

Asymmetry in anodic and cathodic polarization profile for LiFePO_4 positive electrode in rechargeable Li ion battery

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Asymmetric kinetics in the electrochemical charge–discharge reaction has been investigated in the two-phase coexistence system at LiFePO_4 positive electrodes for rechargeable Li ion batteries. The analyses of the electrochemical polarization profiles obtained by galvanostatic-pulse cycles reveals that nucleation and mass-transport is rate determining process for anodic and cathodic (charge and discharge) reaction, respectively, at high-rate conditions. We suggest that present two-phase system of LiFePO_4 – FePO_4 forms core–shell type construction in each particle or agglomerate of particles, where LiFePO_4 prefer to reside at outer shell-region of particles maybe due to smaller interfacial energy with electrolytes.

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1. Introduction

Research and development of olivine type LiFePO_4 positive electrodes for rechargeable Li ion batteries (LIB) have been vital due to its low cost, abundance of mineral resources, safety, and so on.^{1)–3)} Besides, Chung et al.⁴⁾ and Kang et al.⁵⁾ reported fast charge–discharge capability, or high-power density, in LiFePO_4 derivative materials which showed stable cycling at a high current rate of more than 100 C.⁶⁾ Thus, LiFePO_4 is expected to power hybrid and plug-in hybrid electric vehicles as well as portable devices.

To improve further their rate performances, quantitative studies on reaction kinetics are essential. In this respect, one of the key electrochemical behaviors is electrochemical polarization which is defined as a deviation from equilibrium voltage upon charge/discharge. The polarization consists of several components due to internal-resistances in LIB, such as electronic/ionic conductivity, charge-transfer reaction and mass-transport phenomena, and so forth. Several studies contributed to separate these resistance and analyze atomistic level reaction for LIB. For examples, we suggested adatom model to describe Li^+ exchange mechanism at Li|liquid electrolyte| $\text{LiLa}_{1/3}\text{NbO}_3$ system.⁷⁾ Abe et al.^{8),9)} reported the effect of desolvation, systematically. For the two-phase coexistent system, we have reported that nucleation of Li inserted/removed phase plays an important role.¹⁰⁾ In the LiFePO_4 – FePO_4 two-phase coexistence system, numerous reports tried to reveal reaction mechanism due to a practical importance mentioned above and fundamental fascination to understand two-phase coexistence reaction.^{11)–25)} The interfacial energy between two phase boundary,¹⁶⁾ and chemical potential anomaly at the surface of LiFePO_4 ¹⁷⁾ have been investigated to figure out the dependence of compositional range of the miscibility gap¹⁴⁾ upon the particle size. Laffont et al. reported LiFePO_4 – FePO_4 system by high-resolution electron energy loss spectroscopy (HR-EELS), and showed direct

evidence of two-phase coexistence in the single particles.¹²⁾ More recently, Delmas et al. suggested atomistic-level reaction mechanism called ‘domino-cascade model’, where successive *bc* phase-boundary movement along *a*-axis took place during charge–discharge accompanying Li^+ and e^- exchange in the *b* direction.²³⁾ As above, reaction kinetics was intensively investigated from atomistic level viewpoint. Another interesting aspect of the reaction kinetics is asymmetric charge–discharge profile in the LiFePO_4 – FePO_4 system reported by Srinivasan et al.¹⁵⁾ They interpreted asymmetric phenomena by classical shrinking-core model. Recently, Shin et al. investigated origin of asymmetric charge–discharge profiles by in-situ X-ray diffraction (XRD) technique, showing phase transition from FePO_4 to LiFePO_4 during discharge is more difficult to complete than during charge at high C-rate.²⁴⁾ Such asymmetric electrochemical phenomena should link the atomistic level discussion, while discussions on the asymmetric reaction kinetics are limited to date. Hence, present study aims to investigate the asymmetric kinetics between charge and discharge by measurement of polarization profiles during the galvanostatic pulse cycles, and suggest the macroscopic mechanism for kinetics of Li^+ exchange reaction in two-phase coexistent LiFePO_4 – FePO_4 system.

