

Reaction Mechanisms of Cation-Disordered Rocksalt-Type LiMnO_2

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The demand of further increase in energy density of lithium-ion batteries is still growing. Among the lithium-containing transition metal oxides, LiMnO_2 with an orthorhombic zigzag-type layered structure has been extensively studied as potential positive electrode materials. Major drawbacks of LiMnO_2 as electrode materials are found in slow electrode kinetics probably associated with cycle-induced phase transitions and the formation of nanodomains. A observed reversible capacity is generally limited to be less than 200 mA h g^{-1} , which is far from a theoretical capacity of 286 mA h g^{-1} . Recently, as a non-layered system, cation-disordered rocksalt-type oxides, $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$, have been proposed as high-capacity positive electrode materials [1], and this sample with Mn^{3+} does not convert into spinel-like phase.

In this study, to examine the reversibility limit of LiMnO_2 , cation-disordered LiMnO_2 is synthesized from zigzag layered LiMnO_2 by mechanical milling, and electrode performance and phase evolution processes are compared with zigzag layered LiMnO_2 . To improve the electrode performance, the milled sample was further mixed with acetylene black (denoted as "carbon composite"). Well defined diffraction patterns are found for as-prepared LiMnO_2 with the zigzag layered structure. These diffraction patterns are completely lost after mechanical milling, and cation-disordered rocksalt-type LiMnO_2 with low crystallinity is formed [2]. Electrochemical properties of LiMnO_2 with different crystal structures (zigzag layered and cation disordered) are compared in Figure 1. Rocksalt-type LiMnO_2 delivers a large reversible capacity of 260 mA h g^{-1} , which reaches >90% of the theoretical capacity. Moreover, slow kinetics to spinel phase transition was evidenced for rocksalt LiMnO_2 [2].

Charge compensation mechanisms on charge/discharge for rocksalt LiMnO_2 was also examined by XAS. Reversible shift of Mn K-edge XAS spectra is noted as shown in Figure 2. This result suggests that highly reversible Mn cationic redox proceeds, which is the same processes with zigzag layered LiMnO_2 . Therefore, it is concluded that the difference in crystal structures is essential to suppress the unfavorable phase transition with Mn ions as electrode materials.

References

- [1] N. Yabuuchi *et al.*, *Nature Commun.*, **7**, 13814 (2016).
[2] N. Yabuuchi *et al.*, *J. Mater. Chem. A*, **6**, 13943 (2018).

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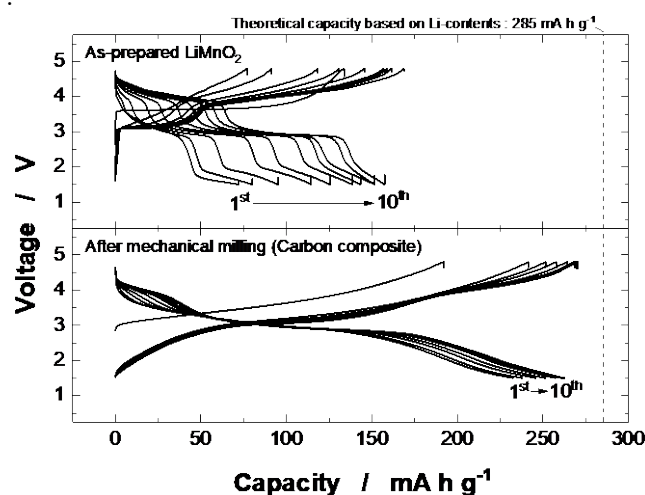


Fig. 1: Charge/discharge curves of LiMnO_2 with different crystal structures (top; zigzag-type and bottom rocksalt-type)

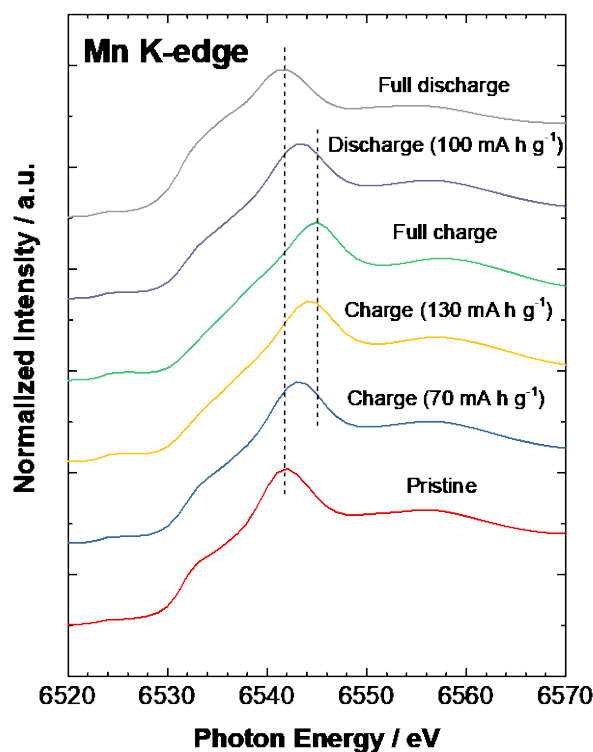


Fig. 2: X-ray absorption spectra at Mn K-edge observed for rocksalt LiMnO_2 on charge/discharge processes.