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Theoretical Studies of the Discharge Mechanism of CuO Cathodes Modified with Bi_2O_3 in Rechargeable Zn/CuO Batteries

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Abstract

Recent studies have shown a significant influence of Bi additives on the cyclability of CuO cathodes in rechargeable Zn/CuO batteries [1,2]. However, the mechanism of this influence is not completely understood. We apply *ab initio* methods based on density functional theory to study the mechanism of interaction of Bi_2O_3 additives with the CuO cathode material. Using the results of our calculations, we examine the structural and chemical changes occurring in CuO and CuO-Bi_2O_3 cathodes during the battery discharge and investigate the possibility of the formation of Bi- and Cu-containing intermediate phases in the cathode.

Introduction

Rechargeable alkaline Zn/CuO batteries are promising candidates for large-scale electrical energy storage because of their relatively low cost, general elemental abundance, and environmental safety. The electrochemical discharge of CuO in an aqueous Zn/CuO battery can be described as follows [3]:

First discharge: $\mathbf{3CuO + 4H^+ + 4e^- \rightarrow Cu + Cu_2O + 2H_2O}$

Subsequent cycle: $\mathbf{Cu_2O + 2H^+ + 2e^- \rightarrow 2Cu + H_2O}$

Both CuO and Cu_2O are p-type semiconductors. The accumulation of Cu_2O in the cathode could lead to a loss of electrical conductivity and the failure of the battery. It has been demonstrated that the addition Bi_2O_3 to the CuO cathode facilitates the electrochemical reversibility of the discharge reaction in a Zn/CuO battery by decreasing the cell resistance and promoting the reduction of Cu(II) and Cu(I) [1].

Research Objectives

- Develop a theoretical model describing the discharge mechanism of CuO cathodes modified with Bi_2O_3 in alkaline Zn/CuO batteries.
- Examine the structural and chemical changes occurring on CuO and CuO-Bi_2O_3 cathodes during the battery discharge.
- Investigate the possibility of formation of Bi- and Cu-containing intermediate phases.

Computational Methods

- Ab initio computational methods based on DFT [4-6].
- Quantum ESPRESSO electronic structure package [4].
- Periodic boundary conditions & plane-wave basis sets.
- GGA-PBE exchange-correlation functional [5].
- DFT+U Hubbard correction (U = 7.5 eV, J = 0.98 eV).

References

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Results and Discussion

Structures & electronic properties of CuO, Cu_2O & CuO_2

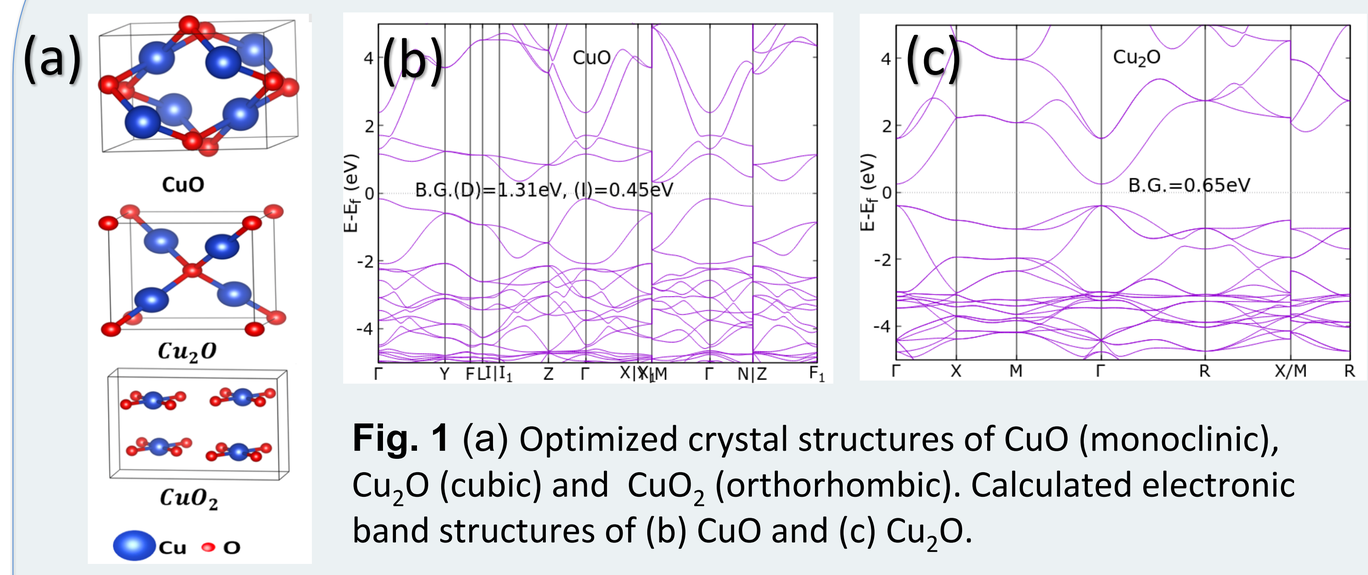


Fig. 1 (a) Optimized crystal structures of CuO (monoclinic), Cu_2O (cubic) and CuO_2 (orthorhombic). Calculated electronic band structures of (b) CuO and (c) Cu_2O.

