

Lithium ion insertion and extraction reactions with Hollandite-type manganese dioxide free from any stabilizing cations in its tunnel cavity

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Abstract

Lithium ion insertion and extraction reactions with a hollandite-type α - MnO_2 specimen free from any stabilizing cations in its tunnel cavity were investigated, and the crystal structure of a Li^+ -inserted α - MnO_2 specimen was analyzed by Rietveld refinement and whole-pattern fitting based on the maximum-entropy method (MEM). The pH titration curve of the α - MnO_2 specimen displayed a monobasic acid behavior toward Li^+ , and an ion-exchange capacity of 3.25 meq/g was achieved at $\text{pH} > 11$. The Li/Mn molar ratio of the Li^+ -inserted α - MnO_2 specimen showed that about two Li^+ ions can be chemically inserted into one unit cell of the hollandite-type structure. As the amount of Li content was increased, the lattice parameter a increased while c hardly changed. On the other hand, the mean oxidation number of Mn decreased slightly regardless of Li content whenever ions were exchanged. The Li^+ -inserted α - MnO_2 specimen reduced topotactically in one phase when it was used as an active cathode material in a liquid organic electrolyte (1:1 EC:DMC, 1 mol/dm³ LiPF_6) lithium cell. An initial discharge with a capacity of approximately 230 mAh/g was achieved, and the reaction was reversible, whereas the capacity fell steadily upon cycling. About six Li^+ ions could be electrochemically inserted into one unit cell of the hollandite-type structure. By contrast, the parent α - MnO_2 specimen showed a poor discharge property although no cationic residues or residual H_2O molecules remained in the tunnel space. Rietveld refinement from X-ray powder diffraction data for a Li^+ -inserted specimen of $(\text{Li}_2\text{O})_{0.12}\text{MnO}_2$ showed it to have the hollandite-type structure (tetragonal; space group $I4/m$; $a = 9.993(11)$ and $c = 2.853(3)$ Å; $Z = 8$; $R_{\text{wp}} = 6.12\%$, $R_{\text{p}} = 4.51\%$, $R_{\text{B}} = 1.41\%$, and $R_{\text{F}} = 0.79\%$; $S = 1.69$). The electron-density distribution images in $(\text{Li}_2\text{O})_{0.12}\text{MnO}_2$ showed that Li_2O molecules almost fill the tunnel space. These findings suggest that the presence of stabilizing atoms or molecules within the tunnel of a hollandite-type structure is necessary to facilitate the diffusion of Li^+ ions during cycling.

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1. Introduction

Several manganese oxides with tunnel structures have been synthesized so far [1–5]. α - MnO_2 has a hollandite-type structure (space group $I4/m$, No. 87) comprising double chains of MnO_6 octahedra forming (2×2) tunnels, as shown in Fig. 1. At present, only α - MnO_2 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 - MnO_2 makes it attractive for various industrial applications such as an electrode material for lithium-ion secondary batteries [2,6–19] and an ion- or molecular-sieve [4,20–26].

Various methods have been used to prepare α - MnO_2 , with different influences on the properties of the products. Most α - MnO_2 samples include cationic

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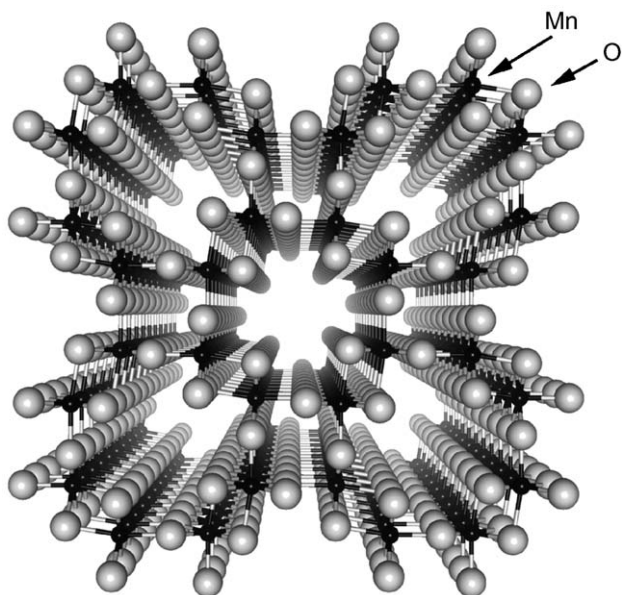


Fig. 1. Schematic drawing of the crystal structure of α - MnO_2 of a hollandite-type structure with space group of $I4/m$ (No. 87). The crystal structure is viewed along the c -axis.

residues such as Li^+ , K^+ , and Ba^{2+} ions in their tunnels because precursors containing such cations are usually used in their synthesis. These residual cations would impede the diffusion of Li^+ ions in the tunnels during electrochemical operation and also reduce the material's ion-exchange capacity. Presumably, if an α - MnO_2 specimen free from any cationic residues could be synthesized, its properties would be improved significantly.

