Stress fields in hollow core–shell spherical electrodes of lithium ion batteries

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This paper presents a comprehensive model coupling the effects of hydrostatic stress, surface/interface stress, phase transformation and the structure of electrodes. First, the governing equation of moving phase interface with hydrostatic stress is established. Under the effect of hydrostatic stress, phase transformation process is much faster, which means phase transformation time is overestimated in previous publications. Then, a cross-scale analysis is presented to investigate the size effect owing to hydrostatic stress, surface stress and interface stress separately, which concludes that the effect of hydrostatic stress is significant for the stress field in microelectrode particles, whereas that of surface/interface stress is highlighted in nano-ones. Finally, an electrochemical variable ‘efficiency’ (ratio of effective capacity over total capacity) is defined. The advantages of hollow structure electrodes on stress and efficiency are analysed. The present model is helpful for the material and structure design of electrodes of lithium ion batteries.

1. Introduction

Lithium ion batteries are the choices of diverse applications, such as electronics and electric cars because of their high capacity, high voltage and long lifetime, and therefore attracted wide research interests [1–6]. During the process of discharge/charge, lithium ions insert into/extract from electrodes, which will cause cyclic deformation. The intercalation and deintercalation...
of lithium ions can induce high stress in the electrode particle [7]. When the stress exceeds the ultimate strength of the material, it will cause the fracture of electrode. In fact, intercalation material particle fracture has been observed in post-mortem microscopy studies [8–10]. Indeed, intercalation-/deintercalation-induced stress and mechanical fracture are key mechanisms for lithium ion battery’s capacity fade and electrode fracture.

Stress generation owing to lithium ions intercalation/deintercalation and electrode fracture has been modelled in the literature. For example, some researchers investigated the effects of different factors on the stress field, e.g. hydrostatic stress [7,11,12], surface stress [13], charge operations [14,15], diffusion coefficients and interfacial reaction rate [16]. Furthermore, others tried to lower the stress by optimizing electrode geometry, e.g. spherical [17], core–shell [18–20], nanowire [21], thin film [22,23], layered plates [24], thin strip [25] and cylinder [26]. Inserting the stress field into the fracture mechanics model, some novel models are developed to predict the fracture of electrode, which will induce the failure of battery. Woodford et al. [27] calculated the stress intensity factor of the initial crack at an electrode’s surface and analysed the effect of crack length. Then, several new models are developed to predict crack propagation [28–30]. Some phenomena observed in working process of lithium ion batteries cannot be described by continuum model. Therefore, some pioneers put the research into atomic scale. Sastry and co-workers [31–34] studied phase transformation, heat generation and dissolution of particles during intercalation by using atomic force microscopy. Gao and colleagues developed the continuum and atomistic models to study the strong coupling of diffusion, stress and solute concentration, and the surface locking instability for atomic intercalation into electrode [35,36]. Suo et al. [37] and Zhao et al. [38] investigated the lithiated silicon’s microscopic deformation mechanism, and lithiation-induced plasticity by using the first principle calculation.

Recently, phase transformation phenomena have been widely observed in many kinds of electrode material during the process of lithium ions’ inserting into the electrodes [39,40]. During the phase transformation, a phase interface is observed between two phases. At the interface, the concentrations of the two phases equal their own equilibrium values. Therefore, a sharp concentration jump appears at the phase interface. Moving boundary models [16,41–44] have been developed to track the movement of this phase interface. But the existing models have not considered the effect of hydrostatic stress on the phase interface. Recently, the effect of hydrostatic stress on the species flux has been pointed out by Zhang et al. [11], and widely accepted in the research field of lithium ion batteries. Because the governing equation of the movement of the phase interface is derived based on the balance of the species flux, the hydrostatic stress should be taken into account in the governing equation of the phase interface.

With a unique doubled surface area, core–shell structure and large internal void, hollow particles have great potential in applications of lithium ion batteries [45]. Some researchers have found that core–shell structure can influence the stress fields and its physical properties. For example, Duan et al. [46,47] analysed the stress fields and morphological evolution of core–shell structures with surface/interface stress. Yoon & Manthiram [48] observed that hollow core–shell mesoporous TiO2 spheres exhibit a high capacity of 200 mAh g\(^{-1}\) with good cyclability and high rate capability. Yao et al. [49] investigated the electrochemical properties of a hollow silicon anode, and achieved a high initial discharge capacity of 2725 mAh g\(^{-1}\) with less than 8% capacity degradation every 100 cycles. Koo et al. [50] used hollow iron oxide nanoparticles as electrodes, and observed high capacity, high coulombic efficiency of 99.7%, great rate performance and excellent stability. However, most of the published works are based on experimental observation, and the comprehensive analysis for the property of hollow spherical electrode has not been developed. To touch the real physical and mechanical process, a theoretical model coupling the effects of hydrostatic stress, surface/interface stress, phase transformation and structural optimization of hollow particles is proposed in this paper.

The remainder of this paper is organized as follows: §2 provides the general mechanical and electrochemical equations of lithium ion batteries during the charge/discharge process. Section 3 derives the governing equation of a lithium ion inserting into a specific hollow spherical LiCoO\(_2\) electrode, including the effect of hydrostatic stress, surface/interface stress
and phase transformation. Section 4 gives the concentrations and stress fields under the effect of hydrostatic stress. In §5, the effects of surface/interface stress are investigated through a cross-scale analysis. In §6, the structure advantages of hollow structure electrodes are analysed. Then, an electrochemical variable ‘efficiency’ is defined. Finally, some conclusive remarks and discussion are given in §7.

2. Formulation

Figure 1 provides a schematic of the concentration distributions of the three stages in the discharge process. At the beginning of the discharge process, there is the \( \alpha \) phase only (figure 1a). As time passes, the concentration of Li ions increases. When the concentration at the outer surface reaches the equilibrium value of \( \alpha \) phase, i.e. \( c_{\text{eq}}^\alpha \), phase transformation begins, which is the beginning of the second stage (figure 1b). In the second stage, the electrode is divided into \( \alpha \) and \( \beta \) phases by an interface \( S_{\alpha\beta} \), which makes the electrode particle a biphase one. The concentrations of the two phases at the interface equal their equilibrium values, i.e. \( c_{\text{eq}}^\alpha \) and \( c_{\text{eq}}^\beta \). Then, the phase interface moves inward. When it reaches the inner surface, the concentration at the inner surface reaches \( c_{\text{eq}}^\beta \). At this time, the phase transformation finishes, and the discharge steps into the last stage, in which there is only a \( \beta \) phase (figure 1c). Note that the charge process is just the opposite process of discharge. In the charge process, the electrode also went through three stages: (i) \( \beta \) phase only; (ii) biphase; and (iii) \( \alpha \) phase only.

