

# Discharge Mechanism of $\text{MnO}_2$ in Deep-Cycle Rechargeable $\text{Zn}/\text{MnO}_2$ Batteries

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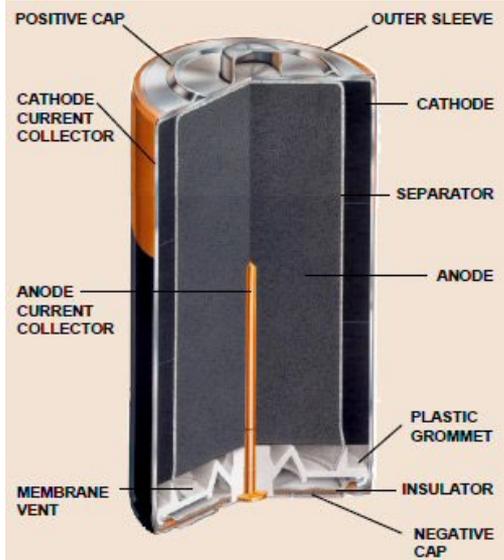
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# Outline

- Introduction
- Rechargeable Zn/MnO<sub>2</sub> batteries for energy storage
- Structural and electrochemical properties of MnO<sub>2</sub>
- Discharge mechanism of the  $\gamma$ -MnO<sub>2</sub> electrode
- Cycling of the Bi/Cu-modified  $\delta$ -MnO<sub>2</sub> electrode
- Summary

# Alkaline Zn/MnO<sub>2</sub> Batteries

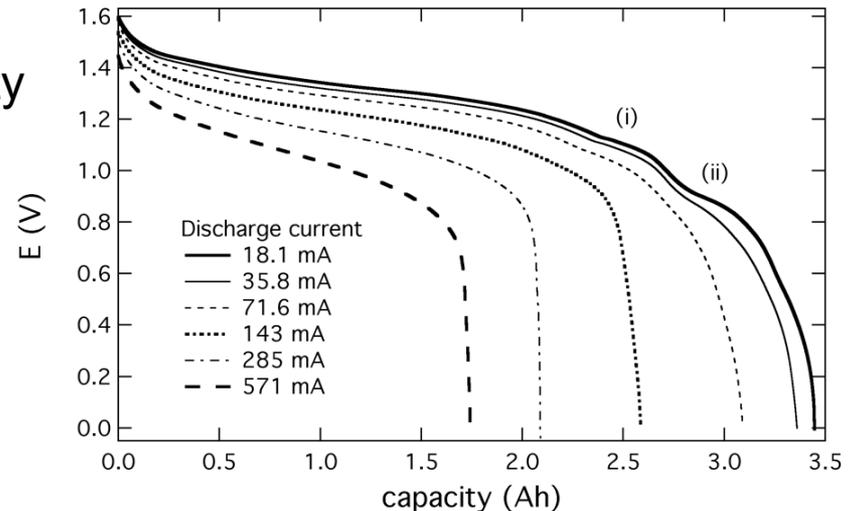
Alkaline Zn/MnO<sub>2</sub> batteries hold great promise for large-scale energy storage due to their high energy density, non-toxicity, non-combustibility, and low cost.



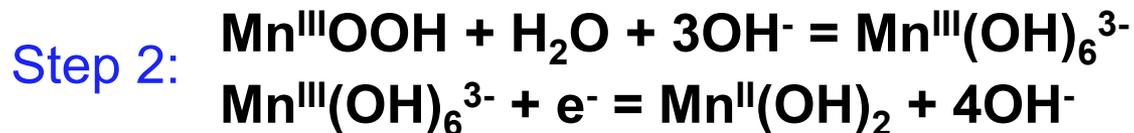
## Zn/MnO<sub>2</sub> batteries

- High energy density
- Low cost per kWh
- Non-toxic
- Non-flammable

## Zn/MnO<sub>2</sub> battery discharge



The reduction of MnO<sub>2</sub> is a two-step process: the first step is H<sup>+</sup> intercalation into the solid structure of MnO<sub>2</sub>; the second step is dissolution and chemical transformation.



