Operando lithium plating quantification and early detection of a commercial LiFePO₄ cell cycled under dynamic driving schedule

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Abstract

Lithium plating is considered one of the most detrimental phenomenon in lithium ion batteries (LIBs), as it increases cell degradation and might lead to safety issues. Plating induced LIB failure presents a major concern for emerging applications in transportation and electrical energy storage. Hence, the necessity to *operando* monitor, detect and analyze lithium plating becomes critical for safe and reliable usage of LIB systems. Here, we report *in situ* lithium plating analyses for a commercial graphite||LiFePO₄ cell cycled under dynamic stress test (DST) driving schedule. We designed a framework based on incremental capacity (IC) analysis and mechanistic model simulations to quantify degradation modes, relate their effects to lithium plating occurrence and assess cell degradation. The results show that lithium plating was induced by large loss of active material on the negative electrode that eventually led the electrode to over-lithiate. Moreover, when lithium plating emerged, we quantified that the loss of lithium inventory pace was increased by a factor of four. This study illustrates the benefits of the proposed framework to improve lithium plating analysis. It also discloses the symptoms of lithium plating formation, which prove valuable for novel, *online* strategies on early lithium plating detection.

Keywords

Lithium plating; Battery degradation modes; Mechanistic model simulations; Incremental capacity; Dynamic stress test;

1. Introduction

In recent years, the increase of duty-loads and cycle-life requirements in electric vehicles (EVs) and battery energy storage systems (BEES) have heightened the need for accurate and reliable control of battery systems. The battery management systems (BMS) are control units consisting of hardware and software, to ensure the correct functioning of the lithium ion battery (LIB) packs. Despite continuous improvements in BMS technology [1,2], catastrophic battery failures have been recently reported [3–6]. Dendrite-induced short circuit caused by lithium plating have been identified as possible factors that triggered several of the reported battery failures [3,5,7]. These unfortunate events have caused massive financial losses affecting manufacturer's and battery industry reputation, and present a major concern for the end-user safety. Therefore, it becomes evident that further improvements in battery monitoring are essential. These developments shall include advanced techniques to *operando* diagnose and predict complex battery degradation mechanisms, including lithium plating formation. Though challenging, the development of these techniques shall bring significant advancement in the battery industry.

Among the various degradation mechanisms occurring in LIBs, lithium plating is considered one of the most detrimental. This is because lithium plating not only catalyzes further degradation but also affects the safety of the battery operation [8–11]. Lithium plating is a phenomenon that occurs during charge, when lithium ions deposit as metallic lithium on the negative electrode (NE) surface instead of intercalating into graphite. Because metallic lithium is highly reactive with the electrolyte, it reacts causing loss of lithium inventory (LLI) [8,12], which reduces the available capacity in a battery. Furthermore, the formed metallic lithium may result in the formation of moss-like deposits and dendrites [13–15] that can eventually grow and pierce the separator which causes a short circuit by connecting the electrodes. This phenomenon could trigger thermal runaway, leading to battery failure [6,16].

The factors that cause lithium plating can be related to: (i) harsh cell operating conditions (e.g., low temperature, strenuous charge, overcharge) [17–20], (ii) cell constructive defects (e.g., poor cell balance, geometric misfits and poor electrolyte formulation) [13,21,22], and (iii) conventional aging of the battery (leading to cell unbalance and/or kinetic degradation) [23–26]. Under lithium plating occurrence, it is also possible that part of the metallic lithium deposited on the anode during charge is recovered as active lithium during the subsequent discharge [13,21,27–29]. This process, known as reversible lithium plating occurs because oxidation (stripping) of lithium is a more facile reaction than lithium deintercalation. When this process occurs, lithium plating does not cause direct capacity loss on the battery because the metallic lithium is then another electroactive phase on the NE electrode [27]. Addressing and quantifying all the aforementioned factors becomes critical to understand and identify the lithium plating phenomenon.

Due to the critical impact of lithium plating on LIB's performance and safety, considerable efforts have been devoted to further elucidate its effects, and to develop techniques for its detection. To detect lithium plating, a division into electrochemical and physical techniques has been proposed [30]. Physical characterization techniques usually involve *ex situ* analyses, and are not therefore practical for implementation in BMS. Hence, focus should be set on *in-situ* techniques. *In situ* electrochemical techniques include: anode potential measurements [20,21,28,31–33], coulombic efficiency [27,34] stripping discharge [21,35], incremental capacity [27,35–37], voltage relaxation [28,35,38] and electrochemical impedance spectroscopy (EIS) [35,36]. Yet successful, some of the reported techniques are not practical for implementation in BMS either because they require expensive or dedicated testing equipment. Similarly, some reported techniques were demonstrated under a specifically-designed testing conditions (i.e., testing at low temperatures, testing of unbalanced cells), to deliberately induce lithium plating and enable its analysis. Therefore, its feasibility in real-world dynamic schemes might be problematic. Finally, detailed studies on the long-term degradation mechanisms that induce lithium plating shall be improved; understanding and

quantifying cell degradation mechanisms becomes critical to facilitate lithium plating detection and prediction. Hence, an advanced, *in situ* and cost-effective technique to detect and quantify lithium plating of commercial batteries under testing still remains to be presented.