(a) Mechanical equations

As discussed above, there is a phase interface \( S_{\alpha\beta} \) in the second stage of the discharge process, illustrated by figure 2. Li ions inserting into and extracting from the electrode particle causes non-uniform distribution, and then induce stress. Before developing the model for this problem, we make some simplifying assumptions: (i) the body force of electrode particle is neglected; (ii) the electrode material is treated as a continuous solid solution with elastic properties; and (iii) the material properties remain constant across the full charge/discharge process.

To describe this mechanics–electrochemical coupling problem, the concentration of Li ions is inserted into the constitutive law. For both \( \alpha \) and \( \beta \) phases, the constitutive law can be written as [51]

\[
\varepsilon^p = \frac{1}{E^p} [(1 + \nu^p)\sigma^p - \nu^p \Theta^p \mathbf{I}] + \frac{\bar{\Omega}^p \Omega^p}{3} \mathbf{I}, \quad (p = \alpha, \beta),
\]

where \( \varepsilon^p \) is the strain tensor of phase \( p \), \( \sigma \) is the stress tensor, \( \Theta^p \) is the trace of \( \sigma^p \) and \( \mathbf{I} \) is the second-order unit tensor. \( E^p \) and \( \nu^p \) are Young’s modulus and Poisson’s ratio, respectively, \( \Omega^p \) is...
Figure 2. Schematic of electrode particle: there is an interface $S_{\alpha \beta}$ between $\alpha$ and $\beta$ phases.

The partial molar volume, $\bar{\rho} = (\rho^p - \rho^0)$ is the change in Li ion concentration from the initial value $\rho^0$ in the electrode particles, and $\rho^p$ is a function of time and position. Here, and in the following, the superscript $p = \alpha, \beta$, denoting the $\alpha$ phase and $\beta$ phase, respectively.

Based on elasticity theory, the equilibrium equation is

$$\nabla \cdot \sigma^p = 0 \quad (2.2)$$

and the geometrical equation is

$$\varepsilon^p = \frac{1}{2} (u^p \nabla + \nabla u^p), \quad (2.3)$$

where $u^p$ is the displacement vector of phase $p$.

Combining equations (2.1)–(2.3), one can obtain the governing equation of each phase. However, to solve this problem, the mechanical equation for the interface is needed. For the interface $S_{\alpha \beta}$ between the two phases $\alpha$ and $\beta$, the equilibrium equation of the interface is [52]

$$[\sigma] \cdot n = -\nabla_s \cdot \tau, \quad (2.4)$$

where $[\sigma] = \sigma^\beta - \sigma^\alpha$, $\sigma^\alpha$ and $\sigma^\beta$ are the stress tensors in phases $\alpha$ and $\beta$, respectively. $\nabla_s \cdot \tau$ denotes the divergence of interface stress $\tau$ at the phase interface. The relationship between interface stress tensor $\tau$ and interface strain tensor $\varepsilon^s$ is

$$\tau = \tau^0 1 + C^s : \varepsilon^s, \quad (2.5)$$

where $\tau^0$ is the constant interface stress which is strain-independent, $1$ is a second-order unit vector in two-dimensional case, and $C^s$ is the interface stiffness tensor. Here and in the following, the super and subscript ‘s’ denotes the interface/surface quantities.

The displacement is continuous at the interface,

$$u^\alpha = u^\beta, \quad (2.6)$$

where $u^\alpha$ and $u^\beta$ are the displacement vectors of two phases, respectively. Solving this boundary value problem, equations (2.1)–(2.3) for $\alpha$ and $\beta$ phases, and equations (2.4)–(2.6) for the interface $S_{\alpha \beta}$, one can obtain the stress profile of the biphase electrode particle.

It is noted that although the stress discontinuity at the phase interface has been discussed in the literature [16,44], the stress discontinuity they addressed are only induced by the concentration discontinuity at the phase interface (cf. figure 1b) and the difference of the material constants between two phases. However, in this paper, the whole electrode particle is divided into three parts: $\alpha$ phase, $\beta$ phase and the phase interface (cf. figure 2). Therefore, the mechanical formulation should include the equations of $\alpha$ phase, $\beta$ phase, equations (2.1)–(2.3), those of the phase interface, equations (2.4)–(2.6). Therefore, the stress discontinuity in this paper is induced by three aspects, different material constants, concentration discontinuity and interface stress. This paper gives the theoretical model to investigate the effect of interface stress at phase interface on the phase transformation of the lithium ion battery. In fact, the effect of the interface stress on the mechanical properties of nanostructured materials and heterogeneous materials has been widely investigated [52–55].
(b) Electrochemical equations

During the process of discharge/charge, Li ions will insert into/extract from cathode particles. This process can be treated as diffusion of lithium ions. The chemical potential gradient is the driving force for the movement. The velocity ($V^p$) of lithium ions in phase $p$ can be written as follows [11]

$$V^p = -M^p \nabla \phi^p, \quad (p = \alpha, \beta), \quad (2.7)$$

where $M^p$ is the mobility of lithium ions, and $\phi^p$ is the electrochemical potential. The species flux ($J^p$) is

$$J^p = c^p V^p = -c^p M^p \nabla \phi^p, \quad (2.8)$$

where $c^p$ is lithium ion concentration in phase $p$. And electrochemical potential ($\phi^p$) in an ideal solid solution is written as [56]

$$\phi^p = \phi^p_0 + RT \ln X - \Omega^p \sigma^p_h, \quad (2.9)$$

where $\phi^p_0$ is a constant, $R$ is gas constant, $T$ is absolute temperature, $X$ is molar fraction of lithium ion and $\sigma^p_h$ is hydrostatic stress, defined as

$$\sigma^p_h = \frac{1}{3} \sigma^p. \quad (2.10)$$

Substitution of equation (2.9) into equation (2.8), species flux can be expressed as

$$J^p = -M^p c^p \left( \frac{RT}{X} \nabla X - \Omega^p \nabla \sigma^p_h \right) = -D^p \left( \nabla c^p - \frac{\Omega^p c^p}{RT} \nabla \sigma^p_h \right), \quad (2.11)$$

where $D^p = M^p RT$ is diffusivity.

