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

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

The authors thank the reviewer for his detailed reading of our manuscript.

Reviewer 2

The authors describe EPR spectroscopy and imaging at L-band of a slid-state battery in a pouch cell format. They demonstrate that it is possible at this frequency to detect a signal even if the cell is placed inside a laminated pouch bag, corresponding to a format that is also used for standard lab experiments or some commercial batteries. While this result is valuable and publication in Magnetic Resonance would be justified, the current state of the manuscript represents various shortcomings that need to be addressed. In particular, the conclusion that "an L-band EPR spectrometer will enable us to locate metallic lithium structures through a standard packaging for batteries with a better spatial accuracy and then will improve the knowledge of Li-metal nucleation processes" is not fully substantiated, since in the presented data only signal is unambiguously discernible that originates from the boundary of the cell. It is not possible to distinguish if Li metal from the center of the cell leads to an observable signal at all.

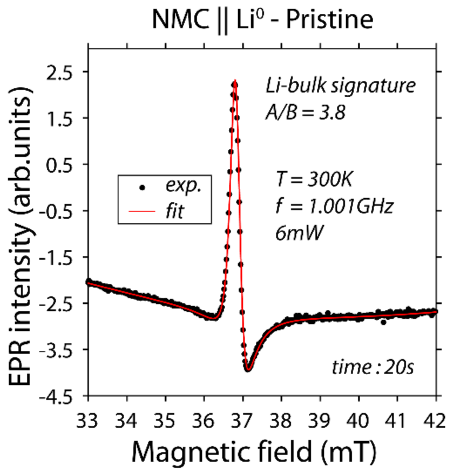
Comment#1: Experimental details are currently insufficient for other laboratories to reproduce these experiments. The exact specification of the used separator and the origin of the different commercial materials should be provided.

Response: *Thank you for this suggestion. NMC= NMC811 ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$) very commonly used by cathode supplier like Umicore for example. SE: Li6PS5Cl can be supplied by NEI. Pouch made of aluminum laminate (120µm) 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) of the revised manuscript.*

Comment#2: 36 mW is a high power level for such a narrow signal, which would generally lead to significant saturation effects. The authors should specify the attenuation caused by the pouch bag. Also, does this high power level cause local heating in the cell?

Response: *We thank the reviewer for this important point. The EPR spectrum of the Li-metal anode is possibly saturated by using a high power, here 36mW, but such power level does not affect the origin of the EPR spectrum observed. In our work, we did not perform an operando measurement for which a preliminary investigation of saturation effects is necessary for monitoring the spectral intensity evolution. Here, we only provide the feasibility to use L-band EPR spectrometer to observe Li-metal structures through a standard and Al-based pouch cell battery. In the case of operando measurements or to quantify lithium aggregates, a small power level will be applied to the sample.*

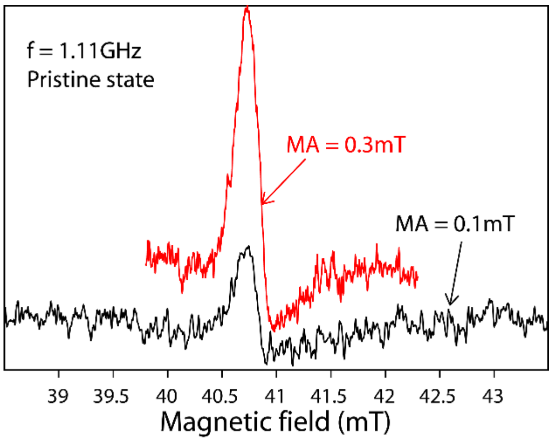
Please, as suggested by the reviewer, we provide below the EPR spectrum of the pristine pouch cell battery NMC811||Li-metal recorded at 6mW displaying the same general pattern (bulk Li-metal) as the one recorded at 36mW.



During our measurements, we did not observe a local heating in the cell.

Comment#3: A modulation amplitude of 0.3 mT is too high if the main signal has a width of 0.3 mT and, more importantly, potentially narrower signals may also occur. Please provide a spectrum recorded with a narrower modulation amplitude to exclude overmodulation effects.

