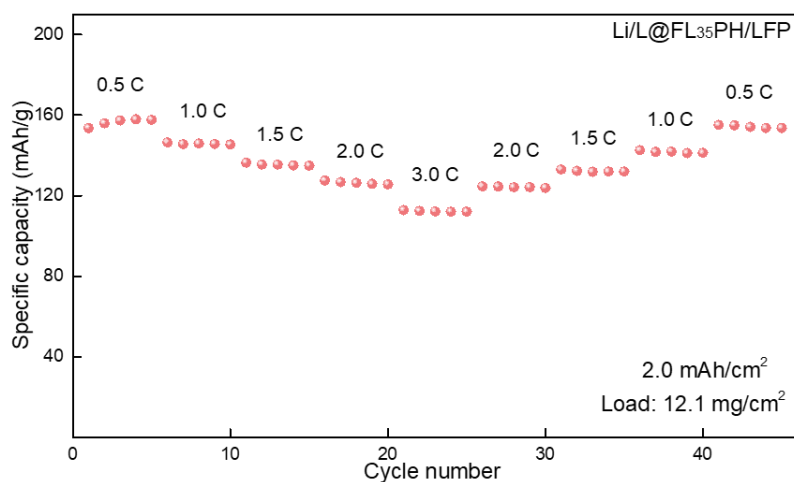
Supplementary Fig.36 The cycling performance of Li|CSEs|LFP batteries at 1.0 C with 0.6 mAh/cm².



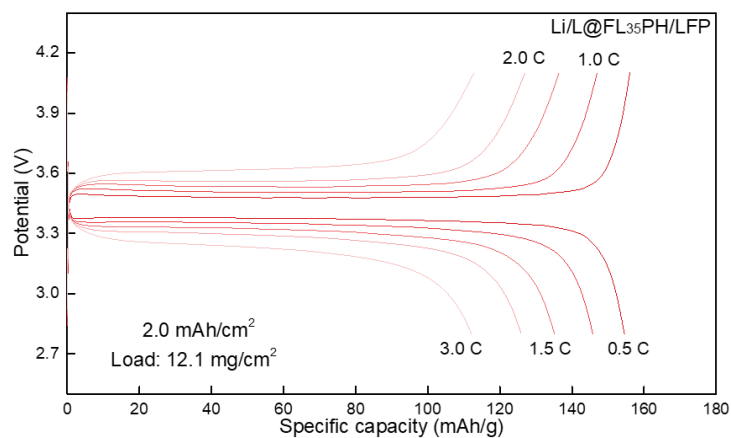
Supplementary Fig.37 The cycling performance of Li|L@FL₃₅PH|LFP batteries at 1.0 C with 2.0 mAh/cm².



Supplementary Fig.38 | Galvanostatic discharge/charge voltage profiles of Li|L@FL₃₅PH|LFP batteries with 2.0 mAh/cm².



Supplementary Fig.39 | The rate performance of Li|L@FL₃₅PH|LFP batteries.



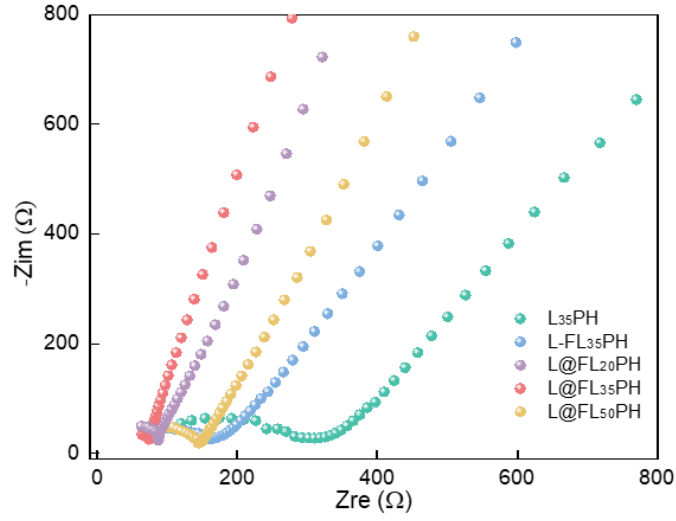
Supplementary Fig.40 | Galvanostatic discharge voltage profile of Li|L@FL₃₅PH|LFP batteries at different rates.

Comment 9. Why choose 35% FeF₃@LLZTO in L@FL₃₅PH sample as a proportion of composition? The relevant optimization and characterization data seem to lack specific explanations. In addition, the L@FL₂₀PH and L@FL₅₀PH samples mentioned in the experimental section have no relevant data in the entire text, and the purpose and significance of their settings are not reflected.

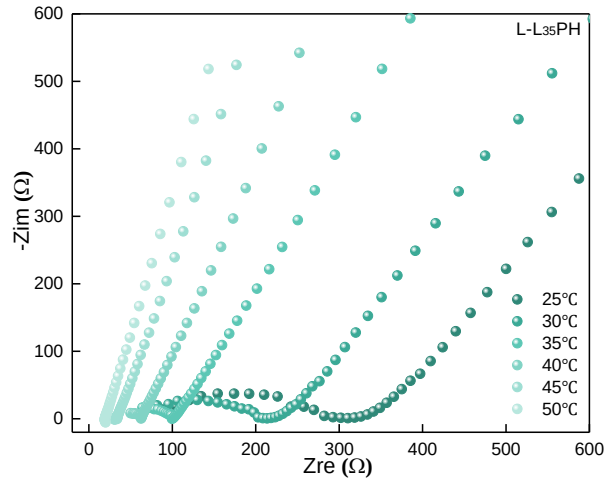
Response:

Thank the reviewer for the comments regarding the content ratio of the inorganic additives. To identify its influence on battery performance, the content has been altered as 20wt.%, 35wt.% or 50wt.% during the stepwise mixing method for CSEs preparation, and they are noted as L@FL₂₀PH, L@FL₃₅PH and L@FL₅₀PH, respectively. By comparing the results of ionic conductivity, the L@FL₃₅PH containing 35wt.% FeF₃@LLZTO has been screened as the targeting electrolyte. Its ionic conductivity was measured as 1.1×10^{-4} S/cm, which is higher than 5.3×10^{-5} S/cm of L@FL₂₀PH and 6.3×10^{-5} S/cm of L@FL₅₀PH (**Supplementary Fig.20**). The results and discussion clarifying the performance variation induced by FeF₃@LLZTO contents have been provided in the revised manuscript as below.

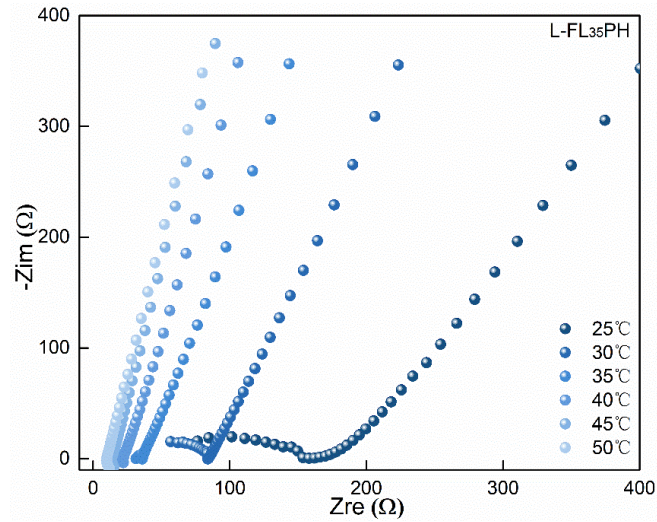
“Then, the influence of TFSI⁻ adsorption concentration on electrochemical performance of CSEs is investigated using Nyquist plots. At room temperature, L@FL₃₅PH with 35wt.% FeF₃@LLTZO content is measured with ion conductivity of 1.1×10^{-4} S/cm, which is one order higher than 5.3×10^{-5} S/cm of L@FL₂₀PH (20 wt.% FeF₃@LLTZO content), 6.3×10^{-5} S/cm of L@FL₅₀PH (50 wt.% FeF₃@LLTZO content), 2.9×10^{-5} S/cm of L-FL₃₅PH and 1.5×10^{-5} S/cm of L-L₃₅PH (**Supplementary Fig.20**). Further analysis on CSEs using electrochemical impedance spectroscopy (EIS) at various temperature from 25 to 50 °C is conducted for calculating Li⁺ diffusion energy barrier (E_a , **Supplementary Figs.21-23**). E_a value of L@FL₃₅PH is measured as 0.35 eV (**Fig.3a**), which is lower than 0.73 eV of L-FL₃₅PH and 1.04 eV of L-L₃₅PH (**Supplementary Fig.24**).”



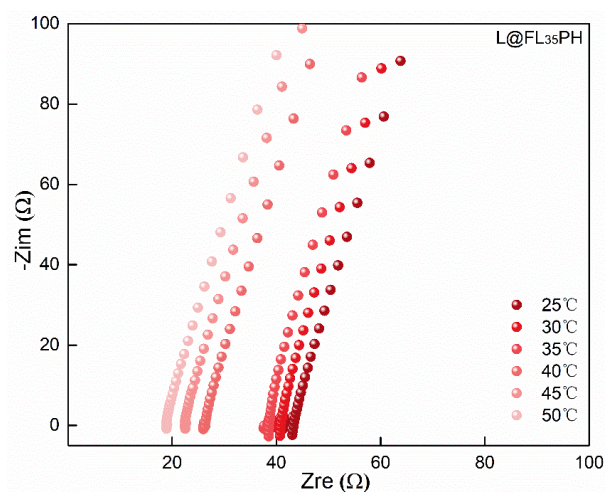
Supplementary Fig.20 | Nyquist plots of SS|CSEs|SS batteries at room temperature.



Supplementary Fig.21 | Nyquist plots of SS|L-L₃₅PH|SS battery at 25-50°C.



Supplementary Fig.22 | Nyquist plots of SS|L-FL₃₅PH|SS battery at 25-50°C.



Supplementary Fig.23 Nyquist plots of SS|L@FL₃₅PH|SS battery at 25-50°C.

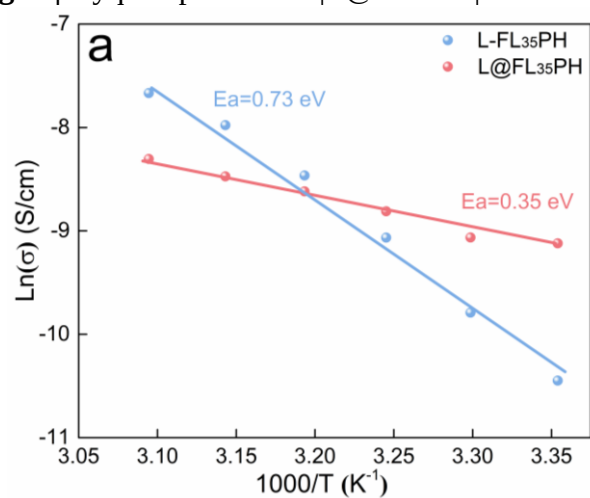
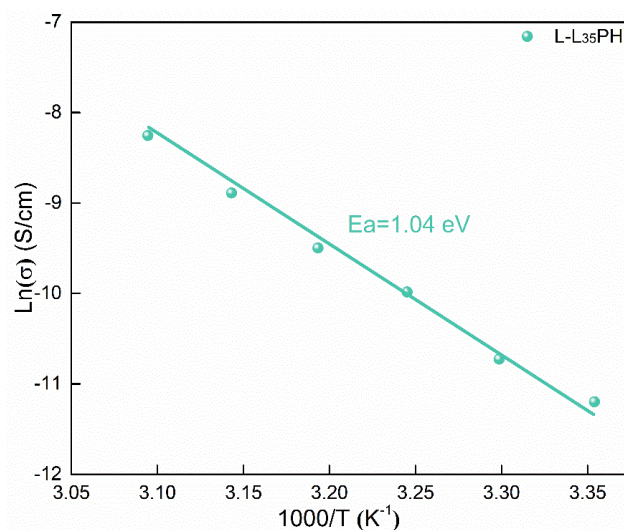


Fig.3 (a) Arrhenius plots of the ionic conductivities of the CSEs at 25°C-50°C.



Supplementary Fig.24 Arrhenius plot of the ionic conductivities of L-L₃₅PH electrolyte at 25-50°C.

Comment 10. There are multiple writing errors in the article, such as “CCD test”

being replaced by “GCD test” and confusion in the annotations in Figure 3d. The article uses “EDS”, while the supplementary materials (SI) use “EDX”. It is recommended that the article and supplementary materials remain consistent and provide the full name when the abbreviation first appears.

Response:

Thank you very much for your comments. The above-mentioned writing errors have been carefully checked and corrected, and we have also carefully checked typos and grammar errors throughout the revised manuscript.

For Reviewer #2:

This work developed a FeF_3 coating on the surface of LLZTO powder via the sol gel method, with the goal of promoting LiTFSI dissociation and forming TFSI⁻ aggregation layer in the LiTFSI/PVDF-HFP composite solid electrolyte. Because of the lack of the discussion about residual DMF solvent, the results of LiTFSI/PVDF-HFP composite solid electrolyte are not sufficient.

