Enhanced Interfacial Proton Migration on BaZr(Y)O₃ by Molten Carbonate: a First Principles Study

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Abstract

Enhanced proton conductivity of Y-doped BaZrO₃ (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 ZrO₂-terminated (100) surface of BaZr(Y)O₃ without and with the presence of MC from a density functional theory (DFT) perspective. The calculations explicitly show that the proton migration on BaZrO₃ 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.

Keywords: Solid oxide fuel cell; molten carbonate; proton conductor; first principles calculation

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I. Introduction

A focus of the recent development of solid oxide fuel cell (SOFC) technology towards 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 ($M = \text{Zr, Ce}$) 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 ($\text{V}_\text{O}^{\bullet\bullet}$) and its interactions with H_2O to produce H^+ -carrying specie of $\text{OH}_\text{O}^\bullet$, which is known as the “Grotthuss mechanism” [9]. Since the hydration reaction is exothermic, lower temperatures favor the formation of $\text{OH}_\text{O}^\bullet$, 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.

$\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.95}$ (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 $\text{OH}_\text{O}^\bullet$ derived from $\text{V}_\text{O}^{\bullet\bullet}$ transfers H^+ to the neighboring carbonate-ion

$(\text{CO}_3)_{\text{CO}_3}^\times$, forming a new proton species $(\text{HCO}_3)_{\text{CO}_3}^\bullet$ in MC phase [10-11], through the following defect reaction (in Kröger-Vink notation):

A subsequent DFT modeling revealed that proton migration in the form of $(\text{HCO}_3)_{\text{CO}_3}^\bullet$ 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).

II. 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 term of electrons was described by the Perdew-Burke-Ernzerhof (PBE) functional [23]. For all surface calculations, a $4 \times 4 \times 1$ 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 $2s^2 2p^4$, C

$2s^2 2p^2$, Zr $4s^2 4p^6 5s^2 4d^2$, $4s^2 4p^6 5s^2 4d^1$ of Y, and Ba $5s^2 5p^6 6s^2$ 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

ZrO₆ octahedron, which has been previously determined as a favorable pathway [33].

III. Results and Discussion

3.1 Adsorption of proton on the ZrO₂-terminated surface

We started calculations by first optimizing the bulk structure with a 6×6×6 k-point mesh using the computational methods described above. The calculated lattice constant of a cubic BaZrO₃ 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 ZrO₂-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-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-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 ZrO₂-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-hollow}, (d) on the top of Zr atom, T_{Zr}, and (e) on the top of hollow site, T_{hollow}.

3.2 Proton migration on the ZrO₂-terminated surface

Next, selected migration pathways and their corresponding energy barriers for the proton migration on the ZrO₂-terminated (100) surface were studied. **It should be pointed out here that the capacity of most DFT packages does not allow to treat the electronic state of proton separately from the supercell. The charge is applied to the whole system. This method of treatment would compromise to some degree the accuracy of the calculated charges, but the reaction pathways and energetics calculated are still reliable. To prove this point, we**

performed two additional NEB calculations for proton rotation around an oxygen atom with one positive charge and without charge (neutral), respectively. The results show that the energy barrier is 0.34 eV for one positive charge system and 0.33 eV for neutral system, indicating that the one positive charge added to the system has very little impact on the energy barrier of proton transport.

Fig.2 shows the migration pathways and energy profiles of H^+ along X-direction (a to b), Y-direction (c to d), and XY direction (e). For the X-direction, two independent migration pathways are possible: linear path $1 \rightarrow 2$ (labeled as “Path-1”) with the shortest migration distance and curved path from $1 \rightarrow 3 \rightarrow 4 \rightarrow 2$ (labeled as Path-2). These two migration pathways and the corresponding energetics are shown in Fig.2 (a) and (b), respectively. “Path-1” includes one-step migration and experiences an energy barrier of 1.660 eV. “Path-2” consists of three steps, marked as I, II, and III. The step I and III are related to H^+ transfer from an oxygen toward a neighboring oxygen with the bond breaking and reforming of $O-H^+$. The step II involves only H^+ rotation around an oxygen with the $O-H^+$ bond connected. The energy barriers of H^+ transfer and rotation are 0.567 eV and 0.326 eV, respectively. Therefore, the overall energy barrier for “Path-2” is 0.567 eV, which is in agreement with the activation energy of 0.69 eV for H^+ transfer observed in $BaZrO_3$ [17], mobility activation enthalpies of 0.41-0.63 eV for protonic defects in cubic perovskite-type oxides [35], activation energy of 0.3-0.6 eV [33] and 0.45-0.65 eV [36] for H^+ migration in BZY electrolytes. Evidently, the proton transfer is the rate-determining step, which agrees well with the experimental and other computational results [17-18, 37-38]. Overall, the results show that proton migration preferentially favors a curved over a straight pathway.

