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, Li$_{1+x}$Mn$_{1-x}$Ti$_x$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

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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.