We have recently succeeded in synthesizing a high-purity and well-crystallized specimen of α - MnO_2 free from any stabilizing cations in its tunnel cavity by a precipitation method using ozone oxidation [27,28]. Using our synthetic method, α - MnO_2 can directly be formed in solutions containing no cations other than Mn^{2+} . Therefore, a high-purity specimen free from any cationic residues in the tunnels can be obtained.

In this work, we investigated ion-exchange and electrochemical properties of the α - MnO_2 specimen free from stabilizing cations in its tunnel cavity. To clarify the structural properties of a Li^+ -inserted α - MnO_2 specimen, we also refined its structure parameters by Rietveld analysis from X-ray powder diffraction data. Furthermore, we visualized electron-density distribution (EDD) in the Li^+ -inserted α - MnO_2 specimen by whole-pattern fitting (w.p.f.) based on the maximum-entropy method (MEM) [29–31]. EDD determined in this way is expected to provide valuable information on the residual atoms or molecules in the tunnel cavity.

Contrary to our expectation, the parent α - MnO_2 specimen showed a poor discharge property although no

cationic residues and residual H_2O molecules remained in the tunnel space. In contrast, the Li^+ -inserted α - MnO_2 specimen exhibited a good charge–discharge property as the cathode. The EDD images in the Li^+ -inserted specimen showed that Li_2O molecules occupy the tunnel space almost entirely. These facts suggest that the presence of stabilizing atoms or molecules within the (2×2) tunnel of the hollandite-type structure is necessary to facilitate the diffusion of Li^+ ions during cycling. We discuss here both electrochemical and chemical lithium ion insertion/extraction reactions with hollandite-type MnO_2 (HMO).

2. Experimental

2.1. Sample preparation

An α - MnO_2 specimen was prepared by the precipitation method using ozone oxidation [27,28]. Scanning electron microscopy (SEM) images of the α - MnO_2 specimen showed that the surfaces of particles were covered almost uniformly with needle-like crystals, which were elongated parallelly to the c -axis, i.e., along the direction of the tunnel (Fig. 2). Details of the preparation and characterization of α - MnO_2 have been reported in previous works [27,28].

A Li^+ -inserted α - MnO_2 specimen was obtained by soaking the parent α - MnO_2 powder in a mixed solution of 0.1 mol/dm^3 LiOH and 0.1 mol/dm^3 LiNO_3 at a 1:1 volumetric ratio. Five grams of the α - MnO_2 powder was immersed in 500 cm^3 of this mixed solution. After 20 d, the ion-exchanged specimen was filtered off without washing with water, and then dried in a desiccator for 1 d. A Li^+ -extracted α - MnO_2 specimen was prepared by immersing the Li^+ -inserted α - MnO_2 specimen in a mixed solution of 0.1 mol/dm^3 HNO_3 and 0.1 mol/dm^3 LiNO_3 .

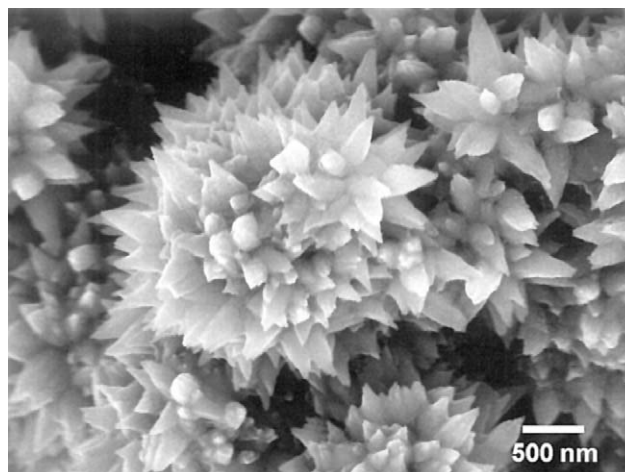


Fig. 2. Scanning electron microscopy image of an α - MnO_2 specimen.

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