

Electronic Band Structure of Li_2CuO_2 and Application to Battery Electrode

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The electronic band calculations of Li_2CuO_2 and Li-deintercalated CuO_2 have been performed by the full-potential linearized augmented plane wave (FLAPW) method within the local spin density approximation (LSDA). It is found that Cu 3d states are strongly hybridized with O 2p states and that Li atom is almost ionized. On the basis of the total energy calculations, we have studied the applicability of Li_2CuO_2 as a rechargeable battery cathode material. The average battery voltage in the chemical reaction process, $\text{Li}_2\text{CuO}_2 \rightarrow \text{CuO}_2 + 2\text{Li}$, is estimated. The structural stability is also discussed.

1 Introduction

Lithium transition-metal oxides are attractive materials due to their application potential as rechargeable battery electrodes. Among them, LiCoO_2 with layer structure is one of favorable cathode materials and currently used as a cathode material in commercial Li-batteries. However, Co element is so expensive that the batteries with LiCoO_2 cathode cost a great deal. Thus, new cathode materials with low cost (Fe, Cu etc.) and high cell voltage ($\sim 4\text{V}$) are desired.

Those with chain structure such as Li_2CuO_2 may function as a cathode material. Li_2CuO_2 is one of the compounds of which electrochemical properties have not been studied in detail. It becomes an antiferromagnet below 8.3K and has an interesting crystal structure of body centered orthorhombic lattice [1], shown in Fig. 1. Each Cu atom is surrounded by four O atoms in the *bc*-plane, and the CuO_4 squares share the edge. The resulting CuO_2 chains along the *b*-axis are stacked along the *a*- and *c*-axes, and these chains are connected by Li ions. We have already performed the electronic band calculations for non-magnetic (NM) and antiferromagnetic (AF) states of Li_2CuO_2 by using the FLAPW method within the LSDA. [2]

Recently, several groups have performed first-principles band calculations of various electrode materials. Aydinol *et al.* calculated the average battery voltages for Li/ LiMO_2 and Li/ LiCoX_2 ($M = \text{Ti, V, Mn, Co, Ni, Cu, Zn, Al; X = O, S, Se}$) cells. [3] Deiss *et al.* calculated the average voltages for $\text{LiC}_6/\text{LiMoO}_2$ cells and $\text{LiC}_6/\text{LiNiO}_2$ cells. [4] Wolverton and Zunger studied Li/Co and Li-vacancy/Co orderings associated with the de-intercalation process of LiCoO_2 , as well as the battery voltage. [5] In these studies the average voltage is predicted theoretically without using any experimental data, by combining the *ab initio* band calculation with basic thermodynamics. These results are in good agreement with experimental results. This fact indicates that first principles band calculation is a useful tool for looking for new cathode materials.

In this paper, first-principles total energy calculations for Li_2CuO_2 , fully Li-deintercalated CuO_2 and metallic Li are carried out. The applicability of Li_2CuO_2 as rechargeable Li-battery cathode is discussed. In Section 2, the detail of electronic band calculation is shown. In Section 3, we discuss the average battery voltage and the structural stability. Lastly, it is found that although Li_2CuO_2 behaves as a cathode

material, the structural stability is not so good, compared with LiCoO_2 and LiNiO_2 .

