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The role of negatively charged oxygen vacancies upon β -MnO₂ conductivity

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ABSTRACT

Recent years have witnessed burgeoning development in the field of electrochemical energy storage and conversion. β -MnO₂, as one of the most promising electrode materials served in batteries and supercapacitors, has stimulated intensive interest. In the present work, using hybrid functional (HSE06) approaches, we have explored the unexpected role of oxygen vacancies upon β -MnO₂ conductivity, by examining the structural properties, vacancy formation energies, and charge-state transition levels. Contrary to most transition metal oxides, we reveal that the oxygen vacancies in β -MnO₂ may act as either acceptors or donors, depending on the position of the Fermi level. The negatively charged oxygen vacancies could serve as shallow electron traps, coupled with fairly low formation energies. On one hand, they would possibly contribute to the *p*-type conductivity of bulk β -MnO₂; on the other hand, they would also form in significant concentrations in *n*-type β -MnO₂, thus acting as potential compensating centers and pinning the Fermi energy to the lower part of the band gap. Moreover, it is shown that the positively charged vacancies would act as deep donors in β -MnO₂ and are therefore unlikely to induce the *n*-type conducting behavior. All these findings suggest that the conductivity of β -MnO₂ could be effectively controlled by the internal defect engineering, which in turn offers new opportunities for manipulating the performance of β -MnO₂.

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1. Introduction

To satisfy the increasing demand for power and energy, access to electrode materials with higher energy storage capacity, faster charge–discharge rates, superior reliability and flexibility has been a focus on the development of the next-generation energy storage devices. β -MnO₂, which is characterized by its high element abundance, low cost, high theoretical capacitance in a wide working potential window [1], and environmentally friendly features, has become one of the most promising candidates for application in various areas, e.g. catalysis [2], lithium batteries [3–5], flexible supercapacitors [6], and so forth. Despite all those favorable characteristics, the poor conductivities and low practical capacitance of β -MnO₂ still hinder its practical applications [7]. Researchers have tried to exploit the full potential of β -MnO₂ via intrinsic and extrinsic modifications [1]. Among them, introducing oxygen vacancies into the bulk is one of the most efficient methods to

improve the electrical conductivity of β -MnO₂ [1]. There are two major strategies to introduce oxygen vacancies into MnO₂, i.e., atomic doping with lower valence state impurity [8,9] and annealing in reducing atmosphere [10]. Unfortunately, it remains a major challenge to introduce the oxygen vacancies into the bulk controllably [1].

Theoretical calculations represent a very powerful and efficient tool for elucidating many defect properties of semiconductors. However, to the best of our knowledge, few theoretically studies have been performed for oxygen vacancy formation in β -MnO₂, and thus, a profound understanding of the electrochemical performance of oxygen-deficient β -MnO₂ at the electronic level is still lacking. Additionally, most previous calculations regarding the properties of β -MnO₂ were within the Perdew–Burke–Ernzerhof [11] (PBE) with Hubbard *U* corrections (PBE + *U*) frameworks. It should be noted that this approach suffers from a severe underestimation of the band gap with predicted values of 0.7–0.8eV [12,13], when compared to the experimental results (1.30eV [14]). In this work, using Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional approach [15,16], the gap is reproduced accurately,

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which is also very important for determining the defect level positions and the defect formation energies. We attempt to reveal the fundamental basis for the conductivity mechanism in oxygen-deficient β -MnO₂ and evaluate its corresponding energetics, structural, magnetic and electronic properties.

In most semiconductors, it is suggested that the oxygen vacancies commonly exist in three different charge states (0, +1 and +2) [17–20], and they are typically considered as donor defects [21–23]. However, Shluger et al. have observed the negatively charged oxygen vacancies in HfO₂, where V_O^{1-} and V_O^{2-} are likely candidates for intrinsic shallow electron traps [24–27]. In this work, we will illuminate the fact that oxygen vacancies behaving as acceptors may not be interpreted as an exception, and reveal some new physical features in β -MnO₂. Using first principle calculations, we find that oxygen vacancies in β -MnO₂ are amphoteric defects, *i.e.* they could be positively and negatively ionized. It turns out that the oxygen vacancies in β -MnO₂ are capable of acting as either acceptors or donors, depending on the position of the Fermi level. Since the acceptor transition level $\varepsilon(0/-1)$ lies near the valence band maximum (VBM) and V_O^{1-} has fairly low formation energy, V_O^{1-} would possibly contribute to the *p*-type conductivity (*i.e.*, hole conductivity) of bulk β -MnO₂; or it would also form in significant concentrations in *n*-type β -MnO₂, thus acting as potential compensating centers. Furthermore, it is demonstrated that the positively charged vacancies are unlikely to cause *n*-type conductivity in β -MnO₂, because the donor levels $\varepsilon(+2/+1)$ and $\varepsilon(+1/0)$ are located deep with respect to the conduction band minimum (CBM). The systematic theoretical investigations may provide an efficient means for predicting the electronic conductivity behavior of β -MnO₂, and may be valuable to guide future experimental research in this direction.

