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THE USE OF NON-DIMENSIONAL PARAMETERS TO STUDY STRESS IN LITHIUM-ION BATTERY ELECTRODE STORAGE PARTICLES

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ABSTRACT

Mechanical degradation is thought to be one of the causes of capacity fade within Lithium-Ion batteries. In this work we develop a coupled stress-diffusion model for idealized spherical storage particles, which is analogous to the development of thermal strains. We then non-dimensionalize the model and identify three important parameters that control the development of stress within these particles. We can therefore use a wide number of values for these parameters to make predictions about the stress responses of different materials. The maximum stress developed within the particle for different values of these parameters are plotted as stress maps. A two dimensional model of a battery was then developed, in order to study the effect of particle morphology.

INTRODUCTION

As lithium ion batteries are sought to power larger devices with longer lifetimes e.g. automobiles, the need to characterize their performance over time has become important. Battery capacity and power output fades over time, with chemical decomposition and side reactions being the primary source of this loss, which can be described as ageing of the battery. The role of stress in ageing is not very well understood, and evidence of particle comminution in batteries has lead to research in this area. In this work we have implemented a coupled stress-diffusion model and used it to develop property maps identifying the effect of different material properties. We have integrated this model with a model for the lithium ion battery in order to recreate the environment around these particles.

NOMENCLATURE

J_{Li} Flux of lithium ions

D_0	Diffusion coefficient
c_{Li}	Concentration of lithium within the particle
c_{max}	Maximum value of lithium concentration
Ω_{Li}	Partial molar volume
σ_h	Hydrostatic Stress
r_0	Particle radius
i_n	Current at particle surface
F	Faradays constant
E	Young's modulus
d_p	Distance between particles
ν	Poisson's ratio
R	Universal gas constant
T	Temperature

Using the assumptions of an ideal material and a concentration dependent mobility we can derive [1,2] the following coupled equation of flux

$$J_{Li} = -D_0 \left\{ \nabla c_{Li} - \left(1 - \frac{c_{Li}}{c_{max}} \right) \frac{\Omega_{Li} c_{Li}}{RT} \nabla \sigma_h \right\} \quad (1)$$

We identify three non-dimensional parameters that govern the stress response of these particles

$$\hat{I} = \frac{i_n r_0}{FD_0 c_{max}} \quad \hat{\Omega} = \frac{\Omega_{Li} E}{RT} \quad \epsilon_{Li}^{max} = \Omega_{Li} c_{max} \quad (2)$$

We further non dimensionalize this equation to arrive at the following equations of mass transport and stress within a spherical particle

$$\frac{\partial \hat{c}_{Li}}{\partial \hat{t}} = \left(\frac{\partial}{\partial \hat{r}} + \frac{2}{\hat{r}} \right) \left[\frac{\partial \hat{c}_{Li}}{\partial \hat{r}} - \hat{\Omega} (1 - \hat{c}_{Li}) \hat{c}_{Li} \frac{\partial \hat{\sigma}_h}{\partial \hat{r}} \right] \quad (3)$$

$$\hat{\sigma}_h = \frac{2\mathcal{E}_{Li}^{\max}}{3(1-\nu)} \left(\int_0^1 \hat{c}_{Li} \hat{r}^2 d\hat{r} - \frac{\hat{c}_{Li}}{3} \right) \quad (4)$$

Where,

$$\hat{r} = \frac{r}{r_0} \quad \hat{t} = \frac{tD_0}{r_0^2} \quad \hat{c}_{Li} = \frac{c_{Li}}{c_{\max}} \quad \hat{\sigma} = \frac{\sigma}{E} \quad (5)$$

Let us consider the case of insertion. We start with an empty particle and apply the dimensionless current to the surface. When the concentration at the surface reaches the limiting value, which is 1, the concentration is held at that point. We refer to this as transitioning from galvanostatic charging to potentiostatic charging. Thus the entire capacity of the battery is utilized without exceeding the limits of concentration, which is similar to what is done experimentally. For insertion the maximum tensile stress occurs in the center of the particle. We plot this stress as a function of the three nondimensional parameters in Figure 1.

