Diffusion stress analysis of spherical shell electrode

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\textbf{Abstract.} Lithium-ion batteries have a wide range of applications in the field of electronics. It is necessary to conduct in-depth study of the impact of diffusion-induced stress to enhance the performance of lithium-ion batteries. In this study, the diffusion-induced stress of spherical shell electrode is investigated. The effect of initial concentration of lithium ions and the size of electrode on the diffusion stress under constant voltage charge and discharge conditions are analysed by employing single phase diffusion model. In this paper, the evolution of the lithium ion concentration in the spherical shell electrode is calculated by controlling the initial concentration of lithium ions, and then the size of the electrode material is changed to explore the radial and circumferential stress of the spherical shell electrode material. It is found that the lower initial concentration of lithium ions can effectively reduce the diffusion stress. The stress variation of the right peak point of spherical shell electrode with lithium ion concentration is further studied. The results show that the smaller the electrode material size, the smaller the diffusion stress.

1. Introduction
Lithium-ion batteries (LIBs), as a widely used clean energy for the 21st century [1], not only provide rechargeable energy for most portable electronic devices, such as mobile phone, heart pacemaker and the like, but also holds the fundamental role to drive the commercialization of electric vehicles, which are the bottleneck of shared traffic economy. The components of the lithium battery include anode, cathode, electrolyte and diaphragm. It is the anode materials which generally includes carbon-based materials, silicon materials and what not play a decisive role in the commercialization and development of the lithium ion battery [2].

High capacity, long life and high security of LIBs are required by increasing demanding applications but the maximum limitation to such properties is lithiation-induced swelling and fracture which leads to mechanical degradation and structural disintegration. To overcome this complication, increasing attention of community has been attracted to nanostructured anodes, such as thin films [3], nanowires [4], hollow nanoparticles [5], and nanoporous structures [6,7]. Due to their small size, the nanostructures enable fast Li transport and accommodate strain, hence mitigating mechanical failure.

Jiang and Li [8] proposed an SPRM technique to quantitatively image the electrochemical current of single LiCoO\textsubscript{2} nanoparticles during cycling with a high sensitivity (50 fA) and fast temporal resolution (20 ms), allowing for studying the phase transition and Li-ion diffusion kinetics at single nanoparticle level. It was found that, while the intrinsic diffusion coefficient was consistent with the prediction from first principles calculations, interior crystallographic structures also played essential roles to affect the Li-ion diffusion kinetics. Additionally, numerous researchers have been dedicated to analyzing the
influence of particle geometry on the diffusion-induced stress. Liu et al. [9] investigated the critical sizes under which the Si electrode can accommodate the strain without failure.

Compared with ordinary particle anodes, the hollow particle anodes show more promising properties due to its simultaneously enhancing the mechanical and structural stability of anodes. Zhao et al. [5] studied silicon anodes of hollow core-shell nanostructures and determine conditions to avoid fracture and debonding regarding the geometry of anodes and state of charge.

In consideration of the analogy between diffusion and heat flow, diffusion stress can be modeled as thermal stress [10]. It is shown that there is a circumferential stress in the surface layer and a tensile stress at the center of the crack. In order to explain the stress evolution, Zhao et al. [11] exhibit an analytical solution of the co-evolving reaction and rigid-plasticity in a spherical particle. The kinetic model and finite element simulation were applied to obtain solutions of the lithium ion concentration distribution, phase interface velocity and the stress evolution [12].

In this paper, the finite difference method is used to study the occurrence and evolution of stress in spherical shell caused by Li-ion diffusion and then we numerically simulate the effect of lithium ion concentration on the diffusion stress by using single-phase diffusion material.

In section 2, an elastic model of a spherical coupled with diffusion stress and curvature effect is proposed. Furthermore, the influence of the lithium ion concentration and the inner and outer diameter of the spherical shell electrode on the diffusion stress was investigated. Finally, the results are analysed and some conclusions about the stress of spherical shell electrode materials are drawn.

