EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE

Energy Storage Unit

Petten, Thursday, 18 November 2021

Dear Editor,

I am contacting you as Co-Author of the manuscript: **" Identification and quantification of decomposition mechanisms in lithium-ion batteries; input to heat flow simulation for modelling thermal runaway"** under revision for publication within the JOVE.

Thank you for the comments received by the Editor of JOVE and by the reviewers that have improved the quality of the potential publication. Please find below the specific questions to these comments and explanations of the amendments taken place.

Reply to the reviewers

TITLE:
Identification and Quantification of Decomposition Mechanisms in Lithium-Ion Batteries; Input to Heat Flow Simulation for Modeling Thermal Runaway
Ibtissam Adanouj[1], Ákos Kriston[2], Vanesa Ruiz[1], Andreas Pfrang[1]

1) **The manuscript needs a thorough proofreading.**

The manuscript was proofread by the co-authors as well as by the internal JRC reviewer to ensure its quality.

2) **Please use American English throughout.**

As a service of the European Commission, we are required to use British spelling.

3) **Please reword for clarity. Formation?**

2 sentences have been merged and modified as below:

These results provided insight into the thermal events happening within a broader temperature range than covered in previously published models and allowed the development of an improved thermal model to depict TR.

4) Please ensure the Introduction include all of the following with citation:

a) A clear statement of the overall goal of this method

b) The rationale behind the development and/or use of this technique

The reason for using STA coupled with GC-MS and FTIR was as explained in the lines number 149-155:

STA allows for the identification of phase transitions during the heating process, along with accurate determination of temperatures and enthalpies associated with these phase transitions, including those without mass change. The combination of on-line FTIR and GC-MS methods with the STA provides a qualitative assessment of gases evolved from the sample during its thermal decomposition. This is the key in identifying thermally induced reaction mechanisms. Indeed, STA/FTIR/GC-MS coupled system allows correlating the mass changes, the heat flow and the detected gases.

c) The advantages over alternative techniques with applicable references to previous studies

d) A description of the context of the technique in the wider body of literature

Advantages of STA/FTIR/GC-MS over other techniques are explained in lines 212-226 and supported by references to other studies:

To the best of the authors' knowledge, there is limited research published on the thermal behaviour of electrode material, using of the exact combination of these analytical instruments STA/FTIR/GC-MS, analytical parameters and sample preparation/ handling to elucidate chemical reaction mechanisms at material level during thermal decomposition. At cell level, Fernandes et al. investigated the evolved gases in a continuous way, using FTIR and GC-MS, in a battery cylindrical cell undergoing an overcharged abuse test, in a closed chamber[62]. They have identified and quantified the gases during this test but the understanding of reaction mechanisms still remains unclear. Furthermore, to develop a TR runaway model, Ren et al. have also conducted DSC experiments at material level to calculate kinetic triplet parameters of exothermic reactions[55]. They have identified six exothermic processes, but the reaction mechanisms were not determined and they did not use coupled gas analysis techniques.
On the other hand, Feng et al. have proposed a three-stage TR mechanism in LIB cell with three characteristics temperatures that can be used as indexes to assess thermal safety of battery[63]. For this purpose, they have used a thermal database with data from ARC. Nevertheless, details of the chemical reactions underlying these three mechanisms are not provided.

e) Information to help readers to determine whether the method is appropriate for their application

This information is provided in lines 157-165:

FTIR and GC-MS have each advantages and limitations. The high sensitivity of GC-MS allows rapid and easy detection of molecules from peaks of low intensity. Furthermore, FTIR data well complement the information provided by MS spectrum patterns to achieve the structural identification of organic volatile species. However, FTIR is less sensitive. In addition, diatomic molecules, such as H_2, N_2, O_2, do not possess a permanent dipole moment and are not infrared active. Therefore, they cannot be detected using infrared absorption. To the contrary, small molecules like CO_2, CO, NH_3 and H_2O can be identified to a high degree of certainty[38] . Altogether, the information provided by these complementary methods makes it possible to gain insight of the gases emitted during thermal characterisation.

5) Reworded please review. Please reword for clarity

This sentence is modified as follows:

Clean energy technologies such as wind energy and solar energy are regarded as best alternatives to a fossil-fuel dominated energy system[3], however, they are intermittent and the storage of energy will help to ensure continuity of energy supply.

6) What kind of energy can be stored… to bring out connection to the energy system.

This sentence is modified as follows:

Properties such as high specific energy density, stable cycling performance and efficiency make lithium-ion batteries (LIBs) promising candidates as electrochemical energy storage system.

7) Reworded please check.

This sentence has been checked after rewording and modifications are accepted.

STA allows for the identification of phase transitions during the heating process, along with accurate determination of temperatures and enthalpies associated with these phase transitions, including those without mass change.

