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# Diffusion of lithium ions and diffusion-induced stresses in a phase separating electrode under galvanostatic and potentiostatic operations: Phase field simulations

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## ABSTRACT

Phase separation in an electrode of a lithium ion battery, which is a phenomenon where an active electrode material is separated into Li-rich and Li-poor phases, exists widely in many active materials and has significant impacts on the diffusion of lithium ions and diffusion-induced stresses. A phase field model is developed to study the phase separation. Firstly, the influences of various energies, such as the free energy of uniform Li-ion concentration, gradient energy and elastic energy, on phase separation are discussed. Secondly, the impacts of charge operation, e.g. galvanostatic and potentiostatic, on Li-ion diffusion and diffusion-induced stresses in a planar phase separating electrode are investigated. Calculations are also made for single phase electrodes based on Fick's law for comparison. The obtained simulation results show that the Li-ion diffusion in a phase separating electrode depends significantly on the phase separating profile and movement of phase boundary, but it is not sensitive to charge operation. The diffusion-induced stresses also separate into high and low stress regions. Finally, based on the diffusion process and diffusion-induced stress, it is suggested that phase separation should be avoided for the sake of fast charging and mechanical reliability.

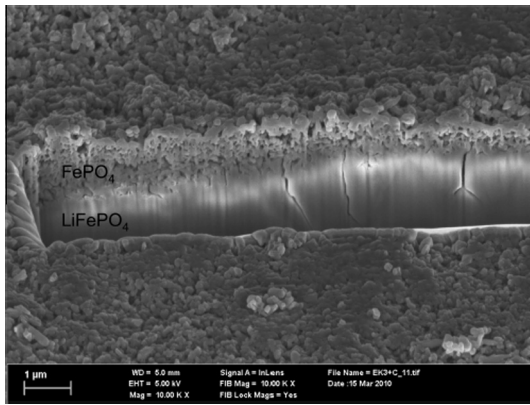
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## 1. Introduction

Diffusion of lithium ions in electrodes is one of the most important issues during the charging and discharging of a lithium ion battery because it is responsible for the spatial distribution of lithium ions in electrodes as well as the increase of diffusion-induced stresses that lead to mechanical degradation of electrode (Zhang et al., 2008; Cheng and Verbrugge, 2010; Zhao et al., 2010). Phase separation in electrodes, a phenomenon that an active material is

separated into Li-rich and Li-poor phases, exists widely in many active materials, such as silicon (Chon et al., 2011; Sun et al., 2013), LiMnO<sub>2</sub> (Lin et al., 2011) and LiFePO<sub>4</sub> (Laffont et al., 2006; Weichert et al., 2012), and it significantly influences the diffusion. Upon lithium insertion or removal, the sharp interface between different phases, called phase boundary, would move within the material and lead to formation of various multiphase structure depending on electrode geometry and state of charge. For example, a core-shell structure formed in an electrode particle with a spherical interface moving towards or away from the center (Sun et al., 2013; Laffont et al., 2006; Ebner et al., 2013), and a layered two-phase structure

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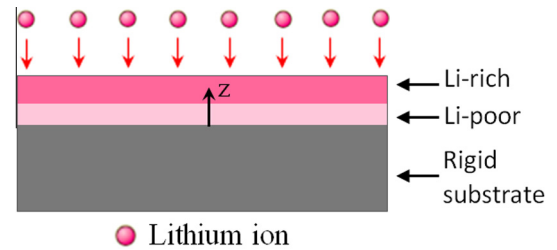


**Fig. 1.** A layered phase separating structure in LiFePO<sub>4</sub> electrode (Weichert et al., 2012).

was found in an LiFePO<sub>4</sub> electrode with a flat phase boundary (Weichert et al., 2012), as shown in Fig. 1.