# Rechargeable Alkaline Zn-MnO<sub>2</sub> Batteries

- In primary Zn/MnO<sub>2</sub> batteries, the discharge reaction is not reversible; the reduction of MnO<sub>2</sub> leads to the formation of hausmannite (Mn<sub>3</sub>O<sub>4</sub>) and hetaerolite (ZnMn<sub>2</sub>O<sub>4</sub>).
- There are two approaches to the development of rechargeable Zn/MnO<sub>2</sub> batteries:
  - 1) Limit DOD to a point below the threshold of formation of Mn<sub>3</sub>O<sub>4</sub> and ZnMn<sub>2</sub>O<sub>4</sub>.
  - 2) Engineer a reversible deep-cycle MnO<sub>2</sub> electrode.
- Recent studies demonstrated the possibility of building long-lasting deep-cycled rechargeable Zn/MnO<sub>2</sub> batteries utilizing birnessite ( $\delta$ -MnO<sub>2</sub>) cathodes stabilized with Bi and Cu additives.

[Yadav et. al, *Nat. Commun.* **8**, 14424 (2017); *J. Mater. Chem. A* **5**, 15845 (2017); *Mater. Today Energy* **6**, 198 (2017); *Int. J. Hydrogen Energy* **43**, 8480 (2018); Gallaway et. al., *J. Electrochem. Soc.* **165**, A2935 (2018)]
- The process of formation of hausmannite and hetaerolite in Zn/MnO<sub>2</sub> batteries is not well understood. The mechanism by which Bi and Cu additives affect the rechargeability and cyclability of Zn/MnO<sub>2</sub> batteries has not been studied in detail.

# Computational Modeling of MnO<sub>2</sub> in Zn/MnO<sub>2</sub> Batteries

## Research Objectives

- Develop a theoretical model describing the discharge mechanism of MnO<sub>2</sub> in deep-cycle rechargeable alkaline Zn/MnO<sub>2</sub> batteries.
- Investigate the possible redox reaction pathways in the MnO<sub>2</sub> electrode.
- Study the mechanism of formation of irreversible reaction products in the MnO<sub>2</sub> electrode.
- Investigate the influence of Bi and Cu additives on the rechargeability and cyclability of the  $\delta$ -MnO<sub>2</sub> electrode.

## Computational Methods

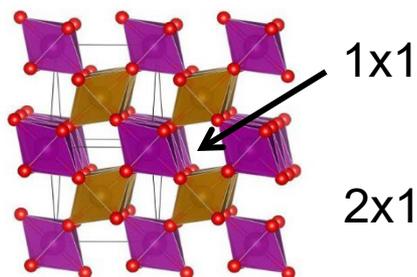
- Quantum ESPRESSO\* electronic structure package
- Density functional theory (DFT)
- Plane wave basis sets
- Spin-polarized calculations
- Vanderbilt ultrasoft pseudopotentials
- Revised generalized gradient approximation (PBEsol)



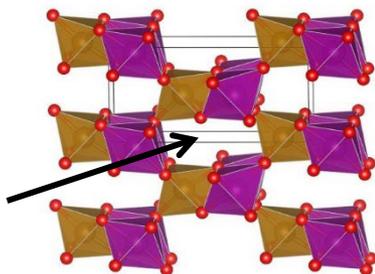
QUANTUM ESPRESSO

\* <http://www.quantum-espresso.org>

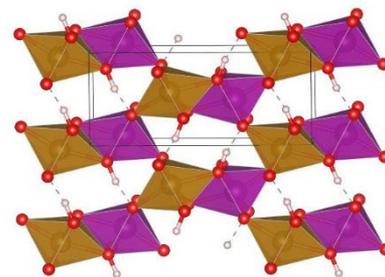
# Structures of $MnO_2$ Polymorphs and Discharge Products



