

Quantifying the Self-Discharge Rate of Solid-State Batteries

Corresponding Author: Professor Juergen Janek

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In this Comment article, Alt and Janek discuss the reversible self-discharge in solid-state batteries due to residual electronic conductivity in the solid electrolytes and develop a quantitative model to predict the reversible losses for several representative solid electrolytes. The results are consistent with a recent experimental study (Ref. 5). The theoretical model is novel and answers a question that the reviewer has struggled for years on how to quantitatively predict reversible capacity loss. Authors are the first to precisely point out the electrochemical stability window (ESW) as the driving force for internal self-discharge and propose an Ohm's-law-like equation for the internal self-discharge current density deriving from a diffusion-driven transport. Given the intense interest in solid-state battery research, the reviewer appreciates the timely report and believes the analysis will stimulate further research on a largely ignored topic, i.e., calendar/shelf life, for solid-state battery development. The reviewer believes the Comment article is ready to be published in the current form. Below are two comments the reviewer would like authors to consider discussing, with the main goal to clarify suggestions/recommendations for future action from the solid-state battery community.

Electronic transport in solid electrolytes. For each solid electrolyte, the authors used a particular electronic conductivity in the model based on literature results. However, as the authors know, electronic transport in Li solid electrolytes has been rarely studied. There are many open questions on whether the electronic conductivity reported in literature, even in the reviewer's work, is the intrinsic electronic conductivity of solid electrolytes. More careful studies are still needed to verify whether the reported value is intrinsic property of the material or due to defects such as grain boundaries, crystallinity, surfaces, non-stoichiometry etc. Knowledge of their Li activity dependence and charge carrier is still missing. It is suggested that authors consider discussing this point to hopefully stimulate more research on this topic, especially by scientists from the solid state ionics community, as understanding and lowering electronic conduction in solid electrolytes is certainly the most important direction to address the challenge of reversible self-discharge. Also, the current article reads like the driving force and average electronic conductivity are independent, but as the authors know, they are related. The average electronic conductivity is determined by the defect equilibria at the corresponding ranges of Li activity or chemical potential. Because the defect equilibrium diagram for sulfide, halide, and oxide can be very different, not just in carrier concentrations but also in the dominant electronic carrier, a larger ESW does not necessarily mean a higher internal self-discharge current.

Effect of interphases. Authors are suggested to further clarify the effect of interphase on the theoretical model. Thinking of a simple circuit model with three resistors in series for electronic transport, R-CEI, R-SE, and R-SEI. One of the assumptions for the model to work, i.e., leakage current is mainly driven by Li chemical potential gradient in the SE, is that R-CEI and R-SEI are much smaller than R-SE. However, this may not always be the case for every solid electrolyte. For example, a Li₂S-rich SEI with an electronic conductivity of 10-12 S/cm and a thickness of 100 nm can have a comparable electronic resistance for a 10 μ m-thick solid electrolyte with an electronic conductivity of 10-10 S/cm. When R-SEI or R-CEI is much larger than R-SE, then the leakage current may be largely determined by the quality of SEI/CEI. While quantifying the electronic resistance of interphases is challenging, this can be tested by quantifying the leakage current at different state of charge (SOC) of solid-state cells, because if the leakage current is solely driven by the chemical potential gradient in the solid electrolyte, it will be SOC-independent, given the limited ESW, for a typical 4 V cell. For the authors' information, in Ref. 5, a 4.2V voltage was used to calculate the average electronic conductivity, 3.5×10^{-10} S cm⁻¹ at 25°C and 7.0×10^{-10} S cm⁻¹ at 60°C, based on the reversible capacity loss. If the ESW, 0.5 V, was used, then the average electronic conductivity would be about one order of magnitude higher. Authors may want to consider expanding the discussion from line 163 to line 169. This can not only help provide critical information on the specific conditions where the model is accurate, but also, more importantly, suggest an important direction to address this challenge by designing electronically insulating interphases. After all, if the electronic conductivity of most promising solid electrolytes turned out to be based on luck rather than design, or there is no way to reduce it, which the reviewer does not hope so, it would still be good to let the solid-state battery community optimistically know that there are still ways to address it.

