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Computational study of electro-convection effects on dendrite growth in batteries

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HIGHLIGHTS

- A mesh-free model is developed to study electro-convection effect on dendrite growth.
- Dendrite growth and flow patterns are qualitatively consistent with previous reports.
- Low viscosity electrolytes can suppress dendrites by increasing ion mass transport.

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ABSTRACT

Dendrite formation on the anode surface of a battery is closely related to the safety and capacity of high energy density batteries, thus suppressing dendrite growth will significantly improve the performance of batteries. Many experimental reports reveal that convection near the dendrite nucleation site can change the local mass transport, and ultimately affect dendrite growth. Investigation of the convection effect in batteries will guide the development of strategies to suppress dendrite growth in a convective electrolyte. Most of the existing electro-convection computational models for dendrite growth studies are based on Eulerian frameworks. These methods have difficulty modeling the moving boundaries associated with dendrite growth and are less computationally efficient in simulating convective fluid motion. In this paper we adopt a mesh-free particle based Lagrangian method to address the challenges of previous grid based Eulerian electro-convection models. The developed model is verified by comparison to analytical solutions, including verification of ion migration and the electric potential. Simulation results show that the predicted dendrite growth and electro-convective flow patterns compare well with experimental results during early dendrite growth stages. Parametric studies reveal that low viscosity electrolytes suppress the dendrite growth by increasing the mass transport of ions near the anode/electrolyte interface.

1. Introduction

Rapid developments in electric-powered-vehicle technologies have significantly increased the demand for high energy density batteries [1,2]. High energy density and longer lifetime batteries are necessary for electric vehicles to achieve practical performance metrics similar to traditional gasoline cars, such as driving range and longevity. Additionally, other applications such as portable electronics and energy-grid backup also require high performance and high volumetric energy density batteries [3,4].

Issues with safety and cyclability currently limit commercial application of advanced high energy density batteries, such as the Lithium-air (Li-air) battery. One main safety and cyclability issue is dendrite formation [5,6]. Dendrites can form on the anode/electrolyte interface after multiple charge/discharge cycles. These formations can: change the scale of the critical physics of the anode; affect the local transport properties; increase Joule heating in the anode; and lead to eventual breakage of the dendrites, which can cause short circuits leading to overheating and potential fires [4,7].

Many computational and experimental studies have investigated dendrite growth suppression [6,8–16], with the main focus of research on improving the operating conditions of batteries, anode surface properties, and ion transport in the electrolyte. Recent publications reveal that electrolytes with tailored properties, such as anisotropic diffusivity or low viscosity, may influence

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ion transport and eventually suppress dendrite growth [14,16].

Experimental studies rely on overall battery performance and imaging of cells after operation to understand the internal physics of the system. Experimental imaging of dendrite growth in an operating battery is very challenging and has only been shown in microscopic cells specifically designed for operation within a microscope [8,17,18]. Computational models can add significant insight into the growth and morphology of dendrites in a battery by resolving the physics at the anode/electrolyte interface. However, due to the complexity of tracking the growth front and the multiphysics nature of the problem, computational models of dendrite growth including convection, migration, and reactions are lacking.

In this paper, we develop a mesh-free particle-based Lagrangian model for the study of dendrite growth in a battery system including the effects of electro-convective flow. The model implementation, e.g., migration and electric potential, are verified individually by comparison with analytical solutions, and the electro-convection dendrite growth model is compared with experimental observations from previous publications. To study the effects of dendrite growth, we perform a parametric study varying the electrolyte viscosities. The results of the parametric study show the same trends as previous experimental reports, and identifies a strategy for suppressing dendrite growth in convective battery systems.

2. Electro-convective flow and dendrite growth in batteries

The basic electrochemical reactions on the anode surface of batteries have the general form [4,19]:

$$A \leftrightarrows A^{+} + e^{-} \qquad [1]$$

As shown in Eq. (1), the direction of the reaction is from left to right during discharge when the anode material A, such as lithium (Li), is oxidized at the anode surface and generates A^{+} (cations) and electrons; conversely, during charge the A^{+} reacts with electrons and deposits solid metal A on the anode surface. At the microscopic scale, the anode surface is heterogeneous, with protrusions and impurities [12,20]. These heterogeneities can serve as nucleation sites for precipitation and have faster deposition rates of cations such as lithium ions (Li^{+}). After several charge/discharge cycles, dendritic structures of the anode metal will form at the surface of the anode, known as “dendrites”.