2. Methodology

According to the electrode material in the process of intercalation of lithium phase change occurs, the electrode material intercalation mechanism can be divided into single-phase lithium insertion and dual-phase lithium insertion. In this article only discusses about single-phase lithium insertion.

For the case of single-phase lithium insertion, there is no phase separation during the charging and discharging process. The intercalation process can be described by the single-phase diffusion model. In the initial stage, the entire electrode is fully charged, and the lithium ions in the electrode are in the highest concentration state; With the discharge, the concentration of lithium ions in the particles gradually decreased, after a long enough time, the electrode loses all of the lithium ions, and the entire electrode is at a low lithium ion concentration.

For spherical shell-shaped electrode particles, the concentration evolution in the particles can be controlled by the following diffusion equation (irrespective of the relationship between the stress distribution and the concentration distribution)

\[
\frac{\partial c}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right)
\]

\[\text{(1)}\]

Fig. 1. (a) Spherical shells filled with lithium ion. (b) Partially discharged spherical shells. (c) Fully discharged spherical shells. (d) A case with an inner diameter a and an outer diameter b.
In order to simplify the solution conditions, researchers usually simplified the entire charging process to constant voltage charging, the lithium ion concentration at the surface of the electrode active particles was always constant, equivalent to the concentration in the electrolyte. For spherical shell-shaped electrode active particles with inner diameter $a$ and outer diameter $b$, the boundary condition can be expressed as

$$
\begin{align*}
&c(r,0) = c_0, \quad r \in [a,b] \\
&c(a,t) = c(b,t) = c_r, \quad t \geq 0 \\
&c(0,t) = \text{finite}, \quad t \geq 0
\end{align*}
$$  \tag{2}

We assume that the same isotropic elastomer. Because the stress reaches equilibrium and the diffusion of lithium ions in the electrode is a very fast process, the electrode particles can be regarded as a quasi-static mechanical equilibrium system at any time. Therefore, without considering the effect of the body force, the spherical coordinate system of the mechanical equilibrium equation is expressed as

$$
\frac{d\sigma_r}{dr} + \frac{2(\sigma_r - \sigma_\theta)}{r} = 0
$$  \tag{3}

where $\sigma_r$ and $\sigma_\theta$ denote radial and toroidal stresses, respectively.

Lithium ions in the electrode active particles in the uneven distribution of the material will cause the electrode material strain, this strain is similar to the strain caused by the uneven heat distribution, by comparing with the thermodynamic constitutive equation, the constitutive equation with the presence of the lithium ion concentration distribution can be,

$$
\begin{align*}
\varepsilon_r &= \frac{1}{2\mu(1+\nu)}(\sigma_r - 2\nu\sigma_\theta) + \varepsilon_r c \\
\varepsilon_\theta &= \frac{1}{2\mu(1+\nu)}(\nu\sigma_r - \sigma_\theta) + \varepsilon_r c
\end{align*}
$$  \tag{4}

where $\mu$ is the material shear modulus, $\nu$ is the Poisson's ratio, $c$ is the lithium ion concentration, $\varepsilon_r$ is the lattice expansion strain caused by the insertion of lithium ions, and $\varepsilon_r$ and $\varepsilon_\theta$ respectively represent the radial strain and the circumferential strain.

Since the spherical shell-shaped electrode particles have symmetry, both the radial strain and the circumferential strain can be determined by the radial displacement $u$:

$$
\begin{align*}
\varepsilon_r &= \frac{du}{dr} \\
\varepsilon_\theta &= \frac{u}{r}
\end{align*}
$$  \tag{5}

By formulas (3), (4) and (5) we can get

$$
\begin{align*}
\sigma_r &= \left(\frac{1}{1-\nu-2\nu^2}\right)\left[\frac{2\mu(1-\nu^2)du}{dr} + \frac{4\nu\mu(1+\nu)u}{r} - 2\mu(1+\nu)^2\varepsilon_r c\right] \\
\sigma_\theta &= \left(\frac{1}{1-\nu-2\nu^2}\right)\left[\frac{2\nu\mu(1+\nu)du}{dr} + \frac{2\mu(1+\nu)u}{r} - 2\mu(1+\nu)^2\varepsilon_r c\right]
\end{align*}
$$  \tag{6}

and
For a single-phase lithium insertion electrode material, the spherical shell-like particle surface is a free boundary of stress when the external constraint is not taken into account, so that the radial stress at the surface is zero and the stress at the intermediate position is finite.

