Electronic Structure and Chemical Bonding of Li and Protons in Spinel Type Manganese Oxides by Cluster Calculation

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(Received July 24, 2000; CL-000702)

A study of the electronic structure and chemical bonding of the Li and proton exchange in spinel-type manganese oxides is performed by a first-principles molecular-orbital method using model clusters composing of 57 atoms. The discrete-variational (DV)-Xα method was employed and Mulliken's population analyses were thoroughly conducted. We found that Li and proton in manganese oxides is highly ionized. Strong covalent interactions between Mn and O can be noted.

Lithium–manganese oxides with a spinel-type structure have received considerable attention as selective adsorbents,[1–3] and cathode materials for advanced lithium batteries.[4,5] Lithium is extracted from spinel lithium manganates by either chemical oxidation or exchange with protons in aqueous solution.[2] These characteristics are probably related to the highly ionized state of lithium in the spinel-type lithium manganese oxides. Because of its technological importance, intensive experimental and theoretical researches have been devoted to the study of the energy band structures and related properties of this compound.[6–8] Their interests have been focused on the average intercalation voltage for a lithium-ion battery. Accordingly even these extensive studies have left very fundamental questions still unanswered: Are Li and hydrogen atoms fully ionized in order to donate the valence electrons to the λ-MnO_2 host, and what is the chemical bonding of λ-MnO_2 by the Li and proton insertion?

In order to formulate guiding principles for the improvement of Li and proton insertion into manganese oxides, fundamental knowledge on the chemical bonding is essential. This study aims to achieve an understanding of the chemical bondings accompanied by Li and proton insertion into λ-MnO_2 using a first-principles linear combination of atomic orbitals (LCAO) method. The advantage of the LCAO method as compared with the plane-wave type method is its straightforward derivation of atomic-orbital components essential for net charges and bond overlap populations through Mulliken's population analysis method.[9] We are especially interested in the charge state of Li and proton and the magnitude of covalency around a Li and hydrogen atoms when they are inserted into the λ-MnO_2 host.

First-principles molecular orbital (MO) calculations by the DV-Xα method[10,11] using the program code SCAT[11] have been performed in order to obtain a chemical bonding. Numerical atomic orbitals (NAO) were employed as basis functions. They were generated and optimized by solving the radial part of the Schrödinger equation for a given environment at each iteration of the self-consistent calculation. All elements of Hamiltonian and overlap matrices were calculated numerically on the basis of the discrete variational integration scheme.[10,11] The detailed computational procedure can be found in the literature.[11] We have chosen model clusters for $LiMn_2O_4$ and HMn_2O_4 as shown in Figure 1. The lattice constants used in the present calculation are a = 8.24Å for $LiMn_2O_4$,[12] a = 8.03Å for HMn_2O_4,[13] respectively. The cluster models are composed of $(Li_5Mn_{12}O_{40})^{33-}$ for $LiMn_2O_4$ and $(H_5Mn_{12}O_{40})^{27-}$ for HMn_2O_4, both having D_{2d} symmetry. The atomic orbitals used in the present study are 1s, 1s–2p, 1s–4p, and 1s–2p for H, Li, Mn, and O, respectively. The formal charges are Li^+, $Mn^{3.5+}$, and O^{2-} for $LiMn_2O_4$, and H^0, Mn^{4+}, and O^{2-} for HMn_2O_4. Each cluster was embedded in Madelung potential generated by point charges outside the cluster. The magnitudes of point charges were chosen in the same way.

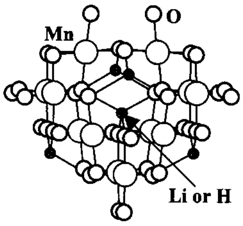

Figure 1. Cluster models, $(X_5Mn_{12}O_{40})^{n-}$ (n=27 for X=H and n=33 for X=Li), of XMn_2O_4(X=H and Li) with a spinel-type structure.

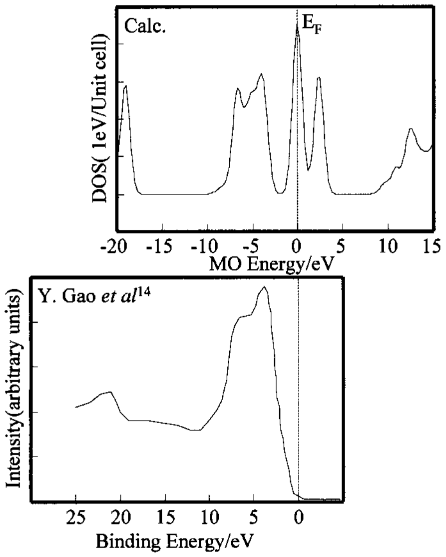

Figure 2. Comparison between the calculated DOS for $(Li_5Mn_{12}O_{40})^{33-}$ and the experimental PES spectrum obtained by Y. Gao *et al*.[14] The Fermi level (broken line) is chosen to be the zero energy.

