Electrochemical study on Mn²⁺-substitution in LiFePO₄ olivine compound

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Abstract

Olivine compounds $LiFe_{1-x}Mn_xPO_4$ $(0.0 < x < 0.4)$ were prepared by the solid-state reaction, and the electrochemical properties were studied in order to examine the effects of Mn^{2+}-substitution. The substitution led to the modification of the electrochemical performance, such as initial capacity, capacity fading and polarization. From the cyclic voltammetry, it was found that the effective Li^+ ionic diffusion coefficient was always larger in the charging process than in the discharging process and that it became larger with an appropriate amount substitution. The structural analysis on the chemical-delithiated compounds exhibited anomalous expansion of the unit cell along *c*-axis with the substitution, while the lattice parameters of the pristine compounds obeyed Vegard's law. The relationship between the Li^+ ion diffusion and the bottle-neck area of (0 1 0) zigzag path was discussed. From the results, it was considered that Mn^{2+} had no direct contribution on the electrochemical reaction but influenced both electronic and ionic conductivities, which led to some modifications in the electrochemical performance.
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1. Introduction

Rechargeable lithium batteries are key components of portable electronic devices such as laptop computer and mobile phone. $LiCoO_2$ has been commercially used in rechargeable lithium-ion batteries because of good performance and stability, but it has some drawbacks associated with material cost and toxicity. Considering practical applications such as electric vehicles, alternative cathode materials with environmental compatibility are strongly required. Among various candidates, $LiFePO_4$ olivine compound have become a promising material, since it has some advantages: low in cost, environmentally benign, and good structural stability. The potential profile of $LiFePO_4$ is very flat (the redox plateau is located at about 3.45 V versus Li/Li⁺), and a relatively high theoretical capacity of 170 mAh g⁻¹ is attained [1,2].

However, one of the main problems, which remove the olivine compound from commercial utilization, is its poor rate capabil-

ity. It is thought that the poor rate performance is attributed to low mobility of Li ions across the $FePO_4/LiFePO_4$ interface and to low electronic conductivity ($\sim 10^{-9}$ S cm⁻²). Several synthesis and processing approaches have been employed to overcome this problem, which includes the particle fining [3], the surface coating of the cathode particle with electrochemically conductive materials such as Ag and carbon [4] and the super-valent cation substitution in Li-site [5]. Based on the idea that the electrochemical reaction in the cathode is composed of series and/or parallel connections of intra- and inter-particle conduction, we have recently proposed the combination of bulk and surface modifications [6], in which the carbon-coating by thermal decomposition of pyrene produced surface modification and the partial substitution of Fe^{2+}/Mn^{2+} enhances the bulk conductivity. It was found that the initial capacity, the capacity fading with cycling and the polarization were significantly improved with the combined modification. Although it is thought that the Mn^{2+}-substitution is one of the effective ways to modify the electrochemical performance of the olivine compound, there is little information about the effect of the substitution on Li^+ ionic diffusion in the olivine compound. In this work, the effects of

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a partial substitution of Fe^{2+} with Mn^{2+} on the electrochemical properties have been studied from the viewpoint of the Li^+ ionic diffusion, and briefly discussed with the structure of the delithiated compound.

2. Experiment

Reagent grade lithium dihydrogen phosphate LiH_2PO_4, ferrous oxalate dihydrate $FeC_2O_4 2H_2O$, and manganese oxalate dihydrate $MnC_2O_4 2H_2O$ were used as raw materials. The stoichiometric amounts of them ($LiFe_{1-x}Mn_xPO_4$ with $0.0 < x < 0.4$) were mixed together by dry milling. The mixture was thermally decomposed at $350\,^\circ C$ in N_2 atmosphere for 3 h, mixed again in ethanol, and then subjected to annealing at $700\,^\circ C$ in N_2 atmosphere for 10 h, followed by furnace cooling down at room temperature. In order to study the compounds in the charged state, the chemical delithiation was carried out using bromine in acetonitrile solution. Olivine powder (3 g) was dispersed in acetonitrile solution (150 ml), bromine (30 ml) was added to it, and then the suspension was mechanically agitated for 3 h at $30\,^\circ C$ in the dark. After the reaction, the products were washed with acetonitrile to remove the residual salts.

