

# Tracking solid electrolyte interphase dynamics using operando fibre-optic infrared spectroscopy and multivariate curve regression

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

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This paper presents the use of the IR-FEWS technique to study the chemical dynamics of electrolytes and the evolution of the solid electrolyte interphase (SEI). While the technique has been previously utilized by the authors to monitor electrolyte evolution (10.1038/s41560-022-01141-3), this work demonstrates an advancement by combining FTIR with the mathematical analysis method MCR-ALS. The manuscript contains numerous detailed errors, please check and correct them.

1. Abbreviations used in the previous text should be used consistently in the following text, e.g. "lithium methyl carbonate" in "Nevertheless, a second component (C6, light green in Figure 6.f.g) is needed to model the end of the charge, which indicates the further formation of lithium methyl carbonate (characteristic band 359 at 1355 cm<sup>-1</sup>)". And the abbreviation "IR-FEWS" used for "To address this issue, we exploit opportunities offered by operando optical fibre IR spectroscopy (IR-FEWS) via the use of chalcogenide fibres embedded into negative electrode materials..." in the abstract is inconsistent with its full terms. Please check carefully.
2. The calculated electrode surface area in the supporting materials should be corrected from "6 cm<sup>-2</sup>" to "6 cm<sup>2</sup>".
3. There is a discrepancy between the description in lines 97-101 and the actual figures in the supporting information. And the chromatograms should match those in the main text or be relabeled to correspond correctly to the times.
4. Line 247 should reference "Figure 3f and Supplementary figure 5" instead of "Figure 3e and Supplementary figure 5". Please check for similar errors throughout the manuscript.
5. Terminology Correction: In lines 352 and 359, "charge" should be corrected to "discharge".
6. The description in lines 393-402 of the main text does not match the figures. Please correct each inconsistency.

Here are some suggestions regarding the content of the manuscript.

7. The text mentions: "The GITT trace is shown in Figure 2b: during reduction, the electrode material initially shows a minor capacity of around 1 mAh (Supplementary figure 2), which we attribute to conversion reaction of surface copper(I) oxide (Cu<sub>2</sub>O), whose presence on a pristine sample was confirmed by X-ray photoelectron spectroscopy (XPS), as shown in Supplementary figure 3.", but the O spectrum of XPS does not mark the characteristic peaks about Cu<sub>2</sub>O, and there is no Cu spectrum to prove the presence of Cu<sub>2</sub>O, please explain in detail.
8. The relationship between different molar concentrations of LiPF<sub>6</sub> and IR absorption spectra is shown. However, it is unclear whether the three EC:DMC ratios impact the results. Please provide experimental evidence to support this.
9. The text does not state what the charging conditions are for different battery systems (Sn|Li, CoO|Li, LTO|Li) and how it takes into account that different batteries take different times to charge. Please add in the text.

10. In the LTO|Li battery system, Fig. 6g shows that the LMC fluctuates more noticeably in the first charge, while in the subsequent cycling experiments there is a noticeable change only in the fourth cycle, please make an interpretation.

11. It's generally accepted that the SEI forms during the first cycle and there should be  $\text{Li}_2\text{CO}_3$  residue at the end of the discharge. However, the C5 component generated during charging and dissolved during discharging in Figure 7f. Please explain.

12. In Fig. 7f, there are significant fluctuations in C6 before the first charge and at the beginning of the charge of the battery, please explain.

Since the combination of IR and MCR-ALS to identify and tune various constituents is a major innovation of the paper, here are some questions and suggestions for this.

13. The MCR-ALS method has limitations when dealing with newly emerging unknown products. If unknown products with spectral peaks similar to those of the target product appear, it may result in peak fitting that significantly deviates from the actual situation, even if the mean squared error (MSE) is low. How does this study address this issue to prevent such occurrences? Since the combination of IR and MCR-ALS is a major innovation of the paper, a more detailed explanation of how this method distinguishes and quantifies the various mixed substances is warranted.

14. In Figure 1b, different lithium salt concentrations significantly affect the relative intensity of the two peaks of EC at  $1800\text{ cm}^{-1}$ . Which spectrum should be used as the standard for fitting during battery cycling? Will the relative concentration changes of lithium ions near the electrode during cycling affect the shape of substances within the spectral range, thereby influencing the results of data analysis?

15. Given the extreme short penetration depth of evanescent waves, how does the experiment ensure good contact between the fiber surface and the electrode material? Otherwise, the monitored substances might not be SEI.

As the combination of IR and MCR-ALS is a major innovation of the paper, it is recommended to supplement the findings with other methods such as ex-situ Raman and nuclear magnetic resonance (NMR) to verify the reliability of using this method to identify and quantify the components of SEI.

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)

What are the noteworthy results?

IR optical fiber measurements demonstrated increased sensitivity to SEI components in electrode materials, compared to traditional FTIR or Raman measurements. The authors further demonstrated that MCR-ALS can identify at least three primary SEI constituents and qualitatively track their growth during battery cycling. This capability was demonstrated in several electrolyte and electrode compositions, indicating that the technique is robust and widely applicable.

Will the work be of significance to the field and related fields? How does it compare to the established literature? If the work is not original, please provide relevant references.

The use of chalcogenide fibers extends existing work using operando FTIR-ATR diagnostics to battery formats beyond coin cells. While casting electrodes directly on an ATR should result in similar SEI detection capabilities for coin cells, optical fibers can be cast into different battery formats, including cylindrical, pouch, and prismatic cells. Thus, optical fiber-based detection methods may be more amenable to studying commercial cell performance.

In one of the earliest applications of FTIR-ATR to operando electrolyte measurements in the anode, Hongyou et al. reported sensitivity to SEI species 1. This result is similar to the authors prior paper (citation 12 in the manuscript) using optical fibers in cylindrical cells, in that they both detect SEI reaction products near  $1675\text{ cm}^{-1}$ . In both of these prior studies, the measured SEI species are likely dissolved species in the bulk electrolyte. I did not find a discussion of how the authors differentiate dissolved SEI species (especially near  $1675\text{ cm}^{-1}$ ) from SEI deposited directly on the electrode. This should be discussed. While a detailed review of experimental SEI characterization techniques is not within the scope of the manuscript, the literature review should be strengthened. In particular, Raman has been used to study SEI evolution 2,3. It would be informative to identify the species detectable by each method as well as the challenges of collecting spectra in situ for each case.

Ex-situ SEI analysis with FTIR has been used extensively. However, there are concerns about the roll electrode preparation, especially washing, has on SEI composition. It seems the fiber optic measurement would be a good way to evaluate the effectiveness of ex-situ SEI analysis. The two methods were compared in supplementary figure 9, showing similar results.

Beyond the obvious benefits of dynamic SEI measurement using their technique, can the authors comment on the performance of ex-situ SEI analysis as compared with in-situ measurements?

The method is demonstrated over several battery charge cycles. Can the authors comment on anticipated issues with using the fiber sensors over tens or hundreds of cycles, which would be needed to study the role of SEI on battery aging?

Does the work support the conclusions and claims, or is additional evidence needed?

The diagnostic technique and data analysis methods are well documented, and the diagnostic performance is impressive. The ability of MCR-ALS to distinguish separate SEI phenomenon is very promising. As the authors acknowledge, isolating SEI species is challenging and thus the MCR-ALS components cannot be definitively identified. Instead, these components are associated with semi-carbonates and  $\text{Li}_2\text{CO}_3$ , but not exclusively.

A reader may question whether the chalcogenide fiber is truly inert and does not participate in the SEI formation process. While the presence of the fiber may have some impact on SEI formation, the authors previous work found the fiber material to be stable in electrolytes during battery cycling (citation 12). It would be good to state this in the paper. Is it possible to evaluate the fiber integrity after in situ testing in this study? The intimate contact between the fiber and active materials could lead to fiber interactions that were not observed in prior experiments (for example, other chalcogenide materials have been used as ion conductors 4). It would be interesting to see if any SEI species were directly deposited on the fiber or only on active materials surrounding the fiber. Along these lines, does the fiber attenuation markedly change during battery cycling? This may be addressed in supplementary figure 9, but it's unclear if the electrode surrounding the fiber is intact after repeatedly washing with DMC.

Are there any flaws in the data analysis, interpretation and conclusions? Do these prohibit publication or require revision?  
I did not find any flaws in data analysis, interpretation, or conclusions.

Is the methodology sound? Does the work meet the expected standards in your field?

Yes.

Is there enough detail provided in the methods for the work to be reproduced?

Yes.