The Photoelectron spectroscopy (PES) for $LiMn_2O_4$ obtained by Y. Gao et al.[14] is compared with our calculation result (Figure 2). As can be seen, the calculated results again show a good agreement with the experimental result. The size of the present clusters is thus confirmed to be sufficient to reproduce the DOS features. The molecular orbital calculation yields discrete molecular orbital (MO) levels. By the molecular orbital calculation, we obtain the discrete MO levels. However, it is convenient for visualization to replace the discrete MO levels are convoluted by Gaussian functions with a full width at a half maximum (FWHM) of 1.0 eV for easy visualization of DOS. The energy scale is shifted to make the Fermi level (E_F) zero. The bond overlap populations between A and B atoms are evaluated as having an energy distribution of overlap population Q_{AB}^{l}, called overlap population diagrams or COOP (crystal orbital overlap population) diagrams. Thus the bond overlap population Q_{AB} between atoms is obtained by summing the Q_{AB}^{l} for all MO levels below E_F. In Figure 3, the partial density of states (PDOS) for each atomic orbital is also plotted. The valence state is principally constructed by O-2s and O-2p bands. However, the O-2p band also notably contains components of Mn-3d orbitals, indicating strong Mn–O covalent bonding.

The partially filled Mn 3d band is located intensively around the E_F. Unoccupied bands above 8 eV are made of Li-2sp and Mn-4sp orbitals. Li-2sp states exhibit much more contributions to the bands than the valence band, suggesting that Li is highly ionized in $LiMn_2O_4$. On the other hand, considerable degrees of Mn-3d, 4s and 4p states are found in the O-2p band. The mixing of O-2*p* states in the Mn-3d band is also notable. The Mn 3d band also involves a considerably large amount of O-2p components making antibonding interactions for Mn–O bonds.

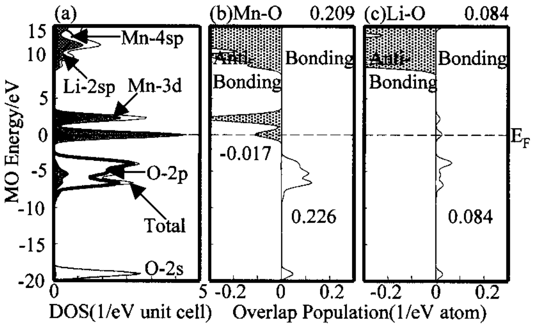

Figure 3. The total and partial density of states(a) and the overlap population diagrams of Mn-O(b) and Li-O(c) bonds for the $(Li_5Mn_{12}O_{40})^{33-}$ cluster.

When Li atoms are tentatively substituted by protons (Figure 4), the filled bands located from –3 eV ~ –10 eV are still mainly composed of O-2p orbitals. The partially filled band located around the Fermi energy is also mainly composed of Mn-3d, O-2p, and H-1s orbitals. Unoccupied bands above 10 eV are made of Mn-4sp orbitals. H-1s states give very slight contributions to the valence band, suggesting that proton is highly ionized in HMn_2O_4. On the other hand, significant amounts of Mn-3d, 4s and 4p states in the O-2p band are found. The mixing of O-2p states in the Mn 3d band is also notable. Accordingly, there are strong marked covalent interactions between Mn and O. This is probably due to the fact that protons in HMn_2O_4 are virtually in the high ionized state and make slight covalent interactions with the surrounding atoms. The presence of protons, therefore, does not significantly affect the valence states of the clusters. The strength of the covalent bonding can be estimated from the overlap population as shown in Figures 3(b,c) and 4(b,c). The values in each figure give the bonding and antibonding contributions to the overlap population between Mn and O, between Li and O, and between H and O. The sum of these two components is shown in the upper-right side of each figure. Figures 3 (b) and (c) clearly demonstrate strong covalent bonding between Mn and O(0.209), and much smaller covalency in Li–O bonds(0.084). The H–O bond in Figure 4(c) has much smaller covalent bonding. This means that the nature of the Mn–O bond is hardly affected by the presence of Li or protons. Mulliken's charges of Li and H are 0.7 and 0.52, respectively, indicating that they are highly ionized.[15] This may be a significant factor in determining the exchange between Li and protons in aqueous solution.

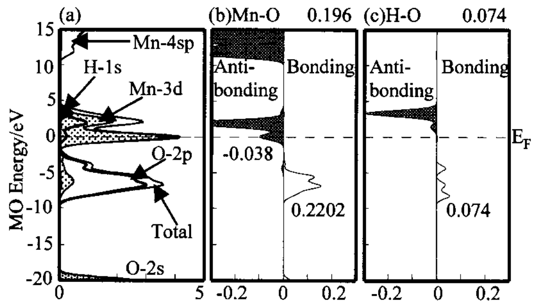

Figure 4. The total and partial density of states(a) and the overlap population diagrams of Mn-O(b) and H-O(c) bonds for the $(H_5Mn_{12}O_{40})^{27-}$ cluster.

In conclusion, the electronic structure and chemical bonding of $LiMn_2O_4$ and HMn_2O_4 have been deterimined by the DV-Xα molecular orbital method using cluster models for $(Li_5Mn_{12}O_{40})^{33-}$ and $(H_5Mn_{12}O_{40})^{27-}$, respectively. We found that the Mulliken's charges of Li and protons in the corresponding clusters are approximately 0.7 and 0.52, respectively. Net charges of Mn and O are hardly affected by Li insertion. This strong covalent bonding is formed between Mn and O with BOP of 0.209, quite different from very slight covalency in Li–O and H–O.

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15 Mulliken charges as well as the overlap populations depend on the choice of the basis functions. However, the variation in their values has been known to be small if we use minimal basis functions in the present DV-Xα method. The values can therefore be used at least for qualitative comparison.