The obtained samples were characterized by powder X-ray diffraction, and the lattice constants were determined using Rietveld refinement (RIETAN-2000). The specific surface area of the product was measured with the BET method. The electrochemical Li^+-intercalation/deintercalation were carried out with a Li coin cell assembled in an Ar-filled glove box. 1.0 M $LiPF_6$ in ethylene carbonate/dimethylcarbonate (EC–DMC) or ethylene carbonate/diethylcarbonate (EC–DEC) and Li foil were used as electrolyte solution and anode, respectively. To fabricate cathode sheet, active material, acetylene black and polyvinyl difluoride binder in *N*-methyl-2-pyrrolidone were mixed in a ratio of 8:1:1 by weight and coated onto Al foil with doctor blade technique. The coin cells were subjected to the galvanostatic charge–discharge cycling in the voltage region from 2.5 to 4.0 V at a constant current of $17\,mA\,g^{-1}$ (0.1 C), and to cyclic voltammetry in the same voltage region, where the sweeping rate was selected in the range from 0.01 to $1.0\,mV\,s^{-1}$.

3. Results and discussion

All products were identified as a single phase of olivine compound (orthorhombic symmetry with *Pnma* space group), irrespective of the substitution degree. The variation of the lattice parameters with the Mn^{2+}-substitution degree is shown in Fig. 1. The lattice parameters increased almost linearly with the amount of Mn^{2+}-substitution, and they obeyed Vegard's law. It indicated homogeneous solid solution formation, and this fact, that the Mn^{2+}-substitution in $LiFePO_4$ was easily attained, corresponded to the atomistic model calculation result [7]. SEM observation showed that the obtained particles were sub-micron in size and irregular in shape, and the BET surface area of them varied within the range of $5.5–7.2\,m^2\,g^{-1}$. These results implied that the particle size and morphology were almost insensitive to the Mn^{2+}-substitution, and it was likely that the variations
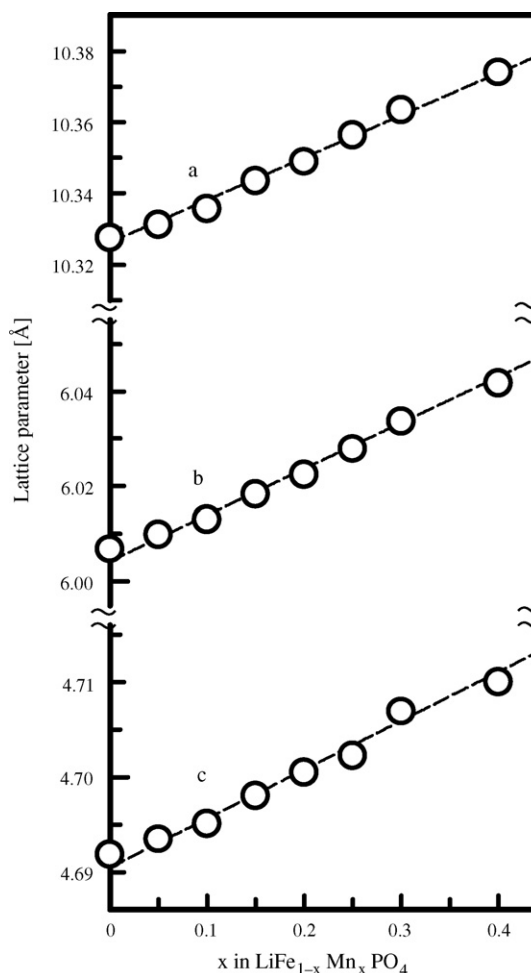

Fig. 1. Variation of lattice parameters with the substitution degree.

of the electrochemical performances with the substitution were attributed to the intrinsic properties of the cathode material, rather than the extrinsic properties such as particle size and morphology.