In all plots we see that the value of maximum stress increases with increasing values of \hat{I} and \mathcal{E}_{Li}^{\max} . The maximum lithiation strain \mathcal{E}_{Li}^{\max} is the parameter that controls all strain magnitudes, including elastic ones, in the extraction or insertion process. Thus an increase in its value leads to a monotonic increase in the value of the maximum stress. As noted by previous authors [3], the value of \hat{I} determines the concentration gradient of lithium within the storage particle, which in turn determines the value of the elastic stress. Therefore, there is a monotonic dependence of the maximum stress on the value of the dimensionless current. We see that a decrease in the value of $\hat{\Omega}$ leads to an increase in the value of stress. This seems counter-intuitive given that $\hat{\Omega}$ is dependent on the partial molar volume and Young's modulus, and an increase in either of these parameters should lead to an increase in stress. This decrease is a result of the contribution of $\hat{\Omega}$ to the diffusive flux, as seen in Equation 3. The stress gradient always aids the diffusion process and is positive radially during insertion (the radial concentration gradient is negative). Thus if the stress gradient is large it can contribute to the concentration gradient and increase the diffusive flux within the particle. Thus as we keep increasing the value of $\hat{\Omega}$, we increase the contribution of the stress gradient, which in turn reduces the concentration gradients in the particle, leading to lower stresses.

However for the case of insertion we do not see a continual increase in stress on decreasing the value of $\hat{\Omega}$, as was seen in the case of extraction [2]. This is because the concentration gradients at the center do not reflect changes at the surface immediately. Concentration gradients take longer to develop at the center, and even after the transition from galvanostatic charging to potentiostatic charging occurs, these gradients continue to rise. Hence in some cases, (Figure 2(a)) we see that the maximum stress occurs after transition, something which was not seen in the case of extraction. One of the positive effects of large values of $\hat{\Omega}$, is that more uniform insertion takes place, resulting in larger average concentrations within the particle when it reaches the transition point (Figure 2(b)). The value of these parameters for lithium manganate, a cathode material, is $\hat{\Omega} = 141$ and $\mathcal{E}_{Li}^{\max} = 0.08$, making these results applicable to existing materials.

In order to study the effects of a battery environment, the model was integrated into a 2-D model for the entire battery [4]. The battery is divided into different regions: anode, composite cathode, separator and current collector. The composite cathode is further divided into storage particles and a combined electrolyte and binder region. The transport of the different conducting species is modeled individually in the different regions in the system. The transport in electrolyte is modeled using the theory of transport in concentrated solutions, while electrons are modeled using Ohm's law. Periodic boundary conditions are applied to the edges of the battery in order to avoid edge effects.

For the storage particles, the coupled stress-diffusion model is used. The particles are assumed to be cylindrical in shape. Butler-Volmer boundary conditions are used to link the surface of the particle to the electrolyte and binder in the composite cathode. Extraction of lithium from the storage particles is carried out using a scheme of galvanostatic charging followed by potentiostatic charging, in order to deplete the particles completely.

In the first set of simulations a single particle in isolation is considered: due to the periodic boundary conditions this is equivalent to a row of particles equidistant from the separator. The particles are kept at a large distance from the separator and collector to avoid the influence of other features of the battery. The horizontal distance between the particles is varied in order to look at the interactions of the particles with each other with results showing no effect of the particle separation on the stress within the particles.

In order to look at the effect of morphology, the particles are now packed close together, i.e. the distance between the particles and the separator and current collector is the same as

between the particles themselves. Three cases are considered, with one, two and three particles. The non-dimensional current is kept the same across the three cases in order to compare results. The difference between the ionic conductivity and the electronic conductivity within the electrode leads to a difference in extraction of lithium from the storage particles. The particle nearest the separator experiences the highest extraction rates, and subsequently the highest stress, as can be seen in Figure 3. As we increase the number of particles, the highest stress experienced by the particle closest to the separator is larger than that experienced in a single particle morphology. This corroborates experimental results which show that particles closest to the separator show greater rates of fracture.

