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Lithium Plating generation and in-operando detection approaches for lithium-ion batteries

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Executive Summary

Lithium-ion batteries, essential for electric vehicle applications, face significant challenges in safety and performance due to degradation mechanisms such as lithium plating. This undesired reaction on the anode limits the battery's fast-charging capabilities, leading to a higher risk of Thermal Runaway. While material improvements in battery design provide some resilience, real-time control strategies are necessary to prevent lithium plating and mitigate Thermal Runaway risks. This study analyzes laboratory-scale lithium plating generation procedures and advanced in-operando detection methods to monitor and manage lithium plating. Methods include impedance analysis, Distributed Relaxation Times (DRT) analysis, voltage relaxation profiling, and incremental Capacity analysis (ICA). Findings from these studies can enhance battery management systems (BMS), offering improved fast-charging control protocols and State of Safety (SoS) monitoring.

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1 Introduction

Lithium-ion batteries (LIBs) have become central to electric vehicle (EV) technology due to their high energy densities and ability to sustain rapid charging cycles. However, these cells are vulnerable to degradation processes that can reduce capacity, efficiency, and, most critically, safety. Lithium plating—a phenomenon where metallic lithium deposits on the anode surface rather than intercalating into it—is one of the most significant degradation processes affecting the safety of LIBs. During charging, lithium ions intercalate into the anode. If the charging rate is too high relative to local diffusion kinetics (particularly at low temperatures), metallic lithium can deposit on the anode surface instead of fully intercalating. This electrochemical process can be induced by several conditions, namely, operating at high SoC levels, operating at low temperatures, operating at high charging C-rates (fast-charge) and a combination between them. Nevertheless, this process is particularly prevalent under high current and low temperature charging. Lithium Plating introduces some risks: capacity reduction, internal resistance increase and an increased likelihood of Thermal Runaway (TR), a hazardous reaction that can lead to fires or explosions. For the EV industry, understanding and detecting lithium plating early is essential for improving charging protocols, optimizing Battery Management Systems (BMS), and ultimately ensuring safe, high-performance energy storage solutions.

This paper reviews state-of-the-art techniques for lithium plating detection, offering a critical comparison to establish the most sensitive methods to Li plating. These detection methods have been developed, tested and validated through laboratory testing. Our systematic approach includes laboratory-scale lithium plating generation to custom-built two electrode coin cells, as well as commercial cells. The findings aim to inform practical applications in BMS, and the adjustment of the test procedures, enabling safer, faster charging while minimizing the risk of TR and extending battery lifespan.

2 Methods for Lithium Plating Detection

Several Lithium Plating detection methods are analyzed in this work. These methods range from detection methods based on voltage measurements, which could be implemented in current BMS, and other detection methods, based on more innovative sensors such as EIS which could be implemented for online or offline detection approaches. Hereby, the analyzed detection methods are briefly described.

2.1 Methods with conventional BMS sensors

The analyzed methods which make use of conventional BMS sensors (voltage and current measurements) are described hereafter.

2.1.1 Voltage Relaxation Profiles (VRP)

Voltage Relaxation Profiles leverage the fact that, immediately after a charging event, a lithium-plated cell exhibits characteristic behavior as lithium “strips” (i.e., re-intercalates or reacts) from the anode surface. During this relaxation, the cell voltage follows a distinctive curve if Li plating has occurred [1–4]. However, long relaxation times (often 1-10 hours**)** may be required to confidently observe these effects, which limits the real-time feasibility in practical EV operation. Nonetheless, these methods can be used offline or periodically to assess whether plating has occurred under extreme fast-charge events or low-temperature conditions.

2.1.2 Incremental Capacity Analysis (ICA)

Closely related to VRP, ICA (also referred to as dQ/dV analysis) highlights subtle features in the charge or discharge voltage curve. When plating occurs, it can manifest as deviations or anomalies in these differential curves [5,6]. While ICA is straightforward and does not require specialized hardware beyond voltage measurement, high-resolution data acquisition is needed for reliable interpretation. In real-world BMS, such high sampling rates are not always feasible, and a data filtering stage must be introduced before analyzing the data. Hence, ICA is typically employed in laboratory diagnostics or for advanced BMS that can record data at sufficiently high resolution.

2.2 Impedance-Based Methods

Impedance-based detection examines how Li plating alters the electrochemical impedance spectrum (EIS) of the cell. Specifically, shifts at low frequencies reflect changes in charge transfer resistance, or the impedance changes during relaxation are a characteristic indicator of plating [7–9]. Tracking impedance at specific transition frequencies has shown potential for detecting early plating events. This can be done either online (during or immediately after charging) or offline (e.g., during rest periods). Recent advances in BMS IC including EIS functionalities could bring these techniques from laboratory to application level. Challenges persist, however, in distinguishing plating effects from other temperature-driven impedance variations, necessitating extensive testing and validation to avoid false positives.

