***Operando* tracing and quantifying inactive Li in lithium metal battery**

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Abstract

Lithium (Li) metal is regarded as the ‘Holy Grail’ anode for the next-generation energy storage systems, but the practical application of Li metal is greatly hindered by its rapid capacity decay and potential safety hazard, both as result from the continuous reactions between Li metal and electrolytes leading to active Li loss in the form of inactive (“electrochemically-dead”) Li metal and the irreversible formation of Li-containing species in the solid electrolyte interface (SEI). Differentiating these two inactive species is challenging, and demands the invention of a quantitative and operando-tracking method that adequately accommodate the intrinsic natures of these species being continuously evolving, highly reactive and moisture-sensitive. Here, we propose and demonstrate a new operando nuclear magnetic resonance (NMR) spectroscopy as a non-destructive,

nuclei-specific tool to quantify the evolution of dead Li metal and SEI separately in anode-free batteries. We identify the failure mechanisms induced by SEI and/or dead Li metal in several popular scenarios such as electrolytes with additives, three-dimensional conductive host and high stripping current density. In addition, we reveal that all cells decay through a general “two-stage” failure mechanism for the Li metal, the first is mainly related to the SEI formation accompanied with the deterioration of Li deposition morphology, which triggers the second stage that is associated with the rapid growth of dead Li metal. Based on this general failure mechanism, future solutions for extending the cycle life of Li metal anode are discussed.

Introduction

Li-ion battery has significantly redefined how we communicate, transport and reside. However, the increasing demand for high-energy-density storage devices in the ever-growing 5G era presents new challenges that lithium-ion batteries can no longer address, and motivates extensive research on exploring the next-generation energy storage materials and chemistries, such as Li metal batteries (LMAs) that include Li||Ni-rich NMC($\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$), Li-oxygen, Li-sulfur, and solid-state Li batteries. The development of all these devices hinges on the successful application of lithium metal anode, which promises higher gravimetric/volumetric energy density than any known anode materials,¹ but suffers from parasitic reactions as evidenced by unsatisfactory coulombic efficiency (CE) and brings risks of safety hazard.²

To extend the cycle life of lithium metal batteries(LMBs), many strategies have been proposed including electrolyte optimization,³⁻⁵ current collector modifications,⁶ and the introduction of an artificial solid-electrolyte interface (SEI).⁷ Nevertheless, the exact failure

mechanism of LMBs remains elusive, as we cannot rationalize why some strategies work well while others don't, and how to enhance the coulombic efficiency above 99.99% is still beyond our reach after such extensive efforts. One of the critical challenges is to distinguish and quantify the various forms of inactive Li microstructures under in-operando conditions. The Li consumption mainly comes from two sources: (1) chemical instability between Li metal and electrolytes, which lead to the formation of SEI species where Li exists as an ion, (2) physical/mechanical instability isolates the dendritic Li metal from the Li metal bulk or current collector during stripping process and results in the formation of dead Li metal in elemental valence (Li^0). These two processes happen sequentially or in parallel. Moreover, their relative ratio changes dynamically during cycling and are largely affected by operating conditions, such as electrolyte formulations and cycle protocols, which may result in entirely different failure mechanisms, and consequently lead to conflicting conclusions depending on which characterizing means employed or at which stage the analysis is applied.

Quantitative analysis of the dead Li metal and SEI is hindered by their confusable morphologies and moisture-sensitivity, which is challenging for most analytic techniques. Recently, Meng et al developed an elegant quantitative ex-situ technique – Titration Gas Chromatography (TGC) to quantify the dead lithium metal and Li^+ containing SEI species, and demonstrated that the dead lithium metal is the culprit of inactive lithium during the initial cycles.⁸ A study combining ^7Li NMR spectroscopy with TGC was then reported to quantify of dead Li metal and SEI component when plating and stripping Li on a copper current collector.⁹ However, it is impossible for such a post-mortem analysis to monitor the