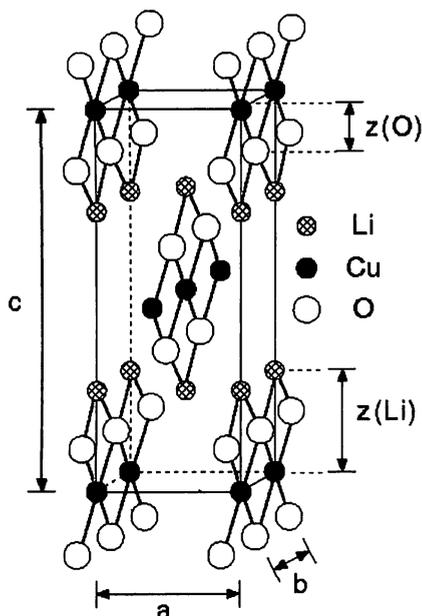


Fig. 1. The crystal structure of Li_2CuO_2

2 Band Calculation

Consider a cell with some host as one electrode and Li metal as the other (See Fig. 2). The anode and cathode electrodes are separated by an electrolyte. The electrolyte allows transfer of Li ions between two electrodes but does not allow for any electron transport. When the battery discharges, Li is intercalated into the cathode compound. Upon charging, the Li ions are removed from the cathode compound.

The chemical reaction is assumed to be $\text{Li}_2\text{CuO}_2 \rightarrow \text{CuO}_2 + 2\text{Li}$. Also assumed that the CuO_2 chains are maintained during the lithium extraction and insertion. In these restrictions, we perform the band calculation for the non-magnetic and antiferromagnetic Li_2CuO_2 and the host metal oxide CuO_2 . And also we perform the band calculation for non-magnetic metallic Li. All band calculations are performed by using the FLAPW method. Program codes TSPACE [6] and Kansai-92 are used. The LDA or LSDA is adopted to construct the exchange and correlation terms of the one-electron potential.

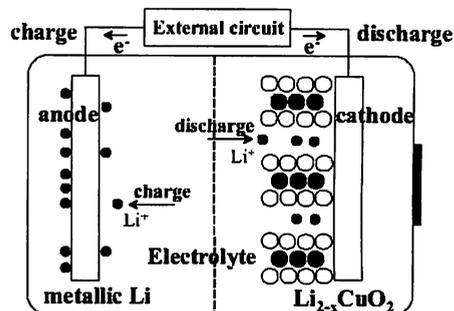


Fig. 2. The schematic picture of electrochemical lithium cell.

2.1 Li_2CuO_2

For constructing the basis functions we use the criteria $l_{max} = 7$ inside the muffin-tin (MT) spheres and $|\mathbf{k} + \mathbf{G}|_{max} = (2\pi/a) \times 3.8$ outside the MT spheres, with \mathbf{k} being a wave vector in the first Brillouin zone (BZ) and \mathbf{G} being a reciprocal lattice vector. The MT sphere radii are taken to be $0.26a$ for all atoms of Cu, O and Li. For the lattice parameters the observed values are used: $a = 3.654\text{\AA}$, $b = 2.860\text{\AA}$, $c = 9.377\text{\AA}$, $z(\text{Li}) = 0.2869c$, $z(\text{O}) = 0.1423c$. The potential is self-consistently determined using 35 (27) meshed \mathbf{k} points in an irreducible 1/8 first BZ for the NM (AF) state. The iteration process is repeated until the calculated total energy of the crystal converges into less than 10^{-3} Ryd. The density of states (DOS) is calculated with the linearly energy interpolated tetrahedron method using the energy eigenvalues at 107 (125) \mathbf{k} points in an irreducible 1/8 first BZ.

For the NM-state, a narrow antibonding band crosses the Fermi level, and this band consists of strongly hybridized Cu $3d_{yz}$ and O $2p_y$ orbitals ($y//b$, $z//c$). The Fermi surface of the NM-state reveals a nesting effect which plays an important role in causing the observed AF magnetic ordering. In the AF-state, the narrow antibonding band in the NM-state is split, and a small gap appears at the Fermi level. The calculated density of states is shown in Fig. 3(a) for NM-state and Fig. 3(b) for AF-state. It has been found that the calculated total energy for the AF-state is lower than that for NM-state.