2.2.1 Online Impedance Monitoring

Some studies track the real part of the impedance (Z’) at specific frequencies—often near the anode’s charge transfer frequency—to detect anomalies that indicate plating [10,11]. The so-called “bathtub” shape of Z’ vs. State of Charge (SoC) can deviate when metallic lithium is deposited. These impedance measurements are measured during charging, so Lithium Plating can be detected in real-time and modify the charging process.

2.2.2 **Distribution of Relaxation Times (DRT)**

DRT analysis is a more advanced technique, offering insights into Li plating by analyzing changes in the battery's impedance spectrum during relaxation after a charging process. Shifts in the DRT peaks (in frequency and/or in intensity) could potentially indicate changes in the anode's charge transfer resistance due to plating [12], but this method typically requires high-resolution impedance data and complex computation. Recent advances in cloud services could mitigate the drawbacks of this technique at application level. Nevertheless, as with other impedance-based approaches, temperature effects and general aging can also shift peaks. Careful multi-parameter monitoring (e.g., temperature, SoC) is crucial to avoid mislabeling.

3 Experimental Setup and methodology

The Devices Under Test (DUTs) used in this study have been a cylindrical 18650 NMC cathode and a prismatic LFP cathode cell. Both cells have been tested to provide insight into the differences between different cathode chemistries. The general characteristics of the DUTs are depicted in Table 1. Prior to testing, the cells were activated with three charge and discharge cycles from 0% SoC to 100% SoC at the standard charging rate of each cell to ensure consistency in performance. The EIS measurements of the commercial cells were conducted using a *Gamry Interface 5000E*.

Table 1: DUT cell characteristics

Parameter	**Cell 1**	**Cell 2**
Format	Cylindrical 18650	Prismatic
Nominal voltage (V_n)	3.7 V	3.65 V
Minimum voltage (V_{min})	2.5 V	2.5 V
Maximum voltage (V_{max})	4.2 V	3.75 V
Nominal capacity (C_n)	2.9 Ah	72 Ah
Charging current (I_{cc})	0.5C (1C max.)	0.25C (1C max.)
Discharging current (I_{dc})	1C (6A max.)	1C (2C max.)
Internal resistance (R_{int})	28 mΩ	0.3 mΩ
Charging temperature (T_{cc})	0 to 50ºC	0 to 45ºC
Discharging temperature (T_{dc})	-20 to 60ºC	-20 to 55ºC
Cathode material	$LiNiCoMnO_2$	$LiFePO_4$
Anode material	Graphite	Graphite
Mass	47 g	1.78 kg

To test the detection methods, custom-built coin cells and the commercial cells have been tested. The coin cells have been assembled with material samples from the commercial cells. From these coin cells, Li plating is electrochemically induced to some of them. This approach allows for a comparative analysis of voltage and impedance techniques, with certainty about which cells have Li plating and which ones do not, targeting parameters that are feasible for Li plating detection. To unequivocally confirm Li plating signatures, typically two- and three-electrode coin cells are built from commercial electrode materials. The coin cells' reduced capacity makes it safer to test different test plans for the generation of Li plating, and its simpler geometry and assembly process makes it easier to introduce a third reference electrode. The coin cells also facilitate the disassembly for posterior visual confirmation of Li plating, making it ideal for validating the Li plating signatures from the electrochemical data. In this work, just two-electrode coin cells have been employed.

The coin cells have been tested to obtain data for voltage relaxation and differential voltage analysis, while the commercial cells have been tested to achieve the data necessary for performing the voltage relaxation and impedance analysis.

4 **Results**

4.1 **Voltage Relaxation**

The voltage relaxation profiles were obtained by measuring the voltage relaxation after the charging process for 10 hours. In this occasion, the Li plating signature will be a distinct voltage plateau during the relaxation of the voltage. The dV/dt of the coin cells have been analyzed at 0.5C, 1C and 2C respectively, for the first cycle and after aging it for 50 cycles. These results are shown in Figure 1, for Cell 1 and Cell 2.

Analyzing the electrochemical data, in the case of Cell 1 (NMC), no Li plating signature is observed at 0.5C (standard charging rate). For 1C charging, initially there are signs of Li plating, but the signature disappears with the aging. As for the highest C-rate, 2C, the distinct voltage plateau is observed even at the first cycle. As for the case of Cell 2 (LFP), no Li plating signature is observed at 0.5C, but clear signs of Li plating showcase at 1C and 2C. However, by means of optical inspection when opening the coin cells (see Figure 2), in the LFP cell, it was observed that plated lithium was present even at 0.5C, which was not visible in the electrochemical data. As for the NMC cell, both electrochemical data and optical inspection correlate with each other. In the NMC coin cells, bright metallic and/or white spots are visible for 1C and 2C anodes, while white salt-like residues were found at the 0.5C cycled coin cells, most likely due to degraded Li metal residues.