The electrochemical performances of $LiFe_{1-x}Mn_xPO_4$ are shown in Fig. 2. The initial capacity increased (from 122 to $133\,mAh\,g^{-1}$) with the substitution degree x up to 0.05, and then gradually decreased (to $106\,mAh\,g^{-1}$) with further substitution. Under assumption that only Fe^{2+}/Fe^{3+} redox contributes the electrochemical reaction, the calculated values were drawn as a dashed line. It was clear that the utilization of Fe^{2+}/Fe^{3+} redox reaction was improved with the substitution. The capacity retention after 20th cycle was enhanced with the substitution, and attained to approximately 98%, which was almost insensitive to the substitution degree. It was also seen that the Mn^{2+}-substitution reduced the polarization that was defined as the separation between charging and discharging plateaus. These results indicated that kinetic limitations on the electrochemical redox reaction were relaxed with the Mn^{2+}-substitution.

In the previous paper, we discussed the improvement of the electrochemical performances with the electronic conduction of the bulk materials [6]. There is another possibility for the relaxation of the kinetic limitation: enhancement of Li^+ ionic diffusion. Then, we evaluated numerically the effective Li^+ ionic
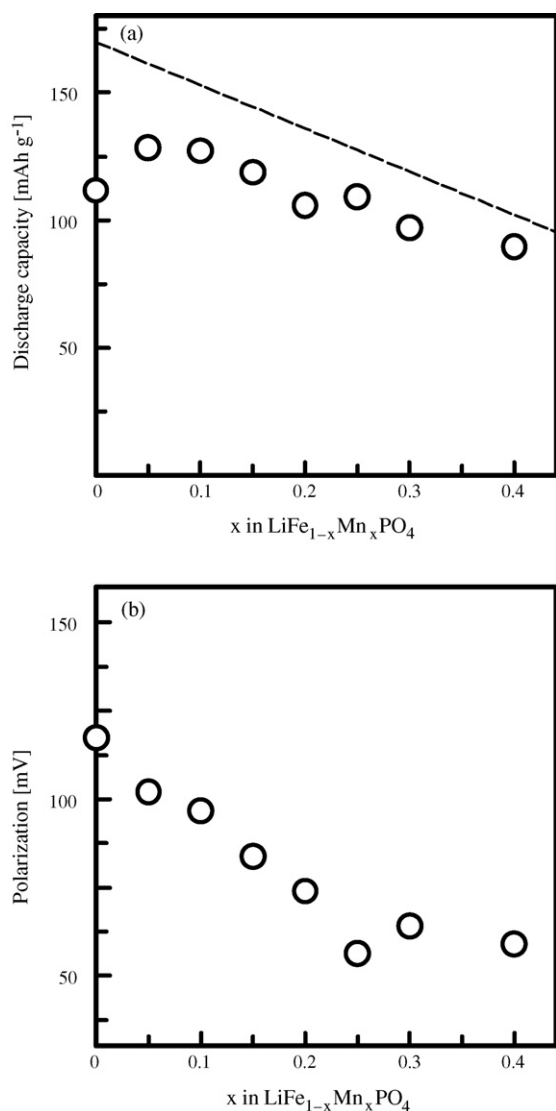
Fig. 3. Cyclic voltammograms of Mn^{2+}-substituted olivine cathode, $LiFe_{1-x}Mn_xPO_4$, with a constant sweeping rate of $0.01\,mV\,s^{-1}$.

20 °C, where the sweeping rate was changed, and typical results are shown in Fig. 4, where the composition was fixed at $x = 0.05$. As the sweeping rate was raised, the oxidation peak shifted higher and the reduction peak shifted lower. Fig. 5 shows the relationship between the peak current and the sweeping rate, and it was found that the peak current was proportional to the square root of the sweeping rate. This suggested that the CV result was related to Li^+ diffusion within the active material. It enabled us to estimated the effective diffusion constant (D_{Li}) of $LiFe_{1-x}Mn_xPO_4$ under assuming a reversible reaction, such that

$$I_p = \frac{0.4463 \times 10^{-3} F^{3/2} A D_{Li}^{1/2} C V^{1/2}}{(RT)^{1/2}}$$

where F is the Faraday constant, R the gas constant, T the operating temperature, V the sweeping rate, C the concentration of Li, and I_p is the peak current on the oxidation and/or reduction process. Generally A denotes the electrode area. But in this

Fig. 2. Variation of (a) initial discharge capacity and (b) polarization with the substitution degree. The dashed line denotes the calculated capacity to the Fe^{2+}/Fe^{3+} redox reaction.

