Comparative Study on the Phase Diagram of $A_x$FePO$_4$ ($A = \text{Li, Na}$)

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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$_{2/3}$FePO$_4$. 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$_{2/3}$FePO$_4$, 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$_7$FePO$_4$. 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(FePO$_4$)$_3$, Na$_{2/3}$FePO$_4$, NaFePO$_4$, and Na$_7$FePO$_4$. In conclusion, guest ion exchange results in dramatic differences in phase diagrams. In Na$_{2/3}$FePO$_4$ case, two-phase mixture FePO$_4$/LiFePO$_4$ will form solid solution phase when the temperature increases beyond 300°C. However, in NaFePO$_4$ 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$_{2/3}$FePO$_4$ (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$_{2/3}$FePO$_4$ (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$_{2/3}$FePO$_4$ (b) Li$_7$FePO$_4$. 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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