LETTER TO THE EDITOR

X-ray Absorption Studies in Spinel-Type $LiMn_2O_4$

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The electronic structure of the spinel-type $LiMn_2O_4$ 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 $LiMn_2O_4$ was determined to be $\sim 4+$. This suggests that the chemical substitution of low valent Li^+ ions into the Mn sites is possible to result in high valence of Mn. © 1997 Academic Press

1. INTRODUCTION

The $LiMn_2O_4$ 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 $LiMn_2O_4$ material 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 $LiMn_2O_4$ compound shows the low toxicity. Therefore, the $LiMn_2O_4$ 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 λ-MnO_2 (6). Normally, the valence of Mn

in the as-prepared $LiMn_2O_4$ 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 $LiMn_2O_4$ 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 $LiMn_2O_4$ 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 manganospinel materials 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 $LiMn_2O_4$ 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 $LiMn_2O_4$ by using the techniques of Mn L_{23}- and K-edge X-ray absorption near edge structure.

2. EXPERIMENTAL

High purity powders of Li_2CO_3 and MnO_2 were weighed in appropriate proportions to constitute the nominal composition of $LiMn_2O_4$. 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 $LiMn_2O_4$ compound has a spinel-based

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crystal structure with a tetragonal unit cell (space group: $Fd3m$) 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 ~ 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 ~ 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 $LiMn_2O_4$ is shown together with MnO_2 (Mn^{4+}) and Mn_2O_3 (Mn^{3+}) standard compounds in the energy range of 635–665 eV. The spectra correspond to $Mn2p^63d^n \rightarrow Mn2p^53d^{n+1}$ 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_3 absorption edge shifts to higher energy, from ~ 642.3 eV in Mn_2O_3 to ~ 643.4 eV in MnO_2. 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
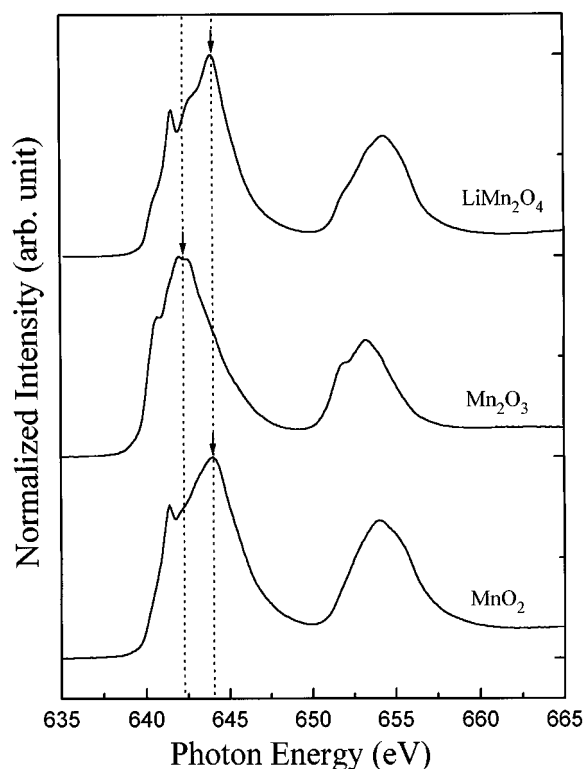

FIG. 1. The Mn L-edge X-ray absorption spectra of $LiMn_2O_4$, MnO_2 (Mn^{4+}), and Mn_2O_3(Mn^{3+}).

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 $LiMn_2O_4$, 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 $LiMn_2O_4$ is ~ 4.

