

## Lithium Dendrite Inhibition on Post-Charge Anode Surface: The Kinetics Role

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### ABSTRACT

We report experiments and molecular dynamics calculations on the kinetics of electrodeposited lithium dendrites relaxation as a function of temperature and time. We found that the experimental average length of dendrite population decays via stretched exponential functions of time toward limiting values that depend inversely on temperature. The experimental activation energy derived from initial rates as  $E_a \sim 6-7$  kcal/mole, which is closely matched by MD calculations, based on the ReaxFF force field for metallic lithium. Simulations reveal that relaxation proceeds in several steps via increasingly larger activation barriers. Incomplete relaxation at lower temperatures is therefore interpreted a manifestation of cooperative atomic motions into discrete topologies that frustrate monotonic progress by ‘caging’.

**Keywords:** Lithium Dendrites, Kinetics, Activation Energy, Annealing.

### INTRODUCTION

Wireless revolution and need for harnessing intermittent renewable energy sources, has created an exponential demand for energy storage devices such as batteries that require long-lasting storage capacity and high-power delivery during last decade [1]. Lithium ( $\text{Li}^0$ ), particularly, anode candidate material with an ideal energy density of 3862 mAh/g, could drastically satisfy this demand. However, due to its relatively low surface energy, it has very high propensity to grow dendrites during consecutive recharging. This phenomenon eventually leads to short-circuiting, overheating the cell and possible ignition of the organic electrolyte as well as creating isolated ‘dead lithium’ crystals. [2]

The current reports have investigated the effect of charging method, [3, 4] current density [5-7], electrode surface morphology [8-10], solvent and electrolyte chemical composition [11-13], electrolyte concentration [5, 14] on dendrite growth. Other methods include the use of powder electrodes [15] and adhesive polymers [16]. Recent studies have tried to explain the dendrite evolution mechanism [17] and have offered impurities as dendrite initiation drive [18, 19]. Current modeling frameworks involve simplifying assumptions that may have fallen short of capturing the comprehensive essentials of dendrite growth. [7, 20, 21]

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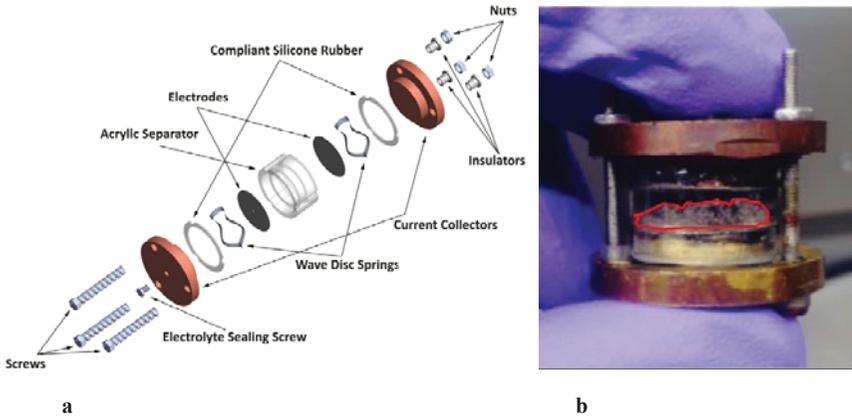
Although the ongoing research tends to extend the battery energy density by developing Lithium-Air and lithium-Sulfur batteries, the dendrite problem remains as a challenging issue in all kinds of rechargeable batteries. [22, 23]

Temperature is a highly accessible parameter with foremost important effect in kinetics. It has been found that cycling at higher temperatures (from -500C up to 400C) can, on average, cause more frequent short-circuiting events up to a factor of 2 [24]. Other results show that the increasing cell temperature enhances the ionic mobilities in favor of dendritic inception and growth [25]. [5, 26] reported that the higher temperatures extends ion depletion layer length which is in agreement with temperature dependence of reaction rates[6]. [27] also pointed out that the probability of ionic reduction in the electrode surface correlates directly to the temperature. In contrast,[28] found that imposing higher temperatures reduces dendrite growth rate relatively to the electrode surface, and could result in more uniform deposition. Although all those approaches are helpful, it is apparent that further progress in tackling this crucial issue should accrue from a full understanding of the dynamics of dendrite growth on Li-metal electrodes. [12, 29, 30]

In our recent work, we have found that applying higher anodic temperatures has a destructive effect for growing dendrites during charging periods [31] and show experimental evidence that higher temperatures during electrodeposition can reduce lithium dendrites to a considerable amount. Acquiring the inherent structural properties of lithium dendrites is one of the hardest problems in the literature and obtaining the energy barrier for the annealing process would represent the dominant coordination number in the dendrite structure. In this paper, we characterize the post-charge annealing of the electrodeposited lithium dendrites and we explain reasons leading to such reduction in details from QM insights.

