Structural and Electrochemical Properties of Doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ as Cathode Material for Lithium ion Batteries

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ABSTRACT :

The electrochemical properties of Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ and pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ olivine cathodes are examined and the lattice parameters are refined by Rietveld analysis. The calculated atomic parameters from the refinement show that Mg^{2+} doping has a significant effect in the olivine LiFeMnPO_4 structure. The unit cell volume is $297.053(2) \text{ \AA}^3$ for pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ and is decreased to $296.177(1) \text{ \AA}^3$ for Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ sample. The doping of Mg^{2+} cation with atomic radius smaller than Mn^{2+} and Fe^{2+} ion induces longer Li-O bond length in LiO_6 octahedra of the olivine structure. The larger interstitial sites in LiO_6 octahedra facilitate the lithium ion migration and also enhance the diffusion kinetics of olivine cathode material. The $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ sample with larger Li-O bond length delivers higher discharge capacities and also notably increases the rate capability of the electrode.

Keywords : Lithium ion battery, Olivine structure, $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ material, Cation doping, Rietveld Analysis.

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Introduction

A series of lithium transition metal phosphates, LiMPO_4 ($\text{M} = \text{Fe}, \text{Mn}, \text{Mn}_y\text{Fe}_{1-y}, \text{Co}, \text{Ni}$), with ordered olivine structure has become one of the most promising cathode materials for lithium ion storage.¹⁻³⁾ The stable nature of the olivine structure is due to the presence of strong covalent P-O bond in the tetrahedral site, which provides good cycle life and excellent safety during lithium ion storage. Among these materials, particular interest towards multi-component LiMnFePO_4 system is due to their favored operating voltage and environmental compatibility. Multicomponent LiMnFePO_4 system combines the advantage of relatively high electronic conductivity of LiFePO_4 and also relatively high voltage of LiMnPO_4 .^{4,5)}

LiMnFePO_4 crystal has an orthorhombic olivine

structure (space group: $Pnma$), in which Li, and Mn (Fe) atoms occupy octahedral 4a, and 4c sites and P atom occupy tetrahedral 4c site. The M atoms occupy zigzag chains of corner shared octahedra running parallel to c-axis in the alternate a-c planes. The structure has a layer of oxygen-sharing MO_6 , parallel to the b-c plane and separated by isolated PO_4 tetrahedra to form an interconnected three dimensional structure and limits the movement of Li ion in one-dimensional channel.^{6,7)} The intercalation of LiMnFePO_4 system proceeds over two voltage plateaus at 3.5 and 4.1 V corresponding to two redox couples $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$, respectively.^{1,8)}

Many approaches have been successfully followed to improve the conductivity and electrochemical performance of olivine structure cathodes.⁹⁻¹¹⁾ Substitution of cations such as Mg^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} and Co^{2+} has been adopted to improve the electrical conductivity and diffusivity of Li ions in olivine system.¹²⁻¹⁴⁾ Low concentration of magnesium doping in olivine

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LiFePO_4 can increase the capacity and cycle performance of the electrode.^{15,16)} Doping of Mg^{2+} ion in olivine structure decreases the lattice misfit near the boundary of $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ / $\text{Fe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ due to the formation of pseudo-one phase reaction during Li extraction.¹⁷⁾

The present work extends our previous report of $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ material, where we studied the pseudo-one phase behavior and smaller lattice mismatch across the boundary leading to smaller volume change in the structure.¹⁷⁾ In this work, crystal structure refinement and electrochemical performance of Mg-doped $\text{LiMn}_{0.48}\text{Fe}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ have been studied in comparison with those of pure $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ material.

2. Experimental

$\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ electrodes were provided by UMICORE. The synchrotron high resolution powder diffraction (HRPD) pattern were measured at the beamline 9B in Pohang Accelerator Laboratory (PAL-II) using a Si(111) double-crystal monochromator multiple detector system (7 analyzer crystals and 7 scintillation detectors) with the wavelength of 1.5475 Å. The step scan of $2\theta = 0.02^\circ/\text{step}$ was used for both samples and the scan speed was $1^\circ/\text{min}$. The synchrotron powder diffraction patterns were refined by Rietveld refinement analysis using the FULLPROF program for accurate determination of unit cell parameters.¹⁸⁾ Endeavor program was performed to illustrate the LiMPO_4 olivine structure and its LiO_6 octahedral site using the input of atomic positions calculated from Rietveld refinement results.

Electrochemical characterization was performed by assembling CR2032 coin cells for galvanostatic charge/discharge measurements. The electrodes were made by dispersing 90 wt.% active material, 5 wt.% carbon black and 5 wt.% polyvinylidene fluoride (PVDF) in *n*-methyl pyrrolidone (NMP) to form a slurry. The slurry was then coated onto aluminium foil and the electrodes were dried in a vacuum oven. The coin cells were assembled in an argon filled glove box with lithium foil as the counter electrode. The electrolytes used were commercially available 1 M LiPF_6 in 1:1 ethyl carbonate (EC): dimethyl carbonate (DMC) solvent.

