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Effect of Irreversible Electrochemical Reaction on Diffusion and Diffusion-Induced Stresses in Spherical Composition–Gradient Electrodes

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Abstract: Composition–gradient electrodes have been proved to have excellent electrochemical performances. The effect of irreversible electrochemical reaction on diffusion and diffusion-induced stresses in such electrodes is investigated. The diffusion equation and mechanical equation considering the electrochemical reaction and the heterogeneous factors are derived, and the distributions of lithium (Li) concentration and stresses in a spherical electrode are obtained under potentiostatic charging. The results indicate that the electrochemical reaction will slow down the diffusion process and enhance the stresses of the electrode. However, the heterogeneous factors of the electrochemical reaction could provide a positive effect on the stresses, which means that the heterogeneous factor is conducive to avoid capacity fading of the battery. The results suggest that the composition–gradient electrodes could be designed to have a decreasing transition form of forward reaction rate and an increasing transition form of the difference of atomic volume between reactants and the reaction product.

Keywords: Composition–Gradient Electrode; Diffusion-Induced Stress; Irreversible Electrochemical Reaction

1 Introduction

There is great interest in developing rechargeable lithium (Li) batteries with higher energy capacity and longer cycle life for applications in portable electronic devices, electric vehicles, and implantable medical devices [1]. The changing or discharging operations of Li-ion batteries would result in volume changes, which can cause mechanical degradation, leading to capacity fading of the batteries. After Prussin [2] first analysed the phenomenon of diffusion-induced stress (DIS) using an analogy method to thermal stresses, many efforts have been made to find out the mechanism of stress generation so as to increase the mechanical durability of batteries.

Cheng and Verbrugge [3] studied the evolution of stress in a spherical insertion electrode particle under potentiostatic and galvanostatic operation. Verbrugge and Cheng [4] investigated stress and strain–energy distributions within electrode particles under periodic potential excitations. Chen et al. [5] established a new model considering the dislocation mechanisms of nanostructured thin film electrode materials involving DIS. Zhao et al. [6] studied the plastic behaviour by formulating a theory that couples large amounts of lithiation and deformation. Hao and Fang [7] developed a model for spherical electrodes covered with shells including the effects of surface/interface stress. Suo and Yang [8] examined the coupling between diffusion and deformation in a bilayer electrode. Li et al. [9] investigated the mechanism of electrochemical performances of composition–gradient electrode by using thermodynamic theory and Fick's law of diffusion.

Besides, there are few works focusing on the stresses induced by electrochemical reaction. Yang [10] first incorporated the volumetric change due to local solid reaction in the theory of DIS and analysed the diffusion–reaction-induced deformation fields in the plate. The results indicated that local solid reaction significantly increases the stress on the surface of the plate. On the basis of Yang's work, Zhang et al. [11] developed a new relation among Li concentration, the fraction of forward reaction product, and the diffusion–reaction-induced stress, which is considered as reversible electrochemical reaction. The calculation result of a cylindrical Li-ion battery electrode shows that the electrochemical reaction has little effect on Li diffusion but enhances the stress significantly, and the reaction-induced stress is much larger than the DIS. Suo and Yang [12] carried out the transient analysis of DIS and evaluated the effect of solid reaction on stress.

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Xie et al. [13] proposed a kinetic model combining Li-ion diffusion through a lithiated phase with chemical reaction at the interface between lithiated amorphous and crystalline silicon.

When one substance diffuses into a solid body, the processes of diffusion and reaction occur concurrently. For example, Kim et al. [14] investigated the insertion mechanism of Li into Mg_2Si anode material for Li-ion batteries. First, they found that the (220) Bragg peak of Mg_2Si was shifted toward lower angles during the Li insertion, which means that the Mg_2Si lattice expands. This result showed that Mg_2Si can be a host matrix for Li intercalation, which proved that Li could diffuse into Mg_2Si. Second, the breakdown of the Mg_2Si structure and the occurrence of the isolation of Mg were observed through X-ray diffraction analyses, which means Mg_2Si was decomposed into Mg and Si, and the reconstruction reaction between Li and Si occurred to form a Li-Si alloy. This result showed that the reaction occurred concurrently during the Li insertion process. Kanamura et al. [15] investigated the structural change of the $LiMn_2O_4$ spinel structure induced by extraction of Li. They found that $Li_xMn_2O_4$ spinel structure provides a high reversibility for the insertion and extraction of Li, which means Li would diffuse into $Li_xMn_2O_4$ and be stored in it. On the other hand, the separation of Mn^{2+} ions from $Li_xMn_2O_4$ was detected by electron paramagnetic resonance, which indicates that $Li_xMn_2O_4$ decomposes through the extraction of Li to form Mn^{2+} compounds as a separate phase. This result could prove the existence of the concurrent reaction. Likewise, the mechanism of the reaction of SnSb with Li was studied by Yang et al. [16]; the decomposition of MoS_2 into Mo and S and the formation of Li_2S were observed by Du et al. [17]. Consequently, the electrochemical reaction plays a vital role in the Li insertion/deinsertion process, and the effect of electrochemical reaction on diffusion and DISs should be taken into account. A Li-ion battery, as an electrochemical system, is operated by current, and a certain amount of current, even though very small, must be passed through the cell. This current will cause an irreversible reaction to occur at the electrodes [18].

