Effects of surface tension and electrochemical reactions in Li-ion battery electrode nanoparticles

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HIGHLIGHTS

- A model for stress diffusion regarding intercalation reactions and surface tension.
- Surface tension induces pressure, providing mechanical stabilization.
- Due to pressure, fewer ions can be inserted and more ions can be extracted.
- Ellipsoidal particles allow for faster (dis)charge but have even lower capacity.

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ABSTRACT

The size- and shape-dependency of the chemo-mechanical behavior of spherical and ellipsoidal nano-particles in Li-ion battery electrodes are investigated by a stress-assisted diffusion model and 3D finite element simulations. The model features surface tension, a direct coupling between diffusion and elasticity, concentration-dependent diffusivity, and a Butler-Volmer relation for the description of electrochemical reactions that is modified to account for mechanical effects. Simulation results on spherical particles reveal that surface tension causes additional pressure fields in the particles, shifting the stress state towards the compressive regime. This provides mechanical stabilization, allowing, in principle, for higher charge/discharge rates. However, due to this pressure the attainable lithiation for a given potential difference is reduced during insertion, whereas a higher amount of ions is given off during extraction. Ellipsoidal particles with an aspect ratio deviating from that of a sphere with the same volume expose a larger surface area to the intercalation reactions. Consequently, they exhibit accelerated (dis)charge rates. However, due to the enhanced pressure in regions with high curvature, the accessible capacity of ellipsoidal particles is less than that of spherical particles.

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1. Introduction

Lithium-ion batteries possess a high potential for the storage of renewable energy and for application in hybrid electric vehicles. They exhibit a high energy density and a low weight, making them valuable for application in mobile electronic devices. Major disadvantage of these batteries is, however, their gradual loss of capacity over lifetime. This decay is caused by an interplay of mechanical degradation and chemical corrosion of the battery electrodes, in particular through formation of a solid-electrolyte interphase (SEI)

that increases the electrode resistivity. The growth processes of the SEI are strongly determined by the chosen electrode material and the composition of the electrolyte [1–3]. Mechanical deterioration, on the other hand, is due to the stresses developing in the electrode materials during intercalation, promoting the nucleation and propagation of cracks in the highly irregular particles; the freshly cracked electrode surface is then exposed to electrolyte, allowing further SEI growth [4].

Modeling the electro-chemo-mechanical behavior of the electrodes during intercalation has received wide attention. Based on the early work of Christensen and Newman [5], many researchers have proposed models for diffusion-induced stresses in electrode particles, among them [6–11]. These models commonly assume constant chemical and elastic constants. However, concentration-

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dependent elastic moduli have been shown to be potentially significant for the stresses arising during diffusion [12—14] and for phase segregation phenomena, where they might suppress spinodal decomposition [15].

Many important electrode materials such as Si exhibit large volume changes during a charge cycle. Corresponding formulations of stress-diffusion models for large deformations, incorporating inelastic effects, have been undertaken, among others, by Refs. [16,17]. The interaction of diffusion and mechanical damage is usually formulated as a monolithic continuum model. An alternative has been described by Barai and Mukherjee [18,19], where the mechanical behavior is modeled through a lattice spring network coupled to a continuum diffusion model. This allows for a straightforward incorporation of defects and a study of their interaction with diffusion and phase segregation.

Volumetric expansion of the active material results in delamination of the electrode; particles (and fragments) disconnected from the electrode will no longer contribute to charge storage, which can be observed macroscopically as capacity loss. Such interactions of intercalation reactions, phase segregation, and crack propagation have been studied recently by Zhao et al. [20], who observed not only enhanced reaction rates at phase interfaces, but also demonstrated that the phase segregation processes can drive crack propagation in the electrode material, further exposing material to the (dis)charge reactions.

Studies on diffusion-induced stresses have been performed mostly on free-standing particles such as spheres or ellipsoids, with few exceptions such as grain boundary diffusion [21], polycrystalline samples [22], or realistic particle geometries obtained from image-based techniques [23,24]. External mechanical effects are usually neglected, a noteworthy exception being the recent contribution by Xu and Zhao [25] who investigated the mechanical interaction of particles embedded in a polymer matrix. They have shown that the mechanical influence that the particles exert upon each other does not only affect the deformation behavior of spherical and cylindrical particles, but also the concentration field within the particles. That is, the compressive stresses cause a local concentration reduction. Attempts at modeling a whole electrode respectively parts thereof, albeit without consideration of mechanical effects, are described in Refs. [26—28].

