Comparative Study on the Phase Diagram of A_xFePO_4 (A = Li, Na)

J. Lu[1], S. Chung[1], S. Nishimura[1, 2], and A. Yamada[1, 2]

[1] The Univ. of Tokyo, [2] ESICB, Kyoto Univ.
Department of Chemical System Engineering,
School of Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-Ku, Tokyo 113-8656 , Japan

Abstract

Phase diagram is of critical importance for predicting and explaining the electrochemical properties of cathode materials. In this study we investigated the phase diagram of a novel cathode material olivine Na_xFePO_4[1,2]. Room temperature phase diagram is firstly established. A series of samples was prepared by sintering mixtures with different proportions of $NaFePO_4/FePO_4$ at 350°C in Ar atmosphere. After cooling down slowly the samples were then subjected to X-ray diffraction. We found two distinct regions in the composition phase diagram of Na_xFePO_4, a two-phase region in the range $0<x<2/3$ and a single-phase region in the range $2/3<x<1$. The range of single (solid solution) phase region is substantially larger than that of Li_xFePO_4[3]. This result is very different from the previous assumption that the region between $Na_{2/3}FePO_4$ and $NaFePO_4$ is two-phase. We further confirmed the temperature dependence of the phase diagram by in-situ X-ray diffraction. Results show that both the solid solution region and two-phase region are very stable until the temperature reaches 500°C (Shown in Figure 1). Above this critical temperature, phases decompose to D1($Fe_7(PO_4)_6$, $NaFe_{3.67}(PO_4)_3$, $NaFeP_2O_7$) or D2(Maricite $NaFePO_4$, $NaFe_{3.67}(PO_4)_3$, $NaFeP_2O_7$). In conclusion, guest ion exchange results in dramatic differences in phase diagrams. In Li_xFePO_4 case, two-phase mixture $FePO_4/LiFePO_4$ will form solid solution phase when the temperature increases beyond 300°C[4,5]. However, in Na_xFePO_4 case, room temperature phases keep stable even at very high temperature (>500°C) in all range of x compositions.

Another interesting phenomena is found in the Mössbauer spectra of the samples Na_xFePO_4 ($0<x<1$). Mössbauer spectra of the intermediate phase $Na_{2/3}FePO_4$ (Figure 2a) was fitted as being composed of three doublets. The presence of two kinds of Fe^{2+} sites (Fe^{2+}(A) and Fe^{2+}(B)) may suggest the existence of Fe^{2+} ordering or structure distortion in the intermediate phase $Na_{2/3}FePO_4$. We also observed the existence of two kinds of Fe^{2+} sites in the solid solution region ($2/3<x<1$), and Fe^{2+}(B) gradually dominates when x increases to 1(Figure 2b).

In summary, room temperature x-ray diffraction patterns of Na_xFePO_4 ($0<x<1$) reveal the two stages of phase change (two-phase region when $0<x<2/3$, single-phase region when $2/3<x<1$) at room temperature. The existence of extended single-phase region ($2/3<x<1$) may have a strong influence on the ionic and electronic conductivity of this novel sodium-intercalation cathode material. High temperature in-situ X-ray diffractions showed the phases which are observed at room temperature are stable up to 500°C. The presence of two kinds of Fe^{2+} sites in Mössbauer spectra leads us to conceive that there may exist Fe^{2+} ordering or structure distortion in the intermediate phase.

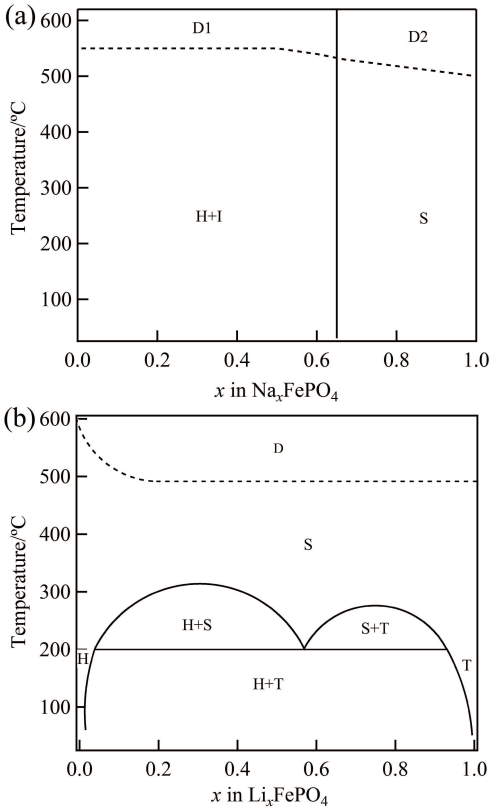

Figure 1. Composition phase diagram (a) Na_xFePO_4 (b) Li_xFePO_4[4,5]. H: Heterosite; T: Triphylite; S: Solid solution phase; I: Intermediate phase; D1/D2/D: Decomposed phases

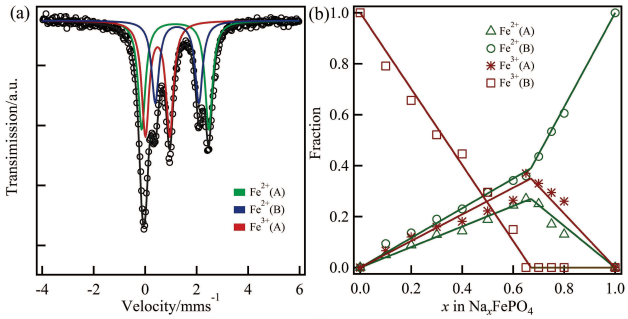

Figure 2. (a) Mössbauer spectra of intermediate phase $Na_{2/3}FePO_4$ (b) Systematic change of Fe sites fraction with x variation

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