At large extraction rates the distribution of lithium in the particle is unequal at different points on the surface. The addition of particles leads to larger differences in the rates of extraction between the particles, as well as between points on the particles themselves. This leads to uneven concentration gradients and stresses within the particles as seen in Figure 4(a) and (b).

ACKNOWLEDGMENTS

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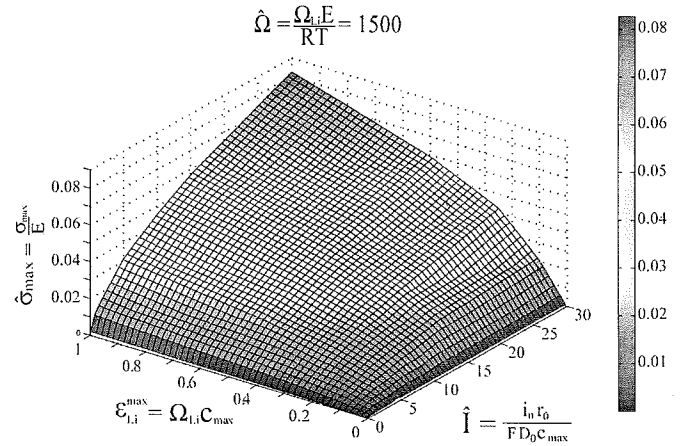


Figure 1(a): Stress map of maximum stress within a spherical particle during insertion plotted for $\hat{\Omega} = 1500$.

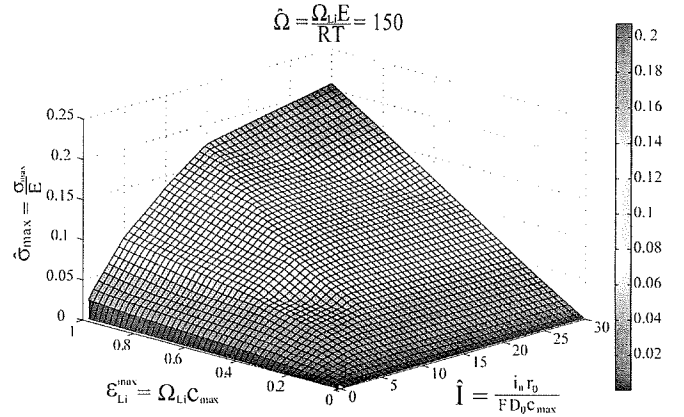


Figure 1(b): Stress map of maximum stress within a spherical particle during insertion plotted for $\hat{\Omega} = 150$.

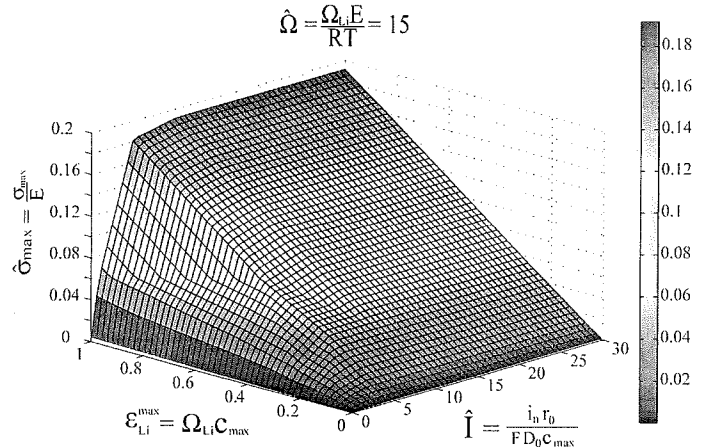


Figure 1(c): Stress map of maximum stress within a spherical particle during insertion plotted for $\hat{\Omega} = 15$.

