Theoretical Studies of the Electrochemical Properties of Zn and ZnO in Rechargeable Zn/MnO₂ Batteries

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Abstract: Zinc is a promising anode material for grid-scale energy storage because of its high gravimetric capacity, low equilibrium potential, non-toxicity, and low cost. The electrochemical performance of Zn anodes in rechargeable alkaline Zn/MnO₂ batteries is influenced by the structure and composition of the ZnO layer formed on the surface of metal Zn during the battery discharge. The crystal structure of ZnO formed in Zn anodes is known to contain defects and impurities, such as Zn and O vacancies, interstitial hydrogen, and alkali metal ions. We apply *ab initio* computational methods based on density functional theory to study the structural and electrochemical properties of Zn and ZnO in rechargeable Zn/MnO₂ batteries. Our calculations show that the formation energies of charged defects and impurities in ZnO are strongly affected by the position of the Fermi level and the applied anode potential. The existence of Zn and O vacancies changes the band structure and optical properties of ZnO. The results of our study suggest that the presence of defects and impurities in ZnO has a significant impact on the electrochemical properties of Zn anodes.

Introduction

Zn has long been recognized as a promising anode material for aqueous rechargeable batteries because of its high theoretical capacity (820 mAh g⁻¹), low redox potential (−0.76 V vs. standard H electrode), high stability in ambient environments, non-toxicity, abundance, and low cost.[1-3] However, Zn anodes have demonstrated low utilization and poor rechargeability in alkaline electrolytes due to the problems associated with surface passivation and dendrite growth.[4-6]

Major challenges for Zn anodes:

- Passivation of Zn with an insulating layer of ZnO.
- Dendrite growth.
- Hydrogen evolution reaction.
- Crossover of Zn²⁺ ions to the battery cathode.

There are two types of ZnO:
- Type I: porous, loose, and white.
- Type II: nonporous, compact, light gray to black.

Research Objectives

The goal of our study is to develop a theoretical model describing the influence of structure and composition of Zn and ZnO on the electrochemical performance of Zn anodes in rechargeable alkaline Zn/MnO₂ batteries and apply this model to evaluate the role of structural defects and impurities in ZnO.

Computational Methods

- *Ab initio* computational method based on DFT.[7-9]
- Quantum ESPRESSO (opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization) electronic structure code.[7]
- Electronic bands & DOS were calculated using PBE+U.
- Optical spectra were computed using TDDFT.
- XRD simulations were performed using VESTA.