dynamic evolution of dead Li metal during electrochemical cycling, or under in operando conditions that simulates an actual battery environment. *Operando* NMR has been used to distinguish the dendritic/mossy Li from the bulk Li metal in Li||LiCoO₂ and Li||Li cells, which demonstrates unique capability in quantifying lithium metal microstructures.¹⁰ The previous study uses excess Li metal, making it difficult in quantifying the dead Li metal as dead Li metal signal may be buried by the strong bulk Li metal signal. Using an excess amount of Li metal (10 times or even 100 times excess) is also not practical in the real application, which results in lower energy density and unvarious cycling performance and potentially misleading failure mechanism.^{11,12} In this regard, many researchers have called for the lithium metal research community to restrain the use of excess lithium metal.¹¹⁻¹³ Anode free batteries (AFBs), in which lithium metal is *in-situ* formed during charge is gaining more research attentions as it avoids using highly reactive Li metal (compatible with current lithium ion battery manufacturing process), and provide high energy density.^{14,15} More importantly, since all the Li resource comes solely from cathode material, the electrochemical performance of AFBs are essentially determined by the efficiency of lithium deposition and stripping without being disillusioned by the excessive Li metal, thus it is an ideal model system for quantitative analysis of the failure mechanism in LMBs.¹⁶

We employed AFBs for *operando* NMR study, and avoided the interference of lithium metal signal commonly observed in previous operando NMR studies. Thus, we observed the deposition and dissolution processes of lithium metal during cycling in real time and quantified the amount of dead Li metal by ⁷Li NMR spectra. Combining the NMR and electrochemistry data, we developed a quantitative model explained in Supplementary

discussion and are able to monitor the live-evolution process of “inactive” Li caused by the dead Li metal and SEI during the cycling process in-operando. The failure mechanisms of AFBs under several typical conditions, including the current density, electrolyte additives, and high-areal current collector, are well-illustrated. On the basis of these studies, we report a two-stage failure process for anode-free batteries.

Figure 1. Schematics of *operando* NMR study on the anode-free battery (AFB) using 1 M $\text{LiPF}_6/\text{EC}:\text{EMC}$ (3:7 by weight) electrolyte. a Operando NMR set-ups. b Schematic of Li metal deposition/stripping on the Cu substrate in the $\text{Cu}||\text{LiFePO}_4$

battery. **c** The first charge (Li deposition) and discharge (Li stripping) cycle curves of operando Cu||LiFePO₄ cell and **d** the corresponding ⁷Li NMR spectra of the Li metal, and **e** their normalized integrals during charge and discharge process. **f** ⁷Li NMR spectra at the cell at OCV, fully charge state and fully discharge state. The integrals at the fully charged state and the fully discharged state are linked to the amount of deposited Li metal and the dead Li metal, respectively.

The Vanishing Li

The chemical shifts of ⁷Li NMR allows us to differentiate metallic Li metal (~ 270 ppm) from diamagnetic Li species in the SEI (~ 0 ppm), as illustrated in **Figure S1**. The ⁷Li NMR signals of SEI overlap seriously with that of electrolyte, making it difficult to be deconvoluted and quantified.¹⁷ Hence, we only focus on the ⁷Li NMR signal of the Li metal for later analysis. **Figure 1** shows the schematic of *operando* NMR setup and the corresponding NMR results during the first cycle. During charge of Cu||LiFePO₄ cell, lithium ions (Li⁺) are reduced to metallic Li and deposit on the Cu substrate; During discharge, deposited Li metal is oxidized to Li⁺ ions with some disconnected from the bulk Li metal or current collector and become dead Li metal (**Figure 1b**). This deposition/stripping process is tracked by operando NMR, as illustrated in **Figure 1d** and **1e**. Upon charge, the increasing ⁷Li NMR signal around 270 ppm corresponds to the continuous deposition of the lithium metal on the Cu substrate, whereas the decreasing signal upon discharge reflects the stripping process. At the end of discharge the remaining Li metal signals is ascribed to the dead Li metal (**Figure 1e**, green line).