In Fig. 2, we present the Mn K-edge X-ray absorption spectrum of $LiMn_2O_4$ in comparison with MnO_2 (Mn^{4+}) and Mn_2O_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_2O_3 by Belli *et al.* (17), the peaks A_1 and A_2 in $LiMn_2O_4$, MnO_2 and Mn_2O_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_{1u} symmetry. There exist two different Mn sites in the spinel structure in $LiMn_2O_4$ and Mn_2O_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
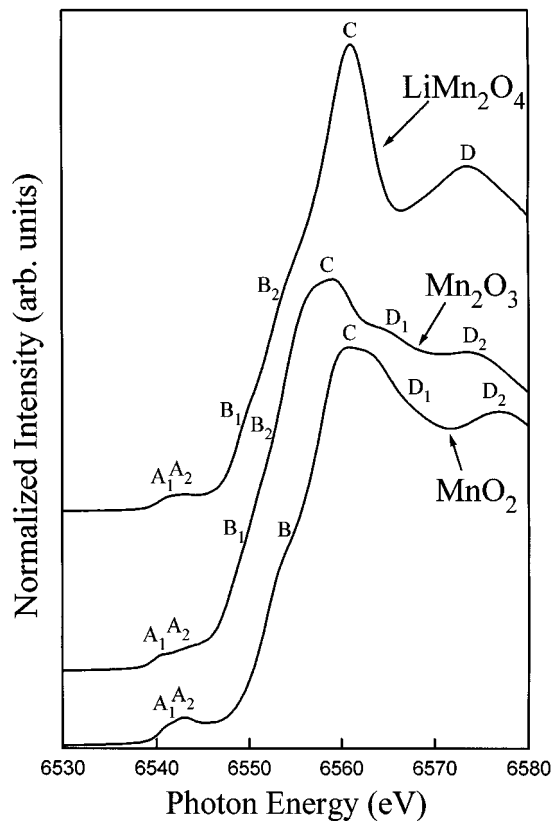
FIG. 2. The Mn K-edge X-ray absorption spectra of $LiMn_2O_4$, MnO_2 (Mn^{4+}), and Mn_2O_3 (Mn^{3+}).

FIG. 3. The first derivative of Mn K-edge X-ray absorption spectra of $LiMn_2O_4$, MnO_2 (Mn^{4+}), and Mn_2O_3 (Mn^{3+}). Inset is the plot of the energy position of the peak A_1 in MnO_2 (Mn^{4+}), Mn_2O_3 (Mn^{3+}), and $LiMn_2O_4$ as a function of the formal oxidation state of Mn ion.

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_2O_3 (Mn^{3+}), and $LiMn_2O_4$ as a function of the formal valence of Mn ion. As was shown, the average Mn valence in $LiMn_2O_4$ is ~4+. It is consistent with the result as determined by the Mn $2p$-edge X-ray absorption spectra. The reason that the valence of Mn increases from 3.5+ (based on the neutral charge of the $LiMn_2O_4$ compound) to 4.0+ may be that the low valent Li^+ ions subsitute into the Mn sites in $LiMn_2O_4$. 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 $LiMn_2O_4$.

In this study, we report the detailed electronic structure of the spinel-type $LiMn_2O_4$ compound probed by the XANES technique. Using the Mn L_{23}- and K-edge XANES spectra, we deduced the Mn valence in $LiMn_2O_4$. This method will help to distinguish charge variations in complex systems
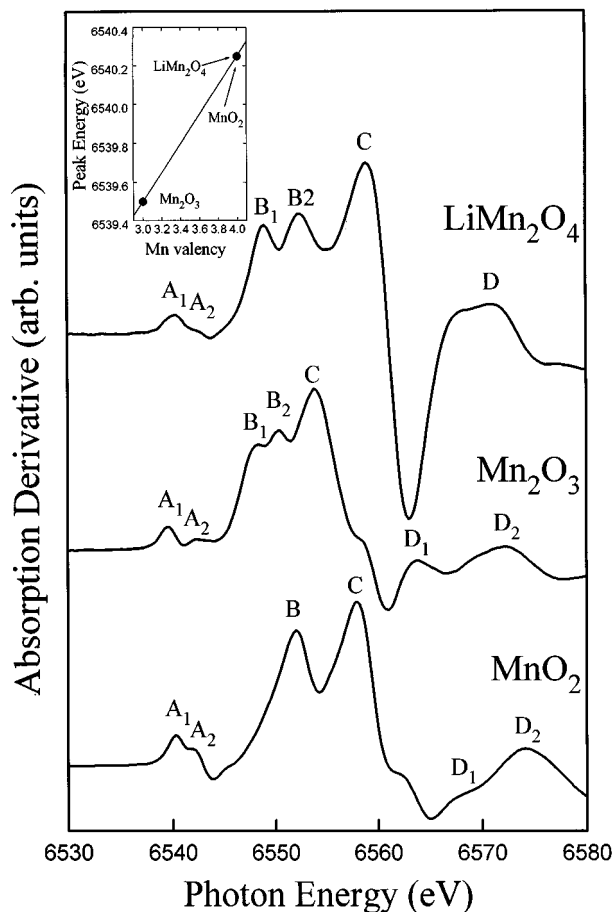
where calculations are difficult or nearly impossible. Based on the XANES studies, we have found the valence of Mn to be ~4+ in $LiMn_2O_4$. This suggests that chemical substitution of Li^+ ions into the Mn sites is an effective route to achieving a high valence of Mn in as-prepared $LiMn_2O_4$ samples.

ACKNOWLEDGMENTS

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