Results and Discussion
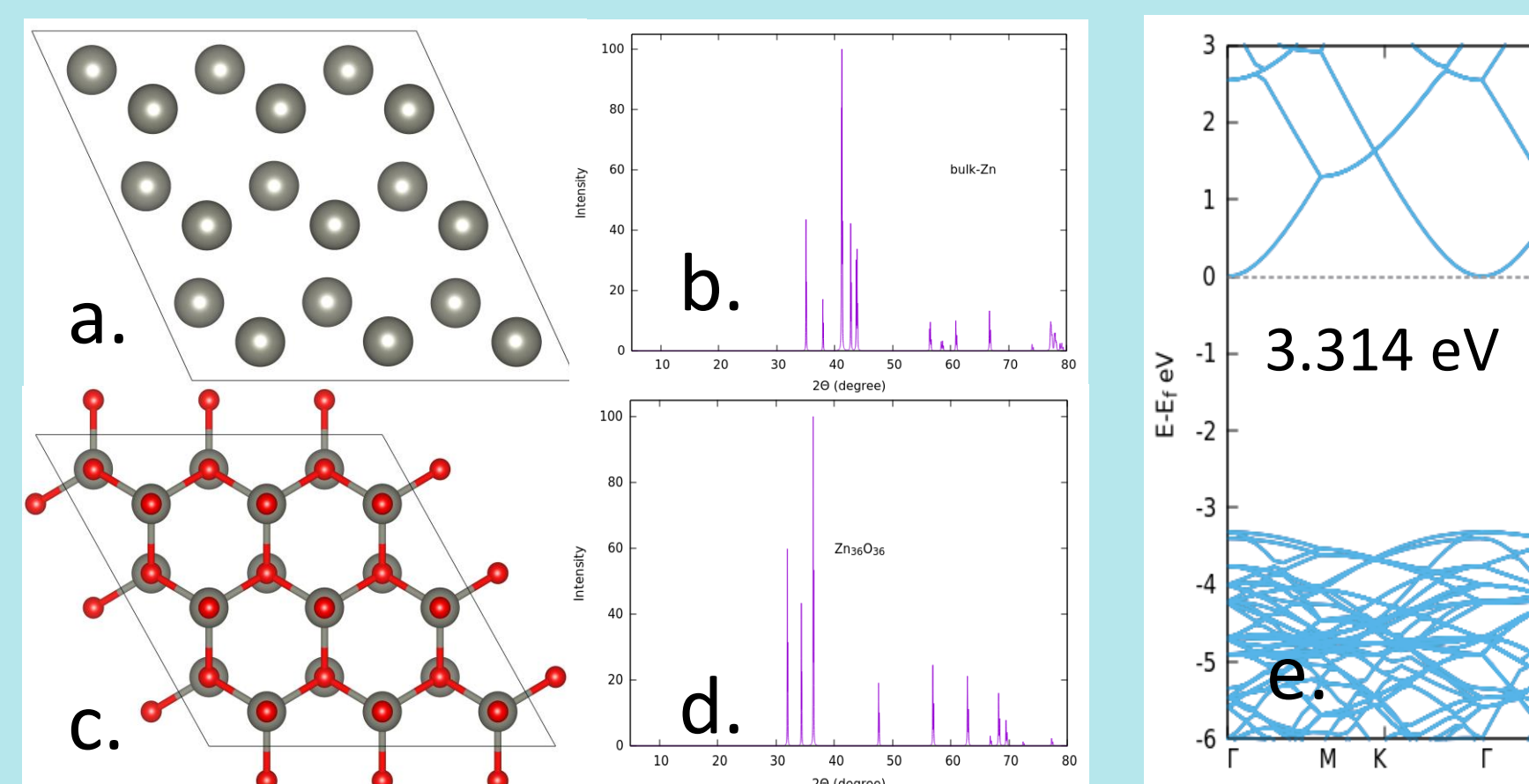
Crystal Structure & Properties of Zn & ZnO

Fig. 1. (a) & (b) Optimized structure and simulated XRD pattern of Zn. (c) , (d) & (e) Optimized structure, XRD pattern, and electronic band structure of ZnO. The calculated direct band gap of ZnO is equal to 3.314 eV.
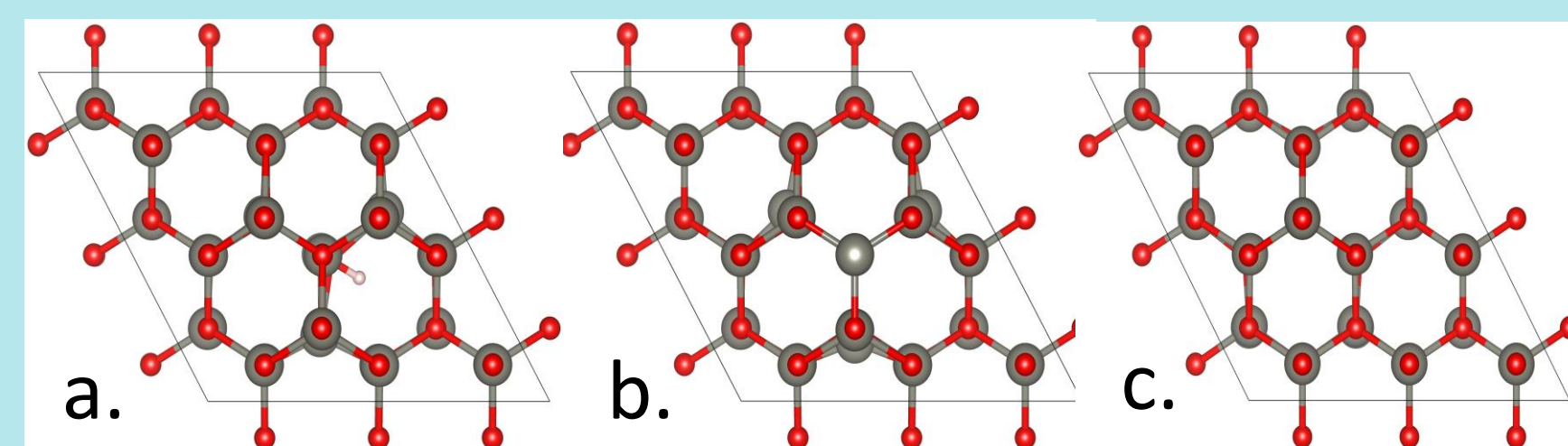
A. Neutral H, O, & Zn defects in ZnO

Fig. 2. Optimized crystal structure of ZnO containing (a) interstitial H atom, (b) O vacancy, and (c) Zn vacancy.

