

Synthesis, Electrochemical Properties, and Reaction Mechanisms of New Lithium-Excess Transition Metal Oxides with Cation Disordered Rock-Salt-Type Structure

N. Yabuuchi,^a M. Takeuchi,^a D. Endo,^b T. Ozaki,^b T. Inamasu,^b J.-Y. Son,^c Y.-T. Cui,^c H. Oji,^c and S. Komaba^a

^aDepartment of Applied Chemistry, Tokyo Univ. of Science
1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan

^bR&D Center, GS Yuasa International Ltd.
1 Inobanba-cho, Nishinosho, Kisshoin, Minami, Kyoto
601-8520, Japan

^cJapan Synchrotron Radiation Research Institute/SPring-8,
1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan

In the past three decades, intensive research efforts have been made to explore new positive electrode materials for rechargeable lithium batteries. Lithium-excess manganese oxides, Li_2MnO_3 , and solid solution phases with LiMeO_2 (Me = Co, Ni, Mn etc.) have recently attracted interest as high-capacity electrode materials. The large reversible capacity partly originates from the participation of oxide ions in the crystal lattice in redox reactions.[1,2] The use of analogy seems to be one strategy to design new high-capacity electrode materials. Therefore, lithium niobium oxide, Li_3NbO_4 , which is classified as cation-ordered rock-salt structure with a cubic-close packed (CCP) oxygen array similar to Li_2MnO_3 , is targeted as a potential new end-member for high-capacity electrode materials.

Figure 1 shows an XRD pattern of Li_3NbO_4 with a schematic illustration of the crystal structure. Framework structure of Li_3NbO_4 consists of Nb_6O_{14} clusters, which further forms a body-centered cubic lattice, and lithium ions are located at remaining vacant octahedral sites. Since Li_3NbO_4 is electrically an insulator, transition metals are substituted for Li^+ and Nb^{5+} . After several trials, it is found that Co^{2+} , Ni^{2+} , Fe^{3+} , and Mn^{3+} can be substituted for Li^+ and Nb^{5+} as shown in Figure 2. Such transition metal substitution is achieved in the series of $\text{Li}_3\text{NbO}_4\text{-MeO}$ (Ni^{2+} , Co^{2+}) and $\text{Li}_3\text{NbO}_4\text{-LiMeO}_2$ (Fe^{3+} , Mn^{3+}) systems with a common CCP oxygen lattice. As shown in Figure 2, the metal substitution influences the clustering of niobium in a CCP oxygen array, leading to the formation of cation disordered rock-salt phases. In general, well-crystallized cation disordered rock-salt phases are known to be electrochemically inactive. Nevertheless, a manganese-substituted sample ($0.43\text{Li}_3\text{NbO}_4\text{-}0.57\text{LiMnO}_2$ or $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_2$ as a layered formulation) shows large reversible capacity with small initial irreversible capacity at 60°C as shown in Figure 3. Initial charge/discharge capacity reaches 300 mAh g^{-1} , which is clearly larger than that of the expected capacity (118 mAh g^{-1}) based on the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox reaction. Therefore, the charge compensation by oxide ions in the crystal lattice, similar to Li_2MnO_3 -based materials, is expected to be achieved.

From these results, we will further discuss reaction mechanisms of the new Li_3NbO_4 -based positive electrode materials for rechargeable lithium batteries.

References

- [1] T. Ohzuku et al., *J. Mater. Chem.*, **21**, 10179 (2011).
[2] M. Sathya et al., *Chem. Mater.*, **25**, 1121 (2013).

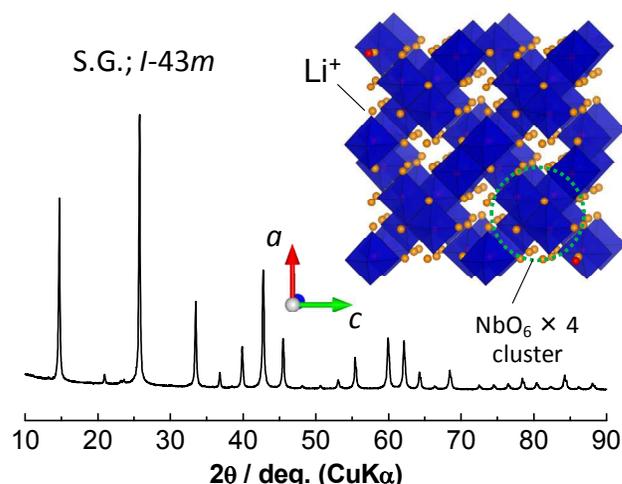


Figure 1. An X-ray diffraction pattern of Li_3NbO_4 . Schematic illustration of the sample is also shown.

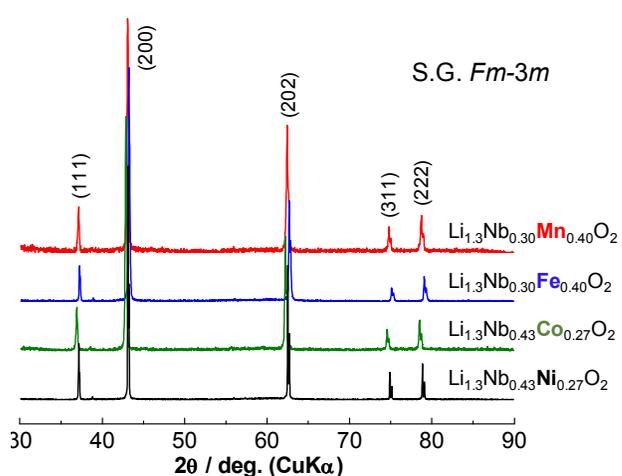


Figure 2. Typical X-ray diffraction (XRD) patterns of $\text{Li}_3\text{NbO}_4\text{-MeO}$ (Me = Ni^{2+} and Co^{2+}) and $\text{Li}_3\text{NbO}_4\text{-LiMeO}_2$ (Me = Fe^{3+} and Mn^{3+}) systems.

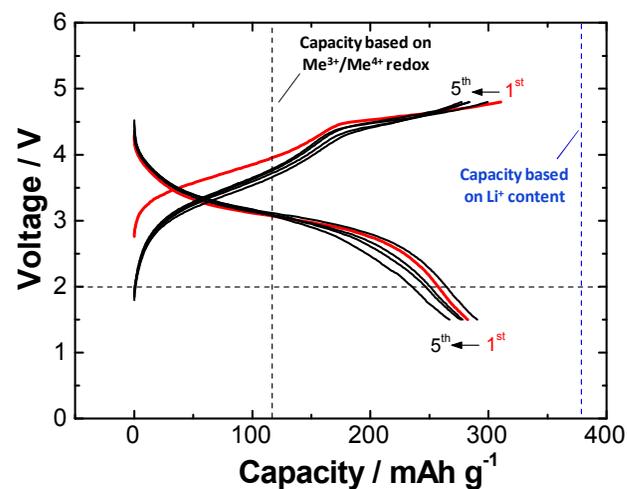


Figure 3. Charge/discharge curves of $0.43\text{Li}_3\text{NbO}_4\text{-}0.57\text{LiMnO}_2$ ($\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_2$) in the voltage range of 1.5 – 4.8 V at a rate of 10 mA g^{-1} at 60°C .

Acknowledgements

This study was in part financially supported by the NEXT program and Grant-in-Aid for Young Scientists (B) (No. 24750186) from the Japanese Ministry of MEXT.