Jason Porter  
Associate Professor  
Department of Mechanical Engineering  
Brigham Young University

#### References

1. Kenichi Hongyou, Takashi Hattori, Youko Nagai, Toshihiro Tanaka, Hiroyuki Nii, Kaoru Shoda, Dynamic in situ fourier transform infrared measurements of chemical bonds of electrolyte solvents during the initial charging process in a Li ion battery, *Journal of Power Sources*, Volume 243, 2013, Pages 72-77, ISSN 0378-7753, <https://doi.org/10.1016/j.jpowsour.2013.05.192>.
2. N. Gogoi, T. Melin, E. J. Berg, Elucidating the Step-Wise Solid Electrolyte Interphase Formation in Lithium-Ion Batteries with Operando Raman Spectroscopy. *Adv. Mater. Interfaces* 2022, 9, 2200945. <https://doi.org/10.1002/admi.202200945>
3. Yeyoung et al, Probing the Evolution of Surface Chemistry at the Silicon–Electrolyte Interphase via In Situ Surface-Enhanced Raman Spectroscopy, *J. Phys. Chem. Lett.* 2020, 11, 1, 286–291
4. Wolfgang Bensch, Thomas Bredow, Hubert Ebert, Paul Heitjans, Sylvio Indris, Sergiy Mankovsky, Martin Wilkening, Li intercalation and anion/cation substitution of transition metal chalcogenides: Effects on crystal structure, microstructure, magnetic properties and  $\text{Li}^+$  ion mobility, *Progress in Solid State Chemistry*, Volume 37, Issues 2–3, 2009, Pages 206-225, ISSN 0079-6786, <https://doi.org/10.1016/j.progsolidstchem.2009.11.007>

(Remarks on code availability)

#### Reviewer #3

(Remarks to the Author)

Leau et al. present a solid body of research in which optical fibre infrared spectroscopy enables operando investigations into battery solid electrolyte interphase (SEI) dynamics. This builds on earlier work by this group in which the optical fibre technique was developed and applied to electrolytes in commercial batteries. The novelty of the new work presented is the emphasis on specifically probing the evolution of SEI, which requires the use of numerical methods to decouple changes associated with the solid and liquid phases – in this case multivariate curve resolution by alternating least squares (MCR-ALS). This is a significant advance considering the notorious complexity of SEI dynamics, and the method presented offers a new way forward to measure and study them.

The quality of the science is generally very high and the presentation is clear. With a few exceptions highlighted below the conclusions are supported by the evidence presented. I would recommend publication, contingent on the following issues being addressed.

## General Comments:

The article is rather long for a communication. Given the large body of work included in the paper, cutting this down will not likely be possible, so an alternative journal may be more appropriate.

The MCR-ALS method is a purely mathematical approach which is implemented without knowledge of whether each of the resulting component spectra can definitively be assigned to an individual chemical species. In this sense these deconstructed spectra are strictly hypothetical so attributing them to a given species based on known band positions comes with the assumption that the number of extracted components is correct. Given the obvious need to minimise the number of components in the numerical analysis, there is a danger some components will be missed and the system oversimplified. This does not undermine the value of the approach for separating different spectral contributions, but some consideration of this should be included in the discussion to make it more balanced.

## Specific Comments:

L21: IR-FEWS not properly defined in abstract.

L99: The MCR-ALS method is based on the assumption that the Beer Lambert Law applies. However, deviations from this may occur at high concentrations, which the authors should acknowledge.

L138: This paragraph is discussing features in Figure 1b, but the text refers to Figure 1d, which is confusing. Also, Figure 1b contains reference to EC<sub>solv</sub> and EC<sub>free</sub> as well as DMC<sub>solv</sub> and DMC<sub>free</sub>. The text should therefore be corrected to specify Figure 1b and the subscripts "solv" and "free" should be defined more generally.

L157: The authors state that the spectrum can be decomposed into four components, corresponding to the solvated and free DMC and EC. Presumably the 2000 cm<sup>-1</sup> to 900 cm<sup>-1</sup> spectral range for the decomposition was selected to deliberately exclude the electrolyte (PF<sub>6</sub><sup>-</sup>) band at 850 cm<sup>-1</sup>? If so, it would be worth stating this explicitly.

L163: Figure 1b legend refers to three different EC:DMC ratios, but it is unclear which spectra are which in the figure.

L188: Capacity is attributed to a conversion reaction on Cu<sub>2</sub>O and the authors refer to XPS data in Supplementary Figure 3 to support this conclusion. However, it is surprising to see that the Cu region of the XPS spectrum is not shown in the figure. The text in the SI (L43) states that copper oxide is observed on the pristine sample and disappears after cycling, but no data is shown to support this.

L195: "Looking at the characteristic negative and positive symmetric absorbance variations observed in the ν<sub>C=O</sub> and ν<sub>OCO</sub> regions reveal the decreases in Li<sup>+</sup> concentration occurring in the electrode during reduction". This statement is potentially quite misleading because the change in these band intensities reflect changes in the solvent and are only indirectly associated with the amount of Li<sup>+</sup>. It would appear as if both the DMC<sub>free</sub> and DMC<sub>solv</sub> bands undergo a decrease intensity with time, but if the amount of Li<sup>+</sup> is decreasing, would the DMC<sub>free</sub> be expected to increase? The analysis later in the manuscript considers this aspect more thoroughly, but care should be taken with the wording at this point.

L214: It is not clear how the authors conclude that "any contribution of product cross-over from the Li metal counter electrode can safely and effectively be disqualified". The data referred to in Supplementary figure 4 shows that there is a negligible change in the two selected band intensities when a cell without the active electrode material is left for several hours at OCV. However, this is an uncharged cell with no current flowing, so no products would be expected to be generated at the Li counter electrode. Hence, the absence of any spectral change is rather unsurprising and says very little about whether product-crossover is affecting the result shown in figure 2d.

L229: The text refers to the 8 components shown in "Figures 3b-e", but Figure 3b is the voltage profile, so the text should presumably say "Figures 3c-f".

L247: The text refers to Figure 3e, but presumably this is meant to be 3f as there is no reference to components C7 and C8 in Figure 3e.

L291: The authors compare the absorbance difference between two separate experiments under different conditions, but this is not wise as the absolute absorbance behaviour is likely to be very sensitive to the precise contact area between electrode particles and the optical fibre, so may vary considerably from experiment to experiment and does not necessarily reflect differences in the SEI chemistry. If the authors wish to quantitatively compare the absorbance in this way, the reported values should include quantified uncertainties derived from multiple experiments to establish if the differences are statistically significant. Alternatively, the absorbance values could be normalised to a chosen peak intensity that is known to not vary between experiments, if such a peak exists. The authors do allude to the dangers of quantitative comparisons later in the manuscript (L364), so this cautionary note should really come earlier as this potentially weakens their argument around the differences between DMC only and EC/DMC if not addressed.

L262: The authors refer to Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, rather than LTO, so this should be made consistent.

L385: The rate C/2.5 is followed by the phrase "2.5 hours per 1 lithium", which may be misinterpreted. Better to say "2.5

hours for complete charging of the LTO". Also, looking closely at Figure 7b, the C rate does not look like it is consistent with C/2.5. A total of 5 charge-discharge cycles are completed in roughly 70 hours, which corresponds to a rate of around C/7.

L448: The authors refer to optical fibre-based Raman scattering in a way that suggests this has not previously been explored, when it has. See, for example, Journal of Power Sources 359 (2017) 435e440 and ChemSusChem 2017, 10, 855 – 861.

(Remarks on code availability)

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Q1: The TAS fiber developed in this paper has a wavelength range of 3 to 13  $\mu\text{m}$ , which, although it can monitor most of the molecular bonding in electrolytes, such as C=O, is not sufficient for monitoring bonding in a wider wavelength range, such as O-O bonding. For the design of sulfur-based optical fibers, what are the ways to extend their infrared monitoring window?

Q2: The analytical range of the MCR-ALS algorithm used in this paper is limited to a window with wave numbers from 2000 to 900  $\text{cm}^{-1}$ , is there any possibility of algorithmic improvement for the nonlinear effects caused by the anionic band at 840  $\text{cm}^{-1}$ ?

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)

The authors have sufficiently addressed all comments from my original review. I recommend the manuscript be published.

(Remarks on code availability)

Reviewer #3

(Remarks to the Author)

All concerns have been addressed in the revised manuscript, so publication is recommended.

(Remarks on code availability)

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**Reviewer #1 (Remarks to the Author):****General comment.**

*This paper presents the use of the IR-FEWS technique to study the chemical dynamics of electrolytes and the evolution of the solid electrolyte interphase (SEI). While the technique has been previously utilized by the authors to monitor electrolyte evolution (10.1038/s41560-022-01141-3), this work demonstrates an advancement by combining FTIR with the mathematical analysis method MCR-ALS. The manuscript contains numerous detailed errors, please check and correct them.*

**General Response:** We thank the reviewer for acknowledging the advancements made in the present work that builds upon our previous efforts. We furthermore appreciate the time spent by the reviewer in rigorously going through our manuscript. We do apologize for the numerous detailed errors as many of these propagated accumulated over months of experimental rounds and self-critical revisions.

