

Study on the Crystal and Electronic Structures of the Layered $\text{Li}_2\text{MO}_3\text{-LiMO}_2$ Materials in Li de-intercalation process

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1 Introduction

The layered $\text{Li}_2\text{MO}_3\text{-LiMO}_2$ materials are one of the promising positive electrode materials of lithium secondary battery because of their large capacity when operated above 4.6 V [1]. In this system, especially, $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$ displays a initial discharge capacity of c.a. 280 mAh/g in the voltage range of 2.5 to 4.8 V and keep a reversible capacity of c.a. 250 mAh/g after 50 cycles [2]. Several papers have reported on the mechanism why these materials show large reversible capacity. However, the initial charge and discharge process are still ambiguous. We have reported on the characteristic structural change during Li de-intercalation for $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ [3-4] using synchrotron radiation. Detailed information on the crystal and electronic structures above 4.6 V is very important in order to improve the calendar life and thermal stability of these materials and, therefore, the structural and electronic changes of $\text{Li}_{1.20}\text{Ni}_{0.17}\text{Co}_{0.10}\text{Mn}_{0.53}\text{O}_2$ (sample A) and $\text{Li}_{1.01}\text{Ni}_{0.49}\text{Co}_{0.21}\text{Mn}_{0.29}\text{O}_2$ (sample B) in Li de-intercalation process were studied in this paper.

2 Experiment

The de-lithiated $\text{Li}_{1.20-y}\text{Ni}_{0.17}\text{Co}_{0.10}\text{Mn}_{0.53}\text{O}_2$ (samples A-series) and $\text{Li}_{1.01-y}\text{Ni}_{0.49}\text{Co}_{0.21}\text{Mn}_{0.29}\text{O}_2$ (samples B-series) were electrochemically prepared using coin-type cells with Li/1M LiPF_6 in EC:DMC(1:2)/samples. Crystal and electronic structures were investigated by synchrotron XAFS (BL7C at PF) measurements. The bondlength were determined using the analysis programs REX2000.

3 Results and Discussion

Figure 1 shows the 1st charge and discharge curves of samples A and B in the voltage range of 2.0 and 4.8 V. The Li/sample A cell showed the 1st charge capacity of 282 mAh/g and gave the characteristic plateau region around 4.5 V. Figure 2 shows the Ni K-edge XANES Spectra of samples A-series and B-series with Li de-intercalation. For samples A-series, Ni K-edge XANES spectra shift to higher energy up to $y=0.4\text{-}0.6$ and then shift to lower energy up to $y=0.93$. This means that the valence state of Ni increased to 4+ and then decreased with Li de-intercalation. For samples B-series, Ni K-edge XANES spectra display continuous shifts to $y=0.88$. This

means that the valence state of Ni increased to 4+ with Li de-intercalation. These results indicated that Li de-intercalated mechanism is different between samples A and B.

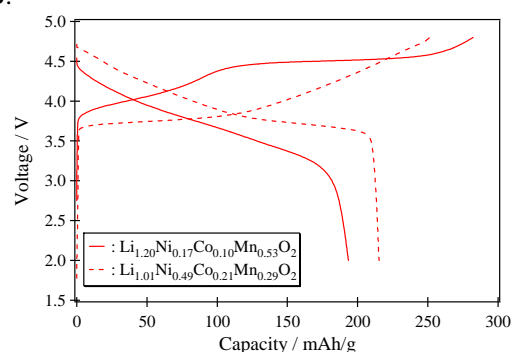


Fig. 1: 1st charge and discharge curves for samples A and B.

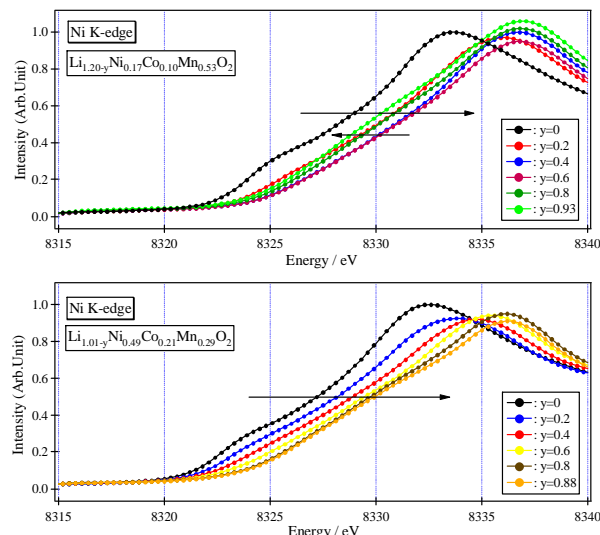


Fig. 2: Ni K-edge XANES Spectra of samples A-series and B-series.

References

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