



Short communication

Open-circuit voltage study on LiFePO₄ olivine cathode

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ABSTRACT

Olivine LiFePO₄ particles were prepared by solid-state reaction using Li₂CO₃, (NH₄)₂HPO₄ and FeC₂O₄•2H₂O as raw materials, and they were coated with an appropriate amount of carbon through thermal decomposition of C₁₆H₁₀ pyrene. Cathodes using the olivine particles were subjected to an open-circuit voltage measurement under the relaxation condition of 24 h at each SOC and DOD states. The electrochemical reaction in the LiFePO₄ cathode was composed of a large plateau around 3.45 V with sloped regions nearby for both the fully charged and discharged states. It was found that the sloped region widths exhibited a hysteresis, that is, they depend on the direction of the redox reaction. Furthermore, both sloped regions became narrower when the operating temperature was raised from 30 °C to 60 °C. These facts implied that the obtained profiles were not in an equilibrium state with a quasi-OCV profile than the real one, and that the potential relaxation in the sloped regions took an extremely long time (more than 24 h).

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1. Introduction

Rechargeable lithium ion batteries are essential energy components of portable electronic devices and being intensively studied for large-scale applications, such as hybrid electric vehicles and plug-in hybrid electric vehicles. Layered rock salt compound LiCoO₂ is used as the cathode material for commercial lithium ion batteries, and LiMn_{1/3}Co_{1/3}Ni_{1/3}O₂ is considered to be a candidate for the cathode material of next generation batteries. But this material includes rare metal Co and is prone to release lattice oxygen at high temperature in the charged state, owing to its chemical instability. Large-scale batteries will be used in demanding applications and require large quantities of cathode material. Considering this, olivine compound LiFePO₄ is one of the most likely candidates for the cathode material of large-scale lithium ion batteries. Olivine structure LiFePO₄ was first proposed by Goodenough and co-workers [1] for its advantageous characteristics of being low cost, non-toxic and environmentally benign, with excellent structural stability. The lithium insertion/extraction reaction is in the form of a two-phase reaction, where LiFePO₄ and FePO₄ are the end members, so the potential profile of LiFePO₄ is very flat and located at 3.45 V versus Li/Li⁺. The theoretical capacity is 170 mAh g⁻¹, which is relatively high compared with other cathode materials.

However, the main problems preventing LiFePO₄ olivine cathodes from commercial utilization are the inherent low electronic and ionic conductivities. Many researchers have studied synthesis and modification of olivine material to overcome these drawbacks. Carbon coating over the particle surface, reducing particle size and cation substitution is commonly employed approaches to improve the electrochemical properties. The carbon coating is usually attained by thermal decomposition of organic materials, and it gives the electronic conduction path formation between cathode particles [2–5]. The particle fining reduces the average diffusion length of the lithium ion, but it brings about a difficulty to succeed high-density composite electrode [6–9]. The substitution of various cations in LiFePO₄ leads to the improvement of the intrinsic electronic and ionic conductivity [10–14]. In our previous work, the electrochemical performance of the olivine cathode was significantly enhanced with both partial substitution of Mn²⁺ and carbon coating [15].

Apart from the surface and bulk modifications, there has been extensive research about the electrochemical reaction mechanism of olivine compound LiFePO₄. The flat potential profile implies a two-phase reaction with LiFePO₄ and FePO₄ as end members, and Li⁺ deintercalation/intercalation models were proposed; a core-shell model by Srinivasan and Newman [16,17] and a domino-cascade model by Delmas et al. [18]. Although most of the redox profile had showed almost constant potential, several recent studies clarified the presence of solid solution regions around both the end members. Delacourt reported a high-temperature phase diagram of Li_xFePO₄, and discussed it using the spinodal

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decomposition concept, where the miscibility gap between the two phases decreased with increasing temperature [19]. It was found by Meethong et al. that the miscibility gap decreased as the particle size was reduced [20,21]. The similar phenomena, that the miscibility gap between the first order phase transition depends on the particle size, were also observed by Kobayashi on the system of Li_xFePO_4 [22] and Wagemaker on the system of anatase Li_xTiO_2 [23]. Both of them indicated that the miscibility gap is reduced with a decrease in the particle size. Further Masquelier and co-workers proposed that olivine particles with average particle size of 40 nm exhibited a single-phase reaction in the whole region [24]. But there was a vital problem; their specimen contained a very large amount of site disorder, and the work enabled us to conclude purely the relationships between the reaction mechanism and the particle size. Apart from these experimental works, Wagemaker theoretically predicted the size-dependent solubility [25], and Van der Ven also predicted the lattice strain effect on the solubility [26] and further discussed the potential profile from the viewpoint of the particle size distribution using numerical calculation [27].

