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Interaction between diffusion and stresses in composition-gradient electrodes

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ABSTRACT

Composition-gradient electrode material is one of the most promising materials in lithium-ion battery resulting from its inhomogeneous mechanical and electrochemical properties. The present work studies the interaction between stresses and diffusion in spherical composition-gradient electrodes. The large deformation theory is adopted to establish the mechanical equations, and the stress-induced diffusion is adopted to establish the diffusion equations. Compared with the interaction effects on lithium-ion distributions and stress distributions in homogeneous electrodes, the results in composition-gradient electrodes may show differences. Three inhomogeneous factors are investigated here—diffusion coefficient, elastic modulus and partial molar volume. When elastic modulus and diffusion coefficient are inhomogeneous, the interaction effects increase the magnitudes of radial stresses initially and then reduce the magnitudes of radial stresses, whose variations are same as the hoop stresses at the electrode center. On the other hand, the interaction effects can reduce the magnitudes of hoop stresses at electrode surface throughout the process of charge. However, when partial molar volume is inhomogeneous, the interaction effects show totally different influences on lithium-ion concentration distributions and stress distributions compared with those in homogeneous electrodes. The interaction effects play a positive role for the decreasing form of partial molar volume $\Omega(R)$, while the opposite conclusion hold for the increasing form of partial molar volume $\Omega(R)$. The results can guide the design of composition-gradient electrode materials.

1. Introduction

Developing advanced energy storage technologies to produce batteries of high energy density and capacity is critical to the applications in large scale energy storage, such as electric-based transportation. The realization of electric-based transportation critically depends on developing solutions to a wide variety of multi-disciplinary problems that limit the design, fabrication, and operational reliability of advanced LIB systems. It is believed that the optimization of electrochemical functions requires a comprehensive understanding of the materials and structural durability in the battery environment. Of major importance are issues which pertain to the prediction and control of the stresses [1–3] and structural damage [4–6] created by the insertion and de-insertion of lithium during electrochemical cycling.

Diffusion-induced stresses, resulting from lithium-ion insertion and de-insertion, were initially studied by Prussin [7]. Then, this kind of thermal analogy method was widely used to investigate the mechanism of stress generation in lithium-ion batteries. Deshpande et al. [8] studied the effects of concentration dependent elastic modulus on diffusion-induced stresses. Yang [9] used theories of dislocation mechanics and plasticity to analyze the effect of dislocations on diffusion-induced stresses. Yang [10] derived the closed-form solutions of the diffusion and forward reaction induced deformation fields in the plate. Zhang et al. [11] investigated the reversible electrochemical reaction on lithium-ion diffusion and stresses in a cylindrical lithium-ion battery electrode.

The literatures mentioned above only analyzed the stresses induced by the lithium-ion diffusion, ignoring the interaction effects of stresses and diffusion. When lithium-ions insert or de-insert into the electrode, inhomogeneous lithium-ion distribution may cause the stress, called diffusion-induced stress; conversely, the stress in the electrode may have great influences on lithium-ion concentration distribution, called stress-induced diffusion. The interaction between stress and diffusion is called interaction effects. Yang [12] considered the interaction between diffusion and chemical stresses in a plate. Hao and Fang [13,14] analyzed the core-shell electrode materials by considering the interaction effects of stress-induced diffusion and diffusion-induced stresses. Wang et al. [15] investigated the effects of chemical stresses on diffusion in a hollow cylinder. It can be concluded that stress-induced diffusion plays an important role in lithium-ion diffusion and stresses.

Here, the interaction effects of stresses and diffusion in a spherical composition-gradient electrode are investigated because the interaction effects may exhibit significant differences in composition-gradient electrodes compared with those in homogeneous electrodes. The novel composition-gradient electrode [16] $LiMn_{1.87}Ni_{0.13}O_4$ delivers a retention of 90.2% after 200 cycles, while the $LiMn_2O_4$ in the same condition

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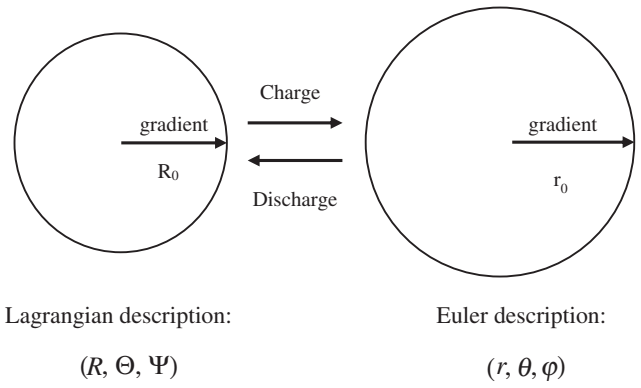

Fig. 1. Illustration of spherical composition-gradient nanoparticle in the Lagrangian form and Eulerian form.

exhibited only 57.8%. Basically, the composition-gradient electrodes [17,18] are lithium cobalt nickel manganese oxide material with layered structure, and high Ni content contributes to higher capacity; high Mn content contributes to higher structural stability; high Co content may lead to high charge and discharge rate. The main cause of high electrochemical performance in a spherical composition-gradient electrode is that the material properties and electrochemical properties change continuously from electrode center to surface. Li et al. [19] formulated a mathematical model to study the inhomogeneous effects on diffusion-induced stresses in spherical composition-gradient electrodes, where the stress field shows significant differences with that in homogeneous electrodes. Specifically, the composition-gradient electrodes are not stress free in the steady-state situation, while this phenomenon is quite different from the stress field in homogeneous electrodes. The stresses at the steady state may have great influences on lithium-ion diffusion, resulting in the arising interests to analyze the interaction effects of diffusion and stresses in spherical composition-gradient electrodes. Combining large deformation theory with diffusion theory, the interaction effects of stresses and diffusion are investigated in this paper. The results can provide more sophisticated foundation in guiding the design of composition-gradient electrode materials.