The following should be involved in the manuscript:

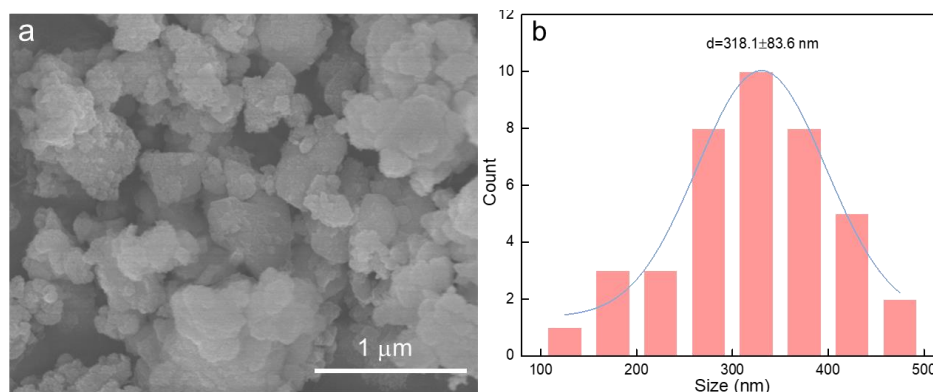
1) Line 490 in the text, “Disperse 500 mg of LLZTO in 20 mL of distilled water,”

Is LLZTO powder a commercial material? The particle size and surface state of LLZTO need to be supplemented in the experimental methods.

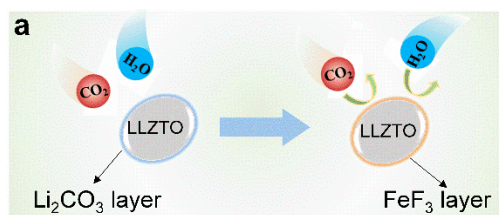
Response:

Thank you very much for your comments. LLZTO powder is a commercial material without further treatment. Following the suggestion, its particle size and surface state of LLZTO have been provided in **Supplementary Fig.1** and the Supporting Information.

“LLZTO particle sizes ranging from 100-500 nm and a rough surface (**Supplementary Fig.1**). As shown in **Supplementary Fig.2**, LLZTO would spontaneously form a layer of Li_2CO_3 on its surface when exposed to air and in contact with CO_2 and H_2O .”



Supplementary Fig.1| (a) SEM and (b) particle size distribution of LLZTO powder



Supplementary Fig.2| (a) Optical photos and schematic diagrams of LLZTO and FeF₃@LLZTO powders

2) Line 498-500 in the text, “Firstly, adding 90 mg (20%), 190 mg (35%) and 360 mg (50%) FeF₃@LLZTO powder was respectively mixed with 60 mg LiTFSI in 2 mL DMF, and dried at 60 °C to obtain LiTFSI@FeF₃@LLZTO powders; then dispersed into a mixed solution of 300 mg PVDF-HFP and 6 mL DMF with magnetic stirring for 12 h.”

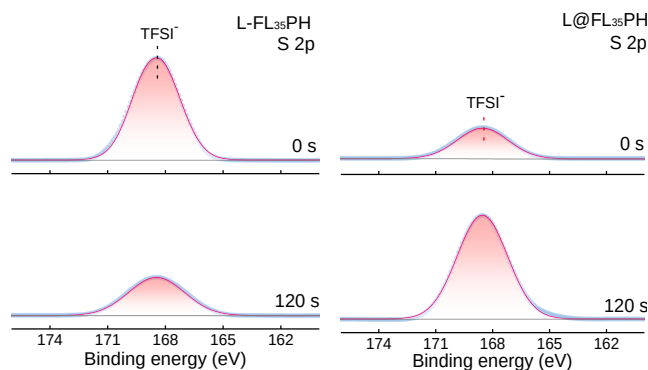
The residual amount of DMF solvent in two kinds of LiTFSI/PVDF-HFP composite solid electrolyte should be determined with DSC analysis, whether DMF residues in L@FL₃₅PH is higher than in L-L₃₅PH.

Response:

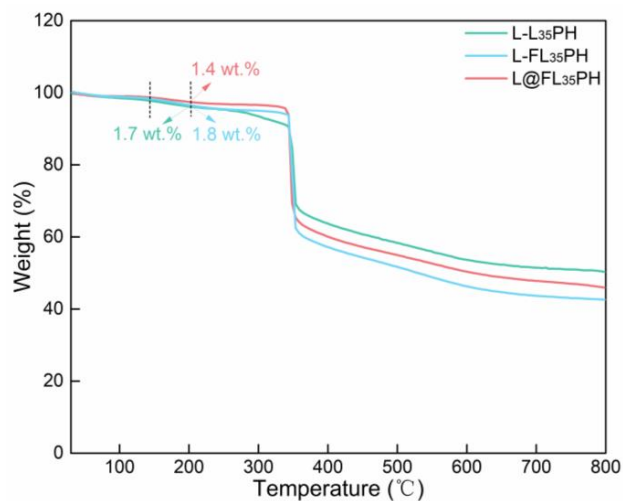
To address comment of the reviewer, the differential scanning calorimetry (DSC) measurements combined with thermogravimetric analysis testing (TGA) have been conducted to identify the DMF residues as shown in **Supplementary Fig.11**. TGA curve shows the slight weight loss of L-L₃₅PH, L-FL₃₅PH and L@FL₃₅PH electrolytes before 140 °C is ascribed to the captured moisture, and the evaporation of residual DMF solvent occurs at 140-200 °C. The DSC curve shows that the melting temperature (T_m) of PVDF-HFP in L@FL₃₅PH, L-FL₃₅PH and L-L₃₅PH appears at 147 °C, and no additional absorption peaks were observed (**Supplementary Fig.12**). Therefore, the weight loss of L@FL₃₅PH (1.4 wt.%) at 140-200 °C is mostly the evaporation of residual DMF, lower than 1.8 wt.% of L-FL₃₅PH. The related discussion has been added in the revised manuscript as following.

“The intensity ratio of TFSI⁻/C-N in L@FL₃₅PH electrolyte is about 2.78, higher

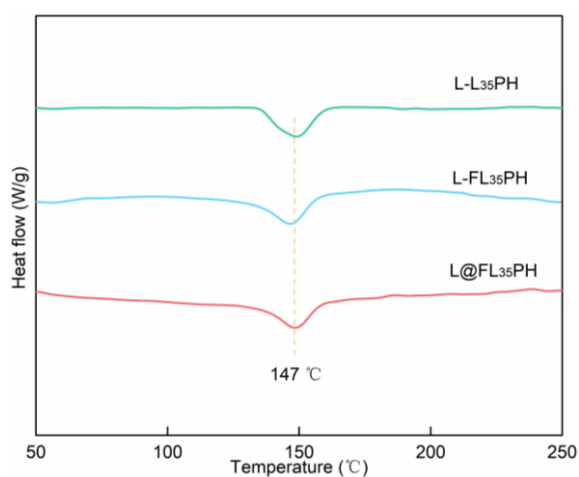
than 0.87 of L-FL₃₅PH electrolyte. It is associated with higher residual DMF and TFSI⁻ concentrations on the FeF₃@LLZTO surface, which coincides with S 2p spectra (**Supplementary Fig.10**) and thermogravimetric analysis testing (TGA) results (**Supplementary Fig.11**). After Ar etching, the intensity of TFSI⁻ peak at 168.3 eV in S 2p spectra increases for L@FL₃₅PH electrolyte, while it alleviates for L-FL₃₅PH electrolyte. It indicates the TFSI⁻ accumulation on FeF₃@LLZTO surface in L@FL₃₅PH electrolyte. Meanwhile, the slight weight loss of the three CSEs before 140 °C is ascribed to evaporation of moisture and residual DMF solvent between 140 °C and 200 °C.^[31] The differential scanning calorimetry (DSC) curve indicates that the melting temperature (*T_m*) of PVDF-HFP in L@FL₃₅PH, L-FL₃₅PH and L-L₃₅PH at 147 °C, without additional absorption peak (**Supplementary Fig.12**). Therefore, the weight loss of L@FL₃₅PH (1.4 wt.%) is close to 1.8 wt.% of L-FL₃₅PH and 1.7 wt.% of LiTFSI-35wt.%LLZTO/PVDF-HFP (L-L₃₅PH). FTIR spectroscopic results demonstrate that the presence of DMF-related free -N-C=O bonds is absent in L@FL₃₅PH and L-FL₃₅PH electrolytes, indicating that the residual DMF was all bound to Li⁺ and there were no free DMF molecules(**Supplementary Fig.13**).^[32] The strong Li⁺-DMF interaction hinders complete DMF evaporation.^[32] The signal peak associated with LiTFSI in the crystalline state is observed at 647 cm⁻¹ for L-FL₃₅PH electrolyte, suggesting some LiTFSI residues. In comparison, the weight loss of L@FL₃₅PH in the range of 200 and 300°C is smaller, owing to its lower TFSI⁻ composition.”



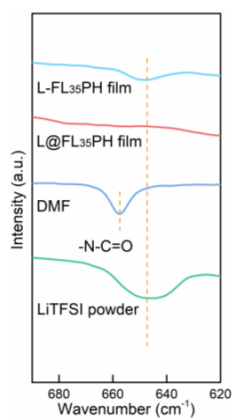
Supplementary Fig.10 | S 2p spectra of L-FL₃₅PH and L@FL₃₅PH electrolytes.



Supplementary Fig.11| TGA curves of L-L₃₅PH, L-FL₃₅PH and L@FL₃₅PH electrolytes.



Supplementary Fig.12| DSC curves of L-L₃₅PH, L-FL₃₅PH and L@FL₃₅PH electrolytes.



Supplementary Fig.13| FTIR spectra of different samples

3) Line 533-541 in the text, “NMC811 and LFP cathodes were prepared using a slurry casting technique. Active material, Super P carbon as a conductive additive and polyvinylidene fluoride were dissolved in N-methyl-2-pyrrolidone with a weight ratio of 8:1:1 to make a slurry and then coated onto a current collector of aluminium foil. The cathodes were dried in a vacuum oven at 110 °C for 12 h. The active loading density of the LFP cathode was 2.0 mg/cm².”

The assembly method of the battery should be described clearly, especially whether liquid electrolyte existed at the cathode interface.

Response:

Thank you very much for your comments. The battery assembly method has been provided in the experimental section of the revised Supporting Information as below.

“The cathode was cut into circular discs with a diameter of 12 mm, and placed at the center of the positive electrode shell. and then sequentially place the composite solid electrolyte membrane, lithium foil, gasket, spring plate, and negative electrode shell. All coin cells were assembled in an argon-filled glove box. During the assembly process, 2 μL (1 M LiTFSI in FEC) was added to the interface between solid electrolyte and electrode to ensure sufficient electrode wetting. All the cells were tested by LAND measurement system within a voltage range of 2.8-4.1 V (LFP) or 2.8-4.3 V (NCM811) at room temperature.”

4) Line 147-151 in the text, “ The C-N peak at 403.7 eV in N 1s spectra represent the residual DMF solvent, while peak at 399.3 eV is attributed to TFSI⁻. Their intensity ratio of TFSI⁻/C-N in L@FL₃₅PH electrolyte was about 2.78, higher than 0.87 of L-FL₃₅PH electrolyte, further proving that the stepwise mixing method could more effectively exert the adsorption effect of FeF₃ on TFSI⁻”.

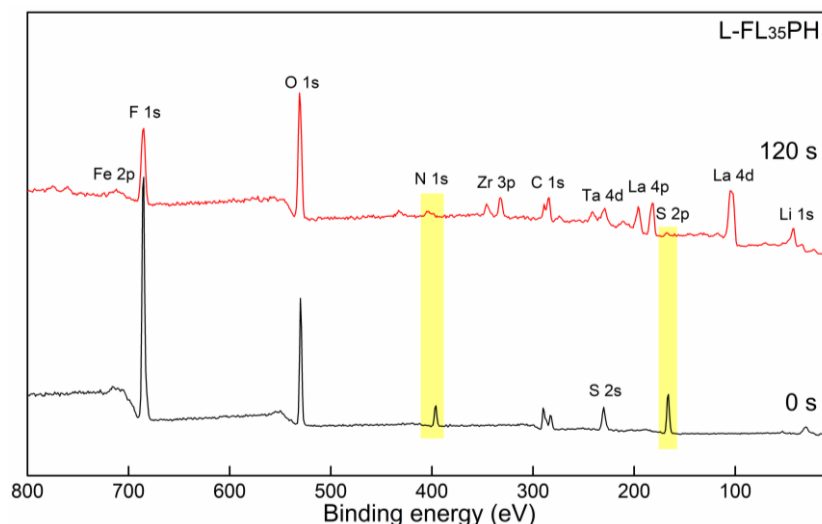
The author should be noticed that more DMF residue in L-FL₃₅PH leads to an increase of C-N intensity, and then reducing the intensity ratio of TFSI⁻/C-N.

