SAND2021-13169D

Ab Initio Studies of the Surface Properties of ZnO Anode Material in Rechargeable Zn/MnO$_2$ Batteries.

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Abstract: Zinc electrodes hold great promise for aqueous batteries. The performance of zinc anodes in rechargeable alkaline Zn/MnO$_2$ batteries is affected by the structure and composition of a solid-state layer of ZnO grown on the surface of metal Zn. Recent studies indicate that the crystal structure of ZnO formed in could contain a large number of defects and impurities, such as O and Zn vacancies and interstitial hydrogen. The presence of defects and impurities in the structure of ZnO has a significant impact on the electrochemical properties and rechargeability of Zn anodes. We apply *ab initio* density functional computational methods to investigate the mechanisms of defect formation in the bulk and on the surface of ZnO. Our calculations show that the formation energies of O and Zn vacancies near the surface of ZnO are lower than those in the bulk ZnO. The energies of hydrogen atoms attached to the surface of ZnO are found to be approximately 1 eV lower than the energies of hydrogen atoms inserted into the bulk ZnO. The results of our study suggest that the surface regions of ZnO have a strong influence on the electrochemical properties of Zn anodes.

Introduction

- Rechargeable alkaline Zn/ MnO$_2$ batteries are an attractive solution for grid-scale electrical energy storage due to their high energy density, non-toxicity, and low cost.[1,2]
- During the anode discharge reaction in alkaline Zn/MnO$_2$ batteries, a solid-state layer of ZnO is grown on the surface of metal Zn.[3]
- The morphology and spatial distribution of ZnO within the anode has a strong influence on the rechargeability and performance of Zn/MnO$_2$ batteries.[3,4]
- Defects and impurities on the surface of ZnO and in the bulk structure of ZnO can significantly alter the electrochemical properties of Zn anodes.
- ZnO formed in alkaline Zn/ MnO$_2$ batteries could contain O and Zn vacancies and interstitial hydrogen.

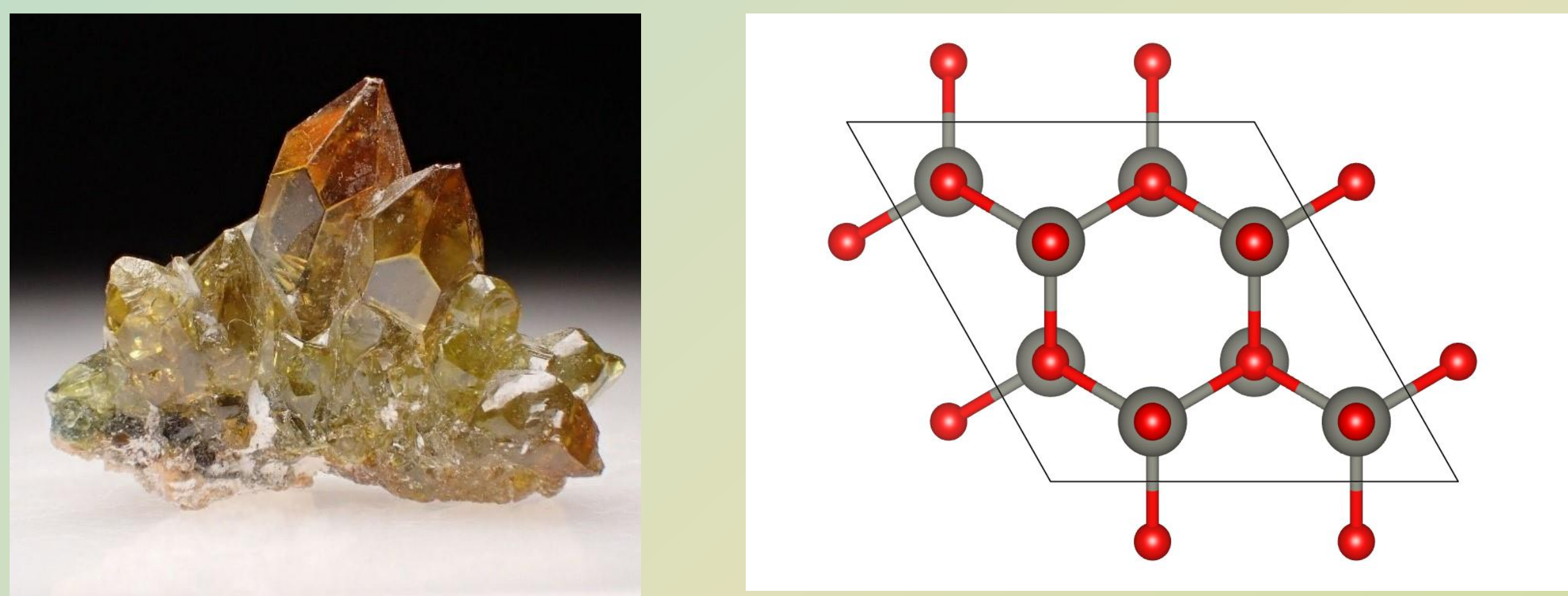

Fig 1. Hexagonal Crystal Structure of Wurtzite ZnO.