Regarding the commercial cell results, no Li plating signature was observed in the voltage relaxation, regardless of the C-rate or temperature. This could be attributed to the voltage resolution and/or sampling time specified in the test procedure, which could not be enough to observe such changes during the voltage relaxation.

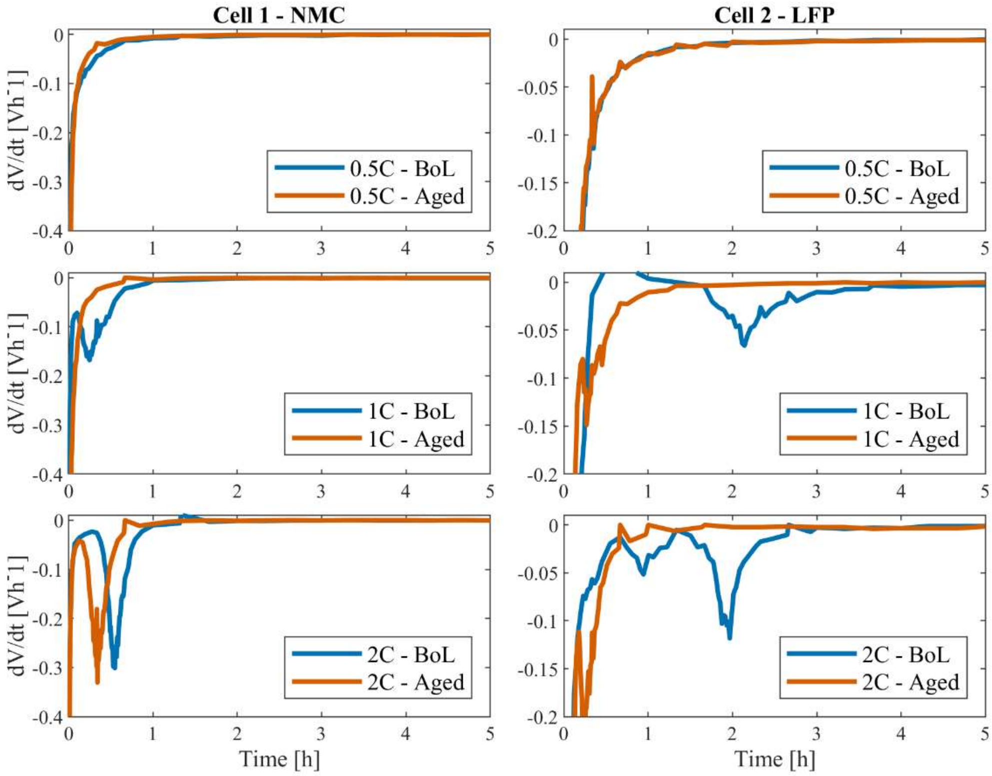

Figure 1: dV/dt during relaxation after a fast charge, Coin Cells.

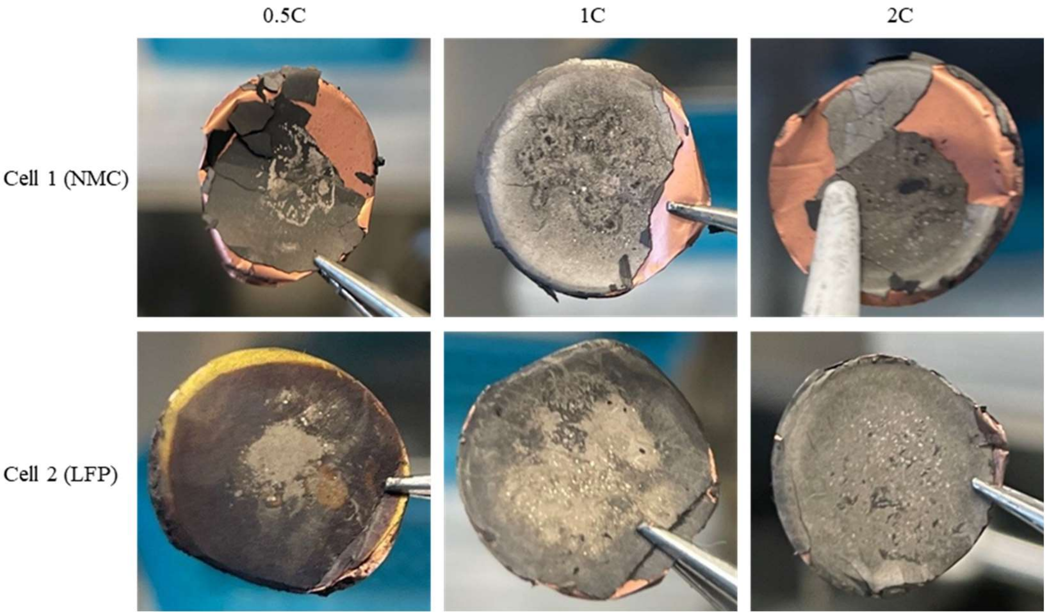

Figure 2: Opened coin cells for visual inspection

4.2 Incremental Capacity Analysis

The Incremental Capacity profiles were obtained by performing a very slow (C/20) discharge just after completing a CC-CV fast charge. In this occasion, for detecting Li plating during the previous fast charge,

