

jz-2022-007686.R1

Name: Peer Review Information for "Oxygen-Enhanced Chemical Stability of Lithium-Mediated Electrochemical Ammonia Synthesis"

First Round of Reviewer Comments

Reviewer: 1

Comments to the Author

The rigorous quantification of electrolyte decomposition byproducts is really interesting. They argue that a stable SEI is essential for high-efficiency lithium-mediated ammonia synthesis (which makes sense). However, I thought some of their arguments weren't fully fleshed out. Not all of their pieces of evidence were really put in context with each other in a way I found convincing. I think some of this might just be an issue with flow and if the paper was organized slightly differently it might be easier to understand the comparisons they're making.

- Abstract: By "ammonia synthesis efficiency," do they just mean Faradaic efficiency? Or does addition of O₂ also increase rate? I know they go into more depth on this in an earlier paper but it feels very vague.

- Abstract: They say addition of O₂ resulted in "less decomposition products" which also isn't very precise as from my reading they were only able to quantify organic products.

P. 4, Line 48 – This feels kind of nitpicky but they're kind of vague about why changes in the electrolyte composition deteriorate the efficiency of the reaction. They say later that changes in the SEI are probably what is changing the FE so it feels odd that they don't specify that until later in the paper.

P. 5, Line 42 – "protecting the highly reactive anode against..." do they mean cathode here?

P. 9-11 – It took me several re-reads to understand the discussion surrounding Fig. S3/Fig. 3b – I think some of the significance of their results could be explained more clearly. My understanding is that addition of O₂ results in a decrease of organic byproducts (and hence an increase of inorganic byproducts?) but only up to a point. However, the later discussion (particularly on p.10, Line 51) leads me to believe that increased O₂ content leads to increased formation (and presumably deposition) of insoluble Li salts. That doesn't track with *decreased* deposition upon increased O₂ concentration. They address this a bit on p.11, line 24, but don't really elaborate on why increasing O₂ concentration eventually decreases production of insoluble Li salts...? This could be an issue with my understanding but I do think they could be more explicit about drawing parallels between visible changes in electrode deposition amounts and their GC-MS results.

P.13, Line 48 – I'm unclear on whether these two arguments are competing or just supplementary explanations on why O₂ improves reaction efficiency. It seems possible that the change in the SEI due to differing electrolyte compositions doesn't actually have that much of an effect compared to inhibition of HER by O₂ (or the other way around).

P.16, Line 38 – is this the total main component or just the main organic component? I think this should be clarified.

P.17, Line 27 – if this is the case, why is there much less visible deposition on the WE surface? Why don't they see lithium oxide derivatives? I'm confused by the argument here.

P.17, Line 34 – I don't see a figure S8 in the SI – am I missing it? I assume they mean Fig. S7, which could be more clearly labeled – I'm unclear on what A, B, and C are on the graphs.

P. 21, Line 4 – The fact that they can't quantify inorganic byproducts undercuts their arguments re: the SEI being more stable at optimal O₂ concentration. The general picture I'm getting is that inorganic byproducts are increased at optimal O₂ concentrations, which results in a more stable SEI and less electrolyte decomposition. But I'm unclear on why inorganic byproducts then decrease upon adding more O₂ (at least that's the impression I get from Fig. S3) and why having a primarily-inorganic SEI would improve FE (if that's the case).

P.22, Line 10 – The argument that O₂ is suppressing HER seems a bit unclear as I'm unsure what the mechanism is – earlier in the paper they seem to argue that O₂ oxidizes potential HER substrates (p.13, Line 48), preventing HER. However, here they say that HER is suppressed because the SEI is so stable. I'm not sure that they've ruled out the possibility that O₂'s role is simply oxidation of HER substrates.

Author's Response to Peer Review Comments:

Response to the Reviewers

Reviewer(s)' Comments to Author:

Reviewer: 1

Recommendation: This paper is publishable subject to minor revisions noted. Further review is not needed.

Comments:

The rigorous quantification of electrolyte decomposition byproducts is really interesting. They argue that a stable SEI is essential for high-efficiency lithium-mediated ammonia synthesis (which makes sense). However, I thought some of their arguments weren't fully fleshed out. Not all of their pieces of evidence were really put in context with each other in a way I found convincing. I think some of this might just be an issue with flow and if the paper was organized slightly differently it might be easier to understand the comparisons they're making.

The authors are very grateful for the Reviewer's comments and suggestions. We have tried to take into account them and clarify the text as much as possible. In advance, we would like to mention that there are only 2 inorganic materials detected by the used methods, specifically NMR: lithium hydroxide and hydrated lithium hydroxide. The rest is about organic byproducts. No possibility for GCMS to say something about inorganic materials, except gases e.g. Ar, CO₂, N₂, He, O₂, H₂O, which we didn't include in this work because they are always present in MS from the atmosphere or carrier gas in GCMS, i.e. He.

- Abstract: By "ammonia synthesis efficiency," do they just mean Faradaic efficiency? Or does addition of O₂ also increase rate? I know they go into more depth on this in an earlier paper but it feels very vague.

The authors appreciate the Reviewer's comment and would like to specify that 'efficiency' is meant for Faradaic efficiency. The abstract was modified.

- Abstract: They say addition of O₂ resulted in "less decomposition products" which also isn't very precise as from my reading they were only able to quantify organic products.

The authors agree that the text has to be more specific and the name 'byproducts' should represent mainly organic compounds detected by GCMS and NMR. By the methods used it was possible to determine mostly the organic molecules. However, also some inorganics e.g. LiOH xH₂O and gases e.g. N₂, He, Ar, CO₂, O₂, which were not included in the story due to their presence in the atmosphere. However, from the previous studies and experience the authors are aware what kind of inorganic materials form after LiMEAS, and it is mainly LiOH xH₂O.

