Phase Transition and Stacking Faults in Na-Extracted Layered Oxides

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Sodium-ion batteries are promising candidates for a stationary energy storage system because of abundant resources of sodium in the world. The electrode materials have been extensively studied and some companies have developed prototype full cells consisting of layered transition metal oxides and non-graphitizable carbon (hard carbon) as a positive and a negative electrode, respectively. Much efforts have been recently devoted to understand the reaction mechanism and further improve electrode performance. However, structure of the layered oxides, especially P2-type phases such as $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$, at fully charged state is unclear and depends on the composition. In this study, phase transition caused by Na-extraction is examined using *ex-situ* synchrotron and *operando* X-ray diffraction (XRD) for P2-$Na_{2/3-x}Ni_{1/3}Mn_{2/3}O_2$ and its Cu-substituted phase.

$Na_{2/3-x}Ni_{1/3}Mn_{2/3}O_2$ and $Na_{2/3}Cu_{1/12}Ni_{1/4}Mn_{2/3}O_2$ with P2-type structure were prepared by a conventional solid-state reaction. *Operando* X-ray diffraction was measured using an in-situ cell (Rigaku) with sample electrodes, 1 mol dm^{-3} $NaPF_6$/PC electrolyte and a counter electrode of Na metal. The XRD patterns for the electrodes revealed that structure of $Na_{2/3-x}Ni_{1/3}Mn_{2/3}O_2$ transformed from P2 into O2-type phase as a two-phase reaction by Na-extraction, while two- and single-phasic P2-OP4 transition was observed for $Na_{2/3-x}Cu_{1/12}Ni_{1/4}Mn_{2/3}O_2$. Furthermore, peak broadening of 10*l* reflection was observed at almost fully charged state for both samples, which is clearly seen in the *ex-situ* synchrotron XRD patterns for $Na_{2/3-x}Ni_{1/3}Mn_{2/3}O_2$ in Fig. 1a. According to study by Lu and Dahn, the peak broadening is assumed to be caused by stacking faults between two choices of O2-type structures (Fig. 1b).[1] The XRD pattern of O2-type phase with stacking faults, where the two choices were selected at random, was calculated using DIFFaX program. The simulated XRD pattern was similar to the observed one, suggesting formation of stacking faults with the two choices. Similarly, a calculated pattern of OP4-type phase with some stacking faults was also close to the observed XRD profile for $Na_{2/3-x}Cu_{1/12}Ni_{1/4}Mn_{2/3}O_2$ after charge to 4.5 V. Relationship between the phase transition accompanying stacking faults and electrode performance will be discussed.

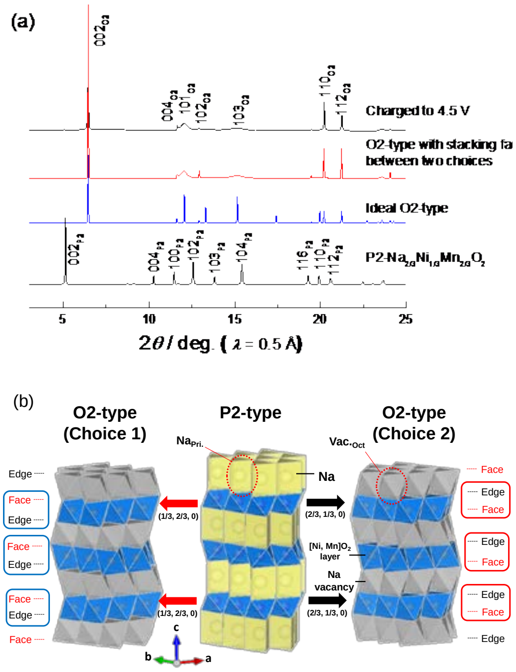

Figure 1. (a) Synchrotron *ex-situ* XRD patterns of $Na_{2/3-x}Ni_{1/3}Mn_{2/3}O_2$ and simulated ones for O2-type phase w/o stacking faults. (b) Schematic illustration of O2-type structure with two choices.

References

[1] Z. H. Lu and J. R. Dahn, *J. Electrochem. Soc.*, **148**, A1225 (2001).