Reviewer #2

(Remarks to the Author)

In this comment, the authors raise an issue that the electronic conductivity of solid electrolytes (SEs) can lead to internal self-discharge (ISD) in solid-state batteries (SSBs). Specifically, they argue that ISD will become more pronounced in commercial SSBs, as the SE layer in the SSBs is typically much thinner than in lab-scale cells. In this context, the authors present a basic model predicting the ISD rate and draw attention to this potential concern. I think this perspective is meaningful, as ISD represents a possible yet overlooked risk in the SSB field. However, before publication, I think the authors should address several potential counterarguments.

1. In my opinion, it has not been convincingly demonstrated that electronic conductivity is the main cause of ISD in SSBs. The authors base their claim on the rate and reversibility of ISD, but these elements are insufficient to point out electronic conductivity as the dominant factor, especially given that electrochemical decomposition of SEs in the cathode is also known to be severe and partially reversible. Moreover, other mechanisms may likewise contribute to ISD. Therefore, I recommend that the authors provide additional discussion clarifying the relative importance of the SEs' electronic conductivity in comparison with other potential ISD-inducing mechanisms.

2. In commercial SSBs, the SE layer will likely incorporate polymeric binders. Thus, the ISD rate estimated solely from SEs might be overestimated, as the insulating nature of the binders could mitigate the electronic leakage. Since this comment emphasizes risks in commercial-level SSBs, I think the authors' ISD model should also account for more practical conditions. In my opinion, additional discussion that considers the reduced electronic conductivity of composite SE layers would make this comment more persuasive.

Overall, this manuscript seems to need additional discussion to support the authors' claims. Nevertheless, if these issues are adequately addressed, I think the comment provides a valuable perspective worthy of publication. There are several minor points to be supplemented.

1. The details and limitations of the ISD model should be further elaborated or included as a supplementary discussion in the supporting information.

2. A brief discussion about the temperature dependence of ISD would be helpful.

3. The authors should consider providing supplementary discussion about the relative importance of the electronic conductivity of the solid-electrolyte interphase (SEI) and cathode-electrolyte interphase (CEI) compared to that of the bulk SE layer.

Reviewer #3

(Remarks to the Author)

In this manuscript authors emphasized that it is imperative that battery research, across both academia and industry, places greater emphasis on the electronic properties of SEs to enable competitive energy densities through the use of thin separators. This includes precise measurement of σ_{e}^- (e⁻) under stable conditions via Hebb-Wagner measurements to estimate internal self-discharge in full-cell SSBs. Equally important is recognizing that SEI and CEI formation not only affect lithium inventory and cell resistance but also influence the internal self-discharge rate by affecting the cell's average σ_{e}^- . Authors imply that only by addressing these intertwined factors of electronic transport, material stability, and long-term storage behavior can "solidified" batteries realistically achieve performance competitive with conventional lithium-ion systems.

It was previously pointed out (<https://doi.org/10.1002/aenm.202204098>) that using Hebb-Wagner approach, anodic decomposition of SE is highlighted as the key source for the overestimated results for the intrinsic electronic conductivity of SEs. Based on the inaccuracy analysis for the Hebb-Wagner approach, it is possible to use this method to measure the intrinsic electronic conductivity of SEs if the applied potential on the blocking electrode is lower than the anodic limit of the SE and if a reversible electrode that is stable with the SE is used. What is different and unique about the approach recommended by authors here?

"Insufficient suppression of electronic transport across solid separators will severely constrain the applicability and competitiveness of practical SSBs – at least in case of long-term storage." How relevant and competitive are SSB in stationary storage for self-discharge of SE to be an issue??

It was previously determined by the voltage dependences of electronic conductivity in LLZO and LYC, that holes, instead of electrons, are the dominant charge carriers for the electronic transport. Does this mean that in these materials self-discharge rate will be slower than in SE materials with n-type conductivity?