By the way, it is required to evaluate the OCV profile after establishing the completion of the relaxation phenomena, because the electrochemical redox includes the kinetic effect (over-potential) and the resulting phases may have some deviations from the equilibrium state. If the equilibrium state is not attained, it is not reasonable to discuss the phase relationship using the OCV profile. In this study, we have experimentally obtained the OCV profile for both the charging and discharging directions at different operating temperatures. Two peculiar phenomena, the irreversibility and curious temperature dependence, are discussed from the viewpoint of the transient stage rather than the equilibrium state.

2. Experimental

LiFePO_4 olivine particles were prepared by solid-state reaction. The stoichiometric amounts of lithium carbonate Li_2CO_3 , ferrous oxalate dihydrate $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ were mixed together by wet ball-milling in organic media (acetone). The mixture was thermally decomposed at 350°C for 5 h under an N_2 flow. Then, an appropriate amount of pyrene $\text{C}_{16}\text{H}_{10}$ (approximately 10 wt.% based on the final product) was added for the carbon coating over the particle surface. The obtained powder was ground and mixed again by ball-milling in acetone. Finally, the mixture was annealed at 600°C in an N_2 atmosphere for 10 h, followed by furnace cooling down to room temperature.

The powder X-ray diffraction patterns were obtained on a Rigaku RINT-1500 diffractometer with $\text{Cu K}\alpha$ radiation at 40 kV and 200 mA. The full diffraction patterns of the products were taken in the 2θ range from 10° to 120° with 0.02° steps to identify the generated phases. The refinement of structural parameters was carried out by Rietveld analysis using RIETAN-2000 [28]. For the estimation of the average particle size, the specific surface area of the products was measured with the Brunauer, Emmett and Teller method.

The active material and acetylene black powders were mechanically dispersed in *N*-methyl-2-pyrrolidone solvent containing PVdF and the obtained slurry was coated onto an Al sheet current collector using the doctor blade technique. After the coated sheets were dried in a vacuum oven at 100°C for several days, these sheets were subjected to roll-pressing and disk electrodes with diameter of 15 mm were punched out. The cathode electrodes consisted of 80% active material, 10% acetylene black and 10% polyvinylidene fluoride in weight ratio. The active material loading was approximately 2.0 mg cm^{-2} and the thickness of the coating layer was approximately 15 μm . A Li coin cell, in which 1.0 M- LiPF_6 in ethyl carbonate/diethyl carbonate (1:1 in weight ratio) and Li metal foil

were used as the electrolyte solution and anode, respectively, was assembled in an Ar-filled glove box. The electrochemical measurements were performed using an HJ1001SM&A charging/discharging tester (HOKUTO DENKO). The cyclic voltammetry was measured at various scanning rates from 0.01 mV s^{-1} to 1.0 mV s^{-1} in the voltage range of 2.5–4.0 V, where the operating temperature was kept at 30°C , allowing us to estimate the apparent Li^+ diffusion coefficient.

The open-circuit voltage was evaluated in both directions starting from the 100% state of charge (SOC) and 100% depth of discharge (DOD). In the case of starting from the 100% SOC (100% DOD), the fully charged (discharged) state was obtained as follows: the cell was galvanostatically charged to 4.0 V (discharged to 2.5 V) at a constant current of 0.1 C and then further charged (discharged) at 4.0 V (2.5 V) under constant voltage until a charging (discharging) current of less than 0.001 C was attained. After the electrochemical discharge (charge) corresponding to 1% Li^+ intercalation (deintercalation), putting the cell into the open-circuit state for about 24 h led to the relaxation approaching the equilibrium state, after which the cell voltage was measured with an electrometer (HOKUTO DENKO, HE-104). These processes were repeated until the cell reached 100% DOD (100% SOC). The above OCV procedures were carried out under a controlled temperature of $30\text{--}60^\circ\text{C}$. In addition to the OCV measurement, the Li^+ diffusion coefficient was estimated by applying the galvanostatic intermittent titration technique to the potential evolution process during the lithiation (delithiation) current flowing.