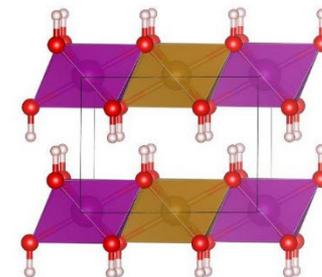
(a)  $\beta$ - $MnO_2$



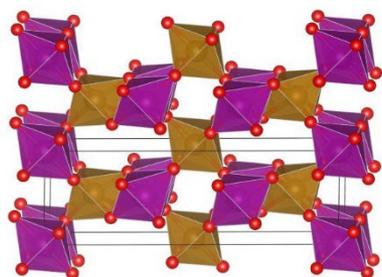
(b)  $R$ - $MnO_2$



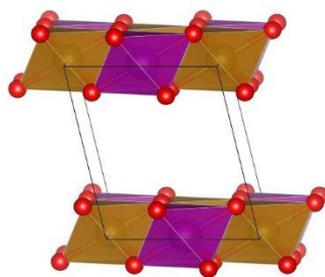
(e)  $\alpha$ - $MnOOH$



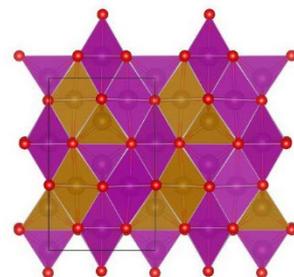
(f)  $Mn(OH)_2$



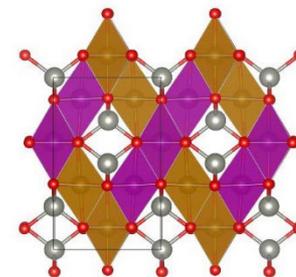
(c)  $\gamma$ - $MnO_2$



(d)  $\delta$ - $MnO_2$



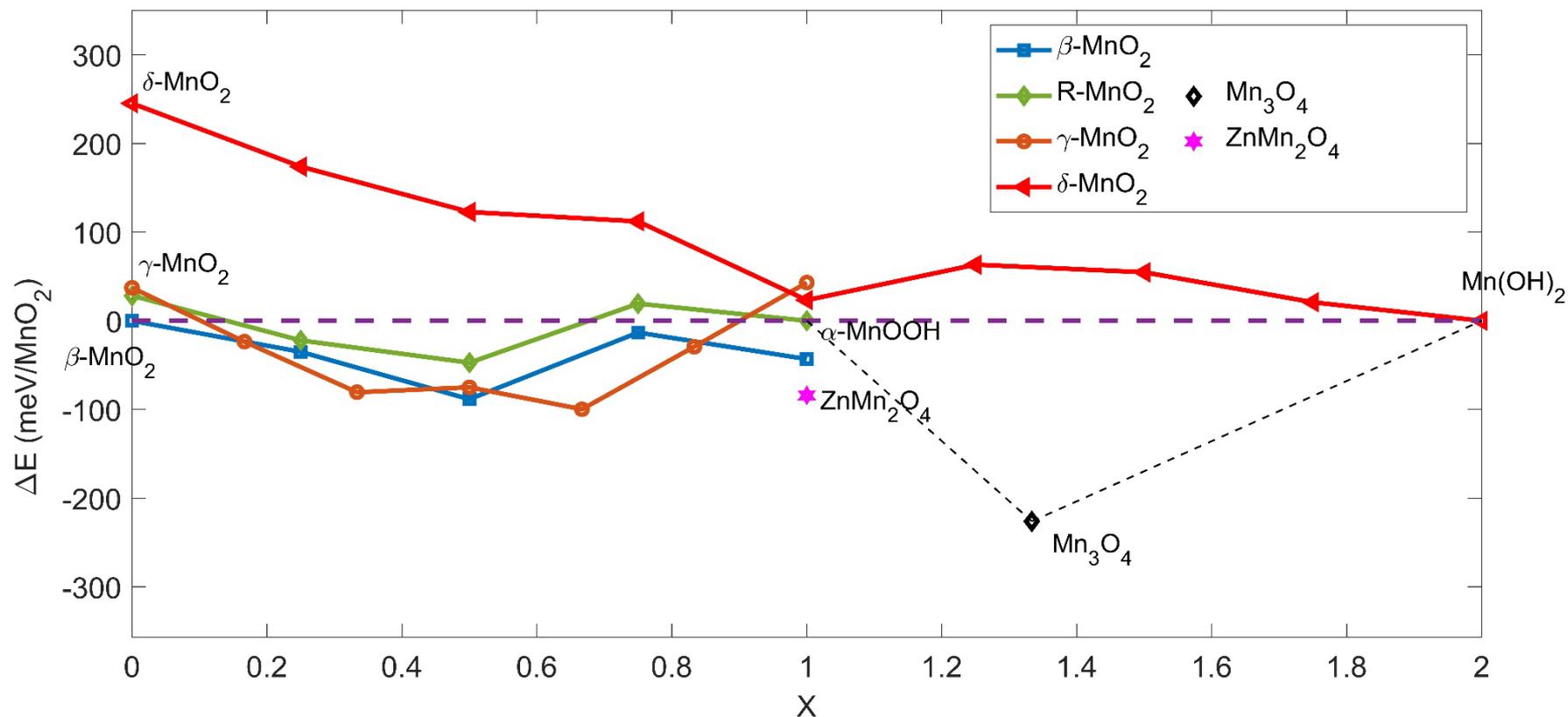
(g)  $Mn_3O_4$



(h)  $ZnMn_2O_4$

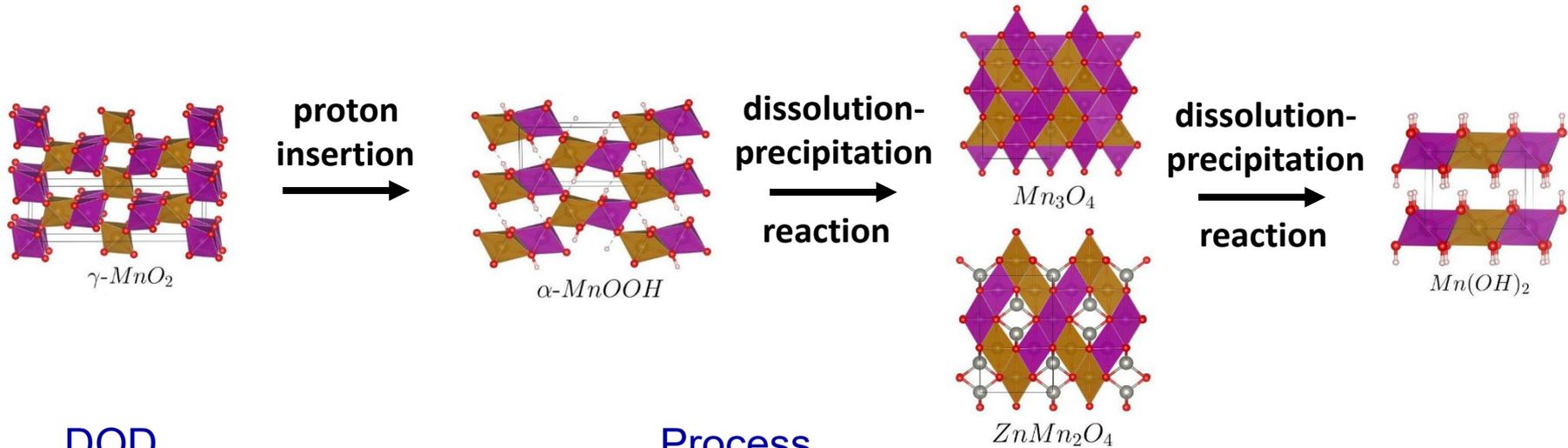
- $MnO_2$  forms a variety of energetically close polymorphic structures.
- The most common form of electrolytic  $MnO_2$  is  $\gamma$ - $MnO_2$ .
- All modeled structures (with the exception of  $Mn_3O_4$ ) are antiferromagnetic.
- Structures of protonated  $MnO_2$  crystals were obtained by inserting  $H^+$  ions into  $\beta$ -,  $R$ -,  $\gamma$ -, and  $\delta$ - $MnO_2$  polymorphs and selecting structures with the lowest total energies.