## **EXPERIMENTAL**

We have used unique manually-made cells for in situ observation and measurement of electrolytic  $\text{Li}^0$  deposits (Fig. 1-a). The cell components and details of the fabrication process have been described before.[32] Round disk electrodes (Area =  $1.6 \text{ cm}^2$ ) were punched from a  $\text{Li}^0$  foil (Aldrich, 99.9%, 0.38 mm thick) that had been cleaned of oxide layers by scraping with a blade and dimethyl carbonate (DMC) in a glove box sparged with argon ( $\text{H}_2\text{O}$ ,  $\text{O}_2 < 0.5 \text{ ppm}$ ). The disk electrodes were mounted on silicone gaskets and pressed against a polymethylmethacrylate (PMMA) electrode separator that kept them  $L = 3.175 \text{ mm}$  apart. The electrolyte, 1 M  $\text{LiClO}_4$  (Aldrich, battery grade, 99.99%, dried for 24 hours at  $90 \text{ }^\circ\text{C}$  under vacuum) solution in propylene carbonate (PC) (Aldrich, 99.7% Anhydrous) was injected into the cell, whereupon the opening was sealed with a Teflon plug.



**Fig. 1: (a)** Component-level view of the cell. **(b)** Dendrites observed by naked eye (red enclosure) from the PMMA separator.

We prepared four oil baths of different thermostated temperatures, using the beakers in the top of hot plates. Simultaneously, four cells were fabricated with the aforementioned procedure and were charged at the rate of  $i=2\text{mA}/\text{cm}^2$  for 24 hours ( $Q=48\text{mAh}$ ) in ambient condition using Biologic instruments (SP-50, VSP). The cells were disconnected, rinsed with isopropyl alcohol and the initial optical observations were done on the post-charge anode surface.

Subsequently, the cells were inserted in the oil baths temperatures and every 24 hours they were taken out and the optical observations on the dendrites are repeated in the cell perimeter. The dendrites lengths typically spanned from  $200\ \mu\text{m}$  to  $3000\ \mu\text{m}$  enabling to observe them with naked eye (Fig. 1-b). The lengths and multiplicities  $[\lambda_i, p_i]$  of the 45 dendrites were measured in series of experiments. The figure of merit is defined as the average weighted lengths of measured dendrites normalized to interelectrode distance  $L$ :

$$\bar{\lambda}(T, t) = \frac{1}{L} \sum_{i=1}^n \lambda_i p_i \quad (\text{E1})$$

where

$$\sum_{i=1}^n p_i = 1 \quad (\text{E2})$$

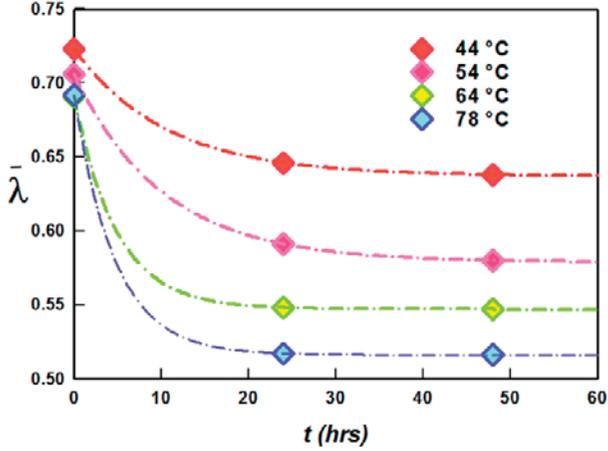


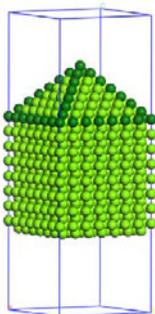
Fig. 2: Average dendrite length  $\bar{\lambda}$  versus bath temperature for 4 various bath temperatures during 48 hours post-charge period.

