# Peer Review File

**Manuscript Title:** Recovery of Isolated Lithium Through Discharged State Calendar Aging

## Reviewer Comments & Author Rebuttals

### Reviewer Reports on the Initial Version:

Referees' comments:

Referee #1 (Remarks to the Author):

The isolated Li at discharge state was found to be recovered after rest. CE test, optical microscopy and TGC were conducted to reveal the Li recovery mechanism, describing an interesting story. However, the included evidence presently cannot strongly support the findings in this manuscript. Several discussion and conclusions in key parts were drawn from citations rather than solid experimental results. Moreover, since various Li recovery mechanism has already been studied in several works, the practical advances of this work needs to be provided. Additionally, the feasibility of such a Li recovery behavior in practical cells still remains unknown, especially during long cycling. Presently, I have major reservations about this paper, and some concerns below should be well addressed before reconsidering the possible publication of this manuscript.
1.Li recovery has been successfully achieved in previous reports with controllable methodology (e.g., Nano Lett. 2022, 22, 9268-9274, Ref. 12 and 18). The advances and advantages of the discharged state calendar aging should be emphasized.
2.Why 12-hour rest is selected? What’s the influence of different duration of rest on the Li recovery and battery performances? The chemical corrosion during aging should not be ignored, which may have influence on the Li recovery.
3.In figure 2g, why newly deposited Li can also be found on the top of the isolated Li that was marked by the author?
4.In the test of operando optical microscopy, the Li plating and stripping behaviors underwent parallel to the electrode, where actually limited pressure was applied to such processes.
5.In addition to visual optical microscopy and citations, more convincing evidence on the Li recovery mechanism should be supplemented (e.g., the chemical properties of isolated Li before and after rest, the components of dissolved SEI in the electrolyte)
6.The dissolution of r-SEI will expose the isolated Li to the continuous corrosion of electrolyte (Adv. Energy Mater. 2023, 2204305; ;Adv. Energy Mater. 2022, 12, 2202012), which seemingly reduces the efficiency of Li recovery. Why the authors deny such influence. Additionally, the dissolving region of r-SEI can be anywhere. Why it must contribute to the reconnection of isolated Li?
7.The solubility of SEI in Li-based battery systems is reported to be limited (Nature Energy 2022, 7, 718-725). When the electrolyte is saturated by the dissolved SEI, will the Li recovery be terminated or failed?
8.Note that few cycles were presented in Li | Cu and LFP | Cu cells. Can this recovery of isolated Li be extended to prolonged cycling?
9.What’s the relation between the electrolyte formulations (including the related solvation ability, Li growth pattern, and SEI chemistry) and Li recovery behaviors? Why LHCE was selected?

Referee #2 (Remarks to the Author):

This article describes an interesting study of the impact of open-circuit rest periods on Coulombic efficiency during complete plating/stripping of Li metal anodes in anode-free configurations using liquid electrolytes. The authors show a Coulombic efficiency >100%, which is attributed to recover of isolated/dead lithium. Further insights are provided through operando optical microscopy.

Overall, this is a valuable study, which will spark interest and discussion among the Li metal anode community. The reviewer is generally supportive of publication, however, several important points should be addressed first:

1) The tone of the discussion is very general. However, the generality of this approach is not discussed in sufficient detail. For example, only on electrolyte was used (LHCE) and only a single set of electrochemical conditions was studied for the coin cells (current density, depth of charge, etc.). How does the recovery of isolated Li depend on these important variables? Is CE >100% always observed, or only under these “optimal” conditions from the paper? In particular, it would be good to show how this performance occurs in various electrolytes (e.g. carbonate, glyme based), which would indicate how general the proposed mechanisms are.

2) In the authors previous work on recovering isolated Li, it was shown that a high current discharge was needed to re-attach the isolated Li to the substrate. Following on point 1 above, was this observed in the case of resting during the discharged state? In other words, was a high current density during the following discharge necessary for the recovery? IF not, why not? Does this affect the conclusions of the previous paper that a high discharge current is needed for the Li migration back to the current collector? More of a direct discussion connecting the conclusions of these two important papers is needed.

3) In general, the Coulombic efficiencies reported in the cycles without resting during discharge have relatively low Coulombic efficiencies (96.2% to 98.2%). First, these seem rather low for the state-of-the-art liquid electrolytes, which can routinely achieve >99% (and even reports up to 99.5%). How does the recovery of the isolated Li depend on the CE of the previous cycles? Is such recovery possible even when very small losses (which are mostly SEI) are present, such as in ~99.5% CE electrolytes? If not, then it seems that this method is mostly relevant for lower CE electrolytes and processes, which is something that should be clearly stated.

4) The authors state that “The uniformity of cycle 11 stripping voltage profile also suggests that electrolyte oxidation is not contributing to the capacity gain (figure 1d insert).”. This was not clear to the reviewer: why does the voltage profile indicate a lack of contribution from electrolyte oxidation? Please explain this more clearly, and include citation(s) if appropriate.

5) The authors state that “However, the documentation of Li isolation and subsequent recovery has eluded past optical studies,5,22–25 likely due to the lack of internal cell pressure in prior optical setups.”. However, in the discussion of the mechanism, the proposed reason for Li recovery relates to the dissolution of the SEI, which should not be pressure dependent. Therefore, the role of pressure needs to be clarified.

6) For the comparison of the optical and standard electrode in figure 2, was the total current adjusted to the reduced electrode surface area of the grid electrode, to keep the local current density the same?

7) In figure 2g, it was not clear how the authors determined that the Li plating outlined in red was really reconnected to the previous isolated Li. How can this be proved? Since the optical microscope is showing a 2-D projection of 3-D geometric data, and the clarity of the zoomed-in images is a bit grainy, it is really hard for the reviewer to conclusively determine that this specific location was a reconnection of the previous isolated Li. It is clear that the previous isolated Li is stripped in panel h, but the authors may want to soften the language of direct visualization of the reconnection in panel g.

8) The reviewer has some doubts about the validity of analyzing of areal ratios of isolated vs. recovered Li in figure 3. First off, it is not clear that the contrast in a specific pixel location in this 2-d projected image (as mentioned above) remains associated with the same specific atoms of Li during cycling. For example, it is known that the position of isolated/dead Li can get "pushed out of the way" during subsequent plating cycles, as seen in cross sectional optical imaging (e.g. in Ref. 25). Therefore, the isolated Li from a previous half-cycle could get displaced by newly plated Li in the following cycle, so the presence or absence of contrast in a specific pixel location would be insufficient evidence that a specific region of plated Li is now recovered, since it can also be displaced. Therefore, the reviewer would caution against quantitatively analyzing the contrast changes of a specific pixel location, which is fixed in space, as a proxy for quantifying recovered Li, since the assumption is that the previously plated Li would have to be rigid, and could not be moved/affected by the subsequent plating and stripping.

9) Please include the video used to generate the data in Figure 3 as a supplemental video file, which will help the reader to visualize the data in Figure 3 more clearly. It would also be helpful to include the data from the rest period in the video, in addition to during plating and stripping. Same goes for the video data for Figure 4, where it would be very helpful to be able to visualize the dissolution of the r-SEI through video data.

10) The Coulombic efficiencies in the full cell are also quite low (~95%), which is below what is needed for a practical battery. This relates to question 3 above, on how generalizable this method is under different electrolytes and cell configurations, especially those with higher CE?

11) The authors state that "This increase in overpotential reflecting an increase in total internal resistance during cycling has been correlated with r-SEI build up.13,30–32". However, it has been shown that the increase in cell resistance after extensive build-up of dead Li results in increased mass transport losses due to reduced electrolyte transport through the compact dead Li layer (Ref. 11). Therefore, this sentence should be updated to include the contribution from mass transport through dead Li, in addition to the buildup of r-SEI, as the reason for increased total resistance during cycling.

12) The proposed mechanism of r-SEI dissolution is interesting, and critical to support the hypotheses of the paper. However, the discussion of this mechanism is rather short. It was not clear

why r-SEI dissolution is occurring. Is this specific to the electrolyte system used? Does it occur across other electrolyte systems (see comment 1 above)? And if so, is it expected, based on the solubility of the r-SEI components in the electrolyte? More of a chemical justification for this r-SEI dissolution is needed to strengthen this discussion.

Referee #3 (Remarks to the Author):

This work by Cui and coworkers presents an evaluation of calendar aging of Li metal anodes in the discharged state. Calendar aging of Li metal is an important topic as Li metal anodes are integral to high energy density, next-generation batteries, and the highly reactive nature of Li metal makes it susceptible to side reactions, aging, etc. The authors make the important point that calendar aging is most often evaluated in the charged state whereas no publications to my knowledge evaluate calendar aging of Li in the discharged state. The manuscript in general is clear and logical.

These authors demonstrate that capacity can be recovered due to isolation and recovery of Li metal and show that the degree of aging can be mitigated through strategic rest protocols. This same conclusion has been demonstrated by Harrison and coworkers albeit for the aging Li metal in the charged state vs discharged state (https://doi.org/10.1021/acsaem.1c00874, https://doi.org/10.1021/acs.jpcc.2c05385). Though one of these papers is cited regarding calendar aging generally, the same mechanism for Li stranding and reconnection is proposed in these works as well as similar conclusions regarding whether rest is applied every cycle or after cycling. The authors should address this.

What these authors add is a clever approach to validating the proposed mechanism that both they and Harrison and coworkers presented through titration gas chromatography and through in-operando optical measurements.

Further, the results presented in this work appear to contradict another publication from Cui and coworkers (https://doi.org/10.1038/s41560-021-00787-9). I request that the authors discuss this prior work within this manuscript.

The authors appear to be thorough, showing error bars with one graph, but not all. I ask that the authors include error bars at least to the SI to demonstrate the repeatability of their results (e.g., error bars not shown in cycling data for Fig. 1d, Fig. 2b, Fig 3g and h, Fig. 4a, and such figures in the SI). Furthermore, I ask that the authors include the number of cells used to calculate error (e.g., were these tests run in duplicate, triplicate, sets of 5, etc.). This will aid in showing that the work in thorough and reproducible.

## Author Rebuttals to Initial Comments:

### Response to Reviewers for "Recovery of Isolated Lithium Through Discharged State Calendar Aging"

We are very grateful to the reviewers for providing valuable feedback that improves our paper. The comments and questions raised by the reviewers have helped us clarify our arguments and demonstrate the reproducibility of our work. We respond to each question raised by the reviewers in blue, and highlight the changes made to our manuscript and SI in grey for removed sections and yellow for added sections.

Referees' comments:

Referee #1 (Remarks to the Author):

The isolated Li at discharge state was found to be recovered after rest. CE test, optical microscopy and TGC were conducted to reveal the Li recovery mechanism, describing an interesting story. However, the included evidence presently cannot strongly support the findings in this manuscript. Several discussion and conclusions in key parts were drawn from citations rather than solid experimental results. Moreover, since various Li recovery mechanism has already been studied in several works, the practical advances of this work needs to be provided. Additionally, the feasibility of such a Li recovery behavior in practical cells still remains unknown, especially during long cycling. Presently, I have major reservations about this paper, and some concerns below should be well addressed before reconsidering the possible publication of this manuscript.

*We thank the reviewer for taking time to review our manuscript and providing very useful feedback aimed at strengthening the novelty, generality, and emphasizing the practical application of this work. To address the concern over solid experimental evidence of isolated Li recovery and its mechanism, we conducted many cycling experiments to demonstrate recovery in several electrolytes spanning different classes of salts and solvent, and at various plating capacities, strip current densities and rest time. Furthermore, new EQCM, XPS and NMR data have been appended to clarify the physical and chemical evolution of the r-SEI and the electrolyte during rest, thereby revealing the effect of r-SEI dissolution on Li recovery during discharge state rest. We have also added a detailed section to highlight the advances of this work in both this response and the main manuscript. Additionally, we have added new data demonstrating recovery in practical pouch cells and recovery during long-duration cycling. Detailed point to point responses to each question are found below.

1.Li recovery has been successfully achieved in previous reports with controllable methodology (e.g., Nano Lett. 2022, 22, 9268-9274, Ref. 12 and 18). The advances and advantages of the discharged state calendar aging should be emphasized.

*This very insightful comment by the reviewer. One major advantage of discharged calendar aging induced recovery is its low cost of implementation in current LMB form factors since it does not require modifications to the battery supply chain or manufacturing process. While previous works have demonstrated capacity recovery, most require electrolyte additives, coatings, or host materials[1,2], which adds to materials and manufacturing costs.

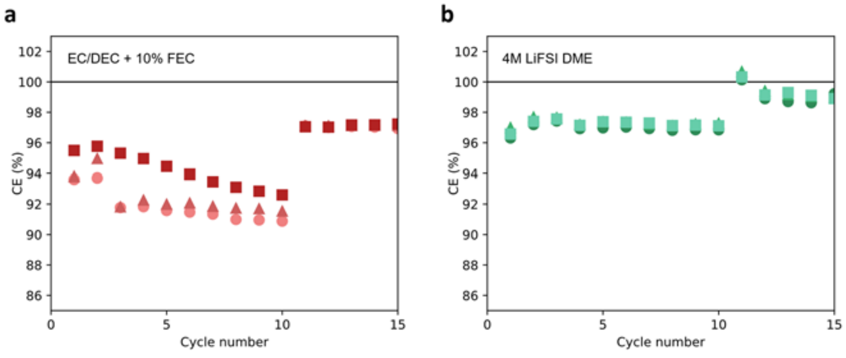
Another advantage of discharged rest is its ability to enable capacity recovery at a wide range of cycling conditions. The data presented in supplementary fig. 2 – 5 reveal that isolated Li recovery is possible cycling in various electrolytes, and at various capacities, strip current densities and rest times.

In reference to the reviewer's comment about the work from Liu et al[3], we would like to point out a few key advantages and differences of our work in comparison to that Nature paper. First, our protocol recovers capacity after discharged rest during the subsequent charging cycle rather than during the high current density discharge step from the prior work done by Liu et al[3]. Because the capacity recovery occurs at different stages of cycling, these recovery mechanisms can operate independently of each other. This claim is substantiated by supplementary fig. 4, which reveals that greater than 100% CE can be achieved after discharged rest, even with discharge current density as low as 0.25mA cm$^{-2}$. To emphasize the advantages of our discharged rest induced recovery, we have added the following sections to the manuscript:

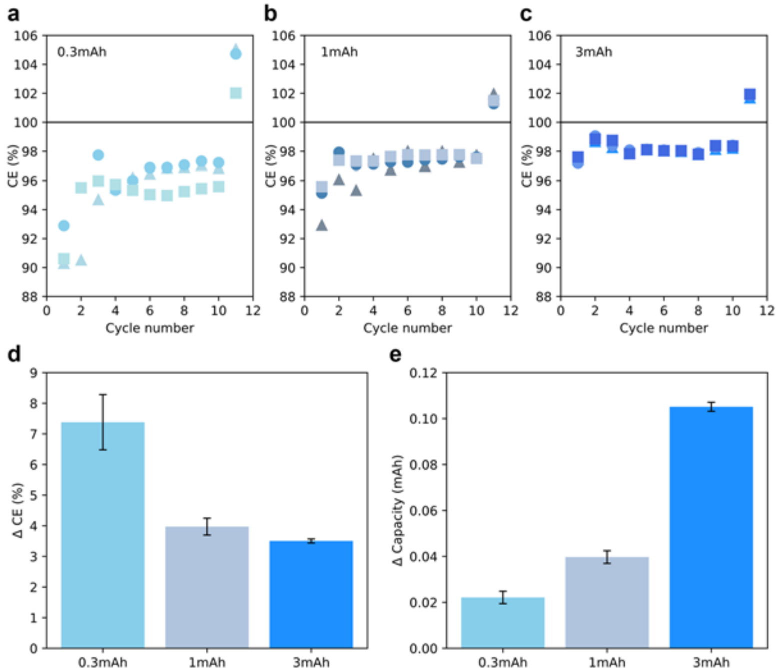
**Revised text on page 4, line 122:** "These experiments help demonstrate the advantages of discharged rest through its high recovery efficacy under a wide range of cycling conditions and its low cost of integration with current LMB technologies. Since the discharged rest cycling protocol does not require additional coatings, electrolyte additives, host materials or modifications to the battery manufacturing process, the significant cycle performance gain with minimal cost helps to lower the barrier of implementation for commercial applications.

**Revised text on page 3, line 109:** "Further experiments cycling with the hybrid protocol using various electrolytes, plating capacities, stripping current densities, and rest times (supplementary fig. 2- supplementary fig. 5) all result in a CE increase for the 11th cycle, demonstrating that post discharged rest capacity recovery is a generalizable phenomenon. An important result of note is the greater than 100% CE observed at a discharge current density of 0.25mA cm$^{-2}$ after discharged resting (supplementary fig. 4a). The significant recovery demonstrated with this low discharge current density strongly suggests that the discharged rest induced capacity recovery mechanism does not overlap with the Li reconnection mechanism found by Liu et al.[14] which utilizes high discharge current density for capacity recovery. These results suggest that there are two different recovery mechanisms."