It is seen from equation (2.11) that the species flux is affected by hydrostatic stress gradient, which has been neglected by some analytical works to obtain the series form solution [13,14,25,26].

The equation of substance conservation is written as

$$\frac{\partial c^p}{\partial t} + \nabla \cdot J^p = 0. \quad (2.12)$$

Inserting equation (2.11) into equation (2.12), the governing equation of Li ion concentration is obtained

$$\frac{\partial c^p}{\partial t} - \nabla \cdot \left[ D^p \left( \nabla c^p - \frac{\Omega^p c^p}{RT} \nabla \sigma^p_h \right) \right] = 0. \quad (2.13)$$

Under galvanostatic operation, the boundary conditions are given as

$$J^p = \frac{i_n}{F}, \quad \text{(active)}; \quad J^p = 0, \quad \text{(inactive)}, \quad (2.14)$$

where $F$ is the Faraday constant and $i_n$ is the current density.

When phase transformation begins, a phase interface appears between $\alpha$ and $\beta$ phases (cf. figure 2). The concentration at either side of the phase interface equals its own equilibrium value

$$c^\alpha_{|S_{\alpha\beta}} = c^\alpha_{\text{eq}}, \quad c^\beta_{|S_{\alpha\beta}} = c^\beta_{\text{eq}}, \quad (2.15)$$

where $c^\alpha_{\text{eq}}$ and $c^\beta_{\text{eq}}$ are the equilibrium concentrations of the $\alpha$ and $\beta$ phases. The movement of the phase interface is assumed to be under the control of the diffusion process in the adjacent phases. A jump material balance is used to track the position of the interface [44], i.e.

$$(c^\alpha_{\text{eq}} - c^\beta_{\text{eq}}) \frac{d\xi}{dt} = J^\alpha - J^\beta, \quad (2.16)$$

where $\xi$ is the position of the phase interface, and $d\xi/dt$ is its moving velocity. It is noted that equation (2.16) is automatically satisfied when there is only one phase in the particle.
Substituting equation (2.11) into equation (2.16), the governing equation of the phase interface is obtained, i.e.

\[
\left( c_{\alpha}^{eq} - c_{\beta}^{eq} \right) \frac{d\xi}{dt} = D^\beta \left( \nabla c^\beta - \frac{\Omega^\beta c^\beta}{RT} \nabla \sigma^\beta + \frac{\Omega^\alpha c^\alpha}{RT} \nabla \sigma^\alpha \right) - D^\alpha \left( \nabla c^\alpha - \frac{\Omega^\alpha c^\alpha}{RT} \nabla \sigma^\alpha \right). \tag{2.17}
\]

It is noted that from equation (2.17) the effect of $\sigma_h$ on the movement of the phase interface is introduced for the first time. To solve this partial differential equation, the initial concentration is uniformly distributed, i.e.

\[
c^\beta(t = 0, x) = c_0, \tag{2.18}
\]

where $c_0$ depends on the process under investigation. For the discharge process, $c_0$ is set as zero; for the charge process, $c_0$ is set as $c_{\text{max}}$.

In summary, for an electrode of a lithium ion battery with arbitrary geometry, the general mechanical and electrochemical equations are derived above. The discharge/charge process can be regarded as a quasi-static process. In each time step, by inserting the concentration of Li ions into equations (2.1)–(2.6), one can compute the stress field. Substituting the stress field into equations (2.13)–(2.17), one can obtain the concentration field.

### 3. Stress fields in hollow spherical electrode

Section 2 provides the governing equations of concentration and stress profile for an electrode with arbitrary geometry in a lithium ion battery. Recently, hollow particles have been used as electrodes in Li ion batteries, owing to their high performance. Figure 3 illustrates the structure of hollow spherical particles, in which $r_1$ and $r_2$ are the inner and outer radii of the hollow particles, respectively. The ratio of inner and outer radii $\xi = r_1 / r_2$. As discussed before, the whole discharge process can be divided into three stages: $\alpha$ phase only (cf. figure 3b), $\alpha$ and $\beta$ phases coexist (cf. figure 3a) and $\beta$ phase only (cf. figure 3c). For the biphase particle, the inner layer is the $\alpha$ phase, whereas the outer one is the $\beta$ phase. There is an interface between $\alpha$ and $\beta$ phases. When this interface moves to the outer/inner surfaces, the biphase electrode particle is reduced to a single phase electrode particle. This section provides the equations of concentration and elastic fields for this specific hollow spherical particle electrodes.

#### (a) Mechanical equations

As an axisymmetric problem, the displacement vector only has radial component $(u)$ and the stress and strain tensors contain two independent components $\sigma_r$, $\sigma_\theta$ and $\varepsilon_r$, $\varepsilon_\theta$ (note $\sigma_\phi = \sigma_\theta$, $\varepsilon_\phi = \varepsilon_\theta$). Under the spherical coordinate, equations (2.1)–(2.3) become
the constitutive law
\[
\varepsilon_r^p = \frac{1}{E_p}\left(\sigma_r^p - \frac{2}{3} v_p \sigma_\theta^p\right) + \frac{\Omega_p}{3} \tilde{c}^p,
\]
and
\[
\varepsilon_\theta^p = \frac{1}{E_p}\left(\sigma_\theta^p - \frac{2}{3} v_p (\sigma_r^p + \sigma_\theta^p)\right) + \frac{\Omega_p}{3} \tilde{c}^p,
\]
the equilibrium equation
\[
\frac{d\sigma_r^p}{dr} + \frac{2}{r}(\sigma_r^p - \sigma_\theta^p) = 0,
\]
the geometrical equation
\[
\varepsilon_r^p = \frac{du^p}{dr}; \quad \varepsilon_\theta^p = \frac{u^p}{r}.
\]
Substituting equation (3.3) into equation (3.1) and equation (3.2), one can obtain the governing equation of displacement
\[
\frac{d^2 u^p}{dr^2} + \frac{2}{r} \frac{du^p}{dr} = \frac{1}{1 - v^p} \Omega_p \left(\frac{2}{r^3} \int_0^1 \tilde{c}^r r^2 dr + A^p + \frac{B^p}{r^2}\right).
\]
The general solution of equation (3.4) is
\[
u^p = \frac{1}{1 - v^p} \Omega_p \left(\frac{2}{r^3} \int_0^1 \tilde{c}^r r^2 dr + A^p + \frac{B^p}{r^3}\right),
\]
where \(A^p\) and \(B^p\) are constants to be determined by the boundary conditions.

