

Synthesis and Electrochemical Studies of Hollandite-type Manganese Dioxide Free from Any Stabilizing Cations in Its Tunnel Cavity

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An open-tunnel oxide, α -MnO₂, with a hollandite-type structure (Fig. 1) is an attractive material for a cathode for rechargeable lithium-ion batteries [1]. At present, only α -MnO₂ is known to have a tunnel structure without any stabilizing cations in its tunnel cavity, whereas the other porous manganese oxides, e.g., romanechite and todorokite, contain some large stabilizing cations in their tunnels. These stabilizing cations impede the diffusion of Li⁺ ions in their tunnels during electrochemical operation. α -MnO₂ would show higher rechargeable capacity and better rechargeability if the specimen without any cationic residues in its tunnel cavity can be synthesized.

We have recently succeeded in synthesizing a high-purity and well-crystallized specimen of α -MnO₂ free from any stabilizing cations in its tunnel cavity by a precipitation method using ozone oxidation [2,3]. Three kinds of acid, a wide variety of their concentration, and ozone-oxidation temperature were tested to produce α -MnO₂. The ozone-oxidation of Mn²⁺ in H₂SO₄ alone provided α -MnO₂, while γ -MnO₂ was always formed in HNO₃ or HCl. Higher reaction temperatures (>70 °C) and higher concentrations of H₂SO₄ (>2 mol/dm³) were necessary for the α -MnO₂ formation. Scanning electron microscopy (SEM) image of the product showed that surfaces of particles were covered almost uniformly with needle-like crystals which were elongated parallel to the c-axis, i.e., along the direction of the tunnel (Fig. 2).

A preliminary electrochemical study of our product was carried out. Lithium ion-exchanged α -MnO₂ showed a good charge-discharge property as the cathode (Fig. 3). All Li⁺ ions inserted in the tunnels were extracted at the initial charge, and the first discharge capacity reached about 250 mAh/g in the voltage range of 4.8–1.0 V. This discharge capacity shows that about 6 Li⁺ ions can be inserted into one unit cell of the hollandite structure. X-ray diffraction study indicated that there is no damage on the hollandite structure after charge-discharge cycling test. A more detailed electrochemical study is currently being carried out.

References:

- [1] C. S. Johnson et al, J. Power Sources **97-98**, 437 (2001) and references therein.
- [2] N. Kijima et al, J. Solid State Chem. **159**, 94 (2001).
- [3] N. Kijima et al, J. Solid State Chem. **177**, 1258 (2004).

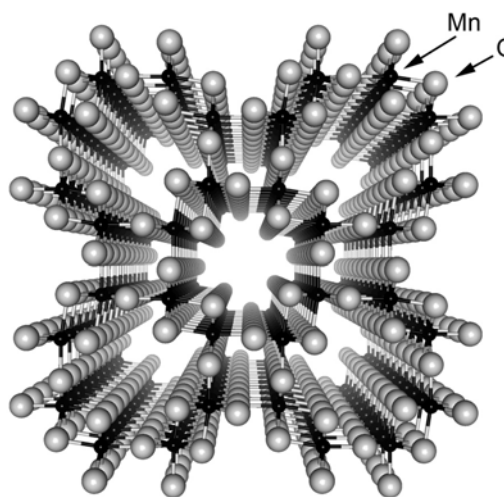


Fig. 1. Crystal structure of α -MnO₂ of a hollandite-type structure with space group of $I4/m$ (No. 87).

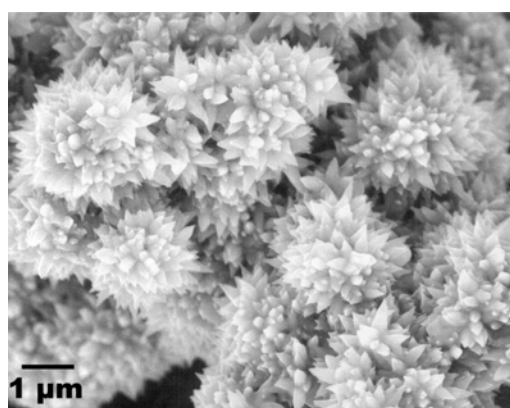


Fig. 2. SEM image of α -MnO₂ product. The specimen is precipitated by ozone-oxidation of MnSO₄ dissolved in 3 mol/dm³ H₂SO₄ for 3 h at 80 °C.

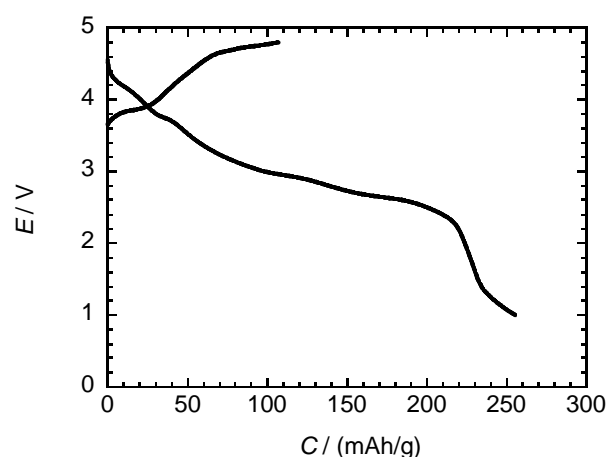


Fig. 3. First charge-discharge curves of Li/Li_xMnO₂ cell with a current density of 10 mA/g.