

## Point-by-point response to reviewers and editor for the manuscript:

*Innovative L-band electron paramagnetic resonance investigation of solid-state pouch cell batteries, by CE. Dutoit, R. Soletti, JM. Doux, V. Pelé, V. Boireau, C. Jordy, S. Pondaven and H. Vezin.*

*This paper used a commercial Bruker L-band (ca. 1 GHz) EPR imager to measure a pouch cell lithium ion battery. This image will stimulate extensive applications of L-band EPR to actual batteries and their performance. The paper, however, requires revision to be more comprehensible about the materials used. As written, it would be difficult for anyone to reproduce this work without direct interaction with the lab that did the preparations.*

We sincerely thank the reviewer for his detailed reading of our manuscript, which allows us to correct an error and to address some points that need to be clarified.

**Comment #1:** *The battery described in this work uses a solid electrolyte and lithium anode. Solid electrolyte LiB are a still developing technology. The majority of LiB in use in personal devices and automotive applications have a liquid electrolyte. There are commercial sources of aluminum encased pouch cells with liquid electrolyte. Could the authors to comment on the feasibility of repeating this experiment with liquid electrolyte LiB? It would have an immediate tie in to the most widely deployed type of pouch cell LiB.*

**Response:** *Thank you for this comment which is absolutely right. Li-ion technology is mainly used in commercial batteries to date. However, our first investigation was performed on two solid-state pouch cell batteries because our initial project was focused on this technology. Following this work, we turned to L-band EPR analysis of lithium-ion pouch cell batteries sealed inside a standard Al-based packaging. It is worth noting that electrochemical performance and EPR of Li-ion cell (non-standard packaging) is well established. We investigated the (de)lithiation process of a graphite anode during cycling of a LiFePO<sub>4</sub>/graphite battery as case study to demonstrate the feasibility of using operando L-band EPR. The results (confidential and which will be the subject of a future paper) shown the nucleation of an EPR peak of Li<sub>x</sub>C<sub>6</sub> during charge which drops to 0 upon discharge. Such a finding is consistent with previous X-band investigations of the graphite (de)lithiation and opens the possibility of using operando L-band EPR as a new device for monitoring redox process.*

**Comment #2:** *Did they select a lithium anode because they thought sensitivity issues would prevent them from directly observing the cathode material EPR at 1 GHz? Typically, the anode is a graphite-based material. There are stated to be increased safety concerns for the solid lithium anode in terms of thermal runaway.*

**Response:** *First, we choose a Li<sup>0</sup> as the anode owing to its high energy density. Secondly, the main idea here was monitoring electrode materials wrapped inside an industrial aluminum-based pouch cell. Lithium metal is easily detected by EPR spectroscopy and appears to be the material of choice in preliminary studies. Furthermore, initially we expected perform operando measurements to detect the nucleation of sub-micrometric lithium particles (like dendrites). However, cycling all-state batteries is not trivial and requires some precise controls. From our good results on the detection of metallic lithium structure through Al-based pouch cell, we performed an operando investigation on a LiFePO<sub>4</sub>/graphite battery (data not shown and which will be the subject of a future paper). We observed, in real time and real conditions, the reversible graphite (de)lithiation showing the good sensitivity of our approach.*

**Comment #3:** The authors should add a section discussing the implications of this first experiment. How would they expect the lithium EPR signal to change as a function of ageing in this pouch cell? What do they think they would see with a graphitic anode pouch cell?

**Response:** In the case of pristine battery with Li-metal as anode, the EPR spectrum expected is asymmetric and is well defined by a Dysonian function. The reason comes from the skin depth, and then from the metal thickness, which determine the EPR line shape. When the metal thickness is much higher than the skin depth the EPR spectrum appears asymmetric. It's the present case at the pristine state for a Li-metal anode. However, upon cycling, some sub-micrometric and/or nanometric lithium particles, such as dendrites, can be formed. Consequently, the EPR reveals a symmetric and intense line shape as reported in the literature with a X-band spectrometer (Niemöller et al. doi: 10.1038/s41598-018-32112-y). At L-band, similar results are expected.

As suggested by the reviewer, we added the following sentences (in red) on page 7.

*“As reported in the literature, during electrochemical cycling, an intense and symmetric EPR spectrum can appear. This feature is the manifestation of an alteration of the metallic anode surface which creates sub-micrometric lithium aggregates. However, in the present work, we did not perform operando measurements and we did not observe an EPR signature of sub-micrometric lithium aggregates.”*

For the graphite anode, we observed the formation of lithiated graphite complexes during charge which disappears during discharge showing the reversible behavior of the graphite lithiation.

**Comment #4:** The EPR audience may not know why these pouch cells are important compared to steel-cased cylindrical cells. For instance, the flexibility in packaging allows pouch cells to be tailored to specific space constraints better than rigid cylindrical cells. The authors don't need to “take down” cylindrical cells, but they could spend a little time answering the “so what?” question, which also helps convey the importance of this first measurement.

**Response:** Thank you for this suggesting. Two sentences have been inserted (in red) on pages 1-2 of the revised paper to clarify these points:

*“Owing to a lightweight aluminum packaging, pouch cells can be used in small portable electronics such as drones, mobile and so on. Compared to rigid cylindrical cells, they offer a good weight to energy ratio.”*

**Comment #4:** What is the composition and availability of NMC, SE, the liquid electrolyte, the pouch batter studied, etc. “An argyrodite-type-sulfide electrolyte” is too vague to be useful.

