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Discharge Mechanism of the γ-MnO_2 Electrode in Shallow-Cycled Zn/MnO_2 Batteries: An Ab Initio Study

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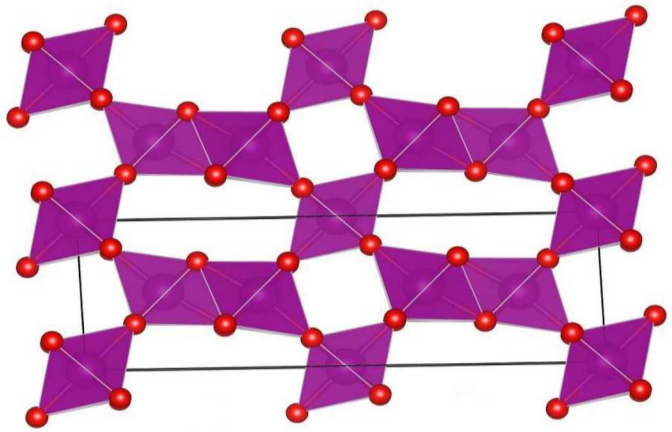
Outline

- **Background and Motivation**
- **Computational Methods**
- **Hydrogen insertion in γ-MnO_2**
- **Summary**

γ-MnO_2"intergrowth"



NM STATE UNIVERSITY

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Background and Motivation

- Alkaline Zn/MnO_2 batteries hold great promise for electrical energy storage and load-leveling power grid applications due to their high energy density, non-toxicity, and low cost.
- Development of commercially viable rechargeable Zn/MnO_2 alkaline batteries has been hindered by a short cycle life due to irreversible changes occurring in the MnO_2 cathode and Zn anode.
- Theoretical studies have been focused on the development of a computational model for accurate prediction of the electrochemical behavior of γ-MnO_2 in Zn/MnO_2 batteries.
- The main objective of this research is to analyze the relationship between the depth of discharge (DOD) and the probability of formation of irreversible redox reaction products in the γ-MnO_2 cathode.

Cathode Half-Cell reaction in Zn/MnO_2 Batteries

Electrochemical reaction (γ-MnO_2 cathode)

I) $Mn^{IV}O_2 + H_2O + e^- \rightarrow Mn^{III}OOH + OH^-$ (Reversible)

II) $Mn^{III}OOH + H_2O + e^- \rightarrow Mn^{II}(OH)_2 + OH^-$

Extensive formation of $Mn(OH)_2$ leads to further convertion of cathode to other forms such as hausmannite

$2MnOOH + Mn(OH)_2 \rightarrow Mn_3O_4 + 2H_2O$

Initial MnO_2 discharge reaction is the proton insertion in solid phase of γ-MnO_2

$MnO_2 + xH_2O + xe^- \rightarrow MnO_{2-x}(OH)_x + xOH^-$ $(0 \leq x \leq 1)$

Computational Methods

- Calculations are done using an *ab initio* computational methods based on density functional theory (DFT).

Kohn-Sham equations:

$$\left(-\frac{\nabla^2}{2} + V_{eff}[n](r)\right)\psi_i(r) = \varepsilon_i\psi_i(r)$$

$$V_{eff}[n](r) = V_{ext}(r) + \int \frac{n(r')}{|r-r'|} d^3r' + V_{xc}[n](r)$$

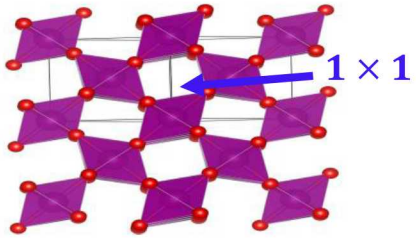
- Quantum ESPRESSO* (opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization) code for electronic structure calculations.
- Exchange correlation functional was approximated by GGA PBEsol.
- Vanderbilt ultra- soft pseudopotentials**
- Spin polarized calculations.