The mechanism of dendrite growth is complicated and not fully understood but many physical factors including operating conditions and material properties have been reported which can affect dendrite growth in batteries. For example, within a Li battery the morphology of Li dendrites has been shown to be strongly dependent on the charging current densities. Li dendrites are more needle-like under low charging current conditions, and more bush-like under high charging currents [8,20].

One strategy for improving the morphology and uniformity of Li deposition is by tuning the anode surface properties via additives or altering the chemical composition of the surface layer [21–23]. Additionally, the dendrite nucleation is reported to be related to many factors such as the solid electrolyte interface, subsurface structures, crystalline impurities, surface tension, electrochemical overpotential, etc. [3,24,25]. However after initial nucleation dendrite growth is mass transport dominated, which has been shown by several groups. Brissot et al. [20] have shown that the average propagation speed of the dendrite front is close to the drift velocity of Li^{+}, which agrees well with the predictions of the dendrite growth model developed by Chazalviel et al. [9]. Nishikawa et al. have observed that the Li^{+} mass transfer rate governs dendrite growth after initiation [12,17]. A computational model developed by Tan et al. demonstrates that dendrite growth in Li batteries can be suppressed by using anisotropic electrolytes to induce directional transport properties of cations which enhance transport through the electrolyte and limit transport across the anode [16].

Several groups have shown that convection also strongly influences the development of dendritic structures. Huth et al. demonstrated the effects from gravity-driven convection and electric field-driven convection on the growth of dendrites, and showed that gravity driven flow can be reduced by a vertical cell configuration [26]. Mocskos et al. and Marshall et al. have reported the detailed analysis of convection effects on the front evolution as well as the branching competition of dendrites in electrochemical deposition [27,28], using both experiments and computational modeling. Parametric studies of varying electrolyte viscosities by Park et al. [14] and Gonzalez et al. [29] have indirectly revealed a relationship between dendrite growth rate and convection. Applying different electrolyte viscosities will directly change the convection velocity, and therefore change ion transport near the surface of dendrites, affecting dendrite growth.

All the previously mentioned studies indicate the complexity of dendrite growth; especially the effects of operating conditions and material properties of both the anode and the electrolyte on growth rate and morphology. However, most of the factors, such as convection and surface reactions are related to the local cation gradients near the anode/electrolyte interface. Thus, the mass transport of the cations is a crucial factor in dendrite growth.

The computational model presented in this study builds off of our previous development of a reactive-transport dendrite growth model [16], and expands the model to consider the effects of the migration and convection of cations on dendrite growth. Convection in the electrolyte changes the concentration gradient of ions near dendrite nucleation sites, and ultimately affects the dendrite growth. The electro-convection dendrite growth model developed in this study demonstrates the complex effects from migration, convection, and reactions on the growth of dendrites in batteries.

3. Computational model development

To understand the effects of convection in the electrolyte on dendrite growth at the anode surface of a Li battery, a computational model of the anode/electrolyte region was developed. The model focuses on the anode/electrolyte interface where the physics significant to dendrite growth occurs, including the transport mechanisms, such as migration and convection, and surface reactions. The simulation domain includes the anode surface as well as a thin diffusion layer within the electrolyte. A finite diffusion layer near the anode/electrolyte interface is a typical assumption in the study of electrochemical systems [19]. Experimental studies support that the majority of reactive mass transport and electrolyte convection during dendrite growth exists in a thin electrolyte layer (~100 μm) near the anode surface [10,18]. The dendrite growth reaction is assumed to be mass transport limited and a first order precipitation reaction is used (Eq. (1)). The model domain is typical of a thin battery cell with an unsupported, incompressible binary liquid electrolyte.

The model schematic is shown in Fig. 1. The simulation domain consists of the anode surface and a diffusion boundary electrolyte layer of thickness L. The anode surface roughness is exaggerated in Fig. 1 to emphasize the heterogeneous nucleation points on the anode surface. Initially the cations (A^{+}) and anions (B^{-}) are uniformly distributed everywhere so the electrolyte is electrically neutral, once a charge potential is applied, the potential difference between the bulk solution (at $y = L$) and anode ($y = 0$) drives the migration of ions. Anions move away from anode, enter the bulk