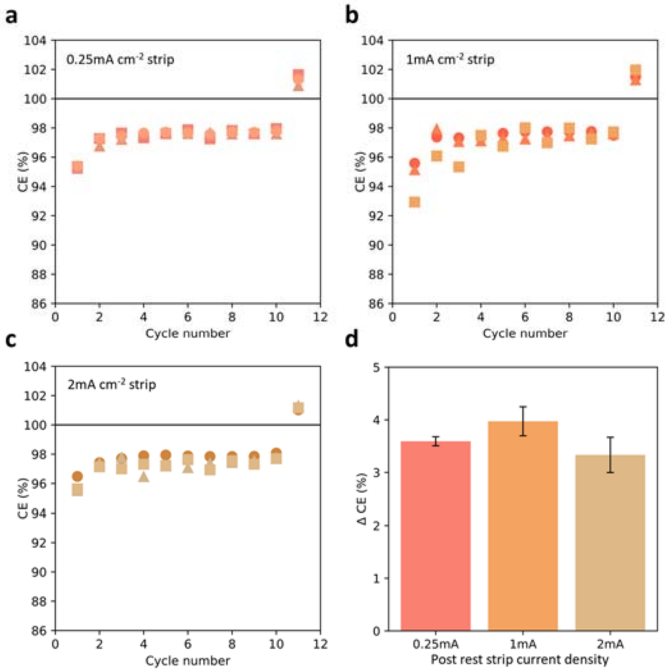
**Supplementary Fig. 2:** CE of Li||Cu half-cells running on the hybrid cycling protocol with 1M $LiPF_6$ EC/DEC + 10% FEC and 4M LiFSI DME electrolytes.



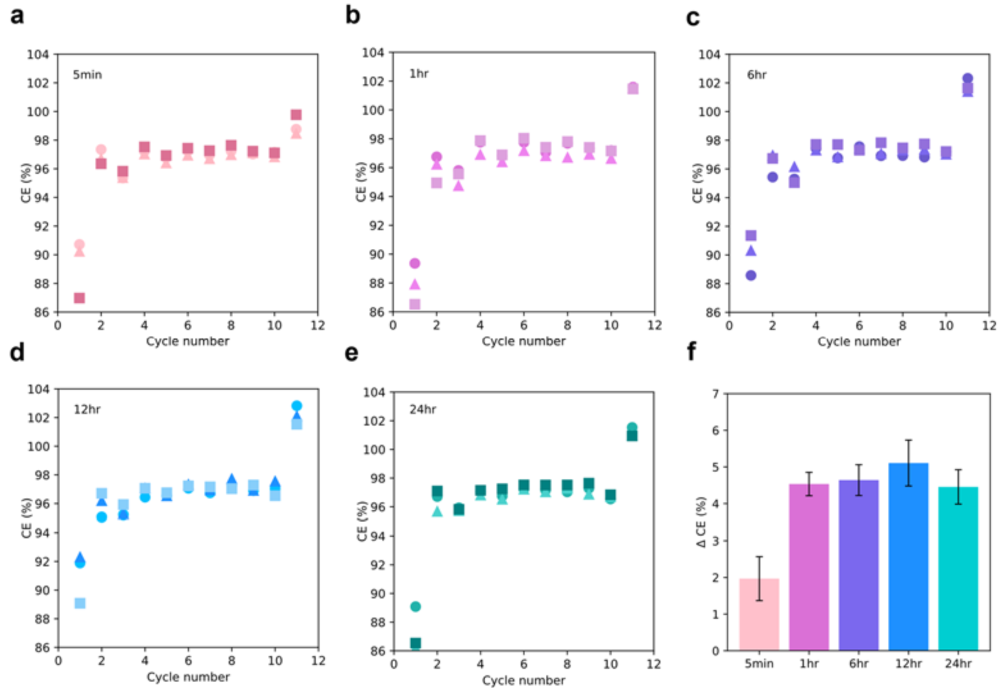
**Supplementary Fig. 3:** CE of Li||Cu half-cells with LHCE running on the hybrid cycling protocol with deposition capacities of 0.3mAh, 1mAh and 3mAh.



**Supplementary Fig. 4:** CE of Li||Cu half-cells with LHCE running on the hybrid cycling protocol with various 11th cycle strip current densities of 0.25mA $cm^{-2}$, 1mA $cm^{-2}$ and 2mA $cm^{-2}$.



**Supplementary Fig. 5:** CE of Li||Cu half-cells with LHCE running on the hybrid cycling with various 11th cycle rest times of 5 minutes, 1 hour, 6 hours, 12 hours, and 24 hours.

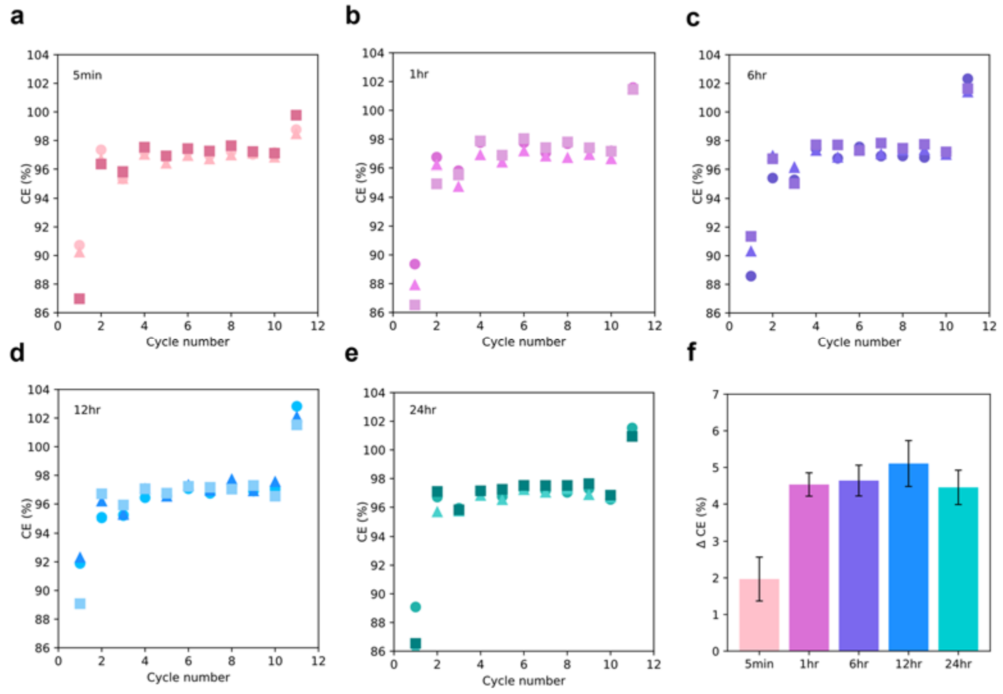


2.Why 12-hour rest is selected? What's the influence of different duration of rest on the Li recovery and battery performances? The chemical corrosion during aging should not be ignored, which may have influence on the Li recovery.

*We thank the reviewer for this important comment to clarify our motivation for selecting 12-hour as the baseline rest period. This was done because 12-hour rest shows the highest ΔCE gain. The optimal discharge rest period was determined by comparing the ΔCE (difference in CE between 11th cycle and 10th cycle) after 10 continuous cycles and various periods of discharged rest (5 minutes, 1 hour, 6 hours, 12 hours, and 24 hours). **The 12-hour discharged rest was selected as the baseline rest period because it produced the highest ΔCE increase as shown in supplementary fig. 5. Additionally, the various discharge resting time data reveals that resting as short as 5 minutes can produce ΔCE jump of approx. 2% after the 10 continuous cycles. The ΔCE increases with increasing rest periods and peaks at 12-hours of rest. At 24-hours of rest, the ΔCE begins to drop slightly, but remains positive. This decrease in capacity recovery is likely driven by the chemical corrosion of active lithium after r-SEI dissolution slows down.** To clarify the impact of corrosion on recovery performance, we have appended the following section to the main text:

**Revised text on page 11, line 318:** “While r-SEI dissolution during discharged calendar aging can help promote the reconnection of isolated Li on the subsequent plating cycle, the concurrent corrosion during rest both reduces the quantity of isolated Li available for recovery as well as thickens the native SEI on isolated Li. These factors can reduce the efficacy of Li reconnection[15,19,20]. Although our tests reveal that corrosion slightly reduces the efficacy of capacity recovery after 24 hours of rest, all cells rested in the discharged state, regardless of rest period demonstrate an increase in CE compared to the continuous cycles (supplementary fig. 5). The minimal decrease in recovery efficacy even after resting for 24 hours indicates that isolated Li recovery, not isolated Li corrosion, is the dominant factor affecting cycle performance after resting in a discharged state. This aligns with the findings from prior corrosion studies which indicate that capacity loss over 24 hour charged state rest makes up less than 20% of total Li capacity. In the case of discharged resting, this implies over 80% of isolated Li should remain recoverable after 24 hours of rest.

**Supplementary Fig. 5:** CE of Li||Cu half-cells with LHCE running on the hybrid cycling with various 11th cycle rest times of 5 minutes, 1 hour, 6 hours, 12 hours and 24 hours.



3.In figure 2g, why newly deposited Li can also be found on the top of the isolated Li that was marked by the author?

Figure 2g depicts the Li and electrode at the end of the second charge cycle. The isolated Li can electronically reconnect with newly plated Li anytime between the start and end of the second charge cycle and become reactivated. After the isolated Li re-establishes electrical contact, new Li can deposit on top of the previously isolated Li during the remainder of the charging step. This set of images and the associated supplementary video 1 help to emphasize that the reconnection of isolated Li is an ongoing phenomenon in LMBs, even during continuous cycling. The purpose of the discharge rest is to increase the quantity of isolated Li which can be recovered through the dissolution of the r-SEI physical barrier preventing Li to Li reconnection.

4.In the test of operando optical microscopy, the Li plating and stripping behaviors underwent parallel to the electrode, where actually limited pressure was applied to such processes.

*We thank the reviewer for this astute comment. While it is true that the plating and stripping directions in our optical setup may differ from standard cells, we believe that the mechanism for isolated Li reconnection observed in the optical cell remains similar to the reconnection that occurs in a standard Li||Cu half-cell and a full anode free cell. In the optical cell, each individual 30µm X 30µm mesh window has a limited volume in which Li can plate. The Li will preferentially plate laterally in these Cu mesh windows as the reviewer has noted. At sufficient capacity, the plated Li will fill up the volume and exert pressure on the surroundings whether it be the sides of the Cu mesh, other active Li, or isolated Li. In the case where actively plating Li applies sufficient pressure on isolated Li, electrical reconnection can be reestablished, reactivating the previously isolated Li. The addition of discharged rest enables dissolution of the r-SEI, decreasing electrically insulating materials in between newly plated Li and isolated Li, increasing the probability of reconnection. The optical cell's inability to perfectly replicate the plating environment and pressure of a standard coin cell may be a shortcoming of this setup. However, we believe this operando optical setup is sufficient for providing good insights into the mechanism of isolated Li recovery in a standard coin cell for two reasons: 1. We report similar CE performance and voltage profiles when comparing the optical cell to the standard coin cell during continuous cycling (figure 2b) 2. We report CE increase after discharged rest of the optical cell which is not seen in the continuously cycled cell (figure 3h.).

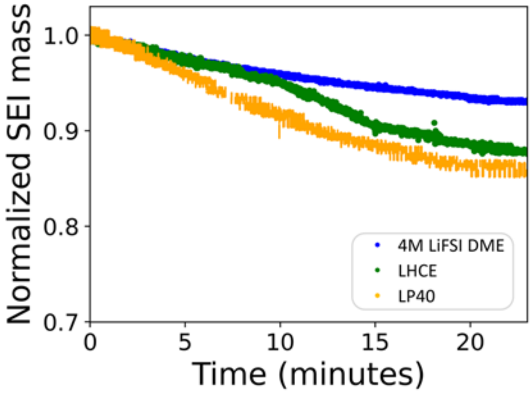
5.In addition to visual optical microscopy and citations, more convincing evidence on the Li recovery mechanism should be supplemented (e.g., the chemical properties of isolated Li before and after rest, the components of dissolved SEI in the electrolyte)

*This is a great point, and we thank the reviewer for bringing this up. To further clarify the Li recovery mechanism, we have carried out new experiments to demonstrate that SEI undergoes significant dissolution during resting for multiple electrolyte chemistries. This is based on experimental results using electrochemical quartz crystal microbalance (EQCM) to measure SEI mass changes during formation and resting at open circuit. Overall, our EQCM data show that significant SEI mass loss is observed for multiple classes of electrolytes tested (supplemental fig. 17). We confirmed our EQCM results with XPS analysis of the r-SEI (supplemental fig. 19), showing that the r-SEI becomes more inorganic after resting, suggesting that organic SEI components are more soluble. Furthermore, we used NMR spectroscopy to analyze electrolytes aged with Li metal and detected additional organic moieties in the electrolyte after aging, confirming that there are organic components in the SEI that dissolve into the electrolyte (supplemental fig. 20). Based on the reviewer's comment, we have added the following to the main text to elaborate upon our mechanism of dead Li recovery:

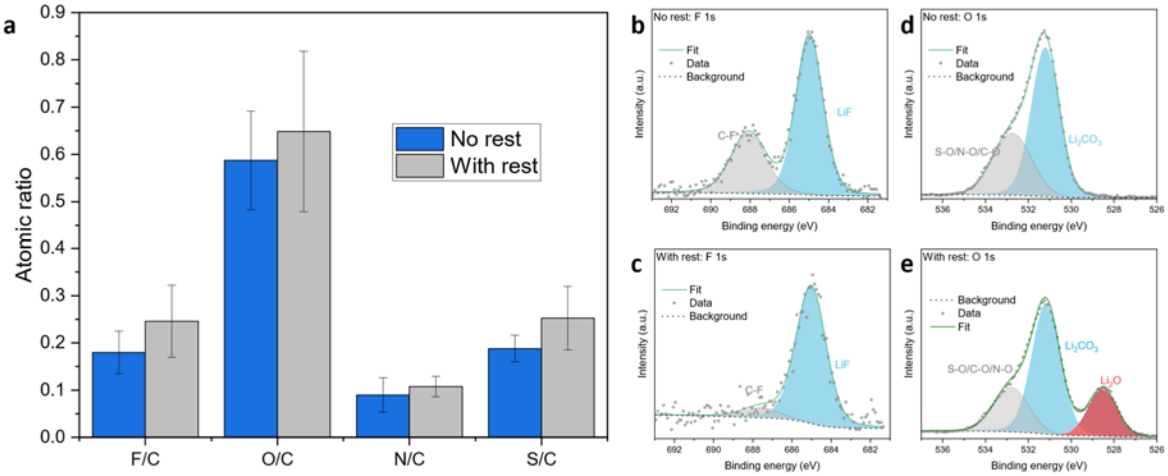
**Revised text on page 10, line 299:** "Additional experiments conducted for this work confirm our optical microscopy results, showing that the SEI undergoes significant dissolution during resting at open circuit voltage. Using electrochemical quartz crystal microbalance (EQCM), we show that significant mass of the SEI is lost during resting at open circuit voltage for multiple electrolyte chemistries (supplementary fig. 17)."

**Revised text on page 10, line 304:** "XPS characterization shows that r-SEI becomes more inorganic after resting at open circuit voltage for all electrolytes tested, suggesting that organic components in the SEI are more soluble than their inorganic counterparts (supplementary fig. 19). To confirm our XPS compositional analysis, we used NMR to analyze electrolytes aged with Li metal and detected additional organic moieties in the electrolyte after aging, confirming that there are organic components in the SEI that dissolve into the electrolyte (supplementary fig. 20)."

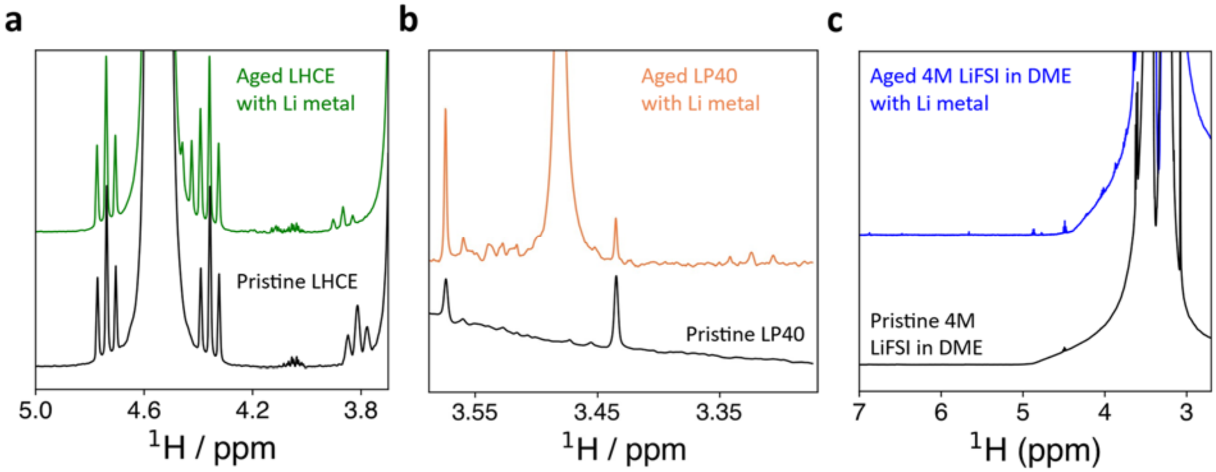
**Supplementary Fig. 17:** EQCM data demonstrating preformed SEI mass loss of various electrolytes during resting at open circuit voltage.



**Supplementary Fig. 19: a.** XPS atomic ratios of the LHCE derived r-SEI formed on Cu current collector after discharge in a Li||Cu cell, examined with and without rest. High resolution F1s spectra of r-SEI b. without and c. with discharged state resting. High resolution O 1s spectra of r-SEI d. without and e. with discharged state resting.



**Supplementary Fig. 20:** NMR analysis of **(a)** LHCE, **(b)** LP40, and **(c)** 4M LiFSI DME in pristine electrolyte and aged electrolyte in Li metal.



