BL-12C/ 2023G028

Study on Charge Compensation Mechanisms for Lithium-excess Rocksalt-type Manganese Oxides with Cationic/Anionic Redox

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1 Introduction

For lithium-ion battery applications, rocksalt-type metal oxides are promising positive electrode materials thanks to their robust three-dimensional host structures based on cation disordered arrangement. Indeed, compared to traditional layered materials, Li-rich metal oxides with the cation-disordered rocksalt structure exhibit superior structural stability using highly reversible multi-electron anionic/cationic redox.

Although higher energy density, which originates from the activation of anionic redox, is obtained for Li-rich Mn-based oxides/oxyfluorides, an unanswered practical issue is found in insufficient reversibility of anionic redox. In this study, charge compensation mechanisms are examined by X-ray absorption spectroscopy.

2 Experiment

$Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$, $Li_{1.2}Nb_{0.2}Mn_{0.6}O_2$, and $Li_{1.1}Nb_{0.1}Mn_{0.8}O_2$ were prepared by a solid-state reaction from Li_2CO_3, Nb_2O_5, and Mn_2O_3. These precursors were heated at 950 °C for 12 h in an argon atmosphere for $Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$ and $Li_{1.2}Nb_{0.2}Mn_{0.6}O_2$ samples, 1050 °C for 1 h for $Li_{1.1}Nb_{0.1}Mn_{0.8}O_2$ sample. Hard XAS spectra were collected with a silicon monochromator in the transmission mode. The intensities of the incident and transmitted X-rays were measured using an ionization chamber at room temperature.

3 Results and Discussion

The crystal structures of the samples were analyzed by X-ray diffraction in Fig. 1. After the calcination, there are no residual phases corresponding to Li_3NbO_4 and $LiMnO_2$, indicating a cation disordered rocksalt phase is obtained for $Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$, $Li_{1.2}Nb_{0.2}Mn_{0.6}O_2$, and $Li_{1.1}Nb_{0.1}Mn_{0.8}O_2$ with a space group symmetry of *Fm*-3*m* in which all cations are located at 4*a* sites. In addition, $Li_{1.1}Nb_{0.1}Mn_{0.8}O_2$ is synthesized as the maximum Mn content in Li_3NbO_4–$LiMnO_2$ binary system. Charge compensation mechanism on electrochemical cycles were examined by XAS study. Note that the irreversibility of electrochemical reaction is noted as shown in Fig. 2. If the irreversible oxygen loss proceeds on charge, this leads to further reduction of Mn^{3+} on discharge. On charge, the energy of XAS spectrum shifts to the higher energy region due to Mn ion oxidation. However, after discharge to 1.5 V, the XAS spectrum is found at a lower energy region in comparison with the pristine electrode. This observation suggests the reduction of Mn ions associated with the oxygen loss on charge.

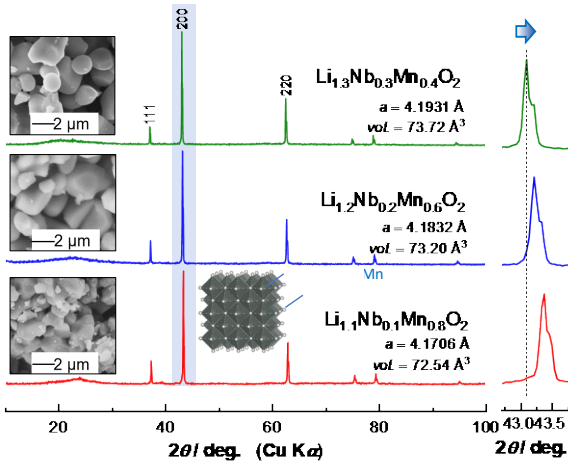

Fig. 1: X-ray diffraction patterns and SEM images of Li-excess rocksalt-type oxides, $Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$, $Li_{1.2}Nb_{0.2}Mn_{0.6}O_2$, and $Li_{1.1}Nb_{0.1}Mn_{0.8}O_2$. A schematic illustration of the cation disordered rocksalt structure is also shown.

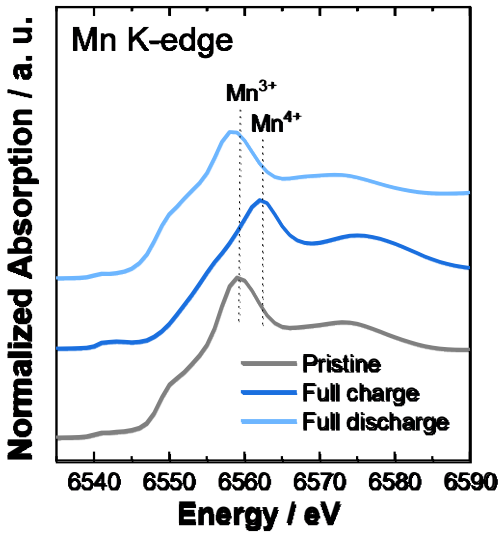

Fig. 2: XAS spectra of $Li_{1.1-x}Nb_{0.1}Mn_{0.8}O_2$ before and after electrochemical cycles in Li cells.

References

[1] Y. Zhang, N. Yabuuchi *et al.*, *Advanced Energy Materials*, **14**, 2304074 (2024).

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