**Specific comments**

**Comment 1.** *Abbreviations used in the previous text should be used consistently in the following text, e.g. "lithium methyl carbonate" in "Nevertheless, a second component (C6, light green in Figure 6.f g) is needed to model the end of the charge, which indicates the further formation of lithium methyl carbonate (characteristic band 359 at 1355 cm<sup>-1</sup>)". And the abbreviation "IR-FEWS" used for "To address this issue, we exploit opportunities offered by operando optical fibre IR spectroscopy (IR-FEWS) via the use of chalcogenide fibres embedded into negative electrode materials..." in the abstract is inconsistent with its full terms. Please check carefully.*

**Response 1.** We apologize for this inconsistency. Corrections have been made accordingly.

**Comment 2.** *The calculated electrode surface area in the supporting materials should be corrected from "6 cm<sup>-2</sup>" to "6 cm<sup>2</sup>".*

**Response 2.** Thank you for noting this oversight. The correction has been made.

**Comment 3.** *There is a discrepancy between the description in lines 97-101 and the actual figures in the supporting information. And the chromatograms should match those in the main text or be relabeled to correspond correctly to the times.*

**Response 3.** Sub-figure labels have been corrected and the color map adapted to match that of the main text.

**Comment 4.** *Line 247 should reference "Figure 3f and Supplementary figure 5" instead of "Figure 3e and Supplementary figure 5". Please check for similar errors throughout the manuscript.*

**Response 4:** Correction has been done. We believe we have caught all similar errors.

**Comment 5. Terminology Correction:** *In lines 352 and 359, "charge" should be corrected to "discharge".*

**Response 5:** The reviewer rightly points out an ambiguity. We have referred to charging on the basis that LTO is primarily used as an anode material and that the material is lithiated during the full charge of the cell. To clarify the ambiguity in the context of a lithium metal half-cell, we have replaced the term with "LTO lithiation".

**Comment 6.** *The description in lines 393-402 of the main text does not match the figures. Please correct each inconsistency.*

**Response 6:** The inconsistency spotted by the referee has been corrected.

**Comment 7.** *Here are some suggestions regarding the content of the manuscript.*

*The text mentions: "The GITT trace is shown in Figure 2b: during reduction, the electrode material initially shows a minor capacity of around 1 mAh (Supplementary figure 2), which we attribute to conversion reaction of surface copper(I) oxide (Cu<sub>2</sub>O), whose presence on a pristine sample was confirmed by X-ray photoelectron spectroscopy (XPS), as shown in Supplementary figure 3.", but the O spectrum of XPS does not mark the characteristic peaks about Cu<sub>2</sub>O, and there is no Cu spectrum to prove the presence of Cu<sub>2</sub>O, please explain in detail.*

**Response 7:** We thank the reviewer for pointing out this ambiguity concerning copper oxide and for giving us the opportunity to clarify it. Reviewer 3 also had the same query, as noted below. Indeed, the XPS O1s spectrum for the pristine sample shows a peak at 529.4 eV, which we highlighted in green in the corrected version, as it had been wrongly attributed to Cu<sub>2</sub>O. By further collecting the Cu2p spectrum (included in Supplementary figure 5.), we

concluded that we were dealing with CuO rather than Cu<sub>2</sub>O. This may appear, at first, incoherent with XRD measurements that reveals the presence of Cu<sub>2</sub>O, and not CuO. Such a discrepancy can be reconciled by keeping in mind that XPS solely probes solely 50-100 Å of the Cu particles surfaces (the most oxidized state of Cu (CuO) while XRD probe a deeper part of the particles (less oxidized Cu (Cu<sub>2</sub>O)). So likely, both oxides are involved in the process. Lastly after cycling (and before cleaning), Cu<sub>2</sub>O and Cu<sup>0</sup> are mainly detected, in line with the previous sequence (Cu<sup>0</sup> → Cu<sub>2</sub>O → Cu) reported for Li-driven conversion reactions (Klein, F. *et al.* Reaction Mechanism and Surface Film Formation of Conversion Materials for Lithium- and Sodium-Ion Batteries: An XPS Case Study on Sputtered Copper Oxide (CuO) Thin Film Model Electrodes. *J. Phys. Chem. C* **120**, 1400–1414 (2016)).

**Comment 8.** *The relationship between different molar concentrations of LiPF<sub>6</sub> and IR absorption spectra is shown. However, it is unclear whether the three EC:DMC ratios impact the results. Please provide experimental evidence to support this.*

**Response 8:** Indeed, the impact of the solvent ratio on spectra cannot be identified from Figure 1b alone. We have therefore followed the referee's suggestion and have now plotted the three EC:DMC ratios separately in Supplementary figure 1, along with the DMC solvent only.

**Comment 9.** *The text does not state what the charging conditions are for different battery systems (Sn|Li, CoO|Li, LTO|Li) and how it takes into account that different batteries take different times to charge. Please add in the text.*

**Response 9.** A paragraph has been added to mention the choice of cycling rate in the text.

"The reduction current was chosen with the intention of observing a sufficient number of reduction events on a reasonable timescale. For Sn, CoO and LTO, it was C/80, C/5, and C/2.5 respectively, (C/N: 1 stoichiometric lithium,  $\Delta x = 1$ , per N hours). It therefore corresponds to a theoretical reduction time of 10 hours and 7.5 hours for CoO and LTO, respectively. We note that the theoretical capacity of the tin electrode was not reached, presumably attributed to the copious SEI formation in the Sn electrode that are coupled with materials rapid and dynamic increase in surface area that is coupled with volume change."

**Comment 10.** *In the LTO|Li battery system, Fig. 6g shows that the LMC fluctuates more noticeably in the first charge, while in the subsequent cycling experiments there is a noticeable change only in the fourth cycle, please make an interpretation.*

**Response 10.** We acknowledge the error in the legends we provided for Figures 7e and f, which adds to the confusion in our conveyed message. LMC appears alone in C7 in figure 7f, while in the C6 component there is also a band of LMC at 1350 cm<sup>-1</sup> (Figure 7e). This accounts for the formation of LMC that we observed during the first 4 cycles as well. The fact that LMC can be found in the two components at the same time was mentioned in the paper "a given chemical species may spread between several MCR-ALS numerical components."

We have corrected the error and clarified the text as follows:

"The two other MCR components model long-term SEI accumulation, with a distinction between the component of the first three cycles (mainly C6, light green, enlisting both Li<sub>2</sub>CO<sub>3</sub> and semi-carbonates, including LMC), and the next two cycles (mainly C7, grey, having a lessened Li<sub>2</sub>CO<sub>3</sub> contribution). More precisely, we attribute C7 to contributions from LMC (bands at 1635 cm<sup>-1</sup>, 1460 cm<sup>-1</sup>, 1355 cm<sup>-1</sup>, and 1104 cm<sup>-1</sup>), predominantly formed at the end of the reduction phase."

**Comment 11.** *It's generally accepted that the SEI forms during the first cycle and there should be Li<sub>2</sub>CO<sub>3</sub> residue at the end of the discharge. However, the C5 component generated during charging and dissolved during discharging in Figure 7f. Please explain.*

**Response 11.** Firstly, we should mention that tracking Li<sub>2</sub>CO<sub>3</sub> can be done by examining Figure 7d, where the associated wavenumber 1525 cm<sup>-1</sup> shows a slow, but steady increase. Secondly, we need to examine how MCR-ALS reconstructs these variations: from the spectral components in Figure 7e, we note that both C5 and C6 contribute to this wavenumber. Indeed, C5 increases alone during LTO reduction. In contrast, during LTO oxidation, the decrease in C5 is counterbalanced by the increase in the C6 component. We apologize for the error in the legends we provided for Figures 7e and f, which had led to the confusion spotted by the referee. It has now been corrected.

**Comment 12.** *In Fig. 7f, there are significant fluctuations in C6 before the first charge and at the beginning of the charge of the battery, please explain.*

**Response 12.** We also note some interesting behavior with C6 before strong periodicity is seen during later stages. In the pre-cycle fluctuations (first 2 hours), while there appears to be some instability, we don't consider these to be significant to any further interpretation because of their small amplitude. Now, if we consider the subsequent fluctuations (t=9h, 24h, 38h, etc) upon reaching low voltage that are not only visible in C5 and C6, but also in Figure 7d (raw data), we presume that these could be due to the formation of other SEI species, undetectable by mid-IR



spectroscopy, but affecting the refractive index in the volume near the sensor surface and thus impacting the penetration depth of the evanescent wave.

