

Elastic-strain effects on the phase separation in LiFePO₄ / FePO₄ system

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Lithium ion batteries are seeing widespread use in large-sized applications such as automobiles, which raises expectations for more high-performance storage batteries, combined with renewable energy technologies, to realize a sustainable society. The performance of lithium ion batteries, with regard to energy density, rate capability, cyclability and safety, has steadily improved since their launch in 1991. Since lithium ion batteries are simply based on the movement of lithium ion between the negative and positive electrodes, the advent of new active materials may dramatically improve the battery performance. The electromotive force of lithium-ion batteries depends on the difference in the chemical potential of lithium atoms between the two electrodes.

Lithium transition-metal phosphates with an olivine structure¹ have attracted much attention as promising positive-electrode materials for Li batteries. In particular, LiFePO₄ shows an acceptably large capacity, although insertion and extraction reactions of Li ions take place at relatively low potentials of 3.42 V vs. Li/Li⁺. Yamada et al.² clearly showed that there are two solid-solution regions outside both endpoints of the miscibility gap at room temperature, and insertion and extraction reactions of Li ions in LiFePO₄ basically undergoes a two-phase equilibrium. Furthermore, it is reported that the miscibility gap shrinks and solid-solution regions extend with reduced size of LiFePO₄ particles. Especially, Gibot et al.³ prepared nano-sized LiFePO₄ particles of about 40 nm, and demonstrated by X-ray diffraction that insertion and extraction reactions of Li ions proceeded forming a solid solution of Li_xFePO₄ over the almost entire composition range, although the electrode-potential variation still indicated two-phase equilibrium.

On the other hand, recently several works reported that the phase separation kinetics are significantly suppressed or retarded, and these interesting phenomena are generally believed to be due to the elastic strain due to the lattice mismatch. Also in our previous papers,⁴ the strain effects have been discussed for negative electrode materials (Sn, Al etc) in Li batteries, which have shown that the electrode potential (open circuit potential) can be significantly affected by the strain energy. Thus, the arguments on a transformation strain by lithiation and delithiation is gradually becoming frequent.

In terms of the elastic strain energy, it is usually considered that the nanoparticles are quite advantageous for the phase separation, because the elastic strain accompanied by the phase separation can be easily released in the vicinity of the particle surface (even without introducing misfit dislocations or mosaicity). Since the surface effects are usually enhanced as the particle size decreases, the phase separation is supposed to be facilitated in such small particles. However, in conflict with this expectation, several recent works have shown that nano-sized particles tend to undergo the single phase reaction. Thus, at the present stage, it is not yet

clarified how the associated elastic strain affects the phase separation during the charge/discharge processes.

In this study, we consider the elastic strain effects on the phase separation kinetics of the LiFePO₄ system, on the basis of the phase-field simulation with Cahn's spinodal decomposition theory and micromechanics theory. On the standpoint of the theoretical simulations, we show several significant features in the phase separation accompanying the coherent strain of this system (e.g. the stability of the anisotropic interfaces in Fig. 1), by summarizing the strain effects on the active materials in the light of previous experimental results and by describing the plausible dynamics mode of the charge/discharge process in the LiFePO₄/FePO₄ system.⁵ Furthermore, we explain why single nano-sized LiFePO₄ particles exhibit a complete single-phase reaction, which is still unclear problem to date. The mechanism of the single-phase reaction can be understood, when we consider the effects of both elastic strain energy and interfacial energy on the phase separation and/or, in the case of spinodal decomposition, a kinetics concept based on the critical or preferred wavelength for stable growth of the spinodal wave that takes account of both effects.

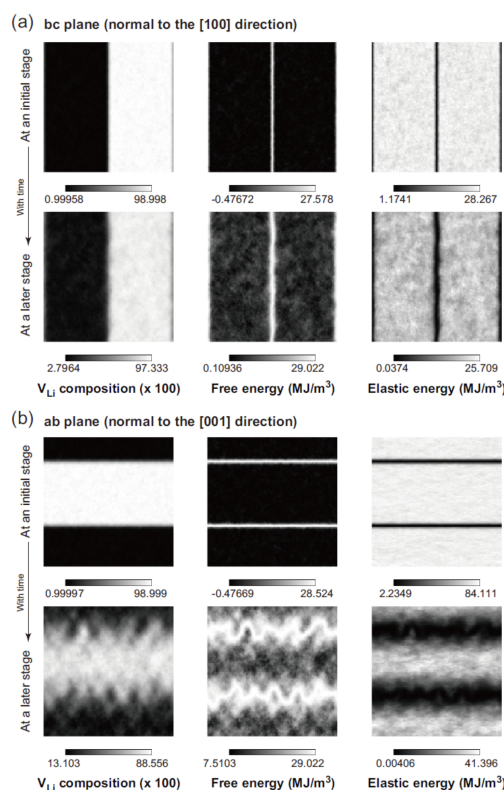


Figure 1. The stability of the anisotropic interfaces: (a) bc plane and (b) ab plane.⁵

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