Response: *We are agreeing with this comment. In our work, we have deliberately chosen to over modulated the EPR signal in order to clearly observe the Li-metal signature. Initially, we had no idea about the L-band EPR line shape, neither the microwave frequency adapted to penetrate the Al-based pouch cell. Consequently, in our first investigation we recorded the EPR spectrum using a microwave frequency ≈1.11GHz for two modulation amplitude values, 0.1mT and 0.3mT respectively. The result is shown below. As we can see, the use of small modulation amplitude values (MA), which limit the signal distortion, provides a low signal-to-noise ratio (S/N). On contrary, even though over-modulation affects the line shape (distortion and broadening), a slightly over-modulation can enhance the S/N ratio and then significantly enhance the sensitivity. Consequently, we chose to keep MA=0.3mT and use a smaller microwave frequency to enhance the S/N ratio. Furthermore, our work was performed on a pristine pouch cell battery. At this electrochemical state, only bulk Li-metal signal expected. However, we are agreeing with the reviewer that during charge and discharge, some sub-micrometric Li-metal particles can appear and a modulation amplitude much smaller will be necessary.*



Comment#4: With a field of view of 30 mm and 512x512 pixels, a resolution of 60 µm would be *expected. Please specify more accurately the limiting factor of the stated resolution of 150 µm, and why the apparent resolution in the images in Fig. 3 appears to be even lower than this value.*

Response: *We thanks the reviewer for this relevant comment which is absolutely right. EPR images were recorded with 200x200 pixels and a field of view of 30mm which corresponds to a resolution of 150 µm.*

The experimental details of EPR imaging is now corrected in the revised manuscript (on page 3, line 69 in red).

Comment#5: Section 2.1: Please provide the thickness of all the components of the cell, as shown in Fig. 2a, including current collectors. For the current collectors, it would be helpful if also the respective skin depth would be stated.

Response: *Our work has been performed through a collaboration with the industrial company SAFT. SAFT does not want to provide such information on the thickness of their electrochemical components. However, in the revised manuscript, we provided some additional details about electrode materials used in this work that will allow other laboratories to reproduce our measurements.*

Comment#6: Section 2.2 (and throughout manuscript): Please provide all units in mT.

Response: *As suggested by the reviewer, we provide all units in mT throughout paper.*

Comment#7: Section 2.3: Please specify the number of radial projections, i.e. how many projections were recorded for the images

Response: *The number of radial projection used for the EPR images is 157. This value is now reported in the revised manuscript (on page 3, line 69 in red).*

Comment#8: Line 78ff: Discussion of Dysonian lineshape is handwavy and incomplete; either provide a more accurate description or just summarize and refer to discussions in the literature

Response: *We thank the reviewer for this point. This shape comes from the microwave field which excites only spins located inside the skin depth and is influenced by the non-uniformity of the microwave field in the metallic structure. For a thickness much higher than the skin depth, the EPR spectrum appears asymmetric while for a thickness lower than the skin depth, a pure Lorentzian (symmetric) shape is obtained.*

As suggested by the reviewer, we included three references in the discussion part of the revised version of the paper (on page 4, line 87). These papers describe the Dysonian line shape of a Li-metal sample as a function of the purity and the thickness of the metallic structure.

We also modified the description of the Dysonian line shape in the revised version (on page 3 lines 81-85} by: "… excited. Consequently, the line shape is influenced by the homogeneous of the electromagnetic field in the metallic structure displaying a Dysonian line shape when a fraction of the electronic spins experiencing the microwave field and a pure Lorentzian in the opposite case for which all the electronic spins are excited "and deleted the sentence: "Furthermore, this phenomenon depends on the spin coherent time T2, in which electron travels on a specific distance δe, named spin depth. In metallic lithium structures, T2 ≈10^{-8}s and then when …*".*

We added "(Dysonian)" on page 4, line 86 (in red) of the revised version: "…the EPR spectrum exhibits an asymmetric (Dysonian) line shape characterized by the ratio A/B…" and "… ≫1 resulting from the

apparent amplitude ratio between its positive lobe and negative lobe (Gourier et al., 1989; Niemöller et al., 2018; Dutoit et al.,2021)" on page 4, lines 86-88 in red of the revised version.

Comment#9: Line 83: a metallic conductor does not cause a 'perturbation of the dielectric'; please state more precisely

***Response:** Thank you for this relevant remark. Usually, a conventional X-band EPR spectrometer is equipped with a microwave cavity similar to a metal box highly conductive. A large and over-sized metallic conductor deposited inside the microwave resonator can provide some difficulties to tune the spectrometer owing to the perturbation of the electromagnetic field inside the resonator and by the presence of the static magnetic field. Dielectric refers to microwave resonator.*

Comment#10: Line 87: Unclear what is meant by "the dielectric is slightly perturbed". Which dielectric is perturbed?

***Response:** The L-band EPR spectrometer used in our work is equipped with a bridge loop-gap resonator. During our experiments, we encountered some minor issues upon inserting the pouch cell about tuning the spectrometer on. Dielectric refers to microwave resonator.*

Coment#11: Fig. 2b: What is the origin of the line shape of the defect signal? The narrow line does not look like the first derivative of a signal one would expect from defects.