Composition–gradient electrodes [19–23], which have a smoothly varying composition gradients for Ni, Co, and Mn extended from the core to the surface within a single-cathode particle, show better electrochemical performance compared with conventional single-phase electrodes [24–27] or core-shell electrodes [28–32]. This article aims at evaluating the usual spherical composition–gradient electrodes and the effect of irreversible electrochemical reaction on diffusion and DISs in the electrodes. To study the influence of the heterogeneous factors in electrochemical reaction alone and exclude the influences of other heterogeneous factors which have been discussed in the previous study [33], the heterogeneous factors of diffusion coefficient, elastic modulus, and partial molar volume are taken as constants. In addition, plasticity [6] and concentration-dependent elastic modulus [34] are not considered in this study. The aim of this work is to reveal the influence of heterogeneous factors in electrochemical reaction on diffusion and stresses, so as to understand the excellent electrochemical performances of composition–gradient electrodes. This work may provide an optimized design of composition–gradient electrode material.

2 Mathematical Analysis

2.1 Diffusion Problem

Consider a cubic control volume of size $\Delta x_1 \times \Delta x_2 \times \Delta x_3$ in the composition–gradient sphere. Despite the heterogeneous material properties, the cube is homogeneous owing to the infinitesimally small size. Consider the electrochemical reaction during Li insertion in the electrode

$$Li + xB \rightarrow LiB_x, \tag{1}$$

where Li is solute atoms, B is the host atoms, and LiB_x is the reaction product. According to the Law of Mass Action of Devereux [35], the forward reaction rate considering the first-order reaction is

$$v = kC, \tag{2}$$

where k is the forward reaction rate constant, and C is the molar concentration of Li. For an irreversible reaction, the rate of removal of diffusing substance is equal to the forward reaction rate. Thus, the mass conservation equation considering the case of symmetrical spheres with respect to the centre is written as

$$\frac{\partial C}{\partial t} = -\frac{\partial (r^2 J)}{r^2 \partial r} - kC, \tag{3}$$

where J is the flux of Li.

The chemical potential in an ideal one-mole solid solution is employed [36]

$$\mu = \mu_0 + R_g T \ln C - \Omega \sigma_m \tag{4}$$

where μ_0 is the potential in a given standard state, $R_g = 8.314$ J/(mol·K) is the universal gas constant, T is the temperature, Ω is the partial molar volume of the

solute, and σ_m is the hydrostatic pressure. The first term on the right side of (4) is invariant of Li-ion concentration. The second term represents the contribution of configurational entropy. The third term describes the effects of the hydrostatic pressure.

The gradient of the chemical potential drives the flux of Li J, which is written as

$$J = -\frac{CD}{R_g T}\frac{\partial \mu}{\partial r}, \tag{5}$$

where $D = D(r)$ is the diffusion coefficient. In the composition–gradient electrode, the diffusion coefficient is a function of the radial coordinate.

Substituting (4) into (5), the flux of Li J is obtained

$$J = -D\frac{\partial C}{\partial r} + \frac{CD}{R_g T}\frac{\partial}{\partial r}(\Omega\sigma_m). \tag{6}$$

Finally, the diffusion equation considering the irreversible reaction is obtained by substituting (6) into (3)

$$\frac{\partial C}{\partial t} = \frac{2}{r}\left(D\frac{\partial C}{\partial r} - \frac{CD}{R_g T}\frac{\partial}{\partial r}(\Omega\sigma_m)\right) + \frac{\partial}{\partial r}\left(D\frac{\partial C}{\partial r} - \frac{CD}{R_g T}\frac{\partial}{\partial r}(\Omega\sigma_m)\right) - kC. \tag{7}$$

If there is no reaction in materials ($k = 0$), the diffusion equation reduces to the classical diffusion equation.

We assume that the initial concentration of the sphere is 0, and for potentiostatic charging, there is a constant concentration C_R at the surface of the sphere. Thus, the initial and boundary conditions are written as follows:

$$\begin{aligned} &C(r, 0) = 0 \\ &C(R, t) = C_R \\ &C(0, t) = \text{finite}, \end{aligned} \tag{8}$$

where R is the radius of the sphere, and C_R is the maximum Li-ion concentration corresponding to the material.

2.2 Mechanical Problem

The Li-ion diffusion process of inserting into or extracting from electrodes will cause volume changes. Experimental evidence has shown that the volume change induced by lithiation of a composition–gradient electrode is not significant [37, 38]. Therefore, the theory of linear elasticity is employed in this study. As for the electrochemical reaction, volume changes also occur due to the atomic volume of reactants being different from that of the reaction product. The volumetric strain caused by diffusion $\varepsilon_{\text{diffusion}}$ is expressed as [2]

$$\varepsilon_{\text{diffusion}} = \Omega C, \tag{9}$$

which means that the volumetric strain is proportional to the molar concentration distribution of Li ions.

