

Peer Review File

Sulfide-based composite solid electrolyte films for all-solid-state batteries



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29th Jan 24

Dear Professor Wang,

Thank you for submitting your manuscript, "Progress and Prospect of Sulfide-Based Composite Solid Electrolyte Films", to Communications Materials. It has now been seen by 4 referees, whose comments are appended below. You will see that while they find your work of interest, some important points are raised. We are interested in the possibility of publishing your study in Communications Materials, but would like to consider your response to these concerns in the form of a revised manuscript before we make a decision on publication.

In particular, Reviewer 3 mentions that the current Outlook section is too vague, and insight should be added into why lithium symmetric cells with sulfide thin films have weaknesses should be discussed; while Reviewer 1 suggests adding why sulfide electrolytes are popular. In addition, Reviewer 4 mentions that important aspects for sulfide-based composite solid electrolyte films should be listed as a Figure, and that the state-of-the-art should be presented.

We therefore invite you to revise and resubmit your manuscript, taking into account the points raised.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

-A response letter with a point-by-point reply to each of the referee comments and a description of changes made. Please include the complete referee report in the response letter. Please note that the response letter must be separate to the cover letter to the editors.

-A marked-up version of the manuscript with all changes to the text in a different colored font. Please do not include tracked changes or comments. Please select the file type 'Revised Manuscript - Marked Up' when uploading the manuscript file to our online system.

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We hope to receive your revised paper within three months; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we will close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Dr Jet-Sing Lee

Associate Editor

Communications Materials

orcid.org/0000-0002-6740-8700

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The authors summarized the progress and prospect of sulfide-based composite solid electrolyte films. The topic is very important for mass production in industry and should attract enough readers in the solid-state battery field. Therefore, I recommend this manuscript to be published on Communications Materials after the following minor revision:

- (1) The topic about halide electrolytes is also popular recently. The authors should emphasize why sulfide electrolytes are chosen.
- (2) The authors have mentioned that "Subsequently, a compact Li₆PS₅Cl-polydopamine film with a thickness of 35 μm and an ionic conductivity of 0.2 mS cm⁻¹ was prepared by cold pressing of Li₆PS₅Cl @polydopamine particles." Please add it in the Table 1.
- (3) Ref.41 and Ref 67 is the same reference, please delete one of them.
- (4) In Ref. 58, the name of "Proceedings of the National Academy of Sciences" should be abbreviated.
- (5) The research of sulfide SSBs is a very hot topic, some important references should be cited, such as Adv. Mater. 2023, 35, 2211047; Adv. Energy Mater.2023,13, 2300962; Nano Letters, 2023, 23, 1, 227;Energy Storage Materials, 2021, 38, 249;Electrochemical Energy Reviews, 2021, 4 (1), 101; Energy Storage Materials, 2018, 14: 58.

Reviewer #2 (Remarks to the Author):

This review paper provides a comprehensive summary of all-solid-state batteries incorporating sulfide composite solid electrolyte films, highlighting on sulfide/polymer composite electrolytes. The introduction presents a thin, flexible, high-energy density sulfide composite electrolyte film achieved by combining a sulfide-based solid electrolyte with excellent ionic conductivity and a flexible polymer solid electrolyte. The ion conduction mechanism of sulfide/polymer composite electrolyte was well explained and systematically categorized the advantages and disadvantages of wet and dry methods employed in their manufacturing process, backed by a comprehensive analysis of their respective performance. Moreover, the paper gave emphasis to the importance of ionic conductivity measurement and Li symmetric battery performance for evaluating and analyzing the manufactured solid electrolyte films.

