Solid State Ionics 289 (2016) 48–54

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Enhanced interfacial proton migration on $BaZr(Y)O_3$ by molten carbonate: A first principles study

Xueling Lei [a,b], Kevin Huang [c,*], Changyong Qin [b,*]

[a] Department of Physics, Jiangxi Normal University, Nanchang, Jiangxi 330022, China
[b] Department of Biology, Chemistry and Environmental Health Science, Benedict College, Columbia, SC 29204, USA
[c] Department of Mechanical Engineering, University of South Carolina, Columbia, SC 29207, USA

ARTICLE INFO

Article history:
Received 26 October 2015
Received in revised form 10 January 2016
Accepted 24 February 2016
Available online 9 March 2016

Keywords:
Solid oxide fuel cell
Molten carbonate
Proton conductor
First principle calculation

ABSTRACT

Enhanced proton conductivity of Y-doped $BaZrO_3$ (BZY) by molten carbonate (MC) has recently been reported. To understand the phenomenon, the present work investigates the pathways and energetics of proton migration along ZrO_2-terminated (100) surface of $BaZr(Y)O_3$ without and with the presence of MC from a density functional theory (DFT) perspective. The calculations explicitly show that the proton migration on $BaZrO_3$ prefers a curved pathway with an energy barrier of 0.567 eV. In the presence of carbonate-ion, the proton migration barrier is remarkably reduced to 0.332 eV, which is in excellent agreement with 0.33 eV of the experimental activation energy for conductivity in the BZY-MC electrolyte. Overall, the enhanced proton conductivity in the BZY-MC composite electrolyte is originated from facile interfacial proton migration between BZY and MC phase.

1. Introduction

A focus of the recent development of solid oxide fuel cell (SOFC) technology toward commercialization is to lower SOFC's operating temperature from the current 700–800 °C to below 600 °C. One key to realize such reduced temperature SOFCs is to discover and employ a high-conductivity solid-oxide electrolyte. One promising class of solid oxide electrolytes is $BaMO_3$ ($M = Zr$, Ce) based perovskite proton (H^+) conductors [1–8]. Unlike conventional intrinsic H^+-conductors such as H_3PO_4, these oxide-based H^+-conductors strongly rely on the oxygen-vacancy ($V_O^{\bullet\bullet}$) and its interactions with H_2O to produce H^+-carrying specie of $OH_O^{\bullet}$, which is known as the "Grotthuss mechanism" [9]. Since the hydration reaction is exothermic, lower temperatures favor the formation of $OH_O^{\bullet}$, thus proton conductivity. This fundamental fact is interestingly synergetic with low-temperature SOFCs, making $BaMO_3$-based materials a promising low-temperature solid electrolyte candidate.

$BaZr_{0.8}Y_{0.2}O_{2.95}$ (BZY) is a representative of well-studied oxide-based proton conductors with reasonably high conductivity [4–8]. Compared with its counterpart $BaCeO_3$, BZY attracts much more attention due to its chemical stability in CO_2-containing atmospheres. However, it is hard to sinter it into a dense microstructure, rendering difficulties for practical use. Recently, we showed that molten carbonate (MC) salts infiltrated into BZY can help produce a dense microstructure [10,11]. More interestingly, such a dual-phase electrolyte exhibited an enhanced proton conductivity. Similar results have also been observed by other groups with excellent SOFC performance [12,13]. In an effort to understand this phenomenon, we proposed that $OH_O^{\bullet}$ derived from $V_O^{\bullet\bullet}$ transfers H^+ to the neighboring carbonate-ion $(CO_3)_{CO_3}^{\times}$, forming a new proton species $(HCO_3)_{CO_3}^{\bullet}$ in MC phase [10,11], through the following defect reaction (in Kröger–Vink notation):

$$H_2O_{(g)} + V_O^{\bullet\bullet} + (CO_3)_{CO_3}^{\times} = (OH)_O^{\bullet} + (HCO_3)_{CO_3}^{\bullet}. \tag{1}$$

A subsequent DFT modeling revealed that proton migration in the form of $(HCO_3)_{CO_3}^{\bullet}$ within a MC phase is a very facile process with low energy barrier [14]. However, how H^+ is transferred across the interface of BZY/MC as suggested by reaction (1) remains ambiguous at this point despite the fact that a range of computational modeling work on H^+ migration and stability in $BaMO_3$-based proton conductors has been reported in the open literature [15–18].