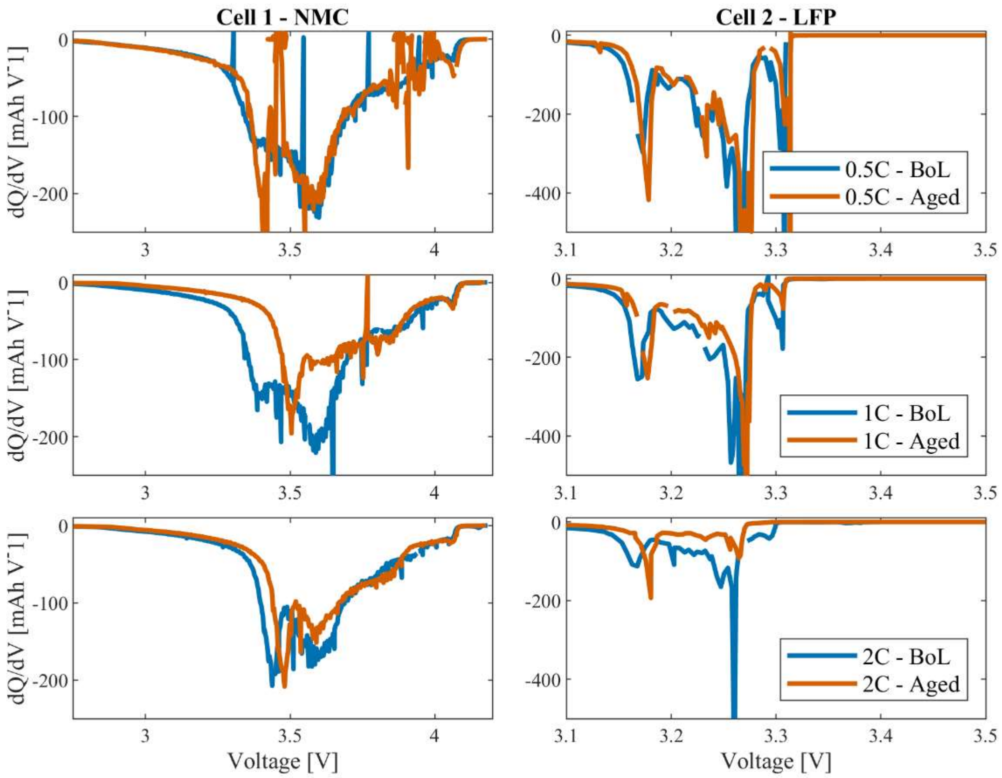

Figure 3: dQ/dV during Li stripping, Coin Cells.

an additional peak is sought for the transition region between Li dissolution plateau and the starting point of graphite Li de-intercalation. The dQ/dV of the coin cells have been analyzed at 0.5C, 1C and 2C respectively, for the first cycle and after aging it for 50 cycles. These results are shown in Figure 3, for Cell 1 and Cell 2.

In the case of the NMC cell, no metallic lithium is observed at 0.5C. At higher currents, plating is observed at 1C after the formation, but not after the aging. On the other hand, Li plating is observed at 2C for all cycles. These results were then confirmed by performing a visual inspection of the coin cells (see Figure 2). However, these peaks are not that clear and could be misleading. As for the LFP cell, clear plating signature is observed for 1C charging rate after formation, although no distinct peaks are found after the aging. As for 2C charging rate, the peaks in the dQ/dV shift and vary in intensity due to incomplete lithiation due to such a fast rate during charge, which complicates the analysis in search for Li plating signatures. In IC analysis, the peaks are found to change at very high rates or after aging, which can complicate the detection of Li plating. Hence, from these results it is concluded that the ICA is less suitable for a diagnosis.

4.3 Impedance analysis during charging

For this analysis, the EIS measurements were performed every 10% charged SoC, with a resting time of 30 minutes. In this analysis, as described in chapter 2, the plating signature will be a “non-bathtub” like behavior and also a decrease in the cell impedance over the cycles. Since impedance changes are expected to happen near the transition frequency, a frequency of 1 Hz is targeted for this analysis. The results for the NMC cell are shown in Figure 4.