Substituting equation (3.5) into equation (3.3), the strain can be obtained
\[
\varepsilon_r^p = \frac{1 + v^p \Omega_p}{1 - v^p} \left(\frac{2}{r^2} \int_0^1 \tilde{c}^r r^2 dr + A^p - \frac{2B^p}{r^3}\right)
\]
and
\[
\varepsilon_\theta^p = \frac{1 + v^p \Omega_p}{1 - v^p} \left(\frac{2}{r^3} \int_0^1 \tilde{c}^r r^2 dr + A^p + \frac{B^p}{r^3}\right).
\]
This equation can be rewritten as
\[
\sigma_r^p = E_p \left(\frac{-2 + v^p}{1 - v^p} \int_0^1 \tilde{c}^r r^2 dr + A^p - \frac{2B^p}{r^3(1 + v^p)}\right)
\]
and
\[
\sigma_\theta^p = E_p \left(\frac{1}{1 - v^p} \int_0^1 \tilde{c}^r r^2 dr + A^p + \frac{B^p}{r^3(1 + v^p)}\right),
\]
where \(c^r_{av} = (3/r^3) \int_0^r \tilde{c}^r r^2 dr\). Note that \(r_1^\alpha = r_1\) and \(r_1^\beta = \xi\).

When the \(\alpha\) and \(\beta\) phase coexist, there is a phase interface appearing at \(r = \xi\). Figure 3a illustrates the phase distribution at this stage, and one can observe that the \(\alpha\) phase is inside, whereas the \(\beta\) phase is outside.

For the hollow spherical electrode particle, equation (2.4) at the interface reduces to
\[
(\sigma_\theta^\beta - \sigma_\theta^\alpha)|_{r=\xi} = \frac{2 \tau_0}{\xi}.
\]
For the isotropic interface, the interface constitutive law equation (2.5) is
\[
\tau_\theta = \tau_\theta^0 + K^\varepsilon_p^\varepsilon_p^\theta,
\]
where \(K^\varepsilon\) is the interface modulus \((\varepsilon_p^\varepsilon_p^\theta = \varepsilon_p^\theta)\).

The displacement continuity equation (2.6) reduces to
\[
u^\alpha|_{r=\xi} = u^\beta|_{r=\xi}.
\]
The stress boundary condition for hollow particles was proposed by Fisher & Svoboda [57]. Actually, this boundary condition can be regarded as a special case of equation (2.4), when the interface is located at the inner and outer surfaces, i.e.

$$\sigma_r^p \mid_{r=r_1} = \frac{2\tau_0}{r_1}; \quad \sigma_r^p \mid_{r=r_2} = -\frac{2\tau_0}{r_2},$$  \hspace{2cm} (3.11)

Combining equations (3.7), (3.8), (3.10) and (3.11), a linear equations system is obtained

$$Z = HY,$$  \hspace{2cm} (3.12)

where $Y^T = (A^\alpha, B^\alpha, A^\beta, B^\beta)$. $Z$ and $H$ are as follows

$$H = \begin{bmatrix}
\frac{E^\alpha}{1 - 2\nu^\alpha} - \frac{2K^\alpha}{r_1} & -\frac{2E^\alpha}{\xi^3(1 + \nu^\alpha)} & -\frac{2K^\alpha}{r_1} & 0 & 0 \\
-\frac{E^\alpha}{1 - 2\nu^\alpha} & \frac{2E^\alpha}{\xi^3(1 + \nu^\alpha)} & \frac{E^\beta}{1 - 2\nu^\beta} - \frac{2K^\beta}{\xi} & -\frac{2E^\beta}{\xi^3(1 + \nu^\beta)} & -\frac{2K^\beta}{\xi^4} \\
0 & 0 & \frac{E^\beta}{1 - 2\nu^\beta} + \frac{2K^\beta}{r_2} & -\frac{2E^\beta}{r_2^3(1 + \nu^\beta)} & + \frac{2K^\beta}{r_2^4} \\
1 & \frac{1}{\xi^3} & -1 & \frac{1}{\xi^3} & 1
\end{bmatrix},$$  \hspace{2cm} (3.13)

and

$$Z = \begin{bmatrix}
\frac{2\tau_0}{r_1} \\
\frac{2\tau_0}{\xi} - \frac{2E^\alpha}{1 - \nu^\alpha} \frac{\Omega^\alpha}{9} \alpha_{\alpha\alpha}(\xi) \\
-\frac{2\tau_0}{r_2} + \frac{2K^\alpha}{1 - \nu^\alpha} + \frac{2E^\beta}{1 - \nu^\beta} \frac{\Omega^\beta}{9} \alpha_{\alpha\alpha}(r_2) \\
\frac{1 + \nu^\alpha}{1 - \nu^\alpha} \frac{\Omega^\alpha}{9} \alpha_{\alpha\alpha}(\xi)
\end{bmatrix}.$$  \hspace{2cm} (3.14)

Solving equation (3.12), one can obtain the constants $A^\alpha, B^\alpha, A^\beta$ and $B^\beta$. Inserting them into equation (3.7), the stress can be calculated. When there is only the $\alpha$ or $\beta$ phase in the electrode particle, $A^\alpha = A^\beta$, $B^\alpha = B^\beta$, and then equation (3.10) is automatically satisfied. In this case, phase interface $\xi$ can be regarded as $r_2$ for an electrode with the $\alpha$ phase only (cf. figure 3b), and as $r_1$ for the $\beta$ phase only (cf. figure 3c). In these two special cases, the interface equilibrium equation (3.8) reduces to the boundary conditions equation (3.11), and is automatically satisfied. In other words, one can obtain the solution of the single phase particle by setting $\xi$ equals $r_2$ ($\alpha$ phase only) or $r_1$ ($\beta$ phase only) in the solution of biphasic particle.