Herein, we report the analysis to *operando* identify and quantify lithium plating on a commercial graphite||LiFePO₄ cell. The cell was tested at ambient temperature using the standard dynamic stress test (DST) driving schedule [39]. We use a framework that merges both electrochemical and computer simulation approaches: the incremental capacity (IC) analysis [40–45] was used to identify and trace the presence of reversible lithium plating and disclose the underpinning causes of cell degradation. The advanced mechanistic model simulations by the ‘*alawa*’ toolbox was used to identify the nature of lithium plating origins, quantify the ongoing degradation modes and quantify the reversible and irreversible part of lithium plating. We further elucidate the rapid performance degradation observed on the test cell, induced by the cycling scheme. The use of the proposed framework advances the understanding of *in situ* lithium plating analyses, and provides a unique tool towards early lithium plating detection.

2. Experimental

2.1. Battery test procedures

The experiments were conducted on a high-power graphite||LFP cell manufactured by A123 Systems (ANR26650M1, 2.3 Ah), using an Arbin BT-2000 battery test station. A Memmert environmental chamber was used to maintain a constant ambient temperature of 23°C throughout testing. The cell was cycled within the limits recommended by the manufacturer: voltage range (2.0 V–3.6 V), and currents below maximum specifications (i.e., 4.3C charge and 30C discharge) [46].

The tests began with the conditioning procedures following the USABC guidelines [39], with an added C/25 charge and discharge cycle. Thereafter, the tested cell was stored for 13 months in the thermal chamber (23°C) at 95% state of charge (SOC), as part of supplementary studies on cell

calendar aging [47]. As the rest period was concluded, reference performance tests (RPT) were carried out. The RPT consisted of standard charges ($CC = 1C$ & $CV = 3.6$ V) with $1C$ and $C/3$ discharge regimes, followed by a CC $C/25$ charge and discharge. Following the RPT, the testing under dynamic conditions was initiated and it consisted in performing fast charge coupled with dynamic pulse-based full discharges. The fast charging scheme consisted of a multi-step method [48], whereas the discharging scheme used a dynamic stress test (i.e., DST) profile as recommended in the USABC manual [39] (see Supplementary Materials, Fig. 1). The DST is a variable-power discharge regime developed by the USABC to simulate expected demands of an EV battery. The DST schedule was scaled to meet the long-term USABC power goal (i.e., 400 W/kg), and repeated every 360 seconds. The resulting maximum C-rates during charge and discharge pulses were of $2C$ and $4C$, respectively, with an average corresponding to a $C/3$ discharge. The average energy throughput per full discharge at beginning of cycling was 8.33 Wh. Every 300 full dynamic cycles, RPTs were carried out to evaluate cell degradation. Data collection intervals were controlled by voltage variation at 5 mV per step during the RPTs, and 20 mV during dynamic cycling.

2.2. Simulation tests

Computer simulations to assess battery diagnosis were performed using the *'alawa* toolbox, developed at the University of Hawaii [49]. The model on which the toolbox is based was described in Ref. [26]. The half-cell data used for the simulations was gathered from Swagelok-type cells and materials harvested from an identical cell (i.e., same cell model, same batch, minimal cell-to-cell variation) as the one tested in this work. The cell disassembly and the half-cell testing were detailed in our previous work [50].

3. Results

3.1. Capacity fade

The tests started with conditioning procedures to determine initial cell performance before and after the storage period. The initial discharged capacity at C/25 was 2.300 Ah. During storage, the cell capacity was reduced from 2.300 Ah to 2.240 Ah (-2.6 %). For sake of comparison with our previous study [50], we will keep 2.300Ah as the 100% normalized capacity.

Fig. 1 displays the evolution of capacity retention at C/25 of the test cell (triangle markers) as a function of cycle number. As dynamic cycling started, the capacity fade evolution followed a discontinuous linear trend divided in two stages. During Stage 1, the normalized capacity followed a downward trend until cycle 600. In Stage 2 (i.e., cycle 900 onwards), the capacity evolution followed a downward trend ~ 4 times steeper. The dashed line shows the projection of the trends. The end-of-life (defined when normalized capacity is below 80% [39]) of the tested cell under dynamic cycling was reached at cycle ~ 1400 . To facilitate comparison and further discussions, **Fig. 1** also displays the capacity retention of an identical cell (i.e., same model, same batch), that underwent a different duty cycle (square markers). This additional cell, which was studied in our previous work [50], was cycled under the same multistep fast charging process, but under constant current discharge at 4C. It will be referred as constant current cycling. The capacity pace of the constant current cycling followed a linear trend similar than of the Stage 1 pace that remained consistent throughout the entire test, reaching the end-of-life after ~ 5000 cycles [50]. As mentioned above, the slight initial capacity difference between the two cells was induced by the calendar aging period.