3. Results and discussion

The obtained LiFePO_4 particles had a specific surface area of $15.6\text{ m}^2\text{ g}^{-1}$, which corresponded to an average diameter of 110 nm, assuming that the particles are spherical in shape. The residual amount of carbon was approximately 1.5 wt.%. The powder X-ray diffraction pattern of the synthesized LiFePO_4 particles is shown in Fig. 1. It was found to be a single phase of orthorhombic olivine compound (*Pnma* space group) with no impurities. The refined lattice parameters were $a = 10.326 \pm 0.002\text{ \AA}$, $b = 6.006 \pm 0.001\text{ \AA}$, and $c = 4.691 \pm 0.001\text{ \AA}$, all of which were in good agreement with the reported values [29].

The cyclic voltammograms were observed at various sweeping rates from 0.01 mV s^{-1} to 1 mV s^{-1} and are shown in Fig. 2. The profiles with sharp current peaks indicate that the electrochemical reaction is attributed to a two-phase reaction. The oxidation (reduction) peak potential shifted toward a higher (lower) voltage as the sweeping rate was raised. The separation between oxidation and reduction peak voltages corresponds to polarization, which is heightened with the current density. In addition, the redox peak currents increased with the sweeping rate. It was seen that the peak currents were proportional to the square root of the sweeping rate, which indicates that the rate-limited process is Li^+ ionic diffusion [30,31]. Hence, it was possible to estimate the Li^+ diffusion coefficient; because the electrochemical reaction of LiFePO_4 is a two-phase reaction, the diffusion coefficient is not a real Li^+ ionic diffusion but a migration rate of the $\text{LiFePO}_4/\text{FePO}_4$ interface [31,32]. The estimated values are listed in Table 1. It was found that the apparent Li^+ diffusion coefficient in the charging process was always slightly larger than that in the discharging reaction. This result was consistent with the previous report, in which the Li^+ extraction reaction was faster than the Li^+ insertion [33].

The OCV profiles during both the charging and discharging processes are plotted in Fig. 3. Most parts of the obtained OCV profiles exhibited an almost constant potential of 3.43 V, indicating that the electrochemical reaction is mainly attributed to a two-phase reaction. However, sloped regions were always observed around both the 100% DOD and 100% SOC states. The sloped pro-

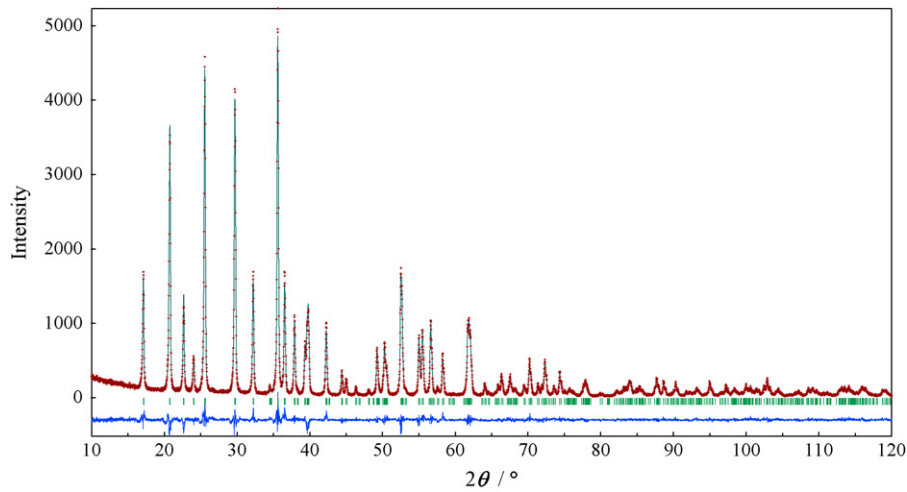


Fig. 1. Powder X-ray diffraction pattern of LiFePO₄/C composite particles. The difference between the observed and calculated profiles and the peak positions corresponding to the orthorhombic olivine phase are also shown, where $R_{wp} = 9.96\%$ and $R_p = 7.22\%$.