Although Li-ion diffusion and diffusion-induced stresses are significantly affected by phase separation, many existing models had assumed that the materials remained in single phase during lithiation and delithiation (Haftbaradaran et al., 2011; Hao and Fang, 2013; Deshpande et al., 2010; Bower et al., 2011; Golmon et al., 2010) and, therefore, they were incapable of revealing the characteristics of Li-ion diffusion in a phase separating electrode. Recently, some researchers investigated phase separation in some cathode particles. For example, Huttin and Kamlah (2012) and Park et al. (2011) studied the phase separation and diffusion-induced stresses in LiMnO<sub>2</sub> particles. Bazant et al. discussed the size dependent spinodal and miscibility gap in nano electrode particles (Burch and Bazant, 2009), effects of coherency strain (Cogswell and Bazant, 2012) and suppression of phase separation (Bai et al., 2011) in LiFePO<sub>4</sub> nanoparticles. Bower et al. (2011) and Deshpande et al. (2011) have also discussed the phase separation in electrode particles. In addition, Di Leo et al. formulated a unified framework of Cahn–Hilliard type diffusion for the application of phase-separating electrode materials (Di Leo et al., 2014). Although these works are very important to the understanding of phase separation, they mainly focused on the morphology of phase separation, especially in electrode particles. The evolutions of phase separating profile and diffusion-induced stress under different charge operations have not been studied. Moreover, literature on phase separation in a film electrode is hardly available.

There are two possible charge operations, i.e. galvanostatic and potentiostatic. The former operation means constant intercalation ionic flux, whereas, in the latter operation the electrode surface is surrounded by invariant lithium ion concentration (Cheng and Verbrugge, 2009). Charge operation is very important to the migration of lithium ions in electrodes as it determines how lithium intercalation takes place. However, the impacts of charge operation on the evolution of Li-ion diffusion and diffusion-induced stress in a phase separating electrode have been hardly discussed. The present paper focuses on



**Fig. 2.** Schematic illustration of the film electrode investigated in this work.

a phase separating film electrode shown in Fig. 2 and simulates the evolutions of Li-ion diffusion and diffusion-induced stresses in the electrode during a lithiation process. The results obtained would be useful for studying: (1) the mechanism of formation of phase separation in a film electrode, and (2) the impacts of charge operation on the evolution of phase separation and diffusion-induced stresses.

## 2. Methodology

The electrode studied in the present study, which is composed of a rigid substrate and an active layer, is shown in Fig. 2. Upon lithiation, lithium ions are inserted into the electrode through the top surface and thereafter diffuse downwards, during which Li-rich and Li-poor phases are formed in the active layer. By considering that the film electrode is large, the Li-ion diffusion is one-dimensional along z-direction.

In the present study, phase field method (PFM) is employed to simulate the electrode of interest, for which the total free energy is written as

$$F = \int (f_{ec} + f_g + f_{ela}) dV \quad (1)$$

where  $f_{ec}$ ,  $f_g$  and  $f_{ela}$  are the densities of homogeneous free energy of uniform Li-ion concentration  $c$ , gradient energy and elastic energy, respectively.

Based on references (Huttin and Kamlah, 2012; Burch and Bazant, 2009), the free energy density  $f_{ec}$  can be expressed as

$$f_{ec} = ac(c_s - c) + 2RTc \ln c + 2RT(c_s - c) \ln(c_s - c) \quad (2)$$

where the three terms on the right hand side of equation account in order for enthalpy of mixing, entropy of mixing valid at low concentration and entropy of mixing responsible for saturation effects, respectively. The factor  $2RT$  accounts for the configurational entropy of both lithium ions and electrons due to low electron mobility (Bai et al., 2011). The factor  $a$  is a constant dependent on the weight of enthalpy,  $c$  is the molar concentration of lithium ions, and  $c_s$  is the saturation concentration at stoichiometric limit.  $R = 8.314472 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  is the gas constant and  $T$  is temperature. It should be noted that  $f_{ec}$  is the most important energy in the electrochemical system. Minimization of  $f_{ec}$  during Li-ion diffusion is the primary cause of phase separation.

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