Response:

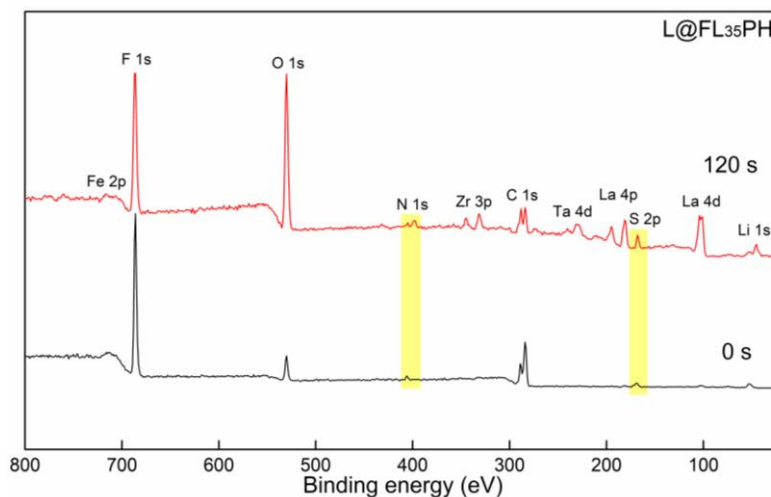
We agree with the reviewer regarding C-N intensity in XPS spectra. The integral area of O=C-N feature associated with DMF in L-FL₃₅PH electrolyte is higher than that of L@FL₃₅PH electrolyte, indicating its more DMF residue. It is also reflected by the TGA and DSC analysis showing 1.8 wt.% DMF residue in L-FL₃₅PH electrolyte, while it is 1.4 wt.% for L@FL₃₅PH electrolyte. The more DMF residue leads to the increased C-N intensity, and the reduced ratio of TFSI⁻/C-N intensities. However, the full spectra illustrate increasing intensity of N 1s and S 2p peaks following collecting depth of L@FL₃₅PH electrolyte, whereas L-FL₃₅PH shows the reverse trend (**Supplementary Figs.8-9**). The result suggests TFSI⁻ gathering on FeF₃@LLZTO surface in L@FL₃₅PH electrolyte, while TFSI⁻ in L-FL₃₅PH electrolyte is predominantly dispersed within PVDF-HFP matrix. This can also reduce the intensity ratio of TFSI⁻/C-N in L-FL₃₅PH electrolyte. Therefore, their intensity ratio of TFSI⁻/C-N in L@FL₃₅PH electrolyte is about 2.78, higher than 0.87 of L-FL₃₅PH electrolyte, which is associated with higher residual DMF and TFSI⁻ concentrations on the FeF₃@LLZTO surface. The above description has been added into the revised manuscript as bellow.

“The variation in TFSI⁻ concentration gradient from surface to bulk between L-FL₃₅PH and L@FL₃₅PH could be further reflected in high-resolution C 1s spectra (**Figs.1e, f**), covering C-F species at 291.8 eV attributed to LiTFSI and PVDF-HFP, C-C/C-H peak at 284.8 eV of PVDF-HFP, and C-S peak at 289.7 eV of TFSI⁻.^[26] At the bulk region, O=C-N species appears at 286.4 eV, as evident for residual DMF solvent in L@FL₃₅PH.^[27] Comparing to L-FL₃₅PH, the intensity ratio of C-F/C-C in L@FL₃₅PH increases from surface to bulk, and the increase in C-S/C-C ratio is much larger than that of the L-FL₃₅PH electrolyte. The result validates that the TFSI⁻ is immobilized on FeF₃@LLZTO particles surface via the stepwise mixing method. The C-N peak at 403.7 eV in N 1s spectra represents the residual DMF solvent, while the peak at 399.3 eV is attributed to TFSI⁻.^[28-29] After being etched for 120 s, the Fe-N

signal is detected at 400.2 eV for the both electrolyte membranes, resulting in the suppressed TFSI⁻ desorption from FeF₃ layer.^[30] The intensity ratio of TFSI⁻/C-N in L@FL₃₅PH electrolyte is about 2.78, bigger than 0.87 of L-FL₃₅PH electrolyte. It associates with higher residual DMF and TFSI⁻ concentrations on the FeF₃@LLZTO surface, which coincides with S 2p spectra (**Supplementary Fig.10**) and thermogravimetric analysis testing (TGA) results (**Supplementary Fig.11**). After Ar etching, the intensity of TFSI⁻ peak at 168.3 eV in S 2p spectra increases for L@FL₃₅PH electrolyte, while it alleviates for L-FL₃₅PH electrolyte. It indicates the TFSI⁻ accumulation on FeF₃@LLZTO surface in L@FL₃₅PH electrolyte. Meanwhile, the slight weight loss of the three CSEs before 140 °C is ascribed to evaporation of moisture and residual DMF solvent between 140 and 200 °C.^[31] The differential scanning calorimetry (DSC) curve illustrates that the melting temperature (T_m) of PVDF-HFP in L@FL₃₅PH, L-FL₃₅PH and L-L₃₅PH at 147 °C, without additional absorption peak (**Supplementary Fig.12**). Therefore, the weight loss of L@FL₃₅PH (1.4 wt.%) is close to 1.8 wt.% of L-FL₃₅PH and 1.7 wt.% of LiTFSI-35wt.%LLZTO/PVDF-HFP (L-L₃₅PH).”



Supplementary Fig.8| XPS spectra of L-FL₃₅PH electrolyte before and after etching.



Supplementary Fig.9 | XPS spectra of L@FL₃₅PH electrolyte before and after etching.

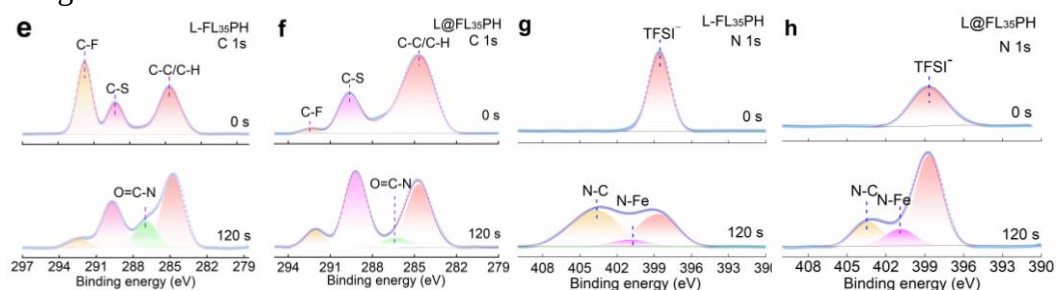
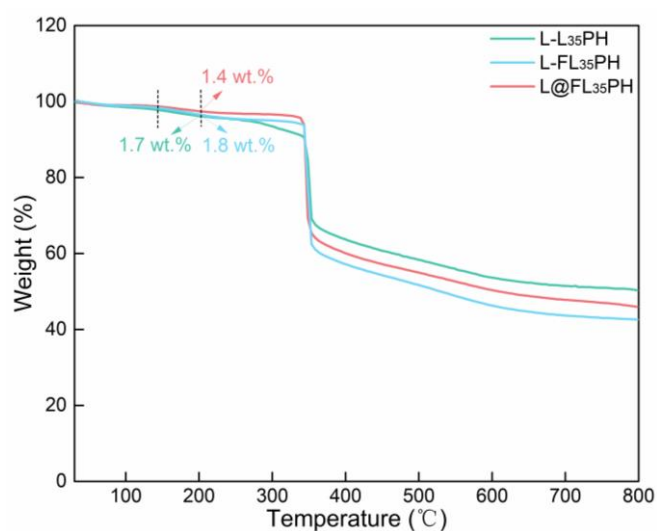
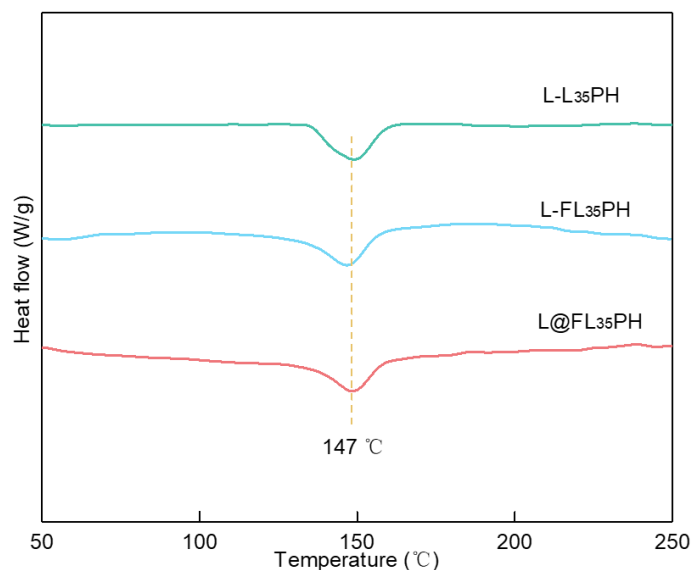


Fig.1 (e-f) C 1s and (g-h) N 1s spectra of L-FL₃₅PH and L@FL₃₅PH before and after etching.



Supplementary Fig.11 | TGA curves of L-L₃₅PH, L-FL₃₅PH and L@FL₃₅PH electrolytes.



Supplementary Fig.12 DSC curves of L-L₃₅PH, L-FL₃₅PH and L@FL₃₅PH electrolytes.

5) Line 339-343 in the text, “The results demonstrated that lithium anode surfaces matched with both electrolytes form dense and uniform SEI components, enriched with LiF_2^- and LiS^- . However, the lithium anode surface matched with L-FL₃₅PH electrolyte led to thick SEI, which is unfavorable for interface impedance.”

It should be discussed the reason of no TFSI⁻ peak in the XPS of L@FL₃₅PH.

Response:

Following the reviewer suggestion, the absence of TFSI⁻ peak in XPS spectra of L@FL₃₅PH is due to the uneven TFSI⁻ distribution gathering on FeF₃@LLZTO surface. This also coincides with 3D reconstruction results of TOF-SIMS (**Fig.4**) showing low TFSI⁻ content on anode surface. The corresponding discussion has been provided in the revised manuscript as following.

“The surface composition of CSEs after 40th cycles is analyzed by XPS. As shown in **Fig.4a**, F 1s spectra appear a signal peak at 687.9 eV corresponding to C-F bond for PVDF-HFP and LiTFSI in both L@FL₃₅PH and L-FL₃₅PH, while LiF peak at 684.8 eV is primarily associated with TFSI⁻ decomposition.^[46] It is evident that is hindered for decomposition on cathodes or anodes in the lower LiF content of

L@FL₃₅PH, which is attributed to the adsorbed TFSI⁻. In N 1s spectra (**Fig.4b**), two peaks ascribed to TFSI⁻ and N-SO₄ are detected at 399.7 eV and 398.8 eV, as the result of TFSI⁻ decomposition.^[28] Similarly, two peaks at 167.2 eV and 165.4 eV in S 2p spectra are related to TFSI⁻ and N-SO₄ (**Fig.4c**), respectively. While the weakening intensity of N-SO₄ peak also reveals TFSI⁻ decomposition.^[47-48] The TFSI⁻ signal of L@FL₃₅PH electrolyte is absent on surface, due to its adsorption on the FeF₃@LLZTO surface. With continuously decomposing TFSI⁻, its concentration at Li anode surface decreases. The peak at 162.1 eV ascribed to Li₂S is collected after decomposing TFSI⁻.^[16] Such result reflects that a thicker SEI layer is established between L-FL₃₅PH electrolyte and Li anode, resulting in interface polarization, lithium dendrite amplification, leading to secondary reactions and cycle life shortening.^[49-50] Thus, fixing TFSI⁻ is a feasible strategy to suppress Li dendrites.

After 40 h cycling, blueshift of S-N bond from 770 cm⁻¹ to 776 cm⁻¹ is observed in FTIR spectra of L-FL₃₅PH, reflecting its enhanced bonding strength. It is ascribed to be aggregation of N-SO₄ after TFSI⁻ decomposition. In contrast, S-N bond almost maintains its position in L@FL₃₅PH, followed by anions migration towards Li anode surface. The time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis reveals chemical evolution of anode during SEI formation (**Fig.4e, f, Supplementary Fig.34**). LiF₂⁻ and LiS⁻ signals in L@FL₃₅PH electrolyte accumulated on the intermediate stage after 25 s sputtering, whereas it is within 100 s time for L-FL₃₅PH. The results indicate that SEI thickness formed on Li anode matches with L@FL₃₅PH electrolyte and is thinner than that with L-FL₃₅PH electrolyte. Furthermore, the intensity of LiS⁻ signal also reflects the aggregated TFSI⁻ decomposition in L-FL₃₅PH electrolyte. The 3D reconstruction in **Fig.4d** reveals the depth distribution of LiF₂⁻, LiS⁻ and NSO₄⁻ fragments. The dense and uniform SEI components is demonstrated on Li anode for the two electrolytes, while L@FL₃₅PH enriches with LiF₂⁻ and LiS⁻. NSO₄⁻ fragments in comparison to L-FL₃₅PH. It further confirms the aggregation of TFSI⁻ species Li anode. The ionic conductivity of LiF at room temperature is measured as 6×10⁻⁸ S/cm calculated by the Nyquist plot (**Supplementary Fig.35**),

indicating that LiF species and thick SEI hinder ion transport.”