***Response:** The EPR spectrum obtained on the NMC811||Si-based pouch cell battery is very different from the EPR signal obtained on the NMC811||Li-metal. This first result provides evidence that L-band EPR spectroscopy can probe electrode materials wrapped up in a standard pouch cell. The EPR spectrum recorded in fig 2b exhibits two paramagnetic species: (i) a very broad line due to the NMC cathode (distortion of the baseline) and (ii) a very weak signal centered at ≈2.001. It is well known that the EPR spectrum of SiO_2 gives a line centered in a g-value range of 1.999-2.0018 (DOI:* 10.1063/1.371996 and DOI: 10.1063/1.369464). *The origin of such weak signal can be easily attributed to SiO_2 defects which are located inside the Si-based anode. We are agreeing that the EPR line does not exhibit the first derivative of a spectrum classically recorded in an EPR experiment. The reason is the phase sensitivity detection is not optimized because the main result expected here was only to compare the both spectroscopic signatures (NMC811||Li-metal compared to NMC811||Si-based).*

Comment#12: Line 115: Conduction EPR images are generally not quantitative, hence quantitativity, as stated in the text, would have to be confirmed with an independent experimental technique. In this case, shielding and eddy current effects most likely affect the signal, thus the signal does not represent spin concentration at all.

***Response**: We thank the reviewer for rising this important point.*

We did not perform a quantitative investigation neither given the number of electron spins detected in the sample because the EPR intensity of lithium metal line does not reflect the total amount of lithium. The reasons are twofold. On one hand, only electrons of energy above the Fermi energy are unpaired (and contribute to the EPR spectrum), i.e. a fraction of about 0.4% of the electrons; on the other hand, for particles larger than several micrometers, only electrons located in the skin depth contribute to the resonance.

On page 6, line 126 of the first version, we used the term "spin concentration" only to describe the signal variation between areas more or less sensitive to the microwave field. What we meant here is "spin concentration seen by the microwave field". We agree with the reviewer that the "true" spin concentration cannot be obtained only by EPR imaging.

Comment#13: Fig. 3. The three projections cannot be congruently combined to a 3D image. What is the reason for this? Concomitant gradients? Please discuss

***Response:** Yes, we think the three projections can be combined to record a 3D image. However, such reconstruction requires the development of a specific algorithm and script using, for example, MATLAB.*

Comment#14: Fig. 3. What is the reason that the noise (or apparent signal?) away from the sample, where there is definitively no Li, is larger than right around the sample?

***Response:** First, it is worth noting that only Li-metal from the negative electrode gives an EPR signal and contribute to the EPR image (fig.3). Secondly, conventional EPR image reconstruction method, such as filtered back projection applied may produce some artifacts in the image. This is the reason why we observe a noise signal away from the anode much larger than around the anode. However, this phenomenon does not modify the presence of higher signal produced by the metallic anode.*

Comment#15: Fig. 3. What was the state of the battery? Was it pristine or had it been cycled?

***Response:** In figure 3 we provide the EPR image of the pristine battery. This image (square form) corresponds to the lithium metallic anode before cycling showing none structural modification.*

Comment#16: Line 121 and Fit. 3: The signal from the center of the anode is not larger than at the edge of the field-of-view, where it represents exclusively noise. Therefore, there is not a "slight variation of EPR intensities", but the signal from the center of the cell cannot be conclusively distinguished from noise at all. It appears that there is only signal caused by the boundary of the cell. This should be discussed in detail.

***Response:** Thank you for this relevant remark. Indeed, the signal from the center part is featureless while the signal from the edge of the anode appears clearly. The reason is shown by Niemöller et al (DOI: 10.1038/s41598-018-32112-y) and comes from the edge effects. In a flat Li-metal sample, local variations of the skin depth can cause a variation of the Li-signal. The edge appear much higher than the center part caused by a shielding effect. Although Li-metal structures are also located in the middle part, their EPR signals are hidden by the signal from the edge.*

As suggested by the reviewer, we deleted "slight" in our sentence "slight variation of EPR intensities" (on page 6, line 132 of the revised version).

Comment#17: Line 135: Li-metal nucleation would lead to a conduction EPR signal with substantially different line width than shown for a pristine Li metal foil. An individual localization would require special measures that further increases the acquisition time. Discuss the feasibility of such experiments in terms of the expected acquisition time, taking also into account the necessary reduction of the modulation amplitude.

Response: *Exactly, in the case of sub-micrometric metallic lithium nucleation, the line shape changes and appears much higher (apparent amplitude), symmetric (due to the skin depth) and sharp. Consequently, the time needed to record such images and locate Li-metal particles could increase significantly. This time depends on the conversion time, sweep time, number of projections, recovery delay. For example, with a conversion time of 10.24ms, 402 projections and a recovery delay of 1.5s, the time needed to record the image of a bulk Li-metal is around96min whereas with a conversion time of 20.48ms, 402 projections and a recovery delay of 1.5s, the acquisition time of micro-aggregates is around 166min.*