While the paper offers a concise overview of sulfide/polymer composite electrolytes, it is acknowledged that the inclusion of recent research studies would substantially improve its capacity to serve as a comprehensive review paper and is recommended to include its findings. Several recent publications have explored sulfide composite solid electrolyte films incorporating various binders. An indicative example of these is evidenced in the following publications; Advanced Energy Materials (2023): 2302596., Journal of Electroanalytical Chemistry 928 (2023): 117032., Chometon, which focus on

optimizing parameters for an effective solvent-free formulation of PEO: LiTFSI: Li6PS5Cl hybrid solid electrolyte. Other recent publications are as follows; ACS Applied Materials & Interfaces, 2023., Kang et al. Mechanically Robust Ultrathin Solid Electrolyte Membranes Using a Porous Net Template for All-Solid-State Batteries. ACS Applied Materials & Interfaces, 2023., and Nano Energy 102 (2022): 107679.

Reviewer #3 (Remarks to the Author):

This manuscript comprehensively summarizes and rationally categorizes the techniques reported to fabricate thin electrolyte films made with sulfides. Figures are crafted with thought and clearly deliver the messages intended. Text is well written, concise, and focused. Overall, this is a compact review which covers a lot of ground without a wall of text. It may be suitable for publication on Commun. Mater. as is, but the following suggestions may further improve the manuscript.

(1) Page 7, two examples are highlighted for binder-solvent systems, but it is not clear how they stand out in terms of design and working mechanism.

(2) Figure 3 is briefly mentioned but not really explained in the main text.

(3) Several performance weaknesses have been mentioned for lithium symmetric cells with sulfide thin films, but no insight has been provided into the reasons why.

(4) Strategies raised in the Outlook section are mostly vague. Something more specific and pertaining to particular challenges such as those in comment #3 would be more helpful.

Reviewer #4 (Remarks to the Author):

Li et al summarized the sulfide-based composite solid electrolyte films for all-solid-state batteries. In this short review, the ionic transport mechanism of sulfide/polymer composite electrolyte films is provided to afford a fundamental for the development of composite electrolyte films with high ionic conductivity. The preparation methods and the properties of sulfide-based composite electrolytes are introduced in detail, and the advantages and disadvantages of each method are also analyzed. The application of

composite electrolyte films in all-solid-state battery is also presented. This is a very important review in the field of materials science. It can be further improved in the following aspects:

1. The most important events in sulfide-based composite solid electrolyte films for all-solid-state batteries should be listed as Figure to help readers to catch the whole scenario of this field.
2. How Li ion transfer through the interfaces between polymer and sulfide solid electrolyte? How about the charge and carrier distribution?
3. The state of the art on the electrochemical performance of all-solid-state batteries based on sulfide-based composite solid electrolyte films should be well presented.
4. The recent advances in sulfide-based composite solid electrolyte films for batteries (e.g. J Energy Chem 2021, 58, 17; Adv Funct Mater 2021, 31, 2101985; InfoMat 2022, 4, e12292; J Energy Chem 2022, 74, 309; WIREs Comput Mol Sci 2023, 13, e1621; Adv Mater 2023, 35, 2206013) should be further highlighted.

A Point-by-Point Response Letter

We greatly appreciate the valuable comments and suggestions from editor and all reviewers. Accordingly, we have carried out extended experiments and made suitable revisions, which we believe have greatly improved our manuscript. The following are our point-by-point responses to all reviewers' comments. The corresponding changes have also been highlighted in the revised manuscript.

Reviewer #1

The authors summarized the progress and prospect of sulfide-based composite solid electrolyte films. The topic is very important for mass production in industry and should attract enough readers in the solid-state battery field. Therefore, I recommend this manuscript to be published on Communications Materials after the following minor revision:

Response: We thank the reviewer for his/her appreciations and positive recommendation to our work, and would also like to thank the reviewer for his/her very valuable comments on the manuscript.

(1) The topic about halide electrolytes is also popular recently. The authors should emphasize why sulfide electrolytes are chosen.

Response: Thank the reviewer for this suggestion. We have added corresponding explanation in the revised manuscript.