Analogously, the volumetric strain caused by reaction $\varepsilon_{\text{reaction}}$ is proportional to the difference of atomic volume between reactants and the reaction product, ω, and the fraction of the reaction product formed, S. Thus, the volumetric strain caused by reaction $\varepsilon_{\text{reaction}}$ is expressed as [10]

$$\varepsilon_{\text{reaction}} = \omega S. \tag{10}$$

The value of ω depends on the material itself. In composition–gradient electrode, the volume contents of different materials change with the radial coordinates, so ω becomes a function of coordinates.

The forward reaction rate represents the rate of removal of diffusing substance. Thus, from (2), we can obtain

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -v = -kC. \tag{11}$$

The fraction of the reaction product formed, S, is proportional to the removal of diffusing substance, so the fraction of the reaction product formed in a time period of t is written as

$$S = \alpha\int_0^t v\mathrm{d}t = \alpha\int_0^t kC\mathrm{d}t, \tag{12}$$

where α is the proportional constant.

Substituting (12) into (10), the volumetric strain caused by reaction $\varepsilon_{\text{reaction}}$ is written as

$$\varepsilon_{\text{reaction}} = \omega\alpha\int_0^t kCd = \varpi\int_0^t C\mathrm{d}t, \tag{13}$$

where $\varpi = \omega\alpha k$ controls the forward reaction. As ω is a function of coordinates, the ϖ here is also a function of coordinates.

As mentioned before, the volumetric expansion of a solid body during the diffusion process is caused by both Li-ion diffusion and electrochemical reaction [14]. Thus, from (9) and (13), the resultant volumetric strain of a solid body is obtained

$$\varepsilon_{\text{volume}} = \varepsilon_{\text{diffusion}} + \varepsilon_{\text{reaction}} = \Omega C + \varpi\int_0^t C\mathrm{d}t. \tag{14}$$

Consider a solid sphere made of linear elastic isotropic gradient material. The sphere's material is graded through

the radial direction. The relationships between strain and radial displacement $u(r)$ are expressed as

$$\varepsilon_r = \frac{\mathrm{d}u}{\mathrm{d}r}, \quad \varepsilon_\theta = \frac{u}{r}, \tag{15}$$

where ε_r and ε_θ are the radial and tangential strain components, respectively.

By using the analogy between thermal stresses and diffusion–reaction-induced stress, the stress–strain relations are

$$\sigma_r = \lambda e + 2\mu\varepsilon_r - (3\lambda + 2\mu)\frac{1}{3}\left(\Omega C + \varpi \int_0^t C\mathrm{d}t\right)$$
$$\sigma_\theta = \lambda e + 2\mu\varepsilon_\theta - (3\lambda + 2\mu)\frac{1}{3}\left(\Omega C + \varpi \int_0^t C\mathrm{d}t\right), \tag{16}$$

where σ_r and σ_θ are the radial and tangential stress components, respectively, e is the elastic volume strain, and λ and μ are Lamé constants, which are denoted by Young's modulus E and Poisson's ratio ν as

$$\lambda = \frac{\nu E}{(1+\nu)(1-2\nu)}, \quad \mu = \frac{E}{2(1+\nu)}. \tag{17}$$

In absence of body force, the equation for static mechanical equilibrium of a sphere is given by

$$\frac{\mathrm{d}\sigma_r}{\mathrm{d}r} + \frac{2}{r}(\sigma_r - \sigma_\theta) = 0. \tag{18}$$

Using (15–18), the Lamé equation in term of the radial displacement considering the electrochemical reaction and the heterogeneous factors is obtained

$$(\lambda + 2\mu)\frac{\mathrm{d}^2u}{\mathrm{d}r^2} + \left(\frac{\mathrm{d}\lambda}{\mathrm{d}r} + 2\frac{\mathrm{d}\mu}{\mathrm{d}r} + \frac{2\lambda + 4\mu}{r}\right)\frac{\mathrm{d}u}{\mathrm{d}r} + \left(\frac{2}{r}\frac{\mathrm{d}\lambda}{\mathrm{d}r} - \frac{2\lambda + 4\mu}{r^2}\right)u = \frac{1}{3}\frac{\mathrm{d}}{\mathrm{d}r}\left[(3\lambda + 2\mu)\left(\Omega C + \varpi \int_0^t C\mathrm{d}t\right)\right]. \tag{19}$$

The traction-free condition for the surface is adopted as

$$\sigma_r(R, t) = 0. \tag{20}$$

The condition of initially stress-free is given as

$$u(r, 0) = 0. \tag{21}$$

The numerical solutions of diffusion and stresses considering the electrochemical reaction and the heterogeneous factors are obtained by using the commercial package COMSOL Multiphysics. The heterogeneous factors of diffusion coefficient, elastic modulus, and partial molar volume are not considered and are taken as constants in this research, as they have been discussed in a previous study [33]. Besides, there are two heterogeneous factors in electrochemical reaction, respectively, forward reaction rate factor k and the difference of atomic volume between reactants and the reaction product ω. The two heterogeneous factors are studied in this work.