We used a new analytical method to calculate the capacity loss due to the formation of dead Li metal (C_{dead}) and SEI (C_{SEI}) based the analysis of the ^7Li NMR integral and the electrochemistry data. The method is explained in details in the **Supplementary discussion**. The total irreversible capacity (C_{Ir}) can be obtained from the electrochemical data as follows,

$$C_{\text{Ir}}(\text{Electrochemistry measured}) = \text{charge capacity} - \text{discharge capacity} \quad (1)$$

Here, we assume that the C_{Ir} is only originating from the dead Li metal and SEI.⁸ Thus, the capacity loss due to the formation of SEI (C_{SEI}) can be calculated by the equation (2):

$$C_{\text{SEI}} = C_{\text{Ir}}(\text{Electrochemistry measured}) - C_{\text{dead}}(\text{NMR measured}) \quad (2)$$

According to the equations (1) and (2), C_{dead} and C_{SEI} can be quantified separately.

In this study, the Li metal deposited on Cu is less than 10 μm that can be fully penetrated by radio frequency (RF), thus, quantitative information about the Li metal can be obtained. We firstly use the baseline electrolyte consist of 1 M LiPF_6 in ethylene carbonate(EC)/ ethyl methyl carbonate(EMC), in which the thickness of deposited Li metal is around 2-3 μm (**Figure S10a**) that is much smaller than the skin-depth of Li metal (10.4 μm) at 9.7 T.¹⁰ **Figure 1d** shows the evolution of Li metal signal in $\text{Cu}||\text{LiFePO}_4$ cell in baseline electrolyte during the first cycle, which was cycled between 2.8 V - 3.8 V at a current density of 0.5 mA cm^{-2} . The selected spectra at 3.8 V and 2.8 V represent the signal of total deposited Li metal and the dead Li metal, respectively. (**Figure 1f**). According to our conversion method, this dead Li metal signal (**Figure 1f**) corresponds to 15 μAh capacity loss (details shown in the **Supplementary discussion**). The total irreversible capacity measured by electrochemistry is 27 μAh (**Figure S2**). Therefore, the capacity loss caused by the

formation of SEI can be calculated to be $27-15=12$ μAh . These capacities are normalized by the 1st charge capacity (**Table 1**), where we conclude that the total irreversible capacity loss in the first cycle is 9.4%, from which 5.2% resulting from the formation of the dead Li metal, and 4.2% due to the formation of SEI layer.

Table 1 Quantified distribution of dead Li metal and SEI with operando NMR in the baseline electrolytes at the first cycle.

	Electrochemistry measured			NMR measured	Calculated
	1 st	1 st	Irreversible	dead Li metal	SEI
	Charge	discharge	capacity		
Capacity / μAh	286	259	27	15	12
Normalized to the first charge capacity / a.u.	100%	90.6%	9.4%	5.2%	4.2%

Figure 2. Operando ^7Li NMR results of $\text{Cu}||\text{LiFePO}_4$ cell in 1 M $\text{LiPF}_6/\text{EC}:\text{EMC}$ (3:7 by weight) electrolyte during cycling: from the first cycle till capacity decay to zero. **a** Voltage-cycle time curves. **b** Evolution of the integral area of the detected Li metal signal with cycle time. The red dots are specified at the end of discharge state for each cycle, which represent the signals of dead Li metal. These signals of dead Li metal are converted into uAh according to the method explained in **Supplementary discussion**, and then normalized by the first charge capacity (here is 286 uAh), denotes as the C_{dead} (%). The capacity loss caused by SEI (C_{SEI}) for each cycle is calculated by $C_{\text{SEI}} = \text{Irreversible capacity} - C_{\text{dead}}$. **c** The evolution of reversible capacity, C_{dead} and C_{SEI} , which can be depicted into two stages according to the different growth rate of dead Li

meal. A schematic of the two-stage process is illustrated in **d-f**.

Operando NMR was also performed on cells with extensive cycling and the amount of dead lithium metal and SEI formed directly determines the cycle life of LMBs. **Figure 2** exhibits the charge and discharge profiles and their corresponding signals of Li metal for the whole cycling process, which spans from the first cycle to the complete cell failure (with capacity decays to 0). The evolution of dead Li metal can be directly observed in a qualitative manner (red dot line, **Figure 2b**) and it appears to be a two-stage process. In the initial 4 cycles, the signal of dead Li metal remains stable around 5%. After that, the dead Li metal signals increase steadily reaching 60% at the end of 30th cycle. This implies that the formation of the dead Li metal in this system is not substantive at the beginning and is not the main reason for the initial capacity decay.