diffusion coefficient with the cyclic voltammetric method at various sweeping rate, which was applied by Fietzek et al. [8]. The cyclic voltammograms of $LiFe_{1-x}Mn_xPO_4$ are shown in Fig. 3, where the sweeping rate was fixed at $0.01\,mV\,s^{-1}$. Both oxidation and reduction current peaks were observed around 3.5 V and the current peak shape implied that the electrochemical lithiation/delihtiation of $LiFe_{1-x}Mn_xPO_4$ cathode proceeded with two-phase reaction. The peak value increased with the substitution degree up to 0.05, took a maximum and then decreased with further increase in the substitution. On the Mn^{2+}-substitution, the oxidation peak position only slightly shifted lower, but the reduction peak potential significantly shifted higher. This implied that the Mn^{2+}-substitution affected the discharge reaction rather than the charge reaction. Additionally, the peak potential separation corresponded to the polarization degree, which was reduced with the substitution.

In order to estimate the effective Li^+ diffusion coefficient in $LiFe_{1-x}Mn_xPO_4$, the cyclic voltammetry was carried out at
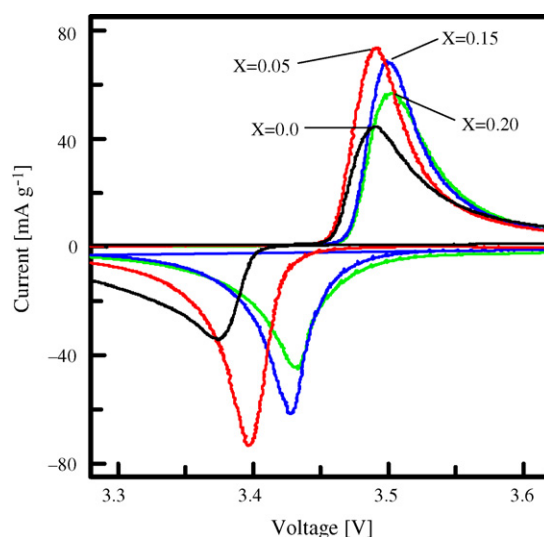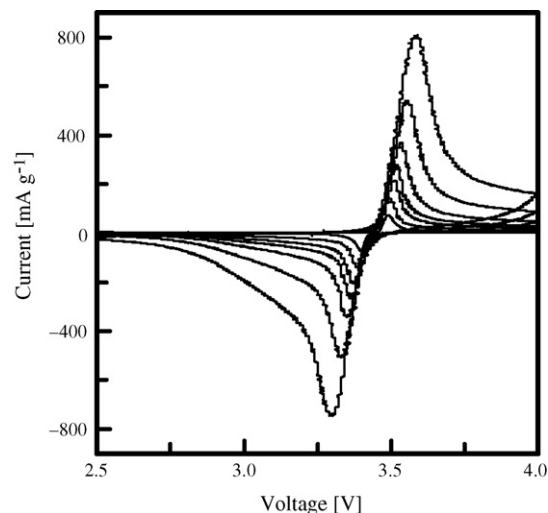

Fig. 4. Cyclic voltammograms of $LiFe_{0.95}Mn_{0.05}PO_4$ cathode with various sweeping rate from 0.01 to $1.0\,mV\,s^{-1}$.
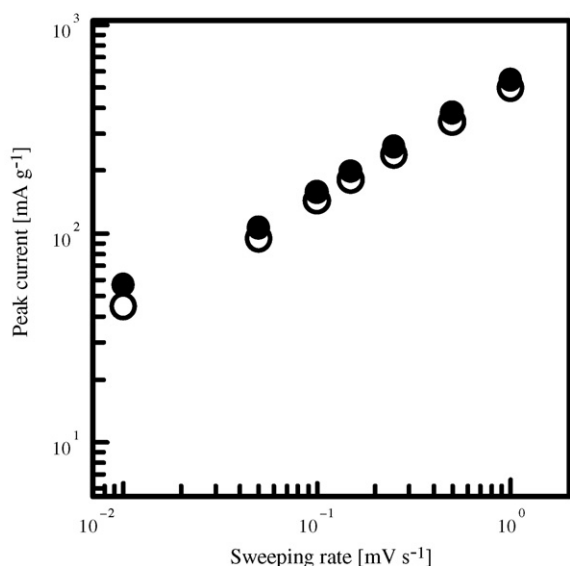
Fig. 5. Peak current values vs. sweeping rate for the cathode of $LiFe_{0.8}Mn_{0.2}PO_4$: oxidation (●) and reduction (○).