The formation energies of neutral H, O, and Zn defects were evaluated using the following equation[10,11]

$$E_{Formation} = E_{Defect,q} - E_{Perfect} - \sum_i n_i \mu_i$$

where n_i - number of defects of element i in a supercell, μ_i - chemical potential of element i, $n_i > 0$ for an added atom, and $n_i < 0$ for a removed atom.

	interstitial H	O vacancy	Zn vacancy
E_f (eV)	0.82	3.72	5.26

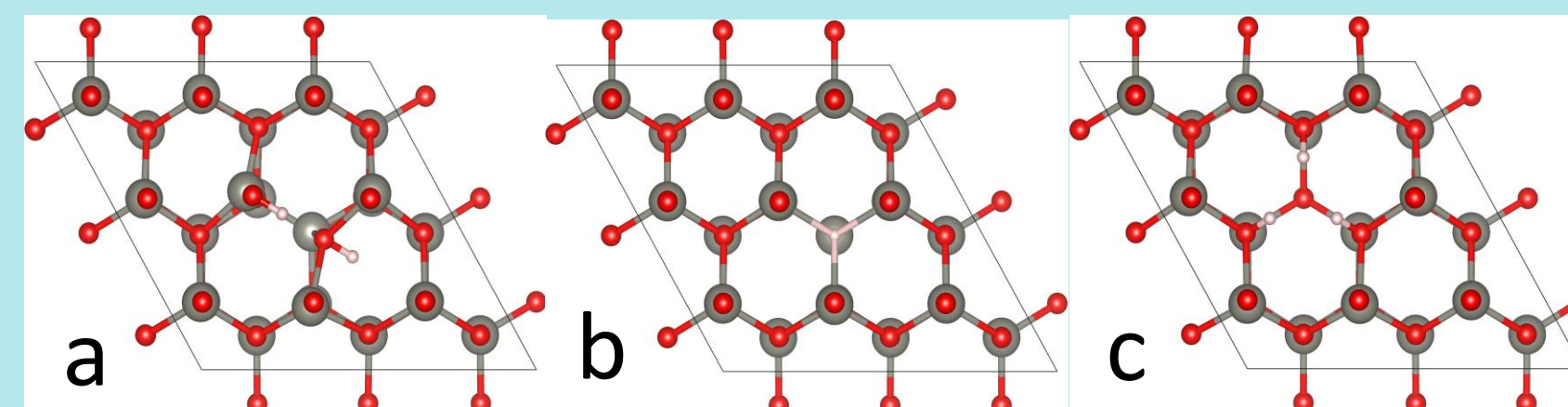### H insertion into pristine & defective ZnO