8) Maybe: For STA?

This sentence has been modified as follows:

The combination of on-line FTIR and GC-MS methods with the STA provides a qualitative assessment of gases evolved from the sample during its thermal decomposition.

9) **Please adjust the highlight to fit to the 3-page limit with headings and spacing. Currently it is more than this. Please ensure that the highlighted section makes a cohesive story for the video. Please remove the redundancy from the protocol steps and make it crisp. Please ensure that each step describes how to perform the action in complete sentence.**

The data evaluation part has been removed from the video script and therefore, is not highlighted anymore. The length of the highlighted text is now 3 pages.

In addition, the text is thoroughly revised to make the story cohesive and crisp and comments of the reviewer are taken into account.

10) **Please ensure each step contains no more than 2-3 actions (comment to paragraph 5.5).**

Following the requirements to limit the highlighted text to 3 pages, section 5.5 and the following sections have been removed from the video script. Our understanding is that the requirements for each step to contain no more than 2-3 actions applies only to the video script part.

11) **How do you figure out where is this?**

Sentence has been modified to make it clear.

After the experiment is completed, open the Netzsch Proteus data treatment program by double-clicking on icon.

12) **Please make substeps (comment to paragraphs 5.5.18-5.5.19, 5.5.21)**

The text in paragraph 5.5.18 has been shortened.

We do not see the added value of including substeps in these paragraphs as each paragraph describes the actions related to one and the same operation. In our view, further breaking down of the text can confuse the reader.

13) **This is not an action, converted to a note instead.**

We agree to keep the text as a note.

14) Please remove the figure legends from the uploaded figures.
Each figure legend should have a one-liner title with all panels combined and also have description of individual panels. Please obtain reprint permission for reference 67 as well.
Please check this is this sample number 5?

The legends have been removed from the figures. Each figure was provided with a one-liner title.

Where applicable, individual panels have also been given a title. The NIST reference spectra are plotted on the basis of the data from NIST Chemistry WebBook[68] . We have used NIST data in the publication[48] in a similar way. Sample number 5 has been checked, as required.

15) As we are a methods journal, please ensure that the Discussion explicitly cover the following in detail in 3-6 paragraphs with citations:

a) Critical steps within the protocol

1. Our research has shown that a lead time, i.e. time elapses between opening of the cell and the STA/evolved gas analysis (including all preparations), has a pronounced effect on DSC curve of the materials. This is likely to be related to unwanted side reactions taking place in the idling cell. An example of such an effect is given in **Fig 12** where DSC curves for graphite electrode with lead time of 2 days and 4 days are compared.

2. Proper assembly and closure of the cell is of utmost importance for successful electrochemical cycling of the cell and hence for preparation of electrodes for STA/GC-MS/FTIR characterization. Whether the cell is properly assembled, closed and connected to the cycler can be seen from voltage vs time profile. **Fig 13** shows a number of cycling profiles for faulty cells and compares those to the 1-cycling profile of the proper cell. Therefore, we consider all steps in the cell preparation as critical.

3. Proper balancing of the electrode capacities is critical importance to avoid overcharging of graphite and Li plating. **Fig 14** compares DSC curves of fully charged and overcharged graphite, clearly showing a substantial effect of overcharging on the thermal behaviour of the material.

A paragraph has been added to the paper (lines 970-1000):

However, we will first discuss the important aspects of this technique, the pitfalls and the troubleshooting we encounter to ensure, from a user perspective, the successful implementation of the method.

*Our research has shown that a lead time, i.e. time elapsed between opening of the cell and the STA/evolved gas analysis (including all preparations), has a pronounced effect on DSC curve of the materials. This is likely to be related to electrolyte evaporation and unwanted side reactions taking place at the surface of the fully charged anode, which is highly reactive, in the presence of trace amounts of oxygen and/or water[72, 73]. An example of such effect is given in **Fig. 12** where DSC curves for graphite electrode with lead time of 4 h, 2 days and 4 days are compared. The DSC profile of the 4-day lead time anode shows significantly smaller exothermic signals, while the curves for 4 hours and 2 days long lead times are very similar.*

*The assembly of a hand-made full Li-ion battery cell with a thin separator and electrode discs of equal diameters is a delicate operation. Therefore, proper assembly and closure of the cell is of utmost importance for successful electrochemical cycling of the cell and hence, for preparation of electrodes for STA/GC-MS/FTIR characterisation. For example, electrode disks misalignment and/or crimped separator can result in significant changes in the cycling behaviour of a full Li-ion cell[74]. Whether the cell is properly assembled, closed and connected to the cycler can be seen from voltage vs time profile. **Fig. 13** shows a number of cycling profiles for faulty cells and compares those to the first cycle of the properly prepared cell. Therefore, we consider all steps in the cell preparation as critical.*