work, A was defined as the contact area between electrolyte and active material, and calculated from the active material weight in the cathode sheet and its specific surface area (BET surface area). These procedures were almost the same as that in the previous work [8], where the effective area of the (0 1 0) planes instead of the overall BET surface area was used. The obtained values of the effective diffusion constant were on the order of 10^{-13} cm^2 s^{-1}, and they were almost in the same order as the reported values [9,10]. The variation of the effective diffusion constant on the oxidation and reduction reactions was shown in Fig. 6, as a function of the Mn^{2+}-substitution degree. First, the effective diffusion constant on the oxidation reaction was slightly larger than that obtained in the reduction process, irrespective to the Mn^{2+}-substitution degree. This implied that the delithiation reaction was faster than the lithiation reaction in the olivine compounds. The similar asymmetric behavior between
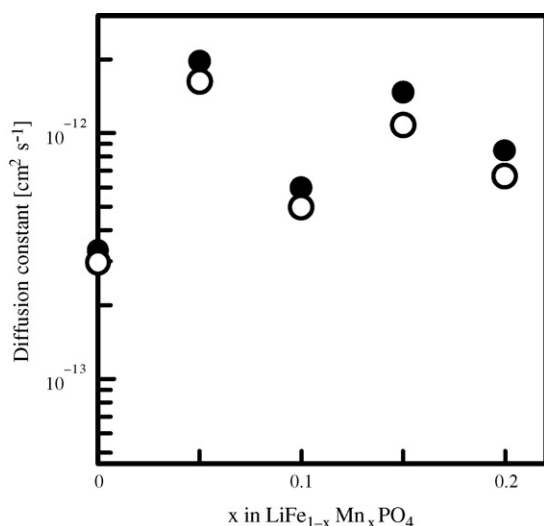
delithiation and lithiation in addition to the path dependent reaction was observed in $LiFePO_4$ cathode [11], where the two-phase reaction between $LiFePO_4$ and $FePO_4$ was described with the shrinking core model. Considering these experimental facts, it was clarified that the electrochemical discharging reaction in the olivine compound was slower than the charging reaction. Next, it was found that the effective diffusion constant in both charge and discharge reactions was increased with the Mn^{2+}-substitution, especially it took a maximum around $x = 0.05$. Therefore, the partial substitution of Fe^{2+} by Mn^{2+} may improve the ionic conduction in olivine compound on both delithiation and lithiation processes. It was also possible to explain the experimental facts about the electrochemical performance improvement of the Mn^{2+}-substituted olivine cathode from the viewpoint of the ionic conduction. Consequently, the Mn^{2+}-substitution in $LiFePO_4$ olivine compound provides the influences on both electronic and ionic conductions, and it results in the improvement of the electrochemical performance of olivine cathode, such as the initial capacity, the capacity retention and the polarization degree. However, it is not possible to quantitatively and separately discuss their contributions.

As many researchers already pointed out, the electrochemical reaction of $LiFePO_4$ compound proceeds in a two-phase reaction between lithiated phase $LiFePO_4$ and delithiated $FePO_4$. The structural investigation on the delithiated compound in addition to the lithiated compound gives us useful information on the ionic diffusion during the electrochemical reaction. Taking account of the upper voltage applied in this work, the chemically delithiation with bromine/acetonitrile solution was carried out. It was found from the powder X-ray diffraction pattern and
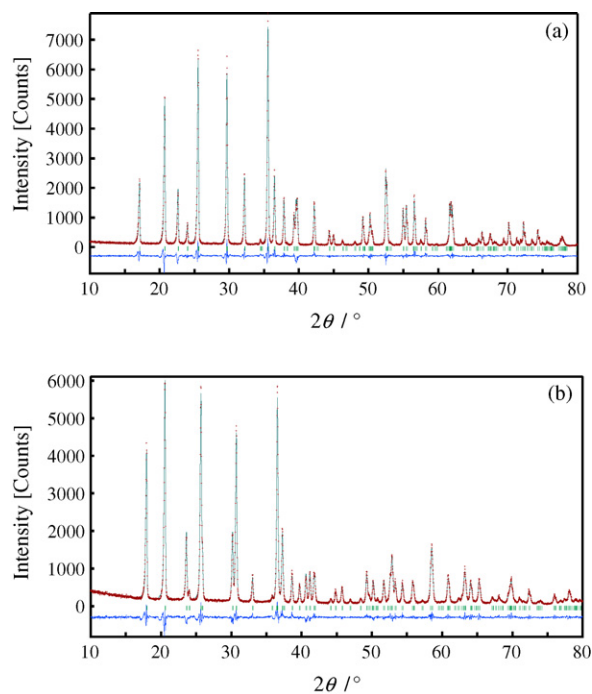