(b) Electrochemical equations

The governing equations of the three stages of the discharge process are different and need to be discussed separately. At the first stage, only the $\alpha$ phase exists, as illustrated by figure 3b. For this axisymmetric problem, the governing equation (2.12) reduces to

$$\frac{\partial c^\alpha}{\partial t} = \frac{D^\alpha}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c^\alpha}{\partial r} - c^\alpha \frac{\Omega^\alpha}{9} \frac{\partial \sigma_h^\alpha}{\partial r} \right).$$  \hspace{2cm} (3.15)

The gradient of the hydrostatic stress can be rewritten as

$$\frac{\partial \sigma_h^\alpha}{\partial r} = -\frac{2E^\alpha}{1 - \nu^\alpha} \frac{\Omega^\alpha}{9} \frac{\partial c^\alpha}{\partial r}.$$  \hspace{2cm} (3.16)

Substitution of equation (3.16) into equation (3.15), the final governing equation is obtained

$$\frac{\partial c^\alpha}{\partial t} = \frac{D^\alpha}{r^2} \frac{\partial}{\partial r} \left[ (1 + \theta^\alpha e^\alpha) r^2 \frac{\partial c^\alpha}{\partial r} \right],$$  \hspace{2cm} (3.17)
where $\theta^\alpha = 2E^\alpha (\Omega^\alpha)^2/[9(1 - \nu^\alpha)RT]$. Rewrite the dimensionless parameter $\lambda^\alpha = \theta^\alpha c^\alpha = \theta^\alpha c_{\text{max}} \cdot c^\alpha/c_{\text{max}}$. Note that $c^\alpha/c_{\text{max}} \in [0, 1]$, $\theta^\alpha c_{\text{max}}$ is a constant. Therefore, the effect of hydrostatic stress depends on the value of $\lambda^\alpha$ and varies with concentration $c^\alpha$.

The initial value of the concentration in the electrode is

$$c^\alpha(r)|_{r=0} = c_0, \quad r \in [r_1, r_2].$$  \hfill (3.18)

The lithium ion flux is inserted into and extracted from the electrode through the outer surface. So the outer surface is active, whereas the inner surface is inactive. Therefore, the specific form of boundary condition equation (2.14) is

$$- D^\alpha (1 + \theta^\alpha c^\alpha) \frac{\partial c^\alpha}{\partial r} \bigg|_{r=r_1} = 0; \quad - D^\alpha (1 + \theta^\alpha c^\alpha) \frac{\partial c^\alpha}{\partial r} \bigg|_{r=r_2} = \frac{i_n}{F}. \hfill (3.19)$$

When the concentration at the outer surface reaches the equilibrium value of the $\alpha$ phase, phase transformation begins. Figure 3a illustrates the biphase hollow electrode particle. Combining the diffusion process of two phases, one can obtain the governing equations from equation (3.17),

$$\frac{\partial c^\alpha}{\partial t} = \frac{D^\alpha}{r^2} \frac{\partial}{\partial r} \left[r^2 (1 + \theta^\alpha c^\alpha) \frac{\partial c^\alpha}{\partial r} \right]$$

and

$$\frac{\partial c^\beta}{\partial t} = \frac{D^\beta}{r^2} \frac{\partial}{\partial r} \left[r^2 (1 + \theta^\beta c^\beta) \frac{\partial c^\beta}{\partial r} \right]. \hfill (3.20)$$

For the hollow spherical particles, the governing equation of the moving interface equation (2.17) reduces to

$$(c^\alpha_{\text{eq}} - c^\beta_{\text{eq}}) \frac{\partial \xi}{\partial t} = D^\beta (1 + \theta^\beta c^\beta_{\text{eq}}) \frac{\partial c^\beta}{\partial r} - D^\alpha (1 + \theta^\alpha c^\alpha_{\text{eq}}) \frac{\partial c^\alpha}{\partial r}.$$ \hfill (3.21)

It is noted that the contributions of $\theta^\alpha$ and $\theta^\beta$ to the movement of the phase interface have been ignored in previous work [44]. This is the first time they have been inserted into the governing equation.

The concentrations at two sides of the interface are equal to their own equilibrium values, i.e.

$$c^\alpha|_{r=\xi} = c^\alpha_{\text{eq}}; \quad c^\beta|_{r=\xi} = c^\beta_{\text{eq}}. \hfill (3.22)$$

At this stage, the concentration of the $\alpha$ phase satisfies the boundary condition at the inner surface, whereas that of the $\beta$ phase satisfies the boundary condition at the outer one, i.e.

$$- D^\alpha (1 + \theta^\alpha c^\alpha) \frac{\partial c^\alpha}{\partial r} \bigg|_{r=r_1} = 0; \quad - D^\beta (1 + \theta^\beta c^\beta) \frac{\partial c^\beta}{\partial r} \bigg|_{r=r_2} = \frac{i_n}{F}. \hfill (3.23)$$

During the process of phase transformation, the phase interface moves inward, which means the $\alpha$ phase decreases, and the $\beta$ phase increases. When the phase transformation finishes, the $\alpha$ phase disappears and only the $\beta$ phase is left in the electrode (figure 3c). The governing equation is

$$\frac{\partial c^\beta}{\partial t} = \frac{D^\beta}{r^2} \frac{\partial}{\partial r} \left[r^2 (1 + \theta^\beta c^\beta) \frac{\partial c^\beta}{\partial r} \right]. \hfill (3.24)$$

The corresponding boundary conditions are given as

$$- D^\alpha (1 + \theta^\beta c^\beta) \frac{\partial c^\beta}{\partial r} \bigg|_{r=r_1} = 0; \quad - D^\beta (1 + \theta^\beta c^\beta) \frac{\partial c^\beta}{\partial r} \bigg|_{r=r_2} = \frac{i_n}{F}. \hfill (3.25)$$

The beauty of the formulation for the hollow spherical particle is that the governing equations (3.17), (3.20), (3.21) and (3.24) are decoupled from the stress field explicitly. This indicates that one can directly compute the concentration field by using equations (3.17)–(3.25). Then, the stress field can be calculated by solving equations (3.7)–(3.12).
Table 1. Material properties of LiCoO$_2$ [44].

<table>
<thead>
<tr>
<th>material property</th>
<th>symbol</th>
<th>unit</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>maximum concentration</td>
<td>$c_{\text{max}}$</td>
<td>mol cm$^{-3}$</td>
<td>0.049943</td>
<td>0.049943</td>
</tr>
<tr>
<td>equilibrium concentration</td>
<td>$c_{\text{eq}}$</td>
<td>mol cm$^{-3}$</td>
<td>0.75$c_{\text{max}}$</td>
<td>0.97$c_{\text{max}}$</td>
</tr>
<tr>
<td>diffusivity</td>
<td>$D$</td>
<td>cm$^2$ s$^{-1}$</td>
<td>$10^{-9}$</td>
<td>$2 \times 10^{-9}$</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>$E$</td>
<td>GPa</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>partial molar volume</td>
<td>$\Omega$</td>
<td>cm$^3$ mol$^{-1}$</td>
<td>19.15169</td>
<td>19.4414</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td>$\nu$</td>
<td>—</td>
<td>0.2</td>
<td>0.16</td>
</tr>
</tbody>
</table>

4. Concentration and stress with hydrostatic stress

Section 3 provides the equations of concentration and stress field. Equation (3.20) is the governing equation of concentration with the effect of hydrostatic stress. To find out the concentration and stress fields with the effect of hydrostatic stress, a hollow spherical electrode is analysed, whose inner and outer radii are 10 and 20 $\mu$m, respectively. Li$_x$CoO$_2$ is used as the electrode material in our simulation because it is the mostly reported electrode material with the phase transformation phenomenon and is the most widely used in industry. The material constants are listed in Table 1. The software COMSOL is used to solve the governing equations of concentration, in which a total of 400 elements are used (see electronic supplementary material).