# Energies of Protonated $\text{MnO}_2$ Polymorphs, $\text{Mn}_3\text{O}_4$ , & $\text{ZnMn}_2\text{O}_4$



- Energies are plotted with respect to pyrolusite-groutite line for  $0 < x < 1$  and groutite-pyrochroite line for  $1 < x < 2$ .
- $X$  is DOD in electron equivalents. The charge of Mn ions is  $4 - x$ .
- Lower energies correspond to more stable structures.
- Hausmannite & hetaerolite are lower in energy than other discharge products.

# Discharge Mechanism of Unmodified $\gamma$ -MnO<sub>2</sub> Electrode



## DOD

$$0 < x \lesssim 0.8$$

$$0.8 \lesssim x < 1$$

$$1 < x < 4/3$$

$$4/3 < x < 2$$

## Process

H<sup>+</sup> insertion into the solid phase of  $\gamma$ -MnO<sub>2</sub>

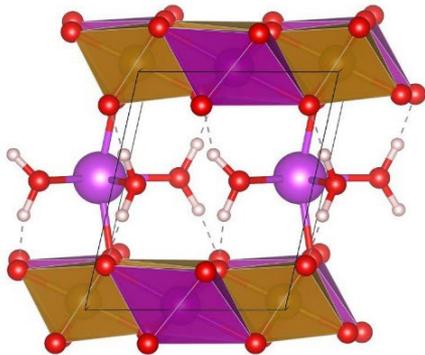
$\gamma$ -MnO<sub>2</sub> breaks down and converts into  $\alpha$ -MnOOH

$\alpha$ -MnOOH converts into Mn<sub>3</sub>O<sub>4</sub> and ZnMn<sub>2</sub>O<sub>4</sub>

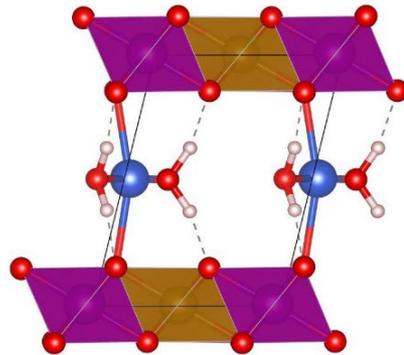
Mn<sub>3</sub>O<sub>4</sub> and ZnMn<sub>2</sub>O<sub>4</sub> coexist with Mn(OH)<sub>2</sub>

- Theoretical predictions are in good agreement with the results of EDXRD studies. [Gallaway et. al., *J. Electrochem. Soc.* **165**, A2935 (2018)]
- Discharge reaction is reversible at low DOD,  $x \lesssim 2(1 - P_r)/(2 - P_r)$ . [Vasiliev et. al., *J. Electrochem. Soc.* **165**, A3517 (2018)]
- Discharge reaction becomes irreversible at high DOD due to the accumulation of highly resistive products (hausmannite and hetaerolite).