2. Experimental

Electrode sheets used in this study consist of active material (LiFePO_4), acetylene black (AB) as electronic conductive agent, and Poly(vinylidene fluoride) (PVdF) as binder at a weight ratio of 50:45:5. The mixture was ball-milled at 2000 rpm for 15 min with agate milling balls. The milled powders were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). We assembled air-tight three-electrode cells in Ar-filled glove box using lithium metal as counter and reference electrodes, and 1 M LiClO_4 in polypropylene carbonate (PC) as electrolyte solution. All the electrochemical tests were performed at 30°C by VMP3 multi channel potentiostat-galvanostat equipped with impedance modules (Bio-logic). Details on cell preparation scheme were described elsewhere.¹⁰⁾

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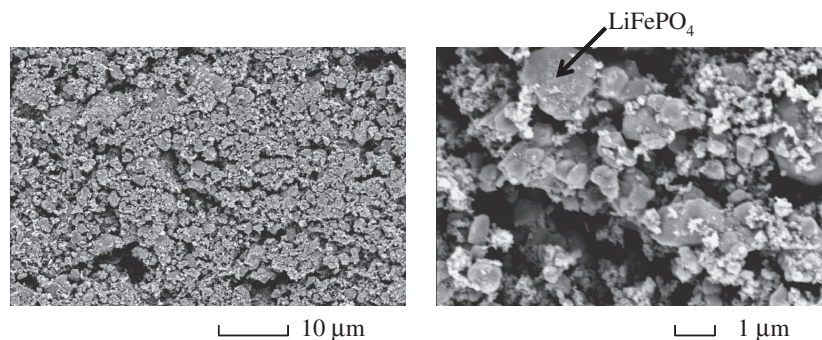


Fig. 1. SEM images of cathode composites of LiFePO₄, acetylene black, and PVdF binder, which was ball-milled, and casted on the Al sheet.

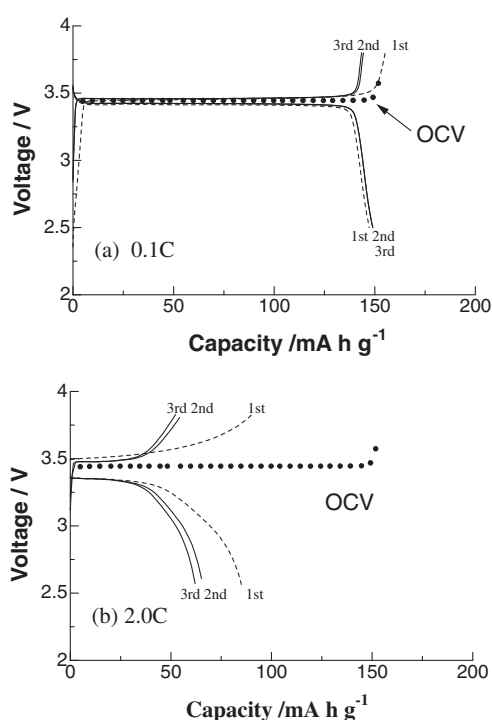


Fig. 2. Voltage profiles during initial three charge and discharge cycles in Li|LiFePO₄ cells.

3. Results

The phase and size of LiFePO₄ crystallite were confirmed to be olivine-type structure and ~ 30 nm, respectively, by the powder XRD.²⁶⁾ Figure 1 shows that the SEM images for cathode composites, LiFePO₄, AB, and PVdF, casted on the Al sheet, in which grain size of LiFePO₄ was ~ 1 μ m.

The assembled three-electrode-cell was cycled three times at 0.1 and 2.0 C with cut-off voltages of 2.5–3.8 V as shown in Figs. 2(a) and 2(b), respectively. Closed circles in the figures represent open circuit voltages (OCV) measured by galvanostatic interrupted titration technique (GITT) with 12 h relaxation. Significant irreversible capacity and capacity fading was not indicated except the irreversible capacity at first charging for these electrodes. Therefore, irreversible electrochemical side-reaction was completed at first-charging reaction. Flat voltage plateau was observed around 3.44 V vs. Li⁺/Li owing to the two-phase coexistent reaction (or miscibility gap), and sloping voltage profile was slightly seen at both ends of the plateau which