(a) Concentration field

Being discharged under 10 A m$^{-2}$ currency density, the concentration field at the three stages is calculated. At the first stage, there is the $\alpha$ phase only. Figure 4a illustrates the concentration at different times in this stage. This stage takes about 2100 s to finish. One can observe that the concentration of Li ions increases with $r$ from the inner surface to the outer one. Equation (3.19) indicates that at the outer surface, the concentration gradient is inversely proportional to the factor $(1 + \theta c)$. The concentration of Li ions increases with time; therefore, the concentration gradient decreases with time. At 50 s, the concentration at the outer surface is about 10 times that at the inner surface. But the concentration is nearly uniform in the electrode at 500 s. At 2106.5 s, the concentration at the outer surface reaches the equilibrium value of the $\alpha$ phase. At this time, one can find that the concentration gradient is so small that the concentration everywhere is close to $c_{\text{eq}}^{\alpha}$.

When the phase transformation happens, an interface is observed between the $\alpha$ and the $\beta$ phases. The phase interface gradually moves from the outer surface to the inner surface. Figure 4b illustrates the concentration distribution when the phase interface is at different positions. Observations show that there is a concentration jump at the phase interface. The concentration at either side of the interface equals its own equilibrium value, i.e. $0.75c_{\text{max}}$ and $0.97c_{\text{max}}$, respectively. Compared with the concentration jump, the concentration gradient is still quite small. With the phase interface moving inward, the concentration and the gradient of the $\beta$ phase keep increasing. When the phase transformation finishes, the concentration at the outer surface is close to $c_{\text{max}}$.

As mentioned above, the governing equation of the phase interface is modified to include the effect of hydrostatic stress. Table 2 lists the time it needs for the phase interface to arrive at different positions. Compared with the conventional models without the effect of hydrostatic stress, the speed of phase interface movement is much faster. This means the time during the phase transformation stage is overestimated by the models without the hydrostatic stress effect.

The third stage begins when the phase transformation finishes. At this time, there is only the $\beta$ phase in the electrode. Figure 4c illustrates the concentration distribution at different times. It takes about 57 s before the concentration at the outer surface reaches $c_{\text{max}}$. This is not only the end
Figure 4. Concentration distribution of the electrode particle: (a) with the $\alpha$ phase only; (b) with both $\alpha$ and $\beta$ phases; and (c) with the $\beta$ phase only. (Online version in colour.)

Table 2. Time needed for the movement of phase interface.

<table>
<thead>
<tr>
<th>position</th>
<th>without hydrostatic stress (s)</th>
<th>with hydrostatic stress (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.9r_2$</td>
<td>23 500</td>
<td>171</td>
</tr>
<tr>
<td>$0.8r_2$</td>
<td>44 950</td>
<td>328</td>
</tr>
<tr>
<td>$0.7r_2$</td>
<td>61 210</td>
<td>452</td>
</tr>
<tr>
<td>$0.6r_2$</td>
<td>73 700</td>
<td>550</td>
</tr>
</tbody>
</table>

of the third stage, but also the end of the whole galvanostatic discharge process. Similar to the first stage, the concentration increases with time while its gradient decreases with time. In addition, the concentration increases with $r$, and is close to $c_{\text{max}}$ everywhere.

(b) Stress field

Owing to the non-uniform distribution of Li ions in the electrode, stress is induced. Because the hoop stress is directly related to the concentration field, the concentration discontinuity at the interface should have a significant effect on the stress field. Figure 5 illustrates the stress field of a hollow spherical electrode with 20 nm outer radius and 10 nm inner radius, which is discharged under 10 A m$^{-2}$ currency density. Physically, the atoms at the interface and surface experience different local environments, and the interface modulus and surface modulus can be different. However, in some situations, it is difficult to determine the interface modulus. In
much of the literature, the same values for interface and surface moduli have been used \[52,57,58\]. Therefore, in our simulation, we use the same value for constant surface and constant interface stress \(\tau^0 = 1\) J m\(^{-2}\), and the same value for the surface modulus and the interface modulus \(K^s = 5\) N m\(^{-1}\) \[13\]. Generally, for the single-phase electrode particle (e.g. LiMn\(_2\)O\(_4\)), the maximum stress inside the particle is about hundreds of MPa \[11,27\]. For the biphase electrode particle (e.g. LiCoO\(_2\)), the stress can be as high as several GPa because of the concentration discontinuity at the phase interface; similar values have been found by the theoretical model \[16\] and by experiment \[59\].

Stresses with and without considering the surface effect are compared. The radial stress increases with \(r\) from the inner surface to the phase interface, and then decreases from the interface to the outer surface. Without considering the surface or interface effect, it is zero at the inner and outer surfaces, and is continuous at the phase interface. For hollow particles, this effect is much more important due to its double surfaces. Under the effect of surface stress, radial stress is positive at the inner surface, and negative at the outer one, which is consistent with the boundary conditions in equation (3.11). A positive stress jump appears at the interface, which satisfies equation (3.8). It is noted that discontinuity of radial stress is caused by interface stress.

The hoop stress is the driving force of crack propagation for the electrode particle, which makes it more important in stress analysis. The hoop stress decreases from the inner surface to the phase interface. With a jump at the interface, the hoop stress changes from a positive to a negative value. It increases from the phase interface to the outer surface. The discontinuity of hoop stress is caused by three aspects: concentration discontinuity at the phase interface, the difference of material properties between two phases and the interface stress. Compared with radial stress, discontinuity of hoop stress at the interface is much higher. The reason for this huge discontinuity is the sharp jump in concentration at the interface. Therefore, one can conclude that the effect of the phase transformation on hoop stress is significant. By comparison, one can find that the surface/interface effect on hoop stress is much smaller.

