

Schematic Investigation on the Electrochemical Performance of Olivine Typed  $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$  Cathode Material for Li-ion Rechargeable Batteries

C.G. Back, S.U. Park, S.J. Oh, and C.W. Lee

Central R&D Center, Hanwha Chemical  
76 Gajeong-Ro Yuseong-Gu, Daejeon 305-804  
South Korea

Since the demonstration of high structural and excellent thermal stabilities of  $\text{LiFePO}_4$  along with its reversible electrochemical lithium insertion-extraction property, the great attention has been paid on isostructural ordered olivine  $\text{LiMPO}_4$  ( $\text{M}=\text{Co}, \text{Ni}, \text{Mn}$ ) as next generation cathode materials because of their high theoretical energy density compared to that of  $\text{LiFePO}_4$ . While the operating voltage of  $\text{LiFePO}_4$  is ca. 3.5V vs.  $\text{Li}/\text{Li}^+$ , that of  $\text{LiMnPO}_4$  is much higher to plateau 4.1V vs.  $\text{Li}/\text{Li}^+$ , which leads to 1.2 times larger theoretical energy density than that of  $\text{LiFePO}_4$  and whose voltage lies within the stability window of the common non-aqueous electrolytes. This advantage is especially important to the large scale applications, especially for electric vehicle and energy storage system. However, there are several obstacles confronted in the commercial development of  $\text{LiMnPO}_4$ . One of the problems is low electric conductivity of  $\text{LiMnPO}_4$ , ca.  $10^{-8}$  times lower than the reported value of  $\text{LiFePO}_4$  ( $10^{-9}$ S/cm) [1], and the capacity at 4.1V is not achieved without Fe coexistence with Mn at the octahedral 4c sites [2]. The other one is the strong electron ( $\text{Mn}^{3+}: 3d4$ ) lattice interactions (Jahn-teller effect) in the charge state, and the resultant elastic limit set by the lattice distortion is suggested as an intrinsic obstacle in generating reversible charge-discharge capacity [3].

In this study, olivine typed  $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$  ( $X=0.2, 0.3, 0.4, 1$ ) is prepared by the world unique process of supercritical hydrothermal process, whose process is known to have superior performance in preparing homogeneous nano-size particles in a continuous process [4], and the electrochemical performance of the cathode materials is schematically investigated with the special focus on the electrochemical property itself, kinetics of Li-ion in the materials, and local structural change with charge-discharge cycles by using electrochemical impedance spectroscopy, X-ray diffraction, and X-ray absorption spectroscopy. In figure 1, powder X-ray diffraction patterns of  $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$  ( $X=0.2, 0.3, 0.4, 1$ ) are presented. All of the diffraction patterns are well indexed to orthorhombic structure with pnma space group, and no second phase is detected. Lattice parameters are calculated by Rietveld refinement analysis on the diffraction patterns and listed in table 1, in which the lattice volume of  $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$  increases with Mn, especially in Li-ion moving direction of a. In Figure 2, the chemical diffusion coefficient of Li-ion in  $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$  are presented for various contents of Mn, which is obtained by using cyclic voltammetry at various scan rate between 0.2mV/s and 2mV/s at 25°C and correlating the peak intensity with the square root of the scan rate [5]. The result shows that the chemical diffusion coefficient of Li-ion during the redox reaction of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  is greatly influenced with the content of Mn in  $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$  as the value significantly decreases with increasing Mn content, from  $\sim 10^{-15}\text{cm}^2/\text{s}$  for  $\text{LiFePO}_4$  to  $\sim 10^{-18}\text{cm}^2/\text{s}$  for  $\text{LiFe}_{0.2}\text{Mn}_{0.8}\text{PO}_4$ , while the chemical diffusion coefficient of Li ion during Mn redox reaction is pretty low in

general, but not much influenced with Mn content. This result suggests that the kinetics of electron and Li ion in  $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$  are greatly affected by Mn content, possible by the strong electron lattice interaction (Jahn-Teller effect) around charged  $\text{Mn}^{3+}$  sites coupled with large local lattice deformation in the bulk crystal.

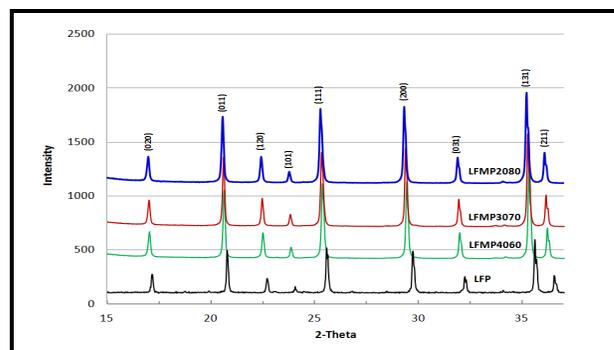


Fig. 1 Powder X-ray diffraction patterns of  $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$  ( $x = 0.2, 0.3, 0.4, 1$ )

Table 1. Lattice parameters of  $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$  ( $X=0.2, 0.3, 0.4, 1$ )

	a(Å)	b(Å)	c(Å)	V(Å <sup>3</sup> )
$\text{LiFePO}_4$	6.0063	10.3276	4.6927	290.8954
$\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$	6.065	10.4048	4.7247	298.1527
$\text{LiFe}_{0.3}\text{Mn}_{0.7}\text{PO}_4$	6.0769	10.419	4.7315	299.576
$\text{LiFe}_{0.2}\text{Mn}_{0.8}\text{PO}_4$	6.0857	10.4295	4.7366	300.6358

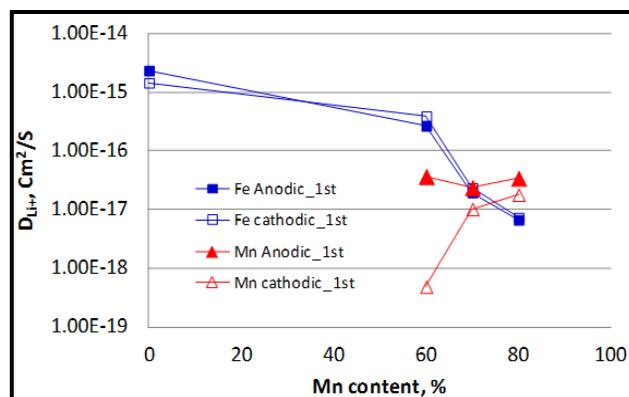


Fig. 2. Chemical diffusion coefficient of Li-ion for  $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$  ( $X=0.2, 0.3, 0.4, 1$ ) at 25°C

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