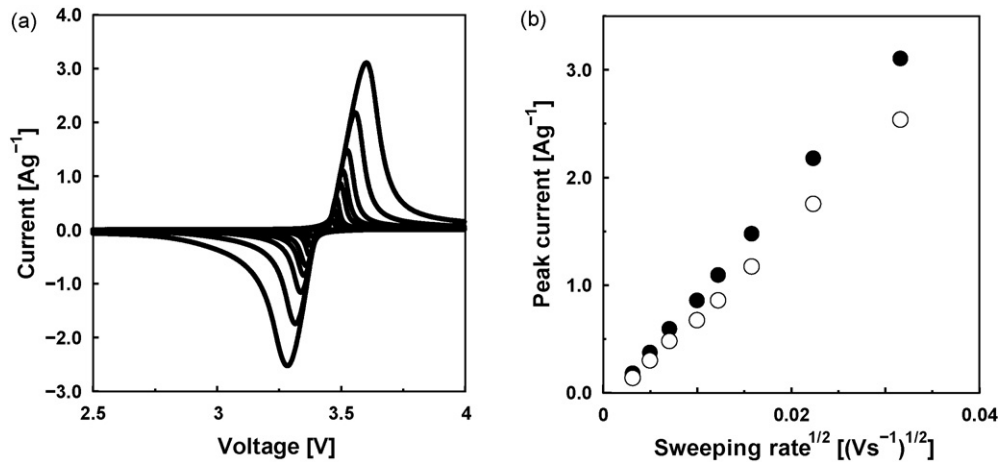


Fig. 2. (a) Cyclic voltammograms under various sweeping rates from 0.01 mVs^{-1} to 1.0 mVs^{-1} for LiFePO₄ particles. (b) Relationship between the square root of sweeping rate and the peak current of oxidation (solid circle) and reduction (open circle).

file regions in olivine cathodes were previously studied by some researchers [20–22,33–35], and were thought to be a characteristic of a single-phase reaction. In other words, the regions are outside the miscibility gap, where the Fe²⁺/Fe³⁺ mixed-valent intermediate phases are realized. Therefore, the electrochemical reaction of olivine compounds consists of not only the two-phase reaction but also single-phase reactions in the vicinity of both the end members. Yamada et al. discussed the electrochemical kinetic of LiFePO₄ olivine compound while taking the presence of these single-phase regions into account [35]. In our previous study on LiFe_{1-x}Mn_xPO₄ compounds [32], the sloped region around the 100% DOD state was always wider than that around the 100% SOC state, and the Mn²⁺ substitution led to the enlarging of these single-phase regions. The previous works pointed out that the single-phase regions were sensitive to the olivine particle size [20–27], and suggested that the miscibility gap becomes narrower with a decrease

in the particle size at room temperature [20–25]. The narrowing of the miscibility gap leads to the reduction of the interfacial strain between the charged phase and the discharged phase, and it promotes the phase boundary migration. Therefore, it is considered that the narrowing results in the enhancement of the rate capability at the olivine nano-particles. The relaxation of the interfacial strain by thermal fluctuation in nano-particle is thought to be one of the reasons for the miscibility narrowing [25,26]. According to the surface free energy, Van der Ven recently proposed that the particle size distribution modifies the potential profile. There, the influence of the particle size distribution is enlarged with a decrease in the average particle size, and it results in the slope profile even in the two-phase reaction [26,27]. Considering this proposal, the sloped profile may not always imply the solid solution region. But in this work, the discussion will be progressed along the solid solution concept.

Table 1
Li⁺ diffusion coefficients evaluated with CV and GITT methods.

GITT method D(Li ⁺) [cm ² s ⁻¹], Around 100% SOC		CV method D(Li ⁺) [cm ² s ⁻¹]		GITT method D(Li ⁺) [cm ² s ⁻¹], Around 100% DOD	
Charging	Discharging	Charging	Discharging	Charging	Discharging
3.21×10^{-17}	1.19×10^{-14}	1.17×10^{-14}	7.16×10^{-15}	8.49×10^{-15}	3.12×10^{-17}

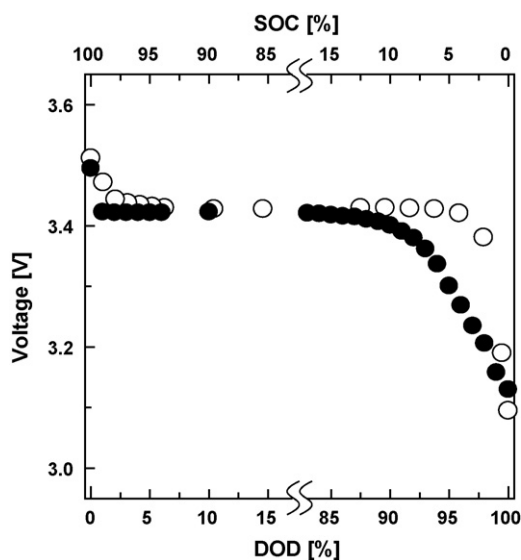


Fig. 3. Open-circuit voltage curves of LiFePO_4 particles: open and solid circles denote the measured values during the discharging and charging process, respectively.

