



Analysis of the dependence of spinodal decomposition in nanoparticles on boundary reaction rate and free energy of mixing



Evgeny Pogorelov^a, Julia Kundin^{b,*}, Michael Fleck^c

^aAdvanced Ceramics Group, University Bremen, D-28359 Bremen, Germany

^bICAMS, Ruhr University Bochum, D-44801 Bochum, Germany

^cUniversity Bayreuth, Metals and Alloys, D-95447 Bayreuth, Germany

ARTICLE INFO

Article history:

Received 19 April 2017

Received in revised form 18 August 2017

Accepted 19 August 2017

Keywords:

Spinodal decomposition

Nanoparticles

Lattice misfit

Phase-field modeling

ABSTRACT

The mathematical model for intercalation dynamics in phase-separating materials (Singh et al., 2008) is a powerful tool for the investigation of the spinodal decomposition in nanoparticles. By means of this model, we conduct a careful mathematical analysis of the intercalation dynamics in nanoparticles to study the dependence of spinodal gap on the boundary reaction rate and the particle size, which can be used for LiFePO₄ battery material application. Consistent with previous investigations, we found that for some range of the boundary reaction rate and the particle size the concentration spinodal gap is not continuous, but it has stable “islands” where no spinodal decomposition is expected. The new important observation is that the presence of an infinitesimally small boundary reaction rate will destabilize nanoparticles even for infinitesimal length. In particular for nanoparticles having the size of order or less than interphase width λ , the spontaneous charge or discharge will occur at the reaction rate of order $0.1 D/\lambda$. The further raise of the intercalation rate will stabilize the system until some size limit of order two diffusion length. The intercalation effects are proven by means of numerical simulations. We also show that the increasing enthalpy of the spinodal mixture as well as increasing elastic energy due to the lattice misfit can destabilize the particles and increase the spinodal gap.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Electrode materials for Li-ion undergo phase transitions during electrochemical cycles. Lithium iron phosphate LiFePO₄ is one of the most intensively studied cathode materials for Li-ion batteries. The insertion/extraction mechanism in LiFePO₄ cathodes occurs through a two-phase solid-solid transformation of first order between Li_xFePO₄ and Li_{1-x}FePO₄ phases with x and $x' \ll 1$. The Li-insertion/extraction process and the spinodal miscibility gap in this system were investigated in many experimental works [1–8]. It was shown that interfacial charge transfer kinetics is very important for the phase transformation behavior in Li-ion batteries including the surface effects and the reduction of the miscibility gap [9–14]. Meethong et al. [5,6] experimentally investigated the particle size effects on the miscibility gap in nanoscale particles and showed the influence of the elastic strain during lithiation/delithiation cycles on the phase transformation behavior. Further investigations of Weeland et al. showed the effect of the coherency strain and surface wetting on the miscibility gap and phase

microstructure in LiFePO₄ nanoparticles [15]. The surface modification techniques such as the carbon coating [9,12] and graphene wrapping [11] can crucially improve the electrochemical power density of the batteries. During the experimental investigation of intercalation phenomena in Li-ion battery cathodes on the nanoscale level, Tang et al. [16] found that, for small particles, the surface effect is more sufficient and cannot be explained by the classic phase-field model. Intercalation phenomena in this case will drastically decrease the efficiency of Li-batteries preventing full charge/discharge cycle.

A number of analytical methods have been proposed in the last decades for a better understanding the phase transformation mechanisms [17–21,23]. One of the most suitable computational methods for modeling the phase transitions in electrode materials is the phase-field modeling [20,24,25,21]. This continuum approach allows the investigation of the phase separation dynamics in nanoparticles and prediction of the various effects including the intercalation waves and effect of coherency strain (see [22] and references therein). In order to incorporate the insertion/extraction mechanism in the phase-field approach, a general mathematical model was proposed by Singh, Ceder, and Bazant (SCB model) [20], which further was successfully used to study phase

* Corresponding author.

E-mail address: julia.kundin@ruhr-uni-bochum.de (J. Kundin).

transformation dynamics in single-crystal nanoparticles [24–27]. The model is based on the classical Cahn-Hilliard (CH) equation, which is a thermodynamically consistent approach to modeling spinodal phase decomposition. Singh et al. proposed to include the reaction or intercalation rate conditions on the boundaries which describe the intercalation of Li^+ in a particle in CH model. The system with these new boundary conditions is called Cahn-Hilliard reaction system (CHR). Burch and Bazant [25] investigated the CHR system using the perturbation theory and found that the miscibility gap as well as the spinodal gap generally shrink as the particle size decreases. Furthermore, the size-dependent spinodal gap continually reduces when the boundary intercalation rate increases. Tang et al. [28] investigated the effect of coherency strain on the phase transition in the presence of intercalation boundary conditions. Dargaville and Farrell [26] examined the full two-dimensional Cahn-Hilliard reaction system including anisotropic strain according to the approach of Cogswell and Bazant [29] and found that the phase separation persists even in small crystals. Bai et al. [22] showed the suppression of phase separation above a critical current in LiFePO_4 cathodes and concluded that a very slow discharge rate could reduce the cycle life of the battery. Then Dargaville and Farrell [27] used the high-rate experimental data to validate the previously developed CHR models and obtained a poor fit by variation of model parameters. Recently, Heo et al. [21] proposed a phase-field model for simulating phase microstructure evolution in the presence of surfaces. In their work, a Khachaturyan microelasticity theory was proposed for the solution of the elastic problem and incorporated in the Cahn-Hilliard equation in a similar way to Cogswell and Bazant [29].