To further elucidate the process of capacity decay, we carry out quantitative analysis on both C_{dead} and C_{SEI} for the whole cycles according to Equation (2). The result shows that the reversible capacity presents a continuous decay while the C_{dead} and C_{SEI} gradually accumulate with prolonged cycles (**Figure 2c**). For the initial 4 cycles (stage I), C_{SEI} dominates in the capacity loss, consuming 28.4% of the overall capacity, while dead Li metal only contributes 5.8%, as illustrated in **Figure 2e**. The average increase rate of dead Li metal can be estimated by $(C_{\text{dead}} / \text{cycle number})$, which shows a low value of 1.5% per cycle in the first initial 4 cycles. In contrast, the increase rate of SEI exhibits a much higher value of 7.1% per cycle. Subsequently, at stage II, C_{dead} increases gradually and becomes the major reason for capacity loss after 10 cycles. The average increase-rate of dead Li

metal at this stage rises to 2.5% per cycle, while the increase-rate of SEI declines sharply to 0.5% per cycle. When the capacity decays to 0, XRD patterns show that LiFePO_4 has been transformed into its completely delithiated FePO_4 (**Figure S3**), indicating all Li ions have been completely extracted from the cathode side and form “dead Li metal” and SEI species at the anode side (**Figure 2f**). At this point, according to our quantitative results, C_{dead} and C_{SEI} consume 60.0% and 40.0% of the active capacity respectively, in the baseline electrolyte based on typical carbonate solvents, presenting a dominated contribution of dead Li metal to the capacity loss, despite the different two-step growth. This two-stage mechanism would be discussed in more detail later on. In addition, we discovered that the newly-formed dead Li metal is metastable and can self-dissolve in the electrolyte during the resting period. This dissolving process accelerates in high temperature environment (**Figure S4**). Analysing the unstable dead Li metal is a great challenge to common post-mortem techniques and highlights the need of operando analytic technique. Here, *operando* NMR technique can capture the highly reactive and transient species, and provide quantitative information about the evolution of the dead Li metal and SEI, allowing us to clearly “visualize” the cell failure process.

Effect of Electrolyte and Cycling Conditions

The electrochemistry performance of LMBs is greatly affected by electrolyte formulations, the choice of current collectors and the cycling condition. The formation of dead Li metal and SEI during the aforementioned conditions may vary. In this part, we evaluate the failure mechanisms in three different conditions: 1) adding FEC additives, 2) using 3D host current collectors (Cu foam) instead of Cu foil and 3) cycling the cell at higher stripping rates (0.5

mA cm⁻² for deposition, 1.0 mA cm⁻² for stripping), and we denote the three cells hereafter as AD-cell, 3D-cell, and HD-cell, respectively. These cells are compared to the baseline cell, which is operated with the baseline electrolyte, Cu foil and moderate stripping rate (0.5 mA cm⁻² for deposition, 0.5 mA cm⁻² for stripping). In the first cycle, the signals of the dead Li metal can be observed in HD-cell but not in AD-cell and 3D-cell (**Figure S6a-S8a**), and the corresponding quantitative results for the first cycle are summarized in **Table 2**. The absence of the dead Li metal in AD-cell and 3D cells can be ascribed to the excellent SEI derived from FEC¹⁸ and the enhanced electron-path provided by the 3D Cu foam⁶, respectively (**Figure S5**). **Figure 3a-3c** show their respective *operando* data for prolonged cycles. Despite the difference observed in the first cycle, all three cells exhibit the continuous accumulation of dead Li metal during cycling. However, their accumulation rates differ. The amount of dead Li metal in the AD-cell and 3D-cell increase slowly, while it increases sharply in the HD-cell. The totally amounts of dead Li metal at the end of the cycle for the three cells are different (dashed line in **Figure 3a-3c**). Based on the *operando* data, we can quantitatively calculate the C_{dead} and C_{SEI} for the three cells. We plot the C_{dead} v.s. C_{SEI} curves to compare the amounts of dead Li metal and SEI in real time (**Figure 3d**). Characteristically, all curves start from the zero point ($C_{\text{dead}} = 0$, $C_{\text{SEI}} = 0$) and approach to the line of $C_{\text{SEI}} + C_{\text{dead}} = 1$ (blue line), illustrating the competitive consumption between C_{dead} and C_{SEI} for the total active capacity. In addition, we divided the **Figure 3d** into two regions: SEI-dominated and dead Li metal-dominated regions, by the line of $C_{\text{dead}} - C_{\text{SEI}} = 0$ (dot black line). The previous results in **Figure 2** for the baseline cell is also plotted in **Figure 3d** as a reference. The baseline curve falls in the dead Li metal-dominated region