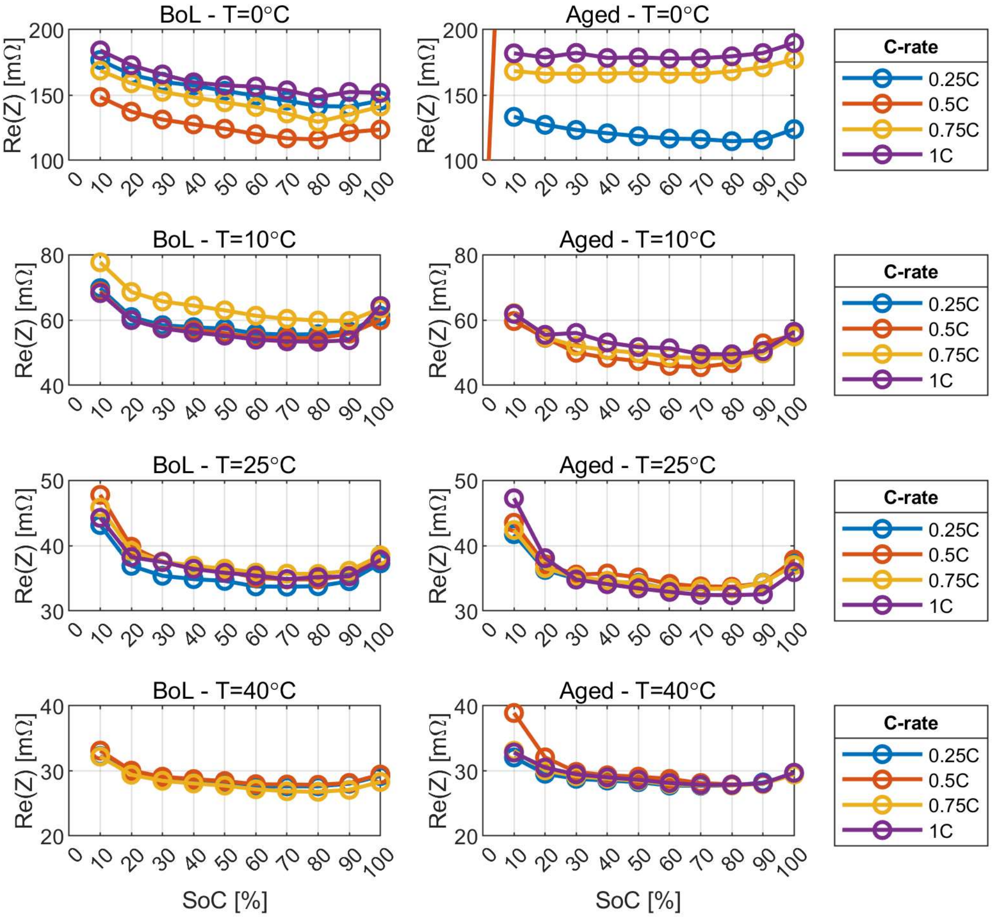

Figure 4: Z’ vs SoC during charging. Different C-rates and temperatures. NMC cell.

Analyzing the data at 25ºC and 40ºC, the expected “bathtub” like behavior is observed, as expected, with no signs of metallic plating. However, at 10ºC, the first signs of Li plating are detected. At BoL, the impedance tendency does not resemble that much the one observed at higher temperatures, and at 60% SoC a mild decrease in the real part of the impedance value is observed. Although this could be a sign of metallic plating, it is so mild that it could be mislabeled as such. On the other hand, observing the impedance after aging, this mild decrease disappears. However, the overall impedance values do decrease with aging, which could be a sign of Li plating. Analyzing this further, if the Nyquist plot is analyzed (see Figure 5), the decrease in the impedance through the whole spectra is confirmed. As for the lowest temperature tested, 0ºC, a decrease is also observed at about 60% SoC. As for the aged cell at this environmental condition, this downward trend is not observed for currents of 0.5C, 0.75C and 1C. This is hypothesized to be caused by dead lithium, which does not participate in the electrochemical reactions anymore. However, at 0.25C, the impedance values do decrease considerably compared to BoL. As seen in the literature, this is a Li plating signature [10]. Focusing on this point further, if the Nyquist plot is analyzed, the decrease in the impedance throughout the whole spectra is observed, confirming this hypothesis.

As for the LFP cell, the same test procedure was followed. In this case, the results were non conclusive. This could be caused due to the setup used or the EIS configuration employed to this higher capacity and very low resistance cell.