3 Results and Discussion

There are few literatures [10, 11] that focus on the forward reaction rate k; thus, a parametric study is carried out at first to determine the selection of k. In an irreversible reaction, the parameter k controls the reaction rate, which determines the impact of the reaction kinetics on the lithiation response. To study the impact of reaction, the Thiele modulus [39] is introduced to describe the relationship between diffusion and reaction rate. The Thiele modulus ϕ for a first-order irreversible reaction is expressed as

$$\phi = \left(\frac{R^2/D}{1/k}\right)^{1/2} \tag{22}$$

where R^2/D is the characteristic diffusion time, and $1/k$ is the characteristic reaction time. The large value of the Thiele modulus represents fast reaction with slow diffusion, and vice versa. Until now, there is no study reporting the material properties of composition–gradient electrodes. Thus, similar to previous studies [9, 40], to evaluate the effects of heterogeneous factors on diffusion and stress of composition–gradient electrodes, we adopt the spatial linear variations of material properties; i.e. the material properties change linearly from the centre to the surface, to simulate the compositional change in space. We assume the electrode is made of $LiMn_2O_4$, whose material properties are listed in Table 1. Moreover, ω is assumed to be equal to the partial molar volume Ω at first. Five values

Table 1: Material properties of $LiMn_2O_4$.

Parameters	Values	Units
E	10×10^9 [7]	Pa
ν	0.3 [7]	/
C_R	2.29×10^4 [7]	mol/m^3
Ω	3.497×10^{-6} [7]	m^3/mol
ω	3.497×10^{-6}	m^3/mol
D	7.08×10^{-15} [7]	m^2/s
α	1 (assumed)	/
R	8×10^{-6}	m

Table 2: Examined ϕ and corresponding k.

ϕ^2	0.01	0.1	1	10	100
k	1.10619×10^{-6}	1.10619×10^{-5}	1.10619×10^{-4}	1.10619×10^{-3}	1.10619×10^{-2}

of ϕ are examined, and the corresponding values of k are listed in Table 2. Then, the distributions of concentration and stresses in the sphere considering electrochemical reaction at a given dimensionless time $\tau = Dt/R^2 = 0.05$ are shown in Figure 1. It is found that when $\phi^2 \leq 1$, the effects of the reaction on distributions of concentration and stresses are negligible. The effects of the reaction are mild when $\phi^2 = 10$, and the effects would be significant when $\phi^2 = 100$. To investigate the effects of heterogeneous factors in electrochemical reaction on diffusion and stresses, the significant impact of the reaction would be helpful. Thus, the forward reaction rate k is chosen to be 1×10^{-2}.

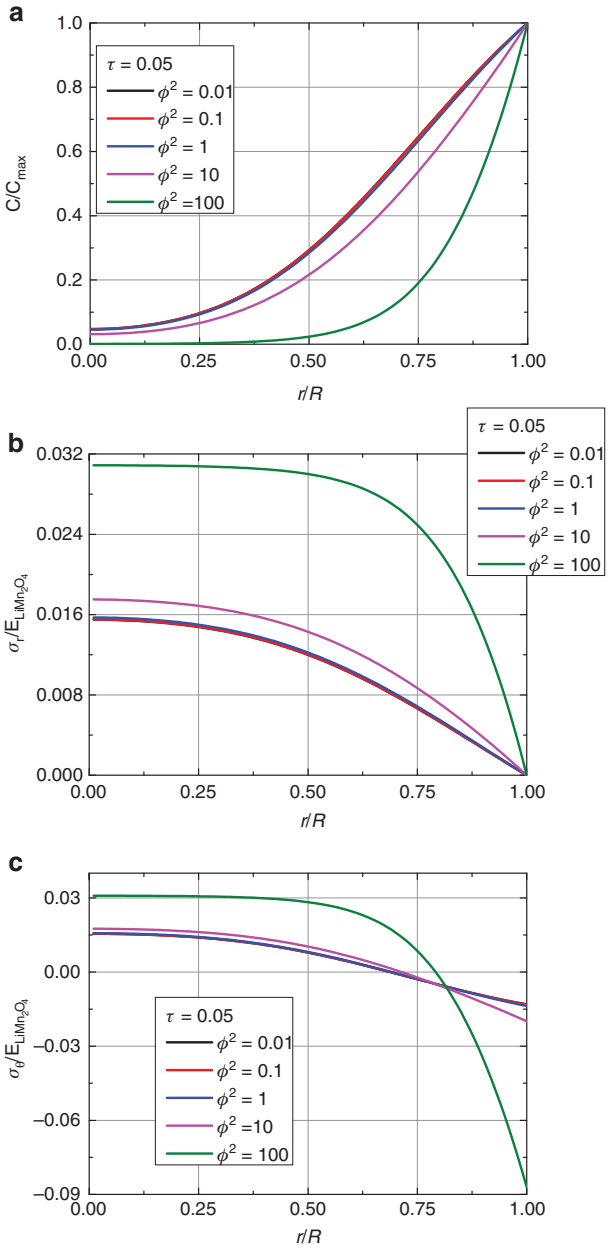

Figure 1: Distributions of (a) concentration, (b) radial stress, and (c) tangential stress in the sphere with different ϕ^2 at $\tau = 0.05$.

Besides, the effect of irreversible electrochemical reaction in homogeneous electrodes is studied by comparing diffusion and stress considering electrochemical reaction and that ignoring electrochemical reaction.