Fig. 1. Evolution of the normalized capacity for the test cell under dynamic cycling, at C/25. To facilitate comparisons, this figure also includes the normalized capacity evolution for another identical cell tested under constant current cycling, particularized at C/25.

3.2. Incremental capacity (IC) and IC peak area results

Fig. 2a presents the evolution of the C/25 discharges voltage vs. capacity curves with cycling. The associated plateaus derived from the first-order phase transformation in the graphite convoluted with the LFP phase transformation are labeled from ❶ to ❺ [26]. The cell voltage signature exhibited severe changes with aging, including the appearance of a high voltage plateau, labeled as ❶ (see **Fig. 2a**, inset panel). To display the cell changes with a higher sensitivity, the IC curves (i.e., $\Delta Q/\Delta V$) were used. The IC curves observation highlighted a strong reduction of peaks ❶ to ❺ overall, arrows on **Fig. 2b**. The intensity decrease for peak ❷ to ❺ seems rather constant but reduction rate differs for peak ❶ where its intensity remained practically constant during the first 600 cycles before plummeting thereafter. Besides these intensity changes, plateau ❶ appearance induced a new peak, peak ❶, to emerge after cycle 600 and its intensity kept increasing after that. The potential difference between peak ❶ and peak ❶ is approximately 80 mV.

Fig. 2. Evolution with cycling during RPT at C/25 discharges of (a) voltage vs. capacity and (b) incremental capacity curves. The inset panel shows a magnification of peak 0.

To investigate the variations in peaks 0 to 5 in more detail and quantify the evolution of the capacity associated with each phase transformation, an analysis of the peak area under each IC peak was carried out [50,51]. **Fig. 3** presents the evolution of the peak area with cycling, in terms of (a) normalized capacity and (b) absolute capacity. As hinted from the observation of the peak intensity, the area under peak 1 ($\int 1$) evolved peculiarly compared to the area under peaks 2-5 ($\int 2-5$): during Stage 1 (i.e., up to cycle 600) $\int 1$ linearly grew, whereas the area ($\int 2-5$) linearly decreased. During Stage 2 (i.e., cycle 900 onwards), $\int 1$ reversed its tendency to follow a sharp

downward linear trend whereas $\int \textcircled{2}-\textcircled{5}$ kept decreasing at the same pace. The $\int \textcircled{1}$ was initially 91.5% and not 100% because of the effect of 13 months calendar aging that induced LLI [52–54], thus reducing $\int \textcircled{1}$ [55]. It has to be noted that the discontinuity in $\int \textcircled{1}$ corresponds to the one observed in the normalized capacity fade, i.e., cycle 600. Moreover, the discontinuity did not affect $\int \textcircled{2}-\textcircled{5}$ which area decrease remained steady throughout cycling.

The evolution of $\int \textcircled{0}$ with cycling is shown in **Fig. 3b**. During the first 600 cycles, no appreciable capacity was measured. However, from cycle 900 onwards, $\int \textcircled{0}$ emerged, showing a slight increase until end of cycling. The effects of $\int \textcircled{0}$ in terms of normalized peak area are also projected in **Fig. 3a**, where the total capacity added for $\int \textcircled{0}$ and $\int \textcircled{1}$ is displayed.

Fig. 3. Evolution with cycling during RPT at C/25 of (a) normalized peak area for $\int \textcircled{1}$, $\int \textcircled{2}-\textcircled{5}$ and the added effects of $\int \textcircled{1} + \int \textcircled{0}$ during Stage 2, and (b) distribution of cell capacity in Ah for full cell, $\int \textcircled{2}-\textcircled{5}$, $\int \textcircled{1}$ and $\int \textcircled{0}$.

4. Discussion

The results presented in the previous section showed that the cell exhibited a peculiar discontinuous capacity fade divided in two stages. It also underwent significant degradation through cycling, as highlighted by the IC curves evolution. To further investigate the origins of the degradation, the evolution of the IC curves are studied in more detail.

We shall begin by analyzing the appearance of peak $\textcircled{0}$ in the IC curves (cf. **Fig. 2b**) and its possible correspondence with lithium plating. The appearance of metallic lithium shall introduce a new active phase to the graphite||LFP system and therefore the appearance of new electrochemical features. According to the literature [21,22,27,35,56], under lithium plating conditions during charge, a characteristic high potential plateau resulting from the lithium-stripping process could emerge in the subsequent discharge. If the plating is reversible, the plateau also appears in the following discharge. In theory, the potential of the Li^0/Li^+ reaction shall sit around 80 mV below the one of graphite stage 1 [57,58]. With the LFP being on a voltage plateau, this potential difference shall be the same in the graphite||LFP system. The measured 80 mV difference between onset potentials of peak $\textcircled{0}$ and peak $\textcircled{1}$ therefore indicates that the new phase is indeed originating from lithium plating.