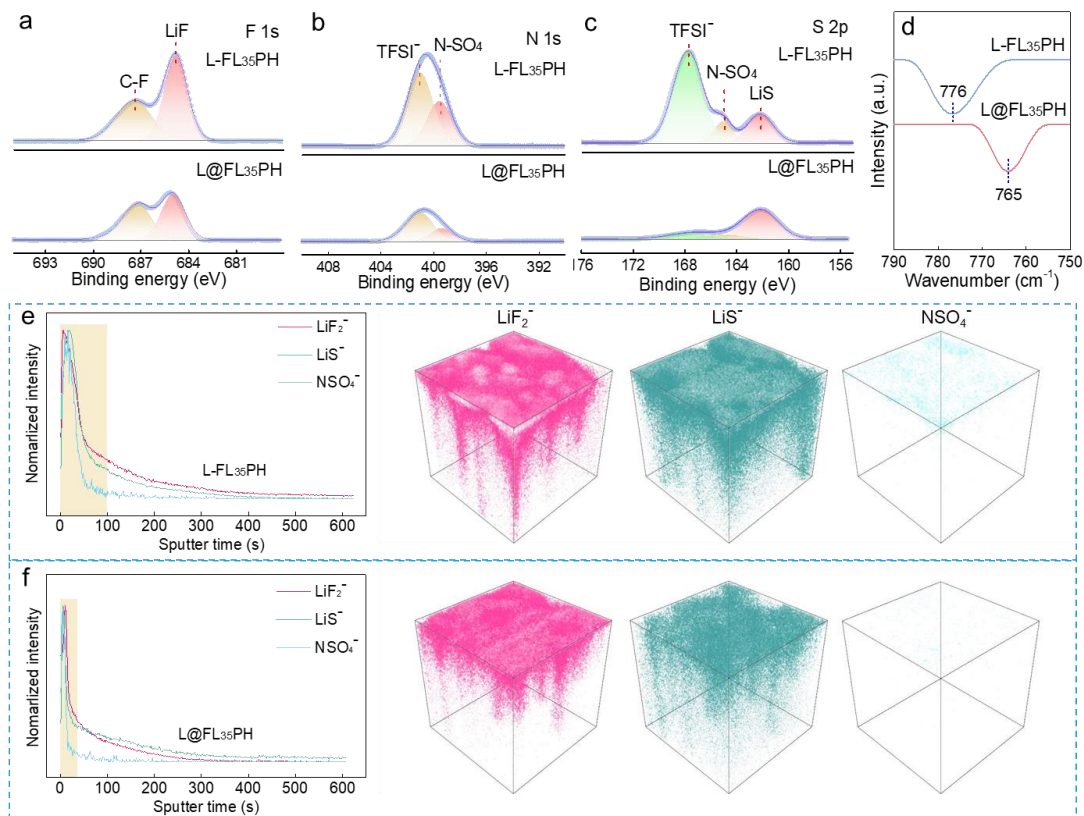
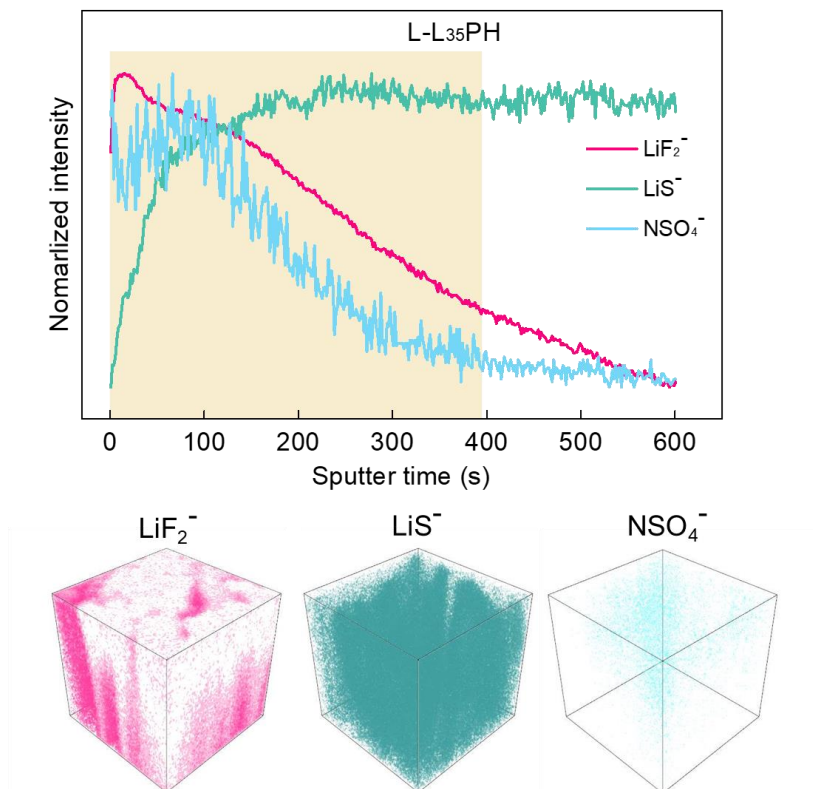
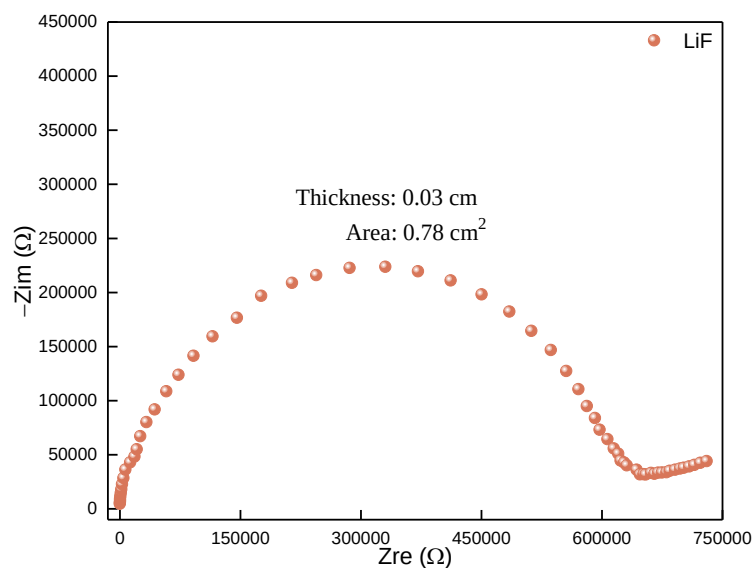


Fig.4 Composition analysis of CSEs and lithium anode surfaces after Li|CSEs|Li cycling for 40 h. XPS profiles of (a) F 1s, (b) N 1s and (c) S 2p, (d) FTIR spectra (e-f) ToF-SIMS depth profiles, with the 3D views of LiF₂⁻, LiS⁻ and NSO₄⁻ in L-FL₃₅PH and L@FL₃₅PH after 40 h.



Supplementary Fig.34 | ToF-SIMS depth profile, with the 3D view of LiF_2^- , LiS^- and NSO_4^- in L-L35PH electrolyte after 40 h



Supplementary Fig.35 | Nyquist plots of SS|LiF|SS batteries at room temperature.

6) Line 92-94 in the text, “This method encounters difficulties in TFSI^- absorption onto FeF_3 particles, which is primarily due to high viscosity and the presence of solid-liquid interface energy.[20] ”

This reference have no any discussions about LiTFSI.

Response:

Thank you very much for your comments. Although the aforementioned reference has not provided discussions about LiTFSI, it demonstrates changes in cation and anion diffusion of LiFSI under electrolytes with different viscosities. The higher viscosities increase proportion of ionic clusters, cation-anion binding strength, but decrease the ion-diffusion coefficient within electrolyte. In addition to the review comment, new references have been cited, including ChemSusChem, 11 3512–3523 (2018). These references clarify the ion dynamics study on TFSI[−] using neutron scattering and dielectric spectroscopy, and demonstrate the increasing electrolyte viscosity as hindrance for ion diffusion, which consistent with the literature results [Angew. Chem. Int. Ed. 62, e2023053 (2023)] .

7) Effect of the differences about DMF residues in the two kinds of CSE film should be discussed

Response:

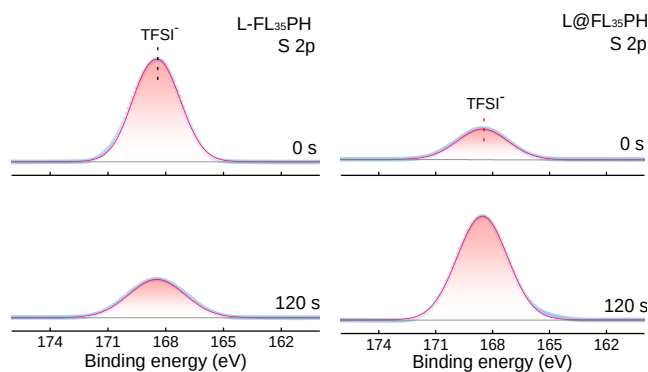
Following the reviewer comment, the TGA and DSC analysis has been conducted to investigate DMF residue. Its content is quantified as around 1.8 wt.% of L-FL₃₅PH and L@FL₃₅PH, and it is higher than 1.4 wt.% of L@FL₃₅PH. DMF residuals generate ionic [Li(DMF)_x]⁺ complexes, which promote ionic conductivity and Li⁺ migration through polymer chain segments. While these complexes hinder complete vaporization of DMF solvent that tends to decompose at high voltage and aggravate interfacial side reactions between electrolyte and Li anode. In response to the above discussion, DMF residuals and their impact on CSEs have been discussed in the revised manuscript as below.

“The intensity ratio of TFSI[−]/C-N in L@FL₃₅PH electrolyte is about 2.78, higher than 0.87 of L-FL₃₅PH electrolyte. It is associated with higher residual DMF and TFSI[−] concentrations on the FeF₃@LLZTO surface, which coincides with S 2p

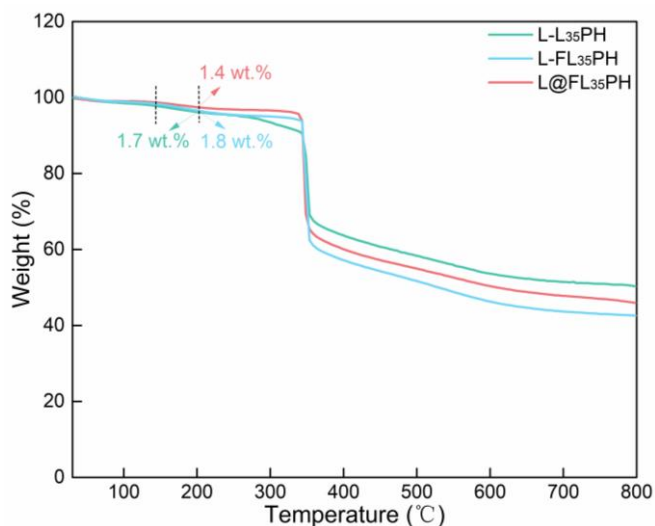
spectra (**Supplementary Fig.10**) and thermogravimetric analysis testing (TGA) results (**Supplementary Fig.11**). After Ar etching, the intensity of TFSI⁻ peak at 168.3 eV in S 2p spectra increases for L@FL₃₅PH electrolyte, while it alleviates for L-FL₃₅PH electrolyte. It indicates the TFSI⁻ accumulation on FeF₃@LLZTO surface in L@FL₃₅PH electrolyte. Meanwhile, the slight weight loss of the three CSEs before 140 °C is ascribed to evaporation of moisture and residual DMF solvent between 140 °C and 200 °C.^[31] The differential scanning calorimetry (DSC) curve indicates that the melting temperature (T_m) of PVDF-HFP in L@FL₃₅PH, L-FL₃₅PH and L-L₃₅PH at 147 °C, without additional absorption peak (**Supplementary Fig.12**). Therefore, the weight loss of L@FL₃₅PH (1.4 wt.%) is close to 1.8 wt.% of L-FL₃₅PH and 1.7 wt.% of LiTFSI-35wt.%LLZTO/PVDF-HFP (L-L₃₅PH). FTIR spectroscopic results demonstrate that the presence of DMF-related free -N-C=O bonds is absent in L@FL₃₅PH and L-FL₃₅PH electrolytes, indicating that the residual DMF was all bound to Li⁺ and there were no free DMF molecules(**Supplementary Fig.13**).^[32] The strong Li⁺-DMF interaction hinders complete DMF evaporation.^[32] The signal peak associated with LiTFSI in the crystalline state is observed at 647 cm⁻¹ for L-FL₃₅PH electrolyte, suggesting some LiTFSI residues. In comparison, the weight loss of L@FL₃₅PH in the range of 200 and 300°C is smaller, owing to its lower TFSI⁻ composition.