Figures 2 and 3 show the distributions of concentration and stresses in the sphere considering electrochemical reaction and that ignoring electrochemical reaction. Comparing Figure 2a with 3a, we can find that the electrochemical reaction slows down the diffusion process, and the effect becomes significant with the increasing dimensionless time. The comparison between Figures 2b and 3b shows a huge increase of stress in the electrode considering the electrochemical reaction, despite the concentration being much less than that ignoring electrochemical reaction, which indicates that the electrochemical reaction plays a vital role in the distributions of radial stress. Furthermore, with the increase of dimensionless time, the differences of the values between the two situations become larger, because the fraction of the reaction product increases with the increasing dimensionless time. For example, the normalized radial stresses at $\tau = 0.01$ are 0.0086 for the situation considering the electrochemical reaction and 0.01 for that ignoring the electrochemical reaction, but the normalized radial stresses at $\tau = 0.2$ become 0.0029 and 0.12, respectively, for the two situations, which means that the gap between the two situations widens. Figure 2c illustrates the distributions of tangential stress in the sphere during Li insertion ignoring electrochemical reaction. It is found that the tangential stress at the surface initially increases and then decreases, which is different from that considering electrochemical reaction. It is important to mention that these results revealing the significant influence of electrochemical reaction on stresses of the electrode are in good accord with the experimental report [41], which observed the mechanical cracking and capacity fading of cycled $LiMn_2O_4$ electrodes due to electrochemical reaction.

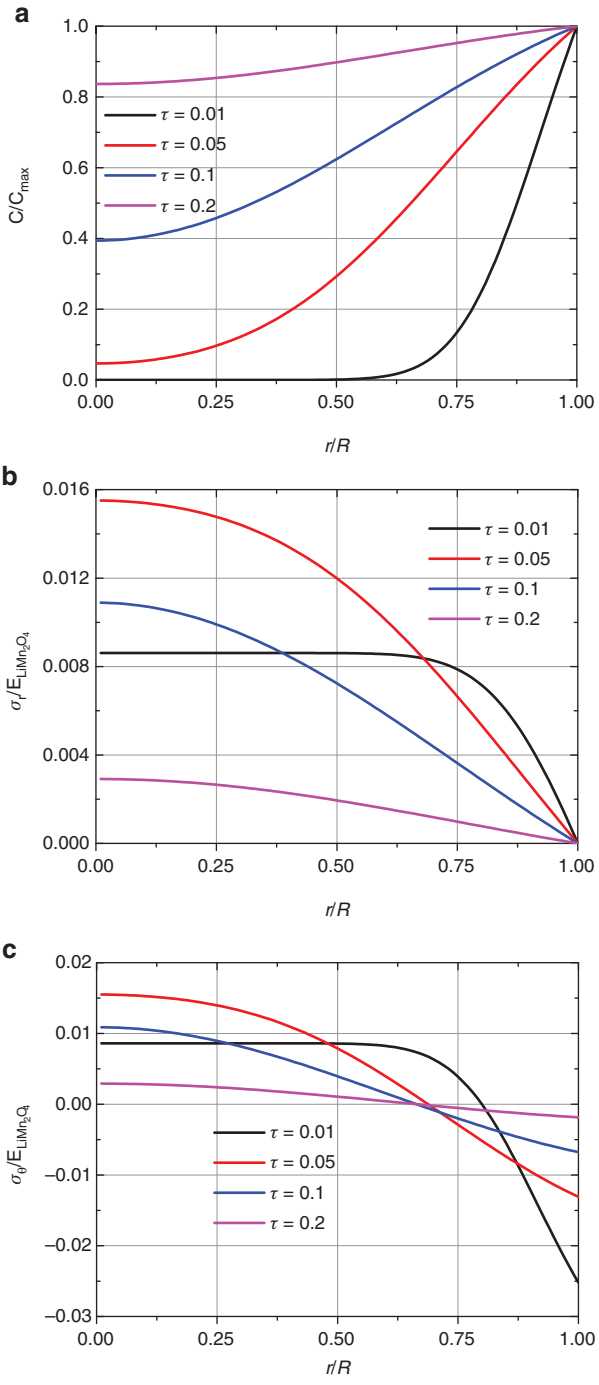

Figure 2: Distributions of (a) concentration, (b) radial stress, and (c) tangential stress in the sphere during the potentiostatic charging process ignoring the electrochemical reaction.