As mentioned in the introduction, lithium plating can origin from different factors influencing the negative electrode: cell constructive defects, hazardous testing and continuous aging. For the test cell, cell constructive defects are discarded since the initial IC cell signatures are in concordance with standard graphite||LFP systems [43,45,50,51], and the preconditioning test results matched with the specifications provided by the cell manufacturer. Hazardous testing is also discarded since cell operating conditions were safe, i.e., ambient temperature was controlled to 23°C throughout entire testing, the charging procedure was validated to be safe [48,50], and DST peak C-rates are

considerably below the maximum cell limits [46]. In the light of these observations, the lithium plating was then induced by the cell continuous aging. To identify which cell aging modes could potentially trigger lithium plating, we subsequently investigated the graphite||LFP system using ‘*alawa*’ mechanistic simulations.

4.1. Loss of negative active material and lithium plating

From the analysis of the impact of the thermodynamic cell degradation modes [26] on a graphite||LFP cell, it appears that only a loss of delithiated negative electrode active material (i.e., LAM_{deNE}) could lead to lithium plating [26]. To visualize this outcome, we carried out ‘*alawa*’ simulations of the cell solely under the effect of LAM_{deNE} to decipher the conditions under which plating could occur.

Fig. 4 illustrates the evolution of a graphite||LFP cell under LAM_{deNE} degradation and its impact on (a) the half-cell matching, (b) the IC signatures, (c) the normalized peak area, and (d) the normalized cell capacity. As a result of LAM_{deNE} , less and less NE is available for reaction and this results in a shrinkage of the NE from its lithiated state (LiC_6), **Fig. 4a**. The shrinkage eventually leads the NE to be fully lithiated before the PE is completely delithiated. The remaining Li-ions in the PE will then not be able to intercalate the NE and will plate at the surface. The effect of lithium plating on the IC signatures is the appearance and subsequent growth of peak ①, as observed in **Fig. 4b**. Peak ① in discharge emerges only under reversible lithium plating conditions [21,22,27,35,56]. In **Fig. 4b**, the simulation shows a theoretical 100% reversible process. The case where both irreversible and reversible lithium plating are present would result in a smaller growth of peak ①. Regardless of the reversible and irreversible amount of lithium plating, the reduction of peaks ② to ⑤ evolves as indicated in the arrows on **Fig. 4b**.

Fig. 4. Evolution of the simulated LAM_{deNE} on a graphite||LFP cell eventually inducing lithium plating, showing, (a) half-cell electrode perspective, (b) IC signature evolution for a 100% lithium plating reversible process, (c) evolution of the peak area, and (d) normalized peak area, as a function of LAM_{deNE} degradation, in percentage.

The normalized peak area (see **Fig. 4c**) illustrates that $\int \mathbf{1}$ first linearly grows to reach a maximum, to then rapidly decreases. $\int \mathbf{1}$ grows because the NE has an excess of relative capacity that falls outside the capacity range of the PE, and because the shrinkage will make this capacity available for intercalation [26]. Since the excess capacity is solely on stage 1, the shrinkage leads to the use of more capacity of this stage and thus an increase of its area. However, as LAM_{deNE} increases, the NE eventually reaches a point where its relative capacity is entirely inside the range of the PE. Consequently, $\int \mathbf{1}$ stops growing and lithium plating is initiated (see **Fig. 4c**). Thereafter,

$\int \textcircled{1}$ decreases rapidly. Contrary to the two-stage evolution of $\int \textcircled{1}$, $\int \textcircled{2-5}$ follows a linear degradation trend throughout cycling.

The evolution of the normalized cell capacity versus LAM_{deNE} is shown in **Fig. 4d**. Prior to the lithium plating occurrence, LAM_{deNE} degradation does not induce capacity fade because the excess capacity is used. Hence, we tend to refer LAM_{deNE} as a “silent” degradation mode in this early degradation stages. This unusual cell behavior occurs because the reduction of $\int \textcircled{2-5}$ is counterbalanced by $\int \textcircled{1}$ increase. Once plating occurs, the capacity loss will be a function of the reversibility of the process (cf. **Fig. 4d**), with the fraction of reversible plating not introducing any capacity loss whereas the fraction of irreversible plating will.

This mechanistic understanding of the impact of LAM_{deNE} can be used to qualitatively estimate the overall cell degradation by comparing experimental results versus *‘alawa* simulations. Both the experimental and the simulated results show great resemblance and in particular, the appearance of peak $\textcircled{0}$ together with the evolution of $\int \textcircled{1}$ are showed in both experimental and *‘alawa* simulations with LAM_{deNE} alone (cf. experimental **Fig. 2b** and **Fig. 3a**, versus simulated **Fig. 4b-c**). We thus identify LAM_{deNE} as the major contributor of cell degradation and the underlying aging mode inducing lithium plating. In addition, the comparison of experimental and simulation results yields a key result: the appearance of lithium plating shall begin at $\int \textcircled{1}$ inflection point. Consequently, lithium plating begins in-between cycle 600 and 900.