Experimental observations suggest that nanostructured electrodes show a better performance [29] and a higher robustness [30] against chemo-mechanical degradation. For instance, Liu et al. [31] observed a strong particle-size dependence of the fracture behavior of Si nanoparticles during first lithiation. In particular, they found a particle size around 150 nm below which cracking did not occur. In order to predict such critical, damage-free particle sizes many contributions in the field of fracture mechanics have been described, among them [32—37].

This size-dependent behavior can be attributed to surface effects that become significant on sub-micron length scales [38]. Classical models of elasticity cannot represent such size-dependent effects. However, they can be extended correspondingly through incorporation of surface elasticity models, tracing back their origins to the work of Gibbs and the contributions of Shuttleworth [39] and Herring [40]. A mathematical theory of surface elasticity has been established by Gurtin and Murdoch [41]. They considered the surface to be an infinitesimally thin layer around a solid body and formulated elastic relations analogous to solid elasticity. Based on their work, surface elasticity effects have been introduced into a host of mechanical problems. An overview of approaches is beyond the scope of this work; however, the reader should refer to the recent works of Chen and Yao [42] and Javili et al. [43], and the references therein.

Consideration of surface effects in diffusion problems has not

received great attention yet. Cheng and Verbrugge [44] were the first to set up an analytical model for diffusion in spherical nanoparticles under surface tension, with the diffusion however being decoupled from the stress field. They observed a shift of diffusion-induced stresses towards the compressive regime, inducing an asymmetry between the charge and discharge behavior of the particle. Deshpande et al. [45] applied that model to the analysis of stresses in nanowire electrodes. McBride et al. [46] formulated a nonlinear continuum thermomechanical model coupling diffusion to surface elasticity and viscoelasticity. Hao et al. [47], DeLuca et al. [48], Zang and Zhao [49], and Liu et al. [50] applied stress-coupled models for diffusion in order to investigate the stress profiles and the charging behavior of hollow nanowires and, in the case of the latter three, hollow nanospheres. These groups employed either constant-concentration or constant-flux conditions in order to represent the intercalation process, apart from DeLuca et al. [48] who employed a Butler-Volmer model for the surface reaction kinetics. However, they did not include mechanical effects. That is, neither of the reported articles comments on the interaction of bulk mechanical behavior and intercalation dynamics.

Aforementioned approaches focused on spherical and cylindrical geometries. There is however a second, geometric degree of freedom by which one can influence the surface area, namely the aspect ratio. The impact of the particle shape on stress-diffusion has been investigated by Stein and Xu [51]. This study showed that prolate, i.e., needle-like particles can significantly equilibrate diffusion-induced stresses through deformation along their semi-major axis. Stein and Xu [52] later analyzed the pressure distribution in spherical and ellipsoidal particles due to surface tension. In spherical particles they observed a uniform hydrostatic stress field which would have no effect in a stress-diffusion problem, as it is the gradient of pressure that acts as driving force for transport. Within ellipsoidal particles, the pressure field due to surface tension is non-uniform [Ibid.], so one should expect altered concentration profiles and hence a different stress distribution in these particles.

The stress state within a particle further affects both the surface reaction rates [53] and the amount of attainable lithiation [54]. Molina Piper et al. [55] investigated the influence of compressive stress on solid-state battery cells and observed a limited initial capacity of strongly compressed cells which however maintained a high usable capacity over many charge cycles. Considering that surface tension induces compression in the electrode particles, one can expect a similar impact on the electrochemical behavior resulting from surface elasticity.

In order to study the impact of surface tension on the electro-chemo-mechanical behavior of electrode particles, we develop a continuum model for the concentration-dependent diffusion in free-standing particles. The model regards constant surface tension, and the intercalation dynamics are modeled through a modified Butler-Volmer relation accounting for mechanical stresses. It can, in principle, be applied for the description of both anode and cathode particles, but in the scope of this work only cathode particles of $LiMn_2O_4$ are regarded. Implementation of the model is based on Isogeometric Finite Element methods [56], using triquadratic Non-uniform rational B-Spline shape functions. This allows for a smooth geometric description of spheres and ellipsoidal particles as well as for a straightforward numerical treatment of higher-order coupling terms arising in non-classical diffusion problems [15,20,51].

The article is structured as follows: the mathematical model for stress-assisted diffusion under surface tension is described in Section 2. Subsequently, the characteristic features of stress-assisted diffusion in solid and hollow spherical particles under galvanostatic conditions are described in Section 3. Thereby, the size effects inherent to diffusion problems are demonstrated. The modification