Fig. 6. Effective diffusion constant vs. substitution degree in $LiFe_{1-x}Mn_xPO_4$: oxidation (●) and reduction (○).

Fig. 7. Powder X-ray diffraction patterns of (a) pristine and (b) chemically delithiated olivine compounds with $x = 0.05$. The difference between the observed and calculated profiles and the peak positions corresponding to the orthorhombic olivine phase are also shown.

the Rietveld refinement, shown in Fig. 7, that the delithiated compound with $x < 0.20$ consisted of a single phase of delithiated olivine with orthorhombic symmetry (*Pnma* space group). The unit cell dimensions were reduced with keeping the original olivine framework. This was because of the transition metal ion was oxidized from Fe^{2+} to Fe^{3+} and the ionic radius became smaller. Compared to the structure of the pristine compound, the lattice parameters *a* and *b* became shorter, but that *c* was elongated in the delithiated phase. These variations along *a*- and *b*-axes were related to the dimension of $(Fe,Mn)O_6$ octahedron, where the M–O bonding length was shortened. On the other hand, the elongation along *c*-axis was attributed to the corner-sharing geometry of the $(Fe,Mn)O_6$ octahedra, and the M–O–M bonding angle was widened on the delithiation process [12]. The refined lattice parameters of the chemical delithiated phase are listed in Table 1. The lattice parameters increased almost linearly with the amount of Mn^{2+}-substitution, where the lattice parameters of the delithiated compound with $x = 0.0$ coincided well with the reported values of fully delithiated $FePO_4$ [13,14]. It was most likely that the oxidation with bromine is strong enough to convert Fe^{2+} to Fe^{3+} but unclear whether the oxidation of Mn^{2+} to Mn^{3+} was occurred. Here, the variation of the lattice parameters with the Mn^{2+}-substitution degree was examined in the following two ways, both of which were based on Vegard's rule. Assuming that the delithiated compounds were members of the solid solution, $FePO_4$ was applied as one of the end members and the other end member was either $LiMnPO_4$ or $MnPO_4$, the lattice parameters of which were already reported in the previous work [14]: $a = 10.44\,\text{Å}$, $b = 6.09\,\text{Å}$, $c = 4.75\,\text{Å}$ for $LiMnPO_4$ and $a = 9.690\,\text{Å}$, $b = 5.93\,\text{Å}$, $c = 4.78\,\text{Å}$ for $MnPO_4$. In the case of the solid solution between $FePO_4$ and $LiMnPO_4$, it was expected that the lattice parameters *a* and *b* increased with the substitution and that *c* decreased. The elongation along *a*- and *b*-axes quantitatively coincided with the experimental result. On the other hand, the shrinkage in the *c*-direction was opposite to the experimentally obtained tendency. In the other case of the solid solution between $FePO_4$ and $MnPO_4$, it was expected that all the lattice parameters decreased with the substitution, and their variations were very different from the results. From the lattice parameter variations in addition to the facts that the redox potential of $LiMnPO_4/MnPO_4$ was above 4.0 V and much higher than the voltage of $LiFePO_4/FePO_4$ electrochemical reaction [15,16], the solid solutions were possibly between $FePO_4$ and $LiMnPO_4$. However, even in the case, it was not possible to explain the lattice shrinkage along *c*-axis. Thus, there was an anomaly in the lattice expansion in the *c*-direction. It
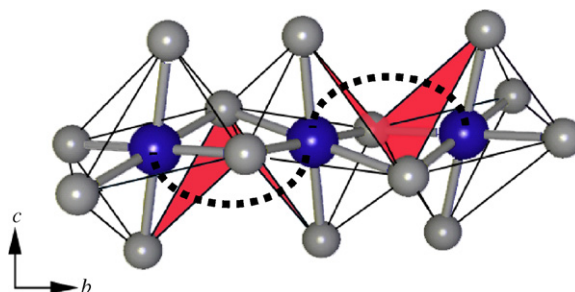