4.2. Quantification of cell degradation mechanisms

While LAM_{deNE} is the main acting mode, cell degradation involved additional aging modes. Indeed, LAM_{deNE} remains “silent” during the initial stage, thus it is failing to explain the experimental capacity loss observed during stage 1. In addition, the non-reversibility of lithium plating might initiate additional degradation during stage 2. The next section aims at fully quantify the degradation modes acting on the cell. To quantify the degradation modes, we divided cell

degradation analysis in two stages: first, prior lithium plating takes place, and second, under the effects of lithium plating. The use of this strategy facilitates the understanding of the underpinning phenomena inducing lithium plating, and facilitates cell emulation process. For the first stage, we used a simulation approach following the procedures shown in our previous works [50,51,59]. For the second stage, we introduced a new approach using a reverse simulation method.

4.2.1. Quantification analysis prior lithium plating

The first clue to infer the degradation modes taking place alongside LAM_{deNE} prior to the appearance of lithium plating is the capacity loss. Indeed, since LAM_{deNE} is silent, we know that at least one non-silent mode is occurring, i.e., LLI, LAM_{liNE} and/or LAM_{liPE} [26]. From the literature we also know that aging caused by LAM in LFP-PE technology can be negligible [54,60–64]. Additional verifications to resolve whether LAM_{liPE} or LLI is taking place were carried out in our previous works [50,51], also concluding that that capacity fade is likely from LLI and not from LAM_{liPE} . Hence LAM_{liPE} is not considered at first. LAM_{liNE} is also unlikely since it reduces the intensity of all peaks further and would overestimate the reduction of peaks ②-⑤ (not shown). This leaves a combination of LAM_{deNE} and LLI as the most likely candidate to explain the observed intensity changes and capacity fade. Furthermore, this combination is common in graphite||LFP degradation, as reported in the literature [50,51,62,65].

Fig. 5 displays the main outcomes of ‘*alawa*’ simulations prior lithium plating takes place for a combination of LAM_{deNE} and LLI. For the simulation to be considered successful, three parameters have to match: the $\int$ ① and $\int$ ②-⑤ evolution, the predicted capacity loss and the overall voltage signature. Some of the parameters can be deciphered from simple observations. As mentioned before, the capacity loss is introduced solely by LLI. Since the capacity loss introduced by LLI is proportional to its extent [26], we can calculate the LLI rate necessary to match the observed capacity loss at $\sim 0.0045\%.\text{cyc}^{-1}$. Moreover, for such small amount of LLI, $\int$ ②-⑤ should not be

affected [26], therefore the decrease of $\int \textcircled{2}-\textcircled{5}$ can be used to directly estimate the pace of LAM_{deNE} at $\sim 0.018\% \cdot \text{cyc}^{-1}$ (**Fig. 5b**).

These values can be verified by looking at the predicted variations of $\int \textcircled{1}$ that is affected by both LAM_{deNE} and LLI, and at the agreement between the full IC curves. **Fig. 5a-b** shows that the chosen parameters provide an accurate representation of experimental $\int \textcircled{1}$ and $\int \textcircled{2}-\textcircled{5}$. **Fig. 5c** shows that the simulated and experimental IC curves are a good fit. All conditions are therefore met and the degradation parameters for stage 1 have been successfully identified.

Fig. 5. Normalized peak area for (a) $\int \textcircled{1}$ and *idem* for (b) $\int \textcircled{2}-\textcircled{5}$, as a function of cycle number in tested cell during RPT at C/25. The experimental data are in solid white symbols, while the simulated results are solid-colored symbols. The combination of the aging modes $\text{LAM}_{\text{deNE}} = 0.018\% \cdot \text{cyc}^{-1}$ and $\text{LLI} = 0.0045\% \cdot \text{cyc}^{-1}$ (black, thicker solid lines) is the best approximation to match the

experimental data. In (c), a comparison of the experimental (markers) vs. the simulated (solid) results of the incremental capacity curves is shown. In (d), the schematic representation of the Graphite||LFP cell shows the evolution with cycling of the simulated aging modes from the conditioning stage to cycle 750.

Based on these results and looking at the electrode balance, it is possible to calculate when the plating started with accuracy, **Fig. 5d**. The simulations revealed that at cycle 750, the fully lithiated state of the NE is aligned with the fully delithiated state of the PE (vertical dotted red line). Hence, subsequent cycling would induce plating as the lithiated NE will shrink below the fully delithiated state of the PE.

4.2.2. Quantification analysis during lithium plating

From the ‘*alawa*’ simulations we estimated that lithium plating takes place from cycle ~750 onwards. The appearance of lithium plating increases the simulation complexity as there exists additional degradation variables to consider, notably the ratio between reversible and irreversible plating. To resolve this complexity, we use a simple method based on a “reverse” simulation strategy and from simple observations. The appearance of peak 0 implies (1) that there is some reversible plating that can be quantified ($\int 0$) and (2) that $\int 1$ is not influenced by the cutoff voltage anymore (no more excess capacity) and therefore correspond to the full stage 1 capacity. Observation (2) also implies that the sum of $\int 1$ and $\int 2-5$ corresponds to the full graphite capacity. This information can be used as input parameters in the half-cell ‘*alawa*’ model to decipher aging quantification.