*In the note following 1.2.1 and the paragraph 2 (Calculation of electrode disc's capacity) in the protocol section, it has been mentioned that proper balancing the electrode disc's areal capacity is an essential requirement prior to full Li-ion battery cell assembling. Therefore, this aspect is of critical importance to avoid overcharging of graphite and Li plating[75–77]. **Fig. 14** compares DSC curves of fully charged and overcharged graphite, clearly showing a substantial effect of overcharging on the thermal behaviour of the material. The overcharged graphite is related to imbalanced electrodes assembly where the cathode's areal capacity (3.54 mAh/cm^2) is higher than the anode's one (2.24mAh/cm^2). As a consequence, the graphite becomes overlithiated and the surplus of Li^+ transported to the graphite matrix can be deposited on the surface as Li metal.*

b) Any modifications and troubleshooting of the technique

Initially, the technique has been optimised. The choice of correct plunger depends on the materials and thickness of cell components. For the system described in this study, we came to the conclusion that the plunger 50 is of a better choice than 150. Therefore, plunger 50 was consistently used in our experiments. The amount of electrolyte also needs to be carefully tuned to ensure good wetting of all cell components and to avoid transport limitations to a maximum degree possible. For the system presented in this study, the optimum amount of electrolyte was shown to be 150 µl.

A paragraph has been added to the paper (lines 1002-1012).

Before launching the experimental campaign, preliminary tests were carried out. The technique has been optimised to troubleshoot problems in order to achieve reliable and reproducible results. Among them, the choice of a correct plunger for EL-CELL electrochemical cell to avoid bending of the separator. The proper plunger height depends on the materials and thickness of cell components[78]. For the system described in this study, we came to the conclusion that the plunger 50 is of a better choice than plunger 150. Therefore, plunger 50 was consistently used in our experiments.
Similarly, the optimal amount of electrolyte needed to be carefully tuned to ensure good wetting of all cell components and to avoid ion transport limitations to a maximum degree possible. Not enough electrolyte results in an increase of ohmic resistance and a loss of capacity[79, 80] . The optimised quantity of electrolyte was found to be 150 µl for the system presented in this study.

c) Any limitations of the technique

Limitations of STA, GC-MS and FTIR are discussed in the introduction section of the paper.

Lines 157-165:
FTIR and GC-MS have each advantages and limitations. The high sensitivity of GC-MS allows rapid and easy detection of molecules from peaks of low intensity. Furthermore, FTIR data well complement the information provided by MS spectrum patterns to achieve the structural identification of organic volatile species. However, FTIR is less sensitive. In addition, diatomic molecules, such as H_2, N_2, O_2, do not possess a permanent dipole moment and are not infrared active. Therefore, they cannot be detected using infrared absorption. To the contrary, small molecules like CO_2, CO, NH_3 and H_2O can be identified to a high degree of certainty[38] . Altogether, the information provided by these complementary methods makes it possible to gain insight of the gases emitted during thermal characterisation.

Lines 192-206:
Another important issue in thermal analysis is the measurement conditions (type of crucible, open/closed crucible, atmosphere) that are affecting the DSC signal to be measured. In this case, the use of a hermetically closed crucible is clearly not suitable for the hyphenated STA/GC-MS/FTIR techniques, which implies the identification of evolved gases. In a semi-closed system, the size of the opening in the perforated crucible lid can have a strong influence on the measurement results. If the size is small, the thermal data is comparable to a sealed crucible[61]. On the contrary, a large hole in the lid is expected to decrease the measured thermal signal because of the early release of low temperature decomposition products. As a result, these

species would not be involved in higher temperature processes[61]. Indeed, a closed or semi-closed system allows longer residence time of the species, transformed from condensed to vapour phase inside the crucible. A laser-cut vent hole of 5 µm in the crucible lid has been selected for the investigation of thermal behaviour and evolved gases of graphite anode and NMC (111) cathode. Considering the size of the laser-cut hole, we assume the system inside the crucible may most probably depict, a simple but reasonable approximation of the dynamic inside both, a closed battery cell and a battery cell venting.