Research Objectives

The goal of this study is to study the possibility of formation of O and Zn vacancies in the bulk ZnO and on the surface of ZnO and analyze the mechanism of hydrogen addition to the crystal structure of ZnO containing surface and bulk defects.

Computational Methods

- *Ab initio* computational methods based on DFT.
- Quantum ESPRESSO (opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization) code for electronic structure calculations.[5]
- Exchange correlation functional was approximated by GGA PBEsol and PBE.[6]
- Calculations were carried out using Vanderbilt ultra-soft pseudopotentials.[7]
- Spin polarization was included in the calculations.

Results and Discussion

To study the possibility of formation of O and Zn vacancies on the surface of ZnO, we calculated the formation energies of ZnO surfaces with different orientation. After that we calculated the formation energies of O and Zn vacancies on the lowest energy surface of ZnO and compared them to the formation energies of O and Zn vacancies in the bulk ZnO. The mechanism of hydrogen addition was investigated by comparing the energies of hydrogen atoms attached to the surface of ZnO and inserted into the bulk ZnO.

A. Surface formation energy

The surface formation energy (Υ) of ZnO was calculated using the following equation:

$$\gamma = \frac{1}{2A}\left(E^S - E^B\right)$$

where:

E^S = DFT energy of the surface

E^B = DFT energy of bulk crystal

A = surface area

The optimizes structures of the three lowest energy surfaces of ZnO are shown in Figure 2.

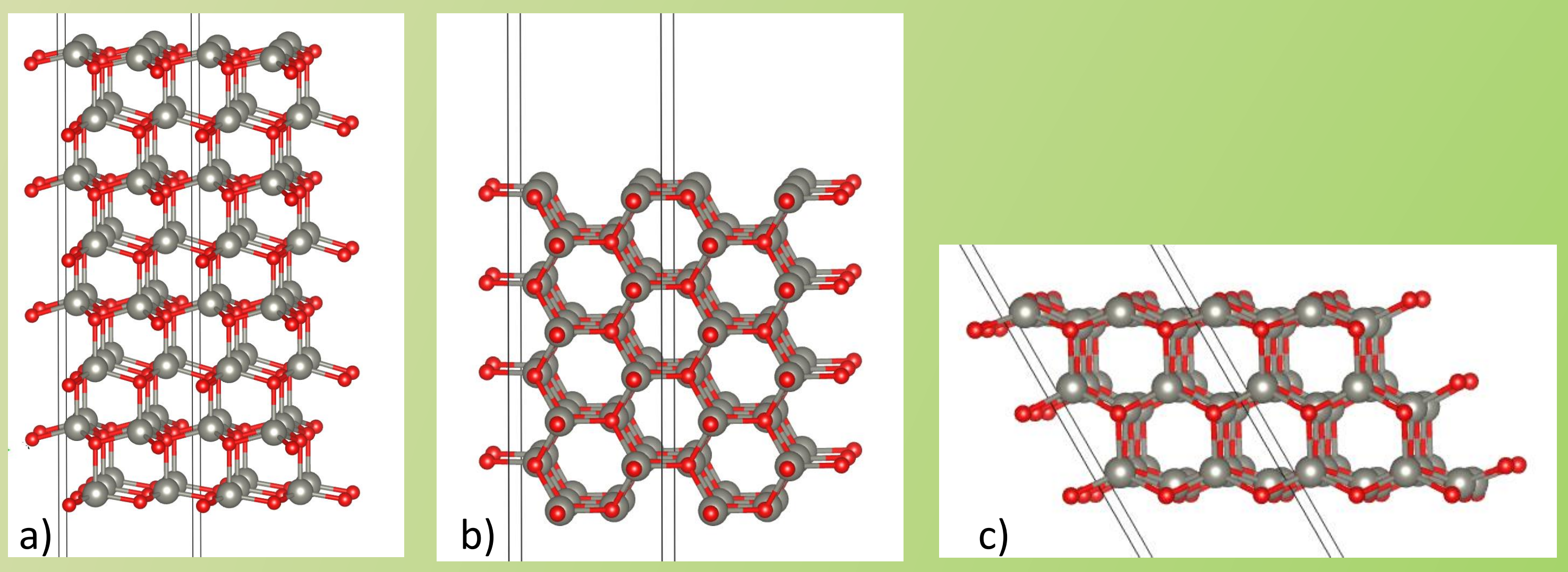

FIG. 2. Optimized lowest energy surfaces of ZnO: a) 0001, b) $11\bar{2}1$, and c) $10\bar{1}0$.