Fig. 6 shows the evolution of the electrodes balance with lithium plating, initiated after cycle 750 (solid line) through cycle 1800 (dashed line). The simulation parameters $\int 0$, $\int 1$ and $\int 2-5$ were set as ‘*alawa*’ inputs to agree with the measured experimental values. This representation highlights that the offset between the PE and NE drastically increase throughout the aging and went from 12.5% initially then 19.8% after cycle 750 to 41% after cycle 1800. These observations can be translated to highlight the impact of reversible and irreversible lithium plating, $Li_{\text{plating rev.}}$ and $Li_{\text{plating irrev.}}$ respectively. Irreversible Li plating contributes to accelerate capacity fade because it promotes

progressive growth of the SEI [20,66,67]. Hence, in the mechanistic model we attribute the SEI growth as a “shifting” of the NE (i.e., same nature as LLI). This explains the increase of the offset, **Fig. 6**. According to the simulations, the LLI degradation rate as lithium plating takes place increased from $\sim 0.0045\% \text{ cyc}^{-1}$ to $\sim 0.018\% \text{ cyc}^{-1}$ because of the passivation of the lithium. On account of the calculated aging modes, the numerical values derived from the simulations, including the evolution of the cell loading ration (i.e., $LR = Q_{NE}/Q_{PE}$) and the offset (i.e., OFS, defined by the NE slippage) [26] are shown in Table 1. Since we previously concluded that aging caused by LAM in LFP-PE technology can be negligible, our simulations did not include LAM_{PE} degradation mode. Hence, the capacity retention of the PE remained constant throughout cycling in our simulations.

Fig. 6. Schematic representation of the Graphite||LFP cell tested under dynamic cycling, showing the evolution with cycling of the simulated aging modes from cycle 750 to 1800.

Table 1. Full cell and individual cell electrode parameters obtained from the simulations.

Reference Performance Test Sequence (C/25)	Full cell	Positive Electrode	Negative Electrode	Loading Ratio (Q_{NE}/Q_{PE})	Offset (%)	Lithium plating
Conditioning	2.30 Ah (100%)	2.62 Ah (100%)	2.49 Ah (100%)	0.95	12.5	No
Beginning of cycling (calendar aged)	2.24 Ah (97.4%)	2.62 Ah (100%)	2.49 Ah (100%)	0.95	14.8	No

Before Li plating (cycle 750)	2.11 Ah (91.7 %)	2.62 Ah (100%)	2.10 Ah (84.3%)	0.8	19.8	Imminent
End of cycling (cycle 1800)	1.55 Ah (67.5%)	2.62 Ah (100%)	1.41 Ah (56.6%)	0.53	41.0	Yes

Based on the results from **Fig. 6**, the overall degradation map can be finalized and is presented in **Fig. 7**. The left axis compares the normalized capacity evolution of experimental versus simulation, whereas the right axis presents the evolution of the calculated degradation modes. First, the effect of the calendar storage (13 months) is represented: the cell lost 2.6% capacity attributed to LLI (only $\int \mathbf{1}$ was reduced). Hence, the initial value of LLI is 2.6%. During the initial 750 cycles, the cell capacity faded linearly and it was solely introduced by LLI (square markers). Despite the fact that LAM_{deNE} (circle markers) is taking place with a pace four times larger than LLI, its contribution to capacity fade remains “silent”. From cycle 750 onwards, the NE becomes the capacity-limiting electrode in the charge regime because of the large NE capacity reduction caused by LAM_{deNE}. The appearance of lithium plating at cycle 750 was accompanied by a four time increase of the rate of LLI attributed to irreversible plating.

Fig. 7. Evolution with cycling of cell degradation. The left axis shows the experimental normalized cell capacity (triangle markers), and the dashed black line shows cell capacity simulation results under the calculated aging modes. The right axis shows the evolution with cycling of the degradation induced by the calculated aging modes (markers and dashed lines).

4.3. Prediction of lithium plating

Coupling the simulation analyses together with the experimental data presented in Section 3, can yield the following facts toward thermodynamic lithium plating prediction:

- Lithium plating incubation can be detected before it manifests by examining the rate of LAM_{deNE} and LLI and the evolution of $\int \text{1}$ and $\int \text{2-5}$. An increase of $\int \text{1}$ indicates symptoms of lithium plating incubation because it implies that the LAM_{NE} is faster than the slippage.
- Lithium plating starts when $\int \text{1}$ reaches its maximum and starts to decrease.

We shall provide a practical application of this understanding: the test cell already showed symptoms of lithium plating incubation on the first RPT carried out at cycle 300. This is determined by examining the IC peak area and a growth of $\int \text{1}$ (cf. **Fig. 3a**). Hence, imagining this was a real case figure, by applying this simple analysis, the usage could have been modified at cycle 300 to a less demanding duty cycle scheme to avoid plating appearance, expand the cell life and increase the overall safety of the system. Equally important, this strategy is cost efficient and simple to implement. Although ‘*alawa*’ simulations were instrumental to demonstrate these results, the actual analysis to predict Li plating does not require further simulations.