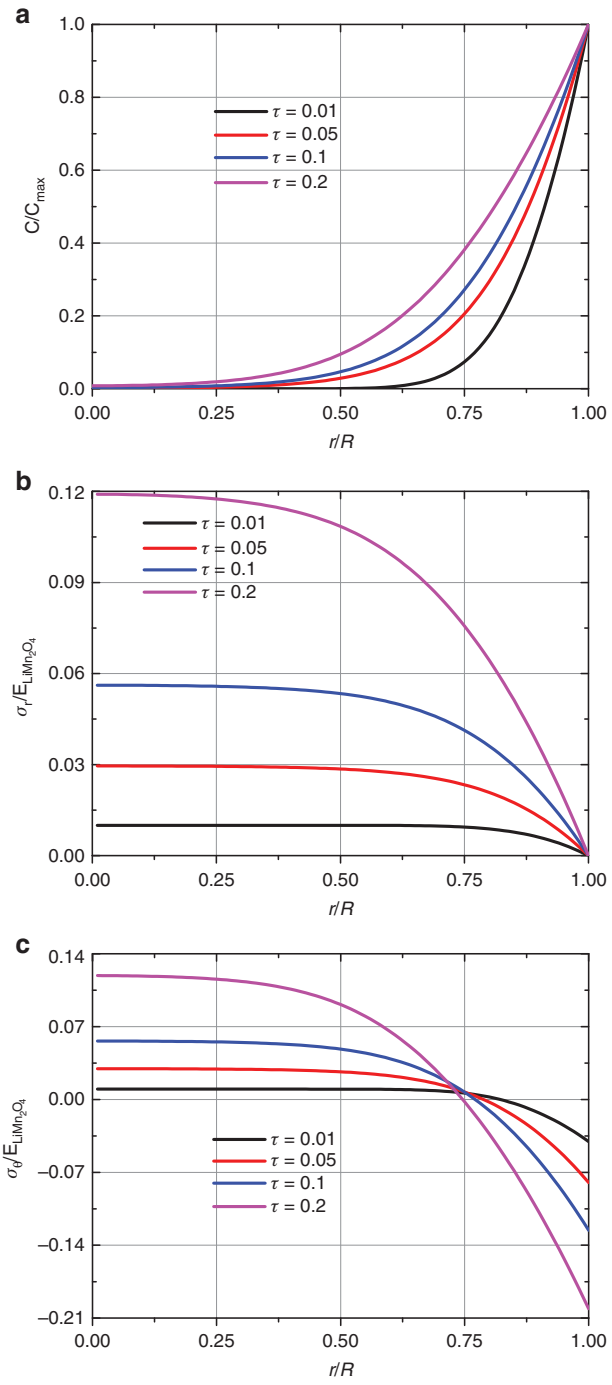

Figure 3: Distributions of (a) concentration, (b) radial stress, and (c) tangential stress in the sphere during the potentiostatic charging process considering the electrochemical reaction.

Figure 4 shows the evolution of the stresses in the sphere at various positions for the two situations. Figure 4a indicates that the radial stresses are tensile for the two situations. The tensile stress keeps growing with time when the electrochemical reaction is considered, while the tensile stress increases first and then decreases to zero when the electrochemical reaction is ignored. With the continuous diffusion of Li into the inner portion of the sphere and the electrochemical reaction, the tangential stress of the sphere gradually changes from tensile to compressive as shown in Figure 4b for the positions of $r/R = 0.75$ (solid line). The evolution of the tangential

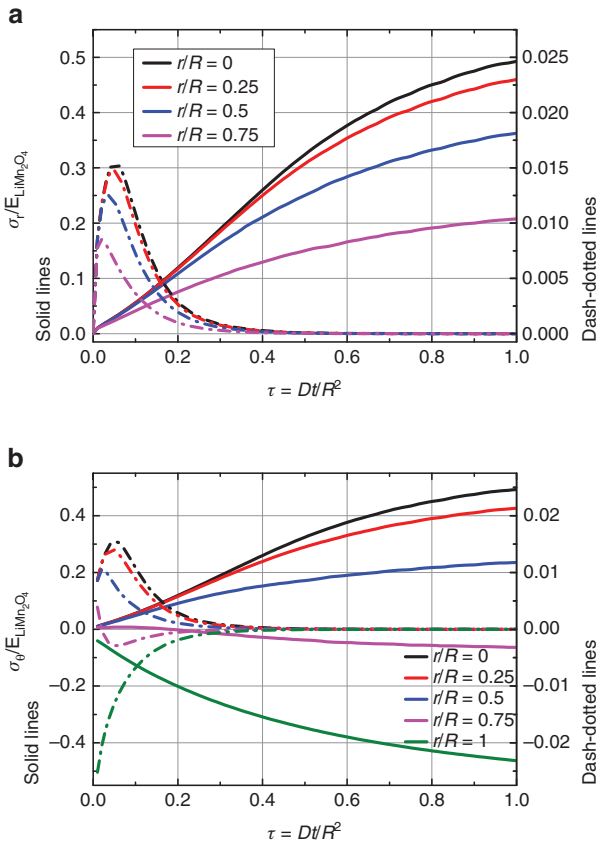

Figure 4: Evolution of the (a) radial stress and (b) tangential stress in the sphere at different positions: situation considering the electrochemical reaction for solid lines, situation ignoring the electrochemical reaction for dash-dotted lines.