"Halides solid electrolytes have emerged as promising candidates due to their good deformability, high ionic conductivity and oxidation stability. However, they also face some challenges due to their high density, expensive raw material cost, and instability in organic solvents. In contrast, sulfide solid electrolytes, especially some lithium argyrodites (e.g. $\text{Li}_6\text{PS}_5\text{Cl}$, $\text{Li}_{5.5}\text{PS}_{4.5}\text{X}_{1.5}$ ($\text{X}=\text{Cl}$, Br), $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{0.8}\text{Br}_{0.7}$), have gained extensive attention due to their abundant raw materials and impressive room-temperature ionic conductivity which is comparable to that of liquid electrolytes."

(2) The authors have mentioned that "Subsequently, a compact $\text{Li}_6\text{PS}_5\text{Cl}$ -polydopamine film with a thickness of 35 μm and an ionic conductivity of 0.2 mS cm^{-1} was prepared by cold pressing of $\text{Li}_6\text{PS}_5\text{Cl}$ @polydopamine particles." Please add it in the Table 1.

Response: Thank the reviewer for this comment. We have now added it in the Table 1.

(3) Ref.41 and Ref 67 is the same reference, please delete one of them.

Response: Thank the reviewer for this comment. We have now deleted one of them.

(4) In Ref. 58, the name of "Proceedings of the National Academy of Sciences" should be abbreviated.

Response: Thank the reviewer for this comment. We have now abbreviated the name of "Proceedings of the National Academy of Sciences".

(5) The research of sulfide SSBs is a very hot topic, some important references should be cited, such as Adv. Mater. 2023, 35, 2211047; Adv. Energy Mater. 2023, 13, 2300962; Nano Letters, 2023, 23, 1, 227; Energy Storage Materials, 2021, 38, 249; Electrochemical Energy Reviews, 2021, 4 (1), 101; Energy Storage Materials, 2018, 14: 58.

Response: Thank the reviewer for this suggestion. We have now cited these references in the main text.

Reviewer #2

This review paper provides a comprehensive summary of all-solid-state batteries incorporating sulfide composite solid electrolyte films, highlighting on sulfide/polymer composite electrolytes. The introduction presents a thin, flexible, high-energy density sulfide composite electrolyte film achieved by combining a sulfide-based solid electrolyte with excellent ionic conductivity and a flexible polymer solid electrolyte. The ion conduction mechanism of sulfide/polymer composite electrolyte was well explained and systematically categorized the advantages and disadvantages of wet and dry methods employed in their manufacturing process, backed by a comprehensive analysis of their respective performance. Moreover, the paper gave emphasis to the importance of ionic conductivity measurement and Li symmetric battery performance for evaluating and analyzing the manufactured solid electrolyte films.

While the paper offers a concise overview of sulfide/polymer composite electrolytes, it is acknowledged that the inclusion of recent research studies would substantially improve its capacity to serve as a comprehensive review paper and is recommended to include its findings. Several recent publications have explored sulfide composite solid electrolyte films incorporating various binders. An indicative example of these is evidenced in the following publications; Advanced Energy Materials (2024): 2302596., Journal of Electroanalytical Chemistry 928 (2023): 117032., Chometon, which focus on optimizing parameters for an effective solvent-free formulation of PEO: LiTFSI: Li₆PS₅Cl hybrid solid electrolyte. Other recent publications are as follows; ACS Applied Materials & Interfaces, 2023., Kang et al. Mechanically Robust Ultrathin Solid Electrolyte Membranes Using a Porous Net Template for All-Solid-State Batteries. ACS Applied Materials & Interfaces, 2023., and Nano Energy 102 (2022): 107679.

Response: We thank the reviewer for his/her appreciations and positive recommendation to our work, and would also like to thank the reviewer for his/her very valuable comments on the manuscript. We have now added the above references in the main text.

Reviewer #3 (Remarks to the Author):

This manuscript comprehensively summarizes and rationally categorizes the techniques reported to fabricate thin electrolyte films made with sulfides. Figures are crafted with thought and clearly deliver the messages intended. Text is well written, concise, and focused. Overall, this is a compact review which covers a lot of ground without a wall of text. It may be suitable for publication on Commun. Mater. as is, but the following suggestions may further improve the manuscript.