In addition, this paragraph has been added to the paper (lines 1014-1045):

As for the limitations of the proposed method, some of them are already discussed in the introduction section of the paper. In addition, regarding the mass spectrometry, the decomposition products are typically analysed using electron ionisation (EI) with quadrupole MS after chromatographic separation by GC. This makes it possible to identify each compound within a complex mixture of evolved gaseous products. However, the chosen settings of the STA/GC-MS limits the detection to small decomposition products with masses below m/z=150 (The m refers to the molecular or atomic mass number and z to the charge number of the ion). Nevertheless, the selected parameters for the STA/GC-MS system are deemed appropriate by the authors for the analysis of released gases coming from electrode materials.
Another potential drawback would be a partial condensation of high boiling point products such as ethylene carbonate in the transfer line (heated at 150 °C). As a consequence, careful purging of the entire systems after each experiment is of importance to avoid cross-contamination of experiments.
With respect to FTIR, the evolved gases are transferred through a heated line at 150 °C to a heated TG-IR measurement cell at 200 °C. The analysis of functional groups appearing in the evolved gases enables the identification of gaseous species. A possible disadvantage of the STA/FTIR coupling is the overlapping signals from the gaseous mixture (several gases evolving at the same time) that results in a complex spectra difficult to interpret. In particular, to the contrary of the STA/GC-MS system, there is no separation of decomposition products prior the infrared absorbance analysis.

The current setup of the gas analysis system allows identification of gaseous compounds which means the method is qualitative. Indeed, the quantification was not addressed in this study which leaves potential for additional chemical information to be harvested. This, however, would require the instruments to be connected in series and not in parallel, i.e. STA/GC-MS and STA/FTIR, to maximise sensitivity and accuracy. In addition, a system for trapping gases after STA analysis would enable the use of GC-MS for quantification after FTIR qualitative characterisation. One could consider the following system: STA/trapped gases/FTIR/GC-MS connected in series. Another consideration is that FTIR could also be used for quantification and cross-validation of quantitative data obtained from GC-MS. The quantification prospect would require anyway further research to determine its applicability in these hyphenated techniques, which was not the scope of our work.

d) The significance with respect to existing methods

The advantages of hyphenated STA/GC-MS/FTIR technique are discussed in the introduction section of the manuscript along with demonstration of the significance of the technique compared to existing methods.

Lines 138-147:

*The set up of this custom-made integrated system is shown in **Fig. 1**. The STA equipment, used in the present study, is located inside a glovebox, which guarantees the handling of components in a protective atmosphere. The latter is coupled with the FTIR and GC-MS via heated transfer lines (150 ˚C) to avoid the condensation of evaporated materials along the lines. The hyphenation of these analytical techniques allows simultaneous study of thermal properties and identification of released gases, providing information of the mechanisms of the thermally induced decomposition reactions. In order to reduce the impact of unwanted chemical reactions in the electrodes during sample preparation further, sample handling and sample loading are performed inside an argon-filled glove box. The disassembled electrodes are not rinsed nor is additional electrolyte added to the crucible.*

Lines 212-226:

To the best of the authors' knowledge, there is limited research published on the thermal behaviour of electrode material, using of the exact combination of these analytical instruments STA/FTIR/GC-MS, analytical parameters and sample preparation/ handling to elucidate chemical reaction mechanisms at material level during thermal decomposition. At cell level, Fernandes et al. investigated the evolved gases in a continuous way, using FTIR and GC-MS, in a battery cylindrical cell undergoing an overcharged abuse test, in a closed chamber[62]. They have identified and quantified the gases during this test but the understanding of reaction mechanisms still remains unclear. Furthermore, to develop a TR runaway model, Ren et al. have also conducted DSC experiments at material level to calculate kinetic triplet parameters of exothermic reactions[55]. They have identified six exothermic processes, but the reaction mechanisms were not determined and they did not use coupled gas analysis techniques.
On the other hand, Feng et al. have proposed a three-stage TR mechanism in LIB cell with three characteristics temperatures that can be used as indexes to assess thermal safety of battery[63]. For this purpose, they have used a thermal database with data from ARC. Nevertheless, details of the chemical reactions underlying these three mechanisms are not provided.

In addition, this paragraph has been added to the paper (lines 1047-1054):

While the present work is qualitative, it offers an improvement on previous work since, as mentioned in the introduction part, the STA equipment is located inside a glovebox, which guarantees the handling of components in a protective atmosphere. Again, to the best of the authors' knowledge, there is limited research published on the thermal behavior of electrode materials, using the exact combination of these analytical instruments STA/FTIR/GC-MS, analytical parameters and sample preparation/handling to elucidate chemical reaction mechanisms at materials level during thermal decomposition. Further details about the *significance of this method are provided in the introduction section.*

e) Any future applications of the technique

This paragraph has been added (lines 1056-1063):

Our research has demonstrated the power of this hyphenated STA/GC-MS/FTIR technique for thermal characterisation of battery materials and the analysis of evolved gases. Obviously, this technique can be applied to different set of materials, for example, to study novel materials, materials properties under extreme cycling conditions, etc. This technique is ultimately suitable to investigate thermal behavior of materials and their thermal decomposition routes and to analyse evolving gases. Another example of such use of this hyphenated STA/GC-MS/FTIR technique is the application to characterisation of energetic materials, including explosives, propellants and pyrotechnics[81].