BL-12C/2015G529

# Study on Reaction Mechanisms of $Li_3NbO_4$-$LiMoO_2$ Binary System by XAS Spectroscopy

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## 1 Introduction

The demand for the increase in energy density of lithium batteries are steadily growing. The use of three-electron redox of transition metals is expected to be a plausible strategy to further increase the energy density of positive electrode materials with less transition metal ions. Historically, three-electron redox reaction of transition metals is reported only for $Cr^{3+}/Cr^{6+}$, *e.g.*, $Li_{1.2}Cr_{0.4}Mn_{0.4}O_2$.[1] In this study, the reaction of $Mo^{3+}/Mo^{6+}$ is targeted as electrode materials. Since conventional layered system, $LiMo^{3+}O_2$, has one mole of Li in the formula unit, only one-electron redox of $Mo^{3+}/Mo^{4+}$ is used. Therefore, $Mo^{3+}$ is diluted in lithium-excess oxide, $Li_3NbO_4$[2] as the model material, according to the chemical formula of $x$ $LiMoO_2$ – $(1 - x)$ $Li_3NbO_4$ binary system. The highest reversible capacity based on $Mo^{3+}/Mo^{6+}$ is expected with $x$ = 0.6 ($Li_{9/7}Nb_{2/7}Mo_{3/7}O_2$) in this binary system.

## 2 Experiment

$Li_{9/7}Nb_{2/7}Mo_{3/7}O_2$ as a metastable phase was prepared by the mechanical milling with a planetary ball mill (Pulverisette 7; Fritsch). A mixture of $Li_3NbO_4$ and $LiMoO_2$ was used as a precursor for mechanical milling. A 0.7 g sample of of $Li_3NbO_4$ and 0.8 g of $LiMoO_2$ were mixed by using a zirconia pot (45 mL) and zirconia balls (15.5 g) at 600 rpm for 12 h. After being milled for 12 h, the mixture was removed from the container and mixed using a mortar and pestle. The mixture was again milled using the zirconia pot and balls at 600 rpm for 12 h. Overall, this process was performed three times, and the total milling time was 36 h.

## 3 Results and Discussion

An X-ray diffraction pattern of $Li_{9/7}Nb_{2/7}Mo_{3/7}O_2$ is assigned to a cation disordered rocksalt structure with low crystallinity. Electrochemical properties of $Li_{9/7}Nb_{2/7}Mo_{3/7}O_2$ before and after mechanical-milling were examined in Li cells. The sample before mechanical-milling shows initial discharge capacity of *ca.* 80 mAh $g^{-1}$, and a voltage profile is the same with $LiMoO_2$ as shown in Figure 1. On the other hand, the sample after mechanical-milling delivers a reversible capacity of *ca.* 290 mAh $g^{-1}$, which nearly corresponds to that of theoretical capacity based on the redox reaction of $Mo^{3+}/Mo^{6+}$. Moreover, three-electron redox of Mo is supported by X-ray absorption spectroscopy without the contribution of Nb for charge compensation as shown in Figure 2.[3].

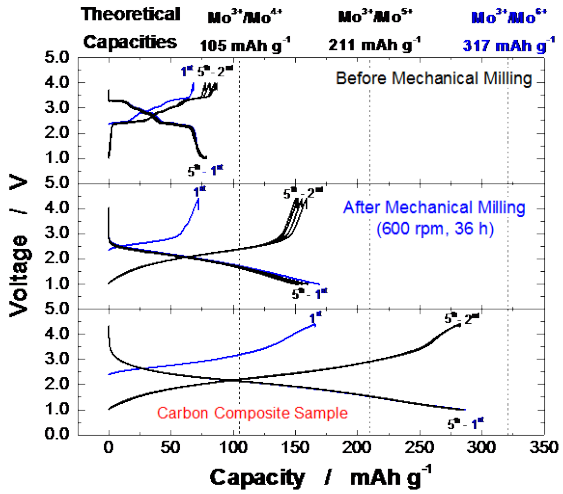


Fig. 1: Charge/discharge curves of the mixture of $Li_3NbO_4$ and $LiMoO_2$ before and after mechanical-milling at a rate of 10 mA $g^{-1}$ at 25 °C. Results of carbon composite sample is also shown.

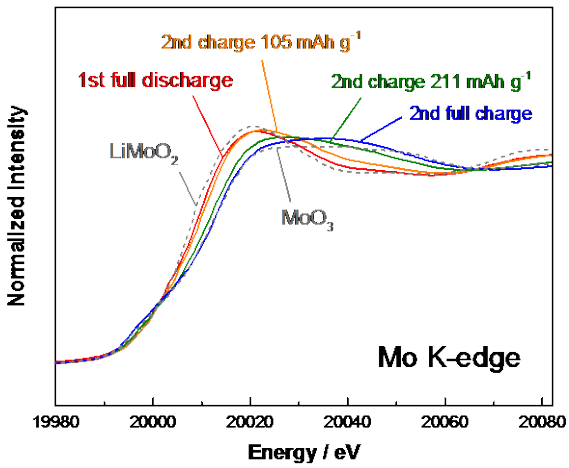


Fig. 2 Changes of XAS spectra of $Li_{9/7-x}Nb_{2/7}Mo_{3/7}O_2$ with reference materials for comparison.

## References

[1] B. Ammundsen *et al.*, *Journal of The Electrochemical Society*, **149,** A431 (2002).
[2] N Yabuuchi *et al.*, *Proceedings of the National Academy of Sciences*, **112**, 7650 (2015).
[3] S. Hoshino et al., and N. Yabuuchi, ACS Energy letters, **2**, 733 (2017).

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