

XAFS Analysis of Lithium Battery Electrode Materials with Tunnel Structure

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Introduction

A great deal of research into the application of α -MnO₂ as an electrode material for lithium-ion batteries has been conducted because α -MnO₂ has large (2×2) tunnels presenting a privileged pathway for Li ion diffusion [1-3]. The α -MnO₂ electrode can be intercalated in lithium cells at about 3 V, and the initial discharge capacity exceeds 200 mAh/g. The chemical and electrochemical lithium ion insertion mechanisms for the α -MnO₂ has been the subject of controversy [2, 3]. To clarify the lithium ion insertion mechanism for the α -MnO₂, X-ray absorption fine structure (XAFS) studies have been made.

Experimental

A well-crystallized α -MnO₂ specimen was prepared by oxidation of MnSO₄ with ozone gas in H₂SO₄ solution at 353 K [1]. A Li⁺-inserted α -MnO₂ specimen was obtained by soaking the parent α -MnO₂ powder in a mixed solution of 0.1 mol/dm³ LiOH and 0.1 mol/dm³ LiNO₃ [2].

Mn K-edge XAFS of both parent α -MnO₂ and Li⁺-inserted α -MnO₂ specimens was measured by transmission mode using synchrotron radiation at beam line BL-9A of Photon Factory. The samples were pelletized with an appropriate amount of BN binder. The REX2000 computer program was used for the analysis of the XAFS data.

Results and Discussion

Figure 1 shows Mn K-edge X-ray absorption near-edge structure (XANES) spectra of the parent α -MnO₂ and Li⁺-inserted α -MnO₂ specimens. No evidence of reduction to lower valent Mn ions was detected by these XANES spectra. This finding shows that no redox process is associated with the chemical lithium ion insertion.

We previously reported a neutron diffraction study of the parent α -MnO₂ specimen [1]. There was no possibility of the existence of Mn³⁺ ions and Mn vacancies in our specimen, and an attempt to determine the position of the proton site responsible for ion-exchange was unsuccessful.

The electron-density distribution (EDD) images show that our parent α -MnO₂ specimen has residual H₂O molecules in the tunnel space [1]. On the other hand, the EDD images of the Li⁺-inserted α -MnO₂ specimen demonstrate that Li₂O molecules exist in the tunnel space [2], as Fig. 2 depicts.

Although small amounts of Mn³⁺ ions and Mn defects would be generated by the lithium ion insertion, most H₂O molecules in the tunnel space seem to be simply replaced by Li₂O molecules. The Li₂O molecules might

be inserted by other mechanisms besides the redox and ion-exchange reactions.

The prelithiated α -MnO₂ specimen has a high initial discharge capacity of approximately 230 mAh/g, although the dehydrated α -MnO₂ specimen with empty tunnels shows a poor discharge property [2]. XAFS investigations of electrochemical Li⁺-inserted α -MnO₂ specimens are in progress.

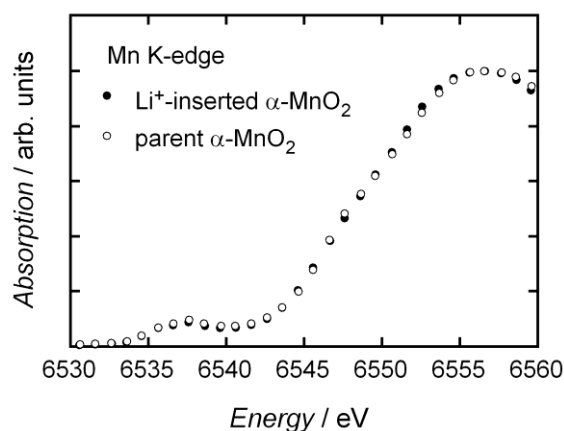


Fig. 1 Mn K-edge XANES spectra of the parent α -MnO₂ and Li⁺-inserted α -MnO₂ specimens.

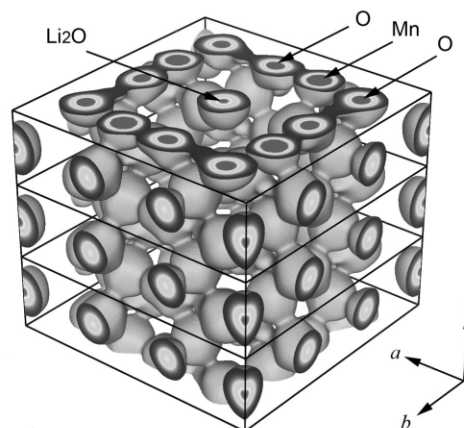


Fig. 2 EDD image of Li⁺-inserted α -MnO₂ specimen. The equi-density level was 0.4 /Å and the solid boxes indicate the unit cells.

References

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