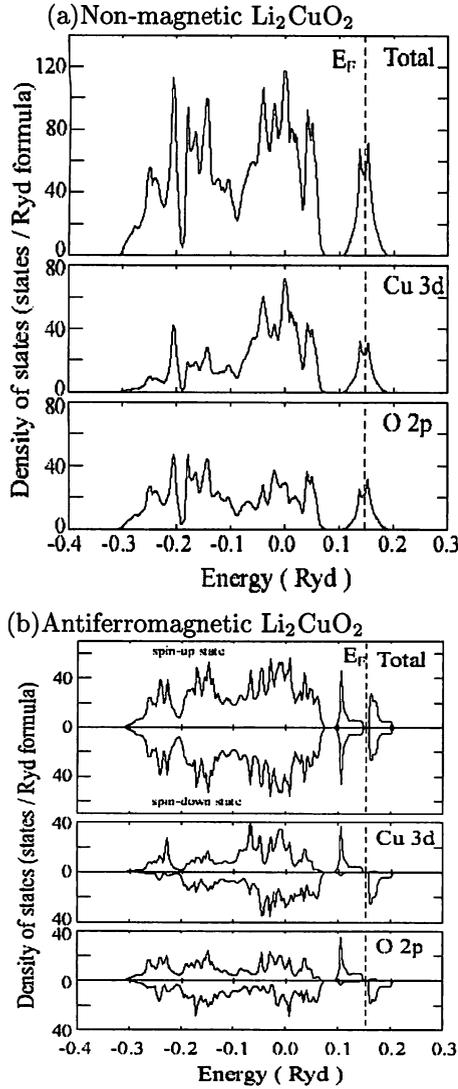


Fig. 3. The density of states of Li_2CuO_2 . (a) for NM state and (b) for AF state. Contributions arising from Cu 3d and O 2p states inside each muffin-tin sphere are also shown.

2.2 Non-magnetic CuO_2

The CuO_2 chains are assumed to be maintained during the lithium extraction, namely we ignore the effect of lattice relaxation, and use the observed lattice constants and positions of Cu and oxygen atoms of Li_2CuO_2 . We use the same criteria for constructing the basis functions, the same MT sphere radii and the same condition for energy convergence as those used in the band calculation of Li_2CuO_2 . The obtained DOS is shown in Fig. 4. The overall feature of the

electronic structure of CuO_2 is similar to that of Li_2CuO_2 .

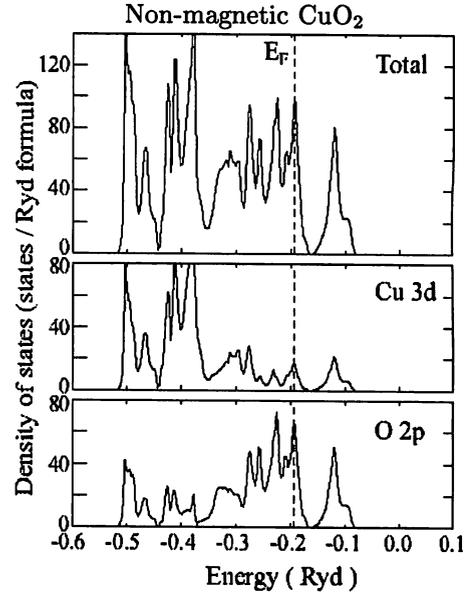


Fig. 4. The density of states for nonmagnetic state of CuO_2 .

2.3 Non-magnetic metallic Li

Metallic Li has a body centered cubic lattice with O_h^9 ($I4/m\bar{3}2/m$) symmetry. For constructing the basis functions, we use the criteria $l_{max} = 7$ inside the MT spheres and $|\mathbf{k} + \mathbf{G}|_{max} = (2\pi/a) \times 4.0$ outside the MT spheres. As the MT sphere radii, we adopted $0.41a$ for Li atom. As the lattice parameter, the observed value is used: $a = 3.510\text{\AA}$. The potential has been self-consistently determined using 55 meshed \mathbf{k} points in an irreducible $1/48$ first BZ for the NM state.