In order to reveal Li⁺ cross-phase transport mechanism, ⁶Li/CSE/⁶Li symmetric batteries with L-FL₃₅PH and L@FL₃₅PH electrolytes were cycled for 60 h at 0.1 mA/cm². Partial ⁷Li⁺ in CSE is substituted by ⁶Li⁺ during cycling, and then Li⁺ transport channels are identified using high-resolution ⁶Li isotope SSNMR.^[14] The fitting result in **Fig.3e, f** indicate three types of Li⁺ environments, i.e., Li⁺ transport within LLZTO (light red peak), interface of FeF₃@LLZTO and PVDF-HFP (blue peak), and PVDF-HFP chains (orange peak).^[45] The fitting results of the ⁶Li NMR spectra before cycling illustrate that the relative content difference of ⁶Li⁺ between the interface and PVDF-HFP in L@FL₃₅PH electrolyte is 1%, which is much smaller than that of L-FL₃₅PH electrolyte (9%), demonstrating the influence of the charge gradient

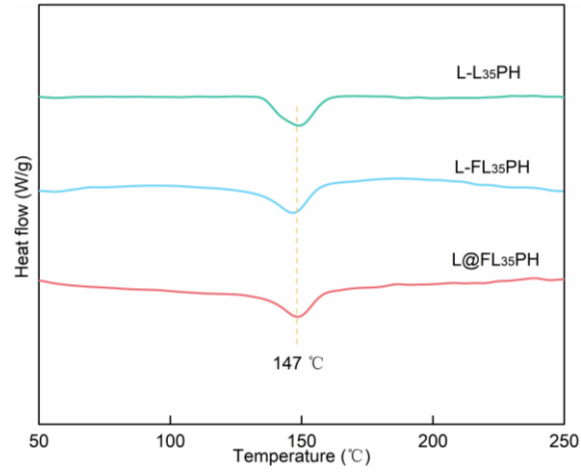
layers on anchoring TFSI⁻ distribution (**Fig.3g**). When cycling with ⁶Li anode, ⁶Li⁺ content within LLZTO for L@FL₃₅PH electrolyte increases from 73% to 87%, while its interfacial feature decreases from 13% to 3%, reflecting Li⁺ transport within LLZTO as the primary mechanism. In comparison, ⁶Li⁺ content within LLZTO changes from 67% to 26% for L-FL₃₅PH electrolyte. Therefore, due to the alleviated CGL effects, the concentrated TFSI⁻ in FeF₃ layer promotes Li⁺ migration through LLZTO particles. Such Li⁺ transport mechanism is further confirmed by the exchange current density of Li|L@FL₃₅PH|Li battery (0.41 mA/cm²) that is two-fold of the Li|L-FL₃₅PH|Li and Li|L-L₃₅PH|Li batteries (**Supplementary Fig.33**).”



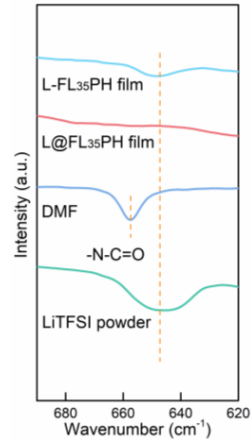
Supplementary Fig.10 | S 2p spectra of L-FL₃₅PH and L@FL₃₅PH electrolytes.



Supplementary Fig.11 | TGA curves of L-L₃₅PH, L-FL₃₅PH and L@FL₃₅PH electrolytes



Supplementary Fig.12 DSC curves of L-L₃₅PH, L-FL₃₅PH and L@FL₃₅PH electrolytes



Supplementary Fig.13 FTIR spectra of different samples

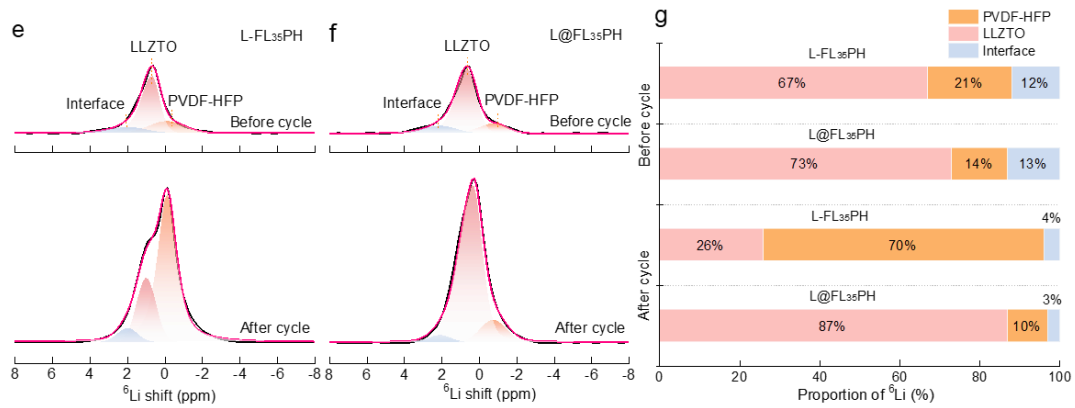
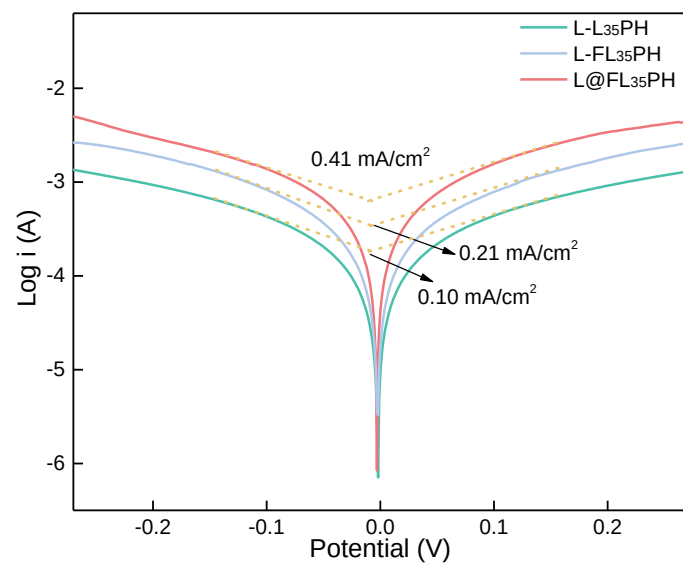


Fig.3 (e-f) The ⁶Li high-resolution Li isotope SSNMR spectra of the L-FL₃₅PH and L@FL₃₅PH electrolytes before and after ⁶Li symmetric cell cycling, and (g) corresponding peak proportions of ⁶Li⁺ with different transport paths.



Supplementary Fig.33 The Tafel curves of Li|L-L₃₅PH|Li, Li|L-FL₃₅PH|Li and Li|L@FL₃₅PH|Li symmetric batteries

For Reviewer #3:

This study addresses the limited ionic conductivity of solid electrolytes in solid-state lithium batteries, focusing on mitigating the space charge layer and enhancing lithium-ion mobility. The authors developed a composite solid electrolyte (CSE) by creating an anion-trapping interface using FeF_3 on the LLZTO surface. This interface promotes LiTFSI dissociation and forms a TFSI^- aggregation layer, improving ionic transport. This is an intriguing study that explores the modification of the solid electrolyte interface. However, some ideas are unclear and require further explanation.

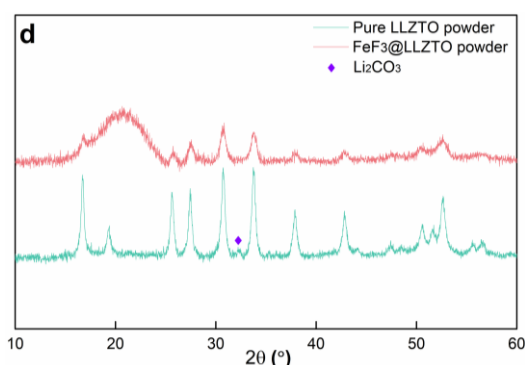
The following are comments and suggestions for improving the manuscript:

Comment I. *To ensure readers can clearly and accurately understand the article, please address the following issues:*

Response:

Following suggestion of the reviewer, we have already revised the manuscript accordingly as following.

(a) In Fig. S1d, kindly label the names of the XRD curves clearly.



Supplementary Fig.2 (d) XRD and XPS spectra of LLZTO and FeF_3 @LLZTO powders

(b) Specify the sample names for L-L₃₅PH, L-FL₃₅PH, and L@FL₃₅PH.

“Figs.1a, b schematically illustrate TFSI^- adsorption modes on FeF_3 fillers. LiTFSI -35wt.% FeF_3 @LLZTO/PVDF-HFP (L-FL₃₅PH) electrolyte is prepared via a

one-pot mixing method, i.e. $\text{FeF}_3@LLZTO$, LiTFSI and PVDF-HFP were blended together in DMF.

While LiTFSI@35wt.% $\text{FeF}_3@LLZTO$ /PVDF-HFP ($L@FL_{35}PH$) electrolyte is obtained through stepwise mixing, followed by LiTFSI absorption onto $\text{FeF}_3@LLZTO$ surface and its integration with N,N-dimethylformamide (DMF) in PVDF-HFP.

Therefore, the weight loss of $L@FL_{35}PH$ (1.4 wt.%) is close to 1.8 wt.% of L- $FL_{35}PH$ and 1.7 wt.% of LiTFSI-35wt.% $LLZTO$ /PVDF-HFP (L- $L_{35}PH$). ”

(c) The location of the 'f' figure is not indicated in Fig. 1.

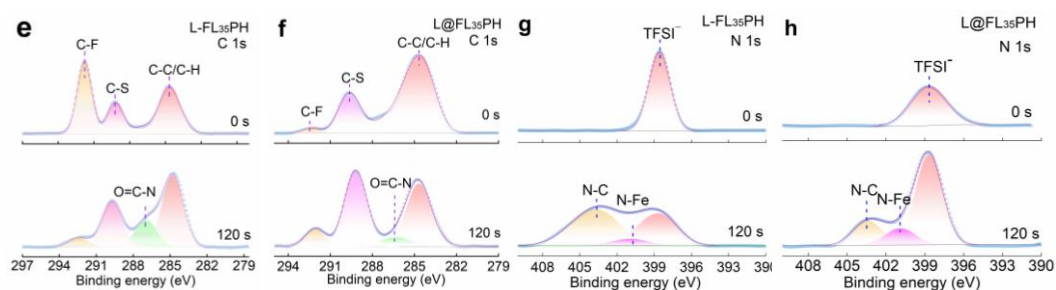


Fig.1 (e-f) C 1s and (g-h) N 1s spectra of L- $FL_{35}PH$ and $L@FL_{35}PH$ before and after etching.

(d) The figures in Fig. 2e and 2f are unclear. Please revise them to align with the corresponding sections in the text.

At the beginning, we would like to revise SCL as the “charge gradient layer (CGL)” for better description on ions gradient distribution at the fillers interface within polymer matrix. The CGL is induced by FeF_3 coating as the charge carriers, which is revealed by the surface zeta potential in **Supplementary Fig. 14c**. It forms a concentrated TFSI^- layer, which is compensated by another Li^+ layer.

The corresponding discussion has been provided in the revised manuscript as following.

“The L- $FL_{35}PH$ exhibits minimal Coulomb interaction on the equilibrium electric field (**Fig.2e**), resulting in thick CGL that impedes Li^+ transport. It hinders Li^+ migration from PVDF-HFP matrix towards $\text{FeF}_3@LLZTO$ particles within CSEs.

While the stepwise mixing method endows L@FL₃₅PH with the concentrated TFSI⁻ on FeF₃@LLZTO surface (**Fig.2f**).”

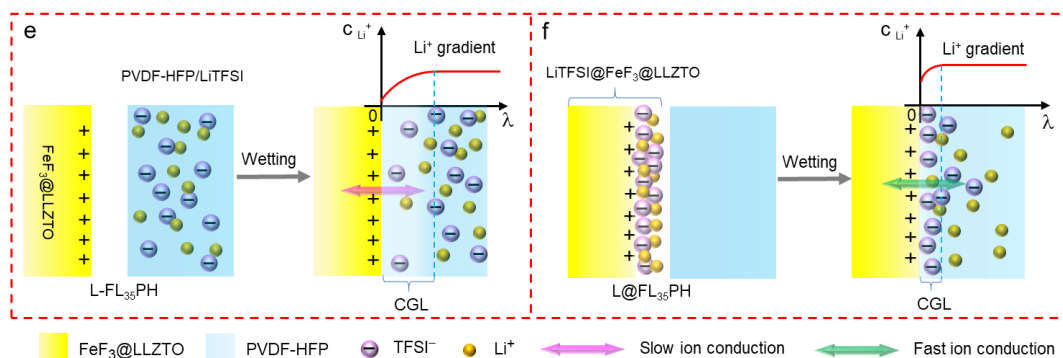
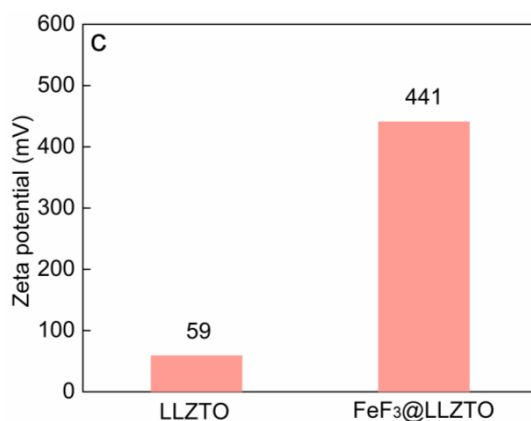


Fig.2 (e-f) The schematic diagram of the effect of CGL thickness on lithium ion transport channels.



