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Ab Initio Studies of the Cycling Mechanism of MnO_2 Cathodes Modified with Bi, Cu, and Mg in Rechargeable Zn/MnO_2 Batteries

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Abstract: Rechargeable alkaline Zn/MnO_2 batteries hold great promise for electrical energy storage and power grid applications due to their high energy density, non-toxicity, and low cost. Bi and Cu additives are known to significantly extend the cycle life and increase the capacity of MnO_2 electrodes in rechargeable Zn/MnO_2 batteries. However, the mechanism of interaction of Bi and Cu with the MnO_2 cathode material is not completely understood. To investigate the influence of chemical additives on the rechargeability and cyclability of MnO_2 electrodes, we calculated the geometries and formation enthalpies for a wide variety of crystal structures of MnO_2 modified with Bi, Cu, and Mg using *ab initio* computational methods based on density functional theory. The results of our calculations suggest that reversible transitions between the layered and spinel phases could play an important role in the cycling mechanism of chemically modified MnO_2 cathodes.

Introduction

Affordable energy storage is essential for efficient integration of renewable energy sources into the electrical power grid. Rechargeable alkaline Zn/MnO_2 batteries represent an attractive solution for large-scale energy storage applications because of their high energy density, non-toxicity, and low cost.[1-3]

Rechargeable Alkaline Zn/MnO_2 Batteries

Advantages

- High energy density (>400 wh/L),
- Cheap and abundant materials,
- Environmentally friendly,
- Incombustible, no risk of fire.

Known Issues

- Relatively short cycle life,
- Capacity degradation due to accumulation of Mn_3O_4 and $ZnMn_2O_4$.[2,3]

Recent studies have shown that Bi and Cu additives can significantly extend the cycle life and improve the performance of rechargeable Zn/MnO_2 batteries.[4,5]

Research Objectives

The goal of this study is to develop a theoretical model describing the discharge mechanism of MnO_2 cathodes in rechargeable Zn/MnO_2 batteries and apply this model to investigate the influence Bi, Cu, and Mg additives on the electrochemical properties of MnO_2.

Computational Methods

- *Ab initio* computational methods based on density functional theory (DFT).
- Quantum ESPRESSO (opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization) electronic structure code.[6]
- GGA PBEsol exchange-correlation functional.[7]
- Vanderbilt ultra-soft pseudopotentials.[8]
- Spin polarized calculations.
- Structural optimization was performed using *ab initio* MD simulations and the BFGS algorithm.

Results and Discussion

A. Discharge Mechanism of Unmodified γ-MnO_2 Electrodes

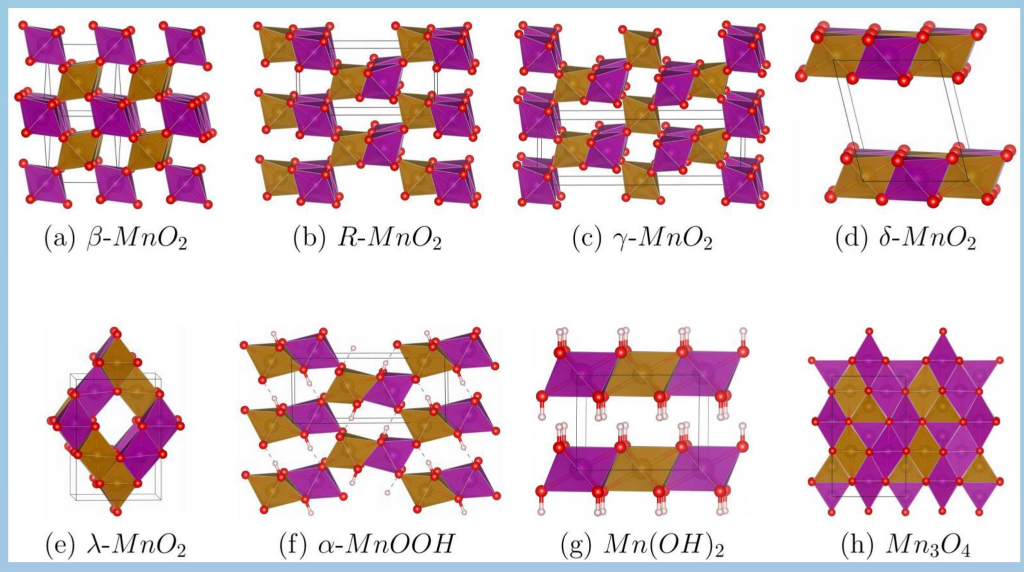

FIG. 1. Optimized crystal structures of β-MnO_2, R-MnO_2, γ-MnO_2, δ-MnO_2 λ-MnO_2, α-MnOOH, $Mn(OH)_2$, and Mn_3O_4.