Is anode free design, that offer significant lowering of chemical potential difference between electrodes, and interface reactivity that can be engineered/controlled, more promising in terms of suppression of electronic conductivity?

Since electronic conductivity stay constant and ionic improves with the temperature can storing SSB at elevated temperatures be beneficial for preventing self-discharge?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Authors have addressed my comments. It can be accepted as is.

Reviewer #2

(Remarks to the Author)

The authors have well addressed the comments so I would recommend accepting the manuscript is.

Reviewer #3

(Remarks to the Author)

The authors have significantly improved the quality and clarity of the manuscript through their revisions. The responses to the reviewers' comments have been thorough, and the changes made have strengthened both the presentation and the scientific rigor of the work. I am satisfied with the current version and am happy to recommend the manuscript for publication.

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Detailed response to reviewers' comments for Nature Energy manuscript NENERGY-25103409

We express our gratitude to the reviewers for their feedback and the time they dedicated to it. We believe that their input has contributed to improving the manuscript, which is highly appreciated. The modifications made in the revised manuscript are indicated in **yellow**. Below, we provide detailed responses (in **blue**) to each of their comments.

Reviewers comments

Reviewer #1 (Remarks to the Author):

Reviewer: In this Comment article, Alt and Janek discuss the reversible self-discharge in solid-state batteries due to residual electronic conductivity in the solid electrolytes and develop a quantitative model to predict the reversible losses for several representative solid electrolytes. The results are consistent with a recent experimental study (Ref. 5). The theoretical model is novel and answers a question that the reviewer has struggled for years on how to quantitatively predict reversible capacity loss. Authors are the first to precisely point out the electrochemical stability window (ESW) as the driving force for internal self-discharge and propose an Ohm's-law-like equation for the internal self-discharge current density deriving from a diffusion-driven transport. Given the intense interest in solid-state battery research, the reviewer appreciates the timely report and believes the analysis will stimulate further research on a largely ignored topic, i.e., calendar/shelf life, for solid-state battery development. The reviewer believes the Comment article is ready to be published in the current form. Below are two comments the reviewer would like authors to consider discussing, with the main goal to clarify suggestions/recommendations for future action from the solid-state battery community.

Authors' Response: We thank the reviewer for the positive report and the valuable corrections/comments that we believe significantly improved the value of our work; please see our detailed response below.

Reviewer: Electronic transport in solid electrolytes. For each solid electrolyte, the authors used a particular electronic conductivity in the model based on literature results. However, as the authors know, electronic transport in Li solid electrolytes has been rarely studied. There are many open questions on whether the electronic conductivity reported in literature, even in the reviewer's work, is the intrinsic electronic conductivity of solid electrolytes. More careful studies are still needed to verify whether the reported value is intrinsic property of the material or due to defects such as grain boundaries, crystallinity, surfaces, non-stoichiometry etc. Knowledge of their Li activity dependence and charge carrier is still missing. It is suggested that authors consider discussing this point to hopefully stimulate more research on this topic, especially by scientists from the solid state ionics community, as understanding and lowering elec-

tronic conduction in solid electrolytes is certainly the most important direction to address the challenge of reversible self-discharge. Also, the current article reads like the driving force and average electronic conductivity are independent, but as the authors know, they are related. The average electronic conductivity is determined by the defect equilibria at the corresponding ranges of Li activity or chemical potential. Because the defect equilibrium diagram for sulfide, halide, and oxide can be very different, not just in carrier concentrations but also in the dominant electronic carrier, a larger ESW does not necessarily mean a higher internal self-discharge current.

Authors' Response: We thank the reviewer for the insightful comments and agree with the points raised. While we believe that most aspects were already briefly addressed in the manuscript, we extended our discussion on these points and have added a clarifying sentence noting that the electronic conductivity (if not controlled by extrinsic impurities) depends on defect equilibria and the local lithium activity.

p. 3: "The average electronic conductivity enters into the description during integration over the ESW, and we like to emphasize that σ_{e^-} cannot be considered constant across the separator but rather depends on the local μ_{Li} , which drives i_{SD} . More precisely, both the local σ_{e^-} and its average $\overline{\sigma_{e^-}}$ depend on factors such as the local lithium activity, resulting defect equilibria and non-stoichiometries that determine the dominant electronic charge carrier, as well as impurities, grain boundaries, and other irregularities that may introduce extrinsic electronic defects. Unfortunately, these aspects remain largely unexplored for many SEs and warrant more detailed investigation."