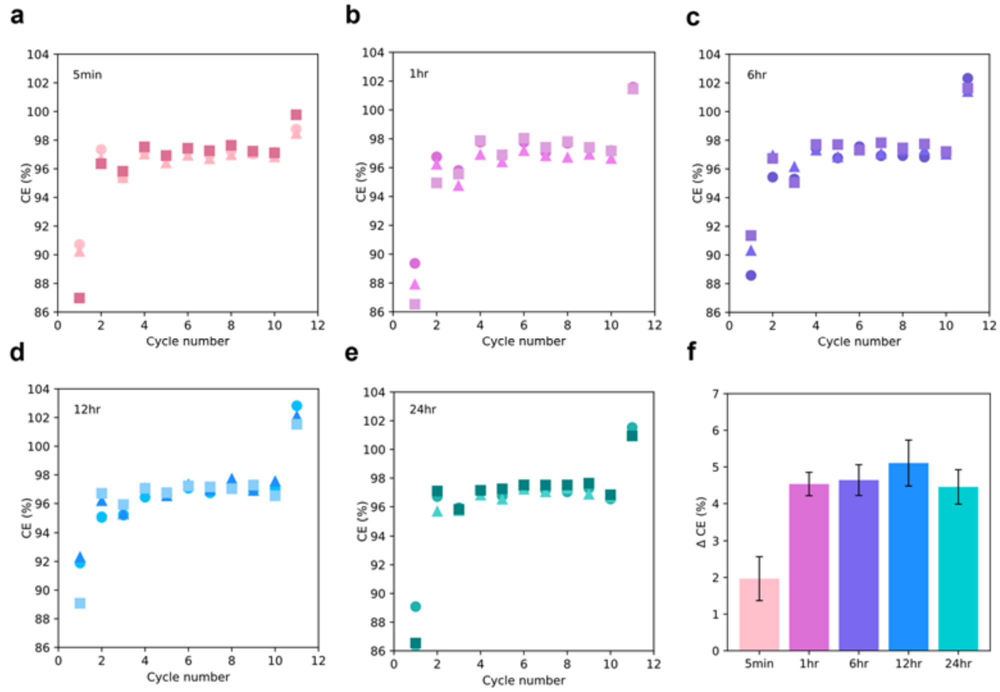
6.The dissolution of r-SEI will expose the isolated Li to the continuous corrosion of electrolyte (Adv. Energy Mater. 2023, 2204305; ;Adv. Energy Mater. 2022, 12, 2202012), which seemingly reduces the efficiency of Li recovery. Why the authors deny such influence. Additionally, the dissolving region of r-SEI can be anywhere. Why it must contribute to the reconnection of isolated Li?

*We thank the reviewer for bringing up this crucial point that was not well addressed in the original manuscript. We want to clarify that we do not deny the effect of corrosion reducing the efficacy of Li recovery. The dissolution of r-SEI and corrosion of isolated Li will occur concurrently during rest in the discharged state. In the process of corrosion, the capacity available for isolated Li available for recovery will decrease due to the reaction of Li metal and electrolyte to form additional native SEI on the Li. However, past corrosion studies have shown the capacity lost to calendar aging does not exceed 20% of the total capacity within the first 24 hours[4–6]. Additionally, the rate of metallic Li loss to corrosion also decreases with increasing rest time for most electrolyte systems. Because the majority of isolated Li remains metallic after discharged resting, it is still available for recovery after discharged state rest. This is supported by supplementary fig. 5f which shows that although the capacity recovered after resting 24 hours is lower than that after resting 12 hours, the 11th cycle CE for 24 hours of rest remains above 100% (supplementary fig. 5e), strongly suggesting the negative impact of corrosion does not offset the positive effects of r-SEI dissolution. This is addressed in the main text:

**Revised text on page 11, line 318:** "While r-SEI dissolution during discharged calendar aging can help promote the reconnection of isolated Li on the subsequent plating cycle, the concurrent corrosion during rest both reduces the quantity of isolated Li available for recovery as well as thickens the native SEI on isolated Li. These factors can reduce the efficacy of Li reconnection[15,19,20]. Although our tests reveal that corrosion slightly reduces the efficacy of capacity recovery after 24 hours of rest, all cells rested in the discharged state, regardless of rest period demonstrate an increase in CE compared to the continuous cycles (supplementary fig. 5). The minimal decrease in recovery efficacy even after resting for 24 hours indicates that isolated Li recovery, not isolated Li corrosion, is the dominant factor affecting cycle performance after resting in a discharged state. This aligns with the findings from prior corrosion studies which indicate that capacity loss over 24 hour charged state rest makes up less than 20% of total Li capacity. In the case of discharged resting, this implies over 80% of isolated Li should remain recoverable after 24 hours of rest.

To address the reviewer's second question, it is correct that the dissolution of r-SEI can occur at any location where r-SEI is in contact with the electrolyte. From the optical cell video, we observe the r-SEI decrease in contrast over time in both areas that are free of and populated by isolated Li. In areas free of isolated Li, r-SEI dissolution does not promote reconnection of isolated Li. However, in areas populated by Isolated Li, the dissolution of r-SEI decreases the physical barriers between isolated Li and the subsequent plating of new Li. With less electronically and ionically insulating r-SEI materials in between active plating Li and isolated Li, there is an increased likelihood of reconnection and capacity recovery.

**Supplementary Fig. 5:** CE of Li||Cu half-cells with LHCE running on the hybrid cycling with various 11th cycle rest times of 5 minutes, 1 hour, 6 hours, 12 hours, and 24 hours.



7.The solubility of SEI in Li-based battery systems is reported to be limited (Nature Energy 2022, 7, 718-725). When the electrolyte is saturated by the dissolved SEI, will the Li recovery be terminated or failed?

* We thank the reviewer for pointing out this missing aspect of this work. Based on the long term 200 cycle data comparing CE of discharge rested cells to continuously cycled cells (supplementary fig. 21), the recovery of Li using discharge resting does diminish significantly by the 100th cycle, most likely due to the saturation of the electrolyte with dissolved r-SEI species. However, by maintaining a CE advantage for 100 cycles, the discharged rest capacity recovery also proves to not be a short-lived phenomenon. The CE advantage maintained for 100 cycles significantly improves the capacity retention of the cell as seen in figure 4i. The advantages of this capacity retention are further discussed in the response to question 8. The following section has been appended to the manuscript to address electrolyte saturation:

**Revised text on page 11, line 332:** “The solubility of r-SEI in the electrolyte has been reported to be limited[40,41]. As a result, prolonged cycling can eventually saturate the electrolyte with soluble r-SEI species, decreasing the efficacy of the discharged rest capacity recovery. The effects of prolonged cycling are tested by comparing the CE (supplementary fig. 21) and cumulative capacity loss (figure 4i) of Li|| Cu half-cells cycled with and without discharged rest over 200 cycles at 1mA $cm^{-2}$ to a capacity of 1mAh. In the first 100 cycles, the continuously cycled cells lose 44% more capacity than the discharge rested cells with an average difference of

0.50mAh. Between cycle 101 and 200, the difference in capacity loss between the two conditions increases by only 0.05mAh to 0.55mAh. The saturation of the electrolyte with soluble r-SEI species during later cycles is likely a contributing factor to the diminishing recovery efficacy. Nevertheless, the substantial capacity recovered by discharged rest in the first 100 cycles has a significant impact on overall capacity retention even during prolonged cycling."

**Furthermore, the rate of electrolyte saturation with soluble species is highly dependent on the electrolyte characteristics and therefore is a tunable property. One of these tunable properties is salt concentration. Electrolytes with higher salt concentrations likely require longer periods for r-SEI dissolution and will reach their saturation limit in less cycles compared to electrolytes with lower salt concentrations. This notion is supported by comparing the difference in capacity recovery between 4M LiFSI DME (supplementary fig. 2b) and LHCE (figure 1d), with the former having a ΔCE increase of approx. 3% and the latter with a ΔCE increase of approx. 4.5% after discharged rest. The higher salt concentration in 4M LiFSI DME electrolyte can hinder the dissolution of species in the r-SEI, subsequently decreasing the amount of isolated Li recovery. The difference in r-SEI dissolution characteristics likely contribute to the significant difference in the ΔCE after discharged rest even though both electrolytes have similar CE during continuous cycling.**

**Supplementary Fig. 2:** CE of Li||Cu half-cells running on the hybrid cycling protocol with 1M $LiPF_6$ EC/DEC + 10% FEC and 4M LiFSI DME electrolytes.

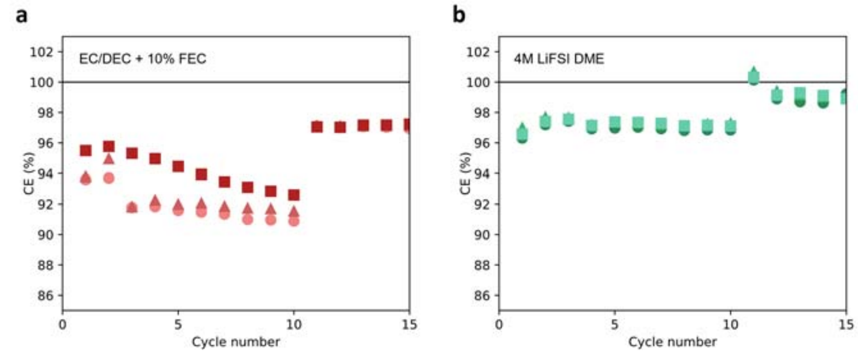
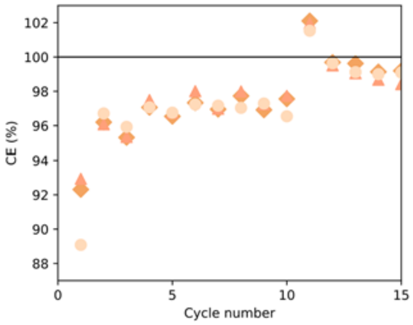


**Figure 1d:** CE of Li||Cu half-cells running on the hybrid cycling protocol for LHCE electrolyte.



**Supplementary Fig. 21:** CE of Li||Cu half-cells with LHCE cycling with 1-hour discharged rest and continuous protocols.

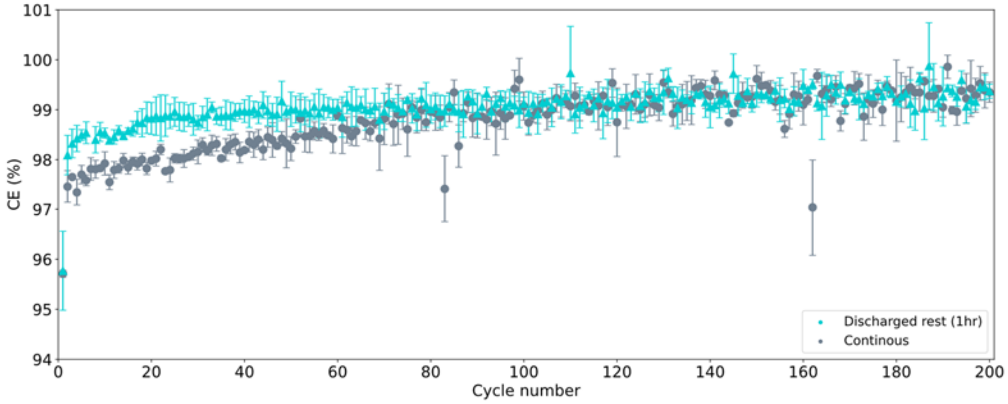
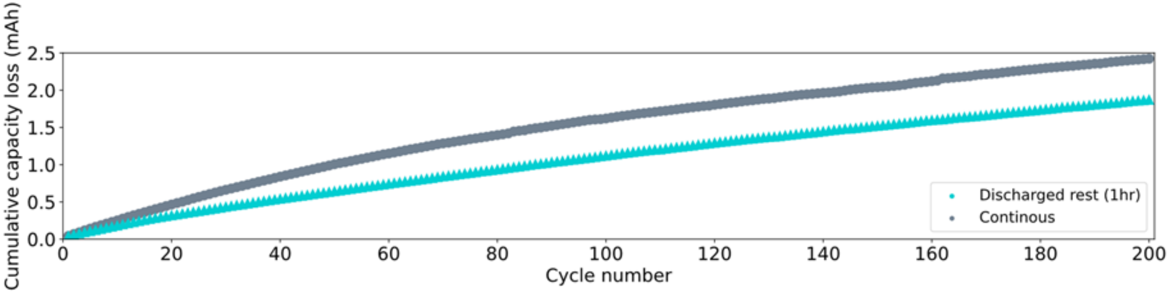


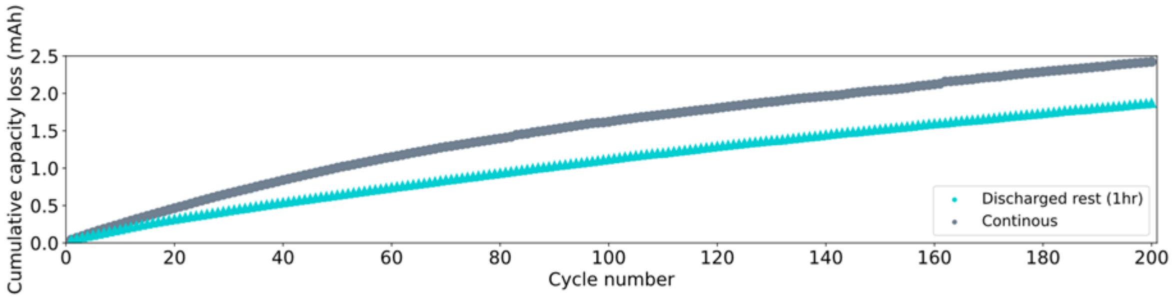
**Figure 4i:** Cumulative capacity loss of Li||Cu half-cells with LHCE running on 1-hour discharged rest, and continuous cycling protocols.



8.Note that few cycles were presented in Li | Cu and LFP | Cu cells. Can this recovery of isolated Li be extended to prolonged cycling?

*We appreciate the reviewer's emphasis on long term cycle performance utilizing the discharged state resting protocol. Much of this question on isolated Li during prolonged cycling is addressed in our response to question 7. However, we would like to emphasize the long-term capacity retention benefit of discharged state cycling in Figure 4i. Without the excess recovery from discharged resting, the continuously cycle cells lost 44% more capacity (1.62mAh vs 1.12mAh) after 100 cycles compared to their rested counterparts. This considerable increase in capacity retention can help substantially prolong the cycle life even if recovery becomes less effective in later cycles.

**Figure 4i:** Cumulative capacity loss of Li||Cu half-cells with LHCE running on 1-hour discharged rest, and continuous cycling protocols.



9.What’s the relation between the electrolyte formulations (including the related solvation ability, Li growth pattern, and SEI chemistry) and Li recovery behaviors? Why LHCE was selected?

*We thank the reviewer for this important question. Electrolyte formulations have a strong effect on Li recovery behaviors. Based on experimental results in this work, recovery of dead Li during resting at open circuit is due to the dissolution of SEI “shells” (referred to as r-SEI). Based on our previous work[6], we show that SEIs that are more inorganic are generally more stable and less soluble, whereas organic SEI components are more soluble. Therefore, the solvation structure of the electrolyte should have direct effects on the solubility of the SEI and Li metal reconnection. SEIs formed using electrolytes with anion-rich Li solvation structure have been shown to be more inorganic compared to electrolytes with solvent-rich Li solvation structure. Therefore, electrolyte formulations that has anion-rich solvation structure, inorganic-rich SEIs (high concentration electrolyte, electrolytes utilizing weakly solvating organic solvents) will generally have less soluble SEIs and less Li recovery during resting at open circuit. This relationship between SEI solubility and Li recoverability is supported by the CE data of supplementary fig. 2, figure 1d and the EQCM data of supplementary fig. 17. Both 4M LiFSI DME and LHCE have similar CEs during continuous cycling, however, 4M LiFSI DME cells have a smaller ΔCE increase after 11th cycle discharged resting compared to LHCE cells. The lower SEI mass loss (solubility) of 4M LiFSI DME SEI compared to LHCE SEI may contribute to the lower recovered isolated Li capacity in 4M LiFSI DME cells compared to LHCE cells.

Additionally, r-SEI dissolution reduces the physical barrier that prevents Li reconnection during subsequent Li metal plating and stripping steps. Therefore, the likelihood of Li recovery will be affected by Li morphology. Electrolyte chemistries that result in dendritic Li plating (e.g. carbonate-based electrolytes) will result in less recovery, as there is a less likelihood of Li being reconnected due to its shape. On the other hand, electrolyte chemistries that promote non-dendritic, low surface area morphologies will result in a higher chance of recovery. We think this is an important point, and we have added the following to emphasize the importance of electrolyte formulations and inactive Li morphology on recovery:

**Revised text on SI page 18, line 376:** “Since organic SEI components are generally more soluble, we believe that electrolyte formulations will have a significant effect on how much inactive Li metal can be recovered (through resting at open circuit voltage). SEIs formed using electrolytes with anion-rich Li solvation structure have been shown to result in more inorganic SEIs. Therefore, electrolyte formulations that have anion-rich solvation structure and inorganic-rich SEIs (high concentration electrolyte, localized high concentration electrolyte, electrolytes utilizing weakly solvating organic solvents) will generally have less soluble SEIs and less Li recovery during resting at open circuit. Different electrolyte formulations can also significantly affect the Li metal plating morphology, and we believe this will also affect the likelihood of Li reconnection. Electrolyte chemistries that result in dendritic Li plating (e.g. carbonate-based electrolytes) will result in less recovery, as there is a less likelihood of Li being reconnected due to its shape. On the other hand, electrolyte chemistries that promote non-dendritic morphologies will result in a higher chance of recovery. However, further studies are needed to quantify how different factors (SEI solubility, Li morphology) affect Li metal reconnection through discharge resting at open circuit."