4.4. Reversible vs. irreversible lithium plating

The ‘*alawa*’ simulations allowed us to quantify the effects of LAM_{deNE} , and to detect the increase of LLI in presence of lithium plating. However, the capacity losses from “normal” LLI attributed to subsequent surface film formation, are not directly distinguishable from irreversible lithium plating. Nonetheless, assuming “normal” LLI rate is constant, as observed in our previous work [50,51], despite the LAM, we can estimate the ratio between the irreversible and reversible lithium plating.

Fig. 8 summarizes the contribution of the total LLI to the capacity fade as a function of cycle number. Assuming “normal” LLI rate is constant, we can extrapolate the calculated rate of LLI (i.e., $0.0045\% \text{ cyc}^{-1}$) up to cycle 1800, as shown in the solid yellow line. Once lithium plating initiates, the pace of LLI is increased. The difference between the extrapolated “normal” LLI and the actual total capacity fade (discontinuous, triangle markers green line) yields the capacity loss induced by irreversible lithium plating (i.e., LLI from $\text{Li}_{\text{plating irrev.}}$, green dotted area). Using this hypothesis, we can estimate the irreversible plating induced up to 20% capacity loss at cycle 1800.

Here we shall recall that only the irreversible part of lithium plating is responsible for direct capacity fade, whereas the reversible part is not (cf. **Fig. 4**). Since the reversible part was measured experimentally (i.e., $\int \text{0}$, red dotted area), the total amount of lithium plating corresponds to the capacity of LLI from $\text{Li}_{\text{plating irrev.}}$ (green dotted area) plus $\int \text{0}$ (red dotted area). This is represented by the squared, red discontinuous line in **Fig. 8**. This line would correspond to the capacity loss associated with 100% irreversible lithium plating. The opposite case where lithium plating is 100% reversible, is defined by the solid yellow line.

From our estimation of the irreversible and reversible capacities we can now calculate the ratio of irreversible/reversible plating to 75/25 at cycle 1800. Since lithium plating is highly dependable on cell electrochemical properties, testing conditions (i.e., temperatures, charging rate) and the degree of cell degradation, the results from other works [22,27,34,68] to estimate irreversible/reversible plating might not be easily comparable. Nonetheless, our approach allows to study and evaluate the nature of lithium plating, with the additional advantage of being *operando* and cost-effective.

Fig. 8. The capacity fade map under C/25 depicting the attributes and contributions to the total capacity fade in the cell as a function of cycle number.

4.5. DST cycling vs. constant current cycling

The rapid performance degradation observed on the test cell is attributed to the DST scheme. Indeed, the fast charging profile used in this work was successfully applied for more than 4500 cycles on the same cell model with discharge rates at 1C and 4C without causing lithium plating [50]. The chosen DST rates were within the manufacturer limits, with an average current of C/3, and a maximum discharge peak of 4C. Therefore, the tested C-rates should not play a major role in cell degradation. In addition, to estimate the equivalent cycles between DST and constant current discharge, we calculated the total discharged capacity that one DST delivers, and compare it to the constant current test. We found that both protocols deliver very similar capacity (see Supplementary Materials, Fig. 2). Therefore, the DST did not imply additional equivalent cycles.

Therefore, the underpinning cause of cell degradation could be related to the vast number of repetitive intercalation/deintercalation processes that the cell undertook. With 10 current sign changes per DST sequence and in average 15 sequences per cycle (18 for a fresh cell, Supplementary Materials, Fig. 1, 10 at end of life), 150 intercalation/deintercalation takes place per cycle. This suggests that the cell experienced more than 250,000 intercalation/deintercalation processes after

1800 cycles. This vast number of partial intercalation/deintercalation processes might have direct consequences on cell degradation as it could affect the architecture of the electrodes (e.g., caused by volume changes, particle stresses, particle isolation, etc.), thus reduce the amount of active material on the NE [8–10,69,70]. Another consideration that could explain rapid cell degradation is that non-uniform charging from DST cycling may result in inhomogeneous distributions of current density, temperatures and SOC gradients, factors that are likely to accelerate cell degradation, and may lead to lithium plating [30,63,71–73]. Further verification via *postmortem* analysis is valuable at this point to detect the level of graphite lithiation and lithium plating, for example by examining the golden and white areas of the graphite, respectively [34,63,74,75]. Regardless of the underpinning cause of cell degradation, when degradation rate is compared to constant current cycling [50], the DST induces a 10 fold increase of LAM_{deNE} rate.

Overall, we determine that DST cycling at the proposed USABC long-term power goal (400 W/kg) causes rapid performance degradation. Still, we shall remark that the test cell achieves the USABC goals for advanced batteries for EVs, projected for 2020 commercialization (i.e., the DST cycle life USABC goal is 1000 cycles before reaching end of life, estimated at 80% of nominal capacity [76]).