at the end (60.0%, 40.0%), indicating more capacities consumed by the formation of dead Li metal. In contrast, when the FEC additive and high surface area current collector are present, these two curves locate all within the SEI-dominated region during the entire cycling process, suggesting that the formation of SEI becomes the major culprit for the observed capacity decay in these two situations. With a higher stripping current density, however, the capacity consumption by the dead Li metal increases significantly to 77.8%, demonstrating that the relative amount of dead Li metal is much more severe when high stripping current density is used. Therefore, *operando* NMR clearly identifies different failure mechanisms of Li metal under various cycling conditions.

Scanning electron microscope (SEM) was further used to investigate the morphology of inactive lithium after at the end of cycling, and the results as shown in **Figure 3e-h**. A fiber-like morphology, full of pulverized dead Li metal (**Figure 3e**), is observed for the baseline cell. However, SEM image of AD cell contains piled-up small particles rather than fibrous dead Li metal, the morphology of which is strongly related to the nature of the SEI (**Figure 3c**).¹ In the 3D cell, the Cu foam after cycling is covered by a film and it is difficult to distinguish dead Li from SEI within that film (**Figure S9**). Based on our NMR results, it is believed the film contains mainly SEI species. In contrast, more substantial dead Li metal is observed in the HD cell, which is not surprising since dead Li metal causes 77.8% capacity loss based on our quantitative analysis of the *operando* NMR data.

Table 2| Quantified distribution of dead Li metal and SEI with *operando* NMR for the first cycle.

	Dead Li metal (%)	SEI (%)
Baseline	5.2%	4.2%
FEC-additives	/	13.8%
Cu foam	/	25.7%
High stripping current density	3.5%	6.3%

254 “/” : no NMR signal of dead lithium metal was observed

255

256 **Figure 3. The impact of FEC additives, Cu foam, and high stripping current density**
 257 **on the formation of dead Li metal and SEI.** *Operando* NMR data under different cycle
 258 conditions: **a** using FEC additive, **b** using 3D Cu foam, **c** applying high stripping current
 259 (1.0 mA cm^{-2}). **d** The normalized capacity loss due to SEI formation (C_{SEI}) versus that due

to the dead Li metal (C_{dead}) in baseline cell consisting of LiFePO₄||Cu cell (grey line), FEC-containing cell (blue line), 3D-Cu foam cell (orange line) and high stripping current density cell (purple line). All curves start from the zero point ($C_{\text{dead}} = 0$, $C_{\text{SEI}} = 0$) and approach to the line of $C_{\text{SEI}} + C_{\text{dead}} = 1$ (blue dot line). Points on this line corresponds to the relative value of C_{SEI} and C_{dead} as the batteries fails completely (capacity decay to 0). The SEI-dominated region and the dead Li metal-dominated region are separated by the line of $C_{\text{SEI}} = C_{\text{dead}}$. **e-f** SEM images of the inactive lithium on the anode substrate after complete cell failure.