To address the reviewer's second question, **LHCE was selected because it is a state-of-the-art electrolyte with a high baseline cycle performance which is relevant for practical LMBs. We believe that further improving cycle performance in an already high performing electrolyte will best demonstrate the efficacy of our discharged state calendar aging capacity recovery technique.** To demonstrate generalizability of the recovery across different electrolytes, we have conducted experiments which show capacity recovery in 1M LiPF$_6$ with EC/DEC and 10% FEC as well as with 4M LiFSI DME (supplementary fig. 2). The cells cycled with **1M LiPF$_6$ with EC/DEC + 10% FEC demonstrated an average ΔCE increase of greater than 5%**. The 11th cycle CE does not exceed 100%, likely due to the carbonate electrolyte promoting growth of high surface area Li morphology which causes faster corrosion as well as increased SEI formation on the isolated Li, both of which reduce isolated Li recoverability. Nevertheless, the CE observed on the 11th cycle after discharged rest is greater than that measured during any prior continuous cycle, strongly suggesting that capacity recovery is taking place. The cells cycled with **4M LiFSI DME do demonstrate greater than 100% CE for the 11th cycle with an average ΔCE jump of greater than 3%.**

**Supplementary Fig. 2:** CE of Li||Cu half-cells running on the hybrid cycling protocol with 1M LiPF$_6$ EC/DEC + 10% FEC and 4M LiFSI DME electrolytes.

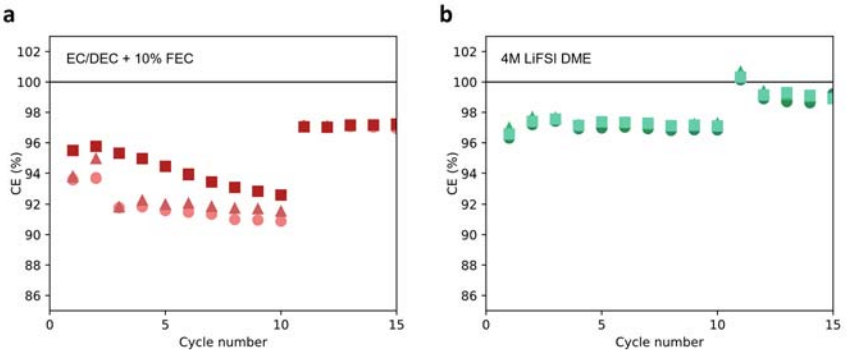
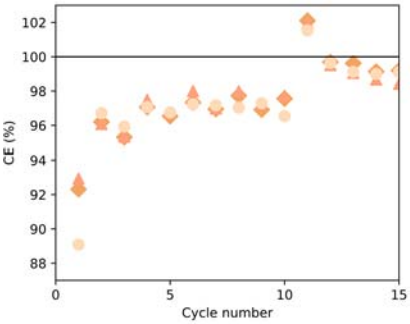
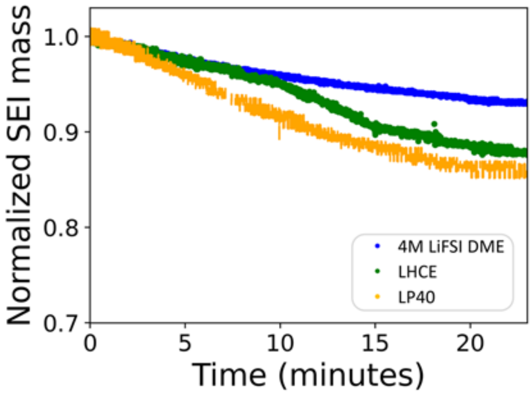


**Figure 1d:** CE of Li||Cu half-cells running on the hybrid cycling protocol for LHCE electrolyte.



**Supplementary Fig. 17:** EQCM data demonstrating preformed SEI mass loss during resting at open circuit voltage.



Referee #2 (Remarks to the Author):

This article describes an interesting study of the impact of open-circuit rest periods on Coulombic efficiency during complete plating/stripping of Li metal anodes in anode-free configurations using liquid electrolytes. The authors show a Coulombic efficiency >100%, which is attributed to recover of isolated/dead lithium. Further insights are provided through operando optical microscopy.

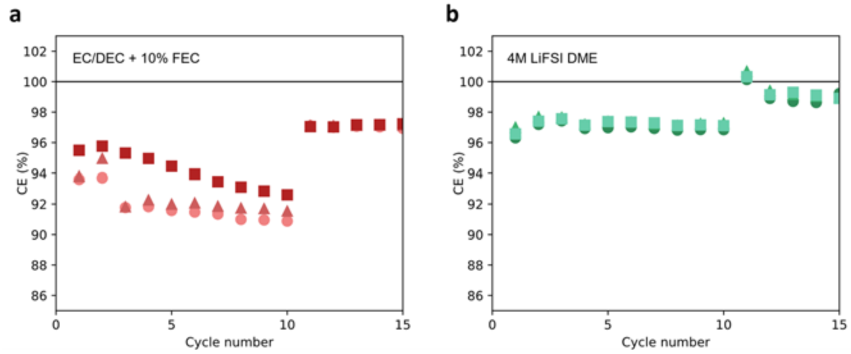
*We appreciate the reviewer for writing detailed and well thought out questions that will help to bolster the evidence for isolated Li recovery through discharged calendar aging. To address the reviewer’s concerns, we have appended additional cycling data with various electrolytes and cycling conditions to demonstrate the generality of isolated Li recovery as well as the ability to recover capacity with discharged resting in cells with a baseline CE >99%. Detailed point-to-point responses to each of the reviewer’s questions are found below.

Overall, this is a valuable study, which will spark interest and discussion among the Li metal anode community. The reviewer is generally supportive of publication, however, several important points should be addressed first:

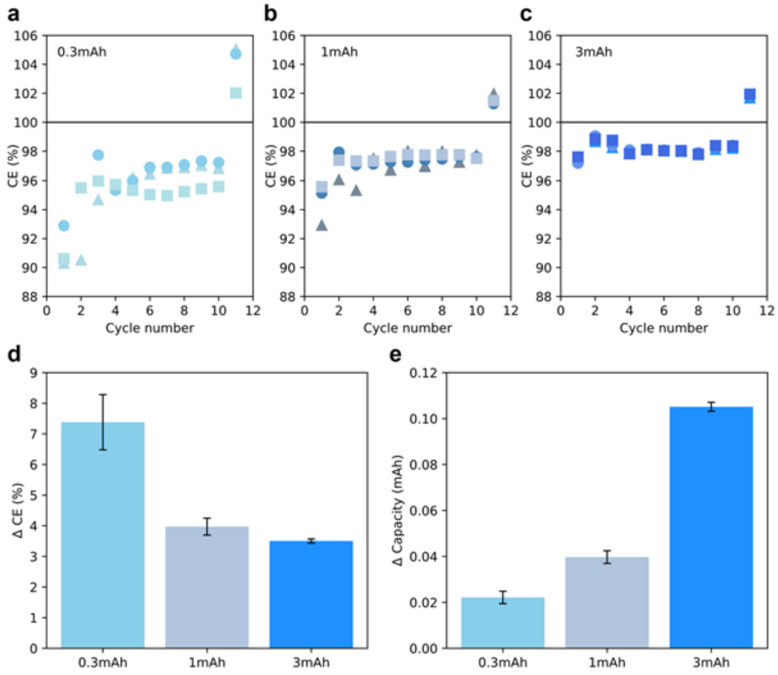
1) The tone of the discussion is very general. However, the generality of this approach is not discussed in sufficient detail. For example, only on electrolyte was used (LHCE) and only a single set of electrochemical conditions was studied for the coin cells (current density, depth of charge, etc.). How does the recovery of isolated Li depend on these important variables? Is CE >100% always observed, or only under these “optimal” conditions from the paper? In particular, it would be good to show how this performance occurs in various electrolytes (e.g. carbonate, glyme based), which would indicate how general the proposed mechanisms are.

We thank the reviewer for this important comment on the generalizability of the discharged state rest recovery. To emphasize the generality of this approach, we have conducted experiments to show that greater than 100% CE can be achieved for rest times ranging from 1 hour to 24 hours, strip current densities ranging from 0.25mA cm$^{-2}$ to 4mA cm$^{-2}$, and capacity ranging from 0.3mAh to 3mAh (supplementary fig 3-5). The only case for LHCE with CE less than 100% was under the condition of a 5-minute discharged rest, likely because 5 minutes is too short for sufficient SEI dissolution to occur, preventing significant reconnection and recovery. Nevertheless, even with just 5 minutes of rest, a 2% increase in CE is observed. To address the generalizability of capacity recovery in various electrolytes, we demonstrate capacity recovery in a carbonate (1M LiPF$_6$ with EC/DEC and 10% FEC) and a glyme based (4M LiFSI DME) electrolyte. The cells cycled with **1M LiPF$_6$ with EC/DEC + 10% FEC demonstrated an average ΔCE jump of greater than 5%.** The 11th cycle CE does not exceed 100%, likely due to the carbonate electrolyte promoting growth of high surface area Li morphology which causes faster corrosion as well as increased SEI formation on the isolated Li[6], both of which reduce isolated Li recoverability. Nevertheless, the CE observed on the 11th cycle after discharged rest is greater than that observed during any prior continuous cycle, strongly suggesting that capacity recovery is taking place. The cells cycled with **4M LiFSI DME do demonstrate greater than 100% CE for the 11th cycle with an average ΔCE jump of greater than 3%.** These results have been appended to the SI as supplementary fig. 2.

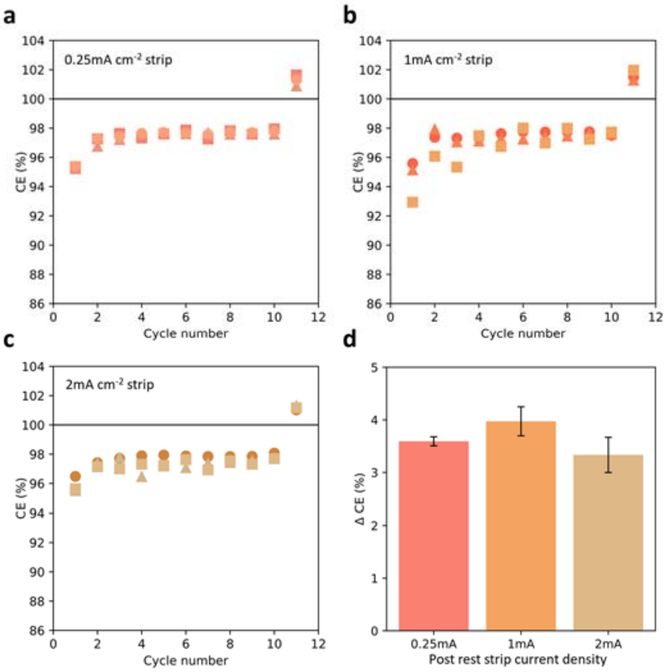
**Supplementary Fig. 2:** CE of Li||Cu half-cells running on the hybrid cycling protocol with 1M LiPF$_6$ EC/DEC + 10% FEC and 4M LiFSI DME electrolytes.



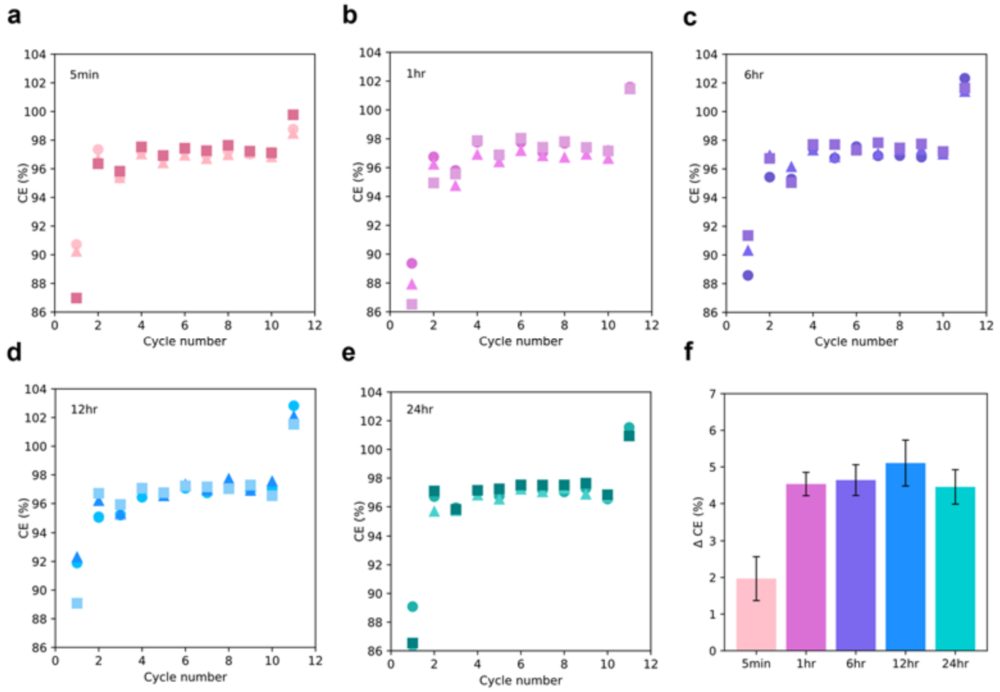
**Supplementary Fig. 3:** CE of Li||Cu half-cells running with LHCE on the hybrid cycling protocol with deposition capacities of 0.3mAh, 1mAh and 3mAh.



**Supplementary Fig. 4:** CE of Li||Cu half-cells running with LHCE on the hybrid cycling protocol with various 11th cycle strip current densities of 0.25mA cm$^{-2}$, 1mA cm$^{-2}$ and 2mA cm$^{-2}$.



**Supplementary Fig. 5:** CE of Li||Cu half-cells running with LHCE on the hybrid cycling with various 11th cycle rest times of 5 minutes, 1 hour, 6 hours, 12 hours and 24 hours.



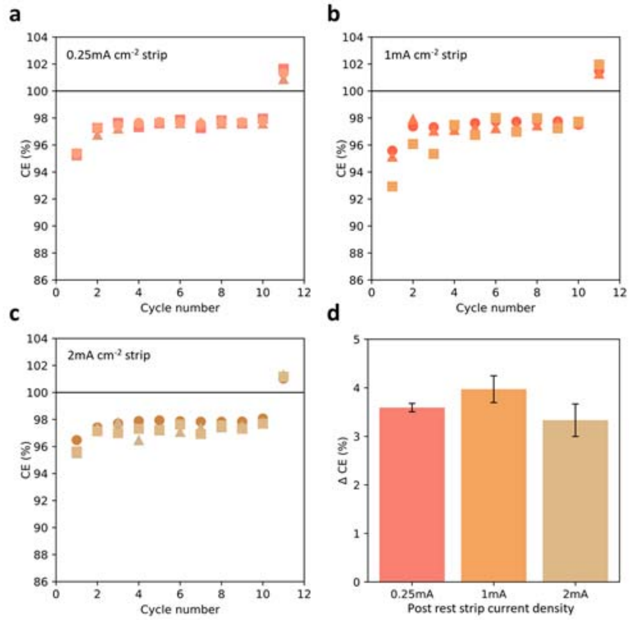
2) In the authors previous work on recovering isolated Li, it was shown that a high current discharge was needed to re-attach the isolated Li to the substrate. Following on point 1 above, was this observed in the case of resting during the discharged state? In other words, was a high current density during the following discharge necessary for the recovery? IF not, why not? Does this affect the conclusions of the previous paper that a high discharge current is needed for the Li migration back to the current collector? More of a direct discussion connecting the conclusions of these two important papers is needed.

*We thank the reviewer for this insightful question that will be important for the distinction between the two works. We find that high discharge current density following discharged calendar aging is not required for the recovery of isolated Li. To substantiate this claim, we cycled cells on a modified version of the hybrid cycling protocol (supplementary fig. 4a) with a low discharge current density of 0.25mA cm$^{-2}$. **The results reveal that although the ΔCE jump does decrease slightly discharging at 0.25mA cm$^{-2}$ (ΔCE = 3.55%) compared to at 1mA cm$^{-2}$ (ΔCE = 3.84%), a CE > 100% is still achieved when stripping at 0.25mA cm$^{-2}$**. Rest induced capacity recovery can still be achieved at low discharge current densities because the mechanism is dependent on the dissolution of the r-SEI during discharged rest rather than a spatial migration under an electric field. The dissolution of the r-SEI reduces the physical barriers between isolated Li and newly plated Li, increasing the likelihood of reconnection and recovery. In contrast, the prior work[3] utilizes high discharge current density without any resting protocol to spatially migrate the isolated Li to the substrate.

Our current results together with previous work show two different recovery mechanisms. A section has been appended to the manuscript to address this distinction.

**Revised text on page 3, line 112:** "An important result of note is the greater than 100% CE observed at a discharge current density of 0.25mA cm$^{-2}$ after discharged resting (supplementary fig. 4a). The significant recovery demonstrated with this low discharge current density strongly suggests that the discharged rest induced capacity recovery mechanism does not overlap with the Li reconnection mechanism found by Liu et al.[14] which utilizes high discharge current density for capacity recovery. These results suggest that there are two different recovery mechanisms."