The reduction of γ-MnO_2 leads to the breakdown of its crystal structure and to the formation of irreversible discharge products, such as Mn_3O_4 and $ZnMn_2O_4$.[9]

B. Cycling Mechanism of δ-MnO_2 Electrodes Modified with Bi and Cu.

The influence of Bi and Cu additives on the cycle life and rechargeability of MnO_2 cathodes can be explained by the formation of intermediate Bi-Mn and Cu-Mn oxides that reduce the rate of accumulation of Mn_3O_4.[10]

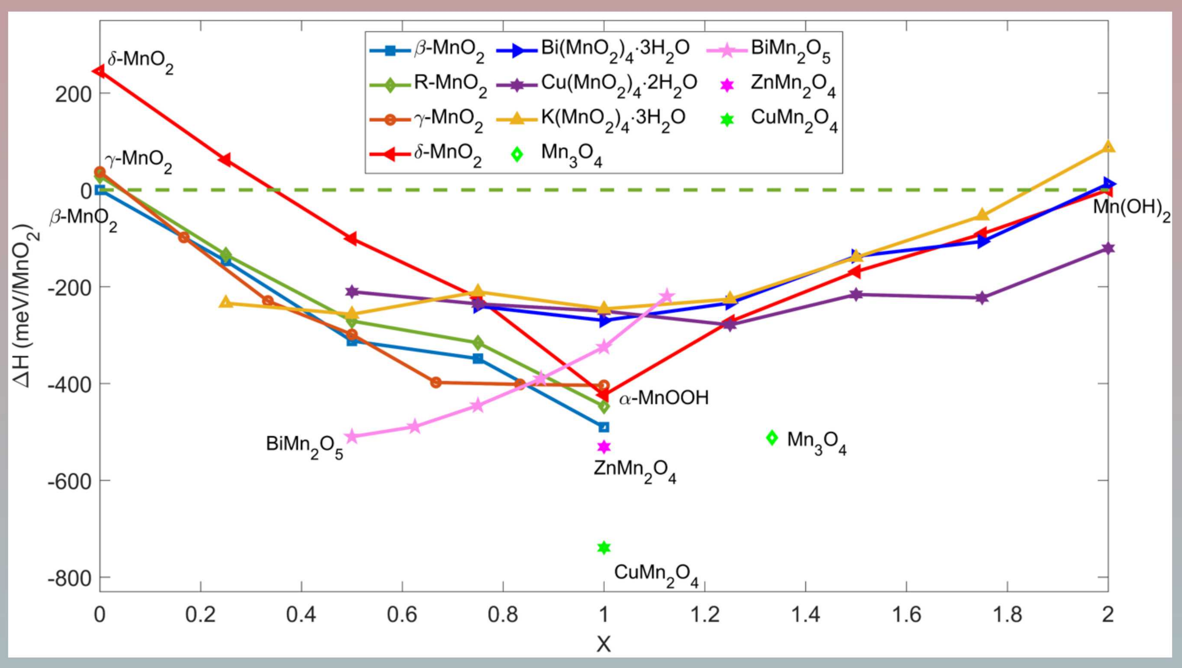

FIG. 2. Calculated enthalpies of protonated β-, R-, γ-, δ-MnO_2 α-MnOOH, $Mn(OH)_2$, Mn_3O_4, $ZnMn_2O_4$, Bi-/Cu- modified MnO_2, $BiMn_2O_5$ and $CuMn_2O_4$. The enthalpies are plotted with respect to the β-MnO_2 (pyrolusite) - $Mn(OH)_2$ (pyrochroite) line.

Cycling mechanism of Bi/Cu-modified δ-MnO_2 cathodes:

- Addition of Bi and Cu suppresses the formation of Mn_3O_4. This effect can be explained by the formation of intermediate Bi-Mn and Cu-Mn oxide compounds.
- Full two-electron reversible redox reaction is possible in δ-MnO_2 cathodes modified with Bi and Cu.
- Accumulation of $ZnMn_2O_4$ in the δ-MnO_2 cathode negatively affects the cycle life of Bi/Cu-modified δ-MnO_2/Zn batteries.