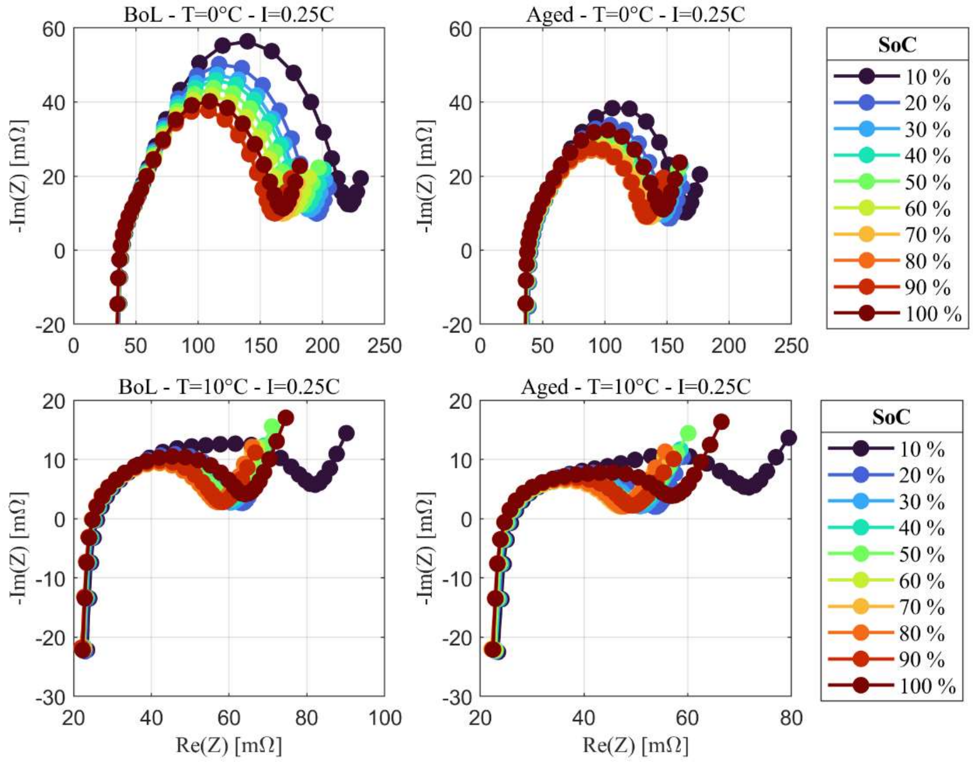

Figure 5: Nyquist plot at BoL and after aging at 0.25C for 0ºC and 10ºC

4.4 DRT analysis

The Distribution of Relaxation Times analysis has been performed to the commercial cells, at BoL and after the aging of 15 cycles, for each C-rate and each temperature. The computation of the DRT has been based on the DRTtools software [13]. Four main peaks are observed through all C-rates and temperatures, named S1 to S4. S1 is attributed to the diffusion process, S2 and S3 are tentatively attributed to cathode and anode charge transfer resistances respectively, while S4 is attributed to the contact resistance. The peak associated to the diffusion process will not be considered for Li plating signatures since its high temperature dependency hardens the detection of Li plating. Same logic applies to the contact resistance peak.

Firstly, the changes in the DRT are analyzed for the EIS measurement just after finishing a fast charge and the EIS after relaxation, both at BoL (see Figure 6). Beginning with the NMC cell, changes are observed in the anode CT peak for 10ºC and 0ºC. At 10ºC, the peak intensity does not change but the frequency shifts to lower frequencies, whereas at 0ºC, the peak intensity does increase, and the frequency mildly decreases. No changes were observed at 25ºC and 40ºC. On the other hand, the cathode CT peak, no changes are observed during relaxation in either case. As for the LFP cell, the anode CT peak mildly increases its intensity, and shifts to lower frequencies also (see Figure 7).