We consider the discussion on p. 5 regarding the consequences of a wide ESW to be sufficient in this context.

p. 5: "A wide ESW stabilizes the SE against degradation in the high-energy full-cell environment with a high OCV. Yet, a wider ESW increases the driving force (i.e., $\Delta\mu_{Li}(SE)/d$) for i_{SD} , potentially increasing SDR and making its suppression more dependent on low average $\overline{\sigma_{e^-}}$. Conversely, narrow ESWs cause formation of interphases at both electrodes that reduce $\Delta\mu_{Li}$ across the SE bulk and, thus, the driving force of i_{SD} (as illustrated in Figure 1)."

Reviewer: Effect of interphases. Authors are suggested to further clarify the effect of interphase on the theoretical model. Thinking of a simple circuit model with three resistors in series for electronic transport, R-CEI, R-SE, and R-SEI. One of the assumptions for the model to work, i.e., leakage current is mainly driven by Li chemical potential gradient in the SE, is that R-CEI and R-SEI are much smaller than R-SE. However, this may not always be the case for every solid electrolyte. For example, a Li₂S-rich SEI with an electronic conductivity of 10-12 S/cm and a thickness of 100 nm can have a comparable electronic resistance for a 10 μ m-thick solid electrolyte with an electronic conductivity of 10-10 S/cm. When R-SEI or R-CEI is much larger than R-SE, then the leakage current may be largely determined by the quality of SEI/CEI. While quantifying

the electronic resistance of interphases is challenging, this can be tested by quantifying the leakage current at different state of charge (SOC) of solid-state cells, because if the leakage current is solely driven by the chemical potential gradient in the solid electrolyte, it will be SOC-independent, given the limited ESW, for a typical 4 V cell. For the authors' information, in Ref. 5, a 4.2V voltage was used to calculate the average electronic conductivity, $3.5 \times 10^{-10} \text{ S cm}^{-1}$ at 25°C and $7.0 \times 10^{-10} \text{ S cm}^{-1}$ at 60°C, based on the reversible capacity loss. If the ESW, 0.5 V, was used, then the average electronic conductivity would be about one order of magnitude higher. Authors may want to consider expanding the discussion from line 163 to line 169. This can not only help provide critical information on the specific conditions where the model is accurate, but also, more importantly, suggest an important direction to address this challenge by designing electronically insulating interphases. After all, if the electronic conductivity of most promising solid electrolytes turned out to be based on luck rather than design, or there is no way to reduce it, which the reviewer does not hope so, it would still be good to let the solid-state battery community optimistically know that there are still ways to address it.

Authors' Response: Excellent comment. We fully agree that interphases can suppress *ISD* if their electronic resistance becomes the bottleneck for electron transport across the separator. We have now incorporated additional discussion on this point and extended our theoretical framework to include both SEI and CEI interphases in SSBs, and believe that this addition significantly improves the impact and quality of our work. Interestingly, our *ISD* model already captures the correct driving force (the ESW) as now thoroughly derived in the SI. In short, if a SE is thermodynamically stable at both negative and positive electrode, then the ESW is wider than the OCV, and the OCV defines the driving force for *ISD* (we consider this as case (i) in the SI). If the SE is not stable at one or both electrodes, then the ESW defines the driving force for *ISD* (considered as case (ii) in the SI). If the resulting *ISD* is too high, protecting interlayers need to be applied (considered as case (iii) in the SI). These lower the voltage range applied to the SE such that again the ESW is met. In case of SEI and CEI formation, the thermodynamics of the corresponding SEI and CEI formation reactions defines the ESW, and the SEI and CEI grow until the electronic flux across all three layers in series, i.e., SEI, SE bulk and CEI, is equal. Then it is sufficient to consider the SE bulk with its electronic partial conductivity, and both SEI and CEI are included implicitly.

p.6: " Interestingly, it is the electronic transport within the SEI and CEI layers that controls their growth rate and will also influence their effect on *ISD*. [...] Ultimately, whether SEI and CEI layers effectively suppress *ISD* in SSBs depends on their $\overline{\sigma_{e^{-},int}}$ and thickness, which are inherently coupled by their diffusion-controlled growth."