Structures & properties of Bi_2O_3 , $CuBi_2O_4$, $CuBiO_2$, & Cu_3BiO_2

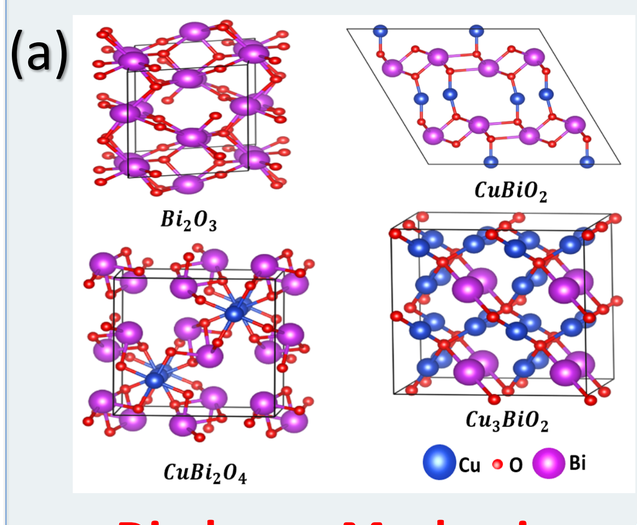
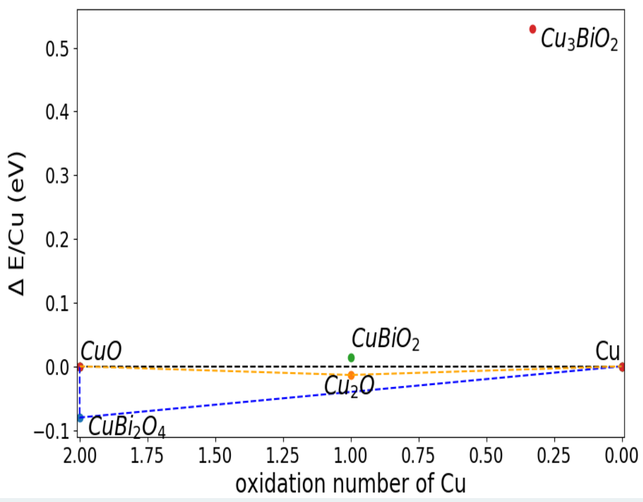


Fig. 2 (a) Optimized crystal structures of Bi_2O_3, $CuBi_2O_4$, $CuBiO_2$, and Cu_3BiO_2. Calculated band structures of (b) $CuBiO_2$ and (c) $CuBi_2O_4$.

Discharge Mechanism of CuO with the addition of Bi_2O_3



$$CuBi_2O_4 = Bi_2O_3 + CuO$$
$$CuBiO_2 = \frac{1}{2}Bi_2O_3 + \frac{1}{2}CuO + \frac{1}{2}Cu$$
$$\frac{1}{3}Cu_3BiO_2 = \frac{1}{6}Bi_2O_3 + \frac{1}{6}CuO + \frac{5}{6}Cu$$

Fig. 3 Calculated formation energies of Cu_2O, $CuBi_2O_4$, $CuBiO_2$, and Cu_3BiO_2 per one Cu atom with respect to the CuO – Cu equilibrium line.

Our calculations predict the energy $CuBi_2O_4$ to be lower than that of a mixture of Bi_2O_3 and CuO, suggesting the possibility of formation of $CuBi_2O_4$ in CuO cathodes modified with Bi_2O_3. The formation energy of Cu_2O is located below the line connecting the energies of CuO and Cu, but above the line connecting the energies of $CuBi_2O_4$ and Cu. It implies that the formation of Cu_2O in discharged CuO cathodes is expected to be energetically favorable, whereas in CuO cathodes modified with Bi_2O_3 the accumulation of Cu_2O during discharge may be partially suppressed.

Summary

We applied *ab initio* density functional computational methods to investigate the discharge mechanism of CuO and CuO-Bi_2O_3 cathodes in rechargeable Zn/CuO batteries. Our calculations indicated the possibility of formation of mixed Cu-Bi oxides in CuO cathodes modified with Bi_2O_3. The results of our study suggested that the presence of Cu-Bi oxides in CuO-Bi_2O_3 cathodes could explain the influence of Bi additives on the reversibility of the discharge reaction in Zn/CuO-Bi_2O_3 batteries.

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