LETTER TO THE EDITOR

X-ray Absorption Studies in Spinel-Type LiMn$_2$O$_4$

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The electronic structure of the spinel-type LiMn$_2$O$_4$ as the cathode material for the application in secondary batteries was probed using both Mn K- and L$_{23}$-edge X-ray absorption near edge structure (XANES) spectra. Based on the energy shifts of the absorption peaks in the XANES spectrum correlated to the effective charge, the valence of Mn in LiMn$_2$O$_4$ was determined to be ~4+. This suggests that the chemical substitution of low valent Li$^+$ ions into the Mn sites is possible to result in high valence of Mn.

1. INTRODUCTION

The LiMn$_2$O$_4$ compound with a spinel-type structure is of interest as a cathode material for rechargeable (secondary) lithium battery applications (1–3). The use of the LiMn$_2$O$_4$ compound as compared to LiCoO$_2$ and LiNiO$_2$ offers the following advantages: (a) Mn is naturally more abundant and cheaper than Co and Ni; and (b) the LiMn$_2$O$_4$ compound shows the low toxicity. Therefore, the LiMn$_2$O$_4$ compound is one of the most promising materials as 3–4 V vs Li/Li$^+$ cathodes for rechargeable lithium batteries. A more advanced design for rechargeable Li batteries is to replace Li metal with a material able to reversibly intercalate Li ions. This has been called the “rocking-chair” battery because Li ions rock back and forth between the intercalation compounds during charge/discharge cycles. However, the deintercalation/intercalation of lithium from/into cathodes of secondary batteries strongly depends on the properties of the hosts of transition-metal elements. Lithium insertion onto Li[Mn$_2$]O$_4$ causes a displacement of the Li$^+$ ions from the 8a (tetrahedral sites) positions onto neighboring interstitial 16c octahedral sites to yield Li$_2$[Mn$_2$]O$_4$ after the insertion of one lithium per spinel unit (4,5). Lithium extraction from Li[Mn$_2$]O$_4$ produces the defect spinel $\lambda$-MnO$_2$ (6). Normally, the valence of Mn in the as-prepared LiMn$_2$O$_4$ materials is recognized to be 3.5+ based on the neutral charge of the compound (7). However, the creation of lithium and manganese vacancies or the substitution of lithium for manganese LiMn$_2$O$_4$ is naturally accompanied by a change of the average oxidation state of manganese. It has been shown that the effective magnetic moment and the electrochemical properties for lithium manganospinels is corrected with the average valence of Mn (7). Therefore, the determination of the Mn valence in the as-prepared cathode material LiMn$_2$O$_4$ becomes important which may give rise to understand the behavior of deintercalation/intercalation of Li ions.

Using advanced synchrotron radiation X-ray sources has promoted a great deal of research in the study of X-ray absorption near edge structures (XANES) spectra of materials (8). The precise knowledge of the lithium manganospinels material is of particular importance for a comprehensive understanding of their electrochemical properties in a lithium battery system. In this work, we have studied the XANES of LiMn$_2$O$_4$ to understand the electronic structure and the valence of Mn ions octahedrally coordinated by oxygens. The measurement of the Mn magnetic moment in the resulting material is a common method in order to determine the valence of Mn ions. Here, we demonstrate a nondestructive method to determine the valence of Mn in LiMn$_2$O$_4$ by using the techniques of Mn L$_{23}$- and K-edge X-ray absorption near edge structure.

2. EXPERIMENTAL

High-purity powders of Li$_2$CO$_3$ and MnO$_2$ were weighed in appropriate proportions to constitute the nominal composition of LiMn$_2$O$_4$. The mixed powders were then sintered at 800°C for 24 h in air. X-ray diffraction analyses carried out with a SCINTAG (XGEN-4000) diffractometer (CuK$\alpha$ radiation) show that the material crystallizes as a pure phase. The LiMn$_2$O$_4$ compound has a spinel-based
crystal structure with a tetragonal unit cell (space group: \textit{Fd3m}) and lattice parameter $a = 8.268(1)$ Å.

X-ray absorption measurements were carried out at the Synchrotron Radiation Research Center (SRRC) on the HSGM beamline for the Mn L-edge measurements, and on the S-05B/W20 X-ray wiggler beamline for the Mn K-edge measurements. Absorption spectra were obtained using transmission mode detection for the Mn K-edge measurements and total electron yield detection for the Mn L-edge measurements.

3. RESULTS AND DISCUSSION

In general, XANES spectra of compounds can be divided into two regions. The absorption features $\sim 10$ eV below the core-level ionization threshold are attributed to transitions from core electrons into unoccupied bound states as well as maxima in the density of states in the conduction band. Absorption features up to $\sim 40$ eV above the ionization threshold are referred to as shape resonance. The sudden enhancement in the X-ray absorption spectrum was ascribed to electronic excitation into quasibound unoccupied orbitals supported by a centrifugal barrier or a ligand induced potential barrier (8, 9). Many recent studies show that multiple scattering of photoelectrons by neighboring atoms is essential for interpreting the higher-energy structure in the XANES spectrum (8, 10–12). The structure of XANES is used as a fingerprint of the local environment of an atom.