(1) Page 7, two examples are highlighted for binder-solvent systems, but it is not clear how they stand out in terms of design and working mechanism.

Response: We thank the reviewer for this comment. In the case of first example, Tan et al. analyzed a variety of sulfides-solvent and sulfides-polymer binder combinations by controlling variables, and investigated their (electro-)chemical compatibility in depth. They found that styrene-ethylene-butylene-styrene (SEBS) polymers exhibited good compatibility with p-xylene (XYL), and was considered as a suitable choice. This is a very typical example involving in selection of suitable solvent-binder pair.

We have now changed the second example as follows. This example represents the thinnest sulfide-based composite electrolyte membrane with relatively high room-temperature ionic conductivity synthesized by tape casting.

“To further improve the ionic conductivity and reduce the thickness of the film, sulfide electrolyte with higher ionic conductivity is chosen. An 8 μm thick $\text{Li}_{9.88}\text{GeP}_{1.96}\text{Sb}_{0.04}\text{S}_{11.88}\text{Cl}_{0.12}$ -poly(methyl methacrylate)/n-butylacrylate composite film with high ionic conductivity of 1.9 mS cm^{-1} was successfully obtained via tape-casting (Nano Lett. 2023, 23, 1, 227–234)”.

(2) Figure 3 is briefly mentioned but not really explained in the main text.

Response: We thank the reviewer for this comment. We have now added relevant description about Figure 3 as follows in the revised main text.

“However, it should be noted that lithium thiophosphates typically undergo severe reaction with polar solvents (Fig. 3a), such as dimethylformamide, leading to sulfide electrolyte decomposition and reduction of the ionic conductivity. This is because sulfides will suffer from nucleophilic attack by the aldehyde group with lone-pair electrons at electronegative oxygen. Consequently, only solvents with low-polarity or non-polarity, such as toluene and xylene, are usually used during wet process. This is because non (or low)-polar solvents exhibit chemical inertness in contact with lithium thiophosphates owing to their negligible donor ability (Fig. 4b and 4c).”

(3) Several performance weaknesses have been mentioned for lithium symmetric cells with sulfide thin films, but no insight has been provided into the reasons why.

Response: We thank the reviewer for this comment. We have now provided insights into the performance weaknesses mentioned for lithium symmetric cells with sulfide thin films in the revised main text.

“While the addition of a polymer binder could enhance the density of sulfide ceramics, there are still some pores that promote the lithium dendrite growth. Additionally, the polymer fails to

completely wrap the sulfide electrolyte particles. Consequently, the sulfide electrolytes undergo reactions with the lithium-metal anode at the interface, resulting in an increase of interface impedance. Moreover, some binders would react with the lithium-metal anode, leading to an elevation of the electronic conductivity and further accelerating the lithium dendrites nucleation and growth. Additionally, the mechanism of lithium dendrite growth in composite electrolyte films need to be further elucidated.”

(4) Strategies raised in the Outlook section are mostly vague. Something more specific and pertaining to particular challenges such as those in comment #3 would be more helpful.

Response: We thank the reviewer for this suggestion. We have now added more specific strategies in the Outlook section, especially a paragraph about how to improve the lithium symmetric battery performance with sulfide thin film. Please see them in the revised main text.

“Additionally, developing new sulfide electrolytes with good stability against polar solvent is also essential. Some strategies, such as doping some soft acid elements into the sulfide electrolyte or substituting soft alkali sulfur with hard alkali oxygen, could be adopted.”

“Improving lifespan and critical current density of lithium symmetric batteries plays a vital role in the practical application of sulfide-based electrolyte films. Several strategies could be considered to achieve this goal, such as developing new binders comparable to the lithium anode, hot pressing of composite film to enhance density, lowering the electronic conductivity of sulfides, and constructing artificial SEI to alleviate the side-reaction between the composite film with lithium-metal anode.”