For the case of single-phase lithium insertion, the diffusion stress can be determined according to the formulas (6) when the concentration distribution in the electrode particles is determined.

3. Results
It is assumed that the charge and discharge process is sufficient and there is no lithium ion remaining in the spherical shell electrode material at the start of charging. Fig. 2 shows the distribution of lithium ion concentration in the spherical shell electrode material. It can be seen that the concentration of lithium ions on both sides is the highest and the concentration of lithium ions in the middle layer is the lowest. Additionally, the concentration of lithium ions in the middle layer gradually increases. Ultimately, the lithium ion concentration of the entire electrode material approaches that of electrolyte.

According to the variation of lithium ion concentration, the displacement and the stress of the spherical shell electrode material is calculated by Eq. (7) and Eq. (6), respectively. For simplicity, we define non-dimensional radial stress ratio and circumferential stress ratio, which can be obtained using the original radial stress ratio and circumferential stress divided by $\sigma_0 = \frac{2\mu_0(1+\nu)}{(1-\nu)}$.

Fig. 3 shows the relationship between the radial stress ratio and radius. It is obvious that when the inner diameter is the same, the stress significantly reduces with the decreasing of outer diameter, which indicates that when the size of the spherical shell electrode cannot be changed, the number of layers of spherical shell can be reduced intentionally to achieve less stress.

Fig. 2. The concentration of lithium ions in the spherical shell electrode material changes when the concentration of lithium ion in the electrolyte ($c_0$) is 1.
Fig. 3. The relationship between the maximum value of the dimensionless radial stress (σ/σ₀) and the dimensionless radius of the spherical shell electrode material (r/b).

After numerous calculations, it is shown in Fig. 3 that two peaks arise, locating at the left peak point and the right peak point, respectively. The maximum stress appeared at the right peak point which is approximate 0.2(b-a) distance from outer surface.

Under different initial concentration of lithium ions, the stress at the right peak point of spherical shell electrode with constant internal and external diameter is calculated and the results are shown in Fig. 4. It can be seen from Fig. 4 that the initial lithium ion concentration has a great influence on the stress of the spherical shell electrode. When the initial concentration of lithium ions decreases, the stress of the material decreases but simultaneously the charging speed lessens.

Fig. 4. The variation of the dimensionless radial stress (σ/σ₀) and tangential stress (σ/σ₀) with time (t) under different initial lithium ion (c₀) concentrations.
Afterwards, the diffusion stress of the spherical shell electrode with a fixed number of layers is simulated. Fig. 5 shows the relationship between the two kinds of non-dimensional stress and the radius. The figure shows that the smaller the size of the spherical shell electrode is, the smaller the radial stress is. Therefore, it is possible to manufacture electrode owning a better mechanical property through controlling the size.

![Fig. 5. The relationship between dimensionless radial stress together with tangential stress and the size of spherical shell electrode under the same initial lithium ion concentration.](image_url)

4. Conclusion
LIBs have the advantages of high energy density, high smooth discharge voltage, excellent cycle performance, environment-friendly and low price. In this paper, the effect of the initial Li-ion concentration and the size of the hollow electrode particles on the diffusion stress is simulated by using the simple continuous diffusion model with spherical shell electrode as the research object.

In this paper, the initial concentration is determined by using the simple continuous diffusion model of the single-phase lithium insertion. Then, the expression of the concentration and diffusion stress in the case of constant pressure charging is deduced. Subsequently, the concentration distribution and the diffusion stress distribution are obtained under various initial concentrations. Present research has shown that lower lithium ion concentrations and smaller spherical shell electrode sizes can result in smaller diffusion stresses, which provides instructions for manufacturing electrode materials for Li-ion batteries.

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