In-Situ XRD Study of Charge/Discharge Dynamic Characteristic of $LiFePO_4$ for Lithium Battery

Yi-Chun Chen (陳宜群) and Chia-Haw Hsu (許家豪)

Materials and Chemical Engineering, Industrial Technology Research Institute, Chutung, Taiwan

$LiFePO_4$ is a promising cathode materieal in lithium ion batteries because it has a good cyclibilty and safty dut to the olivine structure. Fe^{+3}/Fe^{+2} vs. Li/Li^+ is 3.4-3.5V, which causes $LiFePO_4$ has a lower working voltage compared with other cathode materials, such as $LiMnO_2$ (4.7V) and $LiCoO_2$ (3.7V). In order to rise the working voltage, we selected Mn atom to substitute Fe atom in the 4c positions and $LiMn_{0.25}Fe_{0.75}PO_4$ was synthesized. The charge-discharge curve of $LiMn_{0.25}Fe_{0.75}PO_4$ is shown in Fig. 1 and there are two distinct pleteus with different width, corresponding to Mn^{+3}/Mn^{+2} (4.1V) and Fe^{+3}/Fe^{+2} (3.4V), respectively.

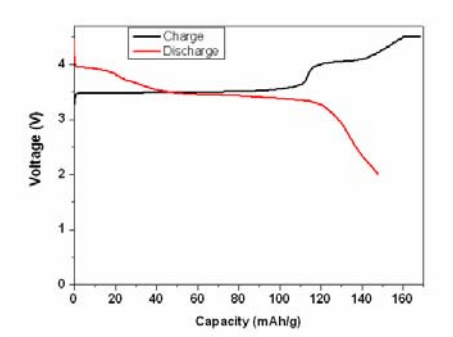

Figure 1.

In order to study the phase diagrams transition of $LiMn_{0.25}Fe_{0.75}PO_4$ during the cell charge-discharge. *In-situ* x-ray diffraction was selected to analysize. *In-situ* x-ray diffraction patterns of $LiMn_{0.25}Fe_{0.75}PO_4$ cell charged from 2V to 4.5V and discharged from 4.5V to 2V are shown in Fig. 2 and Fig. 3, respectively. The peaks are coherent to the $LiMn_xFe_{1-x}PO_4$ Pmnb structure (JCPDF 33-0802) and there are also reflections for Al current collector and is used as an internal standard throughout the experiment.

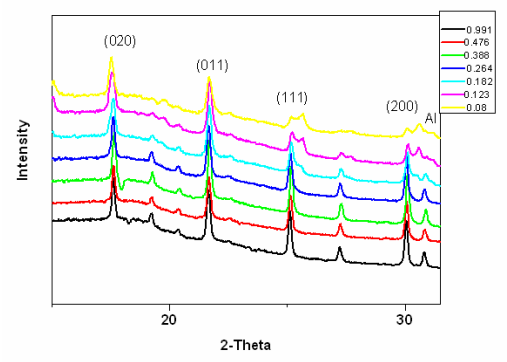

Figure 2.

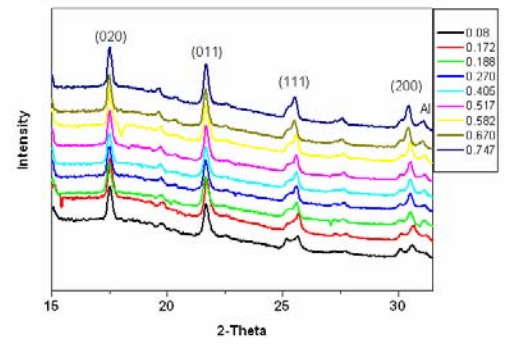

Figure 3.

During the charing process, lithium ions move out from $LiMn_{0.25}Fe_{0.75}PO_4$ and $Mn_{0.25}Fe_{0.75}PO_4$ is formed. Lattice b also increases with the delithiation process, wich reflectes on the XRD patterns. The peaks of $Mn_{0.25}Fe_{0.75}PO_4$ slightly shift to the higher angle and the situation was contrary to the lithiation. By the least square method, lattice constans can be calculated. Fig. 4 shows the lattice constant obtained from least square method as a function of lithium content during the discharge. The lattice parameter b decreases gradually from initial value 9.83Å for x= 0.172 to 0.747Å for x=0.747.

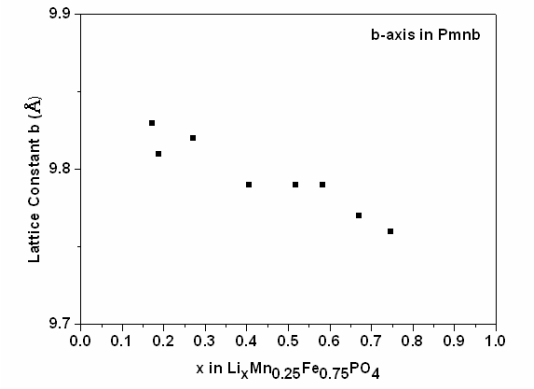

Figure 4.