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Numerical study of grain boundary effect on Li$^+$ effective diffusivity and intercalation-induced stresses in Li-ion battery active materials

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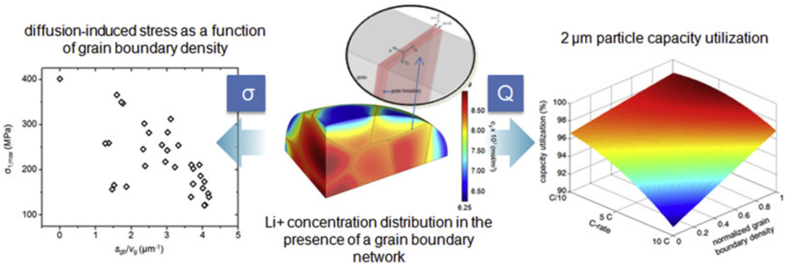
HIGHLIGHTS

- We modeled polycrystalline Li-ion battery active material particles in 3D.
- Developed a FEM approach to capture the effect of grain boundary on Li-ion diffusivity.
- Apparent diffusion coefficient increases with increasing grain boundary densities.
- Grain boundary lowers intercalation stress by reducing the concentration gradients.
- Capacity utilization improves in the presence of a grain boundary network.

GRAPHICAL ABSTRACT



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ABSTRACT

We investigate the grain boundary effect on Li-ion diffusivity and intercalation-induced stress in a single-particle Li-ion cell. The measured activation energy for self-diffusion at the grain boundary is a fraction of that in the lattice due to the loosely packed structure, and this results in a diffusivity that is 3–16 orders of magnitude higher in the grain boundary than in the lattice. To study how grain boundaries affect Li-ion battery performance, grain boundaries are modeled inside ellipsoidal cathode ($LiMn_2O_4$) particles and placed under potentiodynamic and galvanostatic control simulations. A Voronoi grain distribution is employed in modeling grain boundaries. The grain boundary effect on Li-ion diffusivity is evaluated by computing an apparent diffusion coefficient from the cathode particles containing different grain boundary densities. It is shown that the apparent diffusion coefficient increases with increasing grain boundary densities. With enhanced Li-ion diffusivity, particles are found to have higher capacity utilizations, especially under high discharge C-rates. The inclusion of grain boundaries also lowered intercalation-induced stress by reducing the overall Li$^+$ concentration gradients developed within particles during cycling. However, as local Li$^+$ concentration distribution depends on grain boundary network geometries, intercalation-induced stress varied appreciably within the different grain boundary network geometries.

1. Introduction

An ideal secondary battery for hybrid electric vehicles would feature low cost, high gravimetric energy and power densities, an absence of thermal runaway for safety, and minimal capacity

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degradation. High gravimetric power density in particular allows for increased vehicle acceleration and a reduced battery charging time. The power performance of a lithium ion (Li-ion) secondary battery is primarily determined by Li-ion diffusivity in the host electrode materials. In the host electrode material, Li-ion diffusivity is influenced by intercalation-induced stress fields [1–4], phase boundary mobilities [5–7], and crystallographic defects [8,9]. Both thin-film and primary particle Li-ion active materials are polycrystalline materials, which are dense aggregates of single crystals joined by a network of interfacial crystallographic defects known as grain boundaries. It is widely recognized that the grain boundary network in these materials influence their properties, including transport properties. The more loosely packed structures of the grain boundaries result in a higher diffusivity compared to that inside the grain. For polycrystalline materials, the measured activation energy for self-diffusion at the grain boundary is only a fraction of that in the lattice, resulting in a diffusivity that is 3–16 orders of magnitude higher in the grain boundary than in the lattice [10–12]. These experiments have shown that as the average grain size is refined to nanoscale, the grain boundary increasingly dominates the transport properties.

To investigate the grain boundary effect on overall diffusivity, Fisher first modeled a single fast diffusing grain boundary embedded in a semi-infinite bulk of much lower diffusivity [13]. The model and its variants are today widely used in understanding grain boundary diffusion. For simplified polycrystalline geometries, where grain boundaries are lamellar [14] or square matrices [15,16], expressions for an effective diffusion coefficient have been formulated using rules-of-mixture or volumetric averages of the constituent diffusion coefficients. Although the rules-of-mixture method has also been used to study more complex structural effects such as grain size distributions [17] or triple junction densities [18], numerical methods such as molecular dynamics or the Monte Carlo method are more common in studying the effective diffusivity in the presence of grain boundaries. Moreover, effective diffusivities have been classified into different regimes of diffusion kinetics [19,20]. For example, based on the ordering of bulk diffusion length, grain boundary diffusion length, grain boundary thickness, and the average grain size, the overall diffusion kinetics may be determined by grain boundary diffusivity or a mixture of both bulk and grain boundary diffusivities.