Supplementary Fig.14 (c) the surface Zeta potential of LLZTO and FeF₃@LLZTO particles.

(e) Carefully verify the sample names in Fig. 3d.

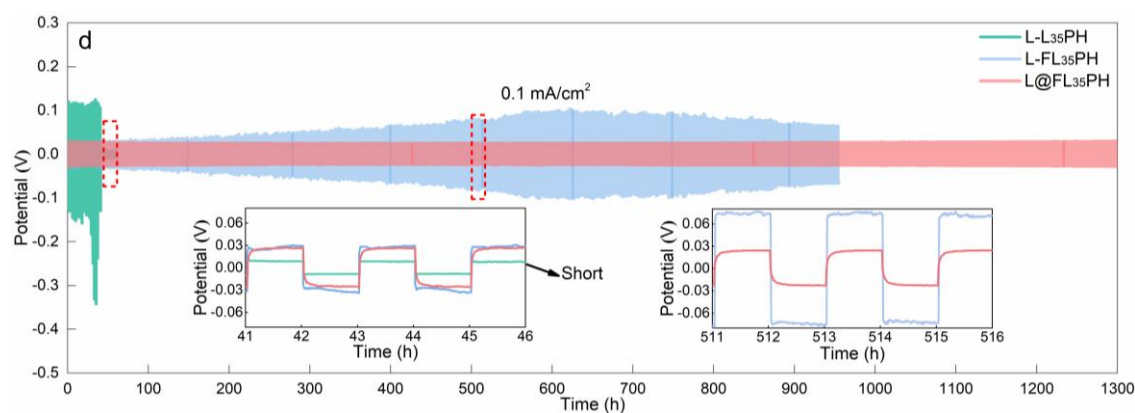
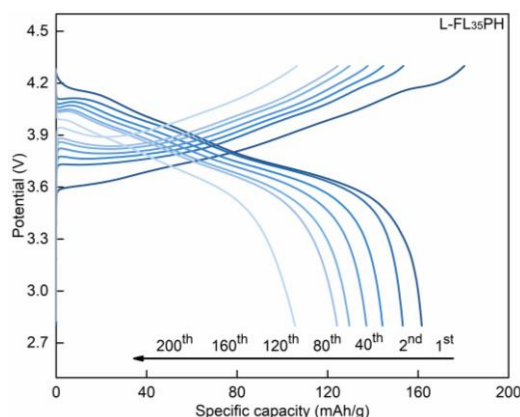
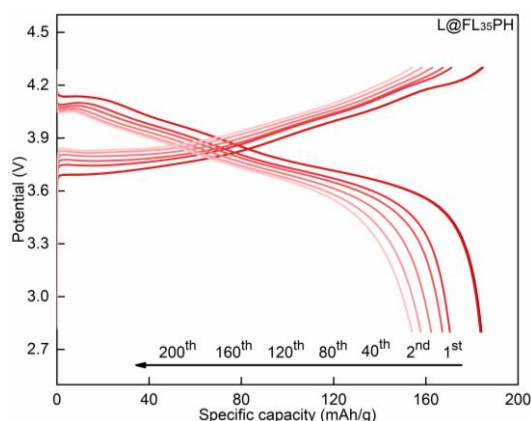


Fig.3 (d) Cycling performances of Li|CSEs|Li batteries with CSEs at 0.1 mA/cm².

(f) Confirm whether the charge-discharge curves in Figs. S27 and S28 correspond to the correct cycle numbers.



Supplementary Fig.41 Charge/discharge curves of L-FL₃₅PH electrolyte at different cycle number



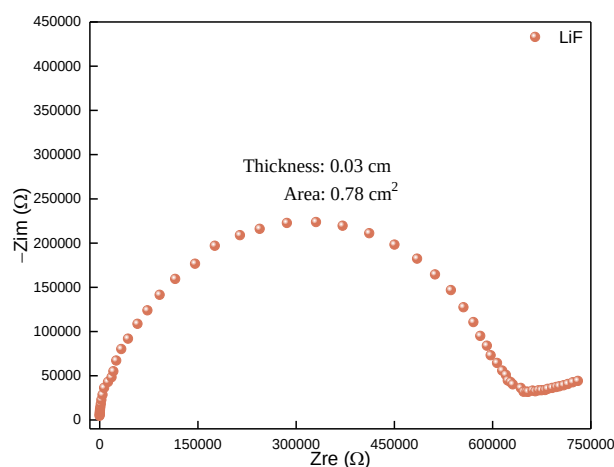
Supplementary Fig.42 Charge/discharge curves of L@FL₃₅PH electrolyte at different cycle number

Comment II. In Fig. 4a, the LiF peak for L-FL₃₅PH is significantly higher than that for L@FL₃₅PH. The authors state in the article, ‘It was evident that lower LiF content was detected for the L@FL₃₅PH electrolyte, mainly due to the fact that most of the immobilized TFSI⁻ could not approach the electrode for decomposition.’ However, in other references, such as Adv. Funct. Mater. 34 (2024) 2311848, it is stated that ‘the in situ organic-inorganic LiF-rich dielectric layer effectively improves the stability and compatibility of the electrode/electrolyte interface, ensuring interfacial lithium conduction while facilitating stable Li⁺ plating/stripping.’ These seem to present conflicting views. How do the authors reconcile these differences?

Response:

Thank you very much for your comments. The positive influence of LiF on stability and compatibility of the electrode-electrolyte interface has been widely validated, and it ensures interfacial Li conduction and facilitates even Li^+ plating/stripping.^[R12-R13] As such, many works have been devoted to promoting LiF formation on anode.^[R14-R15] However, the experimental ionic conductivity of LiF is relatively low, *i.e.* 6×10^{-8} S/cm at room temperature (**Supplementary Fig.35**). The excessive LiF content is unfavorable for ion transport kinetics and hinders battery performance. This is also supported by many studies regarding its influence on inducing Li dendrite growth and increasing interfacial impedance due to its low Li^+ conductivity.^[R16-R17] Therefore, moderate LiF amount is beneficial for improving battery performance. The related discussion has been added in the revised manuscript as below.

“The dense and uniform SEI components is demonstrated on Li anode for the two electrolytes, while L@FL₃₅PH enriches with LiF_2^- and LiS^- . NSO_4^- fragments in comparison to L-FL₃₅PH. It further confirms the aggregation of TFSI⁻ species Li anode. The ionic conductivity of LiF at room temperature is measured as 6×10^{-8} S/cm calculated by the Nyquist plot (**Supplementary Fig.35**), indicating that LiF species and thick SEI hinder ion transport.”



Supplementary Fig.35 | Nyquist plots of SS|LiF|SS batteries at room temperature.

References

- [R12] Tan, J., et al. A growing appreciation for the role of LiF in the solid electrolyte interphase, *Adv. Energy Mater.* 11, 2100046 (2021).
- [R13] Gong, C., et al, Revealing the role of fluoride-rich battery electrode interphases by operando transmission electron microscopy, *Adv. Energy Mater.* 11 , 2003118 (2021).
- [R14] Zhao, J., et al, Surface fluorination of reactive battery anode materials for enhanced stability, *J. Am. Chem. Soc.* 139, 11550–11558 (2017).
- [R15] Zhang, Zhao., et al. Stable all-solid-state lithium metal batteries with Li₃N-LiF-enriched interface induced by lithium nitrate addition, *Energy Storage Mater.* 43, 229–237 (2021).
- [R16] Zhou, S., et al. Tuning the LiF content in the SEI by engineering the molecular structures of porous organic polymers for solid-state lithium metal batteries, *J. Mater. Chem. A* 11, 5636-5644 (2023).
- [R17] Wu, D., et al. Li₂CO₃/LiF-Rich Heterostructured Solid Electrolyte Interphase with Superior Lithiophilic and Li⁺-Transferred Characteristics via Adjusting Electrolyte Additives, *Adv. Energy Mater.* 2200337 (2022).

Comment III. The author mentions, ‘L-FL₃₅PH exhibits minimal Coulomb interaction on the equilibrium electric field (Fig. 2e), leading to a thick SCL that hinders Li⁺ transport.’ What are the criteria for defining a ‘thick SCL’? How does the SCL relate to the formation of the LiF layer?

Response:

We thank the reviewer for providing the constructive suggestion. As explained in Comment I-(d), we have replaced the concept of “space charge layer (SCL)” as “Charge Gradient Layer (CGL)” to better describe the interfacial ion gradient distribution in polymer-based composite matrices. In response to the reviewer

comment, the CGL thickness is determined as the charge gradient distribution between the two heterogeneous components, *i.e.* polymer and fillers. Although this solid-state interface is complicated to experimentally quantify the CGL thickness, the Kelvin probe force microscope (KPFM), Zeta potential measurement, cyclic voltammetry (CV) curves and finite element simulation methods have been employed for qualitative analysis on CGL thickness as demonstrated in **Supplementary Fig.14-17**. Specifically, the surface zeta potential measurements reveal an interfacial charge of 441 mV for FeF₃@LLZTO particles (**Supplementary Fig.14**), indicating that its surface carries higher positive charges than LLZTO particles. Such difference is further supported by the KPFM analysis in **Fig.2c, d**, which indicates the surface potential of -340 mV on L@FL₃₅PH electrolyte that is higher L-FL₃₅PH counterpart. This attenuation in interfacial potential correlates with the enrichment of TFSI⁻ anions at FeF₃@LLZTO particles interface.^[R18] The augmented double-layer capacitance (**Supplementary Fig.15b, d**) of L@FL₃₅PH signifies a denser packing of TFSI⁻ species at the FeF₃@LLZTO surface, thus reducing the CGL thickness.^[R19] Finite-element simulations further corroborate that the elevated charge density at the FeF₃@LLZTO interface, driven by a localized increase in TFSI concentration (0.05 – 0.95 M), coinciding with contraction of ions concentration gradient, thereby diminishing the CGL thickness. (**Supplementary Fig.16-17**).

The CGL in the manuscript originates from the charge concentration gradient at the FeF₃@LLZTO/PVDF-HFP interface, while LiF formation is linked to interfacial reactions between the lithium anode and the composite solid electrolyte. Although CGL and LiF arise from distinct interfacial phenomena, they are intimately coupled through ionic transport kinetics. Specifically, LiF derives from TFSI⁻ decomposition, whereas the FeF₃@LLZTO component suppresses LiF generation by adsorbing TFSI⁻ and restricting its mobility. Concurrently, TFSI⁻ adsorption by FeF₃@LLZTO reduces CGL thickness, facilitating cross-phase boundary Li⁺ transport and diminishing TFSI⁻-mediated competition for Li⁺ diffusion pathways. As a consequence, CGL indirectly modulates TFSI⁻ transport efficiency, thereby influencing LiF formation

dynamics.

To address the comment, the qualitative analyses (KPFM, Zeta potential, CVs) is combined with theoretical simulations (the finite element modeling). The related discussion has been added in the revised manuscript as following.

“The impact of TFSI⁻ adsorption on CSEs surface potential is reflected through KPFM tests as depicted in **Fig.2** and **Supplementary Fig.14a, b**. When comparing to L-L₃₅PH, uniform potential distribution on L@FL₃₅PH and L-FL₃₅PH electrolytes is revealed, illustrating FeF₃ encapsulation on LLZTO improves interface compatibility between organic and inorganic components. The charge-carrying feature of FeF₃@LLZTO particles surface could be recognized by the surface zeta potential that is measured at 441 mV (**Supplementary Fig.14c**). As a reference, the surface zeta potential of LLZTO particles is measured to be 59 mV, indication an isolated FeF₃ coating as the charge aggregated surface. However, the surface zeta potential of L@FL₃₅PH electrolyte is measured at -340 mV, which is much lower than those of L-FL₃₅PH and L-L₃₅PH. It is induced by its higher concentration of TFSI⁻, which decreases potential difference at the organic-inorganic interface, the reduced CGL thickness facilitates Li⁺ transport crossing phase boundaries.^[33] The L-FL₃₅PH exhibits minimal Coulomb interaction on the equilibrium electric field (**Fig.2e**), resulting in thick CGL that impedes Li⁺ transport. It hinders Li⁺ migration from PVDF-HFP matrix towards FeF₃@LLZTO particles within CSEs. While the stepwise mixing method endows L@FL₃₅PH with the concentrated TFSI⁻ on FeF₃@LLZTO surface (**Fig.2f**). The organic-inorganic interface Coulomb interactions is established to decrease CGL thickness. Then, slow unidirectional pathway for Li⁺ transport is transformed into fast bidirectional pathway, and ion transport efficiency is improved. CGL is the charge distribution caused by the electric field intensity at the interface and has an electric bilayer effect.^[34-35] The result indicated that the double-layer capacitance of stainless steel (SS)/celgard/L@FL₃₅PH is 9.4 μF/cm², which is bigger than that of SS/celgard/L-FL₃₅PH (6.5 μF/cm², **Supplementary Fig.15**). The result is ascribed to the enrichment of TFSI⁻ that enhances the surface charge density of FeF₃,

promoting its closer arrangement, thereby compressing the charge layer spacing and simultaneously increasing the capacitance of the double-layer capacitance.^[35] In order to further validate CGL thickness, DFT models with various TFSI⁻ concentrations from 0.05 to 0.95 M have been constructed to simulate Li⁺ concentration, surface potential and charge density on FeF₃@LLZTO surface. The interfacial charge density increases along with TFSI⁻ concentration, resulting in decreasing surface potential and repelling effect for Li⁺ (**Supplementary Fig.16**). Similarly, the introduction of anions leads to the redistribution of charge at the interface, resulting in a decrease in CGL thickness with increasing TFSI⁻ concentration (**Supplementary Fig.17**). This theoretical simulation result is consistent with the KPFM and electric double layer capacity analysis”

