‘Dead’ lithium or back from the ‘dead’?

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The formation and accumulation of ‘dead’ lithium is a major cause of performance decay in lithium metal batteries (LMBs). Writing in *Nature*, Liu et al. demonstrate how dead lithium can be revived based on its response to the electric field during battery operation.

Lithium metal anodes present an exciting opportunity for the development of next-generation batteries with high energy density owing to their large theoretical capacity (3860 mAh/g) and low negative potential (−3.04 V vs the standard hydrogen electrode).[1] Despite the theoretical promise, the practical application of LMBs is confronted with challenges pertaining to safety, degradation and life, predominantly due to the high reactivity of lithium.[2] Major mechanistic limitations include the growth of dendrites during charging, and the generation of solid electrolyte interphase (SEI) through continuous electrolyte consumption. The dissolution of such non-uniform deposition morphologies during discharge results in the formation of isolated metallic structures, commonly known as ‘dead’ lithium.

The accumulation of an electrochemically inactive lithium layer impedes electrolyte transport, poses safety hazards and leads to capacity loss, often necessitating an excess content of lithium in the anode.[3,4] Various techniques including optical microscopy, nuclear magnetic resonance, cryogenic transmission electron microscopy and titration gas chromatography have been used to probe the morphological, chemical, electrochemical and mechanical interactions underlying the formation of dead lithium.[5] Compared to the formation of lithium ions in the SEI, the isolation of inactive lithium has recently also been identified as the dominant degradation mechanism in LMBs.[6] While electrolyte engineering[7] and SEI modification[8] strategies have been proposed to mitigate dead lithium, it is fundamentally still believed that once a metallic structure loses electrical contact, it does not take part in further electrochemical reactions. Contrary to this belief, Liu et al.[9] present the following question: Can isolated lithium respond to the electrical fields in the battery or is it actually 'dead'?

In response to an applied current, the transport of charge carriers, namely the cationic and anionic species in the electrolyte, establishes an electric potential gradient between the electrodes. Despite the loss of electrical connection, Liu et al.[9] theorize that the exposure of isolated lithium to an external electric field would induce a separation of positive and negative charges across its ends. The dynamic polarization of the isolated lithium fragment and the variation in local electrolyte potential result in a potential difference for charge transfer reactions at the interface. For instance, when lithium ions move from the positive to negative electrode during the charging process, the isolated lithium end close to the positive electrode exhibits a negative overpotential that leads to lithium deposition. The positive overpotential at the isolated lithium-electrolyte interface on the other end causes lithium dissolution. Through electronic flow from one side of the isolated lithium to the other, charge conservation is ensured, while enabling the simultaneous occurrence of deposition and dissolution at its ends. This mechanism results in the spatial progression of isolated lithium toward the positive electrode during charge, and toward the negative electrode during discharge. Overall, the isolated lithium structure can be perceived as an electrochemical system in which ions and electrons complete the external and internal circuits, respectively! The proposed dead lithium interaction is of scientific and practical interest not only in the context of LMBs, but also for operational extremes such as fast charging.

Liu et al.[9] examine the electrochemical response of dead lithium using an optical cell with $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC) and lithium electrodes, and an isolated lithium island between them, as shown in Figure 1a. Upon charge and discharge of the NMC-lithium cell (Figure 1b), considerable morphological evolution of the isolated lithium island was observed, illustrative of the electrochemical processes that take place at its ends. During charging, lithium filaments were deposited along with SEI components on the side of the lithium island close to the cathode. The simultaneous dissolution of the isolated lithium end near the lithium electrode results in a net movement of the island toward the NMC electrode (Figure 1c). The morphological transition of the isolated lithium island is opposite during discharge, resulting in its net spatial progression toward the lithium electrode (Figure 1d). Using an electrochemical model, the reaction kinetics at the ends of the isolated island was observed to be much faster than that at the NMC and lithium electrode interfaces. In accordance with the experimental observations, the simulations indicate a transformation of the lithium island into a wedge shape, exhibiting a net movement toward the NMC electrode during charge (Figure 1e) and toward the lithium electrode during discharge (Figure 1f). Since the electric field gradient and ionic transport "scale" with the interelectrode distance[10], the net progression of isolated lithium may be diminished in a realistic cell configuration. Interestingly, as the morphology transforms into a wedge, a resulting increase in the deposition/dissolution kinetics at its ends can be observed. In this regard, it remains to be conjectured how the isolated metal morphology and electrolyte transport be synergistically modulated in order to achieve the desired spatial progression within a realistic length scale.

By designing a four-electrode set up in a coin cell configuration, the authors study the correlation between electrolyte potential difference and current density. The potential difference is measured across a 12-µm distance using two copper mesh electrodes with pre-deposited lithium. It is observed that the electrolyte potential difference remains constant during the charging process and increases from 11.9 to 64.4 mV with an increase in current density from 0.15 to 0.88 mA/cm^2. Consistent with the proposed mechanism, a higher electrolyte potential at the copper mesh electrode near the NMC results in a negative overpotential for the isolated lithium on this side. On the other hand, the overpotential is positive on the isolated lithium side near the lithium electrode. It is inferred that this overpotential is largely dependent on the length of the isolated lithium and exhibits negligible dependence on the width. Importantly, it is observed that the isolated lithium fragments that are oriented in the same direction as the electric field exhibit faster spatial progression than the other filaments.