A Performance-enhancing Strategy and Failure Mechanisms of Li Metal

We find that the two-stage failure mechanism is a universal phenomenon for various operating conditions, as illustrated in **Figure 3d**. The “**f**” shaped profiles are seen for all the cases. In the initial cycles (stage I), all curves locate in the SEI-dominated region and dominantly grow along the axis of C_{SEI} , indicating that the increasing C_{SEI} is the main cause of capacity loss during the initial cycles. The continuous formation of SEI can be attributed to the intrinsic instability of the organic electrolytes at low potential, leading to side reactions at the anode side¹⁹. These side reactions become more severe for cells containing highly reactive additives (AD-cell) and in cell with more exposed electronic conducting surface area (3D-cell). In stage II, these curves start to grow along the axis of C_{dead} , suggesting an increase of dead Li metal formation in the subsequent cycles. The result suggests that minimizing the SEI formation at the initial cycling and controlling the morphology of Li deposits is critical for delaying or suppressing the second “dead Li metal-formation”

Accordingly, we utilized an advanced electrolyte.^{20,21} The combination of high

concentration lithium salt and ether solvent can reduce the reactivity of the electrolyte solvent towards Li metal thus forming a thin and stable SEI layer, and the addition of lithium nitrate as an additive promotes the formation of spherical uniform Li deposits with optimized Li morphology (**Figure S13**).²² Consequently, the capacity retention of in-situ Cu||LiFePO₄ cell is dramatically increased from ~0% (Baseline) to ~50% after 25 cycles (**Figure S14**). Impressively, operando NMR of this system show negligible formation of dead lithium metal, even after 100 hours cycling (**Figure 4a**), only exhibiting the SEI-dominated failure mechanism. After cycling in the advanced electrolyte, the optical images of the residue Li on Cu substrate is black, similarly to the observation reported in other high concentration electrolyte systems.^{3,23} This black residue Li species may be related to a high ionic conductivity SEI (**Figure S15a**). In contrast, some dark grey residues is observed for samples cycled in baseline electrolyte, which is documented to be the dead Li metal covered by thick SEI (**Figure S15b**).²⁴

In summary, we created a NMR-based new technique that enables the comprehensive, quantitative and in-depth investigation on Li metal deposition/stripping in a anode-free battery under operando conditions. Such technique is highly capable of distinguishing and quantify the inactive lithium during the Li deposition/stripping processes, and allows us to identify the real culprit for the rapid capacity decay under various battery conditions. Based on interpretation of the results, we propose three failure mechanisms and present the corresponding simulated operando NMR results in **Figure 4**. In the first mechanism, the Li metal degradation is mainly due to the SEI formation as shown in **Figure 4a**. In this case, the dead lithium metal signal remains around zero, but the maximum of Li metal intensity

decays with cycling time, indicating that the active lithium metal is continuously consumed to form other lithium containing species such as Li containing SEI. This is the case we observed for AFB operating in high performance electrolyte and in cells with FEC additive and 3D current collectors. The other extreme failure mechanism is due to the formation of dead lithium metal, as illustrated in **Figure 4c**. Theoretically, the maximum of Li metal intensity always equals to 1. This is because under this failure mechanism, both active lithium and inactive lithium are metallic lithium, so the total ^7Li NMR signal of the lithium metal remains unchanged. However, in reality, the capacity loss comes from both dead lithium metal and SEI. The last mechanism involves the simultaneously formation of dead lithium and SEI, and the corresponding simulated ^7Li NMR signal of lithium metal signal is shown in **Figure 4b**. Different failure mechanisms could be disclosed with different NMR responses in the operando cells, thus offering a highly capable technique to identify which the failure mechanisms is responsible under a specific cycling condition or electrolyte composition. We believe that this operando technique will be useful in re-evaluate the strategies that have been used to relieve dead Li metal formation in LMBs. In addition, this technique can be extended into other lithium metal-based systems such as Li-oxygen, Li-sulfur, and solid-state Li batteries as well as the sodium counterparts. This noninvasive and versatile *operando* NMR technique can enhance our understanding of Li-metal anodes and contribute to the practical application of Li metal in the next-generation batteries.

Figure 4. Enhancing strategies and schematic of typical failure mechanisms **a** The Li metal intensity varied with cycle time in the *in-situ* Cu||LiFePO₄ cell by using advanced electrolyte. The simulated ⁷Li NMR intensity of lithium metal v.s. cycle time for different typical failure mechanism **b** SEI-failure mechanism. **c** Dead Li metal / SEI mixed failure mechanism. **d** Dead Li metal-mechanism. **e** The corresponding C_{dead} v.s. C_{SEI} curves for three different failure mechanisms.

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391 **Additional information**

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