A detailed study of the OCV profile in this work enabled us to find a few peculiar behaviors. The first one was the irreversibility: the OCV profile measured during the discharging process was different from that obtained during the charging process. The difference was remarkable at the single-phase regions around both the 100% DOD and 100% SOC states, and it was numerically evaluated with the miscibility gap parameters: α for the single-phase region of $\text{Li}_{1-\alpha}\text{FePO}_4$ around 100% DOD and β for the single-phase region $\text{Li}_\beta\text{FePO}_4$ around 100% SOC. The parameter β_{dis} obtained during the discharging process was smaller than that evaluated during the charging process (β_{ch}), while the parameter α_{dis} obtained during the discharging process was larger than that evaluated during the charging process (α_{ch}). It was found that, in both the charging and discharging processes, the sloped profile region width was enlarged in the late stage of the electrochemical reaction. The real OCV profile should be in the thermal equilibrium state, and show a unique profile, which is independent of the measurement process and condition. However, it was clear that the obtained profile exhibited hysteresis. From the above discussion, we conclude that the obtained OCV profiles may not be in an equilibrium state, especially at the late stage of the electrochemical reaction. It is thought that there exists phases with extremely slow relaxation at the late stage of both the charging and discharging reactions. Therefore, it was likely that the obtained sloped region in our OCV profiles did not imply the presence of a real single-phase region. Meethong proposed that the miscibility gap decreased as the particle size was reduced [20,21]. In their works, they presented not the OCV profile but the slow rate profile in their work, and the measurement was interrupted at the current rate less than C/50 in their PITT experiment. Hence, it is afraid that their conclusions are not based on the equilibrium state. On the other hand, Yamada et al. obtained the OCV profile after the 24 h relaxation, which was the same as our experiment, and they did not obtain the hysteresis phenomena. Their electrode composition, thickness and particle loading were almost the same as ours. Only the difference is attributed to the experimental conditions; they carried out the experiment in an Ar-filled glove box. At the current moment, there is no clear reason why the different results were achieved. By the way, it is less meaning to compare our results with the theoretical studies [25–27], because they are always based on the equilibrium state, where the energy minimum condition is achieved.

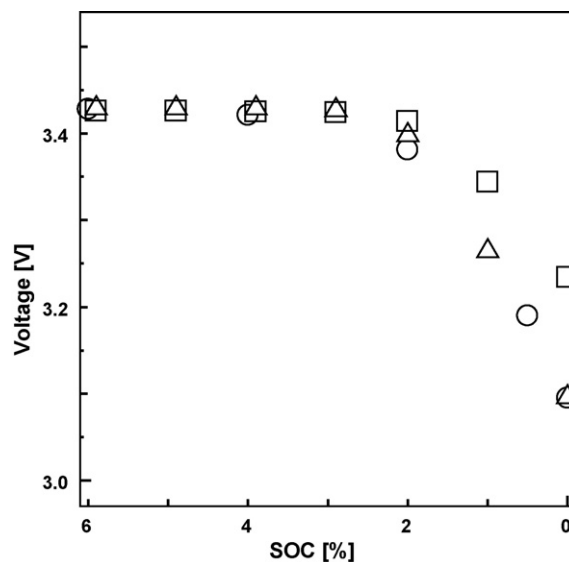


Fig. 4. Open-circuit voltages around 100% DOD measured during the charging process at various temperatures: 30 °C (open circle), 40 °C (open triangle) and 60 °C (open square).

It is considered that the slow potential relaxation in the sloped profile regions is related to the Li^+ ionic diffusion in the cathode material. Assuming that the regions having sloped potential are not the first order but the second order transition, the Li^+ diffusion coefficient at both sloped regions was roughly evaluated with the GITT method, where the voltage response to the constant current was recorded. The calculated Li^+ diffusion coefficients by the GITT method are listed in Table 1, which contains the apparent diffusion coefficients using the CV technique, too. The diffusion coefficient around the 100% SOC obtained during the discharging process was much larger than that obtained during the charging process, and almost agreed with the apparent diffusion coefficient estimated with the CV technique on the charging process. In addition, the diffusion coefficient around the 100% DOD obtained during the charging process was much larger than that obtained during the discharging process, and almost equaled to the apparent diffusion coefficient estimated with the CV technique on the discharging process. From these values, it was clear that the obtained diffusion coefficients in the late stage of both the charging and discharging reactions were extremely small. This may imply that the electrochemical reactions in the late stage of both the charging and discharging processes are kinetically limited. That is, the extremely slow ionic diffusion gives an obstacle to the relaxation in the final sloped region in both electrochemical directions in the olivine cathode material.

