

## Full paper

## Lithium dendrite growth mechanisms in liquid electrolytes



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## ABSTRACT

A unified theoretical framework of dendrite growth kinetics has been developed to account for the coupled effects of electrodeposition, surface tension, and elastic and plastic deformation. The contribution of each driving force is assessed to identify five regimes of lithium growth: *thermodynamic suppression regime*, *incubation regime*, *tip-controlled growth regime*, *base-controlled growth regime*, and *mixed growth regime*, in agreement with the experimental scientific literature. *Tip-controlled growth* shows a linear time-dependence, while *base-controlled growth* shows an exponential time-dependence. A minimum in the growth rate, as a result of the reaction energy barrier increase imposed on the interface by the local elastic energy, is identified in the *mixed growth regime*. Further, two characteristic times are identified: the characteristic deposition time,  $t_d$ , which defines the critical time scale necessary to overcome the electrochemical energy barrier for nucleation, and the characteristic plasticity time,  $t_p$ , which corresponds to the time scale necessary for plastic flow to occur, given a local shear stress. Examples of experimentally reported transitions between *tip-controlled growth* and *base-controlled growth* are readily captured through the proposed framework. While one or more mechanisms may dominate the growth of the electrodeposit, the proposed formulation defines a road map to design dendrite-free, lithium-based anodes as a stepping stone to identify alternate dendrite-free chemistries.

## 1. Introduction

The growth of metallic lithium deposits, broadly referred to as “dendrites,” is a major roadblock in the commercialization of high power and energy lithium-ion batteries [1,2], as well as the emergence of lithium anode-based and lithium-air batteries [3,4]. For currently used commercial graphitic anodes in lithium-ion batteries, dendrites pose a serious safety concern and have resulted in catastrophic failures, particularly at high current densities [5]. In all cases, the safety and performance of existing and emergent rechargeable batteries will determine their success tied to the survival of nascent markets of electricity-based technologies, such as of electric vehicles [6], which would greatly benefit from lithium metal anodes, and the possibility to reduce the charging time from the present 4 and 36 h to 10 min [7,8]. While there has been significant progress in the fast-charging infrastructure, the dendrite growth problem remains the primary bottleneck to implement high energy, fast charging batteries. In this context, thin film (3  $\mu\text{m}$ ) lithium anode batteries have been developed; however, to make them dendrite-free, alternate approaches are required to bring this technology to the main stream [9–11].

Fundamentally, the problem of dendrite growth remains largely unsolved due to the fact that, unlike copper or zinc electrodeposition, lithium grows at current densities one hundred times lower than the

limiting current density, and shifts between, what appears to be, multiple growth mechanisms reported over a wide variety of time and length scales [12]. The inherent electrochemical instability of lithium metal in organic liquid electrolytes, combined with the underlying multiphysical and microstructural complexity of the local environment that each dendrite is subjected to, contributes a great deal of complexities that demand a basic science identification of the individual mechanisms that control its stability and kinetics. These mechanisms result in different lithium morphologies that determine whether the sandwiched separator will be able to arrest the dendrite, or if the dendrite will dissolve back into the electrolyte.

Fig. 1 shows a catalog of electrodeposition experiments where the dendrite was reported to grow either as *tip-controlled* or *base-controlled*. For example, Brissot and Chazalviel reported two regimes of lithium growth, (see ● in Fig. 1): needle-like at low current densities (0.05  $\text{mA}/\text{cm}^2$ ) after 38 h [13], and “arborescent” for high current densities (0.7  $\text{mA}/\text{cm}^2$ ) after 2300 s [14]. Dollé et al. (see ◀ and ▶ in Fig. 1) reported that a single charge cycle at 0.22  $\text{mA}/\text{cm}^2$  produced mossy deposits, while a single charge cycle at 0.5  $\text{mA}/\text{cm}^2$  resulted in elongated dendrite-like microstructures [15]. Orsini et al. demonstrated the growth of lithium microstructures on lithium, copper, and graphite substrates [16]. It was reported that on both lithium and copper, mossy growth was observed for low C-rates (C/5, 0.45  $\text{mA}/\text{cm}^2$ ), while