2. Basic theory

2.1. Governing equation of mechanical equilibrium

When lithium-ions insert or de-insert into the electrode material, the electrode may exhibit large volume change. Two descriptions are adopted: Lagrangian form and Eulerian form. Lagrangian form is based on initial configuration, while Eulerian form is based on current configuration. In a spherical composition-gradient nanoparticle (Fig. 1), a material point at $(R,\ \Theta,\ \Psi)$ in the Lagrangian description moves to $(r,\ \theta,\ \varphi)$ in the Euler description at time t. Based on the above definition, the total deformation gradient tensor is expressed as follow

$$\mathbf{F} = \begin{bmatrix} F_R & & \\ & F_\Theta & \\ & & F_\Psi \end{bmatrix} = \begin{bmatrix} \partial r/\partial R & & \\ & r/R & \\ & & r/R \end{bmatrix}. \tag{1}$$

The total deformation can be decomposed into elastic part $\mathbf{F}^e$ and inelastic part $\mathbf{F}^i$, namely

$$\mathbf{F} = \mathbf{F}^e\mathbf{F}^i. \tag{2}$$

The inelastic volume expansion is caused by lithium-ions intercalation and is assumed to be isotropic [19,20]. As a result, given lithium-ion concentration C in the Lagrangian description, we have inelastic deformation gradient tensor denoted as

$$\mathbf{F}^i = \begin{bmatrix} (1+\Omega(R)C)^{1/3} & & \\ & (1+\Omega(R)C)^{1/3} & \\ & & (1+\Omega(R)C)^{1/3} \end{bmatrix}, \tag{3}$$

where $\Omega(R)$ is partial molar volume of the solute. In a spherical composition-gradient electrode, such as $LiMn_{1.87}Ni_{0.13}O_4$, the material properties change along the radial direction and remain the same along

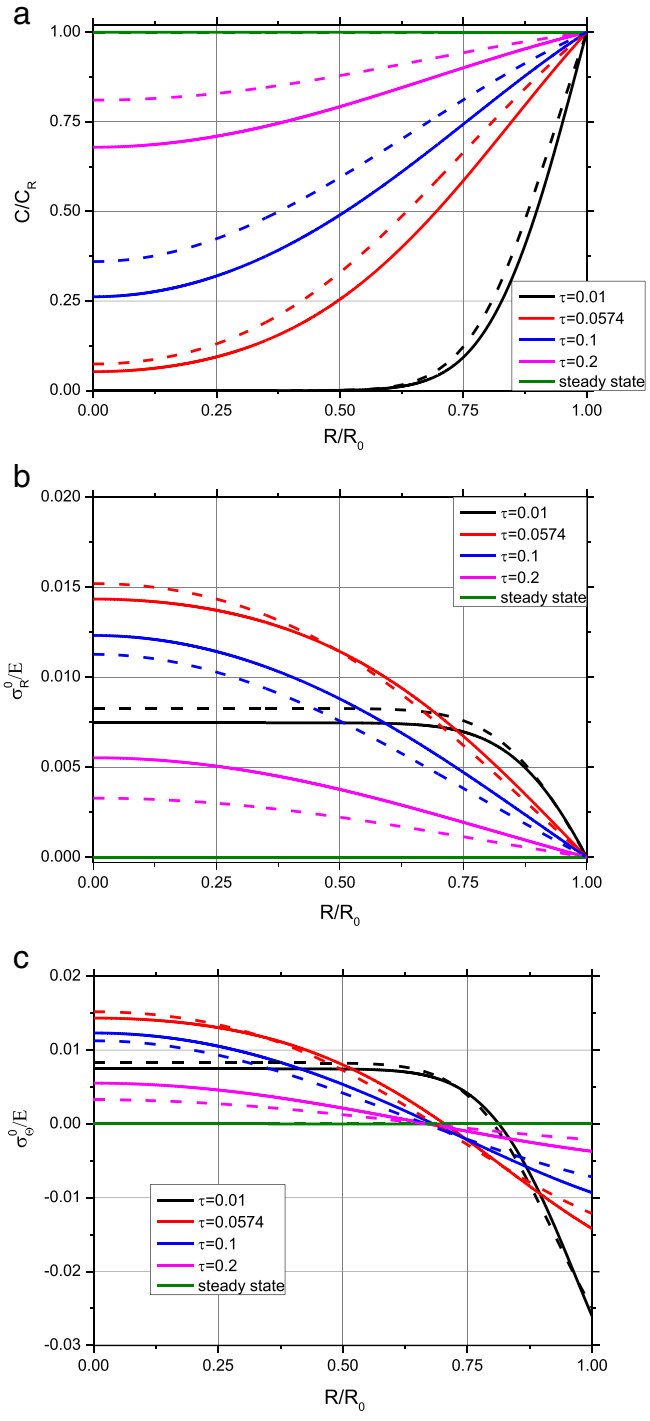

Fig. 2. Illustrations of lithium-ion concentration (a), radial stresses (b) and hoop stresses (c) in homogeneous electrodes at different normalized time. Solid lines represent the results ignoring the interaction effects, while dashed lines represent the results considering the interaction effects.