* http://www.quantum-espresso.org

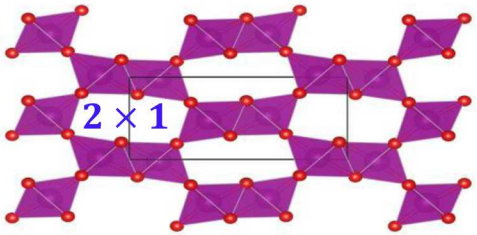
**http://www.physics.rutgers.edu/~dhv/uspp/

Stability of MnO_2 polymorphs

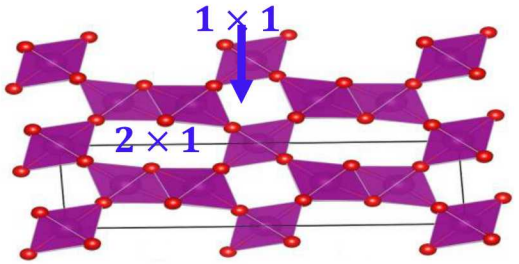
- β-MnO_2 is supposed to be the lowest energy structure



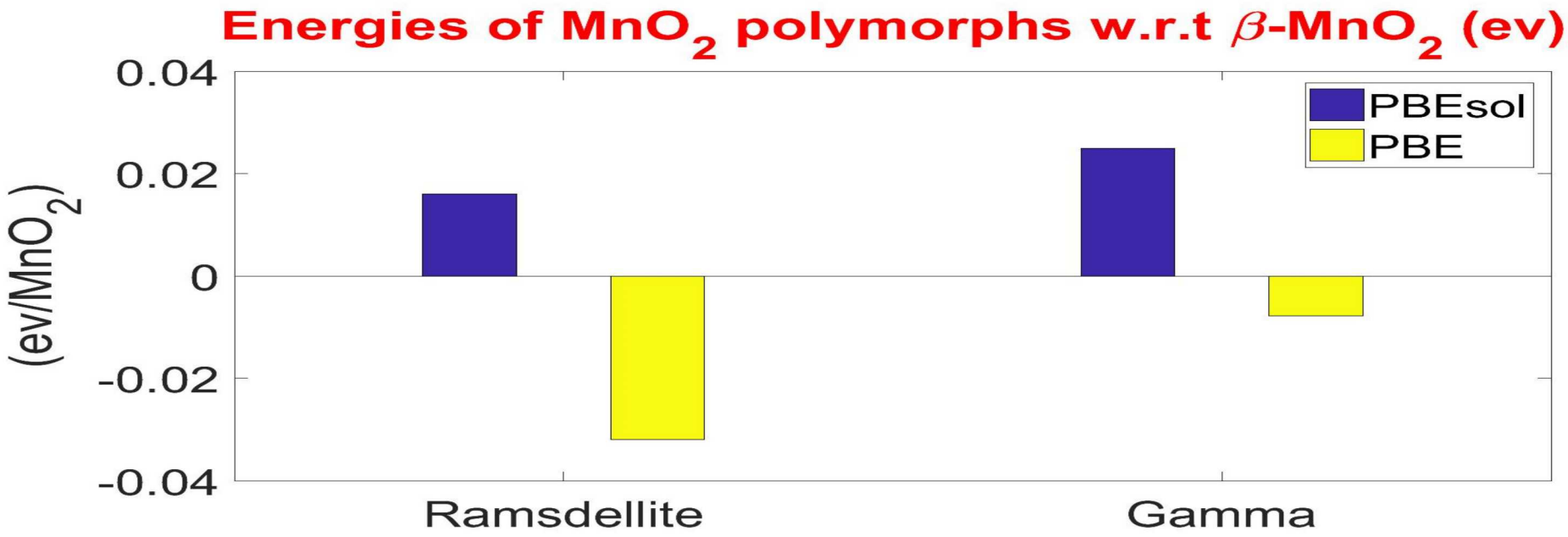
Pyrolusite (β)



Ramsdellite (R)



