*Referee: 1*

*Comments to the Author  
This manuscript reports the analysis of capacity attenuation of lithium-ion batteries under float charging conditions. The authors use various advanced methods to explain the reasons, study the mechanism of LIB degradation in multiple charge/discharge processes, and propose that the negative synergistic effect is the cause of serious failure of lithium-ion batteries during float discharge.   
However, some conclusions of this study are not clear enough and lack characterization. Taking these factors into account, this manuscript needs minor repairs before it can be accepted. The details are as follows:*

Thank you for your general and detailed comments. We wish to express our sincere appreciation to the referee for your insightful comments on our paper. The comments have helped us significantly improve the paper. Here are detailed answers for your comments.

*Q1-1. It is recommended to disassemble the commercial 18650 battery, and conduct an ICP test to determine the positive electrode, negative electrode, electrolyte and other components.*

A1-1. Thank you for your precious comment. The electrodes obtained by disassembling the cell are significantly affected by the residual electrolytes and current collectors, and counter electrode (via cross-talk reactions). For example, we actually found a considerable amount of nickel species on the graphite electrodes, which should not be included in the beginning. The volatile electrolyte components were lost during disassembling in the inert gas atmosphere. Therefore, we assume that accurate composition analysis including trace components by ICP is difficult. On the other hand, the charge-discharge behavior, neutron diffraction, and SEM/EDX data in this study clearly indicate that the positive and negative electrodes are NCA-based and graphite materials, respectively, as described in the manuscript. In the future, we hope to explore ways to more appropriately analyze the cell components by maintaining the internal cell conditions as much as possible.

*Q1-2. Where does the material used in the half battery come from and how to ensure the consistency of the self-assembled battery and the test results of the commercial battery are recommended to be described in detail in the manuscript.*

A1-2. Thank you very much for this important comment. The material used for the half-cells were obtained from the electrodes taken out by disassembling the full cell (fresh and aged) in a glove box under inert atmosphere conditions. The cells after neutron measurement were unsuitable be disassembled due to radioactivation, so the half-cells were prepared by disassembling the fresh and aged cells tests under similar conditions. The aged cell conditions were not definitely identical, but the degraded behavior was essentially the same. We understand that cell disassembling could cause some changes in the components, even if we sufficiently pay attention to the disassembling processes. In the present study, the charge-discharge curves, d*V*/d*Q* curves, and Nyquist plots of the impedance measurements all show that the behavior of the positive and negative electrodes from the disassembled cells can reproduce that of the full cell before disassembling. Therefore, we are sure that these half-cell test results appropriately represent the status of the full cells. The following sentences are added to the revised manuscript.

< Revised sentences >

<In Result and discussion, 3.4 Post mortem analysis>

The cell disassembling could cause some changes in the components, even if we sufficiently pay attention to the disassembling processes. In the present study, the charge-discharge curves, d*V*/d*Q* curves, and Nyquist plots of the impedance measurements all show that the behavior of the positive and negative electrodes from the disassembled cells can reproduce that of the full cell before disassembling. Therefore, we are sure that these half-cell test results appropriately represent the status of the full cells.

The SEM and EDX images of the fresh cell and the cell after the Floating-cycling test are shown in Fig. S14 to S17.

*Q1-3. How do we determine from EIS that the main source of severe deterioration in the float cycle is the positive electrode when testing with a full battery?*

A1-3. Thank you for your comments. As you indicate, the main source of degradation cannot be determined just by the full-cell EIS results. Based on the results of several previous studies [references 39, 40 and 41 in the original manuscript], we inferred that the high-frequency and low-frequency semicircles in the full-cell Nyquist plots correspond to the charge transfer processes at the negative and positive electrode respectively, and that the increase of the low-frequency semicircle in the Floating-cycling cell indicates the increased internal resistance of the positive electrode. This insight was only a conjecture at that moment. After that, we employed operando neutron diffraction analysis and we clarified that the main cause of the capacity degradation in Floating-cycling is the positive electrode. Furthermore, the impedance measurement of the half-cells using the electrodes from the disassembled the cells indicates slight and significant increase in the semicircle originating from the charge transfer processes of the negative and positive electrodes, respectively, in the course of degradation. Therefore, we conclude that the degradation observed in Floating-cycling originates from the positive electrode.

*Q1-4. It is recommended to explain in detail what floating charge is and how the charging process of the battery floating charge is carried out?*

A1-4. Thank you very much for your important comments. Floating charge in this study refers to a charging method in which the cell was charged at a constant current up to the cutoff voltage and maintained constant voltage charging at a minute current value. This preserves the fully charged state by allowing the charge current to flow corresponding to the self-discharge of the cell. The corresponding sentence is revised as follows. The float charging process of the battery is carried out by allowing the cell for CC-charge to 4.2 V at 0.5C and then maintaining the cell at 4.2 V for constant voltage charging during the test period. The procedure is shown in the Experimental section.

< Revised sentences >

<In Introduction>

The LIB cells are often set under continuous (float) charging conditions, which maintains the cell always in the fully charged state compensating the self-discharge, for example, in cellular phone/computer use at home/office connected to commercial power sources and also in power backup applications. It is thus important to understand the phenomena occurring during float charging and to minimize the cell degradation.

