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A Study on Structural Stability in P2- and O3-$Na_x[Fe_{1/2}Mn_{1/2}]O_2$ as Positive Electrode Materials for Sodium-Ion Rechargeable Batteries

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1 Introduction

The demand of the large-scale rechargeable batteries has grown, especially for the load leveling in the electrical grids. In the realm of energy storage, lithium-ion batteries have risen to prominence as key device for green and sustainable energy development, but lithium is classified as a minor metal. In contrast to lithium, sodium is an attractive charge carrier on the basis of elemental abundance, atomic weight, and standard potential. Recently, we have reported sodium iron manganese oxides, P2-type $Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$, consisting of only abundant elements, delivers large reversible capacity (more than 180 mAh g^{-1}) with relatively good capacity retention at room temperature[1]. Whereas O3-type $Na[Fe_{1/2}Mn_{1/2}]O_2$ shows a reversible capacity of only 120 mAh g^{-1} despite larger amount of Na in the composition. In this study, we examined the electronic structure with different stacking order of O3- and P2-type layered sodium iron manganese oxides during charge/discharge by X-ray absorption spectroscopy (XAS) to understand the origin of different reaction mechanism for layered polymorphs.

2 Experimental

Composite positive electrodes consisted of 80 wt% active materials, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVdF), coated on aluminum foil as a current collector. The electrolyte solution used was 1 mol dm^{-1} $NaClO_4$ dissolved propylene carbonate (Kishida Chemical Co. Ltd., Japan) with 2 vol.% fluoroethylene carbonate as an electrolyte additive. Electrochemical testing was conducted using R2032-type coin cells with Na metal as a negative electrode. The coin cells were assembled in an Ar-filled glovebox and cycled at a rate of C/20. After the electrochemical tests, composite electrodes were taken out from the cells, and the electrodes were rinsed with dimethyl carbonate (DMC) and sealed in a water-resistant polymer film in the Ar-filled glovebox.

3 Results and Discussion

X-ray absorption near edge structure (XANES) spectra of P2-$Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$ and O3-$Na[Fe_{1/2}Mn_{1/2}]O_2$ at Fe K-edge during the charge to 4.2 V are shown in Fig. 1(a) and (b), respectively. The spectrum of P2-type phase shifted toward higher energy after the charge from 3.8 to 4.2 V and reversibly shifted back by the discharge to 1.5 V, while that of O3-type gradually shifted during charging and did not completely shift back to its original position, suggesting that the reaction mechanism is different between P2-type and O3-type polymorphs. The change in the intensity of pre-edge peaks is more evident for the O3 sample.. Increase in the pre-edge intensity after fully discharge to 1.5 V for the O3-type phase suggests the irreversible structure changes, presumably Fe migration from octahedral to tetrahedral sites (formed in Na layer by charge) for the O3-type phase. To identify the influence of Fe ion, XANES spectra of O3-$NaFeO_2$ were also collected as shown in Fig. 1(c). Irreversible change in the pre-edge intensity after the charge above 4.0 V was observed for O3-$NaFeO_2$. These results suggest the reversible and irreversible structural change for Fe ions in the P2- and O3-type layered polymorphs, respectively, influencing the electrochemical performance as electrode materials for rechargeable sodium batteries.

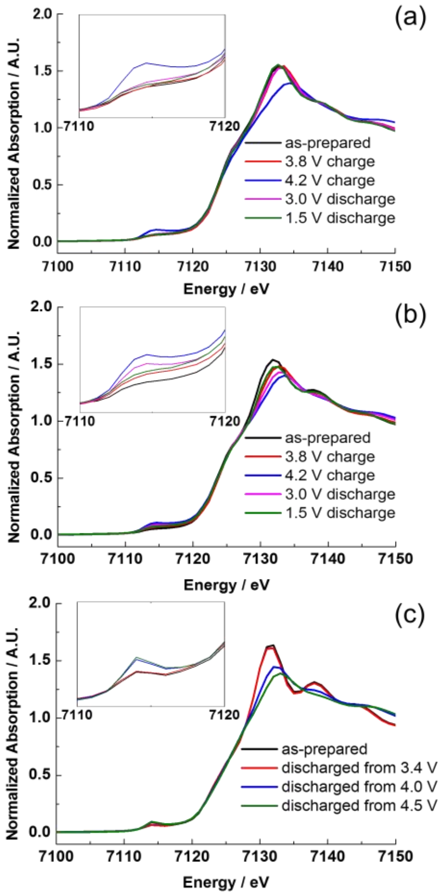

Fig. 1 XANES spectra of (a) P2-$Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$, (b) O3-$Na[Fe_{1/2}Mn_{1/2}]O_2$ at Fe K-edge during the initial charge/discharge cycle in the voltage range of 1.5 V and 4.2 V and (c) O3-$NaFeO_2$ fully discharged to 2.5 V after charge to 3.4, 4.0 and 4.5 V. The insets are expanded views of the pre-edge region.

References

[1] N. Yabuuchi *et al.*, *Nature Mater.*, **11**, 512 (2012).

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