The other peculiar behavior of the obtained OCV profile was its dependence on the operating temperature. Fig. 4 shows the variation of the OCV profile around the 100% DOD state evaluated during the charging process with various operating temperatures. It was shown that the sloped region became narrower as the operating temperature was raised. In addition, as the temperature was incrementally raised, the plateau voltage was correspondingly lower by a few millivolts. Delacourt et al. discussed the presence of the miscibility gap between LiFePO_4 and FePO_4 phases using the spinodal decomposition concept [19] and Van der Ven et al. discussed it through the eutectoid reaction instead of the spinodal one [26]; a single phase was identified in the whole x region above 200 °C. On cooling, the single-phase Li_xFePO_4 was separated into a two-phase mixture, the compositions of which depended on the equilibrated temperature. Moreover, some researchers also reported that the miscibility gap shrinks with an increase in tem-

perature [20–27]. Considering these previous works, the sloped region should be widened as the operating temperature is raised. However, the experimental result shown in Fig. 4 displayed the opposite tendency. It is possible to explain this experimental fact by considering that the relaxation in the sloped profile region is thermally accelerated, because the Li^+ ionic diffusion in the cathode material was promoted when the operating temperature was raised. This is another piece of experimental evidence indicating that the obtained OCV profiles may not be in an equilibrium state, especially at the sloped regions.

From the above discussions, the experimentally obtained profile may be a pseudo-OCV profile rather than a real one, and it is difficult to evaluate the real OCV profile of the LiFePO_4 olivine compound. Hence, it is possible that the single-phase regions around the 100% SOC and 100% DOD states may be much narrower than the proposed one in the previous studies [19–21,35]. More careful attention should be paid for the argument of the relationships among the single-phase reaction regions, the operating temperature and the olivine particle size. However, in this work, the electrochemical reaction mechanism of the LiFePO_4 olivine compound has been discussed only using the OCV profile. Therefore, more study is required for further discussion. Because the regions having small diffusion coefficient correspond to the regions with extremely slow relaxation in the OCV measurement, the Li^+ diffusion kinetics is thought to be a rate-determining step for the potential relaxation. The extremely slow relaxation was also observed in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ system by Wagemaker et al. [36]. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ – $\text{Li}_7\text{Ti}_5\text{O}_{12}$ system also has the first order transition, but exhibits zero strain electrode reaction, which is very different from the olivine compounds. They reached their conclusions using temperature-dependent X-ray diffraction study. Therefore, the structural study may be useful for the clarification of the phase relationship and the kinetics on the electrochemical reaction. We are planning the in situ X-ray diffraction study and studying the structural modification of the olivine compound during the potential relaxation period. These results will be published in the near future.

4. Conclusions

LiFePO_4 olivine particle cathodes were studied with the CV and OCV techniques. The electrochemical reaction of the olivine cathodes consisted of a plateau around 3.43 V, meaning that most of the electrochemical reaction is attributed to a two-phase reaction. However, the sloped profile regions were observed in the vicinity of the two end member compositions. The profiles of the sloped regions exhibited hysteresis: the width of the sloped regions depended on the direction of the electrochemical reaction. This irreversibility was attributed to the Li^+ diffusion kinetics in the sloped regions. It was found with the GITT method that, for both the charging and discharging directions, the Li^+ diffusion coefficient was extraordinarily small at the late stage. In addition, it was detected that the OCV profiles in the sloped profile region were also sensitive to the operating temperature although the temperature dependence contradicted the trend expected from the spinodal decomposition mechanism. The obtained results indicated that the relaxation in the sloped OCV regions was extremely slow and of

thermal-activation type. These experimental studies may have two influences on the research of LiFePO_4 cathodes. In the scientific aspect, it can raise a question in the discussion about the phase relationship using the OCV profile, because the obtained OCV profiles may not be in an equilibrium state. In other technical and industrial aspects, the understanding of the slow kinetics at the late stage of both the charging and discharging processes is expected to be an important way for improving the rate performance and for practical application of the olivine cathode.

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