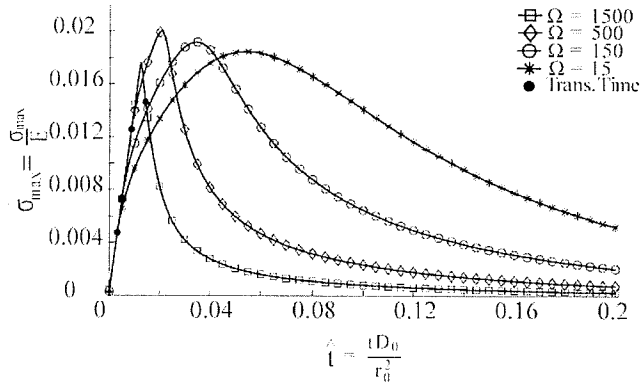


Figure 2(a): Stress histories for different values of $\hat{\Omega}$ plotted when $\hat{I} = 15$ and $\epsilon_{Li}^{\max} = 0.1$.

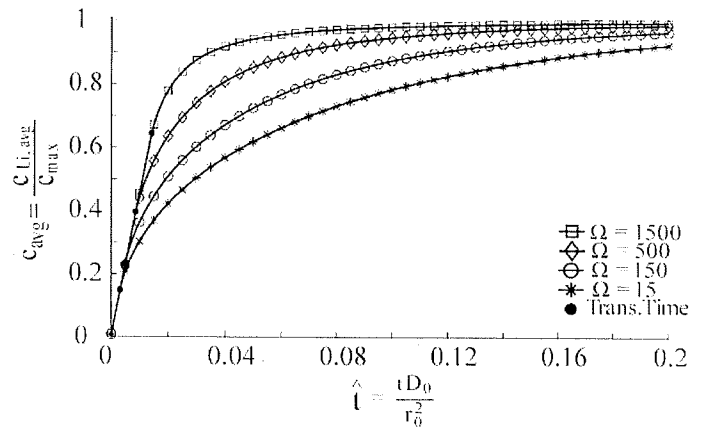


Figure 2(b): Average concentration for different values of $\hat{\Omega}$ plotted when $\hat{I} = 15$ and $\epsilon_{Li}^{\max} = 0.1$.

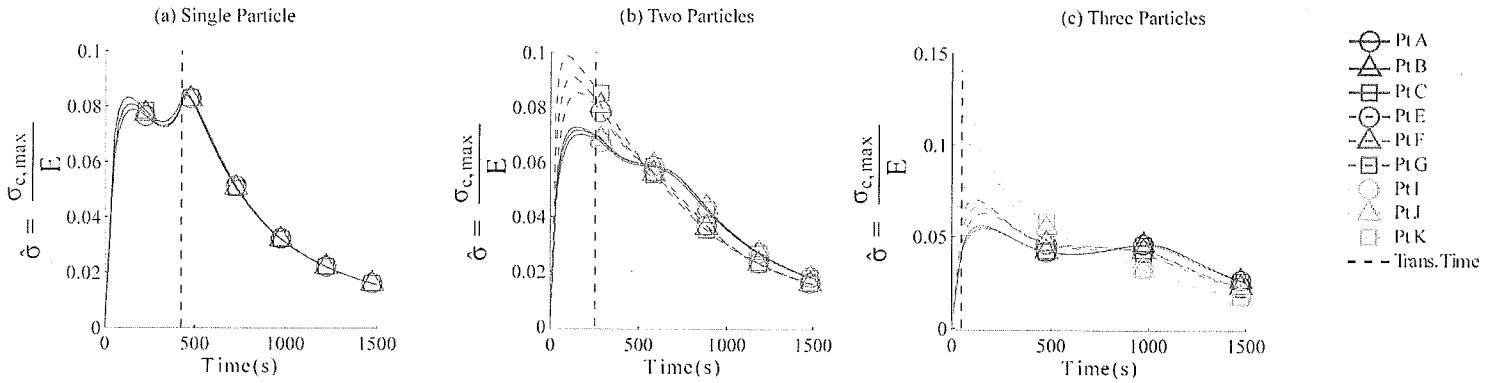


Figure 3: Stress Histories at different points on different particles plotted over time for three different morphologies (a) Single particle morphology (b) Two particle morphology (c) Three particle morphology.