FIG. 3. Optimized structured of (a) 2 H atoms in pristine ZnO (b) 1 H atom in O-vacant ZnO, and (c) 3 H atoms in Zn-vacant ZnO.
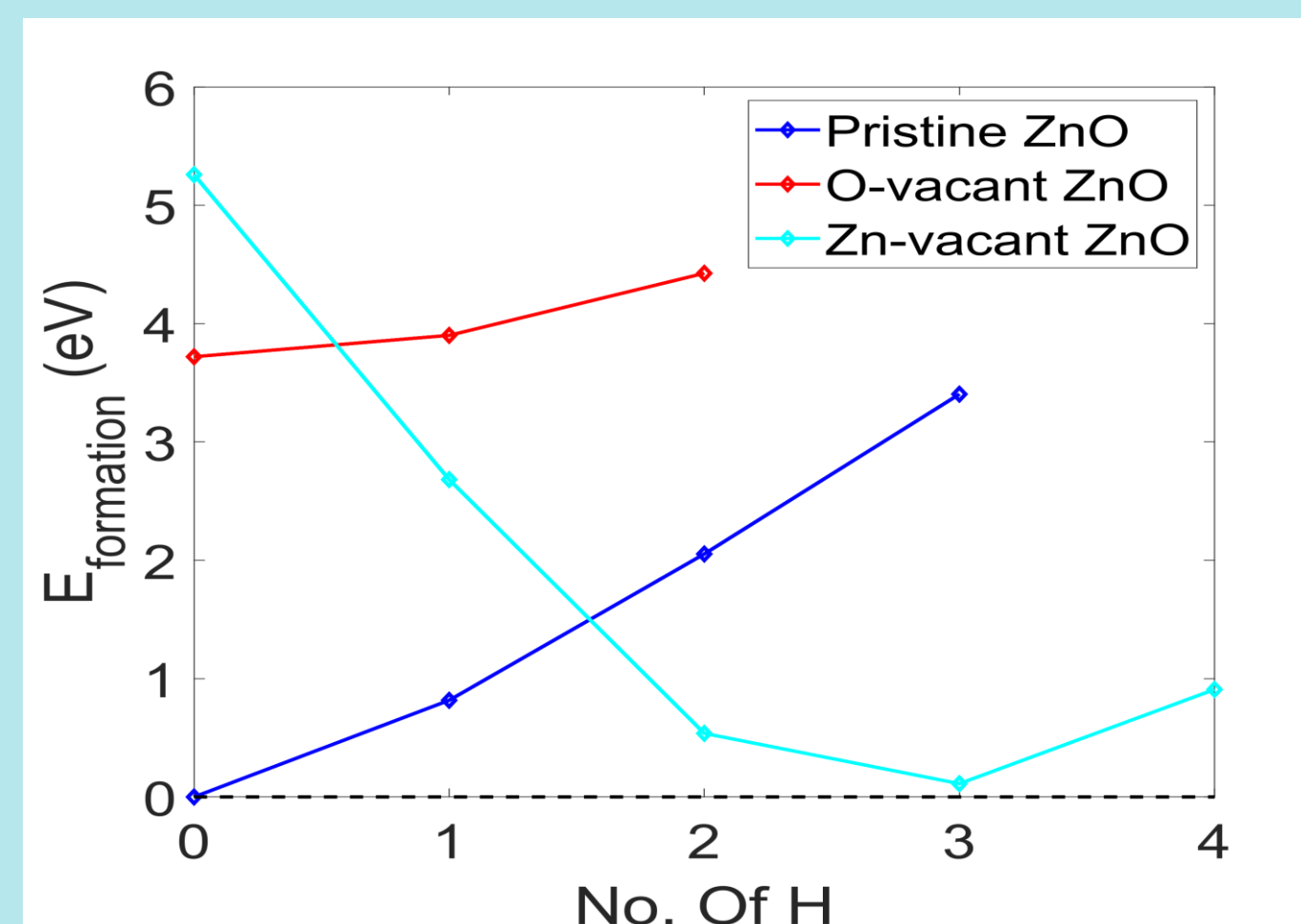

FIG. 4. Formation energies of pristine and defective structures of ZnO containing several inserted H atoms.

Our calculations show that the addition of hydrogen increases the formation energies of O vacancies and decreases the formation energies of Zn vacancies in ZnO. This result suggests that the Zn-vacant structure of ZnO can be stabilized by the inserted hydrogen.