Reviewer #4

Li et al summarized the sulfide-based composite solid electrolyte films for all-solid-state batteries. In this short review, the ionic transport mechanism of sulfide/polymer composite electrolyte films is provided to afford a fundamental for the development of composite electrolyte films with high ionic conductivity. The preparation methods and the properties of sulfide-based composite electrolytes are introduced in detail, and the advantages and disadvantages of each method are also analyzed. The application of composite electrolyte films in all-solid-state battery is also presented. This is a very important review in the field of materials science. It can be further improved in the following aspects:

1. The most important events in sulfide-based composite solid electrolyte films for all-solid-state batteries should be listed as Figure to help readers to catch the whole scenario of this field.

Response: We thank the reviewer for this suggestion. We have now listed the most important events in sulfide-based composite solid electrolyte films for all-solid-state batteries in Figure 6 to help readers to catch the whole scenario of this field. Please see the below figure.



Fig. 6 A brief chronology of development of some important events in sulfide-based composite solid electrolyte films for all-solid-state batteries

2. How Li ion transfer through the interfaces between polymer and sulfide solid electrolyte? How about the charge and carrier distribution?

Response: In the case of composite electrolyte films in which sulfide acts as matrix and polymer is filler, the sulfide phase is mainly responsible for the Li⁺ transport. If ionically insulating polymer binders, such as NBR, poly(styrene-co-butadiene) rubber (SBR), are used, lithium ions could not migrate through the sulfide/polymer binder interface. If the common insulating binders are replaced by the ionically conductive polymer-based electrolytes, lithium ions could migrate through sulfide phase, polymer phase and sulfide/polymer interface phase, and lithium ions preferably diffuse through the sulfide ceramic phase.

In the case of the composite electrolyte in which the polymer acts as the matrix and the sulfide as the filler, there exist a flexible polymer phase, sulfide inorganic phase and polymer/inorganic interfacial phase. The ionic transport mainly occurs in the interfacial phase between the polymer matrix and inorganic fillers, as well as the surrounding polymer phase. The possible ionic transport mechanism is as follows. Nano-sized sulfide solid electrolyte particles with large specific surface area inhibit the crystallization of polymer chain. As a result, a large number of amorphous phases along the surface of the filler are formed in the polymer, thereby enhancing the movement ability of polymer chain and improving the ability of ionic transport. The dissociation of lithium salts is promoted due to the Lewis acid-base interaction between the surface groups of lithium salts and the sulfide fillers, leading to an increase of the lithium ions concentration, and thus the ionic conductivity is improved. In addition, a highly active interfacial layer is formed between the polymer and the sulfide fillers, which in turn lowers the activation energy for ion migration in the interface layer and provides a fast ion conduction pathway.

3. The state of the art on the electrochemical performance of all-solid-state batteries based on sulfide-based composite solid electrolyte films should be well presented.

Response: We thank the reviewer for this suggestion. We have now added some recent cases about the electrochemical performance of all-solid-state batteries based on sulfide-based composite solid electrolyte films as follows in the main text.

“Kang *et al.* coated $\text{Li}_6\text{PS}_5\text{Cl}$ -NBR slurry on a nylon net template to obtain a 31 μm composite film with an ionic conductivity of 0.18 mS cm^{-1} . Based on the above film, the ASSB with LiCoO_2 as cathode and Li as anode displayed specific energy and energy density of 127.9 Wh kg^{-1} and 140.7 Wh L^{-1} , respectively (ACS Appl. Mater. Interfaces 2023, 15, 28064-28072). Similarly, a 45 μm composite film with an ionic conductivity of 0.51 mS cm^{-1} was prepared via coating $\text{Li}_6\text{PS}_5\text{Cl}$ -NBR slurry on a microporous PE separator. With the help of thin film, the $\text{Li} \parallel \text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ full cell delivered a high specific energy of 314 Wh kg^{-1} (Adv. Energy Mater. 2024, 14, 2302596)”

4. The recent advances in sulfide-based composite solid electrolyte films for batteries (e.g. J Energy Chem 2021, 58, 17; Adv Funct Mater 2021, 31, 2101985; InfoMat 2022, 4, e12292; J Energy Chem 2022, 74, 309; WIREs Comput Mol Sci 2023, 13, e1621; Adv Mater 2023, 35, 2206013) should be further highlighted.