*Q1-5. In the EIS test “The semicircles at around 100 Hz increased by the three durability tests, in nearly the same manner, suggesting that the negative electrodes are degraded by a common mode, presumably the SEI formation onto the graphite” What does this mean? Any reference to support this?*

A1-5. We appreciate your comment. Previous studies (Ref.41 in the original manuscript and two additional references shown below) have reported that the semicircle at around 100 Hz in the EIS spectra originates from the negative electrode and it increases with the formation of solid-electrolyte interphase (SEI) on the negative electrode. In our experiments, there were nearly the same impedance increase at around 100 Hz in the Cycling, Floating, and Floating-Cycling. Because all these cells experienced the fully charged states that can cause SEI formation onto the negative electrode, we speculate that the SEI formation is the common degradation modes for these cells. The following references are added to the revised manuscript.

< Revised sentences >

<In Result and discussion, 3.1 Electrochemical evaluation of cell degradation>

The semicircles at around 100 Hz increased by the three durability tests, in nearly the same manner, suggesting that the negative electrodes are degraded by a common mode, presumably the SEI formation onto the graphite41-43.

[42] (additional reference): ﻿T.P. Heins, N. Harms, L.S. Schramm, U. ﻿Schrçder, Development of a new Electrochemical Impedance Spectroscopy Approach for Monitoring the Solid Electrolyte Interphase Formation, *Energy Technol*, 2016, **4,** 1509–1513, ﻿doi:10.1002/ente.201600132

[43] (additional reference): ﻿V.J. Ovejas, A. Cuadras, ﻿Impedance Characterization of an LCO-NMC/Graphite Cell: Ohmic Conduction, SEI Transport and Charge-Transfer Phenomenon Victoria, *Batteries-Basel*, 2018, **4**(3), 43 ﻿doi:10.3390/batteries4030043

*Q1-6. The quantitative analysis of the structure and composition of cathode materials is relatively lacking. Therefore, it is recommended that the authors conduct more characterization, such as XPS and XRD. Recently, some relevant works were published and should be cited, such as Interdiscip. Mater. 2022; 1(3): 323-329.  doi: 10.1002/idm2.12048; Interdiscip. Mater. 2022; 1(3): 330-353. doi: 10.1002/idm2.12043.*

A1-6. Thank you very much for your valuable comment. Because the electrode samples are obtained by disassembling cells that were operated/stored for a long period of time and could be further degraded during the long-term storage in the glove box, we speculate that electrode surface analysis (by XPS for example) leads to no essential information regarding microscopic doping and coatings on the electrodes. For the structural analysis of the electrode, we are sure that the data from operando neutron diffraction showing the structural changes during the full-cell discharging provide much more information than the ordinary XRD measured for the electrodes from the disassembled cell. With the lattice constant evolution during discharging shown in Fig.8 and Fig.9, we made sure the positive electrode of the full cell is an NCA-based material. The particle morphology before and after degradation have been examined by the SEM analysis as shown in Fig.12 and Fig.S14 to S18. As mentioned in A1-1, we hope to explore ways to more appropriately analyze the cell components by maintaining the internal cell conditions as much as possible in the future. The relevant sentences in the manuscript are revised and references you provided are added as shown below.

<Revised sentences>

<In Result and Discussion, 3.4 Post mortem analysis >

Further study is again needed to clarify the detail of the surface film formation mechanism and the cell management as well as new strategies50,51 to suppress these serious degradation modes.

[50] (additional reference): Y. Huang, The discovery of cathode materials for lithium‐ion batteries from the view of interdisciplinarity, *Interdiscip. Mater*, 2022, 1(3) 323-329.

[51] (additional reference): J. Yan, H. Huang, J. Tong, W. Li, X. Liu, H. Zhang, H. Huang, W. Zhou, Recent progress on the modification of high nickel content NCM: Coating, doping, and single crystallization, *Interdiscip. Mater*, 2022, 1(3): 330-353.

*Q1-7. Why is the shift of peak N1 relative to peak P2 related to the potential window shift caused by lithium inventory loss? Is there any basis for that?*

A1-7. Thank you for your comments. The study [Ref.21 in the origoinal manuscript] has shown that the d*V*/d*Q* peak in the midpoint of discharging of a fresh cell with an NCA-like positive electrode and graphite negative electrode corresponds to an overlapping of the peaks from the negative electrode (N1) and the positive electrode (P2). When the lithium extracted from the positive electrode is consumed for the SEI formation and not inserted into the negative electrode, as typically observed for lithium-ion battery degradation known as loss of Li inventory [Ref. 38 in the origoinal manuscript], the state-of-charge positions of the positive and negative electrodes relatively shift and, as a result, the position of the peak P2 remains while the peak N1 shifts to the left-hand side (high state-of-charge side) in the d*V*/d*Q* plot. The cells in our study are also suffered from this loss of Li inventory, which is clarified by the state analysis based on the capacity decrease, impedance measurements, and operando neutron diffraction measurements.

*Referee: 2  
Comments to the Author  
The work analyzes the stability of commercial LIB cells operated under different conditions. For this purpose, the authors employ operando neutron diffraction on commercial cells, impedance analysis and (some) post mortem analysis. The work is very interesting and utilizes state-of-the-art characterization methods. The manuscript was already substantially revised after previous review and shows a high quality at this point. I agree with previous reviewers that there is still some follow-up needed on the post-mortem structural analysis of the "film" on the cathode that is responsible for degradation. However, this can be part of a follow-up work.   
Therefore, I recommend publication in the present state.*

Thank you very much for your careful review and comments on our paper. As you suggested, we intend to clarify the film formation mechanism of the positive electrode during Floating-cycling by exploring a method of disassembling that better preserves the state of electrode and by examining a model experiment to reproduce the film formation in a more sophisticated manner. Thank you again for your reviewing.