In the above, we analysed the effect of hydrostatic stress on concentration and stress. The following text discusses the dependence of its effect on electrode size. For conventional models, the size effect on the stress field in the electrode particle has been analysed \[11,13,27\], which concludes that the stress of the larger electrode particles is higher than that of the smaller ones. However, the size effect induced by hydrostatic stress has not been analysed before. To investigate this effect, a cross-scale analysis is presented here, with particle size \((r_2)\) ranging from 10 nm to 10 \(\mu\)m, with the ratio of inner and outer radii \(\zeta\) remaining 0.5. All the particles are discharged under currency density 10 A m\(^{-2}\).

**Figure 6** illustrates the maximum and minimum hoop stresses of electrode particles with different sizes when the concentration at the outer surface reaches \(c^\alpha_{r_{eq}}\). The stress fields with/without considering the effect of hydrostatic stress are compared. For both models, the...
Figure 6. Variation of stress with size of electrode: (a) maximum hoop stress and (b) minimum hoop stress. (Online version in colour.)

absolute values of maximum and minimum hoop stresses increase with particle size. The maximum hoop stress is tensile, whereas the minimum one is compressive. The stress fields predicted by the two models are almost the same for the nanoelectrode particles. But a great difference is observed when the particles are at the microlevel. Without the effect of $\sigma_h$, the stress becomes quite high and reaches 160 MPa, owing to the large concentration gradient caused by particle size. However, in reality, the stress field is very low under the effect of $\sigma_h$. This is because $\sigma_h$ can lower the concentration gradient to a quite small value. Therefore, one can conclude that the effect of $\sigma_h$ is important for the micro-sized particles, but can be neglected for the nanoparticles. In the discharge process, the concentration increases with time, whereas in the charge process, it decreases with time. Considering that the effect of $\sigma_h$ increases with concentration, one can predict that it will increase with time in the discharge process, whereas it decays with time in the charge process.

In the above, we analysed the effect of hydrostatic stress on the concentration and stress field. One can conclude that the phase transformation process under the effect of hydrostatic stress is much faster, which indicates that the time during phase transformation is overestimated by conventional models without considering the effect of hydrostatic stress.

5. Size effect with surface/interface stress

In §4b, we find that hydrostatic stress can induce the size effect on the stress field of electrode particles. Actually, the size effect is also observed when the interface/surface stress has been taken into account [47,52,55]. Moreover, equation (3.8) implies that the surface/interface stress depends on particle size. A cross-scale analysis is presented here to investigate the size effect on LiCoO$_2$ electrode particle.

(a) Size effect with surface stress

In the first stage, phase transformation does not happen, and the $\alpha$ phase is left. To decouple the effect of phase transformation on the stress field, we analyse the size effect owing to surface stress in this stage. Figure 7 illustrates the maximum ($\sigma_{\theta_{\text{max}}}$) and minimum hoop stress ($\sigma_{\theta_{\text{min}}}$) of particles with different sizes. The variation in particle size is from 10 nm to 10 $\mu$m, whereas $\xi$ is 0.5. The currency density is 10 A m$^{-2}$. Without considering the surface stress, the maximum hoop stress is close to zero for nanoparticles, and increases with the size of electrode. When the size of particle is 10 $\mu$m, the maximum hoop stress has already reached nearly 200 MPa. The minimum hoop stress is always negative. In addition, it is quite close to zero when the particle is at the nanoscale, and then decreases with electrode size. When the size of the electrode particle is 10 $\mu$m, $\sigma_{\theta_{\text{min}}}$ is around $-200$ MPa. When the electrode particle is microsized, the stresses predicted by
Figure 7. Variation of hoop stress with sizes of electrodes: (a) maximum hoop stress and (b) minimum hoop stress. (Online version in colour.)

the model with/without the surface stress effect are almost the same. But when the electrode particle size reaches the nanoscale, there is a big difference between the stresses predicted by the model with/without the surface stress effect. The stress predicted by the model with surface stress shows that $\sigma_{\theta_{\text{max}}}$ becomes negative. And the absolute values of $\sigma_{\theta_{\text{max}}}$ and $\sigma_{\theta_{\text{min}}}$ are quite large. This means the whole particle is under compression. Therefore, if there is flaw or small cracks in the electrode, the stress field will stop them propagating. Moreover, one can conclude that the model without the surface stress effect cannot be applied to predict the stress field of nanoparticles.

(b) Size effect with interface stress

In §2, we concluded that the equation for surface stress at the inner and outer surfaces, equation (3.11), is a special case for the equilibrium equation of the interface, equation (3.8). Considering that the size effect on the stress field owing to surface stresses has been reported above, the size effect owing to interface stresses is expected. Figure 8 illustrates the stress field of electrode particles with different sizes but the same $\zeta = 0.5$. All the electrodes are discharged under $10 \text{ A m}^{-2}$ currency density. It is observed that the radial and hoop stresses both become lower for the smaller electrode particle. For electrode particles whose size is microscale, the discontinuity of radial stress at the phase interface is small. However, when the size of electrode particle reaches the nanoscale, a higher stress discontinuity of radial stress is observed. Therefore, one can conclude that the effect of the interface stress is important for nanoparticles, but can be neglected for particles at the microlevel. Recall that before phase transformation, the hoop stress at the inner surface of the nanoparticle is negative owing to the effect of surface stress (cf. figure 7b). But, the discontinuous concentration turns it into a positive value. Because the positive hoop stress may drive the existing crack to propagate, the biphase stage is the most dangerous.

6. Stress and efficiency of hollow electrodes

Hollow sphere particles are attracting more and more attention owing to their great potential in working as electrode particles. A lot of experiments reported better cyclability, higher rate capability and less capacity degradation compared with solid sphere electrodes [48–50]. Actually, when the inner radius $r_1 = 0$, i.e. $\zeta = 0$, the hollow sphere reduces to a solid one. When the inner radius $r_1$ is close to the outer radius $r_2$, $\zeta \approx 1$, the hollow sphere becomes a thin shell. In the following, we show that the parameter $\zeta (=r_1/r_2)$ can characterize the geometrical property of hollow particles.
Figure 8. Variation of stress fields with sizes of electrodes: (a) $\sigma_r$ and (b) $\sigma_\theta$. (Online version in colour.)

Figure 9. Maximum and minimum hoop stresses: (a) different sizes with same volume and (b) different volumes with same sizes. (Online version in colour.)

