

X-ray absorption fine structure study on Li–Mn–O compounds: LiMn₂O₄, Li₄Mn₅O₁₂ and Li₂MnO₃

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Abstract

The lithium manganese oxide spinel LiMn₂O₄ obtained at different preparation temperatures shows different discharge characteristics. In order to study the difference between the discharge curves of HT-LiMn₂O₄ (HT: high temperature) and LT-LiMn₂O₄ (LT: low temperature), we have analyzed the XAFS (X-ray absorption fine structure) of synthesized LiMn₂O₄ and the products formed from an electrochemical oxidation–reduction process. It was found that, on discharge, the energy shifts of the edge of the X-ray absorption near edge structure (XANES) spectra were different between HT-LiMn₂O₄ and LT-LiMn₂O₄ and were not directly proportional to the discharge capacity. Moreover, the change in the Mn–Mn bond length of HT-LiMn₂O₄ with discharge was greater than that of LT-LiMn₂O₄. © 1997 Published by Elsevier Science S.A.

Keywords: Secondary lithium batteries; Lithium manganese oxide, Spinel structure; X-ray absorption fine structure

1. Introduction

The lithium manganese oxide spinel LiMn₂O₄ has been studied extensively as a promising cathode intercalation material for secondary lithium battery [1]. LiMn₂O₄ prepared at different temperatures has different discharge characteristics. Fig. 1. When LiMn₂O₄ was prepared at a high temperature, LiMn₂O₄ was discharged at about 4 V versus lithium, whereas when LiMn₂O₄ was prepared at a low temperature, a capacity loss occurred around 4 V.

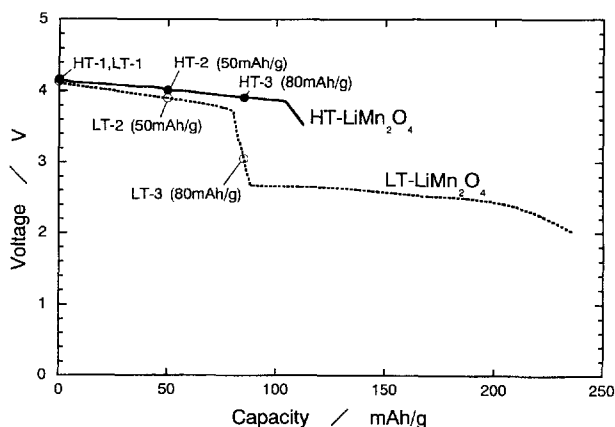


Fig. 1 Discharge curves of HT-LiMn₂O₄ and LT-LiMn₂O₄ in 1 M LiPF₆/EC-DEC.

In order to study the difference between the discharge curves for HT-LiMn₂O₄ and LT-LiMn₂O₄, we analyzed the X-ray absorption fine structure (XAFS) spectra of the synthesized LiMn₂O₄ and the products formed from an electrochemical oxidation–reduction process. Using XAFS measurements, we can obtain information about the absorber–scatterer distance of the specimens.

We analyzed also the XAFS of Li₄Mn₅O₁₂ with a spinel structure and Li₂MnO₃ with a rock-salt structure since these have different Mn oxidation states. Li₂MnO₃ was also investigated.

2. Experimental

Starting materials and heating temperatures for preparing LiMn₂O₄ [2], Li₄Mn₅O₁₂ and Li₂MnO₃ are listed in Table 1.

The discharge of the specimen was performed using a coin-type cell at a current of 3.75 mA/g at room temperature. Metallic lithium was used as the anode, and 1 M LiPF₆ in ethylene carbonate–diethyl carbonate (EC–DEC) was used as the electrolyte. Several Li_xMn₂O₄ specimens having different *x* values were prepared using the electrochemical method as shown in Table 2. For obtaining the HT-1 and LT-1 specimens, the prepared HT-LiMn₂O₄ and LT-LiMn₂O₄ were charged at a current of 3.75 mA/g up to 4.3 V. The

Table 1
Starting materials and heating temperatures for LiMn_2O_4 , $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and Li_2MnO_3

	Li source	Mn source	Heating temperature ($^{\circ}\text{C}$)
HT- LiMn_2O_4 ^a	$\text{LiOH} \cdot \text{H}_2\text{O}$	$\gamma\text{-MnOOH}$	750
LT- LiMn_2O_4 ^b	$\text{LiOH} \cdot \text{H}_2\text{O}$	$\gamma\text{-MnOOH}$	350
$\text{Li}_4\text{Mn}_5\text{O}_{12}$	$\text{LiOH} \cdot \text{H}_2\text{O}$	$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	500
Li_2MnO_3	Li_2CO_3	MnCO_3	850

^a HT high temperature.

^b LT low temperature.