This paper is organized as follows. The detailed calculation methodologies are described in Section 2. We first examine the electronic properties of the oxygen-deficient β -MnO₂ in Section 3.1. Then we address the formation energies, charge-state transition levels (CTL), and structural properties of the oxygen-deficient β -MnO₂, attempting to elucidate the effect of oxygen vacancies upon its conductivity (Section 3.2). In Section 3.3, to better understand the conductivity induced by oxygen vacancies in β -MnO₂, we make a reasonable comparison between oxygen-deficient β -MnO₂ and α -TiO₂ which shares the same rutile structure as β -MnO₂. In Section 4, all major results and findings are summarized.

2. Methodology

2.1. Defect thermodynamics

The defects in semiconductors or insulators usually exist in multiple charge states. The calculations for charged systems are performed within a well-defined methodology, in which a compensating uniform charge background is included to maintain the charge neutrality of the supercell [28]. The formation energy of an oxygen vacancy can be evaluated as [28,29]:

$$E^f[V_O^q] = E_{tot}[V_O^q] - E_{tot}[P] + \mu_O + q \cdot (\varepsilon_{VBM} + E_F) + E_{corr} \quad (1)$$

where $E_{tot}[V_O^q]$ is the total energy of a supercell containing the oxygen vacancy in charge state q , and $E_{tot}[P]$ is the total energy of the corresponding pristine bulk lattice. μ_O is the oxygen chemical potential. ε_{VBM} and E_F are the energy levels corresponding to the VBM and the Fermi level measured from the VBM, respectively. Additionally, E_{corr} is a correction term that accounts for the finite-size effects, including potential-alignment, image-charge corrections and band-filling corrections. The correction schemes considering those three terms were widely applied in the defect calculations for

many materials, unless otherwise stated [30–33].

$$E_{corr} = q\Delta V + \Delta E_{MP} + \Delta E_{bf} \quad (2)$$

The first correction term ($q\Delta V$) is determined by aligning the core levels of atoms far from the defect center in defective cells to that of the pristine bulk [34]. The second term (ΔE_{MP}) account for the spurious electrostatic interactions in the finite-sized cells, for which the Makov-Payne correction scheme is used in this work. The Makov-Payne scheme is typically written as [35],

$$\Delta E_{MP} = \frac{q^2\alpha}{2\varepsilon L} + \frac{2\pi q Q_r}{3\varepsilon L^3} \quad (3)$$

where α is the Madelung constant of the supercell lattice [36,37], ε is the static dielectric constant of the host, L is the linear dimension of the supercell ($L = V^{1/3}$, V is the supercell volume), and Q_r is the second radial moment of the electron-density difference between the defective and pristine cases. Recently, Lany and Zunger have modified the Makov-Payne corrections, claiming that the third-order term is around –35% to the monopole term [29,34]. The static dielectric constant is calculated to be 108 (including ionic contributions) for β -MnO₂ by using density functional perturbation theory (DFPT) [38]. So in our calculations, ΔE_{MP} amounts to 0.01 and 0.05 eV for $q = \pm 1$ and $q = \pm 2$ charged defects, respectively. The third correction term (ΔE_{bf}) is required when the defect states show resonance with the host valence or conduction band. In this case, the formation energy can be corrected by the mixed k -point scheme using the difference between the eigenvalues of the defect-induced band at special k point (weight averaged) and at Γ point [21,39,40].

We also examine the charge-state transition level (CTL), which are defined as [41–43]:

$$\varepsilon(q_1/q_2) = \frac{(E_{tot}[V_O^{q_1}] + E_{corr}[V_O^{q_1}]) - (E_{tot}[V_O^{q_2}] + E_{corr}[V_O^{q_2}])}{q_2 - q_1} - \varepsilon_{VBM} \quad (4)$$

These correspond to the Fermi-level positions at which oxygen vacancy changes its charge state. Note that these values do not depend on the chemical potentials. The position of the CTL given in Eq. (4) corresponds to the thermal ionization energy of a defect, *i.e.*, the acceptor or donor energy [21]. With the aid of experimental techniques, *e.g.* deep-level transient spectroscopy (DLTS) [44] or the temperature-dependent Hall measurements [45], the deep or shallow CTL can be detected, respectively.

The thermodynamic stability condition for β -MnO₂ imposes some restricts on the chemical potentials. The upper limit for oxygen chemical potential μ_O , which corresponds to the energy of O in a gaseous oxygen molecule, was rescaled to zero. Meanwhile, μ_O is subject to a lower limit since β -MnO₂ is required to be thermodynamically stable with respect to the formation of Mn₂O₃. However, since the crystal and magnetic structure of α -Mn₂O₃ are still under debate [46,47], we choose the formation of Mn₃O₄ as the reference for determining the lower limit of μ_O instead. The difference induced by those two choices is expected to be small in the determined region of μ_O . Thus the limitation is as follows:

$$\frac{1}{2} (3E_{MnO_2}^{bulk} - E_{Mn_3O_4}^{bulk} - E_{O_2}^{gas}) < \mu_O - \frac{1}{2} E_{O_2}^{gas} < 0 \quad (5)$$

where $E_{MnO_2}^{bulk}$ and $E_{Mn_3O_4}^{bulk}$ are the total energy of the bulk β -MnO₂ and the bulk Mn₃O₄ per molecular formula, respectively. $E_{O_2}^{gas}$ is the total energy of an isolated O₂ molecule. For the isolated O₂

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