The calculated surface formation energies are listed in Table 1. Our calculations indicated that the most stable surface of ZnO was the $10\bar{1}0$ surface, which had the formation energy of 0.92 J/m^2. This result was consistent with the result of previous calculations carried out by Sung-Ho et. al.[8]

TAB. 1. Surface formation energy of ZnO.

Surface	Formation energy (J/m^2)
0001	1.14
$11\bar{2}0$	1.03
$10\bar{1}0$	0.92

B. Vacancy formation energy

The optimized lowest energy structures of the O and Zn vacancies on the $10\bar{1}0$ surface of ZnO are shown in Figure 3. The formation energies of the O ($\Delta E^S_{(O)}$) and Zn ($\Delta E^S_{(Zn)}$) vacancies on the surface of ZnO were calculated using the following relations:

$$\Delta E^S_{(O)} = E^S_{\{Zn_nO_{(n-1)}\}} - E^S_{\{Zn_nO_n\}} + \frac{1}{2}E_{\{O_2\}} \quad \Big| \quad \Delta E^S_{(Zn)} = E^S_{\{Zn_{(n-1)}O_n\}} - E^S_{\{Zn_nO_n\}} + E_{\{Zn\}}$$

where S denotes the surface and n is the number of Zn and O atoms in the supercell.

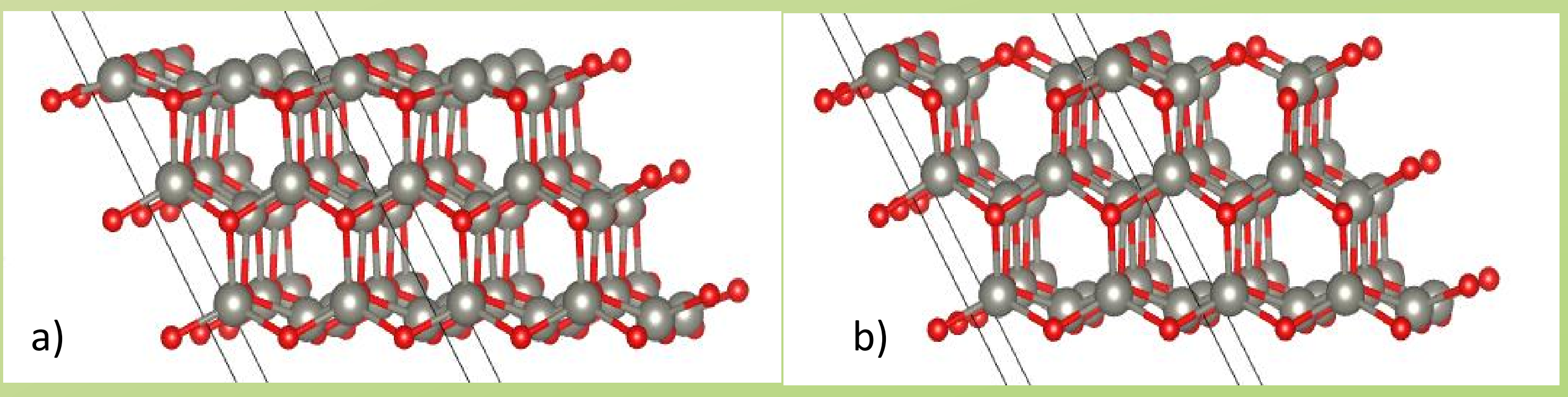

FIG. 3. Optimized structure of the $10\bar{1}0$ surface of ZnO containing (a) oxygen and (b) zinc vacancies.

The formation energies of the O and Zn vacancies on the surface of ZnO and in the bulk ZnO are compared in Table 2. Our calculations show that the O and Zn vacancy formation energies on the $10\bar{1}0$ surface of ZnO are lower than those in the bulk ZnO.

TAB. 2. Formation energies of O and Zn vacancies near the surface and in the bulk ZnO.