**Response:** NMC= NMC811 ( $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ ) very commonly used by cathode supplier like Umicore for example. SE:  $\text{Li}_6\text{PS}_5\text{Cl}$  can be supplied by NEI. Pouch made of aluminum laminate (120 $\mu\text{m}$ ) containing one polyamide layer and one polypropylene layer (supplier: MTI for example).

These details are now included in the experimental section on pages 2-3 (in red).

**Comment #5:** What does it mean that “the different layers were punched”?

**Response:** The different layers were punched means that electrodes and electrolyte layer were cut with a special tool which cuts the layers at the final shape (see an example of a punch : <http://www.hohsen.co.jp/en/products/detail.php?id=116>)

**Comment #6:** It is not evident how “the voltage was then controlled to ensure the pouches were not short circuited.”

**Response:** After the cell is assembled, the voltage is measured with a voltmeter and it was checked that the voltage was above 2V to ensure that there was no short circuit.

We added this detail on page 3, lines 56-57 (in red).

**Comment #7:** Presumably the resonator used was one produced by Bruker. The model/part number should be stated.

**Response:** Yes, the microwave resonator used in our work is a bridge loop-gap resonator produced by Bruker (L Band\_BLGR\_36 mm\_ E1978).

The model/part number is now added in the experimental section (page 3, line 61 in red).

**Comment #8:** What do the authors mean by “can cause serious perturbations of the dielectric”? The context of the statement suggests that they really mean that the conductivity of the metal cell distorts the microwave magnetic and electric field distributions. This is repeated on page 4.

**Response:** Usually, a large metallic sample placed in a X-band microwave cavity, which is simply a metal box, creates a perturbation of the electromagnetic field inside the resonator owing to its high electric conductivity. Such a distortion makes it sometimes difficult to tune the cavity because of the broadening of the “dip” created by the reflected microwave power. That is the reason why, in our previous study at X-band, we used a homemade electrochemical cell EPR silent and two metallic current collectors with a millimeter-sized which do not affect the electromagnetic field.

At L-band, the microwave cavity shape is different (loop-gap shape). Furthermore, we used an electrochemical pouch cell which is much larger than the homemade X-band EPR cell. As a consequence, the current collectors are also much larger. Although the metallic packaging, and the both current collectors create a weak perturbation in the loop-gap resonator, which is challenging here, we were able to tune the cavity and observe an EPR spectrum from the  $\text{Li}^0$  anode.

**Comment #9:** The statement in line 76 that  $T_2$  is approximately  $10^{-9}$  s is inconsistent with the reported results.  $10^{-9}$  s would correspond to about 65G peak-to-peak derivative spectrum. They report 3 G on the next page. In addition, the paper should provide references for the relaxation times.

**Response:** Thank you for this comment, which is right. We have measured the spin-spin relaxation time  $T_2$  and the spin-lattice relaxation time  $T_1$  of an Li-metal anode using FID  $T_2$  decay and FID inversion recovery at X-Band on a Li-Li symmetric battery.

We found  $T_1=T_2$  and a value around  $10^{-8}$ s for the bulk lithium foil as after polarization cycles,  $T_2$  and  $T_1$  of microstructures are in range of  $10^{-6}$  s.

The  $T_2$  value is now corrected in the revised manuscript (page 3, line 81 in red).

**Comment #11:** The caption of figure 2 should include the microwave  $B_1$  at the sample, and the modulation amplitude and frequency used.

**Response:** Yes, thank you, we added the modulation amplitude, frequency and microwave power used in the caption of Fig.2 (page 5).

**Comment #12:** The data described in lines 100-105 are not otherwise presented in the paper, and there is no mention of how they were measured. Possibly the information is from a report in the literature and references should be given.

**Response:** Your remark is absolutely correct. Lines 100-105 describe the EPR result shown in Fig 2(b). In the literature we find a variety of study showing the EPR spectrum of the NMC material. Indeed,  $Mn^{4+}$  gives an EPR peak with a linewidth of around 22mT and  $Ni^{2+}/Ni^{3+}$  create a linewidth broadening. We are agreeing with the reviewer that lines 100-105 must to be clarify.

We modified lines 100-105 (in red) by on page 5 and included a reference in the revised manuscript (ref Tang et al., 2017, page 10).

*“However, as reported in the literature (Tang et al., 2017), at room temperature NMC material exhibits an EPR signal centered at a g-value of around 2.00 with a linewidth of around 22 mT arising from  $Mn^{4+}$ ,  $Ni^{2+}$  and  $Ni^{3+}$ . The manifestation of the NMC is represented by a distortion of the baseline. This distortion is clearly visible in the NMC//Si-based cell but invisible in the NMC//LiO cell due to the intense  $Li^0$  signal”.*

**Comment #13:** The paper should report and comment on problems encountered in this imaging measurement and solutions developed. The primary value of this paper is to say “yes, you can study these metal pouch batteries with commercial instruments.” It is of value to publish as more than a claim to priority only if it contains proper information to make it reproducible.

**Response:** We think the reviewer for this comment.

*Up to now, most of the experiments have been carried out in X-Band on model batteries which, while they have the merit of providing a good understanding of materials in terms of redox, SEI formation and dendritic lithium formation, are clearly a long way from an industrially-produced battery. This work is a first step that shows the feasibility of a commercial device for which we will improve the environment so as to be able to study an entire cell in operando.*

*No problems were encountered with image acquisition. While it is possible to acquire an EPR spectrum, imaging is only a variant of EPR spectrum acquisition, since it involves encoding the signal. The strength of the 40G/cm gradients does not disturb the position of the echo during acquisition. This would perhaps be different with gradients similar to the X band, i.e. 200G/cm.*