Response: Thank the reviewer for this suggestion. We have now cited these references in the main text.

1st Mar 24

Dear Professor Wang,

Your manuscript titled "Progress and Prospect of Sulfide-Based Composite Solid Electrolyte Films" has now been seen again by our referees, whose comments appear below. In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Materials under the open access CC BY license (Creative Commons Attribution v4.0 International License).

We therefore invite you to revise your paper one last time to address the remaining concerns of reviewer 3. At the same time we ask that you edit your manuscript to comply with our journal policies and formatting style in order to maximise the accessibility and therefore the impact of your work.

EDITORIAL REQUESTS

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We hope to hear from you within two weeks; please let us know if the process may take longer.

Best regards,

Dr Jet-Sing Lee

Associate Editor

Communications Materials

orcid.org/0000-0002-6740-8700

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

Accept

Reviewer #3 (Remarks to the Author):

The authors have addressed most comments satisfactorily. Two issues remain:

(1) The purpose of highlighting SEBS for binder-solvent systems remains unclear. The authors explained in the rebuttal that it is an example of "good compatibility" with a nonpolar solvent and (the reviewer presumes) also sulfide electrolytes. However, binders with the same characteristics have been discussed in the preceding paragraph already (i.e., NBR and SBR).

(2) In the added discussion "such as developing new binders comparable to the lithium anode" the authors probably mean "compatible" instead of "comparable".

Reviewer #4 (Remarks to the Author):

It can be accepted now.

A Point-by-Point Response Letter

We greatly appreciate the valuable comments and suggestions from editor and all reviewers. Accordingly, we have carried out extended experiments and made suitable revisions, which we believe have greatly improved our manuscript. The following are our point-by-point responses to all reviewers' comments. The corresponding changes have also been highlighted in the revised manuscript.

Reviewer #1

Accept.

Response: We thank the reviewer for taking time to review our manuscript, and we also appreciate your recommendation for publication of our work.

Reviewer #3

The authors have addressed most comments satisfactorily. Two issues remain:

Response: We thank the reviewer for his/her appreciations to our work, and would also like to thank the reviewer for his/her very valuable comments on the manuscript.

(1) The purpose of highlighting SEBS for binder-solvent systems remains unclear. The authors explained in the rebuttal that it is an example of "good compatibility" with a nonpolar solvent and (the reviewer presumes) also sulfide electrolytes. However, binders with the same characteristics have been discussed in the preceding paragraph already (i.e., NBR and SBR).

Response: We thank the reviewer for this comment. Actually, our purpose does not focus on the SEBS binder. The reason why we highlight this reference is that the authors have analyzed in detail the stability of sulfide electrolytes against different solvents via a variety of characterization techniques. In addition, the obtained film shows good performance with high ionic conductivity and thin thickness. We have now revised our descriptions as follows in the revised main text.

"Tan et al. analyzed the stability of $\text{Li}_7\text{P}_3\text{S}_{11}$ against various solvent pairs by comprehensive methods. They found that p-xylene (XYL) exhibited good compatibility with $\text{Li}_7\text{P}_3\text{S}_{11}$. Additionally, styrene-ethylene-butylene-styrene (SEBS) polymers could be solved into the XYL. Based on the above optimal system, a $\text{Li}_7\text{P}_3\text{S}_{11}$ -SEBS composite film with an ionic conductivity of 0.7 mS cm^{-1} and a thickness of $50 \text{ }\mu\text{m}$ was successfully prepared via tape-casting method".

(2) In the added discussion "such as developing new binders comparable to the lithium anode" the authors probably mean "compatible" instead of "comparable".

Response: We thank the reviewer for this suggestion. We have now changed "comparable" as "compatible" in the revised manuscript.

Reviewer #4

It can be accepted now.

Response: We are grateful to the reviewer for insightful comments and suggestions in improving our work. We also appreciate your time and effort to review our work.