Neutron Powder Diffraction Study of Lithium Battery Electrode Materials with Tunnel Structure

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α-MnO2 has a hollandite type structure comprising double chains of MnO6 octahedra forming (2 × 2) tunnels. At present, only α-MnO2 is known to have a tunnel structure without any large stabilizing cations in its tunnel cavity, whereas the other porous manganese oxides, e.g., romanechite (2 × 3) and todorokite (3 × 3), contain some large stabilizing cations in their tunnels. The open-tunnel structure of α-MnO2 makes it attractive for an application as an electrode material for lithium-ion secondary batteries [1-3]. To clarify the structural properties of a Li inserted α-MnO2 specimen, neutron diffraction investigations have been made in this work.

An α-MnO2 specimen was prepared by the precipitation method using ozone oxidation [1,2]. A Li inserted α-MnO2 specimen was obtained by soaking the parent α-MnO2 powder in a mixed solution of LiOH and LiNO3 [2].

Neutron powder diffraction data were collected at room temperature on the HERMES powder diffractometer installed at the JRR-3M research reactor of the Japan Atomic Energy Agency. The specimens were contained in a cylindrical vanadium cell with an inner diameter of 10 mm. Incident neutrons with a fixed wavelength of 1.8204(5) angstroms were obtained by a vertically focusing (331) Ge monochromator. The powder diffraction data were measured over a 2 theta range of 7-157 degrees with a step interval of 0.1.

The diffraction data were analyzed by the Rietveld method with RIETAN-2000, and the nuclear scattering density distribution of specimens were visualized by the Maximum-entropy-method based Pattern Fitting (MPF).

Figure 1 depicts the Rietveld refinement patterns and the nuclear scattering density distribution images of Li inserted α-MnO2 specimen. These images clearly show the Li and O atoms in the tunnel space.

The Li inserted α-MnO2 specimen showed a good charge-discharge property as the cathode material, although the parent α-MnO2 specimen showed a poor discharge property [2]. These facts suggest that the presence of stabilizing atoms or molecules within the (2 × 2) tunnel of a hollandite-type structure is necessary to facilitate the diffusion of Li ions during cycling.

References

[1] N. Kijima et al., J. Solid State Chem. 177 (2004) 1258.
[2] N. Kijima et al., J. Solid State Chem. 178 (2005) 2741.
[3] N. Kijima et al., Solid State Ionics 180 (2009) 616.

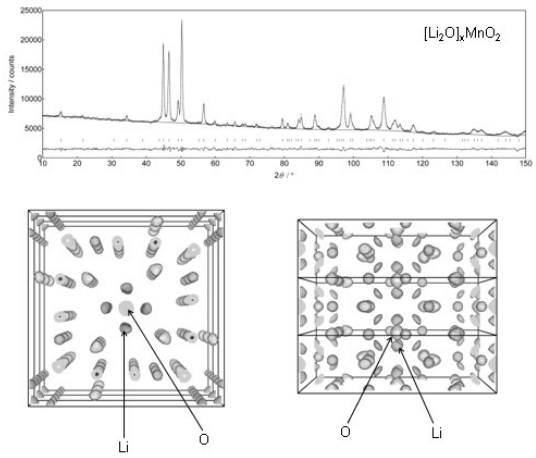

Fig. 1. Neutron powder diffraction patterns and nuclear scattering density distribution images of Li inserted α-MnO2 specimen.