In the present work, we aim to understand the energetics of proton migration across the BZY/MC interface from a DFT perspective. Pathways and energetics of proton migration at the ZrO_2-terminated (100) surface of a pure BZ (BZ: $BaZrO_3$) and a BZ with MC are particularly computed and compared. The results clearly suggest that the presence of MC can significantly enhance the H^+ migration across the surface of BZ (and BZY).

2. Computational method and model

All DFT calculations conducted in this study were performed using a Vienna ab initio simulation package (VASP) [19,20] with the projector augmented wave (PAW) approach [21,22]. The exchange–correlation

---

[*] Corresponding authors.
E-mail addresses: huang46@cec.sc.edu (K. Huang), qinc@benedict.edu (C. Qin).

http://dx.doi.org/10.1016/j.ssi.2016.02.018
0167-2738/

term of electrons was described by the Perdew–Burke–Ernzerhof (PBE) functional [23]. For all surface calculations, a 4 × 4 × 1 Monkhorst–Pack sampling of the Brillouin zone was used [24]. A vacuum region of 15 Å in the *z*-axis direction was created to prevent any interaction between cells. The O $2s^22p^4$, C $2s^22p^2$, Zr $4s^24p^65s^24d^2$, $4s^24p^65s^24d^1$ of Y, and Ba $5s^25p^66s^2$ were taken as the valence electron configurations in the calculations. To ensure a high accuracy, a cutoff energy of 500 eV was chosen for the plane waves. During the structural optimization, all atoms were fully relaxed with a force less than 0.02 eV/Å. Furthermore, the D2 method of Grimme [25] was applied to calculate the dispersion interaction between carbonate-ion and surface, in which the cutoff radius for pair interactions, global scaling factor optimized at the PBE and damping parameter were taken as 15.0 Å, 0.75 and 20.0, respectively. The saddle points and migration pathways with the minimum energy were sought by the nudged elastic band (NEB) method [26]. For all the calculations, spin-polarized and dipole corrections have also been taken into account.

Calculations on energetics and pathways of proton migration were conducted on an 8-layer asymmetrical slab at the ZrO_2-terminated (100) surface. The (100) surface was selected because it has been previously determined to be the most stable surface for $BaZrO_3$ [27,28]. An asymmetrical slab was chosen to maintain a stoichiometric and neutral unit cell, which is an acceptable approach in the study of similar systems. For example, Evarestov et al. [29] showed a negligible difference in surface energy between an asymmetric and symmetric $LaMnO_3$ (110) surface slab. Liu et al. used an 8-layer asymmetric LaMnO-terminated (110) surface of $LaMnO_3$ slab in Ref [30]. Furthermore, previous studies have shown that a total of 8 layers is sufficient to simulate the surface processes on $BaZrO_3$ [27,28,31,32]. In the current model, the bottom 4 layers were fixed to represent the bulk of $BaZrO_3$, whereas the top 4 layers were relaxed and considered as the domain for adsorbed H^+ and CO_3^{2-}. On the other hand, with a ZrO_2-terminated surface, H^+ can be modeled to migrate along the edge of a ZrO_6 octahedron, which has been previously determined as a favorable pathway [33].