B. Charged H, O, & Zn defects in ZnO

The formation energies of charged H, O, and Zn defects were evaluated using the following equation[10,11]
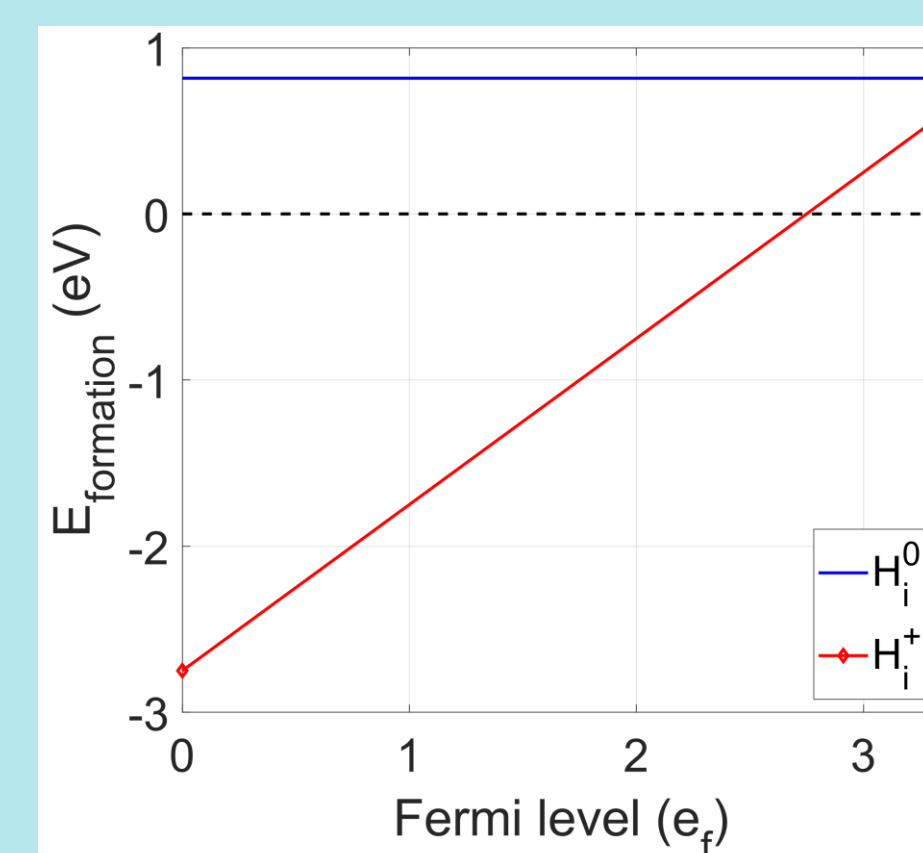
$$E_{Formation} = E_{Defect,q} - E_{Perfect} - \sum_i n_i \mu_i + q(VBM + ef)$$

where q - defect charge, VBM - valence band maximum, and e_f - position of Fermi level with respect to the VBM.

Interstitial H⁺ ion

Fig. 5. Insertion energies of interstitial H and H⁺ into ZnO as a function of Fermi level.

H⁺ ions inserted into the structure of ZnO become stable at a lower Fermi level.

Charged O vacancy state

FIG. 6. Formation energies of neutral and positively charged O vacancies in ZnO.