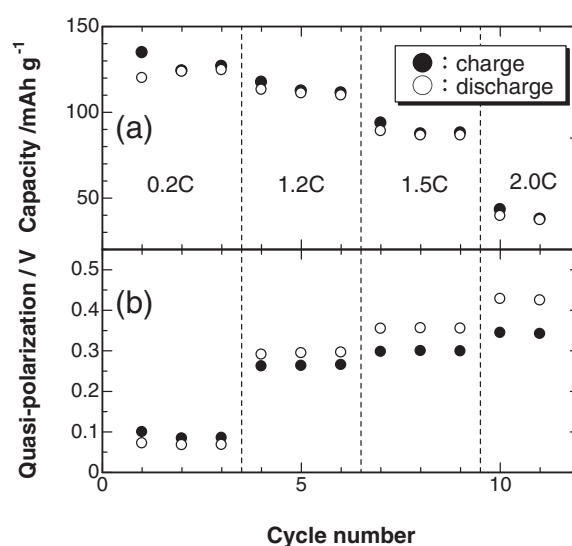


Fig. 3. Variation of capacity retentions and quasi-polarizations for charge and discharge in Li|LiFePO₄ cells.

corresponds to solid-solution region outside the miscibility gap as reported previously.¹⁴⁾ At two phase coexistence region, the OCV is 3.442 V vs. Li⁺/Li at 30°C. Note that OCV plots shown in Fig. 2(a) were corrected by deducting and adding half the difference between relaxed voltages after charge and discharge current pulse at $x \sim 0.5$. The electrode showed the reversible capacity of 150 mA h g⁻¹ which corresponds to 88% of Li ion was removed from the LiFePO₄ lattice, and relatively small and symmetric polarization (less than 0.05 V) against charge–discharge cycles was observed at a low current rate of 0.1 C. On the other hand, polarization became large and asymmetric at high rate charge–discharge cycles of 2.0 C. In particular, discharge curve indicated larger deviation from OCV voltages than charge, which accord with the report by Shin et al.²⁴⁾

We cycled the cell by changing current density every three cycles from 0.2 to 2.0 C, and the corresponding capacity retention and quasi-polarization are shown in Figs. 3(a) and 3(b), respectively. Note that quasi-polarization is defined as a difference between averaged voltage for charge or discharge cycle and OCV, which can roughly estimate the change of polarization with cycling. As seen in Fig. 3(a), capacity retention was reduced with current rates, while capacity difference between charge and discharge is sufficiently small. On the other hand, quasi-polarization was increased with the current density, and the quasi-polarization for discharge became larger than that for charge with

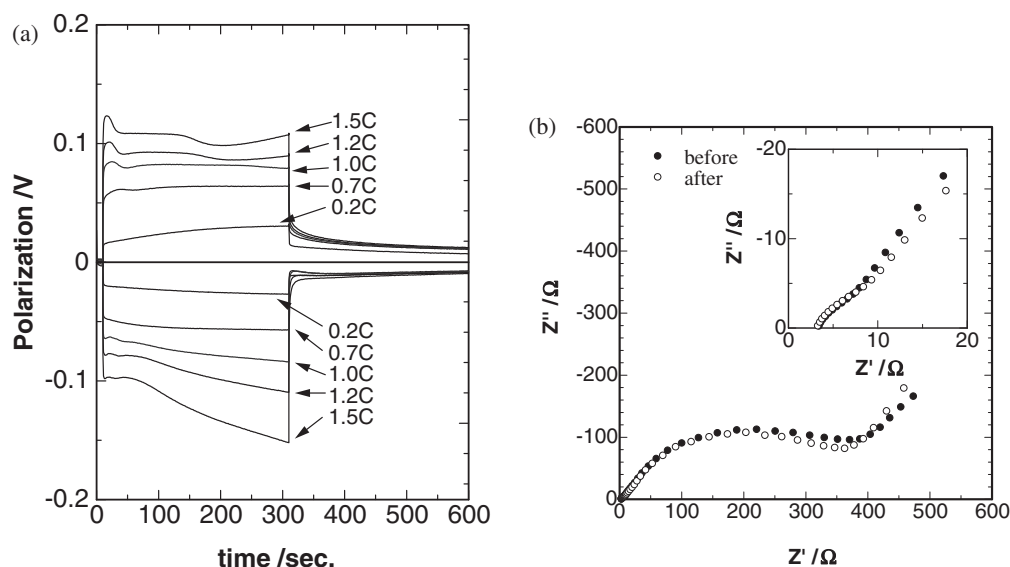


Fig. 4. (a) Polarization profile by galvanostatic charge–discharge pulses (300 s). The horizontal axis was set, such that the timing applying current pulse is zero. (b) Electrochemical AC impedance spectroscopy before and after galvanostatic charge–discharge pulse cycles in Li|LiFePO₄ cell.

increasing current rate. Therefore, present charge–discharge tests support a difference in reaction kinetics between charge and discharge at high rate condition as reported by Srinivasan et al.¹⁵⁾ and Shin et al.²⁴⁾