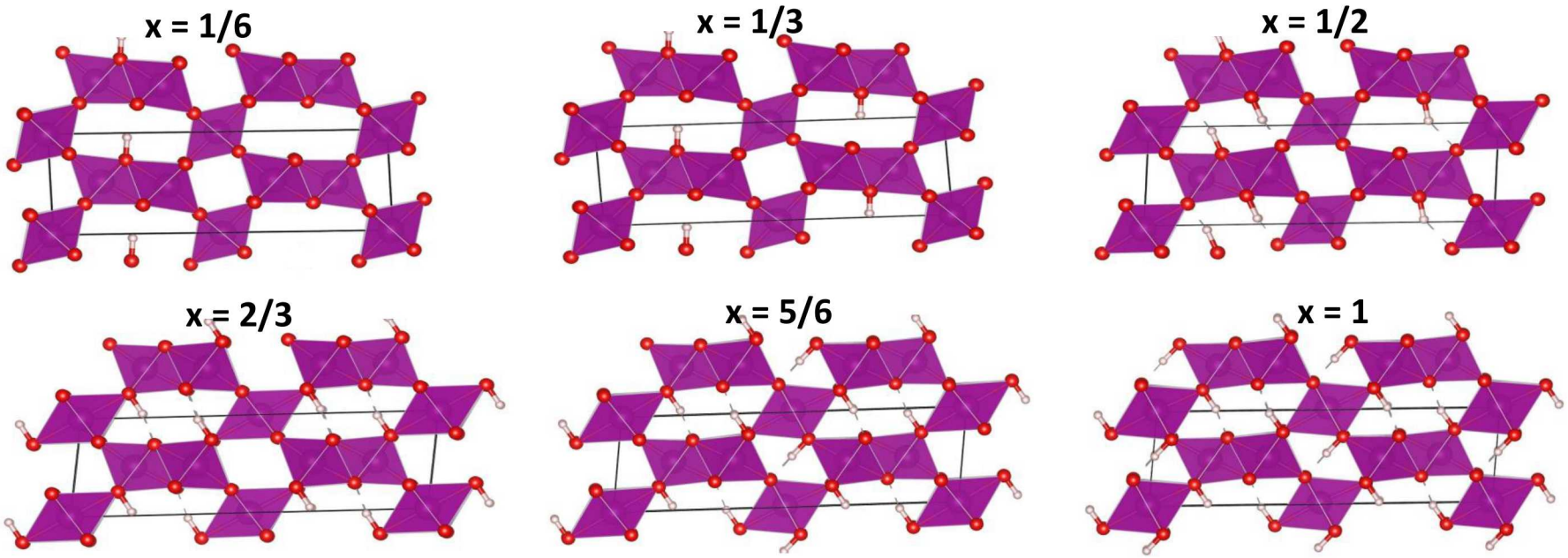
Intergrowth (γ)



- GGA PBEsol xc functional predicts the correct order of the energies of MnO_2 polymorphs

Hydrogen insertion in γ-MnO_2

Calculated Lowest Energy Structures of $MnO_{2-x}(OH)_x$ for $0 \leq x \leq 1$



- Protonation is carried out in three stages:
  - (1) One H atom is inserted in each 2x1 tunnel,
  - (2) Two H atoms are inserted in each 2x1 tunnel,
  - (3) One H atom is inserted in each 1x1 tunnel.
- Protonation produces significant structural distortions in γ-MnO_2.