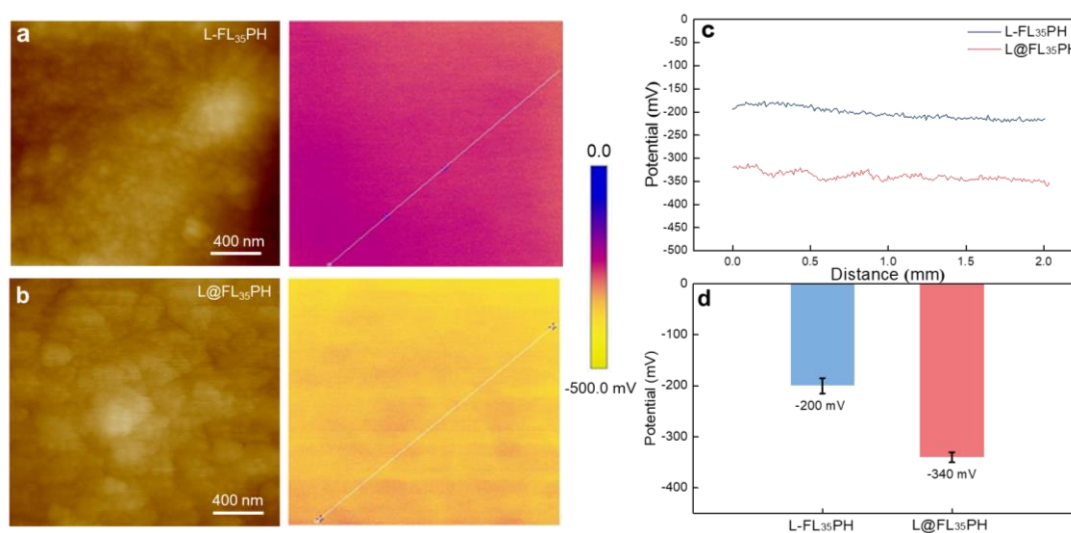
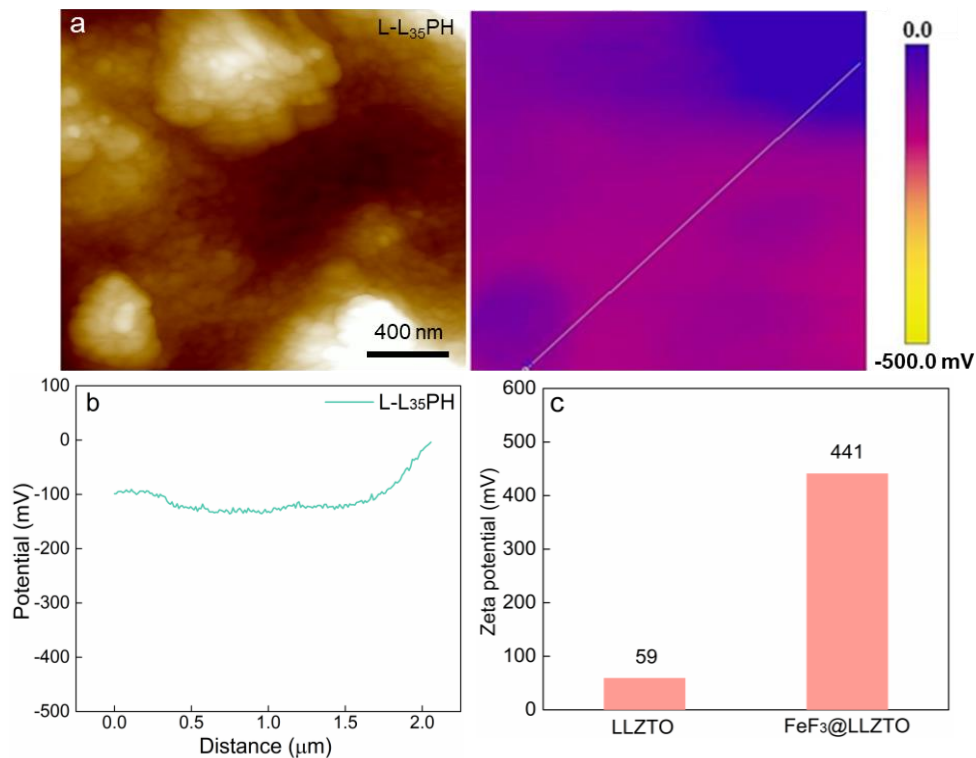
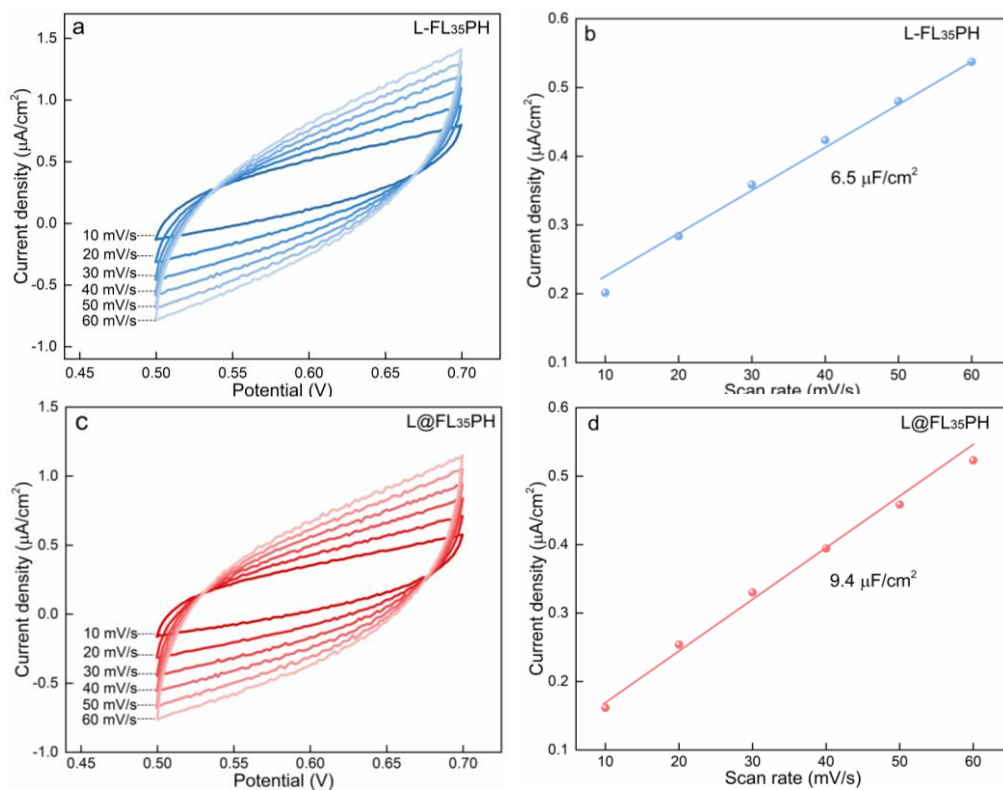


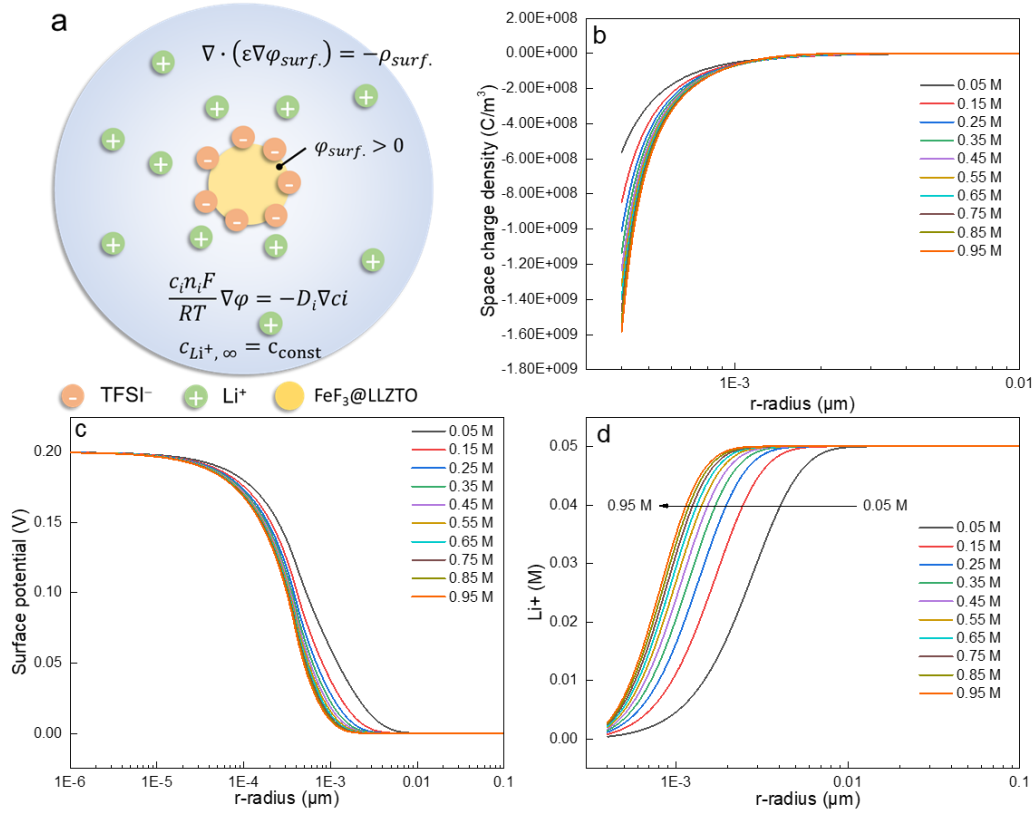
Fig.2 (a-d) Interface potential distribution images of L-FL₃₅PH and L@FL₃₅PH electrolytes.



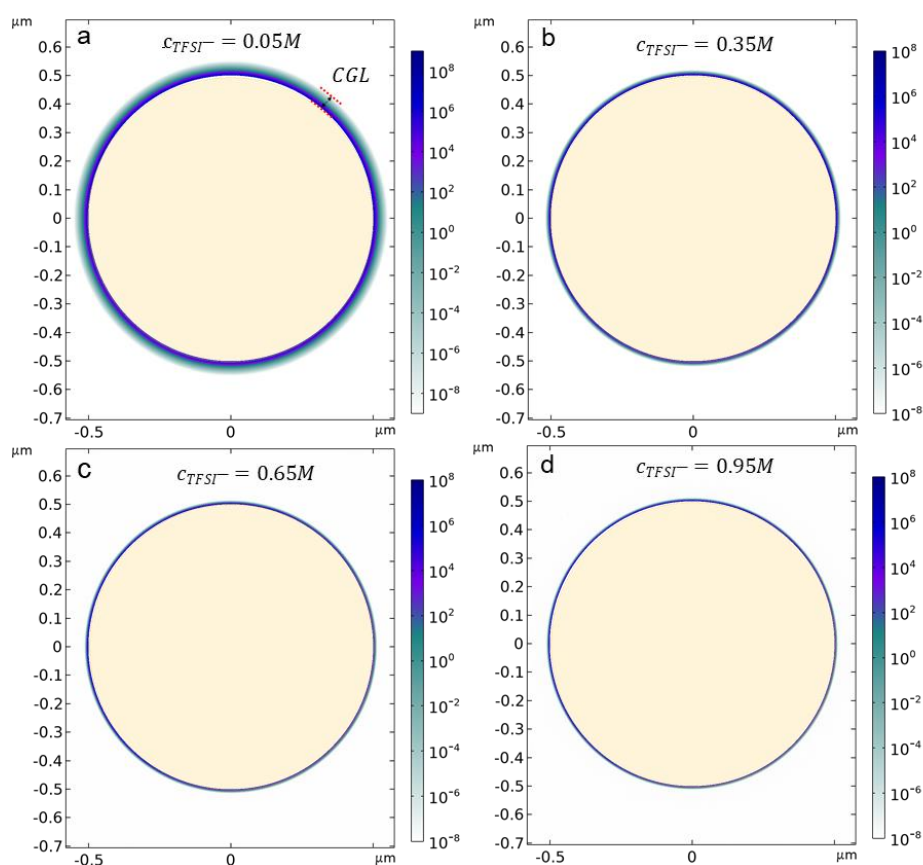
Supplementary Fig.14 (a-b) Interface potential distribution images of L-L₃₅PH electrolyte and (c) the surface Zeta potential of LLZTO and FeF₃@LLZTO particles.



Supplementary Fig.15 (a-d) CV Curve and electric double layer capacitance of SS/Celgard/L-FL₃₅PH and SS/Celgard/L@FL₃₅PH at different scan.



