Photon Factory Activity Report 2012 #30 (2013) **B**

BL-9C/2012G651

XAFS analysis of Lithium-ion battery materials with tunnel-type structure

Kunimitsu Kataoka[1,*],Mikito Mamiya[1], Norihito Kijima[1], Junji Akimoto[1]
[1]Advaced Industrial Science and Technology (AIST), Tsukuba, 305-8565, Japan

Introduction

Lithium manganese oxide $Li_{0.44}MnO_2$ has been extensively investigate as one of the positive electrode materials for secondary lithium batteries [1]. This compound can be prepared by a ion-exchange method using the corresponding sodium manganese oxide $Na_{0.44}MnO_2$ as the parent compound. The electrochemical measurements for $Li_{0.44}MnO_2$ showed an initial discharge capacity of 166 mAh/g between 4.8 and 2.5 V. In addition, the specific capacity and discharge profile were improved by an additional lithium insertion treatment in molten $LiNO_3$-LiOH salt at low temperature ($Li_{0.55}MnO_2$) [2]. Reentry, we have successfully prepared the $Li_{0.81}MnO_2$ sample having the original $Na_{0.44}MnO_2$-type framework structure by LiI treatment of the as-prepared $Li_{0.59}MnO_2$ sample. The electrochemical measurements for $Li_{0.81}MnO_2$ showed an initial discharge capacity of 200 mAh/g between 4.8 and 2.5 V.

To clarify the Li-ion insertion materials of $Li_{0.44}MnO_2$, X-ray absorption fine structure (XAFS) studis have been made.

Experimental

The $Li_{0.44}MnO_2$ sample was prepared from $Na_{0.44}MnO_2$ via Na^+/Li^+ ion-exchange reaction using $LiNO_3$ asa molten salt at 270◦C for 10 h in air. Additional lithium in-serted $Li_{0.59}MnO_2$ sample was next prepared by heating as-prepared $Li_{0.44}MnO_2$ sample in molten $LiNO_3$-LiOH at 270◦C for 10 h in air. The $Li_{0.82}MnO_2$ samples were synthesized by reacting 10mol% excess of LiI (99.9% pure) with the as-prepared $Li_{0.59}MnO_2$ sample in acetonitrile at 80◦C for 5 h and 10 h, respectively. After LiI treatment, the samples were washed with acetonitrile, and then dried at 120◦C for 12 h in a vacuum.

Mn K-edge XAFS of samples were measured by transmission mode using synchrotron radiation at beam line BL-9C of Photon Factory. The Athena software was used for the analysis of XAFS data.

Result and Discussion

The crystal structure of Li_xMnO_2 (x = 0.44 and 0.82) maintains the parent $Na_{0.44}MnO_2$-type tunnel framework as show in Figure 1. The Li-ion of Li_xMnO_2 filled in the tunnel space. About $Li_{0.44}MnO_2$, we have confirmed that it exists in the tunnel space in the previous report [1]. About $Li_{0.81}MnO_2$, chemical composition was confirmed by chemical analysis. The electrochemical measurement result changed surely. However, we were not able to confirm whether excessive lithium was inserted in tunnel space. Because observation of Li-ions is because difficult by powder X-ray diffraction.

Figure 2 demonstrates Mn K-edge X-ray absorption near-edge structure (XANES) spectra of the manganese oxides, $Li_{0.44}MnO_2$ and $Li_{0.81}MnO_2$. Evidence of reduction to lower valent Mn-ions after Li-ion insertion was detected by these XANES spectra. So valence of Mn at $Li_{0.81}MnO_2$ is below $Li_{0.44}MnO_2$. It was confirmed that excess lithium ions are inserted in the tunnel sapce from this result.

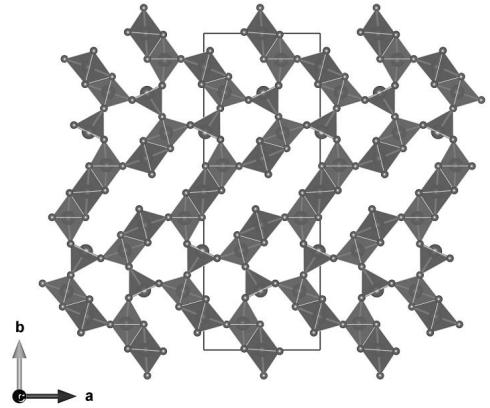

Figure 1. Crystal structure of the $Na_{0.44}MnO_2$-type tunnel framework.

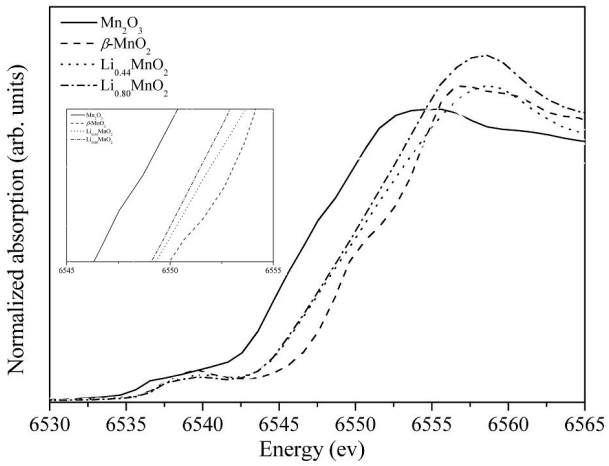

Figure 2. Mn K-edge XANES spectra of the manganese oxides and $Na_{0.44}MnO_2$-type Li_xMnO_2 (x=0.44 and 0.80) .

References

[1] J. Akimoto et al., Electrochem. Solid-State Lett., 8, A554 (2005).
[2] J. Awaka et al., J. Power Sources, 174, 1218 (2007).

kataoka-kunimitsu@aist.go.jp