Type of Defects	O-Vacancy	Zn-Vacancy
Vacancy formation energy on surface	2.91 eV	4.28 eV
Vacancy formation energy in bulk	3.72 eV	5.25 eV

C. Hydrogen attachment and insertion

The optimized structures of H atoms attached to the $10\bar{1}0$ surface of ZnO containing no defects, containing an O vacancy, and containing a Zn vacancy are shown in Figure 4. The hydrogen attachment energy ($\Delta E_{(H)}$) was calculated using the following relations:

$$\Delta E_{(H)} = E^S_{\{Zn_nO_{(n-1)}H\}} - E^S_{\{Zn_nO_{(n-1)}\}} - \frac{1}{2}E_{\{H_2\}} \quad \Big| \quad \Delta E_{(H)} = E^S_{\{Zn_{(n-1)}O_nH\}} - E^S_{\{Zn_{(n-1)}O_n\}} - \frac{1}{2}E_{\{H_2\}}$$

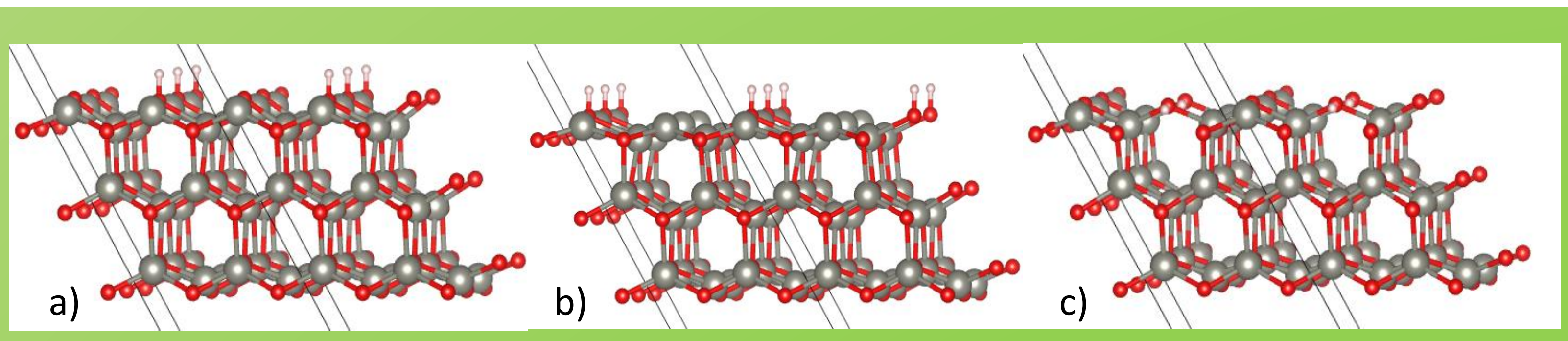

FIG. 4. Optimized structures H atoms attached to the $10\bar{1}0$ surface of ZnO (a) containing no defects, (b) containing an O vacancy, and (c) containing a Zn vacancy.

The energies of H atoms attached to the surface of ZnO and inserted in the bulk ZnO are compared in Table 3. Our calculations predicted negative energies for H atoms attached to the $10\bar{1}0$ surface of ZnO containing no defects, containing an O vacancy, and containing a Zn vacancy. The energies of hydrogen atoms attached to the surface of ZnO were approximately 0.6 – 0.9 eV lower than the energies of hydrogen atoms inserted into the bulk ZnO.

TAB. 3. Energies of H atoms attached to the Surface of ZnO and inserted into the bulk ZnO.

	Pristine crystal (eV)	Crystal with O-vacancy (eV)	Crystal with Zn-vacancy (eV)
Bulk	+0.82	+0.18	-2.57
Surface	-0.63	-0.44	-3.51

Summary

We applied first-principles computational methods based on density functional theory to study the influence of structural defects and impurities, such as O and Zn vacancies and interstitial hydrogen of the properties of ZnO. Our calculations predicted the formation energies of O and Zn vacancies on the surface of ZnO to be 0.8 – 1.0 eV lower than those in the bulk ZnO. The energies of hydrogen atoms attached to the surface of ZnO were found to be negative and approximately 1 eV lower than the energies of hydrogen atoms inserted into the bulk ZnO. The results of our study suggest that the electrochemical properties of Zn anodes in rechargeable alkaline Zn/MnO$_2$ batteries could be significantly affected by presence of defects in the surface region of ZnO.

References

1. N. D. Ingale, J. W. Gallaway, M. Nyce, A. Couzis, and S. Banerjee, Power Sources **276**, 7 (2015).
2. M. B. Lim, T. N. Lambert, and B. R. Chalamala, Mater. Sci. Eng. R Rep. **143**, 100593 (2021).
3. M. J. D'Ambrose, D. E. Turney, G. G. Yadav, M. Nyce, and S. Banerjee, ACS Appl. Energy Mater. **4**, 3381 (2021).
4. M. B. Lim, T. N. Lambert, and E. I. Ruiz, J. Electrochem. Soc. **167**, 060508 (2020).
5. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, *et al.*, J. Phys.: Condens. Matter **21**, 395502 (2009).
6. J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. **100**, 136406 (2008); Erratum *ibid.* **102**, 039902 (2009).
7. D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
8. Sung-Ho NA, et.al., Journal of the Korean Physical Society, **54**,2 (2009): 867-872.

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