Hydrogen insertion in γ-MnO_2

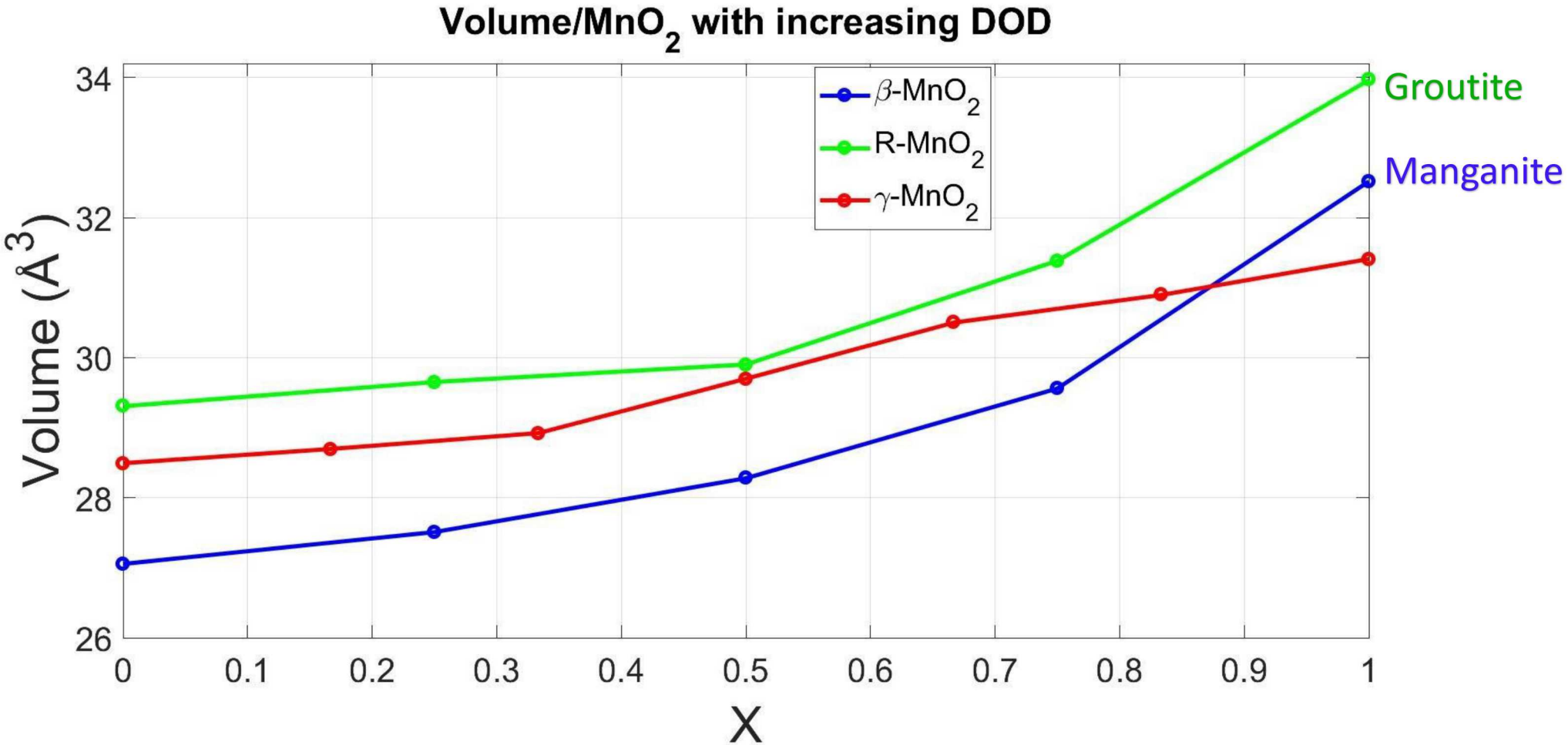
Energy and volume changes of γ-MnO_2 with increase in DOD

S.N	Structure	ΔE (ev)	ΔE/H (ev)	Å^3/MnO_2	ΔV/MnO_2 (%)
1	Mn_6O_{12}	0	0	28.4864	0
2	$Mn_6O_{12}H$	-0.9816	-0.9816	28.6923	0.72
3	$Mn_6O_{12}H_2$	-1.9402	-0.9701	28.9220	1.53
4	$Mn_6O_{12}H_3$	-2.5245	-0.8415	29.6950	4.24
5	$Mn_6O_{12}H_4$	-3.2899	-0.8225	30.5028	7.08
6	$Mn_6O_{12}H_5$	-3.4837	-0.6967	30.8996	8.47
7	$Mn_6O_{12}H_6$	-3.6667	-0.6111	31.4080	10.26