P. 4, Line 48 – This feels kind of nitpicky but they're kind of vague about why changes in the electrolyte composition deteriorate the efficiency of the reaction. They say later that changes in

the SEI are probably what is changing the FE so it feels odd that they don't specify that until later in the paper.

The authors have taken into account the Reviewer's comment and elaborated a bit more in the text.

P. 5, Line 42 – “protecting the highly reactive anode against...” do they mean cathode here?

The authors have made a mistake by ‘anode’ instead of ‘cathode’ and modified the text accordingly.

P. 9-11 – It took me several re-reads to understand the discussion surrounding Fig. S3/ Fig. 3b – I think some of the significance of their results could be explained more clearly. My understanding is that addition of O₂ results in a decrease of organic byproducts (and hence an increase of inorganic byproducts?) but only up to a point. However, the later discussion (particularly on p.10, Line 51) leads me to believe that increased O₂ content leads to increased formation (and presumably deposition) of insoluble Li salts. That doesn't track with *decreased* deposition upon increased O₂ concentration. They address this a bit on p.11, line 24, but don't really elaborate on why increasing O₂ concentration eventually decreases production of insoluble Li salts...? This could be an issue with my understanding but I do think they could be more explicit about drawing parallels between visible changes in electrode deposition amounts and their GC-MS results.

The authors meant that all of the products shown in Fig. 3 are based on GCMS. It means volatile organic molecules, not inorganic salts. Both types of compounds, organic and inorganic, form during LiMEAS. However, the methods used in this study are limited to more or less organic molecules. Introduction of O₂ decreases organic decomposition byproducts and most likely induces more of inorganic oxygenated Li compounds. Their concentration most likely depends on O₂ concentration. However, they cannot be characterized by the methods used in this study.

The authors would like to mention that increasing O₂ concentration eventually does not decrease but increase production and amount of insoluble Li salts. The figure caption was slightly modified.

P.13, Line 48 – I'm unclear on whether these two arguments are competing or just supplementary explanations on why O₂ improves reaction efficiency. It seems possible that the change in the SEI due to differing electrolyte compositions doesn't actually have that much of an effect compared to inhibition of HER by O₂ (or the other way around).

The authors agree on the Reviewer's comment and believe that introduction of O₂ decreases organic and increases inorganic byproducts in the system i.e. Li₂O, Li₂O₂, LiO₂ which are unstable in the presence of H₂O and will turn to LiOH xH₂O. Those 2 arguments are just supplementing O₂ effect. Also, the excess O₂ has an effect on EtOH oxidation on the anode side, which is most likely related to acetaldehyde and acetic acid formation shown in Fig. 3.

P.16, Line 38 – is this the total main component or just the main organic component? I think this should be clarified.

The authors clarified the point in the text specifying that it is the main organic component.

P.17, Line 27 – if this is the case, why is there much less visible deposition on the WE surface? Why don't they see lithium oxide derivatives? I'm confused by the argument here.

The authors do not know and do not want to speculate on this. We assume that by visual inspection of the electrodes is very difficult to say something about the extent of the reaction on just how the electrodes look like after the experiments. The authors tried to comment on the SEM images in the main text, but carefully. However, we know from many previous studies that lithium hydroxides are the main inorganic materials of the deposit on WE since lithium oxide is not stable in the presence of H₂O which is formed during LiMEAS.

P.17, Line 34 – I don't see a figure S8 in the SI – am I missing it? I assume they mean Fig. S7, which could be more clearly labeled – I'm unclear on what A, B, and C are on the graphs.

The authors admit the mistake – Fig. S8 is Fig. S7 in the ESI. A, B, and C on the graphs mean just the parts of the spectrum in different chemical shift regions. The figure captions have been modified.

P. 21, Line 4 – The fact that they can't quantify inorganic byproducts undercuts their arguments re: the SEI being more stable at optimal O₂ concentration. The general picture I'm getting is that inorganic byproducts are increased at optimal O₂ concentrations, which results in a more stable SEI and less electrolyte decomposition. But I'm unclear on why inorganic byproducts then decrease upon adding more O₂ (at least that's the impression I get from Fig. S3) and why having a primarily-inorganic SEI would improve FE (if that's the case).

The authors admit that it is very difficult to comment something from Fig. S3 with respect to inorganic compounds and their amount. We have seen such a formation on the surface of the electrodes several times. We think that the main scope of the paper is organic compounds because the methods used are limited.

The increase of O₂ will not decrease inorganic byproducts, however organic. We assume the excess of O₂ just kills effective lithium and inhibits LiMEAS together with electrolyte decomposition and polyTHF formation, which are both related to metallic Li reacting with THF.

P.22, Line 10 – The argument that O₂ is suppressing HER seems a bit unclear as I'm unsure what the mechanism is – earlier in the paper they seem to argue that O₂ oxidizes potential HER substrates (p.13, Line 48), preventing HER. However, here they say that HER is suppressed because the SEI is so stable. I'm not sure that they've ruled out the possibility that O₂'s role is simply oxidation of HER substrates.

The authors appreciate the Reviewer's knowledge and would like to hear more about HER substrates. We just speculate from what we see by the methods used. Most likely, O₂ is involved in EtOH oxidation. It means the concentration of LiMEAS active EtOH will be reduced and the FE goes up. We know that lower EtOH concentration than 1vol% improves FE but reduces stability of the system i.e. dendrite formation, flaking in the electrolyte etc. Of course, some O₂ is also responsible for effective SEI. However, these studies are ongoing and will be reported in the future.