**Comment 13.** *Since the combination of IR and MCR-ALS to identify and tune various constituents is a major innovation of the paper, here are some questions and suggestions for this.*

13. *The MCR-ALS method has limitations when dealing with newly emerging unknown products. If unknown products with spectral peaks similar to those of the target product appear, it may result in peak fitting that significantly deviates from the actual situation, even if the mean squared error (MSE) is low. How does this study address this issue to prevent such occurrences? Since the combination of IR and MCR-ALS is a major innovation of the paper, a more detailed explanation of how this method distinguishes and quantifies the various mixed substances is warranted.*

**Response 13.** Intrinsically, the method can only distinguish substances whose spectra are sufficiently distinct and whose evolution is sufficiently different. More precisely, in a linear algebra framework, the set of spectra (seen as vectors of  $\mathbb{R}^n$ ) should be linearly independent, as should their temporal contribution. These limits are illustrated by the CoO experiment. The spectrum of DMDOHC is very close to that of DMC, which is understandable given the similarity of these two molecules. Consequently, in Figure 6a and Supplementary figure 22, component C5 (DMDOHC) grows along C1 (DMC<sub>free</sub>) while C2 (DMC<sub>coord.</sub>) shows a stable trend despite transient changes in Li<sup>+</sup> concentration during cell polarization. This suggests that C1 partially accounts for the formation of DMDOHC.

To convey some of these intrinsic challenges to the readers, we have adjusted the discussion section to include these considerations:

“Classic curve fitting approaches cannot be applied to the obtained IR spectra because quantitative differences instantly arise between the static reference samples (synthetic/pure SEI compounds) and dynamically convoluted operando spectra. Instead, an approach without *a priori* knowledge on the SEI composition was adopted where the interpretation is facilitated by employing a limited number of components in the numerical analysis, although admittedly at the risk of oversimplification or exclusion of minor species. As is often the case with numerical-driven methods, a critical posture should be adopted when interpreting the decomposition results, keeping the established literature surrounding the SEI in mind. Nevertheless, we hope this opens the door for groups with stronger chemometrics expertise to pursue work in the direction of robust decomposition algorithms. “

**Comment 14.** *In Figure 1b, different lithium salt concentrations significantly affect the relative intensity of the two peaks of EC at 1800 cm<sup>-1</sup>. Which spectrum should be used as the standard for fitting during battery cycling? Will the relative concentration changes of lithium ions near the electrode during cycling affect the shape of substances within the spectral range, thereby influencing the results of data analysis?*

**Response 14.** This is a good question. The change in Li<sup>+</sup> concentration in the electrode must have some effect on the observed spectra. As explained in the Methods section, this is taken into account in the cycling by including the four spectra in Figure 1d, learnt from the entire concentration dataset, in the MCR-ALS decomposition.

**Comment 15.** *Given the extreme short penetration depth of evanescent waves, how does the experiment ensure good contact between the fiber surface and the electrode material? Otherwise, the monitored substances might not be SEI.*

**Response 15.** The electrode material was dispersed in ethanol and dripped onto the fiber. This operation was done to ensure physical adhesion of the powder on the fiber surface once the ethanol had evaporated. This method was tested on Lithium Iron Phosphate (LFP) material which intrinsically absorbs IR: depositing dry LFP powder on the fiber results in no IR absorption, while using the aforementioned method reveals the material's characteristic bands (see Supplementary figure 32). With future work, this opens a large area for experimental optimization which may indeed, lead to even greater resolution and opportunity for IR-FEWS with battery materials.

**General comment.** *As the combination of IR and MCR-ALS is a major innovation of the paper, it is recommended to supplement the findings with other methods such as ex-situ Raman and nuclear magnetic resonance (NMR) to verify the reliability of using this method to identify and quantify the components of SEI.*

**Response.** This is a well legitimate question bearing in mind the present development of numerous ex-situ and operando analytical technique enlisting either Raman spectroscopy by E. J. Berg, “Elucidating the Step-Wise Solid Electrolyte Interphase Formation in Lithium-Ion Batteries with Operando Raman Spectroscopy. *Adv. Mater. Interfaces* 2022, 9, 2200945. <https://doi.org/10.1002/admi.202200945>) or NMR spectroscopy according to C. Grey elegant work “DNP-enhanced NMR of Lithium Dendrites: Selective Observation of the Solid–Electrolyte Interphase DOI:[10.26434/chemrxiv.10298438](https://doi.org/10.26434/chemrxiv.10298438) ” or by X-ray absorption spectroscopy “Revealing Solid Electrolyte Interphase

Formation Through Interface-Sensitive Operando X-ray Absorption Spectroscopy DOI:[10.26434/chemrxiv-2022-g2bzh-v2](https://doi.org/10.26434/chemrxiv-2022-g2bzh-v2)". Each of these techniques provides specific insights while combined IR optical spectroscopy and MCR-ALS method proposed here provide several information in one, allowing for instance, access to SEI growth and solvation-desolvation phenomena, while offering the possibility of tracking structural variation within the electrode material. Although we acknowledge the value of ex-situ Raman or NMR in establishing SEI composition and the need for pushing the state of understanding to leverage the findings of various spectroscopies, we believe that quantifying the SEI composition via these methods and rigorously linking it to our IR-FEWS data would require colossal amounts of work (at least with present methods). Furthermore, we feel that pursuing this direction would distract from the aim of the paper, which is to demonstrate the relevance of IR-FEWS in the context of tracking the SEI dynamics. Furthermore, it is important to show that our method differs radically from Raman, NMR or X-ray absorption in that it can be implemented in commercial cells working under real conditions to monitor the chemical dynamics of SEI, whereas the other methods cannot. We think this helps position IR-FEWS as an exciting new technology platform for SEI (and battery) analysis, as opposed to serving as a complementary technology to better/longer established methods.

## Reviewer #2 (Remarks to the Author):

### General comment.

What are the noteworthy results?

IR optical fiber measurements demonstrated increased sensitivity to SEI components in electrode materials, compared to traditional FTIR or Raman measurements. The authors further demonstrated that MCR-ALS can identify at least three primary SEI constituents and qualitatively track their growth during battery cycling. This capability was demonstrated in several electrolyte and electrode compositions, indicating that the technique is robust and widely applicable.

Will the work be of significance to the field and related fields? How does it compare to the established literature? If the work is not original, please provide relevant references.

The use of chalcogenide fibers extends existing work using operando FTIR-ATR diagnostics to battery formats beyond coin cells. While casting electrodes directly on an ATR should result in similar SEI detection capabilities for coin cells, optical fibers can be cast into different battery formats, including cylindrical, pouch, and prismatic cells. Thus, optical fiber-based detection methods may be more amenable to studying commercial cell performance.

We thank the referee for recognizing the added value of IR optical measurements within the field of battery. Below, we have responded to each question, and the changes made are highlighted in green in the updated version of the manuscript for easy reference.

### Specific comments

**Comment.1** In one of the earliest applications of FTIR-ATR to operando electrolyte measurements in the anode, Hongyou *et al.* reported sensitivity to SEI species 1. This result is similar to the authors prior paper (citation 12 in the manuscript) using optical fibers in cylindrical cells, in that they both detect SEI reaction products near 1675 $\text{cm}^{-1}$ . In both of these prior studies, the measured SEI species are likely dissolved species in the bulk electrolyte. I did not find a discussion of how the authors differentiate dissolved SEI species (especially near 1675 $\text{cm}^{-1}$ ) from SEI deposited directly on the electrode. This should be discussed.

**Response 1.** This is definitely a well-spotted and very important question we have been asking ourselves for quite some time and for which we believe we have a decent explanation based on additional experiments:

To address this question, we synthesized various known SEI components, such as LMC or LEDC (see Supplementary Figure 14). Each powder was mixed with either a solvent (EC/DMC) or an electrolyte (LiPF<sub>6</sub> EC/DMC) solution and vigorously agitated for 3 hours. The powder was added in a large enough amount (100 mg per 2 mL of solvent/electrolyte) that undissolved powder remain visible even after stirring. After allowing the solution to sediment, the liquid phase was collected and analyzed using FTIR-ATR. The IR spectra for all tests, shown in Supplementary Figure 15, correspond to those of the solvent or electrolyte only, indicating that within the accuracy of the experiment that the relevant SEI components in question are insoluble. This means that the alkyl-carbonates species formed should precipitate, in strong agreement with the experimental observation of a constant IR signal (e.g. presence of alkyl carbonate species) between a fiber that went to a full discharge to 0V and the same fiber that was once removed from the electrode and washed with DMC.