3. Results and discussion

3.1. Adsorption of proton on the ZrO_2-terminated surface

We started calculations by first optimizing the bulk structure with a 6 × 6 × 6 k-point mesh using the computational methods as described above. The calculated lattice constant of a cubic $BaZrO_3$ is 4.25 Å, which is in good agreement with the experimental 4.20 Å [34] and theoretical 4.24 Å [27]. The adsorption behavior of a single proton on the ZrO_2-terminated surface was then studied. A total of five adsorption sites were considered and are schematically shown in Fig. 1: (a) on the top of O atom (upright), T_O, (b) on the top of O atom (tilted to Zr atom), T_{O-Zr}, (c) on the top of O atom (tilted to hollow site), $T_{O\text{-hollow}}$, (d) on the top of Zr atom, T_{Zr}, and (e) on the top of hollow site, T_{hollow}. After a full relaxation, the $T_{O\text{-hollow}}$ configuration (c) is calculated to be the most favorable adsorption site with the lowest energy, indicating that the proton prefers to be on the top of O and tilted to the hollow site. This finding is in agreement with previous understanding on the formation of proton defects, where water from the gas phase dissociates into a hydroxide ion and a proton. The former will then fill an oxygen vacancy, while the latter forms a covalent bond with the lattice oxygen [9]. Moreover, Fig. 1(c) also indicates that the lattice oxygen deviates from its lattice position to the hollow site and that the proton tilts to the hollow site, shortening the distance between proton and its neighboring oxygen. Therefore, this geometry is in favor of the proton migration from an O to its adjacent O, so will reduce the energy barrier of proton transfer.

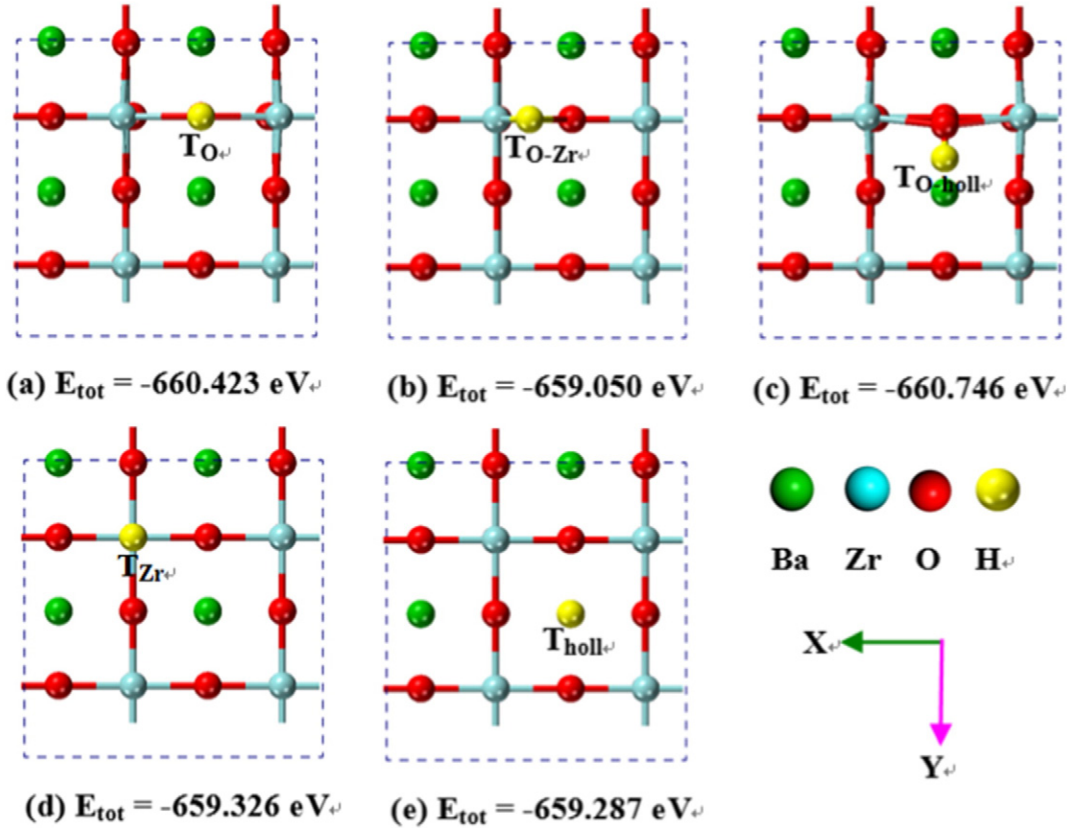

Fig. 1. Optimized structures (top view) and total energy of proton adsorbed on the ZrO_2-terminated (100) surface. (a) on the top of O atom (upright), T_O, (b) on the top of O atom (tilted to Zr atom), T_{O-Zr}, (c) on the top of O atom (tilted to hollow side), $T_{O\text{-hollow}}$, (d) on the top of Zr atom, T_{Zr}, and (e) on the top of hollow site, T_{hollow}.