Charge/discharge cycling test was carried out at room temperature with a battery test station

(WBSC3000, Won-A Tech, Korea). Current rates between C/10 and 20C with voltage window of 2.7-4.4 V (vs. Li/Li+) were selected. The C rate was calculated through weight of active material and its experimental capacity (140 mAhg^{-1}).

3. Results and Discussion

The crystal structure of pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ and Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ material was characterized using high resolution powder X-ray diffraction (HRPD) for precise XRD patterns. The diffraction pattern of the samples was indexed to orthorhombic crystal structure with *Pnma* space group, as shown in Fig. 1. The Mg-doped sample has similar diffraction pattern to that of pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ with negligible amount of impurities.

The atomic parameter for pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ and Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ were refined by Rietveld analysis using the HRPD patterns. The best refinement model was preferred from space group of *Pnma*. The typical HRPD refinement results of both pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ and Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ are shown in Fig. 2(a) and 2(b). The actual refined lattice parameter results of both the samples are listed in Table 1 and 2.

Refinement results are reliable because the weighted profile factor (R_{wp}) and profile factor R_p are less than 10% for both the samples. Refined unit cell parameters of pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ have $a = 10.38914(3)$ Å, $b = 6.05570(2)$ Å, $c = 4.72159(1)$ Å and $V = 297.053(2)$ Å³ and are consistent with the previous reports.¹⁹⁾ For Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ sample, refined unit

Fig. 1. HRPD patterns of pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ and Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$.

Fig. 2. Rietveld refinement patterns of (a) pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ and (b) Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ samples.

Table 1. Rietveld refinement results of pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ sample

$\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$						
Space group		Pnma (62)		Cell volume = 297.053(2) Å ³		
Lattice parameter (Unit : Å)		a = 10.38914(3) Å		$\alpha = 90^\circ\text{C}$		
		b = 6.05570(2) Å		$\beta = 90^\circ\text{C}$		
		c = 4.72159(1) Å		$\gamma = 90^\circ\text{C}$		
Name	Site	x	y	z	B/Å ²	Occupancy
Li	4a	0	0	0	1	0.50
Mn	4c	0.2817(1)	0.25	0.9724(4)	0.96(3)	0.238(1)
Fe	4c	0.2817(1)	0.25	0.9724(4)	0.96(3)	0.238(1)
P1	4c	0.0942(3)	0.25	0.4128(5)	1.43(7)	0.5
O1	4c	0.0963(8)	0.25	0.737(1)	1.3(1)	0.5
O2	4c	0.4542(8)	0.25	0.212(1)	1.3(1)	0.5
O3	8d	0.1636(7)	0.0456(9)	0.2782(8)	1.6(7)	1
Reliability factors		Rp = 6.23%, Rwp = 8.74%, Rexp = 6.17%, chi2 = 2.01, S(Rwp/Rexp) = 1.41				

Table 2. Rietveld refinement results of Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ sample

$\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$						
Space group		Pnma (62)		Cell volume = 296.177(1) Å ³		
Lattice parameter (Unit : Å)		a = 10.378565(17) Å		$\alpha = 90^\circ\text{C}$		
		b = 6.048620(11) Å		$\beta = 90^\circ\text{C}$		
		c = 4.71799(9) Å		$\gamma = 90^\circ\text{C}$		
Name	Site	x	y	z	B/Å ²	Occupancy
Li	4a	0	0	0	1	0.5
Mn	4c	0.2819(1)	0.25	0.9727(2)	0.74(2)	0.23(1)
Fe	4c	0.2819(1)	0.25	0.9727(2)	0.74(2)	0.23(1)
Mg	4c	0.2819(1)	0.25	0.9727(2)	0.74(2)	0.02
P1	4c	0.0937(1)	0.25	0.4140(3)	0.98(4)	0.5
O1	4c	0.0978(5)	0.25	0.7376(9)	0.9(1)	0.5
O2	4c	0.4556(5)	0.25	0.2092(9)	1.1(1)	0.5
O3	8d	0.1634(3)	0.04867(2)	0.2789(6)	1.1(1)	1.0
Reliability factors		Rp = 6.13%, Rwp = 8.52%, Rexp = 6.09%, chi2 = 1.96, S(Rwp/Rexp) = 1.39				

cell parameters are $a = 10.378565(17) \text{ \AA}$, $b = 6.048620(11) \text{ \AA}$ and $c = 4.71799(9) \text{ \AA}$ and $V = 296.177(1) \text{ \AA}^3$. The Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ sample has smaller lattice constants and smaller unit cell volume than pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ owing to the smaller ionic radius of Mg^{2+} ion. Dong *et al.* reported that, substitution of small amount of Mg in LiMnPO_4 nanoplate leads to reduction in volume mismatch across the interface resulting in increase in mobility and electrochemical performance of the electrode.²⁰⁾ Doping of Mg^{2+} ion in $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ structure results in reasonable decrease in the refinement statistical factors such as $R_p = 6.13\%$, and $R_{wp} = 6.09\%$ confirming the doping of Mg^{2+} ion in olivine LiFeMnPO_4 framework.