The XANES spectra of compounds are sensitive to the local symmetry, oxidation state, and electronic structure of the absorbing atom in compounds (8, 12). Therefore, X-ray absorption measurements provide a tool for the determination of metal oxidation states in solids. The technique utilizes discriminating changes in the absorption peaks of an ion in a solid with respect to standard compounds with known oxidation states of that ion. In particular, the chemical shift in the absorption spectra has been applied to determine the site-selective valency of transition-metal compounds (13). In Fig. 1, the Mn L-edge X-ray absorption spectrum of LiMn$_2$O$_4$ is shown together with MnO$_2$ (Mn$^{4+}$) and Mn$_2$O$_3$ (Mn$^{3+}$) standard compounds in the energy range of 635–665 eV. The spectra correspond to Mn$2p^63d^\pi$ $\rightarrow$ Mn$2p^53d^{\pi+1}$ transitions and present two groups of multiplets separated by the spin–orbit interaction of the Mn 2p core hole. The change in spectral shape of the multiplet structure in Fig. 1 is attributed to the variation in symmetry of the ground state (14). In addition, as the oxidation state of Mn increases, the Mn L$_1$ absorption edge shifts to higher energy, from $\sim 642.3$ eV in Mn$_2$O$_3$ to $\sim 643.4$ eV in MnO$_3$. The chemical shift arises from the changes in the atomic valency at the Mn site in compounds. It has been experimentally shown that the energy shift in the X-ray absorption spectrum of the first unoccupied excited state is corrected with the effective atomic charge on the absorbing atoms (8, 12). We have recently been successful in applying this technique to characterize the Mn valence in the (Nd$_{1-x}$Ca$_x$)MnO$_3$ system (15). As shown, the main peak position of the Mn L$_3$-edge in LiMn$_2$O$_4$, as marked by arrows, is close to that in MnO$_2$ with Mn$^{4+}$ in octahedral symmetry. As deduced from Fig. 1, the average Mn valence in LiMn$_2$O$_4$ is $\sim 4$.

![FIG. 1. The Mn L-edge X-ray absorption spectra of LiMn$_2$O$_4$, MnO$_2$ (Mn$^{4+}$), and Mn$_2$O$_3$(Mn$^{3+}$).](image)

In Fig. 2, we present the Mn K-edge X-ray absorption spectrum of LiMn$_2$O$_4$ in comparison with MnO$_2$ (Mn$^{4+}$) and Mn$_2$O$_3$ (Mn$^{3+}$) standards. Figure 3 displays the first derivative of the X-ray absorption spectra corresponding to Fig. 2. Based on the calculations of the molecular excited states of (FeO$_6$)$^{10-}$ by Tossel et al. (16) and the experimental results of MnO$_2$ and Mn$_2$O$_3$ by Belli et al. (17), the peaks $A_1$ and $A_2$ in LiMn$_2$O$_4$, MnO$_2$ and Mn$_2$O$_3$ are ascribed to transitions into the final states of the $t_{2g}$ and $e_g$ symmetries, respectively. The intensities of the $A_1$ and $A_2$ peaks are weak because they are due to the $1s \rightarrow 3d$ quadrupolar transitions. The shoulder B is assigned to excitation from Mn 1s to a $p$-like state of $t_{2g}$ symmetry. There exist two different Mn sites in the spinel structure in LiMn$_2$O$_4$ and Mn$_2$O$_3$, resulting in two different absorption peaks, B$_1$ and B$_2$ (17). The peak C may be due to a “shape resonance” in the continuum part of the spectrum. The
FIG. 2. The Mn K-edge X-ray absorption spectra of LiMn$_2$O$_4$, MnO$_2$ (Mn$^{4+}$), and Mn$_2$O$_3$ (Mn$^{3+}$).

separation between the peak B and the peak C is known to depend upon site symmetry and interatomic distances. The peaks D$_1$ and D$_2$ may arise from multiple scattering resonance of photoelectrons by neighboring atoms and are sensitive to the second shell effects.

The inset of Fig. 3 is the plot of the energy position of the peak A$_1$ in MnO$_2$ (Mn$^{4+}$), Mn$_2$O$_3$ (Mn$^{3+}$), and LiMn$_2$O$_4$ as a function of the formal valence of Mn ion. As was shown, the average Mn valence in LiMn$_2$O$_4$ is $\sim 4+$. It is consistent with the result as determined by the Mn 2$p$-edge X-ray absorption spectra. The reason that the valence of Mn increases from 3.5+ (based on the neutral charge of the LiMn$_2$O$_4$ compound) to 4.0+ may be that the low valent Li$^+$ ions substitute into the Mn sites in LiMn$_2$O$_4$. Based on the neutron diffraction studies, Thackeray et al. (18) have confirmed that around 15% Li ions can substitute into the Mn sites in the lithium manganese oxides with nominal composition LiMn$_2$O$_4$.

In this study, we report the detailed electronic structure of the spinel-type LiMn$_2$O$_4$ compound probed by the XANES technique. Using the Mn $L_{2,3}$ and K-edge XANES spectra, we deduced the Mn valence in LiMn$_2$O$_4$. This method will help to distinguish charge variations in complex systems where calculations are difficult or nearly impossible. Based on the XANES studies, we have found the valence of Mn to be $\sim 4+$ in LiMn$_2$O$_4$. This suggests that chemical substitution of Li$^+$ ions into the Mn sites is an effective route to achieving a high valence of Mn in as-prepared LiMn$_2$O$_4$ samples.

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REFERENCES