Table 2
Preparation of several $\text{Li}_x\text{Mn}_2\text{O}_4$ specimens with different x values by an electrochemical method

Specimen	Charge capacity (mAh/g)	Discharge capacity (mAh/g)	x in $\text{Li}_x\text{Mn}_2\text{O}_4$
HT-1	104	0	0.30
LT-1	104	0	0.30
HT-2	106	50	0.62
LT-2	100	50	0.66
HT-3	108	80	0.81
LT-3	102	80	0.85

charge electricity corresponds to the composition of $\text{Li}_{0.30}\text{Mn}_2\text{O}_4$. For obtaining the HT-2 and LT-2 specimens, the HT- LiMn_2O_4 and LT- LiMn_2O_4 specimens were charged up to 4.3 V and then discharged up to 50 mAh/g, corresponding to the composition of $x = 0.62$ – 0.66 . Moreover, for obtaining the HT-3 and LT-3 specimens, the HT- LiMn_2O_4 and LT- LiMn_2O_4 specimens were charged up to 4.3 V and then discharged up to 80 mAh/g, corresponding to $x = 0.81$ – 0.85 .

The change in the a -axis length of the crystal structure during discharge was examined by X-ray diffraction (XRD) at room temperature. The results nearly coincides with the result reported by Ohzuku et al. [3].

The Mn K -edge X-ray absorption spectra in transmission were obtained at BL7C of the Photon Factory in the National Laboratory for High Energy Physics, Japan. The phase shift and back-scattering amplitude values used for the Fourier-transform calculation were taken from the tables reported by Teo and Lee [4], and McKale et al. [5].

3. Results and discussion

3.1. XANES

The calculated oxidation states of Mn ions for HT- LiMn_2O_4 , LT- LiMn_2O_4 , $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and Li_2MnO_3 are 3.5, 3.5, 4.0 and 4.0, respectively.

The normalized XANES spectra of HT- LiMn_2O_4 , LT- LiMn_2O_4 , $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and Li_2MnO_3 are shown in Fig. 2. The

edge energies of the Mn K -edge are in the order HT- $\text{LiMn}_2\text{O}_4 < \text{LT-}\text{LiMn}_2\text{O}_4 < \text{Li}_4\text{Mn}_5\text{O}_{12} < \text{Li}_2\text{MnO}_3$.

The normalized XANES spectra profile of LiMn_2O_4 is similar to that of $\text{Li}_4\text{Mn}_5\text{O}_{12}$. But the normalized XANES spectra profile of Li_2MnO_3 is not similar to that of LiMn_2O_4 . The normalized XANES spectra profile is presumably affected by the structure factor.

The normalized XANES spectra of HT-1, HT-2, HT-3, HT- LiMn_2O_4 , LT-1, LT-2, LT-3 and LT- LiMn_2O_4 are shown in Figs. 3 and 4. The edge energies of the Mn K -edge are in the order HT- $\text{LiMn}_2\text{O}_4 < \text{HT-3} < \text{HT-2} < \text{HT-1}$ and LT- $\text{LiMn}_2\text{O}_4 < \text{LT-3} < \text{LT-2} < \text{LT-1}$. The order of the edge energies of the Mn K -edge indicates that the oxidation state of Mn decreases with discharge. The edge-energy shift of the XANES spectra are not directly proportional to the discharge

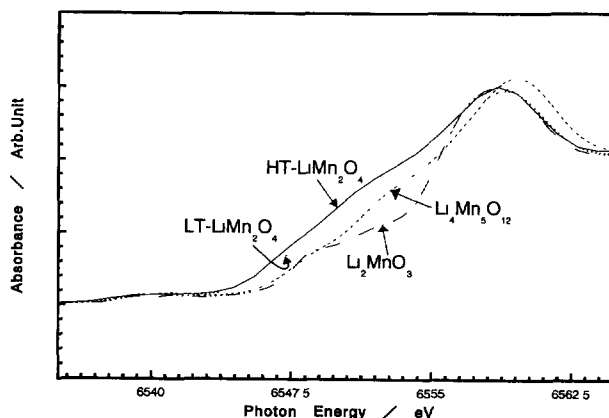


Fig. 2. The normalized XANES spectra of Li-Mn-O compounds

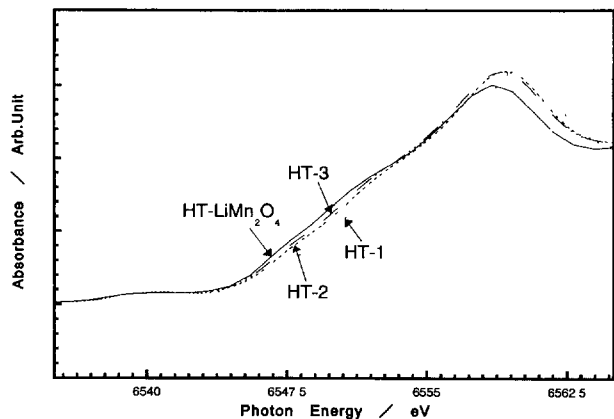


Fig. 3. The normalized XANES spectra of HT-1, HT-2, HT-3 and HT-LiMn₂O₄.