$$SOC = \frac{c_{Li}}{c_{max}} \quad T = 100 \text{ s}$$

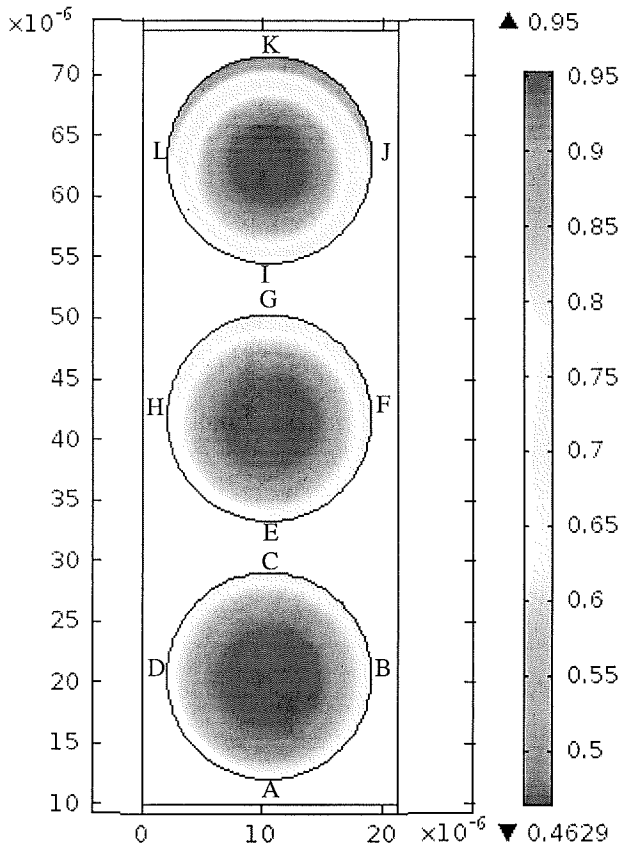


Figure 4(a): Concentration profile at the start of transition ($t = 100\text{s}$) from galvanostatic charging to potentiostatic charging for $\hat{\Omega} = 150$, $\hat{I} = 15$, $d_p = r_0/2$ and $\epsilon_{Li}^{\max} = 0.1$.

$$\hat{\sigma} = \frac{\sigma_{c,\max}}{E} \quad T = 100 \text{ s}$$

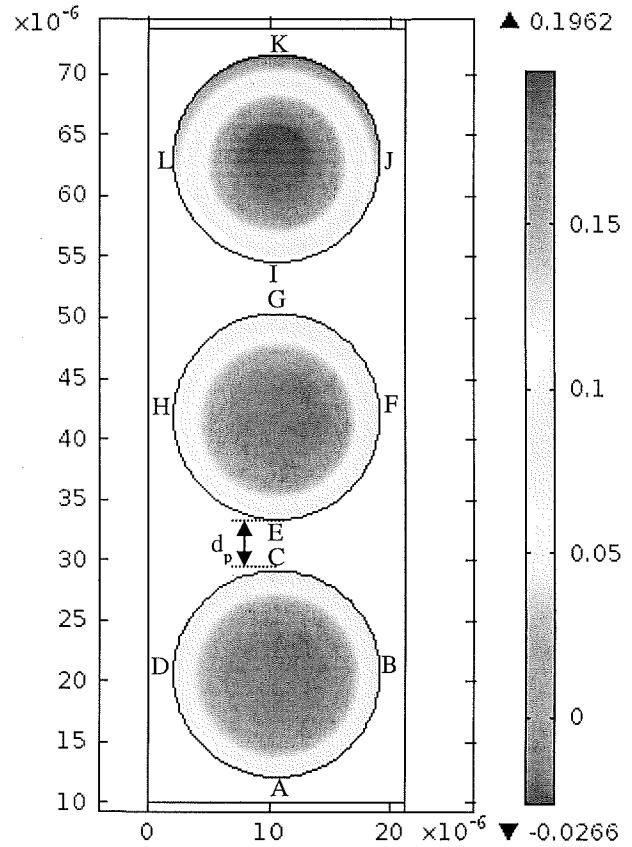


Figure 4(b): Stress profile at the start of transition ($t = 100\text{s}$) from galvanostatic charging to potentiostatic charging for $\hat{\Omega} = 150$, $\hat{I} = 15$, $d_p = r_0/2$ and $\epsilon_{Li}^{\max} = 0.1$.