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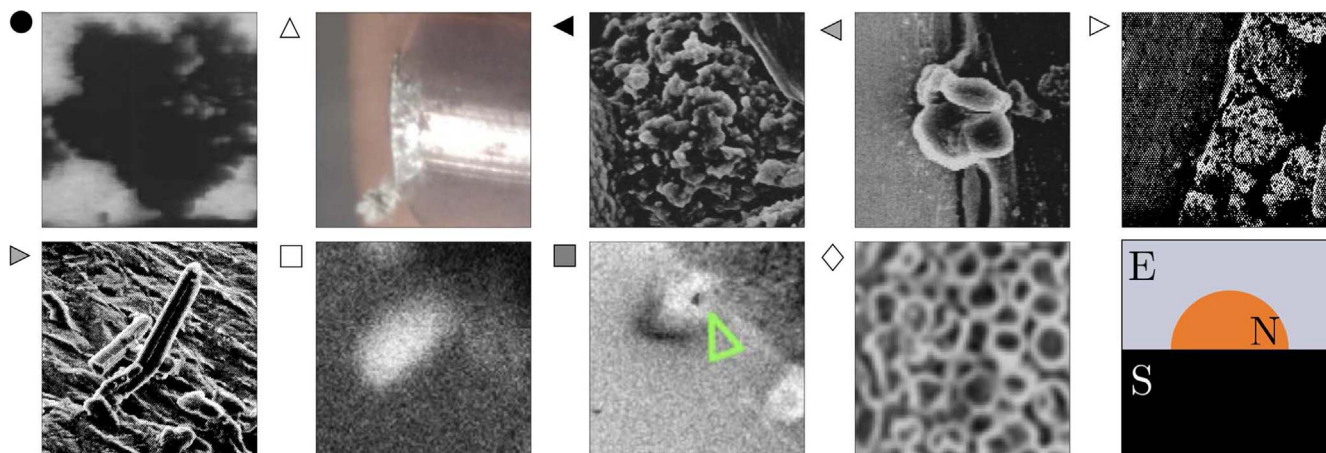


Fig. 1. Catalog of different dendrite microstructures. Experimental results illustrate two main growth mechanisms: *tip-controlled growth* and *base-controlled growth* of lithium electrodeposits, as reported in scientific literature: ● corresponds to experimental data of “bush-like” and “tree-like” dendritic growth for two different applied current densities, as reported by Brissot et al. [14]; △ corresponds to experiments as performed by Crowther and West [19], where the dendrite is initially *tip-controlled* and transitions to *base-controlled growth* at later times; ◀ corresponds to *base-controlled growth* experiments and ▶ to *tip-controlled growth* experiments as reported by Dollé et al. [15]; ▷ corresponds to *base-controlled growth* data and ◁ to *tip-controlled growth* data as reported by Orsini et al. [16]; ◇ corresponds to electrodeposit growth experiments for different applied current densities as reported by Cui et al. [21]; □ corresponds to *base-controlled growth* data and ■ to *tip-controlled growth* data as reported by Li et al. [23]. Finally, bottom right inset shows a schematic representation of a representative hemispherical cap-shaped nucleus, N, deposited on a flat substrate, S, immersed in a liquid electrolyte, E.