The schematic illustration of olivine LiMPO_4 crystal structure is performed using Endeavor program. Fig. 3 explains the detailed view of orthorhombic unit cell ($D_{2h}^{16} - Pmn2_1$), which accommodates four units of LiMPO_4 . Lithium and transition metal ions occupy 4a and 4c sites of octahedra and oxygen ions arranged in the hexagonal close packed structure. Most probable path of lithium ion migration along [010] direction is shown in the scheme. Octahedral 4a positions are occupied by Li^+ ions, which form one dimensional chain along b axis. The Li ion transport along 1D channel is favored due to the basic geometry of olivine structure. Detailed structural analysis shows that, migrating ions follow curved trajectory path between the adjacent lithium LiO_6 octahedra.²¹⁾

Fig. 4 represents the local structure changes in LiO_6 octahedral site for both pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ and Mg-

doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ material. The schematic view of LiO_6 octahedral sites were shown using Endeavor program with the input of atomic positions from Rietveld refinement results. The lengths of Li-O bonds in LiO_6 octahedra for pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ are $\text{Li-O1} = 2.199 \text{ \AA}$, $\text{Li-O2} = 2.09 \text{ \AA}$, and $\text{Li-O3} = 2.166 \text{ \AA}$ and those for Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ are $\text{Li-O1} = 2.201 \text{ \AA}$, $\text{Li-O2} = 2.093 \text{ \AA}$, and $\text{Li-O3} = 2.167 \text{ \AA}$. It has been noticed that, Li-O bond lengths for $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ sample become longer due to Mg doping in the structure. Moreover, longer Li-O bonds have smaller binding energy leading to easy lithium ion migration.²⁰⁾

Fig. 5 shows the first charge/discharge profile of pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ and Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ samples at C/10 rate with the cut off voltage between 2.7 and 4.4 V. There is an existence of two distinct plateaus in both the samples, which is consistent with the previous reports.^{7,8)} First plateau region around 3.5 V corresponds to $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple and second plateaus around 4.1 V corresponds to $\text{Mn}^{2+}/\text{Mn}^{3+}$ redox couple.^{1,22)} Initial charge/discharge capacities of Mg-

Fig. 3. Schematic illustration of LiMPO_4 ($M = \text{Mn, Fe}$). The dotted circles denote the most probable path for Li ion migration.

Fig. 4. Li-O bond length in LiO_6 octahedra of $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ structure.

Fig. 5. The first charge/discharge curves of pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ and Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ at $C/10$ rate.

Fig. 6. The discharge curves of (a) pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ and (b) $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ at different C rate.

doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ are 152.2 mAhg^{-1} and 146.3 mAhg^{-1} and for pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$, charge/discharge capacities are measured as 144.7 mAhg^{-1} and 134.1 mAhg^{-1} . It is observed that, Mg-doped sample shows less polarization and high capacity than pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ material due to larger Li-O bond length and easier lithium ion migration.

Fig. 6(a) and 6(b) shows the galvanostatic dis-

charge profile of pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ and Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ electrodes at various C rates between $C/10$ and $20C$ in the voltage region of 2.7 and 4.4 V. This shows a considerable retention in the capacity for Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ sample at different C rates. Even at $20C$ rate, discharge capacities of pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ and Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ are 95.4 mAhg^{-1} and 107.8 mAhg^{-1} , respectively. It is observed that, better rate capability of $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ material is due to larger Li-O bond in the LiO_6 octahedra. Hence, the longer Li-O bond facilitates faster Li ion migrations, and enhanced the electrochemical performance of cathode material even under high C rates.

Conclusion

The crystal structure and electrochemical performance of pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ and Mg-doped $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ have been investigated to analyze the role of cation doping in olivine framework. The Mg-doped sample showed similar HRPD pattern to that of pure $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ with negligible amount of impurities in the structure. Rietveld refinement showed that, doping with smaller atomic radius of Mg^{2+} ion in $\text{LiFe}_{0.48}\text{Mn}_{0.48}\text{Mg}_{0.04}\text{PO}_4$ induced shrinkage in unit cell volume. The doping of Mg^{2+} cation with ionic radius smaller than Mn^{2+} and Fe^{2+} ion induces longer Li-O bond length in LiO_6 octahedra of the olivine structure. Furthermore, the Li-O bond lengthening in LiO_6 octahedral site makes lithium ion migration easier, which is beneficial for better electrochemical performance and rate capability of multi-component olivine structure.

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