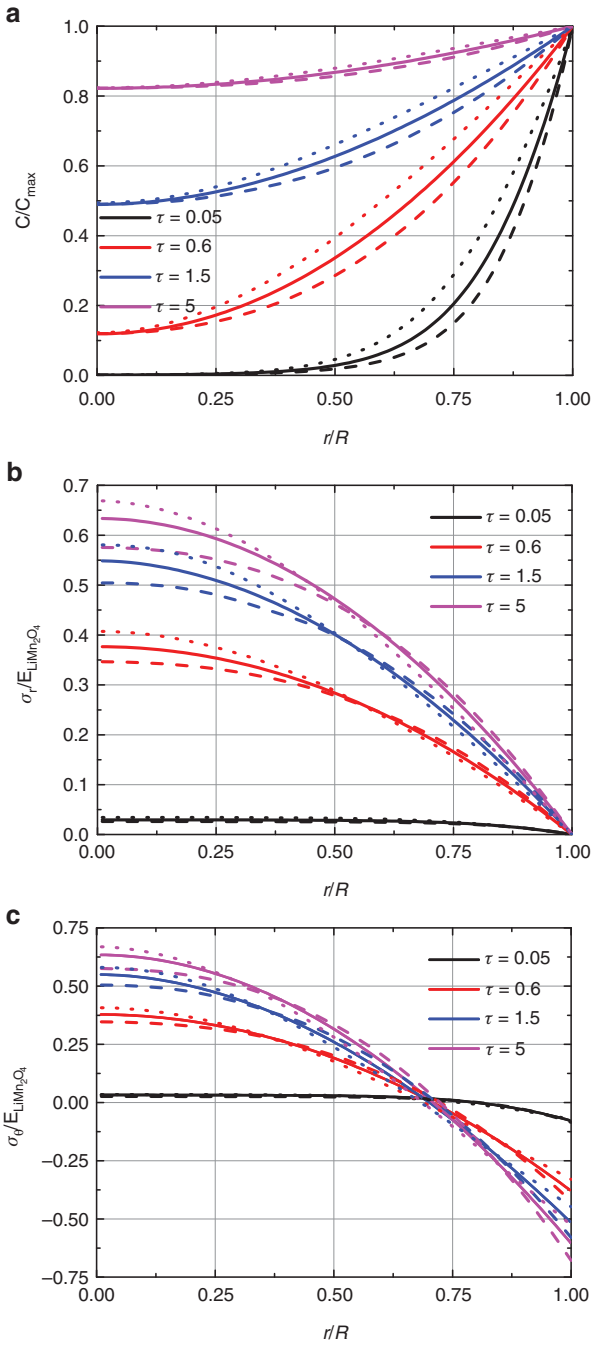

Figure 5: Effects of heterogeneous $k(r)$ on the distributions of (a) concentration, (b) radial stress, and (c) tangential stress during the potentiostatic charging process: homogeneous $k(r)$ for solid lines, $k(r)$ increases from $0.5k$ at the centre to $1.5k$ at the surface for dashed lines, $k(r)$ decreases from $1.5k$ at the centre to $0.5k$ at the surface for dotted lines.

stress when the electrochemical reaction is ignored is similar to that of the radial stress.

Then, the heterogeneous factor $k(r)$ of the electrochemical reaction in composition–gradient electrodes is studied. To investigate the influence of $k(r)$ alone, the other heterogeneous factors are taken as constants listed in Table 1. Because of the designability of the volume contents of the compositions, the material parameters could be designed to be functions of positions by arranging specific distributions of component contents. Thus, $k(r)$ is assumed to change linearly from the centre to the surface, and two forms of linear functions are studied, respectively, the increasing transition form of k ($0.5k$ at the centre to $1.5k$ at the surface): $k(r) = \frac{k}{R}r + 0.5k$; and the decreasing transition form of k ($1.5k$ at the centre to $0.5k$ at the surface): $k(r) = -\frac{k}{R}r + 1.5k$. The effects of heterogeneous $k(r)$ during the potentiostatic charging process are shown in Figure 5. The solid lines, dashed lines, and dotted lines represent the homogeneous, increasing, and decreasing forms of $k(r)$, respectively. The results indicate that the heterogeneous $k(r)$ have influences on both Li-ion diffusion and stresses. Figure 5a shows the distributions of concentration in the sphere. It is found that the increasing form of $k(r)$ slows down the diffusion process, while the

decreasing form of $k(r)$ speeds up the process, and with the increase of dimensionless time, the effect becomes slight. Figure 5b and c show the distributions of radial and tangential stresses in the sphere. The increasing form of $k(r)$ decreases the stresses at the centre of the sphere but increases the stresses near the surface, and the effect of reducing stress at the centre is more significant. The reason for this phenomenon is that the increasing form of $k(r)$ leads to the increasing form of $\varpi(r)$, and the smaller ϖ near the centre results in the smaller $\varepsilon_{\text{reaction}}$; the larger ϖ near the surface results in the larger $\varepsilon_{\text{reaction}}$. Opposite conclusions hold for the decreasing form of $k(r)$.

Finally, the heterogeneous factor $\omega(r)$ of the electrochemical reaction in composition–gradient electrodes is studied. The $\omega(r)$ is also assumed to change linearly from the centre to the surface, and other heterogeneous factors are taken as constants. Likewise, two forms of linear functions are studied, respectively, the increasing transition form of ω (0.95ω at the centre to 1.05ω at the surface): $\omega(r) = \frac{0.1\omega}{R}r + 0.95\omega$; and the decreasing transition form of ω (1.05ω at the centre to 0.95ω at the surface): $\omega(r) = -\frac{0.1\omega}{R}r + 1.05\omega$. Figure 6a illustrates the distributions of concentration in the sphere. It is found that the increasing form of $\omega(r)$ could accelerate the diffusion process, while the decreasing form $\omega(r)$ slows it down. This is because the tensile hydrostatic pressure is positive for the diffusion, and the tensile hydrostatic pressure for the increasing form of $\omega(r)$ is larger, leading to the acceleration of diffusion. Figure 6b and c show the distributions of radial and tangential stresses in the sphere. We found that the increasing form of $\omega(r)$ increases both the radial stress and tangential stress, while the decreasing form of $\omega(r)$ decreases the stresses. The effects of the heterogeneous $\omega(r)$ on the distributions of stresses become slighter during the charging process.