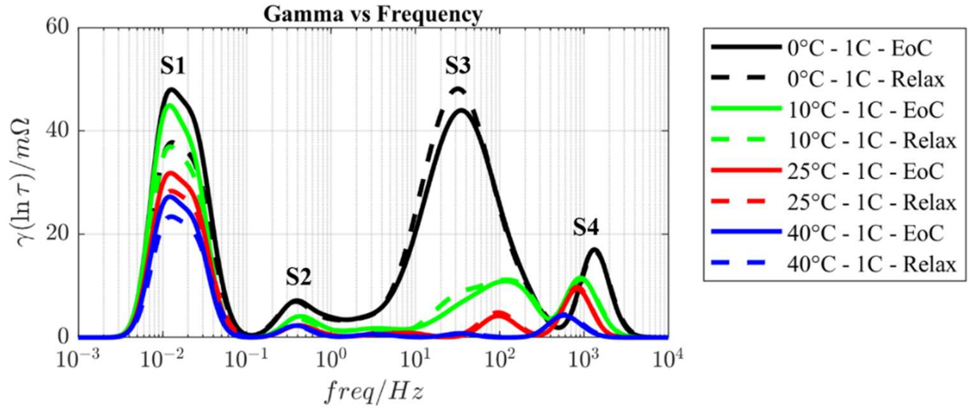

Figure 6: DRT plots after the End of Charge and relaxation of 10 hours. NMC cell

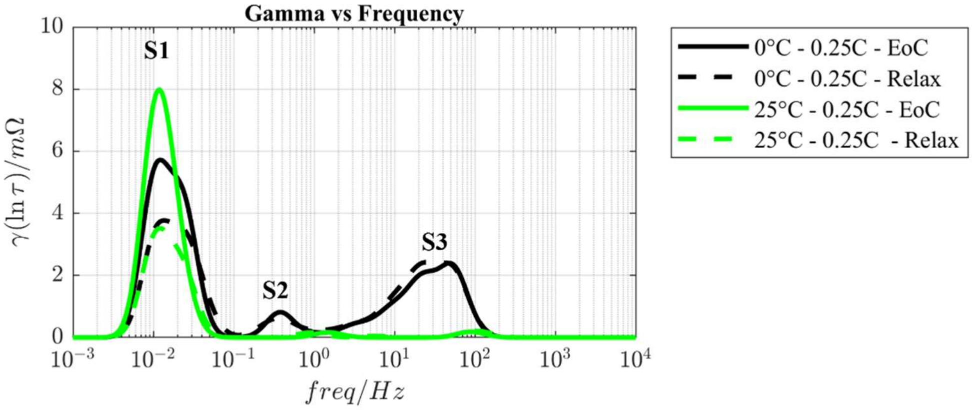

Figure 7: DRT plots after the End of Charge and relaxation of 10 hours. LFP cell.

Secondly, the changes in the DRT due to aging are analyzed just after finishing the charge, for different C-rates and temperatures, just for the NMC cell in this case (see Figure 8). Starting at 0ºC, and focusing on the anode CT peak, different behaviors are observed for the different charging C-rates. At 0.25C, the peak intensity decreases. However, at the rest of the tested C-rates the intensity increases. At 10ºC, the peak intensity of the anode CT decreases at every C-rate. Furthermore, a shift towards lower frequencies is also observed, which correlates with the findings in the literature [10]. As for 25ºC and 40ºC tests, no changes in the DRT were observed.

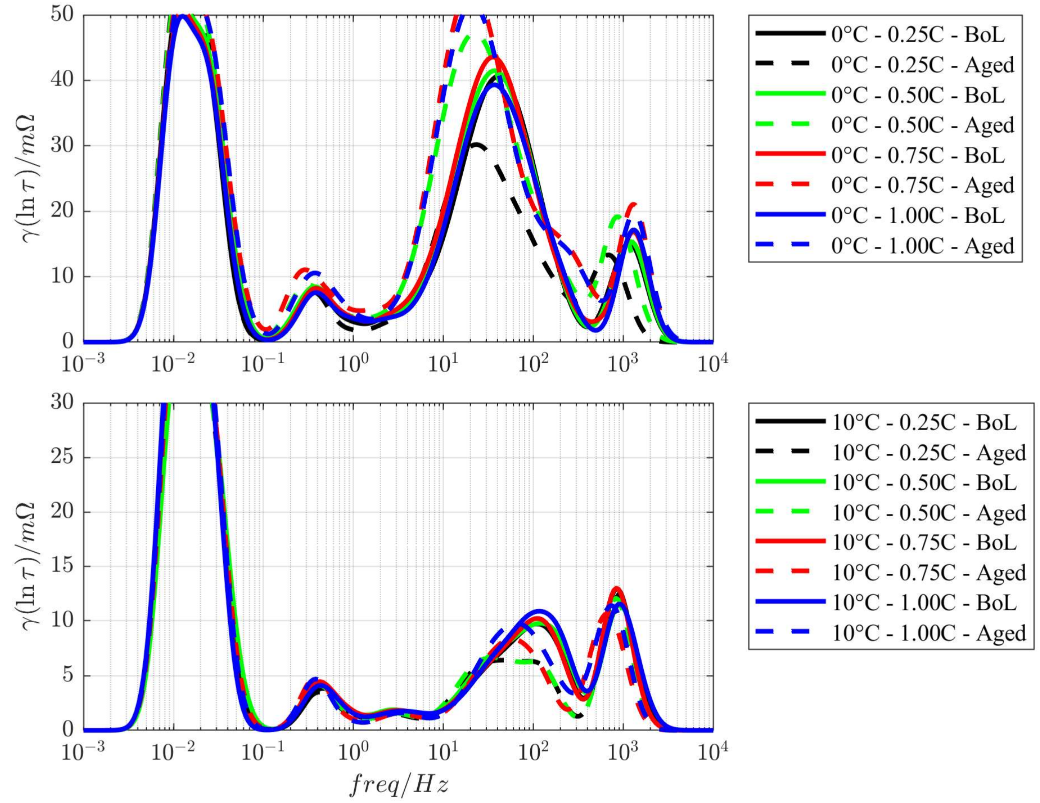

Figure 8: DRT plots at BoL and after the aging for 0ºC and 10ºC at different C-rates. NMC cell.