(a) Stress analysis

Figure 9a illustrates the maximum and minimum hoop stresses of hollow particles with different $\zeta$ but the same volume $1.1 \times 10^4 \mu m^3$. It indicates that the absolute values of maximum and minimum hoop stresses both decrease with $\zeta$. The stress of the particles with $\zeta = 0.05$ is 20 times more than that with $\zeta = 0.95$. One can conclude that the advantages of hollow electrode particles will be strengthened in thin shell structures. To highlight the effect of particle structure, no interface/surface and hydrostatic stresses are considered.

Figure 9b illustrates the maximum and minimum hoop stresses of hollow particles with the same outer radius, $13.82 \mu m$, but different inner radii. The absolute values of maximum and minimum stresses decrease with $\zeta$. Observations show that the thinner the shell is, the smaller the stress is. One can imagine that there will not be any stress if the shell thickness is close to zero, because no concentration gradient can be observed in such a single layer shell.

In summary, the hollow structure electrodes can significantly reduce the stress field of an electrode. The hoop stress decreases with the thickness of the shell. Because the tensive hoop stress is the driving force for the crack to propagate in the electrode, the smaller the thickness of the shell, the lower the failure possibility of the lithium ion batteries.

(b) Efficiency analysis

At the end of galvanostatic charge, there is some residual capacity. Without a constant voltage charge to extract the residual lithium, this part of the capacity will be wasted. To characterize the effective capacity of the battery, a variable $\eta$ (ratio of effective capacity to total capacity), which
characterizes the efficiency of the battery is defined as

$$\eta = \frac{\text{Cap}_t - \text{Cap}_\text{re}}{\text{Cap}_t},$$

(6.1)

where \(\text{Cap}_t\) is total capacity, and \(\text{Cap}_\text{re}\) is residual capacity. Note that \(\text{Cap}_\text{re} \geq 0, \eta \leq 1\). By performing the potentiostatic charge, \(\text{Cap}_\text{re}\) can reduce to zero, and \(\eta\) will become 1. But for the galvanostatic charge, \(\text{Cap}_\text{re}\) is always greater than zero.

Section 6 characterizes the advantages of hollow spherical electrodes on a stress field. For this special electrode particle, the total capacity is

$$\text{Cap}_t = \frac{4\pi}{3} Q \rho \Omega c_{\text{max}}(r_3^3 - r_1^3),$$

(6.2)

where \(Q\) is the theoretical capacity of the electrode material, and \(\rho\) is its density. The residual capacity of the electrode particle is

$$\text{Cap}_\text{re} = 4\pi Q \rho \Omega \int_{r_1}^{r_2} r^2 \, dr.$$  

(6.3)

Substitution of equation (6.2) into equation (6.1) yields

$$\eta = 1 - \frac{3\int_{r_1}^{r_2} r^2 \, dr}{c_{\text{max}}(r_3^3 - r_1^3)}.$$  

(6.4)

In the following, we take \(\text{Li}_x\text{Mn}_2\text{O}_4\) as an example to analyse the efficiency of the electrodes. The necessary material properties are provided by Woodford et al. [27]. Figure 10 illustrates variation of \(\eta\) with \(\zeta\). One can observe that \(\eta\) increases with \(\zeta\). When the shell is thin enough, i.e. \(\zeta\) is close to 1, \(\eta\) approaches 1, i.e. the battery is fully charged. This indicates that the effective capacity can be high enough without constant voltage charge, as long as the shell is thin enough. Moreover, the effects of currency density and particle size on efficiency are analysed. In figure 10a, the electrode particles have the same size, i.e. \(r_2 = 20\ \mu\text{m}\), but are charged under different currency densities. Observations show that \(\eta\) decreases with currency density. When currency density \(i_n = 5\ \text{A m}^{-2}\), the efficiency \(\eta\) is above 96%. In figure 10b, the particles with different sizes are charged under the same currency density, i.e. \(i_n = 20\ \text{A m}^{-2}\). One can observe that \(\eta\) decreases with particle size. For the electrode particle whose size is small enough (e.g. \(r_2 = 5\ \mu\text{m}\)), the efficiency \(\eta\) is higher than 96%. One can conclude that the high effective capacity can be obtained by using small electrode particles and low currency density.

In the above, we analysed the stress and efficiency of hollow electrode particles. One can conclude that the hollow electrode particle significantly reduces the stress. At the end of galvanostatic charge, hollow electrode particles can help to reduce the remaining lithium. However, the particle size of the hollow structure is larger than that of the solid one with the
same volume. Therefore, at the electrode level, the electrode with the hollow structure is larger than the one with the solid structure to obtain the same capacity.

7. Conclusion

This paper provides the governing equation for concentration and stress of an electrode with arbitrary geometry. The hydrostatic stress and surface/interface stress are coupled in the governing equation. The interface stress at the phase interface during phase transformation is firstly introduced. In addition, this is the first time of presenting the governing equation of phase interface movement under the effect of hydrostatic stress. The equations are then reformulated for specific hollow spherical electrode particles. COMSOL software is used to solve this mechanics–electrochemical coupling problem. Conclusions are summarized as follows:

1. Under the effect of hydrostatic stress, the phase transformation process is much faster, which means the time during phase transformation has been overestimated in previous publications. Through a cross-scale analysis, we found that the effect of hydrostatic stress is extremely significant for particles at the microlevel. Owing to the concentration discontinuity at the phase interface, a sharp jump in hoop stress is found.

2. The size effects owing to surface/interface stresses are analysed. The discontinuity of radial stress at the phase interface is observed for nanoparticles. The cross-scale analysis indicates that the effect of surface/interface stresses are significant for nanoelectrode particles, but can be neglected for the micro ones.

3. For nanoelectrode particles, before phase transformation happens, the electrode particle is under compression, which helps to reduce the danger of crack propagation. However, during phase transformation, the concentration discontinuity at the phase interface changes the hoop stress at the inner surface into high tension.

4. The structural advantage of the electrode particle is analysed, and one can find that the stress field is highly dependent on $\zeta (=r_1/r_2)$, and the stress decreases with shell thickness $(r_2 - r_1)$. A variable $\eta$ to characterize the efficiency (ratio of effective capacity over total capacity) of a battery is defined. $\eta$ increases with $\zeta$. When the thickness of a hollow electrode particle is small enough, $\eta$ is close to 1. Dependence of $\eta$ on currency density and electrode size is also investigated. One can use lower currency density and smaller electrode size to increase battery efficiency, and therefore lengthen the working time of the battery.

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References