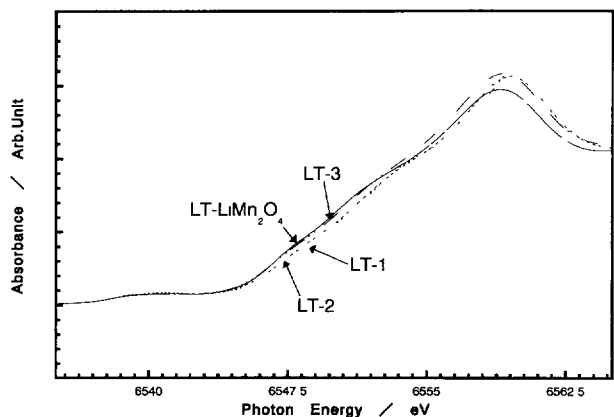


Fig. 4. The normalized XANES spectra of LT-1, LT-2, LT-3 and LT-LiMn₂O₄.

capacity. Meanwhile, we clearly observed the difference between the edge-energy shifts of the XANES spectra for the HT-LiMn₂O₄ and LT-LiMn₂O₄.

3.2. EXAFS

We analyzed the EXAFS spectra of HT-LiMn₂O₄ and LT-LiMn₂O₄ and calculated the bond lengths of Mn–O and Mn–Mn. In comparison with Li₄Mn₅O₁₂, the higher oxidation states of Mn shorten the Mn–Mn bond length.

The bond lengths of Mn–O and Mn–Mn calculated by Fourier filtering and curve fitting are shown in Figs. 5 and 6. The bond lengths of Mn–O and Mn–Mn in the HT- and LT-compounds increase on discharge. The change in bond length for Mn–Mn is greater than that for Mn–O. The change in bond length for Mn–Mn is greater for HT than LT.

Concerning the fact that, on discharge, the edge-energy shift in the XANES spectra was not directly proportional to the discharge capacity, and the Mn–Mn bond-length change for HT-compounds was greater than that for LT-compounds,

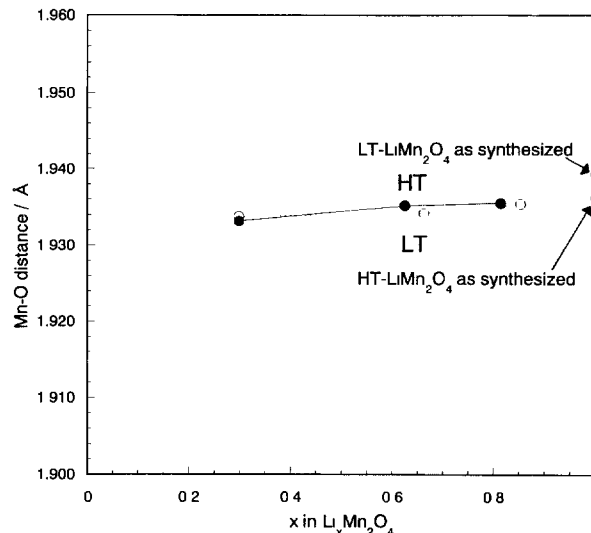


Fig. 5. Change in Mn–O distance and *x* value in Li_{*x*}Mn₂O₄.

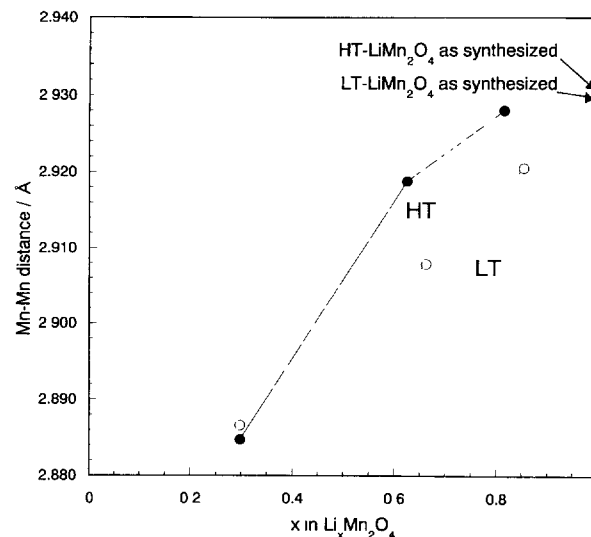


Fig. 6. Change in Mn–Mn distance and *x* value in Li_{*x*}Mn₂O₄.

it is presumed that, on discharge, the edge-energy shift in the XANES spectra is affected by the discharge capacity, but the relationship between the edge-energy shift and discharge capacity is presumably affected by other factors, such as structure factors.

In order to clarify the relationship between the edge-energy shift and the discharge capacity, further work is needed.

4. Conclusions

It was found that, on discharge, the edge energy shift of the XANES spectra was different for the HT- and LT-compounds and was not directly proportional to the discharge capacity. Moreover, the change in the Mn–Mn bond length

for the HT-compounds was greater than that for the LT-compounds.

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