dendritic growth was observed at high C-rates (1C, 2.2 mA/cm<sup>2</sup>). However, for graphite anodes, high C-rates (2C, 0.1 mA/cm<sup>2</sup>) only roughened the anode surface. Arakawa et al. were the first to propose that lithium “extrudes” from the base [17]. Experimentally, it was observed that lithium pushes out towards the counter electrode from the base, where the morphology of the tip remains largely unchanged. The authors predicted different morphologies as a function of the Laplace pressure on the electrodeposit and its surface tension. Hollenkamp et al. used Raman spectroscopy to distinguish growth at the tip and from the base and demonstrated that the tip morphology remains unchanged during *base-controlled growth* [18]. Seminal experiments by Crowther and West (see △ in Fig. 1) showed the transition from *tip-controlled* to *base-controlled* in a single galvanostatic recharge cycle [19], where the growth rate was shown to be proportional to the Butler-Volmer current density, consistent with Monroe and Newman [20]. Recent experiments by Cui et al. [21] (see ◇ in Fig. 1) confirmed the observations as well as predictions by Ely [22], and most recently by Bazant, Li et al. [12,23] (see ■ and □ in Fig. 1). Transitions between experimentally reported growth mechanisms from *base-controlled* to *tip-controlled* [12] or from *tip-controlled* to *base-controlled* [19], clearly outline that the mechanisms for growth are a function of the underlying time-dependent conditions that dendrites are subjected to. Also, additional driving forces are at play during dendrite growth due to the lightning rod-like shielding effects of a highly conductive elongated metallic electrodeposit [24,27].

The first dendrite growth model was developed by Barton and Bockris, who proposed that ion transport in front of the dendrite tip is limited by diffusion. The authors demonstrated the existence of a critical overpotential and described the growth of silver dendrites in liquid electrolytes. Diggle and Bockris further extended the model for higher overpotentials and showed transitions between spongy and dendritic morphologies as the overpotential increased [28]. Aogaki and Makino followed a Mullins-Sekerka type description to show dendrite growth due to the electrochemical instability at the electrode interface for diffusion-limited electrodeposition [29,30]. Chazalviel, Fleury, and Rosso demonstrated that dendrites formed due to deviations from electroneutrality at the electrochemical interface [31–33]. Dendrite propagation velocity was shown to be equal to the anion velocity and proportional to the electric field in the electroneutral region of the electrolyte. Dendritic growth was attributed to depletion of ions near the anode interface at current densities higher than the limiting current density. At lower and battery-relevant current densities, Monroe and

Newman predicted the dendrite tip velocity and extended the Butler-Volmer relation to incorporate elastic deformation to assess the separator stiffness necessary to block dendrite penetration [20,34]. Newman also demonstrated the effect of elastic energy on the electrochemical interface to hinder dendrite growth. Ferrese and Newman further incorporated the effects of plastic deformation of lithium and examined lithium movement on the anode during charge-discharge cycles [35–37]. Ely and García rationalized the contributions from these apparently disconnected mechanisms and unified its description into a generalized electrochemical analytical framework that identified three regimes of dendrite stability and growth [22]. Srinivasan et al. recently resolved tensile and compressive stresses and assessed the propensity of dendrite penetration under elastic deformation [38].

In spite of the great deal of experimental evidence highlighting the unequivocal existence of *tip-* and *base-controlled growth* of lithium, there is no fundamental framework that explains clearly the observations. In this context, a generalized electrochemical and chemomechanical theory of dendrite growth kinetics is presented herein that quantitatively identifies the different regimes of lithium growth. Predicted regimes and time-dependent growth behavior are in excellent agreement with experiments that have reported *tip-controlled* and *base-controlled growth*, and the conditions that lead an isolated dendrite to switch from one mechanism to the other one are explained.

## 2. Theory

Define the total Gibbs free energy of transformation of a hemispherical electrodeposit that forms on an electrically charged mechanically stressed substrate, with a contact angle of 90° as shown in the bottom right inset in Fig. 1. Here, the chemical, electrical, and mechanical contributions to the bulk free energy of transformation are embodied by the expression:

$$\Delta G_T = \frac{2\pi}{3} \left( \Delta G_f + \frac{zF\eta}{\Omega} + \frac{1}{2} \overleftrightarrow{\sigma} \cdot \overleftrightarrow{\varepsilon} \right) r^3 + 2\pi\gamma r^2 \quad (1)$$

Used symbols are summarized in Table 1. The state of stress of such an electrodeposit is described by a symmetric rank two tensor, which for a hemispherically symmetric cap is simplified in the diagonalized reference system as,

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