



Research papers

Influence of concentration-dependent diffusivity on lithium plating: Polarization, stability, and dendrite formation in phase-field simulations

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ABSTRACT

Lithium dendrite issues significantly impede the development of high-energy-density secondary batteries with a lithium anode. The widely-used classical Sand's limiting current density, predicting lithium dendrite formation during plating, relies on constant diffusivity. However, overlooking realistic ion transport dynamics, like concentration-influenced diffusivity, often results in discrepancies between analytical predictions and experiments. To better understand the origin of the observed inconsistency, our study presents a phase-field method for solving the dynamics of ion transport in electrolytes during anode surface migration in plating. The model integrates the Stewart–Newman diffusivity for concentration-influenced ion transport dynamics and the Butler–Volmer equation for electrochemical kinetics at the anode-electrolyte interface. In addition to phase-field simulations, we performed a steady-state analysis of the concentration distribution in electrolytes, determining the limiting current density. Verification confirms strong agreement between the phase-field model and analytical predictions. Our two-dimensional phase-field simulations further reveal that the varying diffusivity, dependent on concentration, plays a crucial role in plating stability and the resulting lithium morphology. Results of this study provides valuable insights for resolving the observed discrepancies in the onset of lithium dendrite formation between experiments and the classical Sand's formula.

1. Introduction

Lithium metal, owing to its high theoretical capacity and low electrode potential, shows promise as an anode material for next-generation high-energy-density secondary batteries [1–4]. However, its high reactivity with electrolytes often leads to unstable plating, causing irregular deposits known as lithium dendrites during battery cycling. The appearance of lithium dendrites presents challenges to the safety and performance of the battery, contributing to increased impedance, reduced energy capacity, shortened lifespan, and the risk of short circuits and cell explosions. Hence, the dendrite formation is a primary issue that needs to be resolved before the commercialization of the batteries coupled with a lithium anode [5,6].

Experiments discovered a strong correlation between dendrite morphology and plating current density. Examples include tip-growing fractal dendrites at high current densities, surface-growing mossy dendrites at intermediate current densities, and root-growing lithium whiskers at low current densities [7–10]. Among these irregular lithium deposits, fractal dendrites present significant safety concerns since their sharp tips and rapid growth can easily penetrate separators [7–12]. The formation of these dendrites is found to be closely related to the

depletion of ions near the anode surface at a current above a certain threshold [7–10].

During plating, continuous consumption of lithium ions at the anode surface, caused by electrochemical reactions such as ion reduction and electrolyte decomposition, results in a considerable decrease in concentration at the anode surface, particularly at high current densities. Whereas the electrochemical reaction rate is determined by current density, the dynamics of how ions move in the electrolyte is complicated by factors such as electrolyte formulation, additives, salt concentration, and temperature [13–17]. Due to limitations in the electrolyte's ion transport rate, a concentration gradient forms near the anode surface, known as concentration polarization. When the current density exceeds the limiting current density, the rate of lithium-ion consumption at the anode surface surpasses the ion transport rate. This imbalance leads to a depletion of lithium ions at the anode surface over a prolonged plating period. The depletion intensifies non-uniform lithium ionic flux near the surface, promoting a transition from mossy dendrite growth to fractal dendrite growth [18–20].

The limiting current density, serving as a safety threshold for the plating process, defines the onset current density that triggers the

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