On the other hand, in a few literature papers (e.g. Hongyou, K. *et al.* Dynamic *in situ* fourier transform infrared measurements of chemical bonds of electrolyte solvents during the initial charging process in a Li ion battery. *Journal of Power Sources* **243**, 72–77 (2013)), as well as our earlier Nature Energy manuscript, we indirectly monitor SEI formation in commercial Na-ion cells via the detection of semi-carbonate species in liquid electrolyte. To reconcile these extremes we contend that the SEI formation occurring in a liquid environment enlists a “nucleation → precipitation” process whereby diffusion of species plays a key role. To have greater insights on the mechanistic of this process we have prepared a comprehensive study and manuscript whose preliminary results provide evidence how temperature, electrolyte amount, impurity, and current are impacting the SEI formation, with a core part of this being the distinction of “nucleation” and/or “diffusion” processes, in addition comments about their solubility, in general. However, this text is still in preparation and has not been submitted yet. Nevertheless, considering our experimental conditions we are convinced that we are indeed probing the solid electrolyte interphase. However, we acknowledge that we cannot fully exclude the chance that soluble molecules could also interfere with the IR absorbance signal. In light of this discussion we have slightly modified the text with the following addendum:

“While these observations confirm that the SEI is indeed insoluble within the accuracy of the experiment, a few literature papers have reported detecting semi-carbonate in liquid electrolyte via infrared spectroscopy<sup>21,37</sup>. This apparent paradox can be resolved by proposing that a nucleation-precipitation process is likely occurring during SEI formation. Therefore, while precipitated species are the major contributors to the SEI’s signature, minor contributions from soluble molecules cannot be totally excluded.”

**Comment 2.** *While a detailed review of experimental SEI characterization techniques is not within the scope of the manuscript, the literature review should be strengthened. In particular, Raman has been used to study SEI evolution 2,3. It would be informative to identify the species detectable by each method as well as the challenges of collecting spectra in situ for each case.*

**Response 2.** We agree with the referee’s comments that Raman spectroscopy is a valuable complementary technique for studying the structure and composition of chemicals. In response, we have added the following two paragraphs to the introduction (highlighted in green in the main text) to enhance the literature review with Raman spectroscopy studies on batteries. These additions cover both traditional in-situ microscopy and operando fiber-based designs:

“Conversely, Raman spectroscopy has proven to be a valuable tool for characterizing the SEI by detecting lower-wavenumber vibrational modes of molecules. For instance, Gogoi et al. investigated *in situ* the reduction EC to lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) on a gold film electrode<sup>9</sup>. However, the Raman effect is weak compared to IR absorption despite plasmonic enhancement techniques, including tip probes<sup>10</sup>, nanoparticles<sup>11</sup> or nanostructured substrates<sup>12</sup>, and requires laser light sources operating in the visible region which can potentially damage the SEI samples. For brevity, we direct interested readers to more comprehensive reviews on progress with operando optical spectroscopy of the SEI found elsewhere, e.g. Meyer et al<sup>13</sup>.”

“Using ultrafine double fibre probes and hollow-core microstructures fibres respectively<sup>18–20</sup>, Yamanaka *et al.* and Miele *et al.* overcame the double challenge of sample excitation and Raman photon collection. They implemented operando fibre-based Raman spectroscopy to pouch cell configuration, evidencing electrolyte composition change and gas bubbles formation. However, their setup depends on an external microfluidic system to pump the electrolyte through the fibre and enhance the signal, limiting both continuous monitoring and the ability to track changes in the electrode materials themselves.”

**Comment 3.** *Ex-situ SEI analysis with FTIR has been used extensively. However, there are concerns about the roll electrode preparation, especially washing, has on SEI composition. It seems the fiber optic measurement would be a good way to evaluate the effectiveness of ex-situ SEI analysis. The two methods were compared in supplementary figure 9, showing similar results. Beyond the obvious benefits of dynamic SEI measurement using their technique, can the authors comment on the performance of ex-situ SEI analysis as compared with in-situ measurements?*

**Response 3.** We appreciate the referee highlighting the importance of operando characterization compared to post-mortem analysis.

Indeed, in Supplementary Figure 13 (ex-Suppl.Fig.9), we compared operando and ex-situ IR measurements. After obtaining the operando spectrum, the cell was opened under an Argon atmosphere, repeatedly rinsed with DMC, and dried. The operando spectra at the end of cycling and the ex-situ IR spectra show similar IR signatures. However, the absorbance of the bands is generally lower in the ex-situ IR spectra, particularly for the bands corresponding to electrolyte solvents, which is expected as the ex-situ sample was dried.

Given the reactive nature of the electrolyte and SEI, we believe that operando characterization with IR fiber can effectively and rapidly confirm the studies conducted through post-mortem analysis. Additionally, the destructive nature of postmortem analysis limits the ability to examine global and dynamic phenomena. The operando technique will aid in identifying the chemical pathways leading to SEI formation and the intermediate species involved in these reactions. Nevertheless, it is also encouraging to see that ex-situ experiments can be validated in agreement with operando work.

**Comment 4.** *The method is demonstrated over several battery charge cycles. Can the authors comment on anticipated issues with using the fiber sensors over tens or hundreds of cycles, which would be needed to study the role of SEI on battery aging?*

**Response 4.** While the first cycles are crucial for observing the SEI formation, it is valid to question our ability to monitor cell aging. As illustrated from data in the LTO experiment depicted in Figure 7, we can already envision extend our work to >10<sup>1</sup> - 10<sup>2</sup> cycles. Our main limitation at the moment comes from the hardware, which does not support multiple simultaneous experiments, preventing long-term cycling studies. In this context, we would like to design optical and automation systems to facilitate the sequential testing of multiple cells. Additionally, we could consider focusing on a specific portion of the infrared spectra and utilize miniaturized infrared sensors like Near-Infrared (NIR) sensors for long term aging. Another challenge with aging experiments is that they are expected to

generate a large volume of data, likely revealing only minor changes over time, which could be difficult to analyze. We believe that a machine learning-based, or some kind of ‘big-data’ approach will be necessary to effectively analyze this data.

### General comment (2<sup>nd</sup> part)

Does the work support the conclusions and claims, or is additional evidence needed?

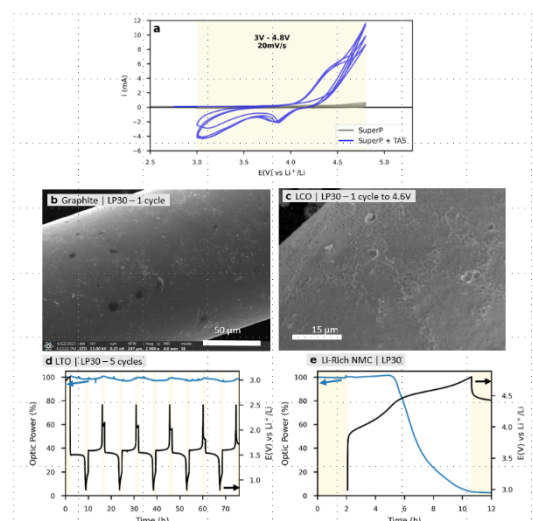
The diagnostic technique and data analysis methods are well documented, and the diagnostic performance is impressive. The ability of MCR-ALS to distinguish separate SEI phenomenon is very promising. As the authors acknowledge, isolating SEI species is challenging and thus the MCR-ALS components cannot be definitively identified. Instead, these components are associated with semi-carbonates and  $\text{Li}_2\text{CO}_3$ , but not exclusively.

As we understand it, this question was initially intended to the referee as part of their general comment. We thank again the referee for the acknowledgement of our work.

### Specific comments (2<sup>nd</sup> part)

**Comment 5.** A reader may question whether the chalcogenide fiber is truly inert and does not participate in the SEI formation process. While the presence of the fiber may have some impact on SEI formation, the authors previous work found the fiber material to be stable in electrolytes during battery cycling (citation 12). It would be good to state this in the paper. Is it possible to evaluate the fiber integrity after in situ testing in this study? The intimate contact between the fiber and active materials could lead to fiber interactions that were not observed in prior experiments (for example, other chalcogenide materials have been used as ion conductors 4).

**Response 5.** The reviewer rightly questions the stability of the fiber when embedded in the electrode rather than in the electrolyte. To address this question, we investigated the reduction and oxidation stability of the electrode via cycling voltammetry over the 0 – 4.8 V voltage range. To carry these experiments we ground TAS fiber with carbon Super to increase both the surface area and the contact between the fiber and the carbon and therefore its reactivity. When cycling over the 0-2V range no obvious differences could really be detected comparing the TAS-containing carbon electrode and the TAS-free carbon electrode. This is confirmed by the SEM picture of a TAS fiber that has been cycled to 0 V. In contrast, on oxidation we note the onset of a minor oxidative current that starts at 4.2 V and then increases strongly (Blue curve) upon further increasing the oxidation current while under the same conditions the TAS-free cell barely shows any oxidation current. This is indicative of a degradation of the TAS fiber at high voltage (>~4.3 V) and this is confirmed by the corrosion pits observed on the SEM picture of a fiber being cycled to 4.6 V. To further confirm this range of stability we made two LTO/LP30/Li metal and Li-rich-NMC/LP30/ Li metal cells each having TAS fibers in the LTO and Li-rich NMC electrodes, respectively. Note the constancy of the optic power guided through the fiber upon cycling for the LTO-based cell, while the optical power drastically drops for the Li-rich NMC cell at a voltage of nearly 4.3V, coinciding with the onset of the oxidation current observed by cyclic-voltammetry measurements. For sake of completeness, we should emphasize that the overall stability window (0-4.3V) may change depending upon the electrolytes used.