Fig. 8. Schematic configuration of LiO_6 octahedra in olivine structure. The dotted lines denote the most probable path for the Li^+ migration. The bottlenecks are represented as the shaded sections.

is possibly that the substitute Mn has no contribution to the electrochemical delihtiation/lithiation (oxidation/reduction) but acts as a stabilizer of the framework structure. In order to more precisely discuss the lattice parameter variation, the information about the valence state of the transition metal ions are required. It is thought that the Moessbauer spectroscopy is useful for determining the valence state of Fe ions, and that the valence state of Mn ions may be evaluated with XPS analysis. The studies on the valence state of them are now being carried out.

It was clear that the Mn^{2+}-substitution had great influence on the structure of both the pristine and delithiated compounds, where the structural framework remained unchanged during the delithiation, and the lattice parameters increased linearly with Mn^{2+}-substitution. In order to examine the relationships between the Li^+ ionic diffusion constant and the structural modifications, the oxygen coordination geometry was studied with the Rietveld refinement results. In orthorhombic olivine structure, the oxygen atoms are arranged in a slightly distorted, hexagonal close-packed arrangement. The phosphorous atoms occupy tetrahedral sites, while the transition metal and lithium atoms occupy octahedral sites. The MO_6 octahedra are linked through common corners in the *bc*-plane, and the LiO_6 octahedra form edge-sharing chains along the *b*-axis. Fig. 8 shows the schematic configuration of LiO_6 octahedra in olivine structure. It is pointed out that in this structure, Li^+ migration occurs between adjacent Li sites along *b*-axis in zigzag form [7,17]. There are bottlenecks along this migration path, and the bottleneck structure consists of LiO_6 octahedral faces, the size and relaxation of which play important roles for Li^+ migration. This situation is similar to the Na^+ conductivity in other framework structure or NASICON-type phosphate compounds, where the ionic conductivity was understood by the steric considerations and the chemical interaction of the mobile cation with the anionic framework. According to the steric considerations, the space provided for the mobile cation to move is important and the effective area of LiO_6 octahedral face. The effective cross-section area of LiO_6 octahedral face was evaluated from the Rietveld refinement results, for both the pristine and the chemically delithiated phases. The results were plotted in Fig. 9 as a function of the substitution degree. From these figures, the effective cross-section area in the charged, delithiated compound was much larger than that in the discharged, pristine compound irrespective to the substitu-

Table 1
Refined lattice parameters of the chemically delithiated olivine compounds with various substitution degrees, *x*

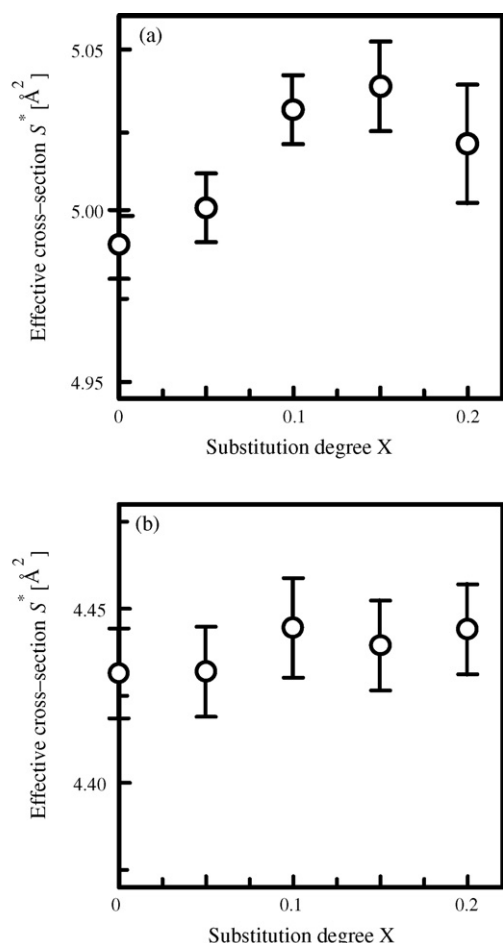| x	a (Å)	b (Å)	c (Å)
0.00	9.8135(2)	5.7878(1)	4.7808(1)
0.05	9.8463(3)	5.8111(2)	4.7883(1)
0.10	9.8651(4)	5.8260(2)	4.7896(2)
0.15	9.8855(4)	5.8416(3)	4.7917(2)
0.20	9.9012(7)	5.8573(4)	4.7968(3)