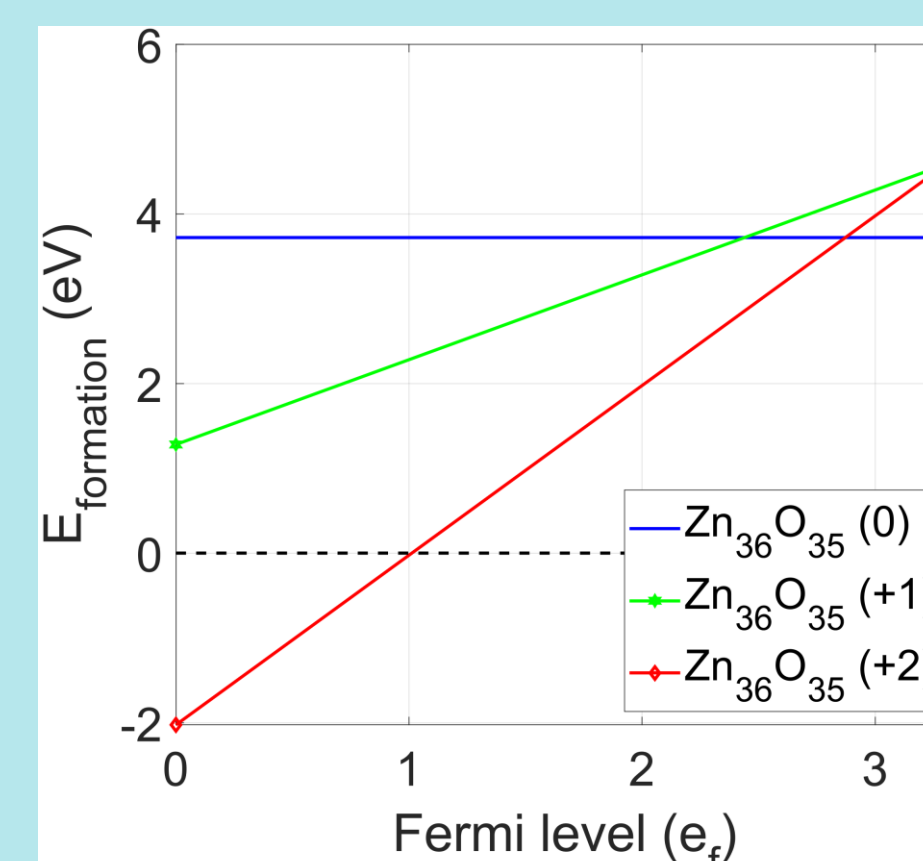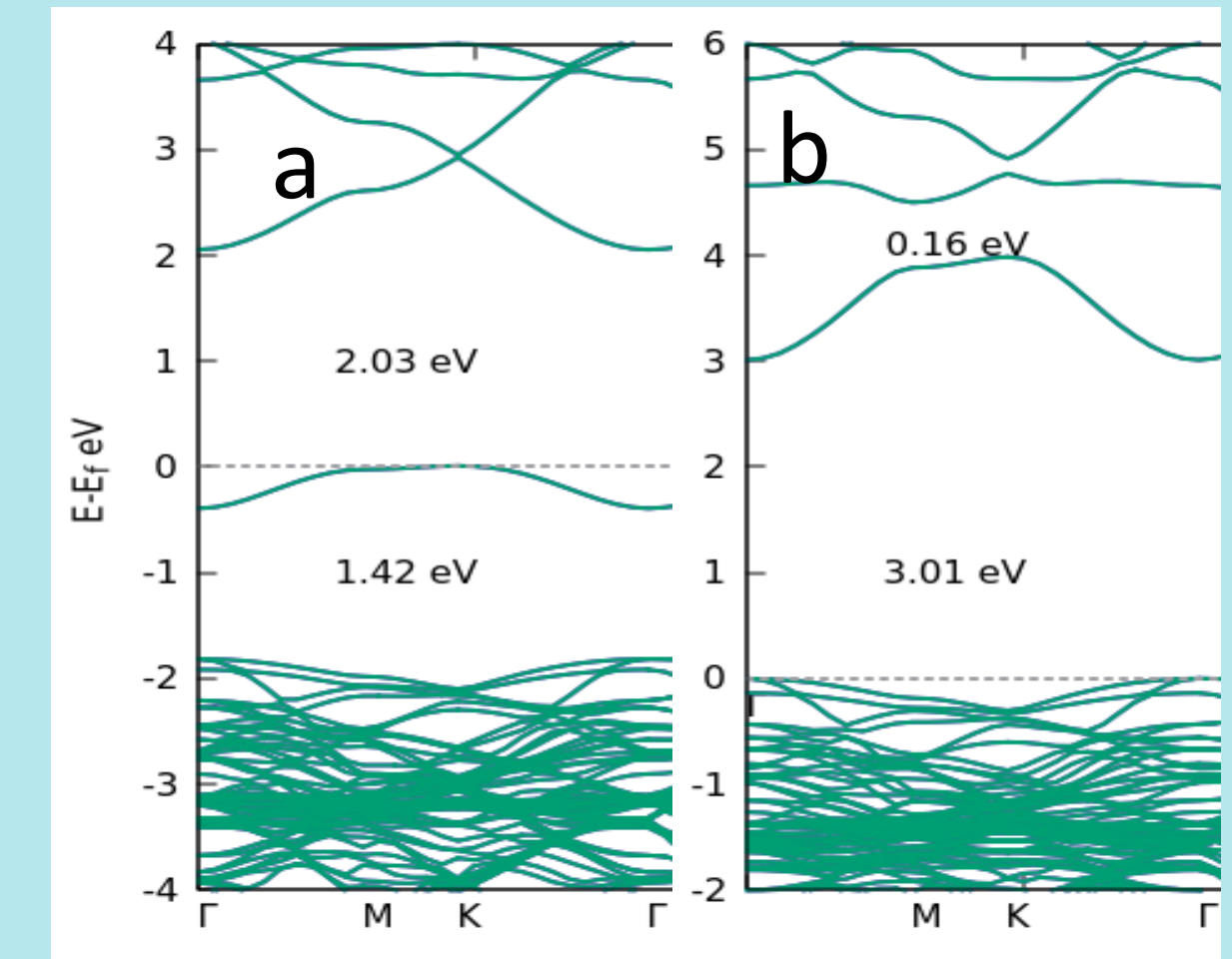Positively charged O vacancies with the charge +2 become stable in ZnO at a lower Fermi level

FIG. 7. Calculated band structures of ZnO containing neutral & charged O vacancies.

