

XAFS Analysis of Lithium Battery Electrode Materials with Tunnel Structure

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Introduction

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., romanachite (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 lithium ion insertion mechanism for the α -MnO₂, X-ray absorption fine structure (XAFS) studies have been made.

Experimental

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].

Electrochemical measurements were carried out using lithium cells. The working electrode consisted of 80 wt% α -MnO₂ specimen, 15wt% acetylene black, and 5 wt% polytetrafluoroethylene powders. The counter electrode was Li foil, and the separator was a microporous polypropylene sheet. The electrolyte was a 1 mol/dm³ solution of LiPF₆ in blended ethylene carbonate and dimethyl carbonate. The cells were constructed in a stainless-steel test cell. Charge-discharge cycles were performed with a potentiostat/galvanostat.

Mn K-edge XAFS of electrodes was measured by transmission mode using synchrotron radiation at beam line BL-9A of Photon Factory. The REX2000 computer program was used for the analysis of the XAFS data.

Results and Discussion

Figure 1 shows the discharge-charge curves for the Li⁺-inserted α -MnO₂ specimen over the first 10 cycles. The Li⁺-inserted α -MnO₂ specimen reduced topotactically in one phase. An initial discharge with a capacity of approximately 230 mAh/g was achieved, and this discharge capacity showed that about six Li⁺ ions could be inserted into one unit cell of the hollandite-type structure.

Figure 2 demonstrates Mn K-edge X-ray absorption near-edge structure (XANES) spectra of the the Li⁺-inserted α -MnO₂ electrodes. Evidence of reduction to lower valent Mn ions after discharge was detected by these XANES spectra. Valence of Mn at 2 V is above 3+ because the chemical shift of the electrode was between those of MnO₂ and Mn₂O₃.

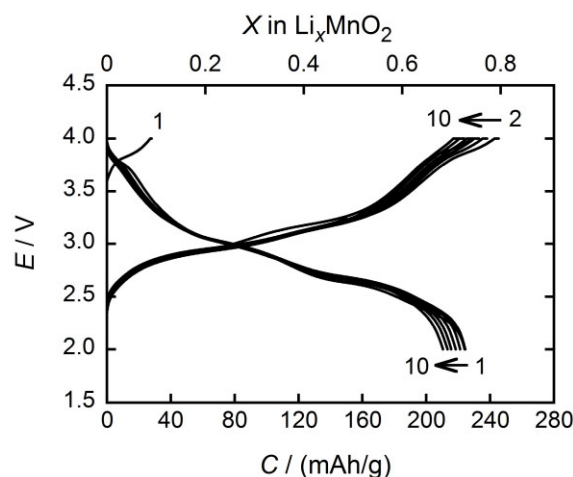


Fig. 1 Charge-discharge curves for Li⁺-inserted α -MnO₂ specimen with a current rate of 10 mA/g.

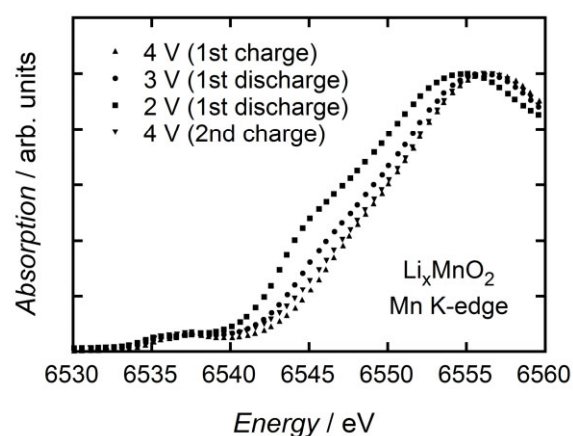


Fig. 2 Mn K-edge XANES spectra of the Li⁺-inserted α -MnO₂ electrodes.

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.

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