Fig. 9. Variation of effective cross-section area with the substitution degree: (a) the delithiated phase (charged state) and (b) the pristine phase (discharged state).

tion degree. The larger bottleneck area brought about the faster Li^+ ionic migration. According to Newman's core–shell model of the olivine electrode [11], the Li^+ diffusion in the delithiated compound shell around the lithiated core plays a important role on the charging process, while the Li^+ diffusion in the lithiated shell covering the delithiated core is important on the discharging process. It seemed to coincide with the fact that in $LiFePO_4$ olivine cathode, the Li^+ extraction reaction from $LiFePO_4$ phase is faster than the Li^+ insertion reaction into $FePO_4$ phase, that is, the charge reaction is readily taken place than the discharge reaction. The other feature found in these figures was that the effective cross-section area increased with the substitution, especially for the charged compounds. In the chemically delithiated compound, the effective cross-section area increased with the substitution degree, took a maximum around $x = 0.15$, and then decreased with further increase in the substitution degree. For the pristine compounds, the bottleneck area only slightly increased with the substitution. According to the steric consideration, the widening of the bottleneck area (expansion of the cross-section area) can provide large space for Li^+ migration, resulting in large diffusion constant. However, the variation of the diffusion constant with the substitution degree did not correspond quantitative to that of the effective cross-section area versus the substitution degree. It can be attributed to the evaluation of the oxygen sub-

lattice arrangement from the X-ray diffraction pattern, therefore, more precise information using neutron diffraction are required for detail discussion on the relationship between the bottleneck area and the ionic diffusion constant.

4. Conclusion

The electrochemical properties of $LiFe_{1-x}Mn_xPO_4$ olivine compounds were studied with galvanostatic charge–discharge and cyclic voltammetry. It was found that Mn^{2+}-substitution had some influences on the electrochemical performance of the olivine cathode: the enhancement of the initial capacity, the suppression of the cycle fading, and the lowering of polarization during the redox reaction. They were attributed partly to the increment in the electronic conductivity of the bulk. It was found from the cyclic voltammetry that the other contribution is related to the modification of the ionic conduction with the substitution. The effective diffusion constant, evaluated from CV signals on various sweeping rates, exhibited larger values in the charging reaction than those in the discharging process. The reduction peak potential rather than the oxidation peak potential were sensitive to the Mn^{2+}-substitution, and the substitution affected the ionic diffusion during both the delithiation and lithiation processes. The effective diffusion constant was maximized around the substitution degree of $x = 0.05$. From these results, it was thought that the Mn^{2+}-substitution had no direct contribution to the electrochemical reaction but enhances both electronic and ionic conductivities. Consequently, the substitution may release somehow the kinetic limitation, resulting in the Fe^{2+}/Fe^{3+} redox efficiency in the olivine cathode.

It was possible to explain the variation of the ionic diffusion constant with substitution degree from the viewpoint of the structural modifications. For the pristine compounds, the lattice parameters obeyed Vegard's law and the unit cell was expanded with the substitution. On the other hand, for the delithiated phase, an anomalous expansion along c-axis was detected with the substitution. An elongation of the lattice in the c-direction may result in the widening of the space provided for Li^+ ionic diffusion. The situation was similar to the NASICON-type phosphate compounds, and it was possible to understand the ionic conductivity from the steric aspect.

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