**Electrochemical stability of TAS fibre :** a, CV of TAS:SuperP powder mix (blue curve) and SuperP powder (grey curve) between 3V and 4.8V; b, ex-situ SEM image of a TAS fibre cycled to 0V in a graphite|LP30 half-cell; c, of a TAS fibre after 1 cycle in a LCO|LP30 half-cell, with 4.6V cut-off potential; d, Evolution of the optic power transmitted through the fibre compared to its initial value (left axis, blue) and cell potential (right axis, black) during ‘long-cycling’ operando experiment of LTO|LP30 cell; e, same with a Li-Rich NMC|LP30 cell.

With this completed, the main text was amended as follows and Supplementary figure 16 now included:

Finally, while the long-term chemical stability of TAS glass in the electrolyte was previously demonstrated<sup>21</sup>, it should be further considered within the intimate contact of the electrode. Hence, the integrity of the fibre in the conditions of the article was verified on scanning-electron microscopy (SEM) images after cycling, and equally demonstrated by the stability of the optic power transmitted over the course of the experiment, as detailed in Supplementary Figure 16.

**Comment 6.** It would be interesting to see if any SEI species were directly deposited on the fiber or only on active materials surrounding the fiber.

**Response 6.** As the fiber is not electronically conductive, it is not expected to have any reduction directly on the surface of the fiber without the electrode coating. However, in all our experiments, the fiber was fully covered by the electrode slurry containing the active material. In this context, XPS analysis of recovered fiber fragments confirmed the presence of SEI components, such as  $\text{Li}_2\text{CO}_3$  and  $\text{LiF}$  directly on the surface of the fiber (see Supplementary Figure 6).

**Comment 7.** Along these lines, does the fiber attenuation markedly change during battery cycling? This may be addressed in supplementary figure 9, but it's unclear if the electrode surrounding the fiber is intact after repeatedly washing with DMC.

**Response 7.** This is a follow-up to question 4 that deals with issues encountered upon cycling with IR fibers and the attenuation and condition of the fiber after washing with DMC. Concerning the attenuation, besides what was discussed above in Response 4, we want to stress that it is more dependent on the surface morphology of the fiber rather than on glass composition variation (see answer 5), as the conductive electrode coating on the fiber dictates the path for electrons and hence, subsequent reactions. Considering the supplementary figure 13 (ex-Suppl. Fig. 9) mentioned by the reviewer, the spectra were plotted without any baseline correction, meaning no attenuation changes of the fiber during cycling. Moving from the attenuation of the fiber by itself to the absorbance of the fiber surrounding environment, we obviously see changes when washing with DMC simply because some fragments of the electrode are washed away. Moreover, another source of absorbance change upon cycling is the formation of a SEI that will also affected the surrounding RI environment and therefore the penetration of the evanescent wave. We fully acknowledge the dynamic challenges for pinpointing spatio-temporal reactions, but considering the richness of the information collected, this also makes the whole IR-FEWS approach so attractive and promising.

### **General comment (3<sup>rd</sup> part)**

*Are there any flaws in the data analysis, interpretation and conclusions? Do these prohibit publication or require revision?*

*I did not find any flaws in data analysis, interpretation, or conclusions.*

*Is the methodology sound? Does the work meet the expected standards in your field?*

*Yes.*

*Is there enough detail provided in the methods for the work to be reproduced?*

*Yes.*

*Jason Porter*

*Associate Professor*

*Department of Mechanical Engineering*

*Brigham Young University*

### *References*

- 1. Kenichi Hongyou, Takashi Hattori, Youko Nagai, Toshihiro Tanaka, Hiroyuki Nii, Kaoru Shoda, Dynamic in situ fourier transform infrared measurements of chemical bonds of electrolyte solvents during the initial charging process in a Li ion battery, Journal of Power Sources, Volume 243, 2013, Pages 72-77, ISSN 0378-7753, <https://doi.org/10.1016/j.jpowsour.2013.05.192>.*
- 2. N. Gogoi, T. Melin, E. J. Berg, Elucidating the Step-Wise Solid Electrolyte Interphase Formation in Lithium-Ion Batteries with Operando Raman Spectroscopy. Adv. Mater. Interfaces 2022, 9, 2200945. <https://doi.org/10.1002/admi.202200945>*
- 3. Yeyoung et al, Probing the Evolution of Surface Chemistry at the Silicon–Electrolyte Interphase via In Situ Surface-Enhanced Raman Spectroscopy, J. Phys. Chem. Lett. 2020, 11, 1, 286–291*
- 4. Wolfgang Bensch, Thomas Bredow, Hubert Ebert, Paul Heitjans, Sylvio Indris, Sergiy Mankovsky, Martin Wilkening, Li intercalation and anion/cation substitution of transition metal chalcogenides: Effects on crystal structure, microstructure, magnetic properties and  $\text{Li}^+$  ion mobility, Progress in Solid State Chemistry, Volume 37, Issues 2–3, 2009, Pages 206-225, ISSN 0079-6786, <https://doi.org/10.1016/j.progsolidstchem.2009.11.007>*

### Reviewer #3 (Remarks to the Author):

*Leau et al. present a solid body of research in which optical fibre infrared spectroscopy enables operando investigations into battery solid electrolyte interphase (SEI) dynamics. This builds on earlier work by this group in which the optical fibre technique was developed and applied to electrolytes in commercial batteries. The novelty of the new work presented is the emphasis on specifically probing the evolution of SEI, which requires the use of numerical methods to decouple changes associated with the solid and liquid phases – in this case multivariate curve resolution by alternating least squares (MCR-ALS). This is a significant advance considering the notorious complexity of SEI dynamics, and the method presented offers a new way forward to measure and study them.*

*The quality of the science is generally very high and the presentation is clear. With a few exceptions highlighted below the conclusions are supported by the evidence presented. I would recommend publication, contingent on the following issues being addressed.*

#### **General comment.**

*The article is rather long for a communication. Given the large body of work included in the paper, cutting this down will not likely be possible, so an alternative journal may be more appropriate.*

*The MCR-ALS method is a purely mathematical approach which is implemented without knowledge of whether each of the resulting component spectra can definitively be assigned to an individual chemical species. In this sense these deconstructed spectra are strictly hypothetical so attributing them to a given species based on known band positions comes with the assumption that the number of extracted components is correct. Given the obvious need to minimise the number of components in the numerical analysis, there is a danger some components will be missed and the system oversimplified. This does not undermine the value of the approach for separating different spectral contributions, but some consideration of this should be included in the discussion to make it more balanced.*

**Response.** We sympathize with the referee regarding the length of the document due to the numerous examples we had to take into account to fully convey our message. Unfortunately, our efforts to shorten the document were not sufficient. We have tried to be more concise in the revised version. In addition, we are fully aware of the various risks and challenges associated with the MCR-ALS method with regard to the possible attribution of individual chemical species. Indeed, such numerical analysis, widely applied to handle spectra other than IR spectroscopies, can oversimplify electrolyte decomposition products. Hence the importance of creating a library of IR reference spectra as we have done in our study complemented with testing of various mixtures. A comment has been added in the revised version:

Classic curve fitting approaches cannot be applied to the obtained IR spectra because quantitative differences instantly arise between the static reference samples (synthetic/pure SEI compounds) and dynamically convoluted operando spectra. Instead, an approach without *a priori* knowledge on the SEI composition was adopted where the interpretation is facilitated by employing a limited number of components in the numerical analysis, although admittedly at the risk of oversimplification or exclusion of minor species. As is often the case with numerical-driven methods, a critical posture should be adopted when interpreting the decomposition results, keeping the established literature surrounding the SEI in mind. Nevertheless, we hope this opens the door for groups with stronger chemometrics expertise to pursue work in the direction of robust decomposition algorithms.

#### **Specific comments**

**Comment L21.** IR-FEWS not properly defined in abstract.

**Response L21.** IR-FEWS has now been defined in the abstract more clearly as IR fiber-optic evanescent wave spectroscopy (FEWS).

**Comment L99.** The MCR-ALS method is based on the assumption that the Beer Lambert Law applies. However, deviations from this may occur at high concentrations, which the authors should acknowledge.