For clarity, and to keep this response concise, we also refer the reviewer to the detailed treatment now provided in the Supplementary Information (SI).

Reviewer #2 (Remarks to the Author):

Reviewer: In this comment, the authors raise an issue that the electronic conductivity of solid electrolytes (SEs) can lead to internal self-discharge (ISD) in solid-state batteries (SSBs). Specifically, they argue that ISD will become more pronounced in commercial SSBs, as the SE layer in the SSBs is typically much thinner than in lab-scale cells. In this context, the authors present a basic model predicting the ISD rate and draw attention to this potential concern. I think this perspective is meaningful, as ISD represents a possible yet overlooked risk in the SSB field. However, before publication, I think the authors should address several potential counterarguments.

Authors' Response: We thank the reviewer for the positive reception and evaluation of our work; please see our detailed response below.

Reviewer: 1. In my opinion, it has not been convincingly demonstrated that electronic conductivity is the main cause of ISD in SSBs. The authors base their claim on the rate and reversibility of ISD, but these elements are insufficient to point out electronic conductivity as the dominant factor, especially given that electrochemical decomposition of SEs in the cathode is also known to be severe and partially reversible. Moreover, other mechanisms may likewise contribute to ISD. Therefore, I recommend that the authors provide additional discussion clarifying the relative importance of the SEs' electronic conductivity in comparison with other potential ISD-inducing mechanisms.

Authors' Response: We understand the reviewer's concern and have therefore clearly defined *internal* self-discharge (ISD) in SSBs, distinguishing it from other processes. Reversible degradation at the negative or positive electrode alters the lithium inventory but does not constitute self-discharge in the sense of an internal (minor) electronic short-circuit, as it arises from destructive material instabilities. Precisely, (ir-)reversible capacity loss caused by SE redox reactions has to be distinguished from reversible charge loss due to the inner electronic short-circuit. From our perspective, and as defined in the manuscript, the only mechanism of *internal* self-discharge (*i.e.*, charge loss) is insufficiently suppressed ("parasitic") electronic conductivity, which drains charge across the separator without external load (similar to redox-shuttle processes in LIBs). We use the following definition in our work:

p. 2: "*ISD* leads to a reduction in the battery's state-of-charge (SoC) under stationary conditions. This reversible *internal* charge loss is fundamentally distinct from (ir-)reversible capacity loss caused by chemo-mechanical degradation of active materials and chemical degradation of SE during cycling. In contrast, *ISD* reduces energy efficiency but does not damage the SSB; it represents a minor *internal* electronic short-circuit and must be distinguished from irreversible degradation reactions that permanently deplete the lithium inventory."

Reviewer: 2. In commercial SSBs, the SE layer will likely incorporate polymeric binders. Thus, the ISD rate estimated solely from SEs might be overestimated, as the in-

ulating nature of the binders could mitigate the electronic leakage. Since this comment emphasizes risks in commercial-level SSBs, I think the authors' ISD model should also account for more practical conditions. In my opinion, additional discussion that considers the reduced electronic conductivity of composite SE layers would make this comment more persuasive.