Supplementary Fig.16 (a) Establishing TFSI⁻ in FeF₃@LLZTO hypothesis model of surface aggregation, (b-c) the change of charge density, surface potential and Li⁺ concentration with varying the TFSI⁻ concentration around FeF₃@LLZTO in the range of 0.05-0.95 M.



Supplementary Fig.17 The relationship between the thickness of CGL and the concentration of TFSI⁻ on the surface of FeF₃@LLZTO.

References

[R18] Zhao, L., et al. Rationally coordinating polymer enabling effective Li-ion percolation network in composite electrolyte for solid-state Li-metal batteries, *Energy Storage Mater.* 68, 103360 (2024).

[R19] Hang Luo, et al. Interface design for high energy density polymer nanocomposites, *Chem. Soc. Rev.* 48, 4424 (2019).

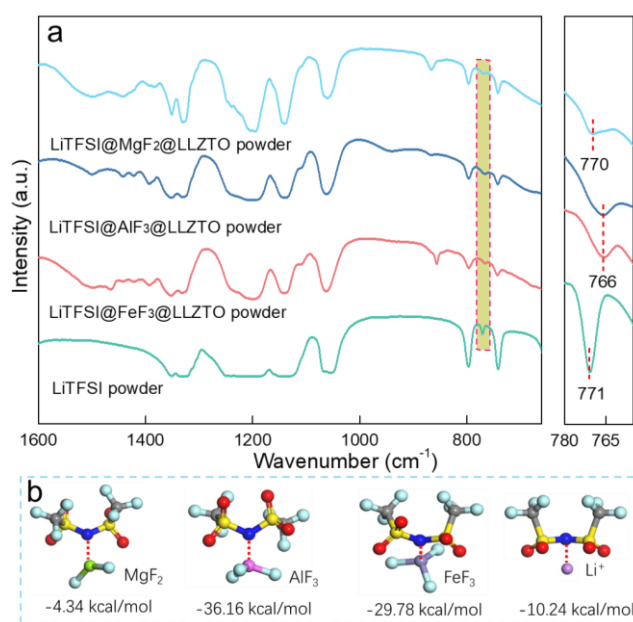
Comment IV. The selection of FeF₃ is based on its electronic defect characteristics, but has it been evaluated against other materials with similar properties? For example, could MgF₂ or AlF₃ serve as potential alternatives.

Response:

Thank you very much for your comments. To address this comment, we have prepared $\text{MgF}_2@\text{LLZTO}$ and $\text{AlF}_3@\text{LLZTO}$ through a similar procedure. The related discussion has been added in the revised manuscript as following.

“Supplementary Note 5: Against other materials with similar properties

We have prepared $\text{MgF}_2@\text{LLZTO}$ and $\text{AlF}_3@\text{LLZTO}$ through a similar procedure. As shown in **Supplementary Fig.7**, FTIR results illustrate that the peak corresponding to the S-N bond of $\text{LiTFSI}@\text{MgF}_2@\text{LLZTO}$ shifts from 771 to 770 cm^{-1} , while the peak blueshift to 766 cm^{-1} is identified in $\text{LiTFSI}@\text{AlF}_3@\text{LLZTO}$. Such result coincides with $\text{LiTFSI}@\text{FeF}_3@\text{LLZTO}$. According to DFT calculations, the binding energy of $\text{MgF}_2/\text{TFSI}^-$ (−4.34 kcal/mol) is weaker than that of $\text{Li}^+/\text{TFSI}^-$ (−10.24 kcal/mol), while the binding energy of $\text{AlF}_3/\text{TFSI}^-$ (−36.16 kcal/mol) or $\text{FeF}_3/\text{TFSI}^-$ (−29.78 kcal/mol) is stronger than that of $\text{Li}^+/\text{TFSI}^-$. This method is universally applicable, yet variations in the results arise from differences in the composition of the metals and their respective binding energies.”



Supplementary Fig.7| Interactions between MgF_2 and AlF_3 with TFSI^- .

RESPONSE TO REVIEWERS' COMMENTS

We thank all the reviewers for their valuable comments on our manuscript. Their constructive suggestions for improvement have certainly raised the quality of our manuscript. In order to address the reviewers' concerns, we have addressed their comments point by point below.

For Reviewer #1

All issues have been properly resolved, and I am satisfied with the revised manuscript.

Response:

We would thank the reviewer for the positive response on acceptance of our work.

For Reviewer #2

The authors have added many important explanations to the revised manuscript, however, several points listed below should be supplemented to understand the work more clearly:

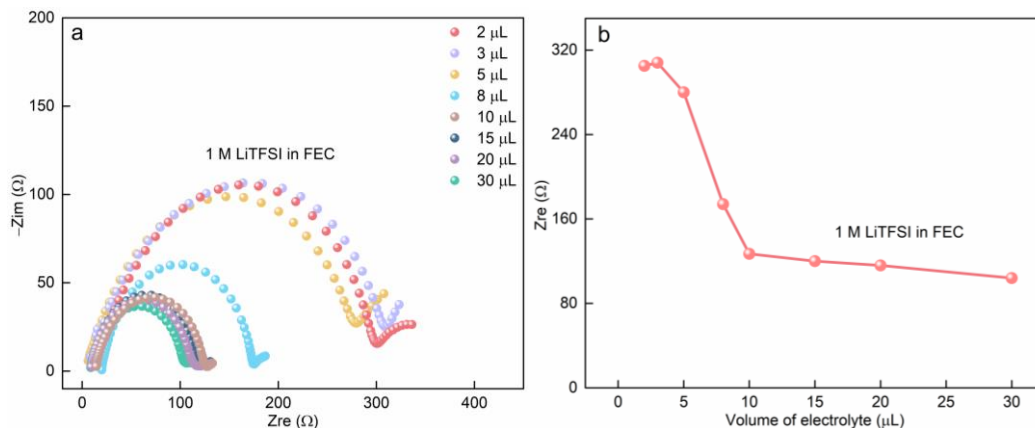
1. Whether an electrolyte with FEC and LITFSI (1 M LiTFSI in FEC) was added as the interface infiltration agent on both sides of the CSEs in all tested cells? If it is, the discussion should be supplemented for the explanation of EIS in the Fig.3?

Response:

We thank the reviewer for recognizing our previous revision. In battery measurements, small amount of liquid electrolyte containing 1 M LiTFSI in FEC solvent has been added onto both CSEs sides as the interface infiltration agent. Following the reviewer suggestion, discussions have added, to clarify the influence of adding liquid electrolyte on EIS spectra. The supplementary experiments have been also conducted through altering its volume ranging from 2 to 30 μL as plotted in **Supplementary Fig. 32**.

In the Manuscript:

“Additionally, the critical permeation threshold is also investigated as the key factor for the interface charge transfer. It is identified through recording the impedance changes with adding various quantity of liquid electrolytes as the interface infiltration agent. As illustrated in **Supplementary Fig. 32**, the impedance value undergoes a slight change around 305 Ω below 5 μL volume. When increasing to over 8 μL , it is reduced down to 177 Ω , as evident for the wetting-percolation threshold for liquid electrolytes onto CSEs. Given so, below the threshold of 8 μL , the electrolyte-electrode interactions are dominated by interfacial wetting effects, rather than bulk-phase ionic percolation.”



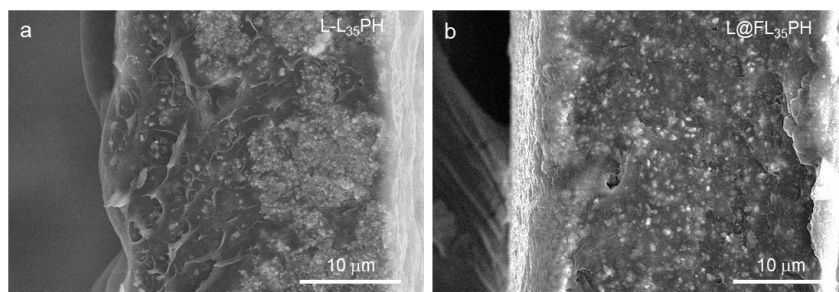
Supplementary Fig. 32 | (a-b) The impedances changes of the Li|L@FL₃₅PH|Li symmetric batteries with adding various volumes of liquid electrolyte (1 M LiTFSI in FEC solvent).

2. If possible, the cross-sectional images of the electrolyte membrane should be added to illustrate the distribution of LLZTO particles.

Response:

Following the reviewer comment, the cross-sectional morphology of L-L₃₅PH and L@FL₃₅PH electrolytes have been collected to illustrate the distribution of LLZTO particles as shown in **Supplementary Fig. 5**. The corresponding descriptions have been also provided in the revised manuscript as below.

“In addition, cross-sectional morphology analysis of L@FL₃₅PH electrolyte reveals a discernible absence of particle aggregation phenomena (**Supplementary Fig. 5**). Particle agglomeration leads to an uneven fracture surface of L-L₃₅PH electrolyte.”



Supplementary Fig. 5 | (a-b) The cross-sectional morphology of L-L₃₅PH and L@FL₃₅PH electrolytes.

3. Line 581 in the text, it should be added the dry conditions for the electrolyte film.

Response:

Thank you very much for your comments. the dry conditions for the electrolyte film have been provided in the **experimental section** as below.

“Firstly, adding 90 mg (20wt.%), 190 mg (35 wt.%) and 360 mg (50wt.%) $\text{FeF}_3@LLZTO$ powder was respectively mixed with 60 mg LiTFSI in 2 mL DMF, and dried at 60 °C to obtain LiTFSI@ $\text{FeF}_3@LLZTO$ powders; then dispersed into a mixed solution of 300 mg PVDF-HFP and 6 mL DMF with magnetic stirring for 12 h. The LiTFSI@ $\text{FeF}_3@LLZTO$ /PVDF-HFP composite solid electrolyte was obtained by pouring onto a glass plate, and dried in a vacuum oven at 60 °C for 12 h. Then the films was named L@FL₂₀PH, L@FL₃₅PH and L@FL₅₀PH electrolytes, respectively, according to the different $\text{FeF}_3@LLZTO$ powder contents.”

This work developed a FeF₃ coating on the surface of LLZTO powder via the sol gel method, with the goal of promoting LiTFSI dissociation and forming TFSI- aggregation layer in the LiTFSI/PVDF-HFP composite solid electrolyte. Because of the lack of the discussion about residual DMF solvent, the results of LiTFSI/PVDF-HFP composite solid electrolyte are not sufficient.

The following should be involved in the manuscript:

1) Line 490 in the text, “Disperse 500 mg of LLZTO in 20 mL of distilled water,”

Is LLZTO powder a commercial material? The particle size and surface state of LLZTO need to be supplemented in the experimental methods.

2) Line 498-500 in the text, “Firstly, adding 90 mg (20%), 190 mg (35%) and 360 mg (50%) FeF₃@LLZTO powder was respectively mixed with 60 mg LiTFSI in 2mL DMF, and dried at 60 °C to obtain LiTFSI@FeF₃@LLZTO powders; then dispersed into a mixed solution of 300 mg PVDF-HFP and 6 mL DMF with magnetic stirring for 12 h.”

The residual amount of DMF solvent in two kinds of LiTFSI/PVDF-HFP composite solid electrolyte should be determined with DSC analysis, whether DMF residues in L@FL35PH is higher than in L-L35PH.

3) Line 533-541 in the text, “NMC811 and LFP cathodes were prepared using a slurry casting technique. Active material, Super P carbon as a conductive additive and polyvinylidene fluoride were dissolved in N-methyl-2-pyrrolidone with a weight ratio of 8:1:1 to make a slurry and then coated onto a current collector of aluminium foil. The cathodes were dried in a vacuum oven at 110 °C for 12 h. The active loading density of the LFP cathode was 2.0 mg/cm².”

The assembly method of the battery should be described clearly, especially whether liquid electrolyte existed at the cathode interface.

4) Line 147-151 in the text, “ The C-N peak at 403.7 eV in N 1s spectra represent the residual DMF solvent, while peak at 399.3 eV is attributed to TFSI⁻. Their intensity ratio of TFSI⁻/C-N in L@FL₃₅PH electrolyte was about 2.78, higher than 0.87 of L-FL₃₅PH electrolyte, further proving that the stepwise mixing method could more effectively exert the adsorption effect of FeF₃ on TFSI⁻”.

The author should be noticed that more DMF residue in L-FL35PH leads to an

increase of C-N intensity, and then reducing the intensity ratio of TFSI-/C-N.

5) Line 339-343 in the text, “The results demonstrated that lithium anode surfaces matched with both electrolytes form dense and uniform SEI components, enriched with LiF₂ – and LiS–. However, the lithium anode surface matched with L-FL35PH electrolyte led to thick SEI, which is unfavorable for interface impedance.”

It should be discussed the reason of no TFSI peak in the XPS of L@FL35PH.

6) Line 92-94 in the text, “This method encounters difficulties in TFSI– absorption onto FeF₃ particles, which is primarily due to high viscosity and the presence of solid-liquid interface energy.[20]”

This reference have no any discussions about LiTFSI.

7) Effect of the differences about DMF residues in the two kinds of CSE film should be discussed