3 Application to battery electrode

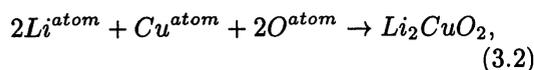
The average voltage V_{av} is proportional to the change of Gibbs's free energy ΔG . ΔG can be approximated by the change of internal energy ΔE , because $P\Delta V$ is of the order of $10^{-5}\Delta E$, and $T\Delta S$ is the order of the thermal energy which is also much smaller than ΔE at room temperature. Therefore, V_{av} (per Li) is given by

$$V_{av} = -\frac{1}{e} \frac{\Delta E}{\Delta x} = -\frac{(E_{tot}^{\text{Li}_2\text{CuO}_2} - E_{tot}^{\text{CuO}_2} - 2E_{tot}^{\text{Li}})}{2e}, \quad (3.1)$$

where Δx refers to the number of the transferred lithium ($\Delta x=2$). The total energies of fully lithiated Li_2CuO_2 , fully delithiated CuO_2 and metallic Li, which are calculated by FLAPW method in Section 2, are used.

The V_{av} is estimated as 4.46V per Li for the NM state of Li_2CuO_2 and 4.51V for AF-state of Li_2CuO_2 . In our study we assumed that the chemical reaction goes to fully lithiated Li_2CuO_2 from fully delithiated CuO_2 and metallic Li, namely mean process of chemical reaction, such as one Li extraction process, is ignored.

Next to discuss the stability as cathode material, the cohesive energy is estimated. In the chemical reaction expressed by the following process



the cohesive energy is given by

$$E_{coh}(\text{Li}_2\text{CuO}_2) = 2E_{tot}(\text{Li}) + E_{tot}(\text{Cu}) + 2E_{tot}(\text{O}) - E_{tot}(\text{Li}_2\text{CuO}_2). \quad (3.3)$$

On the basis of the FLAPW band calculation, the cohesive energy for Li_2CuO_2 is evaluated as 12.2eV, and also that for CuO_2 is 3.9eV. In conclusion, although the structural stability of CuO_2 is not so good, Li_2CuO_2 is one of new possible cathode materials for 4V class secondary Li batteries. For more quantitative argument, an effect of the lattice relaxation in Li extraction process should be taken into consideration. And a study of the process in which Li is extracted partially from Li_2CuO_2 is remained as a future problem.

4 Conclusion

On the basis of the electronic band structures of Li_2CuO_2 , CuO_2 and metallic Li calculated by using the full potential LAPW method and the local density approximations, an applicability of Li_2CuO_2 as rechargeable Li-Battery cathode has been studied.

The average voltage V_{av} is obtained as 4.46V per Li for the non-magnetic state of Li_2CuO_2 and 4.51V for the antiferromagnetic state of Li_2CuO_2 . The cohesive energy for Li_2CuO_2 and that for CuO_2 are estimated to be 12.2eV and 3.9eV, respectively.

Although the structural stability of CuO_2 is not so good, Li_2CuO_2 is one of new possible cathode materials for 4V class secondary Li batteries

References

- [1] F. Sapiña, J. Rodríguez-Carvajal, M. J. Sanchis, R. Ibáñez, A. Beltrán and D. Beltrán: *Solid State Commun.* **74** (1990) 779.
- [2] N. Tanaka, M. Suzuki and K. Motizuki: *J. Phys. Soc. Jpn.* **68** (1999) 1684.
- [3] M. K. Aydinol, A. F. Kohan, G. Ceder, K. Cho and J. Joannopoulos: *Phys. Rev. B* **56** (1997) 1354.
- [4] E. Deiss, A. Wokaun, J. -L. Barras, C. Daul and P. Dufek: *J. Electrochem. Soc.* **144** (1997) 3877.
- [5] C. Wolverton and A. Zunger: *Phys. Rev. B* **57** (1998) 2242.
- [6] A. Yanase: *Fortran Program for Space Group* (Shokabo, Tokyo, 1995) 1st ed., in Japanese.