**Supplementary Fig. 4:** CE of Li||Cu half-cells running with LHCE on the hybrid cycling protocol with various 11th cycle strip current densities of 0.25mA cm$^{-2}$, 1mA cm$^{-2}$ and 2mA cm$^{-2}$.



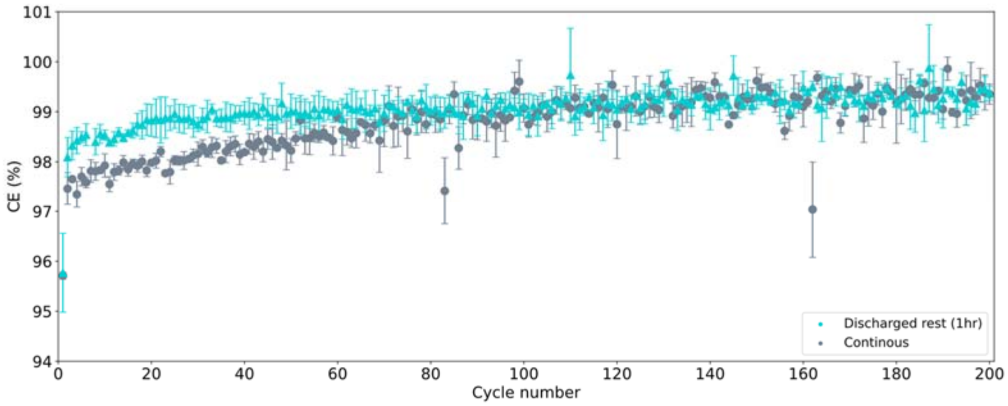
3) In general, the Coulombic efficiencies reported in the cycles without resting during discharge have relatively low Coulombic efficiencies (96.2% to 98.2%). First, these seem rather low for the state-of-the-art liquid electrolytes, which can routinely achieve >99% (and even reports up to 99.5%). How does the recovery of the isolated Li depend on the CE of the previous cycles? Is such recovery possible even when very small losses (which are mostly SEI) are present, such as in ~99.5% CE electrolytes? If not, then it seems that this method is mostly relevant for lower CE electrolytes and processes, which is something that should be clearly stated.

We thank the author for noting this detail about electrolyte performance. There are two factors that should be considered when comparing the CE reported in the original LHCE work by Ren. et al.[7] and the short cycle CE we report in this work. The first factor is the cycle number. The greater than 99.3% CE in the original LHCE published by Ren. et al. was achieved by averaging over 300 cycles compared to the CE of this work which was averaged over 20 cycles in figure 1c. Initial cycle CEs are typically lower than late cycle CEs because

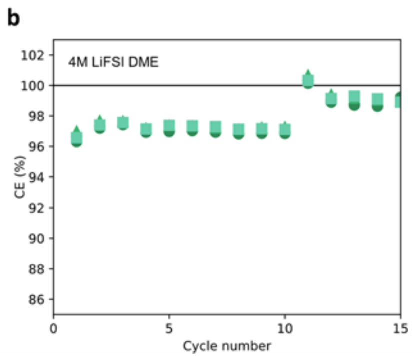
SEI and dead Li capacity losses are more pronounced in the early stages of cycling. This is supported by supplementary fig. 21 showing continuously cycled cell CE increasing over 200 cycles. This increase in CE over cycling is elucidated when comparing the average CE of the first 100 cycles at 98.4% and the average CE between cycle 101 and 200 at 99.2%. Because of the large capacity loss experienced in the earlier cycles, the average CE we report over 20 cycles can be expected to be lower than that averaged over 300 cycles. A second factor which can contribute to the difference in CE is the cycle current density. It has been reported that higher current density plating generates higher surface area morphologies which are associated with lower cycle performance[8]. In the original LHCE work, cells were cycled with an areal capacity of 1.0mAh $cm^{-2}$ and current density of 0.5mA $cm^{-2}$. In this study, while the areal capacity is the same, the current density is double that of the original study at 1mA $cm^{-2}$. In addition to the higher capacity losses which occur at earlier cycles, the higher current density likely also contributes to the lower CE we report compared to the original study.

The reviewer also brings up the important point that the quantity of isolated Li recovery possible is dependent on the CE of prior cycles, with higher CEs corresponding to lower quantities of isolated Li formation. We believe that discharged rest recovery is relevant even for the state-of-the-art electrolytes because they have higher capacity losses during initial cycles. To supplement this claim, we performed additional cycle testing on 4M LiFSI DME (supplementary fig. 2b), which along with LHCE are both considered state-of-the-art liquid electrolytes with greater than 99% average CE electrolytes[9]. While running on the hybrid discharged state rest protocol, both high performing electrolytes demonstrate capacity recovery on the 11th cycle with greater than 100% CE. This capacity recovery observed for both 4M LiFSI DME and LHCE helps to demonstrate the efficacy of the discharged resting protocol for state-of-the-art liquid electrolytes.

**Supplementary Fig. 21:** CE of Li||Cu half-cells with LHCE cycling with 1-hour discharged rest and continuous protocols.



**Supplementary Fig. 2b:** CE of Li||Cu half-cells running on the hybrid cycling protocol with 4M LiFSI DME electrolytes.



4) The authors state that “The uniformity of cycle 11 stripping voltage profile also suggests that electrolyte oxidation is not contributing to the capacity gain (figure 1d insert).”. This was not clear to the reviewer: why does the voltage profile indicate a lack of contribution from electrolyte oxidation? Please explain this more clearly, and include citation(s) if appropriate.

*We thank the reviewer for pointing out this unclear statement. To correct this, we have removed “The uniformity of cycle 11 stripping voltage profile also suggests that electrolyte oxidation is not contributing to the capacity gain (figure 1d insert).” from the manuscript.

5) The authors state that “However, the documentation of Li isolation and subsequent recovery has eluded past optical studies,5,22–25 likely due to the lack of internal cell pressure in prior optical setups.”. However, in the discussion of the mechanism, the proposed reason for Li recovery relates to the dissolution of the SEI, which should not be pressure dependent. Therefore, the role of pressure needs to be clarified.

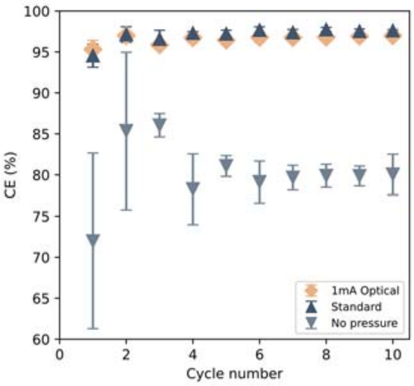
*The reviewer makes a very good point that the role of pressure for isolated Li recovery is not adequately addressed in the manuscript. The goal of this study is not to better understand how stack pressure affects cycle performance, but rather to demonstrate that discharged rest can induce additional isolated Li recovery, even in systems with a high baseline cycle performance. However, based on the conclusion from past studies[10–12] and our own experimental results (supplementary fig. 7a), stack pressure is an important contributing factor to high cycle performance. Therefore, an optical setup designed to observe isolated Li recovery and maintain high baseline CE must have stack pressure comparable to that of a standard coin cell in which isolated Li recovery is electrochemically observed in.

Unfortunately, most optical setup platforms developed in prior studies cannot simultaneously satisfy the requirement of optical compatibility and sufficient stack pressure on the electrodes. We believe stack pressure is an important criterion which enables increased contact between isolated Li and the electrode, a necessary condition for recovery. Additionally, there is not an easy method of measuring the stack pressure in a coin cell. Therefore, we decided the best way to observe isolated Li recovery while maintaining high cycle performance is by modifying a coin cell to be optically compatible. By using most of the coin cell components and maintaining the form factor, the optical cell stack pressure remains similar to that of a standard Li||Cu coin cell. This is supported by the CE data in figure 2b showing the comparable CE performance of the optical cell vs the coin cell over 10 cycles.

This shortcoming on addressing the role of pressure is being addressed in the manuscript by replacing “However, the documentation of Li isolation and subsequent recovery has eluded past optical studies,5,22–25 likely due to the lack of internal cell pressure in prior optical setups.” With:

**Revised text on page 6, line 169:** “To observe this recovery phenomenon, an optical cell with characteristics and properties close to a standard coin cell is required. Pressure is an important factor in high performance cycling[29–32] and recovery of isolated Li because pressure can enhance contact between Li and the electrode, increasing the likelihood of stripping and recovery. Many optical cell platforms have been developed to elucidate important properties of Li metal plating and stripping[6,33–36], but the application of pressure was not essential for these studies. Since the goal of this optical cell is to closely replicate the CE and capacity recovery of a high performing Li||Cu coin cell, pressure is an essential criterion which must be satisfied. The importance of stack pressure for high performance cycling is illustrated in supplementary fig. 7a, which demonstrates that cells cycled with stack pressure have an average CE 15% higher than cells cycled without stack pressure.”

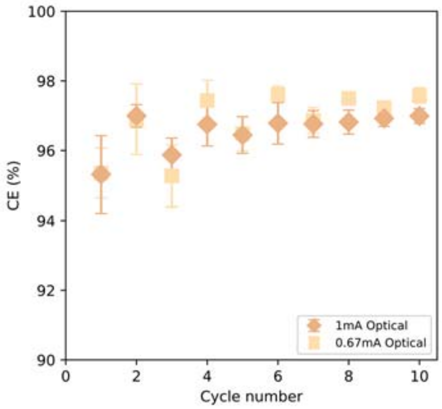
**Supplementary Fig. 7a:** Comparison of the CE between optical cells, standard coin cells, and no pressure coin cells all with LHCE.



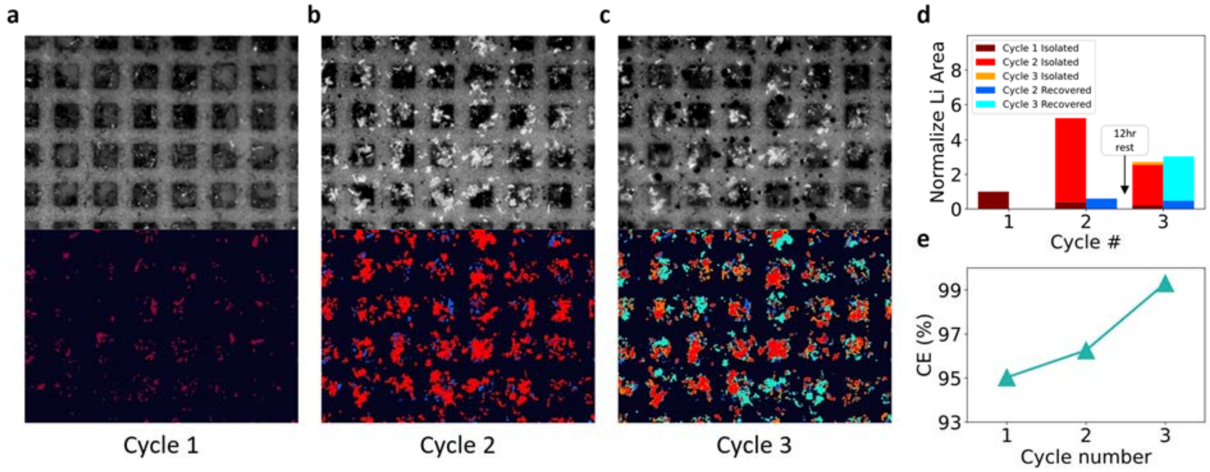
6) For the comparison of the optical and standard electrode in figure 2, was the total current adjusted to the reduced electrode surface area of the grid electrode, to keep the local current density the same?

The current density for the experiments in figure 2 and figure 3 were not adjusted to compensate for reduced surface area. The total frontal electrode surface area of the Cu mesh is calculated to be 2/3 that of a standard Cu current collector. Therefore, to maintain a local current density of 1mA $cm^{-2}$ on the copper mesh, the applied current needs to be decreased from 1mA to 0.67mA. To address the reviewer’s concern, we compared the cycle performance of three optical cells cycled at 1mA vs three optical cells cycled at 0.67mA (supplementary fig. 7b). The results show the CE for both currents are very similar. Additionally, we added an optical cell experiment with a reduced discharge current of 0.67 mA to enable a local current density of 1mA $cm^{-2}$ on the copper mesh (supplementary fig. 14). The result of the lower current local density experiment showed a similar result to that run at the higher current density with increased isolated Li recovery after discharged resting. The similar results demonstrated by both experiments cycling at 1mA vs 0.67mA suggest that the difference between cycling at these two current densities is negligible.

**Supplementary Fig. 7b:** Comparison of the CE between optical cells run at 1mA $cm^{-2}$ and 0.67mA $cm^{-2}$ with LHCE.



**Supplementary Fig. 14:** Colored areal maps of dead and recovered Li for the end of each cycle in the discharged state with cycle 3 discharged at a current density of 0.67mAh $cm^{-2}$. Maroon, red, and orange correspond to inactive Li formed from cycle 1, 2 and 3 respectively. Blue and cyan correspond to recovered Li from cycles 2 and 3 respectively. Optical cell utilized LHCE.



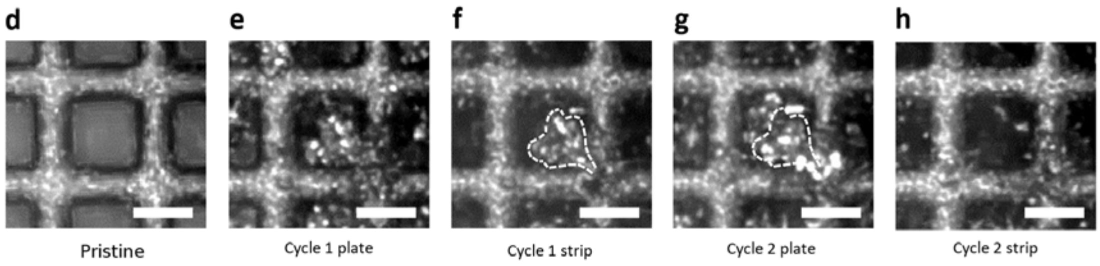
7) In figure 2g, it was not clear how the authors determined that the Li plating outlined in red was really reconnected to the previous isolated Li. How can this be proved? Since the optical

microscope is showing a 2-D projection of 3-D geometric data, and the clarity of the zoomed-in images is a bit grainy, it is really hard for the reviewer to conclusively determine that this specific location was a reconnection of the previous isolated Li. It is clear that the previous isolated Li is stripped in panel h, but the authors may want to soften the language of direct visualization of the reconnection in panel g.

*The reviewer has a good point that the location of reconnection cannot be pinpointed with a 2D projection. The section has been modified to:

**Revised text on page 6, line 195:** "At the end of the first stripping cycle, a large isolated Li deposit (delineated by the white outline) is left behind due to the electronic disconnection between the Li deposit and Cu electrode (figure 2f). During the second cycle plating, fresh Li is seen depositing in the Cu mesh window. This is followed by new Li growth sprouting from the previously isolated Li deposit, indicating electrical reconnection of the isolated Li deposit with the electrode (figure 2g)."

**Figure 2:** Optical images of the Cu mesh and separator taken in the pristine state (d), cycle 1 plate (e), cycle 1 strip (f), cycle 2 plate (g) and cycle 3 strip (h). Optical cell utilized LHCE.



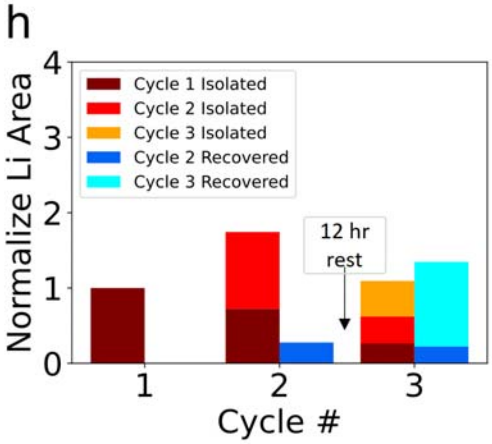
8) The reviewer has some doubts about the validity of analyzing of areal ratios of isolated vs. recovered Li in figure 3. First off, it is not clear that the contrast in a specific pixel location in this 2-d projected image (as mentioned above) remains associated with the same specific atoms of Li during cycling. For example, it is known that the position of isolated/dead Li can get "pushed out of the way" during subsequent plating cycles, as seen in cross sectional optical imaging (e.g. in Ref. 25). Therefore, the isolated Li from a previous half-cycle could get displaced by newly plated Li in the following cycle, so the presence or absence of contrast in a specific pixel location would be insufficient evidence that a specific region of plated Li is now recovered, since it can also be displaced. Therefore, the reviewer would caution against quantitatively analyzing the contrast changes of a specific pixel location, which is fixed in space, as a proxy for quantifying recovered Li, since the assumption is that the previously plated Li would have to be rigid, and could not be moved/affected by the subsequent plating and stripping.

*The reviewer brings up a valid concern that isolated Li can be pushed out of the way or displaced during subsequent plating cycles when observed in past optical cell works[13]. While the displacement of Li cannot be completely prevented, one major advantage of the coin cell optical setup is the ability to confine isolated Li within the Cu mesh window, greatly mitigating isolated Li displacement. This is supported by supplementary video 2-3 which allows for the tracking of Li deposits shown in fig 3a-f through plating and stripping. The videos demonstrate that most areas marked as recovered Li are locations of isolated Li recovery rather than isolated Li displacement. We have included two zoomed in videos of areas with high Li recovery to highlight that the recovery rather than displacement dominates (supplementary video 4-5).