$\Delta E = E(Mn_6O_{12}H_n) - E(Mn_6O_{12}) - \frac{n}{2} E(H_2)$; n = 1,2,…,6

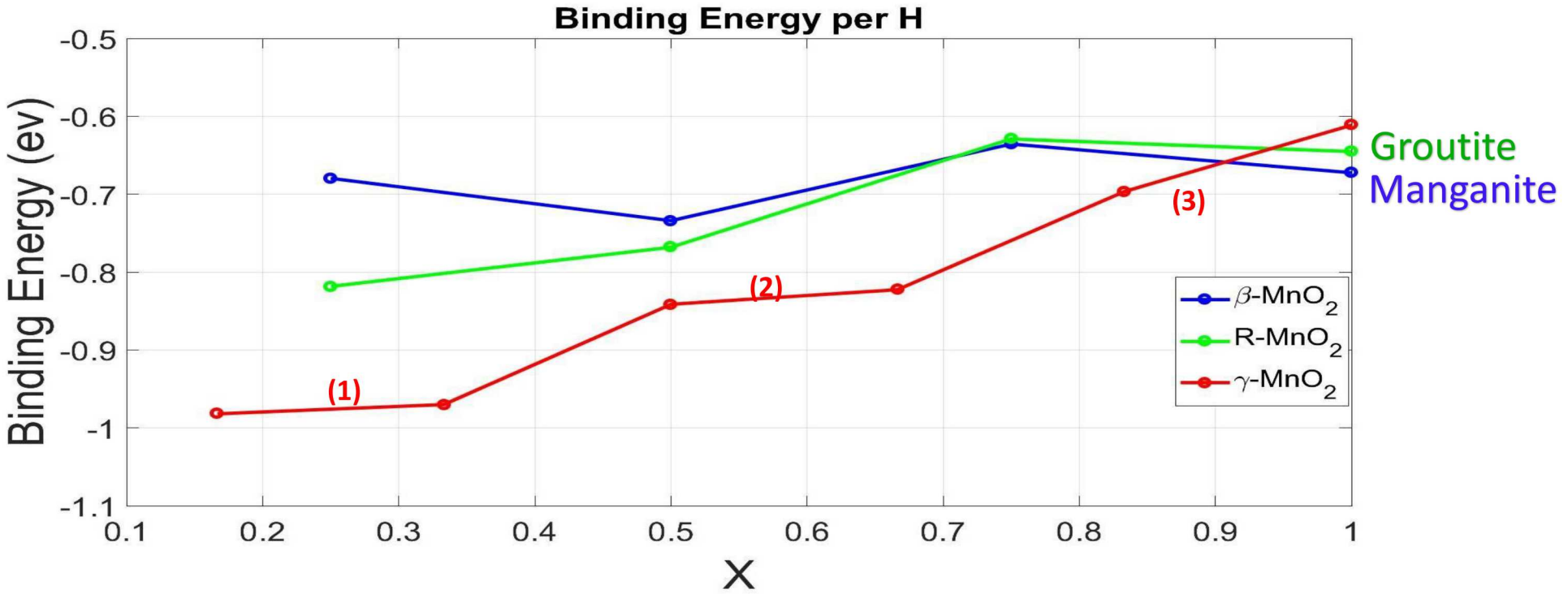
$\Delta V = [V(Mn_6O_{12}H_n) - V(Mn_6O_{12}H_{n-1})] / V(Mn_6O_{12}H_{n-1})$; n = 1,2,…,6

- Energy of H-insertion is lower for 2x1 tunnels than for 1x1 tunnels.



- Initial volumes: $V_\beta < V_\gamma < V_R$
- Volume of protonated MnO_2 phases increases nonlinearly with increasing DOD.
- For large DOD volume of protonated β-MnO_2 becomes larger than volume of protonated γ-MnO_2

Binding energy comparison with other forms of MnO_2



- For protonated γ-MnO_2 binding energy per H atom decreases significantly with increasing DOD.

$$|E_b^{stage1}| > |E_b^{stage2}| > |E_b^{stage3}|$$

- Protonated γ-MnO_2 is more stable for small value of X and becomes less stable for large X than other forms of MnO_2
- Protonation of 1x1 tunnels may leads to structural breakdown of $MnO_{2-x}(OH)_x$

Summary

- Energy of H-insertion is lower for 2x1 R-MnO_2 tunnels than for 1x1 β-MnO_2 tunnels.
- Protonation produces significant structural distortions in MnO_2 polymorphs.
- Initially, inserted protons occupy 2x1 tunnels of γ-MnO_2
- Protons insertion into 1x1 tunnels may lead to breakdown of γ-MnO_2.
- Battery life cycle can be extended by limiting protonation to one H atom per 2x1 tunnel.

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