These results could provide an optimized design of composition–gradient electrode material. More particularly, to have a better charging performance, the composition–gradient electrode could be designed to have a decreasing transition form of $k(r)$ and an increasing transition form of $\omega(r)$; to have a better cycling performance, the electrode is supposed to be designed with an increasing transition form of $k(r)$ and a decreasing transition form of $\omega(r)$. It should be noted that the material properties of the composition–gradient electrode are determined by the spatial distributions of three compositions of Ni, Co, and Mn. Once the material properties of each single composition are known, the specified transition form could be achieved. For example, to have a decreasing transition form of $k(r)$, the volume content of a composition with a high value of k can be constructed to be high near the centre and low near the surface.

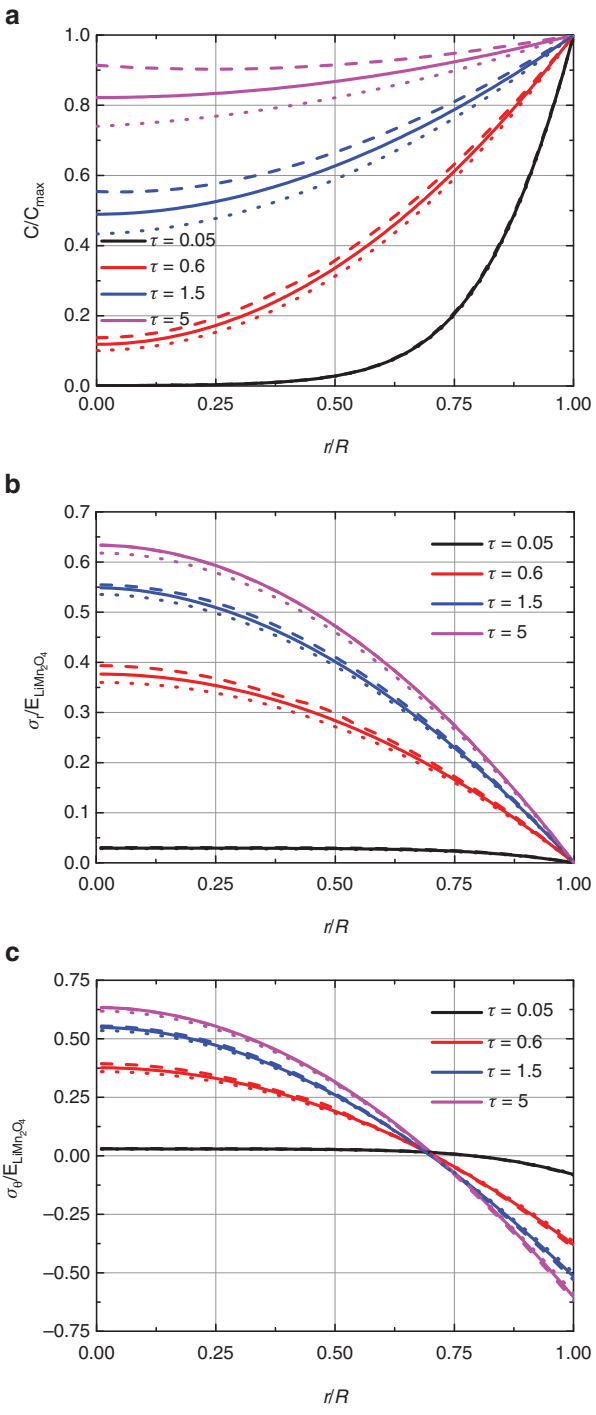

Figure 6: Effects of heterogeneous $\omega(r)$ on the distributions of (a) concentration, (b) radial stress, and (c) tangential stress during the potentiostatic charging process: homogeneous $\omega(r)$ for solid lines, $\omega(r)$ increases from 0.95ω at the centre to 1.05ω at the surface for dashed lines, $\omega(r)$ decreases from 1.05ω at the centre to 0.95ω at the surface for dotted lines.

4 Conclusions

The effect of irreversible electrochemical reaction on diffusion and DISs in spherical composition–gradient electrodes is investigated by formulating a diffusion equation and a mechanical equation considering the electrochemical reaction and the heterogeneous factors. The heterogeneous factors $k(r)$ and $\omega(r)$ are discussed. The results indicate that the electrochemical reaction has a significant effect on diffusion and will enhance the stresses of the electrode, leading to the mechanical degradation and capacity fading of the battery. However, the heterogeneous factors would have a positive effect on the stresses. When the $k(r)$ decreases from $1.5k$ at the centre to $0.5k$ at the surface, the electrochemical reaction would have a positive effect on the diffusion process and reduce the tensile tangential stress at the surface, which is conducive to avoid surface crack. Likewise, when the $\omega(r)$ is a decreasing form, the stresses would be reduced.

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