C. Reversible phase transitions in MnO_2 cathodes modified with Cu and Mg.

During electrochemical reduction, δ-MnO_2 can undergo a transition from a layered birnessite phase to spinel. A spontaneous layer-to-spinel phase transition is believed to be the origin of capacity fading in rechargeable batteries utilizing δ-MnO_2 cathodes.[11] Recent studies indicated a possibility of the inverse phase transition from spinel to a layered birnessite structure. The inverse spinel-to-layer phase transition appears to be mediated by the presence of metal ions and interstitial water.[12]

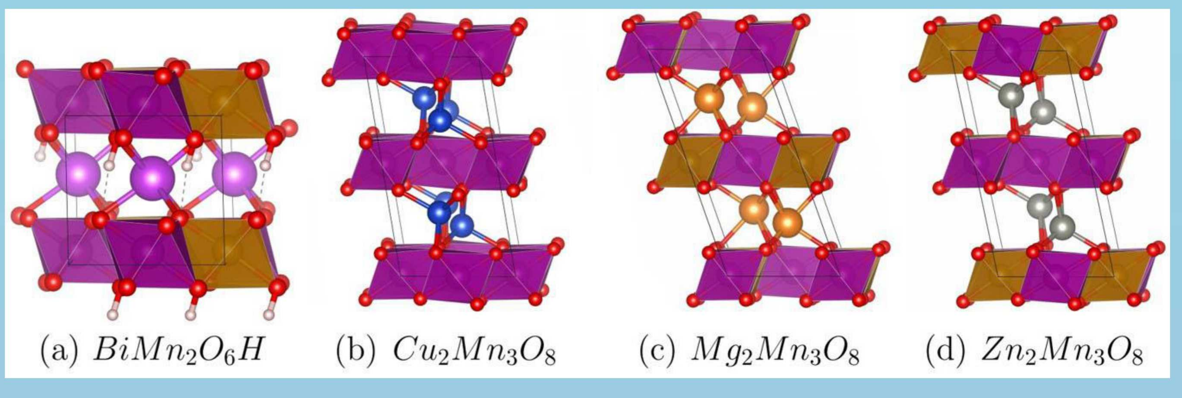

FIG. 3. Optimized crystal structures of layered Mn oxides containing Bi, Cu, Mg, and Zn ions.

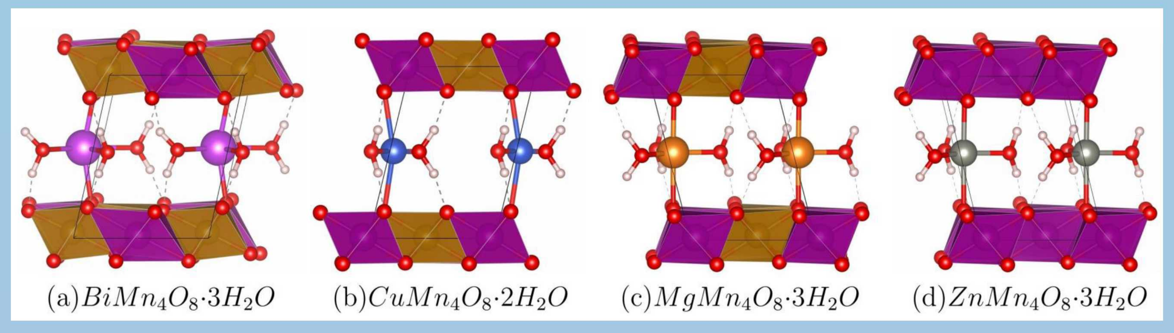

FIG. 4. Optimized crystal structures of hydrated Bi-, Cu-, Mg-, and Zn-intercalated δ-MnO_2 birnessite compounds.