Authors' Response: We fully agree with the reviewer that polymer binders and other additives or contaminants can strongly influence the electronic conductivity of (composite) separators and probably reduce its value. We have therefore expanded our discussion of this point on p. 5. At the same time, we would like to emphasize that our work introduces a theoretical framework for describing ISD in SSBs based on fundamental assumptions about these systems, which are now also elaborated in the SI.

p.5: "Consequently, this highlights the need for targeted materials optimization to further reduce $\overline{\sigma_e^-}$ in SEs and enhance shelf life. In commercial scenarios, systematic studies on the impact of polymer binders and other additives on the separator's $\overline{\sigma_e^-}$ are essential, as they enable the processing of thin-separator architectures compatible with high-energy cells and potentially reduce the separator's $\overline{\sigma_e^-}$. Additionally, impurity levels in SEs must be understood and controlled, as common carbon-based contaminants from production are suspected to substantially increase the materials' $\overline{\sigma_e^-}$."

Reviewer: Overall, this manuscript seems to need additional discussion to support the authors' claims. Nevertheless, if these issues are adequately addressed, I think the comment provides a valuable perspective worthy of publication. There are several minor points to be supplemented:

1. The details and limitations of the ISD model should be further elaborated or included as a supplementary discussion in the supporting information.
2. A brief discussion about the temperature dependence of ISD would be helpful.
3. The authors should consider providing supplementary discussion about the relative importance of the electronic conductivity of the solid-electrolyte interphase (SEI) and cathode-electrolyte interphase (CEI) compared to that of the bulk SE layer.

Authors' Response: We thank the reviewer for the points raised.

1. We have added further details and fundamental assumptions of our *ISD* model to discussions throughout the main text. While real separators and SSBs may deviate from these idealized assumptions, as explained to the reader and highlighted in our discussion, the proposed model provides a quantitative framework to describe and analyze *internal* self-discharge currents and rates. Many factors causing deviations remain largely unexplored for numerous SEs, warranting further investigation (see also p. 4 on electronic conductivity). Additional assumptions of our *ISD* model for each cell component or layer, not covered in the main manuscript, are now also provided in the SI.

p. 3: “Here, we consider a homogeneous separator, free of grain boundaries, additives (e.g., polymer binders), and impurities under stationary conditions, which could otherwise influence electronic transport across the separator and its average electronic conductivity ($\overline{\sigma}_{e^-}$).”

p.8: “As shown, *internal* self-discharge can be readily described and analyzed using the proposed model. However, critical scientific data on electronic transport, non-stoichiometries, impurity levels, contaminations, and related materials parameters remain scarce.”

2. We have now included a brief sentence on the temperature-dependence of ISD.

p. 5: “Moreover, *ISD* increases at elevated temperatures, resulting in higher *SDR*, as $\overline{\sigma}_{e^-}$ likely rises with the enhanced mobility of electronic charge carriers and temperature-induced formation of more electronic defects (defect equilibria).”

3. In line with reviewer 1, we now provide a more thorough and quantitative discussion on the role of SEI and CEI on *ISD* and resulting self-discharge rates. For clarity, and to keep this response concise, we refer the reviewer to our detailed response to Reviewer 1 above and the detailed treatment now provided in the Supplementary Information (SI).

Reviewer #3 (Remarks to the Author):

In this manuscript authors emphasized that it is imperative that battery research, across both academia and industry, places greater emphasis on the electronic properties of SEs to enable competitive energy densities through the use of thin separators. This includes precise measurement of " σ_{e^-} " under stable conditions via Hebb-Wagner measurements to estimate internal self-discharge in full-cell SSBs. Equally important is recognizing that SEI and CEI formation not only affect lithium inventory and cell resistance but also influence the internal self-discharge rate by affecting the cell's average (σ_{e^-}). Authors imply that only by addressing these intertwined factors of electronic transport, material stability, and long-term storage behavior can “solidified” batteries realistically achieve performance competitive with conventional lithium-ion systems.

Authors' Response: We appreciate that the reviewer agrees with our view and perspective. In line with reviewers 1 and 2, we now provide a more thorough and quantitative discussion on the role of SEI and CEI on ISD and resulting self-discharge rates. Please see our detailed response to Reviewer 1 above.

Reviewer: It was previously pointed out (<https://doi.org/10.1002/aenm.202204098>) that using Hebb-Wagner approach, anodic decomposition of SE is highlighted as the key source for the overestimated results for the intrinsic electronic conductivity of SEs.

