Operando ^{1}H MRI reveals dead lithium in a symmetric Li|Li cell

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Introduction: Reversibly plating and stripping lithium metal holds promise for high-energy-density batteries but is plagued by the formation of dendritic structures that compromise safety and cycle life. Indirect ^{1}H MRI, which images the proton-rich electrolyte displaced by metallic deposits, offers a non-invasive, three-dimensional view of dendrite morphology and evolution [1]. Here, we apply this technique to a symmetric Li|Li cell undergoing a plating–stripping cycle, enabling direct visualization of dendrite growth and dissolution in situ. By tracking volumetric changes and tip-velocity dynamics, operando ^{1}H MRI yields quantitative insights into lithium plating kinetics, which can be then used to evaluate electrolyte performance and the transient processes underlying dendrite formation.

Methods: A symmetric Li|Li cell (electrode gap 15 mm, 1 M $LiPF_6$ in EC:DMC) was imaged using a four-echo RARE sequence, while a galvanostat supplied ±1.5 mA; current was reversed after 20 h. Binary dendrite masks were generated by histogram-based thresholding and connected-component filtering, yielding time-resolved volumes, tip-velocity maps, and front heights.

Results and discussion: Dendrites nucleated as dense "moss" and transitioned to branched structures within ~10 h, consistent with a Sand's time prediction of 4.7 h at the applied current. Front height on the initially plated electrode reached ≈ 5 mm, with tip velocities in line with the predictions of Chazalviel [2]. Upon current reversal, only the freshest dendrite tips dissolved, indicating lithium passivation by SEI. The counter-electrode then grew new dendrites that mirrored the first cycle. Volumetric growth rates and tip velocities in the second half-cycle exhibited a slight delay, likely due to a present Li^+ concentration gradient.

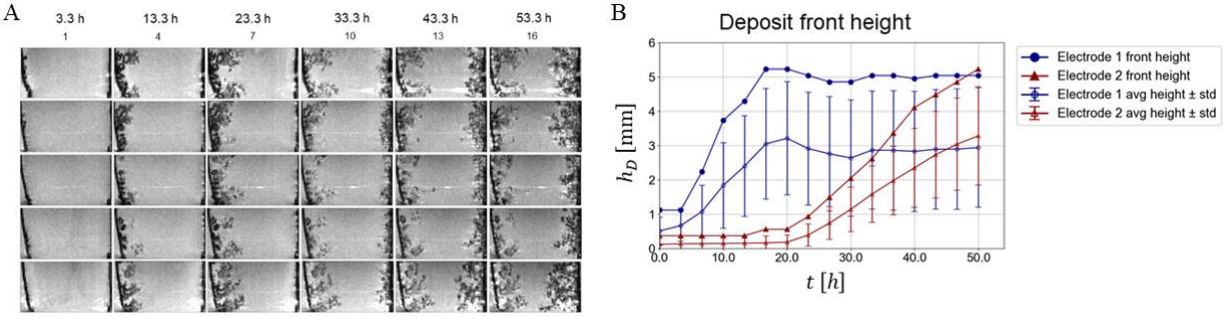

Figure 1. (A) Time-lapse of MRI slices at various depths. (B) maximum and average front height of the deposits.

Conclusion: Operando ^{1}H MRI directly shows that polarity reversal strips only the most recently deposited lithium, leaving a substantial "dead-Li" structure in place. Although tip velocities and bulk growth rates are unaffected by the reversal, the persistent scaffold poses a continuing short-circuit risk. These findings highlight both the diagnostic power of ^{1}H MRI for battery research and the limited efficacy of simple current-reversal protocols at rehabilitating lithium-metal anodes. Future work will combine simultaneous impedance spectroscopy and ^{7}Li concentration mapping to correlate the electrochemical and structural signatures of inactive lithium.

References:

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