Nowadays, the Li-ion battery technology is being developed in two main directions according to the suggestions of experimental and theoretical studies: (i) decreasing the size of cathode particles to nanoscale prevents spontaneous decomposition to some level and improves the power density; (ii) the use of various nano- or micro-coating changes the boundary reaction rate with obvious influence on the charging rate.

In the present work, we focus on the Li intercalation in LiFePO_4 nanoparticles for Li-ion battery applications. We conduct a detailed analysis of the influence of the boundary reaction rate on the size and structure of the spinodal Li concentration gap. The influence of the elastic strain is also investigated. The paper is organized as follows: in Section 2, we briefly describe the model equation. Then, in Section 3, the procedure of linear stability analysis which we use to find the spinodal gap as a function of the composition and particle size is presented. The results of the numerical calculation of the spinodal gap for various boundary conditions and strain energy contributions are presented in Section 4.

2. Model description

2.1. Bulk equations

The general SCB model for intercalation dynamics [20] describes three-dimensional systems with intercalation flux boundary conditions. The intercalant influx is imposed perpendicular to all surfaces of a nanoparticle with a local rate, R . Experiments in real LiFePO_4 nanoparticles which have plate-like form showed that the kinetic processes of the phase transition are strongly anisotropic [4,7,8]. Based on experimental and theoretical studies, Delmas et al. [8] suggested a “domino-cascade” mechanism of the phase transition, which is explained by the existence of structural constraints at the reaction interface. According to this approach, the concentration modulations occur in [100] direction with a uniform concentration profile in two other directions while the intercalation/deintercalation reaction occurs along the [010]

direction. However, this is just the case at the phase boundary. These findings make the application of the one-dimensional model presented in Ref. [25] for the analysis of spinodal decomposition by perturbation theory convenient.

Here, we rewrite the basic equations of SCB model for the one-dimensional system following Ref. [25] to make our further analysis consistent and clear. The classical Cahn-Hilliard type chemical potential of the investigated system is

$$\mu = \frac{\partial g_{\text{hom}}(c)}{\partial c} - K \frac{\partial^2 c}{\partial x^2}, \quad (1)$$

where g_{hom} is the free energy and K is the gradient parameter. The free energy in the CH model can be written as

$$g_{\text{hom}}(c) = ac(1-c) + k_B T [c \log c + (1-c) \log(1-c)] + E_{\text{coh}}, \quad (2)$$

where a is the enthalpy of mixing per site, k_B is the Boltzmann constant, T is the temperature, and E_{coh} is the elastic energy due to the lattice misfit defined as [21]:

$$E_{\text{coh}} = \frac{1}{2} \int_V \frac{d^3 k}{(2\pi)^3} [B(\hat{\mathbf{n}}) \hat{c}^2], \quad (3)$$

where $B(\hat{\mathbf{n}})$ is a function of the direction $\hat{\mathbf{n}}$ in the reciprocal space and \hat{c} is Fourier transform of the concentration.

Following Ref. [25], we define the flux of Li^+ ions as

$$J = -\rho c M \frac{\partial \mu}{\partial x}, \quad (4)$$

where M is a mobility parameter and ρ is the bulk density. The dependency on the concentration makes the behavior of the system asymmetric. Therefore, the center of instability range is shifted to $c_0 > 0.5$. Note that some authors prefer to use a symmetric model [28].

The time evolution of the concentration is given through the continuity equation

$$\frac{\partial c}{\partial t} + \frac{1}{\rho} \frac{\partial J}{\partial x} = 0. \quad (5)$$

Employing the above equations, we obtain the fourth-order equation for the concentration

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(c M \frac{\partial}{\partial x} \left(\frac{\partial g_{\text{hom}}}{\partial c} - K \frac{\partial^2 c}{\partial x^2} \right) \right). \quad (6)$$

2.2. Boundary conditions

We consider a particle of the size $[0; L]$. The boundary conditions on the left and on the right side are the following

$$\left. \frac{\partial c}{\partial x} \right|_{x=0,L} = 0 \quad (7)$$

$$(J - \rho_s R)|_{x=0} = 0, \quad (J + \rho_s R)|_{x=L} = 0, \quad (8)$$

where R is the insertion reaction rate which depends on the difference between the boundary value of the chemical potential μ and the “external” chemical potential $\mu_e = \text{const}$:

$$R = R_{\text{ins}} \left(1 - \exp \left(\frac{\mu - \mu_e}{k_B T} \right) \right), \quad (9)$$

Here, R_{ins} is the rate parameter and ρ_s is the surface density.

For the solution of the elastic problem, the zero surface traction boundary conditions are applied. These conditions result from the relaxation of coherency strain energy at surfaces of nanoparticles.

Download English Version:

<https://daneshyari.com/en/article/5453041>

Download Persian Version:

<https://daneshyari.com/article/5453041>

[Daneshyari.com](https://daneshyari.com)