To understand the reaction kinetics further, polarization profiles by interrupted galvanostatic charge and discharge cycles were measured and analyzed. Another fresh cell was cycled at 0.1 C for three cycles to complete irreversible side reaction, and it charged from full-discharged condition for 5 h at 0.1 C (which corresponds to nominal composition of Li_{0.5}FePO₄) and relaxed for 12 h under open circuit condition. In this state, two phases of LiFePO₄ and FePO₄ coexisted with 1:1 molar ratio. Then, galvanostatic anodic and cathodic (charge and discharge) pulses were alternately applied for 300 s with intermitting relaxation for 12 h (galvanostatic-pulse cycles). Various current density of the galvanostatic pulses were set from 0.2 to 1.5 C.

The obtained polarization–time profiles are shown in Fig. 4(a). For the comparison purpose, the time (horizontal axis) is aligned such that the onset of current pulse is zero. The larger and smaller voltages against OCV correspond to the electrochemical polarization during charge and discharge, respectively. Note that the AC impedance measurement was performed before and after galvanostatic-pulse cycles, and no marked change in the impedance spectra was seen as shown in Fig. 4(b). Hence, the electrode|electrolyte interfacial condition was unchanged, or did not decay, during galvanostatic-pulse cycles.

4. Discussion

According to the theories in the electrochemistry,²⁷⁾ the polarization consists of at least three components as follows: (1) electronic and ionic conduction, (2) charge transfer reaction at the electrode|electrolyte interface, and (3) mass-transport process (such as concentration gradients driven diffusion). In this respect, the polarization profiles during current pulse are roughly divided into two parts. First one corresponds to the time range from 0 to several or tens of seconds, in which the components (1) and (2) would be included. After the components of (1) and (2) appeared, the component (3) is followed in the polarization curve. We inferred that the large portion of the immediate voltage rise (drop)

for the charge (discharge) current pulse was due to the poor electronic conductivity in LiFePO₄ as was pointed out in the previous papers.^{2),4)}

The voltage profiles are characterized by following two points: (i) The cusps were observed at the very initial parts of charging pulses, and (ii) the profiles were asymmetric between charge and discharge pulses, especially at higher rate conditions. In detail, the cusps referred as the feature (i) were related to the nucleation that a FePO₄ (LiFePO₄) crystalline-phase domain was formed in the LiFePO₄ (FePO₄) domain by charge (discharge).¹⁰⁾ This feature was less significant at lower rate condition and discharge pulse. The feature (ii) indicates a difference in reaction kinetics between charge and discharge at higher rate condition. [At sufficiently low rate condition, the voltage profiles were almost symmetrical as seen in Fig. 4(a).] In contrast to the clear characteristics of the nucleation during charge pulse, the large mass-transport driven polarization was observed during discharge pulse which was seen as the sloping voltage profile at 1.5 C in discharge from ~50 to 300 s.

Here, we adopted the core–shell phase separation mechanism as depicted in Fig. 5(A) by referring Laffont et al.'s paper¹²⁾ in order to account for the difference in the reaction kinetics between charge and discharge. In this model, we assumed that the FePO₄ phase (Li-poor phase) prefers to locate an inside of a particle due to large energy penalty at electrolyte|electrode interfaces. In this case, the core–shell phase separation is stable at equilibrium as shown in Fig. 5(A), where FePO₄ and LiFePO₄ phases formed at core and shell region of the particles, respectively. This core–shell phase separation model is analogous to classical core-shrinking model, but there is a difference that FePO₄ occupies always core of the particles. In fact, present model of FePO₄-core and LiFePO₄-shell arrangement can be supported by the Laffont et al.'s observation.¹²⁾

For charging [Fig. 5(B)], the Li ions were removed from LiFePO₄ phase, forming FePO₄ phase. Since the LiFePO₄ phase covers up the surfaces of the electrode particles, the nucleation of the FePO₄ phase may occur firstly. [See Step 2 in Fig. 5(B)] Due to the interfacial energy between FePO₄ nuclei and electrolytes, the nucleation process may expense relatively large energy.