**Response L99.** Yes, indeed the reviewer's point is well understood. To avoid lengthening the manuscript too much, we addressed this question in Supplementary Figure 2. Here we present the variation of absorbance as a function of electrolyte concentration in LiPF<sub>6</sub>, which we track by the PF and DMC bands up to 2M concentration. Note the linear variation of the DMC band in contrast to the PF band that deviates from linearity beyond 1M. With this result, we feel it is justified to use a 1M salt concentration in our experiments while focusing MCR-ALS on the solvent bands.

**Comment L138.** This paragraph is discussing features in Figure 1b, but the text refers to Figure 1d, which is confusing. Also, Figure 1b contains reference to EC<sub>solv</sub> and EC<sub>free</sub> as well as DMC<sub>solv</sub> and DMC<sub>free</sub>. The text should therefore be corrected to specify Figure 1b and the subscripts "solv" and "free" should be defined more generally.

**Response L138.** We thank the reviewer for catching these oversights. These confusions between text and figures, as well as those concerning the correct use of subscripts, have now been corrected. The revised sentence reads as “a separation of several bands corresponding to free and Li-coordinated solvent molecules, referred to as  $DMC_{free}$  and  $DMC_{coord}$ , respectively” coherent with our previous paper.

**Comment L157.** The authors state that the spectrum can be decomposed into four components, corresponding to the solvated and free DMC and EC. Presumably the 2000  $cm^{-1}$  to 900  $cm^{-1}$  spectral range for the decomposition was selected to deliberately exclude the electrolyte ( $PF_6^-$ ) band at 850  $cm^{-1}$ ? If so, it would be worth stating this explicitly.

**Response L157.** This question is a continuation to the referee comment regarding L99 which we supplement as follows: Indeed, as observed in Figure 2, since the PF band deviates at concentrations above 1 molar  $LiPF_6$  salt while that of DMC remained linear up to 2M, we decided to exclude extended analysis of the PF band and to carry out this study focusing on the coordination bands of the solvent only. We have now modified the text to mention it explicitly:

“The spectral range was restricted to 2000  $cm^{-1}$  to 900  $cm^{-1}$ , excluding the anion band at 840  $cm^{-1}$  as this deviates from linearity at salt concentration higher than 1 molar, as shown in Supplementary Figure 1.”

**Comment L163.** Figure 1b legend refers to three different EC:DMC ratios, but it is unclear which spectra are which in the figure.

**Response L163.** We thank the reviewer for raising this issue, and indeed, it was also a point raised by Reviewer 1 as well. We agree with the referee that the impact of the solvent ratio on the spectra cannot be identified from Figure 1b alone. For clarity, the three different EC:DMC ratios we mentioned are now plotted separately in Supplementary figure 1, alongside DMC solvent only.

**Comment L188.** Capacity is attributed to a conversion reaction on  $Cu_2O$  and the authors refer to XPS data in Supplementary Figure 3 to support this conclusion. However, it is surprising to see that the Cu region of the XPS spectrum is not shown in the figure. The text in the SI (L43) states that copper oxide is observed on the pristine sample and disappears after cycling, but no data is shown to support this.

**Response L188.** This question was also asked by Reviewer 1 (question 7), so we'll share the same answer: Indeed, the XPS O1s spectrum for the pristine sample shows a peak at 529.4 eV, which we highlighted in green in the corrected version, as it had been wrongly attributed to  $Cu_2O$ . By further collecting the Cu2p spectrum (included in Supplementary figure 5.), we concluded that we were dealing with CuO rather than  $Cu_2O$ . This may appear, at first, incoherent with XRD measurements that reveals the presence of  $Cu_2O$ , and not CuO. Such a discrepancy can be reconciled by keeping in mind that XPS solely probes the 50-100 Å of the Cu particles surfaces (the most oxidized state of Cu (CuO) while XRD probe a deeper part of the particles (less oxidized Cu ( $Cu_2O$ )). So likely, both oxides are involved in the process. Lastly after cycling (and before cleaning),  $Cu_2O$  and  $Cu^0$  are mainly detected, in line with the previous sequence ( $Cu^0 \rightarrow Cu_2O \rightarrow Cu$ ) reported for Li-driven conversion reactions (Klein, F. *et al.* Reaction Mechanism and Surface Film Formation of Conversion Materials for Lithium- and Sodium-Ion Batteries: An XPS Case Study on Sputtered Copper Oxide (CuO) Thin Film Model Electrodes. *J. Phys. Chem. C* **120**, 1400–1414 (2016)).

**Comment L195.** “Looking at the characteristic negative and positive symmetric absorbance variations observed in the  $\nu C=O$  and  $\nu CO$  regions reveal the decreases in  $Li^+$  concentration occurring in the electrode during reduction”. This statement is potentially quite misleading because the change in these band intensities reflect changes in the solvent and are only indirectly associated with the amount of  $Li^+$ . It would appear as if both the  $DMC_{free}$  and  $DMC_{solv}$  bands undergo a decrease in intensity with time, but if the amount of  $Li^+$  is decreasing, would the  $DMC_{free}$  be expected to increase? The analysis later in the manuscript considers this aspect more thoroughly, but care should be taken with the wording at this point.

**Response L195.** We thank the referee for the opportunity he/she offers us to stress that changes in the band amplitude can result from two effects. On one hand, changes in  $Li^+$  concentration affect the ratio between  $DMC_{free}$  and  $DMC_{coord}$ , causing variations in the opposite direction, while on the other, these bands can both decrease in intensity due to the formation of an SEI during reduction, as this limits the amount of solvent/electrolyte detected by the fiber under such conditions. We realized that our statement may have come too soon in the original text, thus we modified it by replacing decrease for variations in the sentence above.

**Comment L214.** It is not clear how the authors conclude that “any contribution of product cross-over from the Li metal counter electrode can safely and effectively be disqualified”. The data referred to in Supplementary figure 4 shows that there is a negligible change in the two selected band intensities when a cell without the active electrode material is left for several hours at OCV. However, this is an uncharged cell with no current flowing, so no products would be expected to be generated at the Li counter electrode. Hence, the absence of any spectral change is rather unsurprising and says very little about whether product-crossover is affecting the result shown in figure 2d.



**Response L214.** It is well documented that a SEI spontaneously forms on the surface of lithium metal in contact with the electrolyte, even in absence of applied current. Perhaps this should be considered chemical SEI reactions, as opposed to electrochemical. Thus, it was prudent for us to verify that with any open circuit test cell experiment (i.e. Li-metal/separator/TAS fiber), shows no crossover. Still, we agree with the reviewer that we had perhaps over-interpreted our results, which is why we decided to change our sentence from the strongly worded original statement “can safely and effectively disqualified” to a more modest, but thorough “...seems to disqualify chemical oxidation of the Li-metal counter electrode as a source of any deposited products on the reference electrode”.

**Comment L229.** The text refers to the 8 components shown in “Figures 3b-e”, but Figure 3b is the voltage profile, so the text should presumably say “Figures 3c-f”.

**Response L229.** Thank you for catching this error. A correction has been made. As we noted with another reviewer, this manuscript has been strengthened in numerous self-critical rounds before our 1<sup>st</sup> submission, so several figure/legend errors propagated unknowingly.

**Comment L247.** The text refers to Figure 3e, but presumably this is meant to be 3f as there is no reference to components C7 and C8 in Figure 3e.

**Response L247.** Correction has been made.

**Comment L291.** The authors compare the absorbance difference between two separate experiments under different conditions, but this is not wise as the absolute absorbance behaviour is likely to be very sensitive to the precise contact area between electrode particles and the optical fibre, so may vary considerably from experiment to experiment and does not necessarily reflect differences in the SEI chemistry. If the authors wish to quantitatively compare the absorbance in this way, the reported values should include quantified uncertainties derived from multiple experiments to establish if the differences are statistically significant. Alternatively, the absorbance values could be normalised to a chosen peak intensity that is known to not vary between experiments, if such a peak exists. The authors do allude to the dangers of quantitative comparisons later in the manuscript (L364), so this cautionary note should really come earlier as this potentially weakens their argument around the differences between DMC only and EC/DMC if not addressed.

**Response L291.** We fully share the referee concerns about quantitative comparisons. So as per his/her suggestion we added a full paragraph in the “tuning electrolyte composition section” (using bold here for emphasis), which now reads as

“However, herein with the sole use of DMC solvent, the increase of the 1640 cm<sup>-1</sup> semi-carbonates band is generally limited to the reduction events (highlighted with purple arrows in Figure 4b), with an absorbance after 18 hours of testing plateauing at 0.008 absorbance units, versus 0.016 absorbance units for the previous EC/DMC mixture electrolyte (Figure 2d), and still increasing thereafter. Quantitative comparison between experiments should be taken cautiously, as variations in sample preparation can lead to dispersion in observed absolute intensities. However, similar trends were observed when duplicating experiments. More importantly, the low voltage ‘steps’ evolution of DMC solvent contrasts with the previous reduction of EC/DMC, which not only showed an increase during reduction but also during OCV periods.”