## SIMULATIONS

We have used the Reactive Force Field (*ReaxFF*) for simulating and verification of experimental results which is based on bond order [33] and we have trained reactive force field model for lithium subsequently<sup>1</sup>. [34]

Due to amorphous nature of lithium dendrites we have considered an ideal case of initial pyramid morphology that consists of 15 layers of Li bulk ( $7 \times 7 \times 15$ ) and 6 layers of Li pyramid leading to single atom tip (Fig. 3). The size in x and y direction is  $24.57 \text{ \AA}$  and in z direction is  $38.61 \text{ \AA}$ . A  $30 \text{ \AA}$  vacuum space is built to avoid the interactions between the slab and its images. Since nano-scale structures usually exhibit very low melting point comparing with that in bulk phase, we fixed the bottom ten layers to avoid the unrealistic melting.

<sup>1</sup> Simulation parameters available upon request.



**Fig. 3:** The simulation pyramid tip model. (24.57 Å x 24.57 Å x 38.61 Å)

Using the optimized structure we relax the x and y direction at 50 K to adjust the pressure to 1 bar by expanding or compressing the box in x and y directions. The obtained structures were then heated up to target temperatures, 350K, 400K and 450K during 200 ps NVT (i.e. constant number of atoms, volume and temperature) calculations, 0.25 fs time step, were carried out at evaluated temperature using Nose hover temperature control with a damping constant of 25 fs. [35] The simulation parameters are given in Table 1.

x, y dimension (Å)	24.57
z dimension (Å)	38.61
Cube layers	7x7x15
Tip layers	15
Domain width (Å)	24.57 × 24.57
Domain height (Å)	10.53Å
Target temperatures (K)	350, 400, 450 (-melting point)
Simulation time (ps)	200
Simulation time step (fs)	0.25
Damping constant (fs)	12.5

**Table 1:** Model parameters

## DISCUSSION

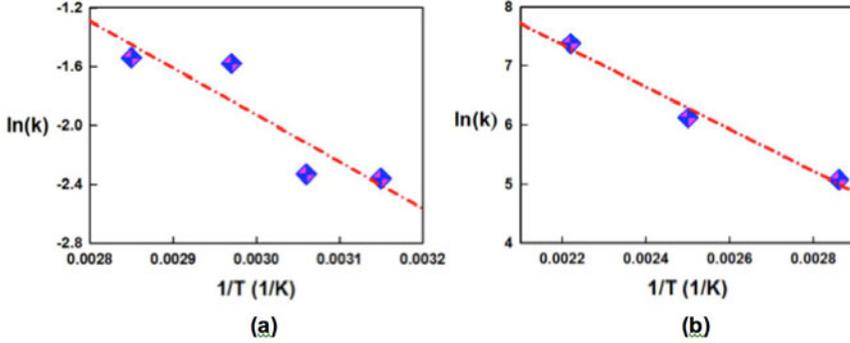
We interpret that the degradation (reduction) of lithium dendrites follows the first-order kinetics and we ascribe the following:

$$\bar{\lambda}(T, t) = \lambda_{\infty} + a \exp(-k(T) t) \quad (\text{E3})$$

The reduction rate  $k$  in our experiments shows to be affected by temperature  $T$ . Considering Arrhenius relation for kinetics, we have the following equation:

$$k(T) = k(T_0) \exp\left(\frac{E_a}{k_B} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad (\text{E4})$$

Hence by plotting the  $\log(k)$  versus temperature reciprocal  $1/T$  we can interpret the exponential coefficient. (Fig. 4)



**Fig. 4:** Interpolation of experimental (a) and computational (b) annealing of dendrites versus reciprocal of temperature with first order Arrhenius kinetics. The effective activation energies  $E_a$  are  $6.3 \pm 2.1$  kcal/mole and  $7.1 \pm 0.9$  kcal/mole respectively.

The experimental results revealed that typically shorter dendrites were formed at higher imposed temperatures (Fig. 2) which are consistent with previous studies [24, 28]. It's also apparent that average dendrite length,  $\bar{\lambda}$ , versus time  $t$  in certain temperature,  $T$ , converges to a constant. This trend is expected as letting the system sit for considerably higher time will saturate the system and all possible re-arrangements have been done.

Additionally, the calculated energy barrier is for surface diffusion (9.715 kcal/mole) in is lower than the bulk diffusion (11.185 kcal/mole). However, the difference is so small, it is highly possible that both of these mechanisms occur in the realist conditions.

## CONCLUSIONS

In this paper, we observed the reduction of lithium dendrites in higher temperatures. We calculated the activation energy of 6-7 kcal/mole for dendrites annealing to more stable and toward crystalline phase. We verified the energy barrier via developing a ReaxFF model. The result is useful for understanding the structural propertie and kinetics. Further work is under progress to understand the mechanism of reduction and evolved instabilities before dendrite collapse.

## ACKNOWLEDGMENTS

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