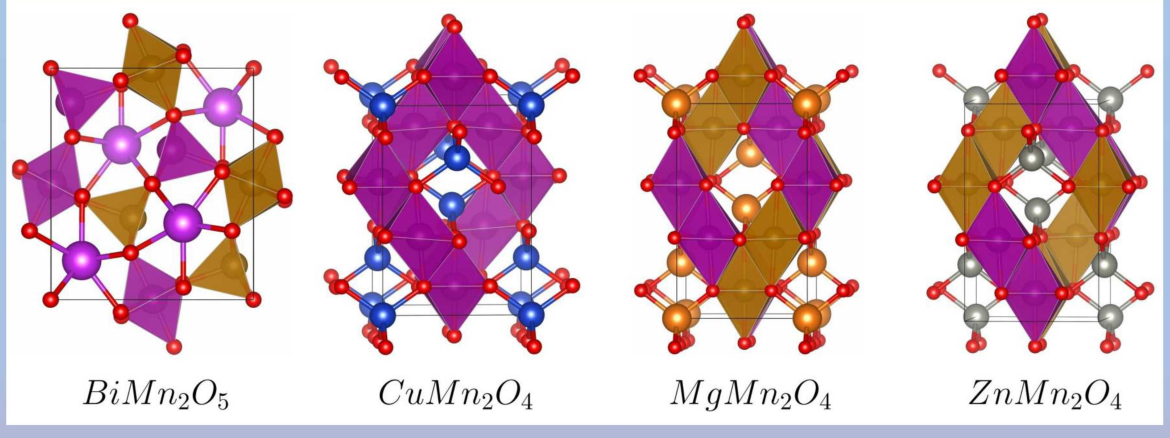

FIG. 5. Optimized crystal structures of $BiMn_2O_5$ and Cu-, Mg-, and Zn-containing spinel phases ($CuMn_2O_4$, $MgMn_2O_4$, and $ZnMn_2O_4$).

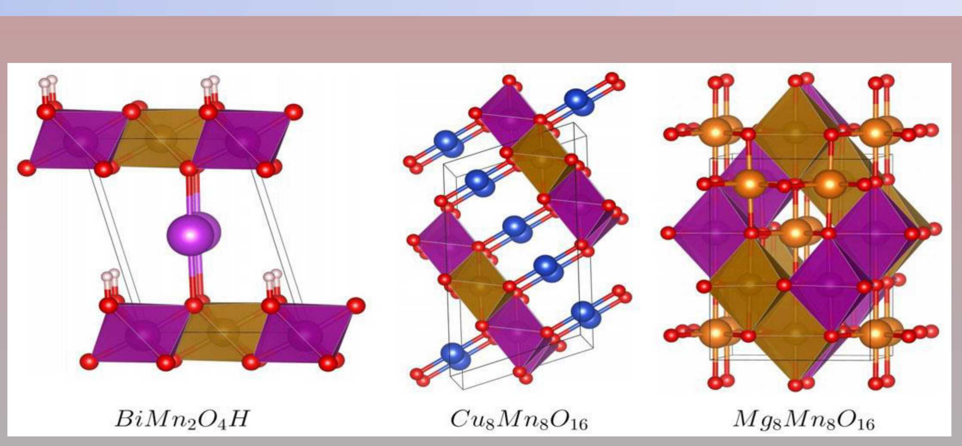

FIG. 6. Optimized crystal structures of $BiMn_2O_4H$, $Cu_8Mn_8O_{16}$, and $Mg_8Mn_8O_{16}$.

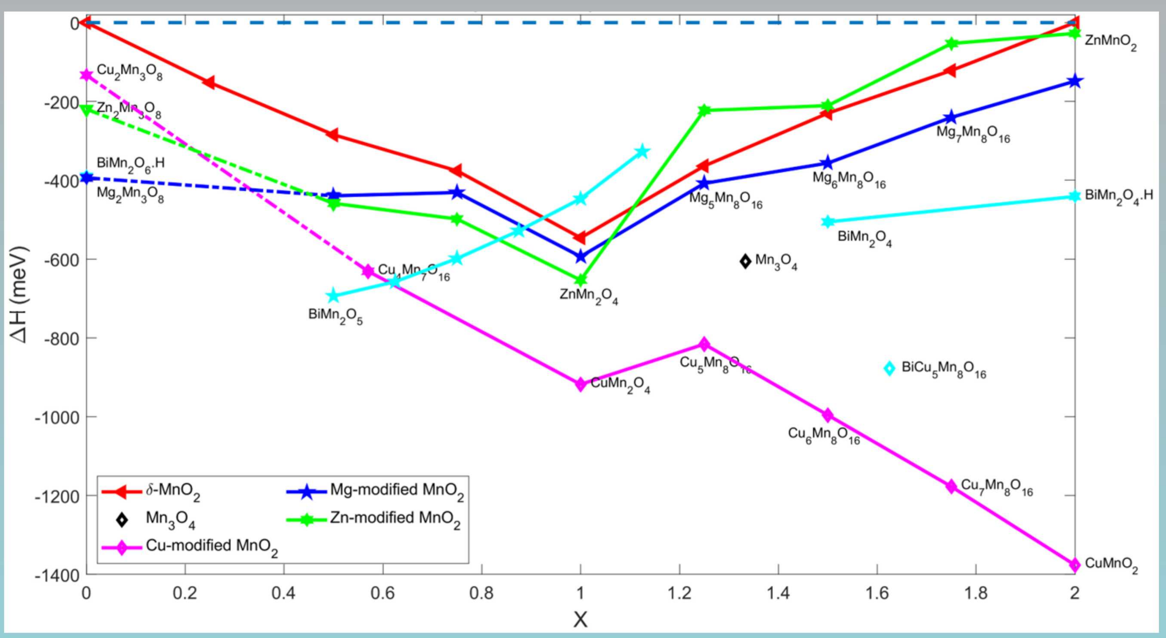

FIG. 7. Calculated enthalpies of manganese oxide compounds containing Bi, Cu, Mg, and Zn ions. The enthalpies are plotted with respect to the λ-MnO_2 (spinel) - $Mn(OH)_2$ (pyrochroite) line.