In the few instances where isolated Li deposits have a significant displacement, the previous isolated Li location would be marked as “recovered” at the pre-displacement location as “dead” as a new location. In this case, the recovered to isolated ratio for this specific Li deposit would be around 1 and therefore would not be counted toward isolated Li or recovered Li. However, the ratio of cycle 3 recovered to cycle 3 isolated for the hybrid rested cell in supplementary fig. 12h is much higher than 1, strongly suggesting Li recovery. An additional section has been appended to Supplementary fig. 12 to address the movement of Li.

**Revised text on SI page 13, line 264:** “Since the areal map data does not incorporate the volume and movement in Li deposits, the R/I ratio is an approximation for the quantity of recovered and isolated Li rather than the exact amount. The optical cell cannot resolve Li deposit thickness and only account for the frontal area facing the camera. Therefore, the difference in capacity lost and recovered based on Li thickness difference cannot be resolved. This thickness variability is likely to be small since the cell stack pressure helps to limit the thickness range. In the instances where isolated Li deposits have a significant displacement, the previous isolated Li location would be marked as “recovered” at the pre-displacement location as “dead” as a new location, even though no recovery had taken place. However, one major advantage of the coin cell optical setup is the ability to confine isolated Li within the Cu mesh window, greatly mitigating isolated Li displacement. This is supported by supplementary video 2-3 which allows for the tracking of Li deposits shown in fig 3a-f through plating and stripping. Furthermore, the recovered to isolated ratio for this specific Li deposit would be approx. 1 and therefore would not be counted toward isolated Li or recovered Li. Although the optical areal maps cannot perfectly quantify Li capacity, the area of Li recovered and lost extracted from the areal maps with and without rest match closely with the trends observed in the CE and TGC data, making the optical cell and the areal map a useful tool to study Li loss and recovery.”

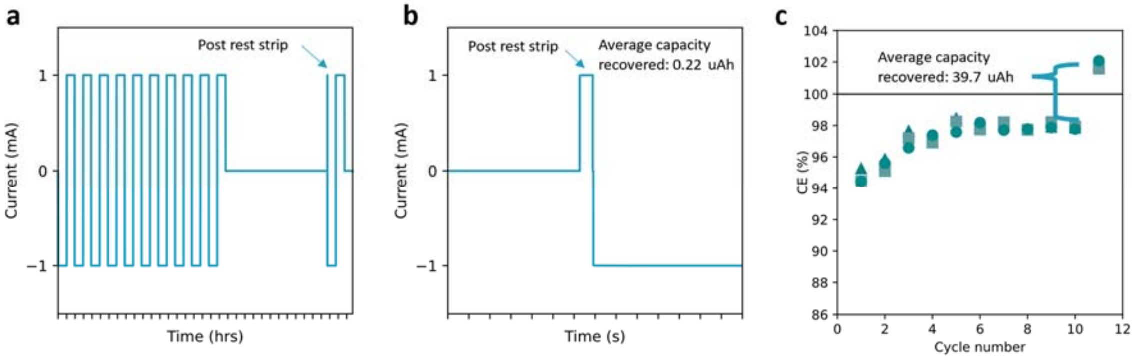
**Supplementary Fig. 12h:** plots of the areas occupied by dead and recovered Li for cell 2 hybrid resting cycle. Optical cell utilized LHCE.



9) Please include the video used to generate the data in Figure 3 as a supplemental video file, which will help the reader to visualize the data in Figure 3 more clearly. It would also be helpful to include the data from the rest period in the video, in addition to during plating and stripping. Same goes for the video data for Figure 4, where it would be very helpful to be able to visualize the dissolution of the r-SEI through video data.

*The videos used to generate the data in Fig 3a-c and Fig 3d-f have been added as supplementary video 2 and supplementary video 3. The video used to generate Fig 4e-h has been added as supplementary video 6. We also note that the wetted surface on the windows changes during rest. In the case where Li is ionically disconnected due to lack of wetting rather than being electronically disconnected from the electrode, re-wetting of the Li during rest can contribute to capacity recovery. To test whether wetting contributes to the recovered capacity, we ran a hybrid protocol with a discharge to 1V at 1mA cm$^{-2}$ step after 12 hours of discharge rest before charging. If the wetting changes observed during rest contribute to Li recovery, this extra discharge step should contribute to a non-negligible amount of capacity. This experiment shows the post rest strip contributes to 0.22µAh of capacity, while the subsequent plating and stripping cycle contributes to over 100 times more capacity recovery at 39.7µAh. This result strongly suggests that the wetting change which occurs during rest does not significantly contribute to capacity recovery (supplementary fig. 15).

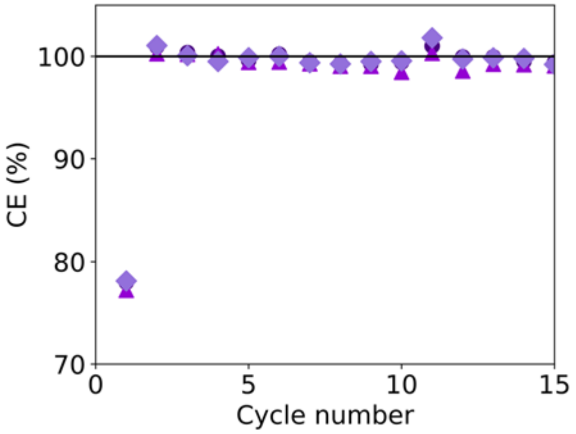
**Supplementary Fig. 15:** hybrid cycle protocol with added post discharge rest strip step to test for recovery from change in electrode wetting during discharge rest. Cells utilized LHCE.



10) The Coulombic efficiencies in the full cell are also quite low (~95%), which is below what is needed for a practical battery. This relates to question 3 above, on how generalizable this method is under different electrolytes and cell configurations, especially those with higher CE?

*The reviewer brings up a valid concern about the low performance observed on our anode free coin cells setups. To address this concern, we cycled 200mAh anode free pouch cells which better approximates cycling in practical anode free cells. The pouch cell set up achieved CE > 99.5% for the cycles 2-10 cycles prior to discharged resting which aligns much better with the expected baseline performance in LHCE (supplementary fig. 16). Furthermore, the anode free pouch cells also demonstrate isolated Li recovery with greater than 100% CE after discharged resting running on the hybrid protocol on the 11th cycle.

**Supplementary Fig. 16:** CE of $LiFePO_4$ (LFP) anode-free pouch cells running with LHCE on a modified hybrid cycle with rest between the 10th and 11th cycle.



11) The authors state that “This increase in overpotential reflecting an increase in total internal

resistance during cycling has been correlated with r-SEI build up.13,30–32”. However, it has been shown that the increase in cell resistance after extensive build-up of dead Li results in increased mass transport losses due to reduced electrolyte transport through the compact dead Li layer (Ref. 11). Therefore, this sentence should be updated to include the contribution from mass transport through dead Li, in addition to the buildup of r-SEI, as the reason for increased total resistance during cycling.

*This is a good suggestion from the reviewer. “This increase in overpotential reflecting an increase in total internal resistance during cycling has been correlated with r-SEI build up.” Has been revised this section to:

**Revised text on page 10, line 284:** “This increase in overpotential observed during cycling has been correlated with the buildup of both isolated Li and r-SEI impeding mass transport.”

-

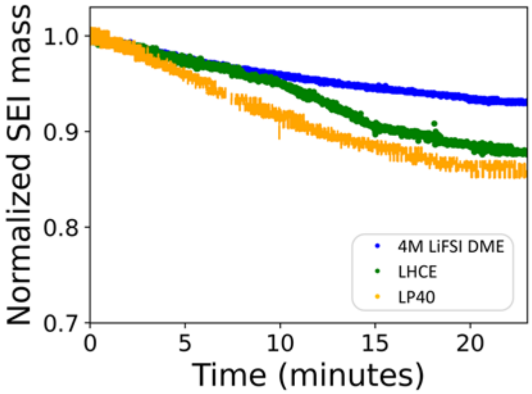
12) The proposed mechanism of r-SEI dissolution is interesting, and critical to support the hypotheses of the paper. However, the discussion of this mechanism is rather short. It was not clear why r-SEI dissolution is occurring. Is this specific to the electrolyte system used? Does it occur across other electrolyte systems (see comment 1 above)? And if so, is it expected, based on the solubility of the r-SEI components in the electrolyte? More of a chemical justification for this r-SEI dissolution is needed to strengthen this discussion.

*This is a great point and is critical for our proposed work. Based on our previous work[14] and additional experimental work done for this current manuscript, we show that significant portions of the SEI are soluble across multiple electrolyte chemistries. The solubility of the SEI was quantified using EQCM, showing that the SEI undergoes significant mass loss during resting at open circuit (supplemental fig. 17). This was further supported by XPS compositional analysis showing that the r-SEI becomes more inorganic after resting, suggesting that organic SEI components are more soluble (supplemental fig. 19). To confirm our XPS compositional analysis, we used NMR to analyze electrolytes aged with Li metal and detected additional organic moieties in the electrolyte after aging, confirming that there are organic components in the SEI that dissolve into the electrolyte (supplemental fig. 20). To confirm the generality of SEI dissolution, we showed that it is prevalent in ether-based electrolytes (LiFSI-DME system), ranging from high concentration electrolyte (4M LiFSI in DME), LHCE (TTE) and carbonate-based electrolyte (LP40). This is reflected in our additional experimental data showing the generality of inactive Li metal recovery through open circuit resting at discharged state. We included the following to further explain the mechanism of inactive Li metal recovery through r-SEI dissolution:

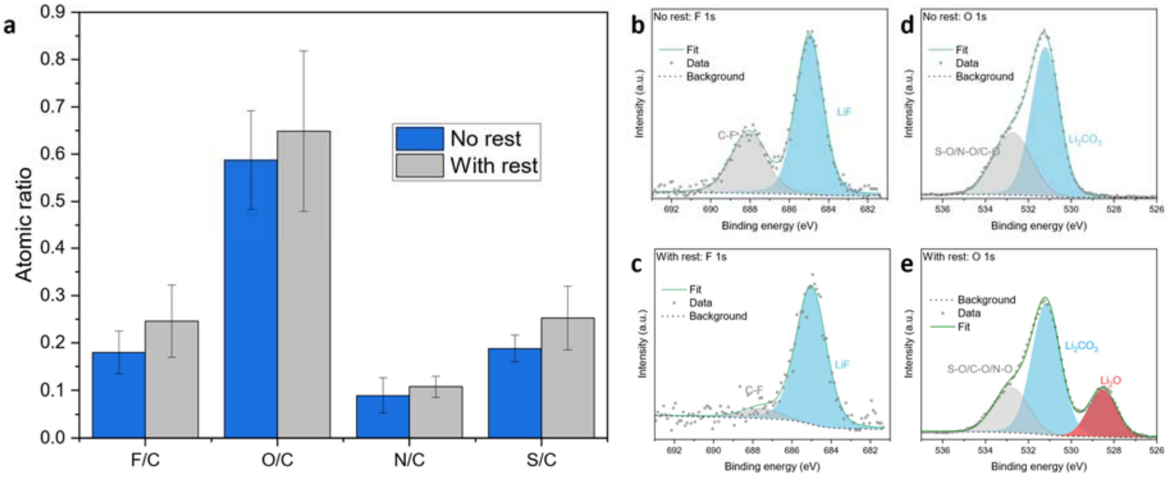
**Revised text on page 10, line 299:** “Additional electrochemical and chemical experiments support the observation of r-SEI dissolution during resting at OCV. Using electrochemical quartz crystal microbalance (EQCM), we show that significant mass of the SEI is lost during resting at OCV for multiple electrolyte chemistries (supplementary fig. 17)

**Revised text on page 10, line 304:** “XPS characterization shows that r-SEI becomes more inorganic after resting at OCV for all electrolytes tested, suggesting that organic components in the SEI are more soluble than their inorganic counterpart (supplementary fig. 19). To confirm our XPS compositional analysis, we used NMR to analyze electrolytes aged with Li metal and detected additional organic moieties in the electrolyte after aging, confirming that there are organic components in the SEI that dissolve into the electrolyte (supplementary fig. 20)."

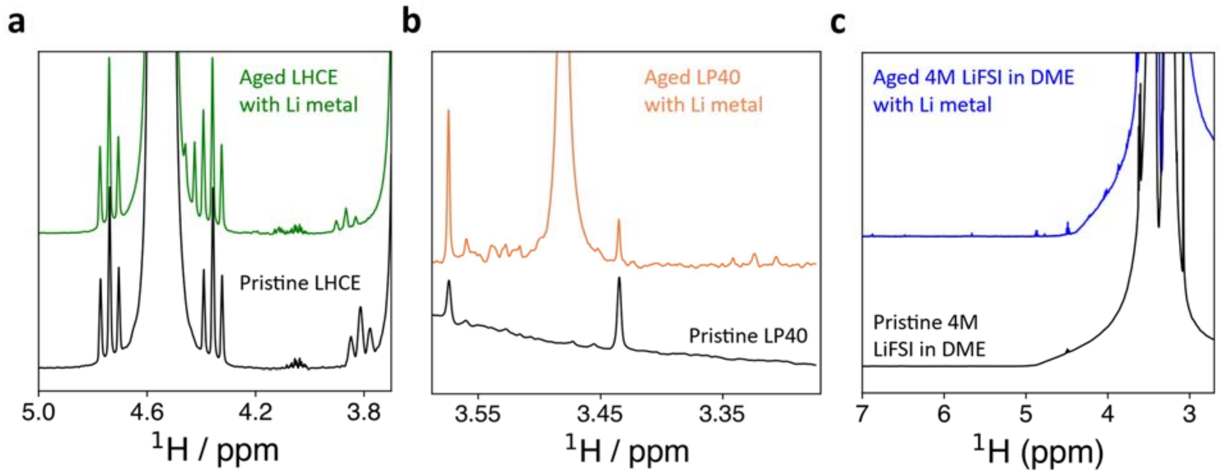
**Supplementary Fig. 17:** EQCM data demonstrating preformed SEI mass loss during resting at open circuit voltage.



**Supplementary Fig. 19:** XPS atomic ratios of the discharged Cu current collector of Li||Cu cell with and without rest



**Supplementary Fig. 20:** NMR analysis of **(a)** LHCE, **(b)** LP40, and **(c)** 4M LiFSI DME in pristine electrolyte and aged electrolyte in Li metal.



Referee #3 (Remarks to the Author):

This work by Cui and coworkers presents an evaluation of calendar aging of Li metal anodes in the discharged state. Calendar aging of Li metal is an important topic as Li metal anodes are integral to high energy density, next-generation batteries, and the highly reactive nature of Li metal makes it susceptible to side reactions, aging, etc. The authors make the important point that calendar aging is most often evaluated in the charged state whereas no publications to my knowledge evaluate calendar aging of Li in the discharged state. The manuscript in general is clear and logical.

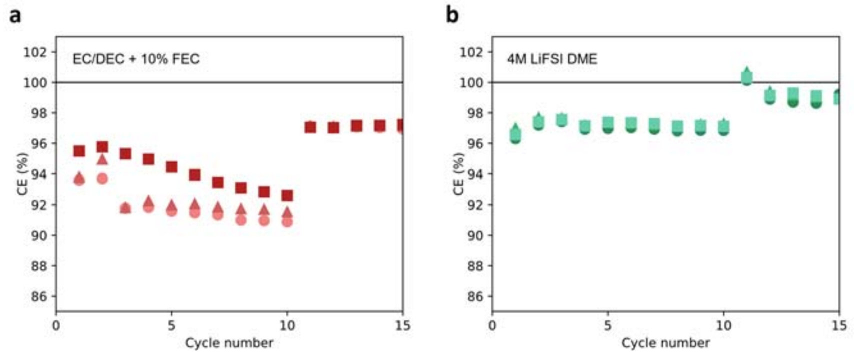
*We thank the reviewer for taking time to provide this valuable feedback. To address the reviewer's comments, we have appended new sections and new cycling data to clarify the novelty of our current work on isolated Li recovery with discharge resting to help differentiate it from past works. To demonstrate the generalizability of our Li recovery mechanism, we conducted cycling over a dozen cycling experiments in various electrolytes, and with various plating capacities, strip current densities, and rest time. Three cells were run for each cycling condition to further emphasize the repeatability of the capacity recovery.

These authors demonstrate that capacity can be recovered due to isolation and recovery of Li metal and show that the degree of aging can be mitigated through strategic rest protocols. This same conclusion has been demonstrated by Harrison and coworkers albeit for the aging Li metal in the charged state vs discharged state (https://doi.org/10.1021/acsaem.1c00874, https://doi.org/10.1021/acs.jpcc.2c05385). Though one of these papers is cited regarding calendar aging generally, the same mechanism for Li stranding and reconnection is proposed in these works as well as similar conclusions regarding whether rest is applied every cycle or after cycling. The authors should address this.