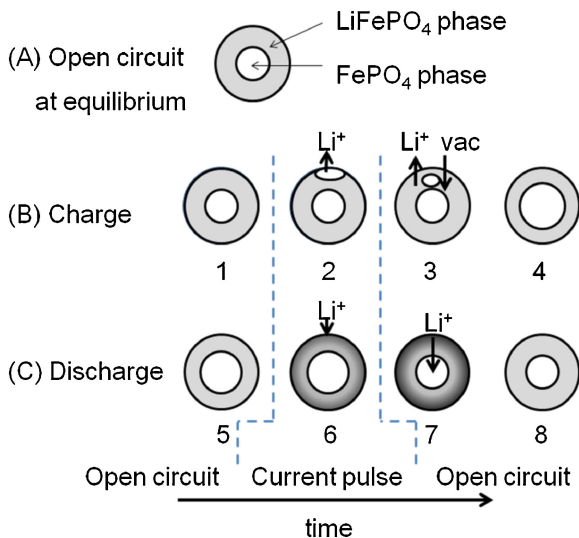


Fig. 5. (Color online) (A) Core-shell model of the particle where LiFePO₄ and FePO₄ phases coexist. (B) Proposed reaction model of Li⁺ removal and (C) insertion from/into LiFePO₄-FePO₄ particle. Grey-scale gradient at the shell of particle indicate concentration graduation of Li⁺ in LiFePO₄ phase [see panel 6 and 7 in (C)].

However, once nuclei of FePO₄ phase formed on the surfaces of the LiFePO₄ particles, following nuclei growth process does not need an excess energy for Li⁺ removal. As a result, the cusp of the voltage profile appeared at the very initial part of the current pulse.¹⁰⁾ [Fig. 4(a)] As mentioned above, mass-transport driven polarization appears generally at a later part of a current pulse. However, no significant increase was seen in the voltage profile for the charge in Fig. 4(a). (One can see flat voltage profile after the cusp related to nucleation.) This would be explained by present model in Fig. 5(B). Since LiFePO₄ phase is condensed at surface region, migration distance of Li⁺ from inside to outside of particles is rather short. Hence, the resulting mass-transport driven polarization is small for charging. (We consider that domain movement of FePO₄ may not relate to the polarization profile, because LiFePO₄ phase is only involved in electrochemical Li removal reaction at charging.) On the other hand, discharge reaction occurs as Li⁺ exchange between electrolyte and FePO₄ phase. Since FePO₄ phase reside at the inside of the particle, mass-transport (or FePO₄ phase movement) may proceed ahead of the nucleation reaction. Therefore, sloping polarization curve due to mass-transport became significant at the high rate condition. In addition, LiFePO₄ phase at the shell of particle can absorb extra Li ion to some extent at the beginning of discharge, since LiFePO₄ phase at two-phase coexistent equilibrium state may possess Li⁺ vacancy sites as described by Li_{1- α} FePO₄ ($\alpha \sim 0.05$ at ambient temperature) according to Yamada et al.¹⁴⁾ [Fig. 5(C)] This suppresses the nucleation process, and therefore, the cusp in polarization profile for discharge is faint comparing with that for charge. However, it is worthy to note that present model in Fig. 5 assumes isotropic diffusion of Li ions in the particle, although anisotropic one-dimensional Li jump in the lattice is commonly known.²⁸⁾⁻³¹⁾ This isotropic diffusion stems from the fact that the LiFePO₄ grains does not composed of primary particles (or single crystallites), but agglomerations of small crystallites, since grain size ($\sim 1 \mu\text{m}$) is much larger than the crystallites ($\sim 30 \text{nm}$) as mentioned above. Therefore, Li⁺ exchange assumed to be occurred in isotropic direction. In such way, the asymmetric

polarization profile between charge and discharge pulse may strongly depend on size and morphology of LiFePO₄ particles, since the distribution of two-phase domains are affected by the electrolyte|electrode interfacial energy. For example, Dokko et al. succeeded to control the morphology with facets in the various directions of LiFePO₄,³²⁾ so that the two-phase domain distribution in the LiFePO₄ particles and resulting reaction kinetics may be different from the present case. Further systematic studies are needed to understand the Li⁺ uptake/removal reaction in two-phase coexistent system.

5. Summary

Asymmetric voltage profile during charge and discharge reaction in the LiFePO₄-FePO₄ system have been studied by galvanostatic cathodic and anodic current pulse cycles. The observed polarization profiles indicated that nucleation and mass transportation are rate-determining process during charge and discharge, respectively, at high-rate condition. Our proposed model assuming that the LiFePO₄ and FePO₄ phases prefer to reside at the outside and the inside of particle, respectively, accounts well for the observed present electrochemical polarization profiles.

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