Nevertheless, it should be stressed that our technique makes it easy to carry out operando studies. In this case quantitative comparisons can be made, as the positioning of the electrode-fiber remains unchanged during cycling.

**Comment L262.** The authors refer to Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, rather than LTO, so this should be made consistent.

**Response L262.** Correction has been made.

**Comment L385.** The rate C/2.5 is followed by the phrase “2.5 hours per 1 lithium”, which may be misinterpreted. Better to say “2.5 hours for complete charging of the LTO”. Also, looking closely at Figure 7b, the C rate does not look like it is consistent with C/2.5. A total of 5 charge-discharge cycles are completed in roughly 70 hours, which corresponds to a rate of around C/7.

**Response L385.** There are two conventions in the literature concerning the definition of the C-rate. One defines that C/N corresponds to the full capacity of the battery in a time span of N hours, or another in which C/N corresponds to the capacity associated to the sole uptake of one Li per unit formula in a time span of N hours. We have chosen the second convention: thus, knowing that Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> inserts up to three lithium ions per unit of formula, and taking into account the second convention C/2.5 corresponds to a theoretical charge/discharge time of 7.5 hours, close to what is observed experimentally. While we see no error within the work itself, we have modified our wording in the text to eliminate any such confusion.

**Comment L448.** The authors refer to optical fibre-based Raman scattering in a way that suggests this has not previously been explored, when it has. See, for example, *Journal of Power Sources* 359 (2017) 435e440 and *ChemSusChem* 2017, 10, 855 – 861.

**Response L448.** We thank the reviewer for this relevant reference which we included in the introduction section:

Using ultrafine double fibre probes and hollow-core microstructures fibres respectively<sup>18–20</sup>, Yamanaka *et al.* and Miele *et al.* overcame the double challenge of sample excitation and Raman photon collection. They implemented operando fibre-based Raman spectroscopy to pouch cell configuration, evidencing electrolyte composition change and gas bubbles formation.

**Reviewer 1 (Remarks to the Author)****General comment.**

Q1: The TAS fiber developed in this paper has a wavelength range of 3 to 13  $\mu\text{m}$ , which, although it can monitor most of the molecular bonding in electrolytes, such as C=O, is not sufficient for monitoring bonding in a wider wavelength range, such as O-O bonding. For the design of sulfur-based optical fibers, what are the ways to extend their infrared monitoring window?

**Response 1.**

The referee shows interest in extending transparency window of sulfur-based glasses. For this, one must consider that the long-wavelength transparency limit of glass forming materials is governed by the energy of their phonon modes. In the case of sulfur-based glass, the limit of the transmission range lies at 11.53  $\mu\text{m}$  for  $\text{As}_2\text{S}_3$  (see table 1.3 in ISBN 978-0-85709-356-1, reproduced below). To extend the monitoring windows, heavier atoms must be used: Se and Te: for instance,  $\text{As}_2\text{Se}_3$  transmission range is extended to 17.5  $\mu\text{m}$ .

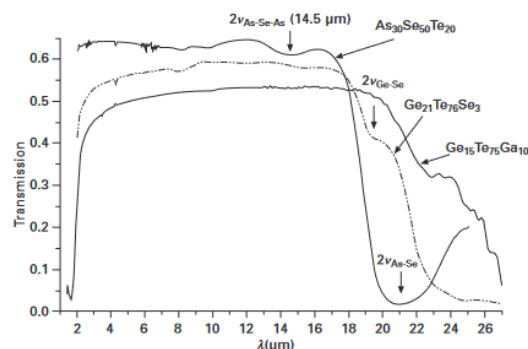
For TAS glass, the transparency spectrum measured on a 2 mm-thick disk reveals a long-wavelength transparency edge at 18  $\mu\text{m}$  ( $555\text{ cm}^{-1}$ ), associated with a  $2\nu_{\text{As-Se}}$  mode (see figure 1.7 in ISBN 978-0-85709-356-1, reproduced below). However, in a fiber geometry, the longer optical path results in a saturation of this low intensity mode at 14.5  $\mu\text{m}$  ( $2\nu_{\text{As-Se-As}}$ ), giving the range reported in this paper.

Extending further the window to monitor the O-O bonding, as suggested by the referee, would require Germanium-based glasses, such as  $\text{Ge}_{21}\text{Se}_3\text{Te}_{76}$ , which was previously demonstrated for IR-FEWS up to 14  $\mu\text{m}$  (10.1016/j.optmat.2010.11.025). In this work, we preferred the  $\text{Te}_{20}\text{As}_{30}\text{Se}_{50}$  composition, which is better established in terms of fabrication and stability toward crystallization.

Table 1.3 Properties of some chalcogenide glasses ( $T_g$ , glass transition temperature;  $T_c$ , onset of crystallization temperature;  $n$ , refractive index;  $n_2$ , non-linear refractive index)

Glass	Transmission range*, ( $\mu\text{m}$ )	$T_g$ ( $^{\circ}\text{C}$ )	$T_c - T_g$ ( $^{\circ}\text{C}$ )	$n$ ( $\lambda$ , $\mu\text{m}$ )	$n_2 \times 10^{-18}$ ( $\text{m}^2/\text{W}$ )
$\text{As}_2\text{S}_3$	0.62–11.53	185	–	2.42 (3)	4–6
$\text{As}_2\text{Se}_3$	0.85–17.5	178	147	2.83 (3)	14–30
$\text{As}_{40}\text{S}_{30}\text{Se}_{30}$	0.75–12.5	180	–	2.61 (3)	14.5
$\text{As}_{40}\text{Se}_{40}\text{Te}_{20}$	1.23–18.52	140	–	2.9 (5)	>20
$\text{GeSe}_4$	0.75	163	–	2.48 (1.55)	13
$\text{Ge}_{25}\text{Sb}_{10}\text{S}_{65}$	0.65–11.0	315	>200	2.25 (1.55)	2–5
$\text{Ge}_{30}\text{As}_{10}\text{Se}_{30}\text{Te}_{30}$	1.2–17.0	260	225	2.8 (10.6)	>20
$\text{Ge}_{21}\text{Te}_{76}\text{Se}_3$	2–20	160	123	–	–
$\text{Ge}_{15}\text{Ga}_{10}\text{Te}_{75}$	2–25	172	$\geq 113$	3.415	–

\* At  $1\text{ cm}^{-1}$  absorption coefficient.



1.7 Transparency spectra of  $\text{As}_{30}\text{Se}_{50}\text{Te}_{20}$ ,  $\text{Te}_{76}\text{Ge}_{21}\text{Se}_3$ , and  $\text{Te}_{75}\text{Ge}_{15}\text{Ga}_{10}$  glasses (thickness is 2 mm).

Reproduced from Adam, J.-L. & Zhang, X. *Chalcogenide Glasses: Preparation, Properties and Applications*. (2014).

Q2: The analytical range of the MCR-ALS algorithm used in this paper is limited to a window with wave numbers from 2000 to 900  $\text{cm}^{-1}$ , is there any possibility of algorithmic improvement for the nonlinear effects caused by the anionic band at 840  $\text{cm}^{-1}$ ?

**Response 2.** Despite the non-linear dependence of the anionic band between 0.0 M and 2.0 M, its variations shown in Supplementary Fig. 11 appear linearly correlated to the changes in the solvation bands. This can be explained considering the relatively small variations of the salt concentration (not quantified here). Therefore the concentration/absorbance dependence is approximated as linear around LP30 concentration. Restraining the calibration spectra to electrolyte compositions closer to LP30 would possibly overcome this nonlinear effect. However, in this work, we chose to keep this wide range of composition which facilitates the separate identification of  $\text{DMC}_{\text{free}}$ ,  $\text{DMC}_{\text{coor}}$ ,  $\text{EC}_{\text{free}}$ ,  $\text{EC}_{\text{coor}}$ .

Furthermore, other non-linear IR-FEWS absorbance behaviors due to the fiber geometry have previously been quantitatively modeled (see Katz et al., 10.1364/AO.33.005888). Using these optical models, we envision the possibility of establishing better correspondences between the reference electrolyte spectra and the electrode-embedded operando spectra to further improve SEI/electrolyte decoupling.

**Reviewer 2 (Remarks to the Author)**

*The authors have sufficiently addressed all comments from my original review. I recommend the manuscript be published.*

**Reviewer 3 (Remarks to the Author)**

*All concerns have been addressed in the revised manuscript, so publication is recommended.*