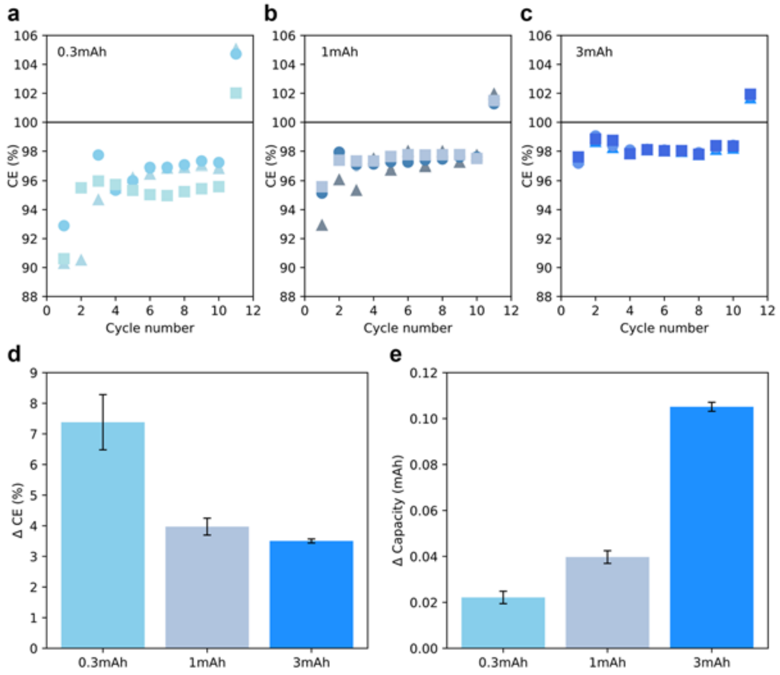
*We thank the reviewer for this well thought out comment emphasizing past works on aging and cycling. The work done by Harrison and coworkers[15,16] demonstrates the important phenomenon that some capacity lost while resting in the charged state can be recovered in a subsequent cycle and proposes that recovery is achieved through the reconnection of dead Li. These studies help illustrate that the detrimental effects of aging LMBs in the charged state can be mitigated. We like to emphasize that the central point of our work on discharged state rest recovery is not to mitigate the degree of capacity loss due to aging, but rather to improve overall cycle performance and capacity retention beyond that of continuously cycled cells and elucidate the mechanism for Li recovery. This increase in cycle performance is illustrated in figure 1b, figure 1c, figure 1d, figure 3h, figure 4a, and figure 4i, all of which show cycles with discharged rest displaying higher CE than continuous cycles. The performance benefits of discharged rest are further generalized in supplementary fig. 2-5, showing that capacity recovery post discharged rest can be observed cycling with various electrolytes, current densities, capacities, and rest times. In addition to the central focus of improved cycle performance, the first-time optical demonstration of Li reconnection and recovery during continuous cycling and elucidation of the mechanisms for isolated Li recovery helps to further differentiate this work from prior studies. We have added the following section to the manuscript to highlight contributions from Harrison and coworkers.

**Revised text on page 2, line 56:** "Additionally, studies by Merrill et al.[16,24] on intermittent charged state resting suggest that some active Li lost during charged state resting as isolated Li can be reconnected on the subsequent cycle. Although the average cycle performance of cells rested intermittently in the charged state remains below that of continuously cycled cells, the studies help emphasize that the detrimental effects of corrosion on LMB cycle performance can be mitigated."

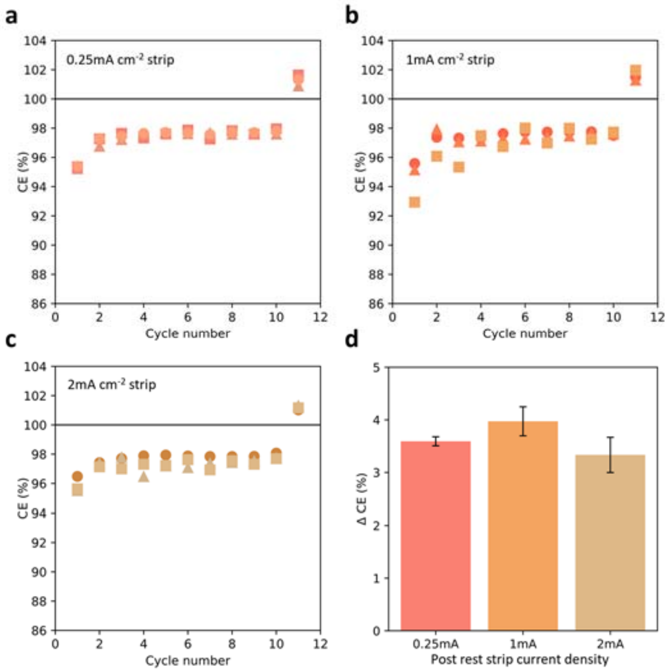
**Supplementary Fig. 2:** CE of Li||Cu half-cells running with LHCE on the hybrid cycling protocol with 1M $LiPF_6$ EC/DEC + 10% FEC and 4M LiFSI DME electrolytes.



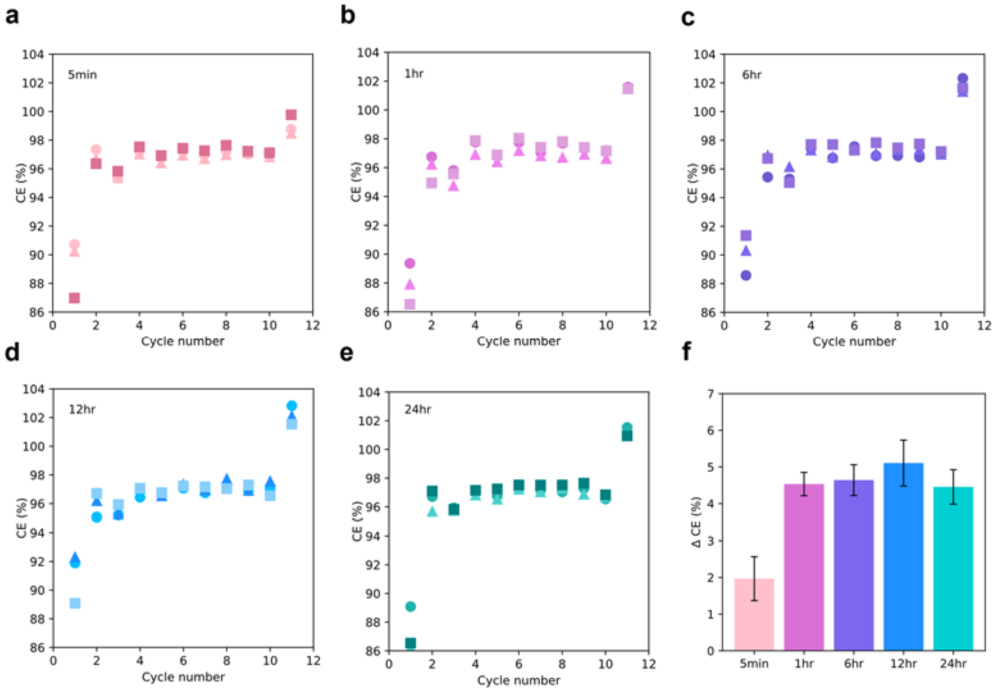
**Supplementary Fig. 3:** CE of Li||Cu half-cells running with LHCE on the hybrid cycling protocol with deposition capacities of 0.3mAh, 1mAh and 3mAh.



**Supplementary Fig. 4:** CE of Li||Cu half-cells running with LHCE on the hybrid cycling protocol with various 11th cycle strip current densities of 0.25mA cm$^{-2}$, 1mA cm$^{-2}$ and 2mA cm$^{-2}$.



**Supplementary Fig. 5:** CE of Li||Cu half-cells running with LHCE on the hybrid cycling with various 11th cycle rest times of 5 minutes, 1 hour, 6 hours, 12 hours and 24 hours.



What these authors add is a clever approach to validating the proposed mechanism that both they and Harrison and coworkers presented through titration gas chromatography and through in-operando optical measurements.

*We are very grateful that the reviewer appreciates the wide-reaching impact of our work. We also thank you for acknowledging that our in-operando mechanistic insights shed light on some of the important work by Harrison and coworkers.

Further, the results presented in this work appear to contradict another publication from Cui and coworkers (https://doi.org/10.1038/s41560-021-00787-9). I request that the authors discuss this prior work within this manuscript.

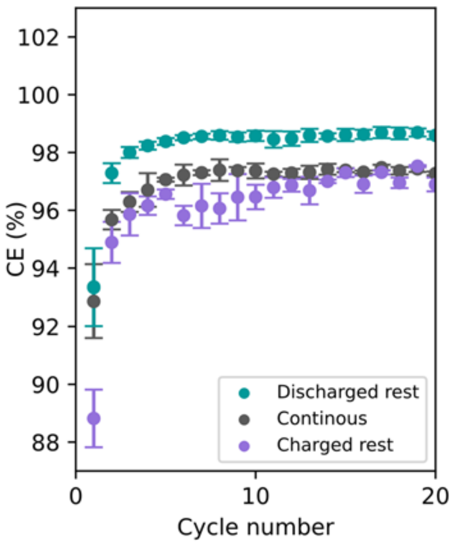
*This is a good point by the reviewer that needs to be better emphasized to clearly differentiate the conclusions of the prior Li corrosion work against the findings of the current isolated Li recovery work. **In the prior corrosion study, it was found that charged state resting enables corrosion of active Li. During charged state aging, active Li can react with electrolyte to generate more SEI or become electrically disconnected forming isolated Li;** both corrosion pathways decrease the quantity of active Li on the anode, leading to a decrease in CE. **In this current work, resting takes place in the discharged state where there is no active Li to corrode. Instead, the exposed r-SEI dissolves into the electrolyte over time, thereby decreasing the physical barrier to reconnection. This increases the likelihood for the subsequent plating cycle to reconnect with the isolated Li, leading to an increase in CE.** We also acknowledge that isolated Li can corrode during discharged resting, but longer term discharged rest experiments of 24 hours (supplementary fig. 5f) still show greater than 100% CE following rest, with only a small decrease in ΔCE compared to the maximum observed recovery at 12 hours. This difference in environment between prior charged state rest work and the current work is highlighted in this section of the manuscript.

**Revised text on page 3, line 80:** "Calendar aging anode-free electrodes in the discharged state and the charged state exposes the electrolyte to two distinctive electrode environments during rest (figure 1a). In the discharged state with the active Li stripped away, the electrolyte interacts only with isolated Li and residual SEI shells from prior cycles (r-SEI) during rest. In the charged state, the active Li remains on the electrode and can be corroded by the electrolyte during rest, decreasing active Li capacity and generating excess SEI."

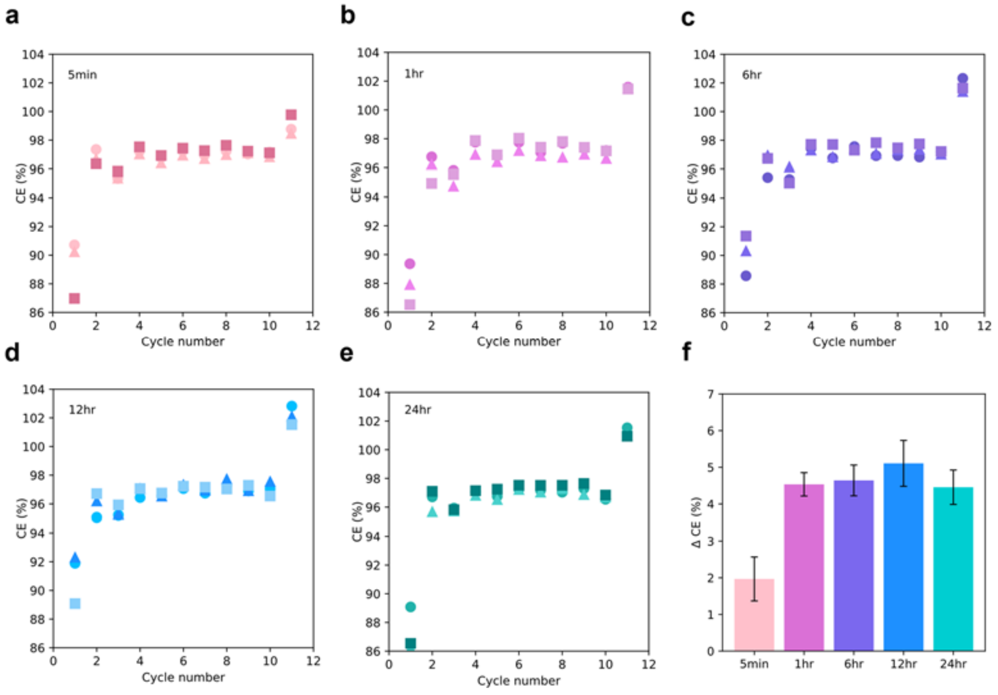
The cycle performance difference between the charged state calendar aging work and the current discharged state work is highlighted in figure 1c, showing the superior CE of discharge state rested cells compared to charge state rested and continuously cycle cells. We have appended another section to the manuscript discussing the effect of isolated Li corrosion and r-SEI evolution during discharged state resting, and how these effects can impact cycle performance.

**Revised text on page 11, line 318:** "While r-SEI dissolution during discharged calendar aging can help promote the reconnection of isolated Li on the subsequent plating cycle, the concurrent corrosion during rest both reduces the quantity of isolated Li available for recovery as well as thickens the native SEI on isolated Li. These factors can reduce the efficacy of Li reconnection[15,19,20]. Although our tests reveal that corrosion slightly reduces the efficacy of capacity recovery after 24 hours of rest, all cells rested in the discharged state, regardless of rest period demonstrate an increase in CE compared to the continuous cycles (supplementary fig. 5). The minimal decrease in recovery efficacy even after resting for 24 hours indicates that isolated Li recovery, not isolated Li corrosion, is the dominant factor affecting cycle performance after resting in a discharged state. This aligns with the findings from prior corrosion studies which indicate that capacity loss over 24 hour charged state rest makes up less than 20% of total Li capacity. In the case of discharged resting, this implies over 80% of isolated Li should remain recoverable after 24 hours of rest."

**Figure 1c:** CE of Li||Cu half-cells running with LHCE on cycling protocols with discharged state rest, no rest (Continuous) and charged state rest.



**Supplementary Fig. 5:** CE of Li||Cu half-cells running with LHCE on the hybrid cycling with various 11th cycle rest times of 5 minutes, 1 hour, 6 hours, 12 hours and 24 hours.

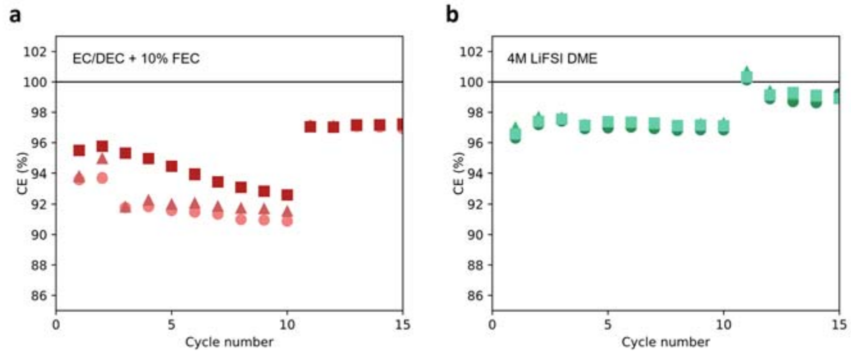


The authors appear to be thorough, showing error bars with one graph, but not all. I ask that the authors include error bars at least to the SI to demonstrate the repeatability of their results (e.g., error bars not shown in cycling data for Fig. 1d, Fig. 2b, Fig 3g and h, Fig. 4a, and such figures in the SI). Furthermore, I ask that the authors include the number of cells used to calculate error (e.g., were these tests run in duplicate, triplicate, sets of 5, etc.). This will aid in showing that the work in thorough and reproducible.

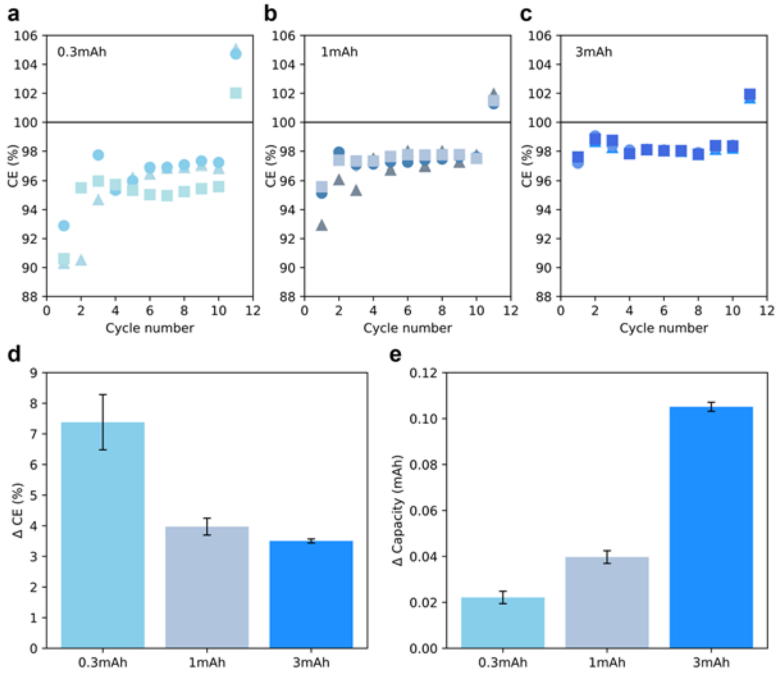
*We thank the review for this suggestion. To address these concerns on reproducibility, we have run additional cycling experiments with the hybrid protocol using various electrolytes, plating capacities, stripping current densities, and rest times (supplementary fig. 2- supplementary fig. 5). Three cells were cycled for each condition, all of which demonstrated an improvement in CE on the 11th cycle after discharged resting. **In plots where a single cycle condition is displayed such as in figure 1d, figure 4a, and supplementary fig. 2- Supplementary fig. 5, we have opted to include the raw CE data for all three cells cycled to emphasize the reproducibility of the ΔCE jump transitioning from continuous cycling to discharged rest cycling. For plots comparing different cycling conditions or cell form factors such as figure. 1c, we have chosen to plot the average CE for the three cells with error bars to prevent overcrowding of each plot with too much data. We believe that representing data comparing different conditions with the average CE and error bars enables the differences or similarities in performance to be more easily understood.** Additional optical cell cycle data and accompanying error bars have been added to figure. 2b.