Based on the inaccuracy analysis for the Hebb–Wagner approach, it is possible to use this method to measure the intrinsic electronic conductivity of SEs if the applied potential on the blocking electrode is lower than the anodic limit of the SE and if a reversible electrode that is stable with the SE is used. What is different and unique about the approach recommended by authors here?

Authors' Response: We fully agree with the reviewer that the Hebb-Wagner approach has its pitfalls that require particular care in any measurement of the electronic partial conductivity in Hebb-Wagner-type cells. However, our manuscript does not deal with measurements of electronic conductivities. In fact, we rather highlight that careful measurements, like the ones reported in the mentioned reference, are necessary and crucial for the proper description of any electronic effect in SSBs. Such carefully determined values of the separator's electronic conductivity can then be used in our model to quantify and describe ISD. The mentioned paper is already cited in the original version (reference #11).

Reviewer: “Insufficient suppression of electronic transport across solid separators will severely constrain the applicability and competitiveness of practical SSBs – at least in case of long-term storage.” How relevant and competitive are SSB in stationary storage for self-discharge of SE to be an issue??

Authors' Response: We understand the reviewer's perspective regarding the relevance of SSBs for long-term or stationary storage. At present, however, the future deployment scenarios and operating conditions for SSBs remain uncertain (and in competition to conventional Li-ion batteries). With our manuscript, we aim to highlight the importance of electronic properties and self-discharge processes in SSBs, and to stimulate further investigations; including those directed toward stationary applications. We therefore believe that extended discussion of this topic is outside of the scope of our comment.

Reviewer: It was previously determined by the voltage dependences of electronic conductivity in LLZO and LYC, that holes, instead of electrons, are the dominant charge carriers for the electronic transport. Does this mean that in these materials self-discharge rate will be slower than in SE materials with n-type conductivity?

Authors' Response: In fact, depending on defect equilibria and lithium activity, either electron holes or electrons can dominate the electronic current. However, many factors such as charge carrier density, mobility, and concentration affect the overall electronic conductivity, making it difficult to predict which carrier would lead to faster or slower self-discharge under given conditions. We therefore consider a detailed discussion of this point to be redundant, relying on fundamental knowledge of the reader, and outside the scope of our manuscript. Especially, it could risk confusing rather than clarifying the topic to the reader at this point. As written above, the in-depth discussion of electronic properties of specific solid electrolytes is an important subject for future research. We like to point out that the study and better understanding of electronic properties of

oxygen solid electrolytes as membranes in solid oxide fuel cells (SOFC) was an important prerequisite on the way to stable systems.

Reviewer: Is anode free design, that offer significant lowering of chemical potential difference between electrodes, and interface reactivity that can be engineered/controlled, more promising in terms of suppression of electronic conductivity?

Authors' Response: We hope our response below addresses the reviewer's concern, although we struggle to fully understand this comment. We apologize for any confusion if our reply does not fully resolve the reviewer's concern or question.

Since lithium metal is formed at the negative electrode of an anode-free cell during the first charging cycle, we believe that our *ISD* model for SSBs applies equally to both conventional and anode-free cell designs. Thus, we do not expect that an anode-free design alone will effectively suppress electronic conductivity, if stored in the charged state, without additional modifications to the cell architecture.

Reviewer: Since electronic conductivity stay constant and ionic improves with the temperature can storing SSB at elevated temperatures be beneficial for preventing self-discharge?

Authors' Response: Both ionic and electronic conductivity are expected to increase with temperature, as charge carrier mobilities improve and in particular electron-hole pair formation is supported. The resulting effect on self-discharge critically depends on the relative enhancement of ionic versus electronic transport. Accordingly, we believe that elevated temperatures are unlikely to suppress self-discharge. Additionally, elevated temperatures can also accelerate decomposition and interphase formation, which may either enhance or mitigate self-discharge depending on their (electronic) properties.

p. 5: "Moreover, *ISD* increases at elevated temperatures, resulting in higher *SDR*, as $\overline{\sigma_e^-}$ likely rises with the enhanced mobility of charge carriers."