

# A Study on Reaction Mechanisms by X-ray Absorption Spectroscopy in $\text{Na}_x\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ as Positive Electrode Materials for Sodium-ion Batteries

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## 1 Introduction

Na-ion batteries are promising candidates as a next generation energy storage device because of the materials abundance and high energy performance. However, averaged operating potential of  $\text{Na}_x\text{MeO}_2$  is usually lower than that of  $\text{Li}_x\text{MeO}_2$ , resulting in lower energy density compared with that of Li-ion system. Among the layered oxide cathode materials, P2-type  $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  is a promising candidate as a high potential positive electrode material because of the operating potential of 3.6 V vs.  $\text{Na}/\text{Na}^+$  based on the  $\text{Ni}^{2+/4+}$  redox couple.<sup>[1]</sup> This material has another crystal polymorph of P3-type layered oxide reported as a low temperature phase.<sup>[2]</sup> In these materials, valence of Ni and Mn is expected to be divalent and tetravalent, respectively. P3-type material is, therefore, also expected to exhibit high operating potential. In this study, we examined the electronic structure of transition metals in P3- and P2-type  $\text{Na}_{2/3-x}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  during charge/discharge by X-ray absorption spectroscopy (XAS) and revealed relationship between crystal structure and electronic structure.

## 2 Experiment

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  $1 \text{ mol dm}^{-1}$   $\text{NaPF}_6$  dissolved propylene carbonate (Kishida Chemical Co.Ltd., Japan). 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 diethyl carbonate (DEC) and sealed in a water-resistant polymer film in the Ar-filled glovebox.

## 3 Results and Discussion

From X-ray absorption near edge structure (XANES) spectroscopy of P3- and P2-type  $\text{Na}_{2/3-x}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  at Ni K-edge, energy shift toward higher energy was observed after charge to 4.5 V and reversibly shifted back by discharge to 2.0 V, which indicates that Ni was oxidized and reduced during charge and discharge processes for both materials. Next, XANES spectra at Mn K-edge during charge to 4.5 V for P3- and P2-phases are shown in Fig. 1(a) and (b), respectively. No energy shift was observed before and after the charge to 4.5 V in P3-type phase, suggesting that Mn does not participate in the redox reaction during charge and discharge processes

for P3-type phase. On the other hand, the spectrum of P2-type phase shifted toward higher energy after charge to 4.0 V. However, no shift was observed after further charge to 4.5 V. These results indicate existence of  $\text{Mn}^{3+}$  in initial composition of P2-type phase and the reversible redox reaction during charge and discharge even though Mn was expected to exist as tetravalent ion in initial composition of P2-type  $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ . In spite of the same composition between P3 and P2 phases, valence of manganese ion before electrochemical Na extraction is different, which would influence on the electrochemical properties as positive electrode materials for Na-ion batteries. Consequently, the difference in electronic state of manganese ions in between P2- and P3-type phases is found by XAS study. To elucidate the charge/discharge mechanism between P3- and P2-type  $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ , further detailed analysis on XAS, especially EXAFS combined with ex-situ XRD, is required.

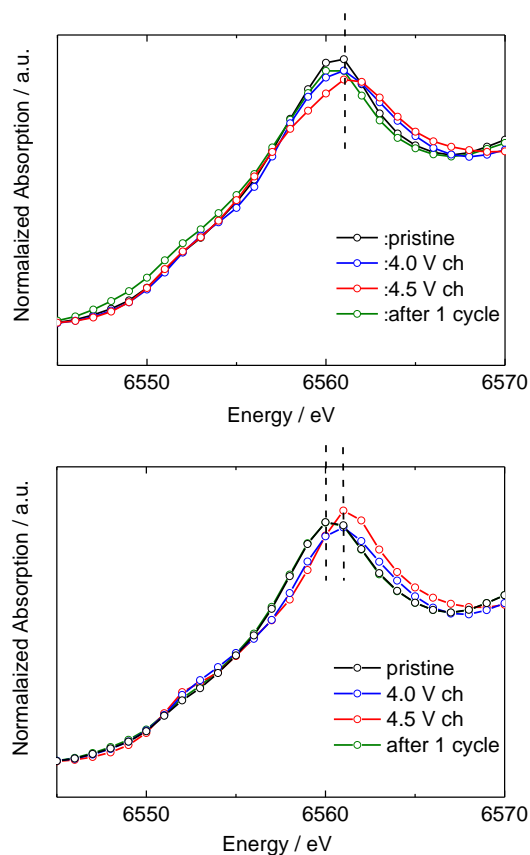


Fig. 1 XANES spectra of (a) P3- and (b) P2-type  $\text{Na}_{2/3-x}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  at Mn K-edge during 1st cycle.

References

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