Based on various experimental studies, the role of grain boundaries in Li-ion active materials has been postulated. For example, in a $LiCoO_2$ thin-film where grains are oriented in a preferred (0 0 3) direction that lithium ions have difficulty diffusing through, grain boundaries may facilitate lithium ions to diffuse into the bulk [21]. A study with *in situ* scanning probe microscopy (SPM) also showed that the formation of (LiF) particles at the grain boundaries lead to reduced lithium ion flux into the active material, as reflected on cyclic voltammograms [22]. Conversely, other studies suggest that grain orientations have a more significant influence on the overall Li-ion diffusivity than the grain boundary density, especially for materials with two dimensional lattice diffusion mechanisms such as $LiCoO_2$ [23] and V_2O_5 [24]. In one study, using the electrochemical strain microscopy (ESM) method, relatively higher Li^+ diffusivity was observed in certain grain facets and grain boundary-like features in a $LiCoO_2$ thin-film [25]. Another study showed that Sn-containing grain boundaries may be used as intercalation sites among inactive $SnMn_3C$ grains [26]; it demonstrates that grain boundaries may be utilized in controlling large volume expansion/contraction in metal anodes, which lead to energy capacity degradation. Indeed, many Li-ion active materials, including metal-alloys [27,28], $LiCoO_2$ [29], $LiMn_2O_4$ [30], and $LiFePO_4$ [31], undergo reversible lattice expansion during charging/discharging. Hence, internal strains/stresses may develop, leading to a gradual loss of energy capacity by dislocations, microcracks [29,31], or isolation of the active material from the current collector [32]. Several models have been developed to estimate the intercalation-induced stress in Li-ion active materials during charging/discharging [1–3]. These models show that intercalation-induced stress is roughly proportional to the concentration gradient developed in the particle. Because a grain boundary network can modify the concentration distribution within active materials, it would also affect intercalation-induced stress and its associated energy capacity degradation.

Although various postulations have been made in regards to the role of grain boundaries in Li-ion active materials, the effect of grain boundaries in Li-ion batteries has never been studied systematically. This is possibly due to difficulty in controlling the grain boundary density without affecting material phase and grain size/orientation distributions. Furthermore, in composite electrodes, the porosity can complicate the analysis. To study grain boundary effect on Li-ion battery performance, we model ellipsoidal cathode particles embedded with grain boundaries using a finite element method approach. By integrating a Fisher-type grain boundary model with a Li-ion stress-diffusion model, the role of grain boundary on overall Li^+ diffusivity, intercalation-induced stress, and energy capacity utilization is investigated. We have the following objectives:

1. To develop an electrochemical–mechanical model that considers grain boundaries in Li-ion active materials
2. To investigate the grain boundary effect on Li-ion battery performance including lithium ion diffusivity, intercalation-induced stress, and capacity utilization

2. Methods

To investigate grain boundary effect on overall lithium diffusivity as well as intercalation-induced stress, a Fickian diffusion equation coupled with a Hookean stress–strain constitutive equation was solved. Diffusion–stress coupling was achieved by including the elastic energy of the solute in the chemical potential [3,33,34].

Diffusion–stress model in the grain domain – Lithium ion diffusion is driven by the chemical potential gradient. For a given lithium ion concentration and hydrostatic stress gradients, the diffusion flux for a dilute or ideal system is given by Zhang et al. [3]

$$\mathbf{J}_g = -D_g\left(\nabla c_g - \frac{\Omega c_g}{RT}\nabla\sigma_h\right) \tag{1}$$

where subscript g indicates the grain or bulk domain, D_g is the diffusion coefficient, c_g is the concentration, Ω is partial molar volume, R is the universal gas constant, T is temperature, and σ_h is hydrostatic stress, defined as $\sigma_h = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$ (where σ_{ij} is the element in the stress tensor). Substituting Eq. (1) into the mass conservation equation, the following species transport equation in the grain domain was obtained

$$\frac{\partial c_g}{\partial t} + \nabla\cdot\left[-D_g\left(\nabla c_g - \frac{\Omega c_g}{RT}\nabla\sigma_h\right)\right] = 0. \tag{2}$$

In the cubic $Li_xMn_2O_4$ $(0 < x < 1)$ phase, the lattice parameter of the host material was assumed to change linearly with the amount of ions inserted [35]; this results in intercalation-induced stresses. Therefore, the stress can be calculated using a thermal-analogy