Neutral and charged O vacancies produce defect states inside the band gap of ZnO. The defect state is located near the middle of the bang gap for the neutral vacancy but is shifted upward for a positively charged vacancy.

Charged Zn vacancy state

FIG. 8. Formation energies of neutral and charged Zn vacancies in the presence of 3 inserted H atoms.

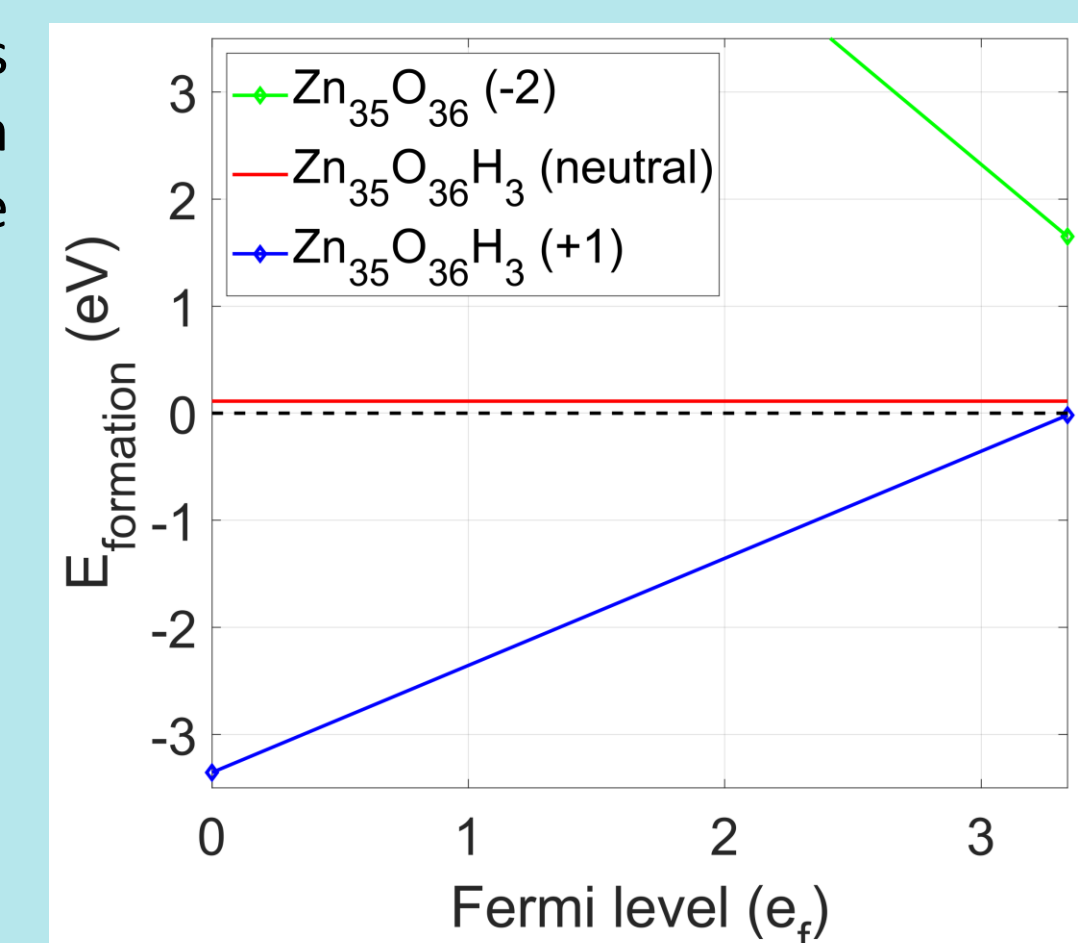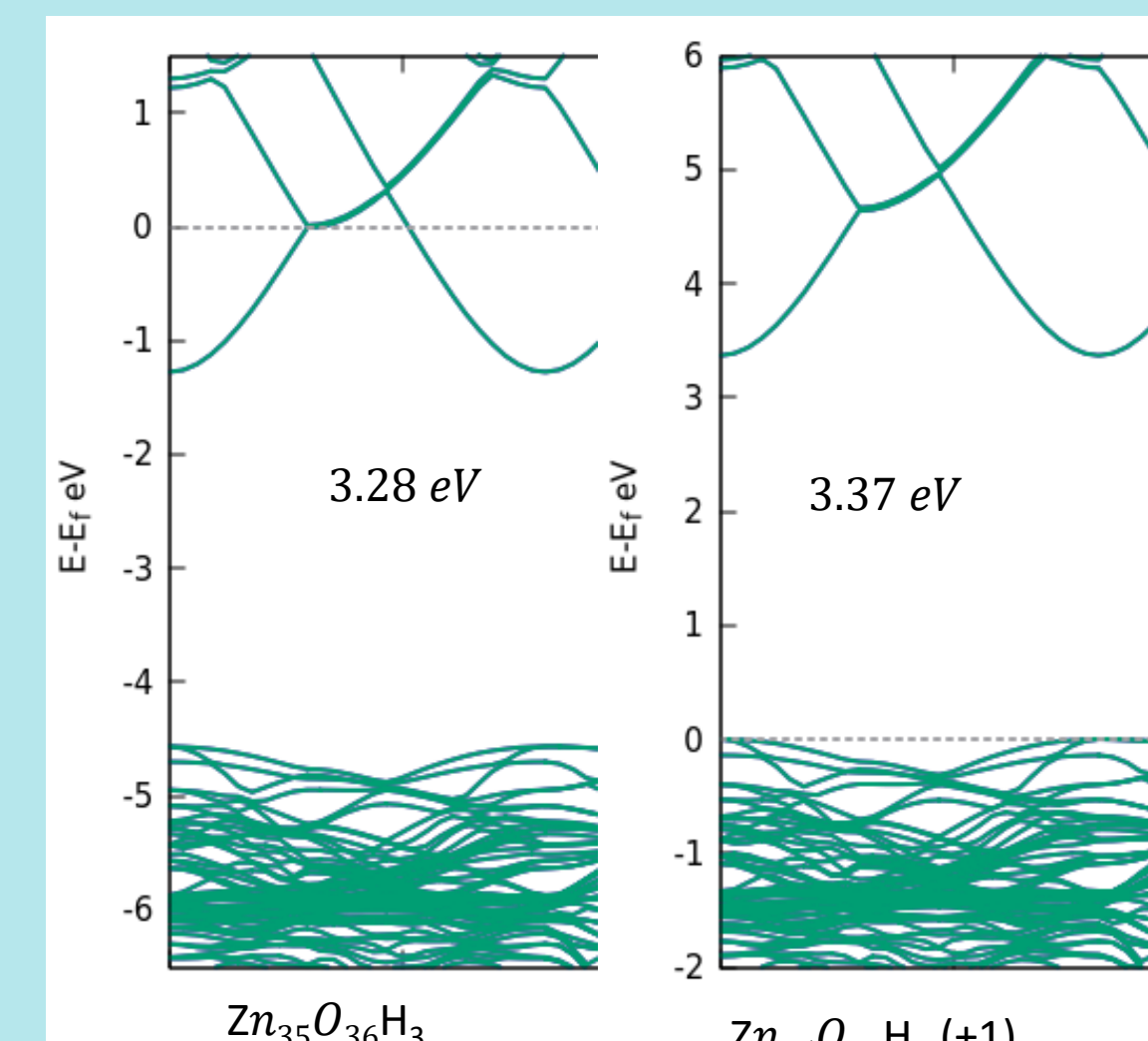Positively charged Zn vacancies in ZnO become stable in the presence of inserted hydrogen.

FIG. 9. Calculated band structures of ZnO containing neutral & charged Zn vacancies in the presence of inserted hydrogen.

Neutral and charged Zn vacancies slightly change the size of the band gap of ZnO, but do not produce defect states inside the band gap.

Summary

We applied first-principles computational methods based on density functional theory to study the structural and electrochemical properties of Zn and ZnO in rechargeable Zn/MnO₂ batteries. Our calculations demonstrated that the electrochemical properties of Zn anodes could be significantly influenced by the presence of defects and impurities in the crystal structure of ZnO. The formation energies of neutral O and Zn vacancies in ZnO were found to be 3.72 eV and 5.26 eV, respectively. The addition of hydrogen increased the formation energies of O vacancies and decreases the formation energies of Zn vacancies in ZnO. The formation energies of charged defects in ZnO were strongly affected by the position of the Fermi level. The computed electronic band structures showed that O vacancies produced defect states inside the band gap of ZnO. The mid-gap defect states could be responsible for the light absorption in visible range, which was observed in experimental studies of Zn anodes.

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