We have also performed further optical cell experiments with a lower discharge current density 0.67mA $cm^{-2}$ (supplementary fig. 14) to supplement figure. 3g and figure. 3h. This additional data helps to emphasize the repeatability of observing isolated Li recovery in the optical cell.

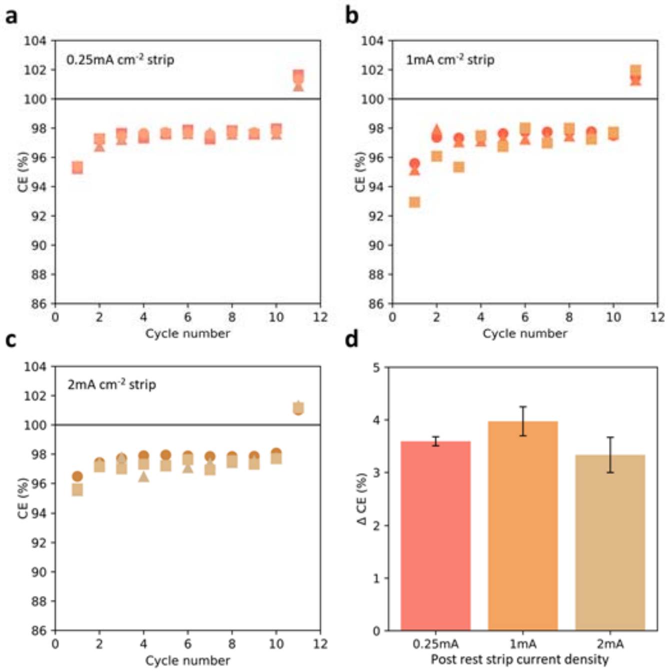
**Supplementary Fig. 2:** CE of Li||Cu half-cells running on the hybrid cycling protocol with 1M $LiPF_6$ EC/DEC + 10% FEC and 4M LiFSI DME electrolytes.



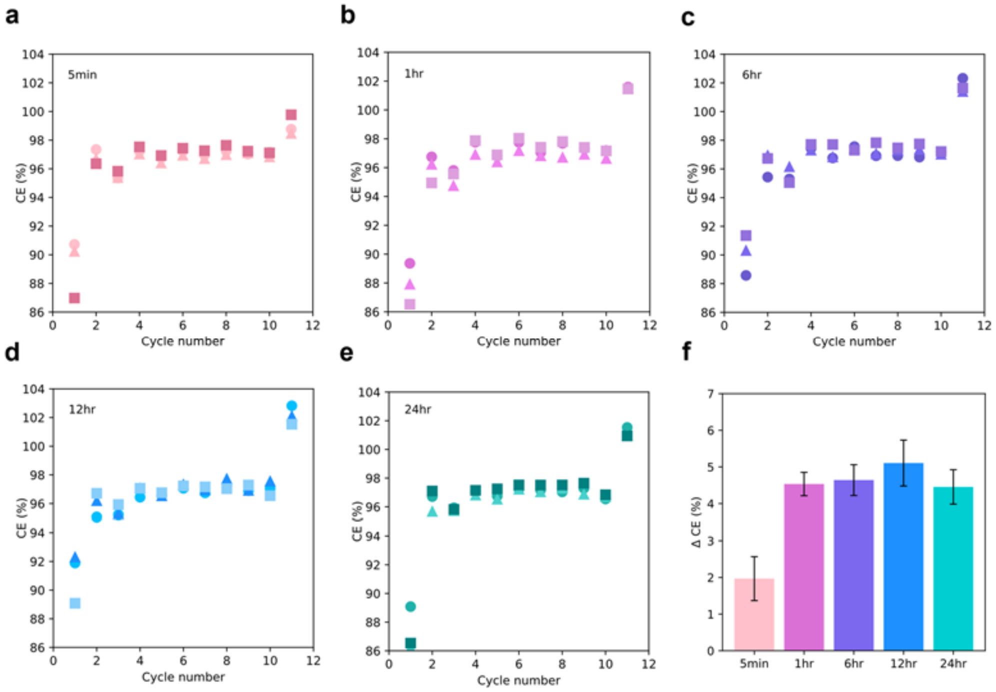
**Supplementary Fig. 3:** CE of Li||Cu half-cells running with LHCE on the hybrid cycling protocol with deposition capacities of 0.3mAh, 1mAh and 3mAh.



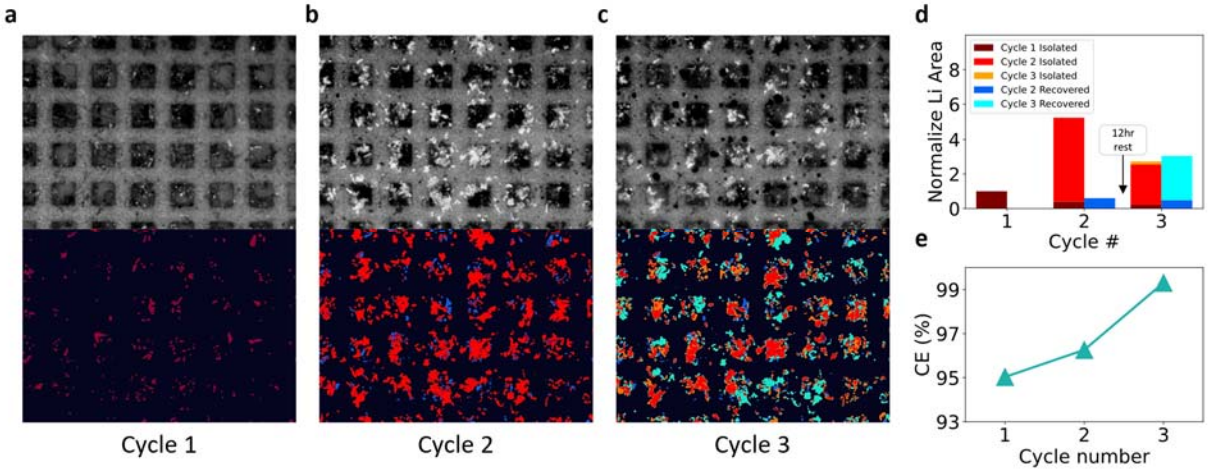
**Supplementary Fig. 4:** CE of Li||Cu half-cells running with LHCE on the hybrid cycling protocol with various 11th cycle strip current densities of 0.25mA $cm^{-2}$, 1mA $cm^{-2}$ and 2mA $cm^{-2}$.



**Supplementary Fig. 5:** CE of Li||Cu half-cells running with LHCE on the hybrid cycling with various 11th cycle rest times of 5 minutes, 1 hour, 6 hours, 12 hours and 24 hours.



**Supplementary Fig. 14:** Colored areal maps of dead and recovered Li for the end of each cycle in the discharged state with cycle 3 discharged at a current density of 0.67mAh cm$^{-2}$. Maroon, red, and orange correspond to inactive Li formed from cycle 1, 2 and 3 respectively. Blue and cyan correspond to recovered Li from cycles 2 and 3 respectively. Optical cell utilizes LHCE.



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16. Merrill, L.C. et al. Role of Coatings as Artificial Solid Electrolyte Interphases on Lithium Metal Self-Discharge. *J. Phys. Chem. C* **126**, 17490-17501 (2022).

**Reviewer Reports on the First Revision:**

Referees' comments:

Referee #1 (Remarks to the Author):

Zhang et al. proposed a Li recovery strategy by simple cycling protocol, which is of novelty and importance. Additionally, we thank the authors for point-to-point responses to our questions. Though we still have some different understanding in terms of the relation among Li corrosion and Li reconnection, this manuscript after revisions fits better with the high scope of Nature. After carefully reading the revised manuscript and response letter, we would like to support the publication of this work after addressing several remaining concerns below.
1. When referring to literature on Li recovery, several strategies have been proposed, such as electrode polarization, redox mediators. Such strategies are suggested to be classified and discussed (e.g., chemical recovery, electrochemical recovery, physical reconnection) to indicate the advances and significance in the studies of Li recovery.
2. The Li recovery is validated in anode-free Li metal batteries. Can such a finding be extended to typical batteries with Li metal anodes (e.g., LiFePO4 | Li)?
3. It's wondering whether the properties of current collector/substrate will influence the reuse of isolated Li in addition to the cycling protocol. Can the author provide some prospects on this perspective referring to the relevant publications (e.g., supplementing extra conductive network of metal nanoparticles).
4. In figure 4i, cells with and without rest exhibited similar cumulative capacity loss in the initial 10 ~cycles, while great difference can be observed in the following cycling. What's the reason?
5. Li of 2 mAh (~ 10 µm) has been lost after 200 cycles even with the adoption of discharge resting. In anode-free and Li-limited full cells, the practical significance of such an electrochemical protocol for long-life batteries remains to be further validated. Additionally, the cycling capacity profiles of LiFePO4 anode-free cells should be supplemented.
6. TGC is reported to be able to quantify the Li0 and Li+ in the isolated Li. In the selected electrolytes of this work, is Li0 the dominant component compared to Li+, which will largely decide the significance of Li recovery by reconnection.

Referee #2 (Remarks to the Author):

The reviewer is satisfied with the revisions and supportive of publication.

## Author Rebuttals to First Revision:

# Response to Reviewers for "Recovery of Isolated Lithium Through Discharged State Calendar Aging"

We are very grateful to the reviewer for providing valuable feedback that improves our paper. The comments and questions raised by the reviewer have helped us clarify our arguments and spark thoughts about future work. We respond to each question raised by the reviewer in blue, and highlight the changes made to our manuscript and extended data in yellow for

Referees' comments:

Referee #1 (Remarks to the Author):

1. When referring to literature on Li recovery, several strategies have been proposed, such as electrode polarization, redox mediators. Such strategies are suggested to be classified and discussed (e.g., chemical recovery, electrochemical recovery, physical reconnection) to indicate the advances and significance in the studies of Li recovery.

*This is a great point. We have classified prior Li recovery work into their distinct categories of electrochemical and chemical strategies to parse out their contributions. Additionally, we further distinguish our Li recovery mechanism as a physical and electrochemical process in which dissolution of residual SEI during discharged resting (physical change) lessens the physical barriers to Li reconnection enabling increased isolated Li recovery on the next plating cycle (physical/electrochemical change). To address this point, we have added the following section to the main manuscript:

**Revised text on page 2, line 39:** To combat LMB capacity loss, recent studies have unveiled new techniques to recover capacity in LMBs previously thought to be irreversible. Electrochemical strategies include applying high discharge current densities to promote dynamic spatial migration of i-Li towards reconnection with the electrode.[1] Chemical strategies include using iodine redox to free Li trapped in SEI and i-Li[2] and employing polymer coatings to preferentially induce Li-ion reduction to Li metal to increase the probability of i-Li reconnection. [3]

**Revised text on page 4, line 229:** The reactivation of i-Li is both an electrochemical and physical process which requires plated Li metal to break through the SEI and reconnect with the i-Li. Therefore, Li plating morphology, which affects the surface area and force applied on i-Li, can affect i-Li recoverability. This work introduces an additional physical process of r-SEI dissolution during discharged resting to promote increased i-Li reconnection and recovery.

2. The Li recovery is validated in anode-free Li metal batteries. Can such a finding be extended to typical batteries with Li metal anodes (e.g., LiFePO4 | Li)?

*We thank the reviewer for the comment. Our electro-physical Li recovery mechanism could be applicable for Li metal anodes ($LiFePO_4$ | Li) as isolated Li will still be generated during cycling. However, this will not be observed in the electrochemical cycling data as the CE will always be close to 100%, due to the excess Li metal reservoir in anode of $LiFePO_4$ | Li cells. However, once the active excess Li is consumed during cycling leaving only isolated Li and SEI on the anode, the discharge rest protocol can be implemented to recover some isolated Li capacity, extending the cycle life of the LMB. The following section has been appended to the main manuscript to address the reviewer's question.

**Revised text on page 3, line 168:** The discharge resting protocol may also be relevant for full cells with excess lithium. Once the active excess Li is consumed during cycling leaving behind isolated Li and SEI, discharge rest can potentially enable recovery of some isolated Li capacity to prolong cycle life. However, the investigation of discharge resting in different cell formats is left as a subject of future studies.

3. It's wondering whether the properties of current collector/substrate will influence the reuse of isolated Li in addition to the cycling protocol. Can the author provide some prospects on this perspective referring to the relevant publications (e.g., supplementing extra conductive network of metal nanoparticles).

*This is also another great point. We believe the properties of the current collector / substrate will have a significant effect on isolated Li recovery. Previous reports have shown that current collector modifications can effectively change Li plating morphologies[3,4]. Since the reconnection depends on plated Li physically reconnecting to dead Li, the shape of the subsequent plated Li (hence plating morphology) will affect the amount of isolated Li recovered. For example, modified current collector that generate "chunky" Li metal plating morphology could potentially result in more Li recovery (after discharge resting), due to a higher Li metal coverage and a higher chance of dead Li reconnection. However, further study is needed to investigate the full effects of current collector modifications on isolated Li recovery through discharge resting. To address this point, we have added the following in the main manuscript:

**Revised text on page 4, line 232:** This work introduces an additional physical process of r-SEI dissolution during discharged resting to promote increased i-Li reconnection and recovery. Components such as current collector[4] or coatings[5] can also be designed to alter Li morphology to increase efficiency of i-Li recovery. The investigation of cell component modification for i-Li recovery is a potential avenue for future studies.

4. In figure 4i, cells with and without rest exhibited similar cumulative capacity loss in the initial 10 ~cycles, while great difference can be observed in the following cycling. What's the reason?

*From the cumulative capacity loss plot (figure 4i), it may not be too apparent that there is a significant difference in the first 10 cycles. However, the plot of CE vs. cycle index (from which the cumulative capacity loss plot is calculated from, extended_source_data_Fig8c) show that the difference in CE between Li || Cu cell cycled with discharge resting compared to continuous cycling are much higher in the 1st to 10th cycle compared to between the 101st to 110th cycle. Additionally, the difference in the cumulative capacity loss in the first 10 cycles while smaller are not significantly different from the subsequent grouping of 10 cycles. Cells with and without rest exhibit a difference in cumulative capacity loss of 0.069mAh for cycles 1-10, 0.076mAh for cycles 11-20, 0.084mAh for cycles 21-30 and 0.069mAh for cycle 31-40 (calculated from source_data_Fig4i). Cells running on the discharged resting protocol have a smaller pool of isolated-Li to recover from during initial cycles compared to later cycles; this can be a contributing factor to why the initial 10 cycle cumulative capacity loss difference is smaller than that of later cycles.

5. Li of 2 mAh (~ 10 μm) has been lost after 200 cycles even with the adoption of discharge resting. In anode-free and Li-limited full cells, the practical significance of such an electrochemical protocol for long-life batteries remains to be further validated. Additionally, the cycling capacity profiles of LiFePO4 anode-free cells should be supplemented.

*This is a great insight by the reviewer on the significant loss accrued in Li||Cu coin cells. While futures studies are needed to further optimize such a protocol for commercial use, the switching of form factors from Li||Cu coin cells to anode free pouch cells (Extended Data Fig. 1b) significantly increase the baseline CE > 99% in just the first 10 cycles while still displaying i-Li recoverability with CE > 100%. This improvement in initial cycle performance can decrease the overall capacity loss over long term cycling. However, as the reviewer pointed out, further investigation into the effect of cathode loading, N/P ratio, electrolyte amount etc… on Li recovery will determine and validate the practicality of discharge resting for long life Li metal batteries. Additionally, we have added the cycling capacity profiles to the extended data Fig. 8b as requested.

6. TGC is reported to be able to quantify the Li0 and Li+ in the isolated Li. In the selected electrolytes of this work, is Li0 the dominant component compared to Li+, which will largely decide the significance of Li recovery by reconnection.

*Based on previous work using TGC to quantify Li capacity loss[5,6], it was shown that at CE >95%, majority of the capacity loss is due to SEI formation and growth (hence Li+). Based on our results in this work using LHCE and 4M (both of which has CE >95%), significant boost in CE can be observed using our discharge resting protocol to recover isolated Li. This suggests that even in high performing electrolytes, i-Li formation can entail a significant portion of the overall capacity loss. Ultimately, we believe that both SEI formation (and growth) and dead Li generation needs to be minimized to achieve cycle life (CE > 99.99%) that is practical for commercial deployment. To address this point, we have added the following in the main manuscript:

**Revised text on page 3, line 104:** While SEI generation is the dominant pathway for capacity loss in high performance electrolytes such as LHCE, the loss of 0.175mAh to i-Li formation over 10 cycles demonstrates the significance of capacity lost to Li disconnection and the importance of minimizing and reactivating i-Li even for high performing electrolytes.

## Reference

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2. Jin, C. et al. Rejuvenating dead lithium supply in lithium metal anodes by iodine redox. *Nat. Energy* **6**, 378-387, (2021).

3. Ma, C. et al. Chemically Induced Activity Recovery of Isolated Lithium in Anode-free Lithium Metal Batteries. *Nano Lett*. **22**, 9268-9274 (2022).

4. Oyakhire, S.T. et al. Electrical resistance of the current collector controls lithium morphology. *Nat. Comm.* **13,** 3986 (2022).

5. Xiang, Y. et al. Quantitatively analyzing the failure processes of rechargeable Li metal batteries. *Sci. Adv*. **7**, eabj3423 (2021).

6. Fang, C. et al. Quantifying inactive lithium in lithium metal batteries. *Nature* **572**, 511-515 (2019).