5 Discussion

After analyzing several Li plating detection techniques for two different cathode chemistries, some conclusions and observations are derived from this study. From the electrochemical data analysis, it is observed that the VRP method is the most sensitive from the galvanostatic cycling methods, especially for the LFP chemistry. The ICA showed that in some occasions the peaks change at high rates or after aging, which may complicate the analysis and decrease the effectiveness of this method for diagnosing Li plating. A VRP analysis is easier to perform than ICA in a real applications, since it is more probable to have a long resting period rather than a C/20 discharge, which will most likely happen only in a laboratory. Furthermore, in some cases, the metallic lithium was detected at BoL, but not after the aging. This is hypothesized to be caused due to dead lithium not participating in the electrochemical reactions anymore. Finally, it must be highlighted that the VRP method can be implemented in current BMS, since it only needs cell voltage monitoring, but its use is restricted to diagnosing metallic lithium after it has occurred, so no actions can be taken during operation to avoid it happening in the first place.

On the other hand, the impedance analysis during charging can potentially solve this limitations, and develop a charging control strategy to avoid such aging mechanisms. The results obtained from this study are promising, since the Li plating signatures are observed during the charging process. Impedance analysis can also be carried out after the charging process by means of a DRT analysis. Meaningful changes are observed at lower to medium frequencies, in the peak presumably referring to the anode CT process at temperatures below 25ºC, which some correlate to previous findings in the literature while others do not. More thorough testing must be performed to validate which changes are caused due to metallic lithium. DRT analysis also provides more aging information about the cell, but its heavy computational needs for performing the deconvolution limits its use to cloud-based diagnosis tools. In Table 2, a summary of the tested methods and their key challenges are presented.

Table 2: Summary of the tested Li plating detection methods and their key challenges for implementation

Method	Requirements	Real-time	Key challenges
Voltage Relaxation	Cell voltage	No – diagnosis after charging	Long resting periods needed, not always available.
Incremental Capacity	Cell voltage, current	No – diagnosis after charging	Very slow discharging rates needed right after a fast charge. Almost impossible in a real application.
Impedance during charging	EIS at single frequency	Yes – performed online or every X% charged SoC	Specific HW needed capable to measure EIS online, otherwise the charging speed is drastically reduced. Distinguish plating signatures from SoC/Temperature changes.
DRT	EIS, whole spectra or specified frequency ragne	No – diagnosis after charging	Specific HW needed. Heavy computational load. Restricted to cloud-based diagnosis tools.

6 Conclusions and future lines

This study presents the findings of the analysis of several Lithium Plating detection methods, which have been tested on NMC and LFP commercial cells. Both in-operando and offline Li plating detection strategies have been analyzed, focusing on voltage/current-based methods for offline detection and impedance-based methods for online and offline detection methods. These analyses have been performed on coin cells and commercial cells in order to validate and confirm the metallic lithium signatures in the cycling data. The voltage relaxation method has been proposed as a method which can be currently implemented in some BMS with relatively good accuracy for diagnosis plated lithium after a fast charge. This method has been proven to be more sensitive than Incremental Capacity analysis and easier to implement, so this one would be ruled out for real applications. As for impedance-based methods, these have been found to provide the most information for Li plating detection, both online and offline. However, for ultimately achieving an accurate, robust charging control and a diagnosis tool every detection method analyzed in this work should be performed in both coin cells and commercial cells, and be compared accordingly. The tests presented in this work represent preliminary testing for adjusting the test procedures. For the coin cells, the impedance measurements shall be performed, to two electrode and three electrode coin cells for confirming the plating signatures. The coin cells with a third reference electrode will help to correlate and confirm the Li plating signatures in the galvanostatic cycling data. As for the commercial cells, the voltage relaxation profiles shall be tested again, adjusting the measurement resolution and the IC analysis performed. Afterwards, these cells should be opened for visually confirming the presence of metallic lithium, as it has been done with the coin cells. Finally, the findings of the testing from the commercial cells shall be cross-checked and correlated to those from the coin cells.

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Presenter Biography

Jon Perez received the B.S. degree in electrical engineering in 2020 at Tecnun University of Navarre, Donostia – San Sebastian, Basque Country, Spain. In 2022, he received the M.Sc degree in Energy and Power Electronics from Mondragon University, Mondragon, Basque Country, Spain. From 2022 onwards, he is pursuing a PhD degree in applied engineering at CIDETEC Energy Storage. His research interests are focused on lithium-ion batteries aging detection, SoX algorithms and early detection of Thermal Runaway and other failures.