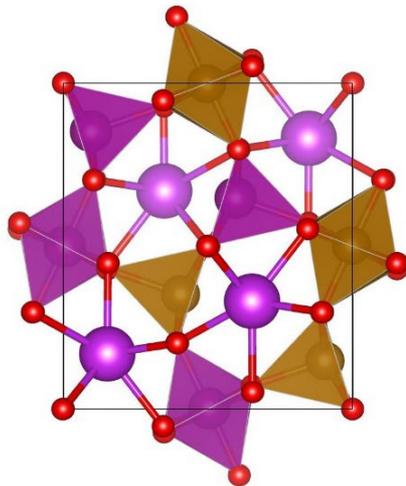
# Structures of Bi/Cu-Modified $\delta$ -MnO<sub>2</sub> and Bi/Cu-Mn Oxides



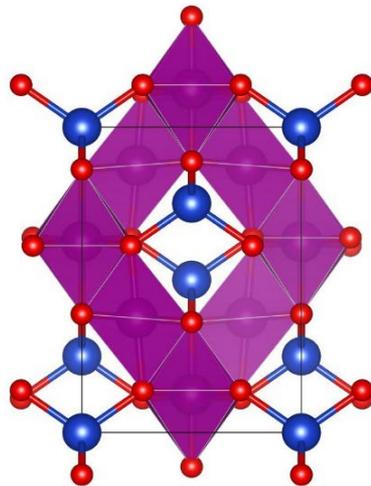
(a)  $Bi(Mn_2O_4)_4 \cdot 3H_2O$



(b)  $Cu(Mn_2O_4)_4 \cdot 2H_2O$



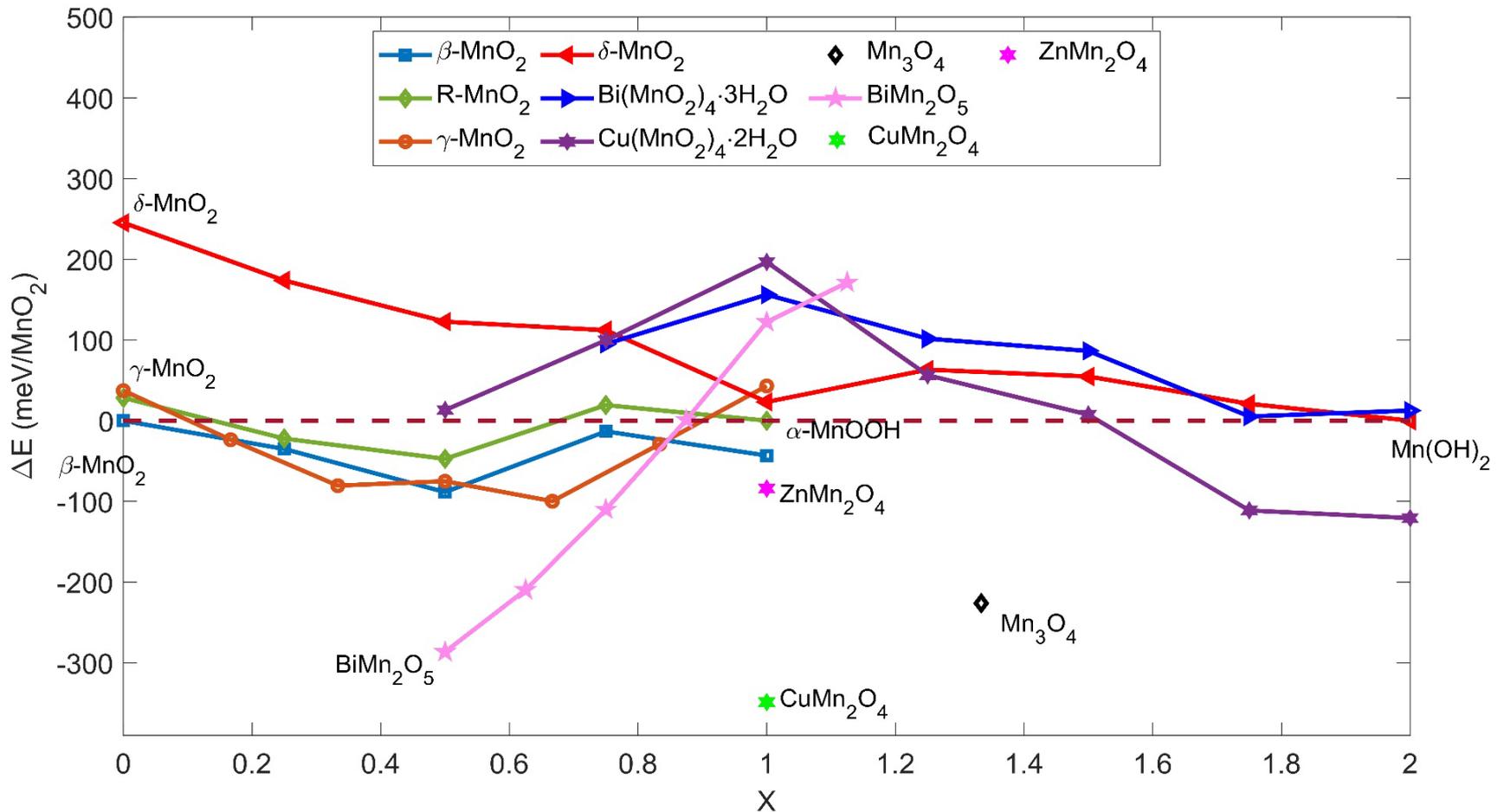
(c)  $BiMn_2O_5$



(d)  $CuMn_2O_4$

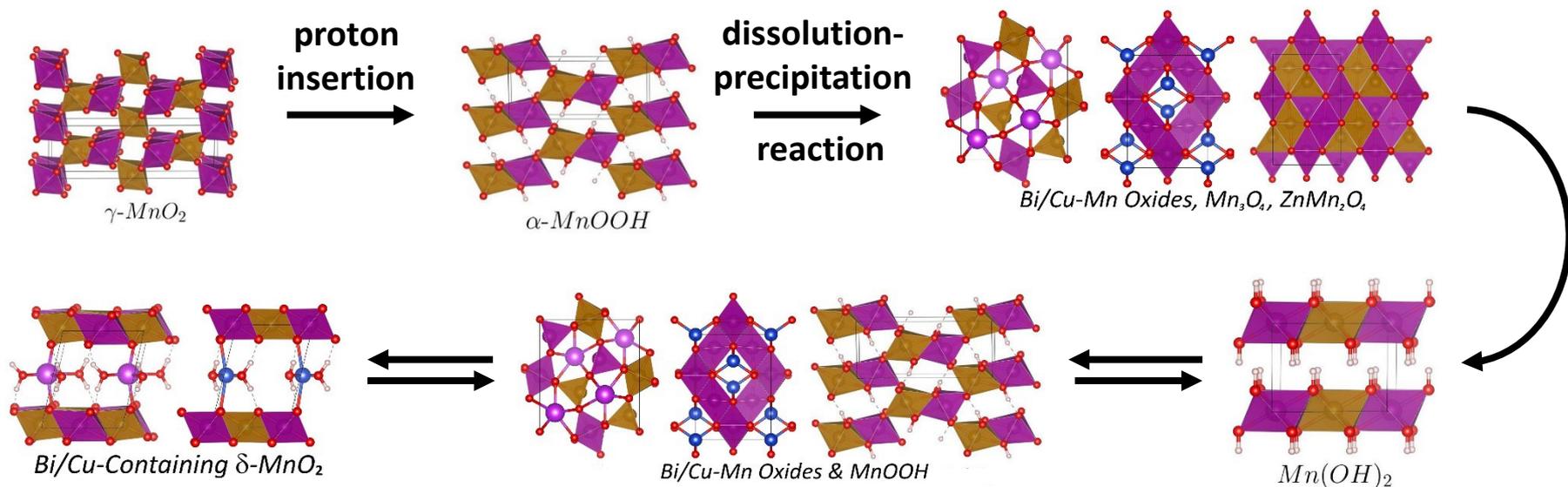
- Several different types of Bi-Mn and Cu-Mn oxide and hydroxide structures have been considered.
- Structures of Bi, Cu, and K-intercalated hydrated  $\delta$ -MnO<sub>2</sub> were modeled using MD simulations followed by structural relaxation.
- Protonated structures of Bi, Cu, and K-intercalated  $\delta$ -MnO<sub>2</sub> were obtained by inserting H<sup>+</sup> ions into the low energy positions and repeating MD simulations.
- Optimized structures of BiMn<sub>2</sub>O<sub>5</sub> and CuMn<sub>2</sub>O<sub>4</sub> were obtained using the BFGS algorithm.