Proposed mechanism of reversible phase transitions in modified MnO_2 cathodes:

- Mn oxide compounds containing Cu and Mg ions can undergo reversible layer-to-spinel-to-layer phase transformations.
- The inverse phase transformation from spinel to a layered structure is assisted by the presence of interstitial water in Cu-, and Mg-intercalated δ-MnO_2 birnessite compounds.
- Reversible layer-to-spinel-to-layer phase transitions could explain the influence of Bi and Cu additives on the electrochemical properties of MnO_2.

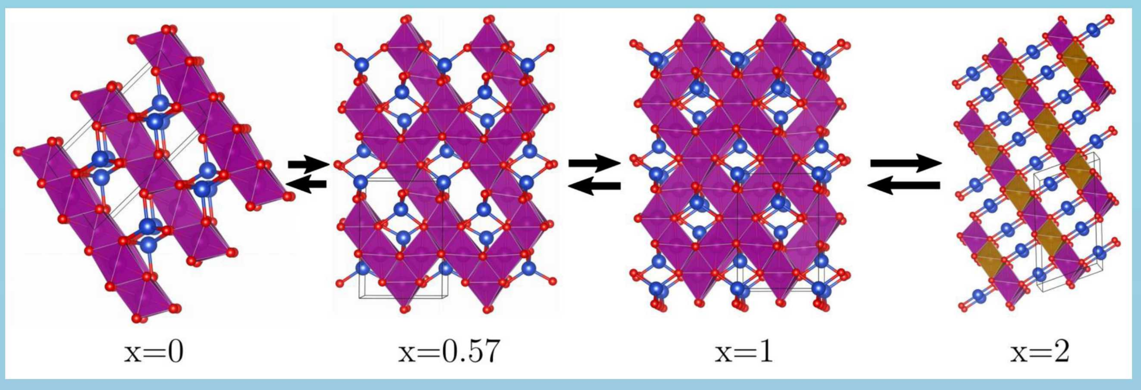

FIG. 8. Schematic illustration of reversible transitions between the layered and spinel phases of Cu-modified manganese oxides.

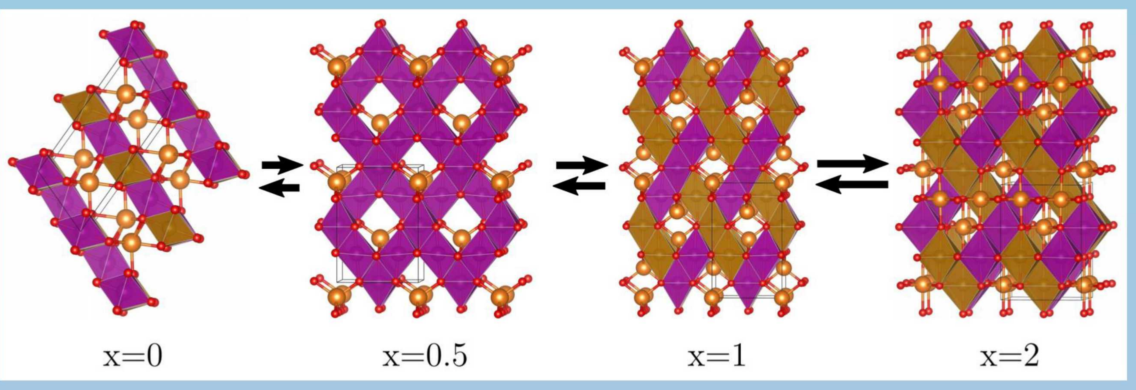

FIG. 9. Schematic illustration of reversible transitions between the layered and spinel phases of Mg-modified manganese oxides.

Summary

We applied first-principles computational methods based on density functional theory to investigate the electrochemical properties of Bi-, Cu-, and Mg-modified MnO_2 cathodes in rechargeable Zn/MnO_2 batteries. The results of our calculations suggest a possibility of reversible transitions between the layered and spinel phases of Mn oxides containing Cu and Mg ions, which could play an important role in the cycling mechanism of chemically modified MnO_2 cathodes.

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