5. Conclusion

In this study, the aim was to attain the challenging necessity for lithium plating detection and quantification in lithium ion batteries. We proposed a framework that merges electrochemical and mechanistic simulation techniques, and applied it to a commercial $LiFePO_4$ cell cycled under a dynamic driving schedule. The use of the proposed framework allowed us to *in situ* identify the ongoing aging modes acting on the cell, detect and quantify the reversible and irreversible part of lithium plating, and provide a unique tool towards early lithium plating detection.

We coupled incremental capacity and the analysis of the peak area to identify and quantify the presence of a new phase transformation in the cell voltage signature. This new phase appeared from reversible lithium plating occurrence. We then studied the nature of lithium plating origins, to observe that gradual cell degradation, and not a sporadic event, led the cell to plate. The mechanistic model simulations (‘*alawa* toolbox with harvested half-cell data) allowed us to *operando* identify the ongoing aging modes, estimate the irreversible amount of lithium plating, and project half-cell degradation on each individual electrode throughout cycling. The results showed that large loss of active material on delithiated negative electrode (LAM_{deNE}) eventually caused cell imbalance, leading to over-lithiate the negative electrode, subsequently inducing lithium plating. The quantitative analysis also showcases the detrimental effect of lithium plating; the loss of lithium inventory (LLI) was increased by a factor of four.

The results of this investigation illustrate the critical importance of tracking cell aging mechanisms to identify and predict lithium plating. As revealed, batteries can have a two-stage capacity fade trend, where the second stage has a steeper rate, attributed to the side-effects of lithium plating. This two-stage trend presents a major concern in real-world battery systems. In fact, unless a detailed aging analysis is carried out, the sudden trend change seems unexpected. To understand and predict this sudden change, an evaluation of the “silent” modes (i.e., LAM_{deNE}) is required. We showed that lithium plating incubation symptoms can be tracked by examining the rate of LAM_{deNE} and LLI. An early detection of lithium plating has unique advantages; it can be used in battery systems to reduce the duty-cycling scheme requirements, hence avoiding further degradation and prolonging cycle-life. This simple, *in situ*, and cost efficient strategy can be easily implemented to improve battery management system (BMS) functions for diagnosis and prognosis.

This work also demonstrates the potential of the ‘*alawa* toolbox to estimate the irreversible and reversible parts of lithium plating. The presented framework could be used by researchers focused on the correlation of cell design parameters (i.e., cell chemistry, electrolytes and electrode architecture)

with lithium plating appearance. A first estimation of the reversible and irreversible ratio could be easily attained without carrying out laborious, ex-situ experiments, thus accelerating the research processes.

To conclude this work, we discussed the plausible underlying causes of cell degradation under the used driving scheme. The analyses indicated a probable connection of rapid cell aging with vast repetitive intercalation/deintercalation processes derived from regenerative braking. Future work will investigate the relationship between the number and intensity of the intercalation/deintercalation processes, and its effects on cell degradation. Additional validation via cell disassembling and *postmortem* analysis is to be expected. This shall further elucidate the effects of dynamic cycling and lithium plating, to evaluate the convenience of using regeneration schemes.

Glossary

Table 2. Abbreviations and nomenclature

Abbreviations and nomenclatures	
BESS	Battery energy storage system
BMS	Battery management system
C/n	Rate in a test regime to charge or discharge the rated capacity in ‘n’ hours
DST	Dynamic stress test
EIS	Electrochemical impedance spectroscopy
EV	Electric vehicle
GIC	Graphite intercalation compounds
IC	Incremental capacity or $\Delta Q/\Delta V$
LAM	Loss of active material
LAM _{deNE}	Loss of active material on delithiated negative electrode
LAM _{dePE}	Loss of active material on delithiated positive electrode
LAM _{liNE}	Loss of active material on lithiated negative electrode
LAM _{liPE}	Loss of active material on lithiated positive electrode
LAM _{NE}	Loss of active material on negative electrode

LIB	Lithium-ion battery
Li _{plating irrev.}	Irreversible lithium plating
LFP	Lithium iron phosphate
LR	Loading ratio, defined as the ratio of the capacity of the negative electrode over the capacity of the positive electrode (Q_{NE}/Q_{PE})
NE	Negative electrode
OFS	Offset between electrode loadings introduced by initial SEI formation and subsequent aging and degradation
PE	Positive electrode
Q	Capacity in general, also for the full cell and rated when appropriate
RPT	Reference performance test
SEI	Solid electrolyte interface
SOC	State of charge
USABC	United States advanced battery consortium

Acknowledgments

The University of Oviedo is grateful for funding provided by the Science and Innovation Spanish Ministry and FEDER, under the Projects TIN2014-56967-R, TEC2016-80700-R (AEI/FEDER, UE), and by the Principality of Asturias Government under Project FC-15-GRUPIN14-073. The Hawaii Natural Energy Institute is grateful for funding by the Office of Naval Research (ONR) Asia Pacific Research Initiative for Sustainable Energy Systems (APRISES) award number N00014-13-1-0463.

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