Effects of Al^{3+} Ion Doping of the Lithium Iron Phosphate

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In order to reveal the doping effect on the electrochemical properties of $LiFePO_4$, a solution method was employed to prepare pure olivine structure $LiFePO_4$, Al^{3+} ions doped $LiFe_{1-x}Al_xPO_4$ ($0.01 \le x \le 0.1$), $LiFeAl_yPO_4$ ($0.01 \le y \le 0.05$), and $Li_{1-z}Al_zFePO_4$ ($0.01 \le z \le 0.05$) powders. The beam line of NSRRC-01C2 was used to analysis the crystalline structures of the prepared powders and the lattice parameters were obtained with GSAS (General Structure Analysis System).

The calculated lattice parameters are shown in Table 4-1. When the amounts of Al^{3+} doping are low, the volume of the unit cell and the cross-section of diffusion (bc plane) increase with increasing amount of Al^{3+} doping that will be beneficial for lithium ion battery performance.

For samples with high Al^{3+} doping level, $x \ge 0.07$ in $LiFe_{1-x}Al_xPO_4$ and $z \ge 0.05$ in $Li_{1-z}Al_zFePO_4$, the lattice parameters and the lattice volume decrease with increasing amount of Al^{3+} doping. That might be attributed to the second phase formation in the powders. In order to confirm the guesstimate, the XRD patterns, shown in Fig. 4-1, were performed by the beam lines of 01C2 of the National Synchrotron Radiation Research Center of Taiwan. It is found that there are diffraction peaks corresponding to $AlPO_4$ and AlP phases in the pattern of $LiFe_{0.9}Al_{0.1}PO_4$ sample. The result is caused by the charge unbalance in the sample and limited tolerance of $LiFePO_4$ lattice to Al^{3+} ions doping. The formation of AlP may be attributed to the excess Al^{3+} and the reducing atmosphere during the heat treatment.

Table 4-1

Lattice constants of pure and $LiFe_{1-x}Al_xPO_4$ powders.

Configurations	Lattice parameter				
	a(Å)	b(Å)	c(Å)	bc(Å^2)	V(Å^3)
$LiFePO_4$	10.3186(4)	6.0102(5)	4.7096(0)	28.31	292.07
$LiFe_{0.99}Al_{0.01}PO_4$	10.3194(0)	6.0124(7)	4.7131(3)	28.34	292.42
$LiFe_{0.97}Al_{0.03}PO_4$	10.3231(5)	6.0191(3)	4.7172(7)	28.39	293.11
$LiFe_{0.95}Al_{0.05}PO_4$	10.3311(4)	6.0212(5)	4.7192(3)	28.42	293.56
$LiFe_{0.93}Al_{0.07}PO_4$	10.3172(3)	6.0121(2)	4.6977(2)	28.24	291.39
$LiFe_{0.90}Al_{0.10}PO_4$	10.3203(5)	6.0137(2)	4.7101(3)	28.33	292.32

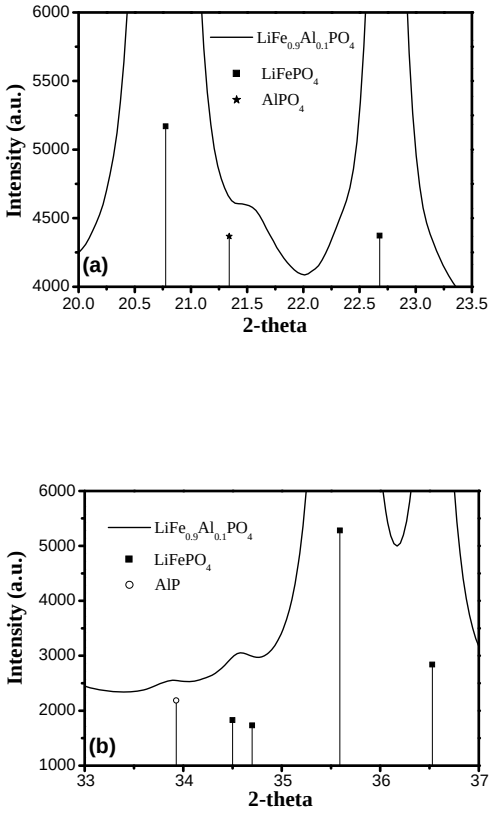

Figure 1. The enlargements of the XRD pattern of $LiFe_{0.9}Al_{0.1}PO_4$ powder performed with 01C2 beam-line of NSRRC and the standard patterns of (a) $AlPO_4$, (b) AlP