By leveraging the observed migration of isolated lithium toward the anode during discharge, can it potentially be recovered? Using NMC-graphite cells with isolated lithium, the authors demonstrate the recovery mechanism through three distinct stages. Following the initial stage of spatial progression, the isolated lithium forms electrical contact with the graphite anode, leading to an increase in cell voltage. Subsequent reconnection of the isolated lithium is correlated with a further increase in cell voltage and results in additional capacity when compared to an NMC-graphite cell without isolated lithium. Furthermore, the recovery process is demonstrated in copper-lithium half cells with pre-formed isolated lithium. By employing a formation cycle that generates dead lithium via fresh lithium deposition on the copper substrate and subsequent stripping, the efficacy of the recovery mechanism and its dependence on the stripping current is examined. The reactivation of the pre-formed lithium is confirmed in the following cycle that exhibited a Coulombic efficiency greater than 100%.

Efficient recovery of dead lithium relies on the rate of its spatial progression that in turn depends on the reaction kinetics at the interface. By increasing the stripping current in the formation step from 2 to 5 mA/cm^2 that presents a larger overpotential for the dissolution/deposition reactions, an improvement in the recovery percentage of dead lithium from 17.6% to 31.7% is observed. However, a further increase in current density reduces the recovery amount due to the enhanced rate of corrosion. Based on this mechanistic correlation, the authors propose a short, fast lithium-stripping step that activates the recovery of isolated lithium after deposition. For NMC-lithium full cells, using a 2-min fast-discharging step that promotes migration of the previously generated dead lithium toward the anode, notable improvement in cell capacity and Coulombic efficiency with respect to a non-activated cell is achieved. Such an increase in cycle lifetime has also been realized under faster-charging conditions.

This study presents a stimulating insight into the electrochemical response of dead lithium, and its implication in lithium metal batteries. In addition to an electric field, it may be conjectured that the reaction kinetics of the isolated lithium can potentially be modulated through its morphology and orientation. These aspects are further connected to the interface chemistry and electrolyte interactions that govern the earlier growth of the electrodeposit. While very high stripping currents may adversely affect the recovery process, the desired progression of dead lithium may still be achieved under moderate currents by leveraging electrolyte transport and thermal field. This study by Liu et al.[9] opens a fundamental avenue toward interrogating the role of dead lithium under operational extremes in lithium metal batteries.

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Declaration of Interests

The authors declare no competing interests.

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Figure Title and Legend

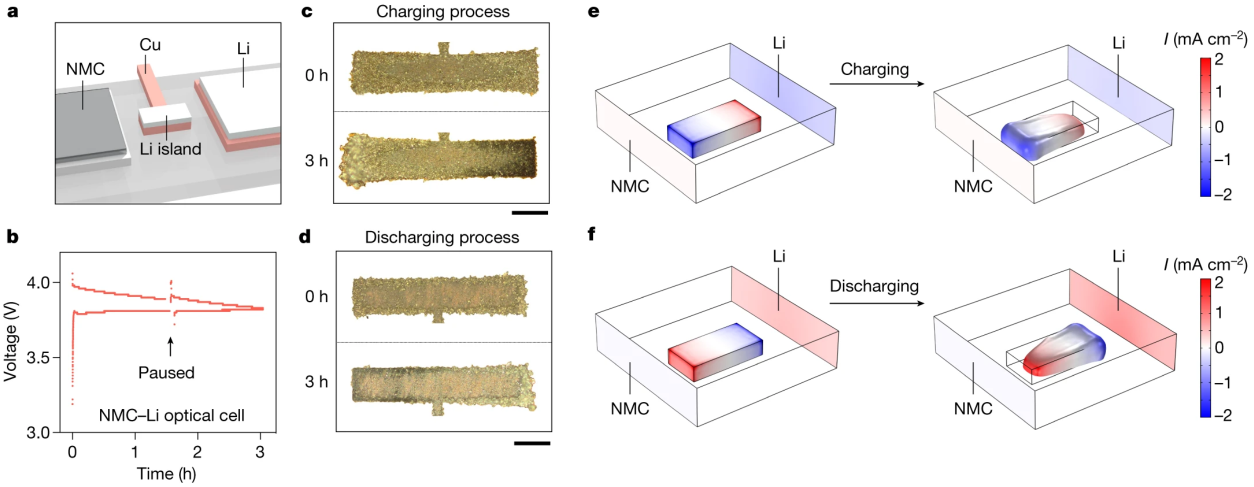

Figure 1. Morphological evolution of the isolated lithium island.

(a) Optical cell configuration with isolated lithium between the NMC and lithium electrodes. (b) Voltage profile of the NMC-lithium cells. Optical images of the isolated lithium island during (c) charge and (d) discharge. Current density distribution on the isolated lithium surface during (e) charge and (f) discharge. Reproduced with permission from Liu et al.[9] Copyright 2021 Springer Nature.