# Energies of Protonated $\text{MnO}_2$ , Bi/Cu-Modified $\delta\text{-MnO}_2$ , and Bi/Cu-Mn Oxides



- Energies are plotted with respect to pyrolusite-groutite line for  $0 < x < 1$  and groutite-pyrochroite line for  $1 < x < 2$ .
- $X$  is DOD in electron equivalents.
- Lower energies correspond to more stable structures.

# Discharge-Charge Cycle of Bi/Cu-Modified MnO<sub>2</sub> Electrode



- Bi-Mn and Cu-Mn oxides are lower in energy than  $\text{MnO}_2\text{H}_x$  discharge products.
- $\text{BiMn}_2\text{O}_5$  and  $\text{CuMn}_2\text{O}_4$  are lower in energy than Bi/Cu-intercalated  $\delta\text{-MnO}_2$ .
- Addition of Bi and Cu to  $\text{MnO}_2$  suppresses the formation of  $\text{Mn}_3\text{O}_4$  and  $\text{ZnMn}_2\text{O}_4$ .
- Discharge reaction is reversible over the DOD range of  $0 \leq x \leq 2$ .
- After the first cycle,  $\gamma\text{-MnO}_2$  is converted into Bi/Cu-modified  $\delta\text{-MnO}_2$ .
- Theoretical predictions agree with the results of experimental studies.

[Gallaway et. al., *J. Electrochem. Soc.* **165**, A2935 (2018)]

[Yadav et. al, *Nat. Commun.* **8**, 14424 (2017); *J. Mater. Chem. A* **5**, 15845 (2017);  
*Mater. Today Energy* **6**, 198 (2017); *Int. J. Hydrogen Energy* **43**, 8480 (2018)]

# Summary

- *Ab initio* density-functional studies of the electrochemical properties and discharge mechanism of  $\text{MnO}_2$  in deep-cycle rechargeable alkaline  $\text{Zn}/\text{MnO}_2$  batteries.
- At low DOD, the electrochemical reduction of  $\gamma\text{-MnO}_2$  in alkaline  $\text{Zn}/\text{MnO}_2$  batteries is governed by  $\text{H}^+$  insertion into the crystal structure of  $\text{MnO}_2$ .
- At high DOD, the crystal structure of  $\gamma\text{-MnO}_2$  breaks down forming  $\alpha\text{-MnOOH}$ . After that, the electrochemical reduction of  $\text{MnO}_2$  becomes irreversible due to the accumulation of  $\text{Mn}_3\text{O}_4$  and  $\text{ZnMn}_2\text{O}_4$ .
- The addition of Bi and Cu to  $\text{MnO}_2$  suppresses the formation of  $\text{Mn}_3\text{O}_4$  and  $\text{ZnMn}_2\text{O}_4$  in the battery cathode. This effect can be explained by the formation of intermediate Bi-Mn and Cu-Mn oxide compounds, such as  $\text{BiMn}_2\text{O}_5$ ,  $\text{CuMn}_2\text{O}_4$ , and other similar structures during the battery discharge.
- Full two-electron reversible redox reaction is possible in  $\gamma\text{-MnO}_2$  and  $\delta\text{-MnO}_2$  cathodes modified with Bi and Cu. After the first cycle,  $\gamma\text{-MnO}_2$  is converted into Bi/Cu/K-intercalated  $\delta\text{-MnO}_2$ .

# Acknowledgements

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