(a)

(b)

(c)

Fig.2 Migration pathways and energy profiles for H^+ migration along X direction (a to b), Y direction (c to d), and XY direction (e). The migration pathways are marked with arrows.

Fig.2 (c) and (d) show two more different migration pathways, labeled as “Path-3” and “Path-4”, for H^+ migration along the Y-direction. These two pathways represent H^+ migration along a linear and zigzag pattern, respectively. Fig.2 (c) shows that “Path-3” follows migration sequence $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$, consisting of a H^+ rotation step (I) followed by a transfer step (II) via the top of hollow site. The former needs to overcome an energy barrier of 0.326 eV, while a much higher energy barrier of 2.187 eV for the latter. The high energy

profile suggests that H^+ migration via this pathway be energy prohibitive. Fig.2 (d) shows the “Path-4” via $1 \rightarrow 2 \rightarrow 4 \rightarrow 3 \rightarrow 1$, consisting of a H^+ rotation step (I) followed by two transfer steps (II, III). The highest energy barrier for H^+ migration is 0.569 eV, indicating that the zigzag pathway is the favorable route for H^+ migration.

From the symmetry viewpoint, we also consider XY-direction as the “Path-5” for H^+ migration. Fig.2 (e) shows “Path-5” following a migration sequence of $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$, which consists of two H^+ rotation steps (I and III) and two H^+ transfer steps (II and IV). The highest energy barrier for this type of H^+ migration is 0.567 eV, also indicating a favorable pathway.

Based on the DFT analysis above, we now can conclude that H^+ migration on the ZrO_2 -terminated (100) surface of $BaZrO_3$ favors a curved pathway, involving both transfer and rotation of proton conduction mechanism.

3.3 Proton migration on the ZrO_2 -terminated surface with Y-doping

For practical use, Y-doping on Zr-site of $BaZrO_3$ is necessary to introduce oxygen vacancies, and the latter is the source of proton species $OH_O^\bullet$. In general, the dopant ion and oxygen vacancy tend to form defect clusters. For example, Mather and Islam [39] studied energetics of defect clusters including (i) simple pair clusters of a neighboring dopant ion and oxygen vacancy ($M_{Ce}'V_o''$) and (ii) neutral trimer clusters ($M_{Ce}'V_o''M_{Ce}'$) centered on oxygen vacancy. To have the vacancy nearby the dopant would also make the cluster model simple for least computation cost. To justify the selection of oxygen vacancy (V) with the nearest Y in a cluster, we performed energetics calculations of a neutral trimer cluster (ii) with two Y

positions: nearest and a distant V site. The results indicate that the energy of cluster with a distant Y site is 0.227 eV higher than the nearest scenario. Therefore, the model cluster with far separate oxygen vacancy and yttrium dopant is not worth further investigation.

The model for the ZrO_2 -terminated (100) surface with an yttrium on the Zr-site is shown in Fig.3 (a). We assumed that an oxygen vacancy will be created next to yttrium and this allows to examine its effect on energy barrier of H^+ migration.

Fig.3 Migration pathways and energy profiles for H^+ -migration along Y direction at Y-doped

ZrO_2 -terminated (100) surface. The migration pathways are marked with arrows.

According to the coordination environment, two types of O, denoted as A and B, are identified in the model. The A-type O bonds with Y to form a half YO_6 octahedron on the surface, while the B-type O bonds with Zr to form another half ZrO_6 octahedron on the surface. To compare with the energy barriers of H^+ migration on a perfect surface of ZrO_2 , H^+ migration along Y-direction (“Path-4”) at the defective surface was examined. The migration

pathway via $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5$ includes four steps: step I and IV represent H^+ rotation around A- and B-type O, respectively; step II and III represent H^+ transfer between two A-type O and between A- and B-type O, respectively. Energy barriers of the four migration steps are given in Fig.3 (b), with 0.266, 0.533, 0.523, and 0.340 eV for step I, II, III and IV, respectively. The total energy barrier for H^+ migration along this pathway is, therefore, 0.533 eV, which is not significantly different from 0.567 eV of the perfect surface, implying that the effect of yttrium on the energy barrier of H^+ migration on the surface is negligible. Therefore, the following DFT calculations of MC effect on H^+ migration were primarily conducted on a perfect BZ surface with ZrO_2 -termination.

3.4 Proton migration at the ZrO_2 -terminated surface/MC interface

To understand the observed enhanced proton conductivity of BZY by MC, we further calculated the energy barrier of H^+ migration at the interface consisting of a ZrO_2 -terminated (100) surface and MC using the method described above. Initially, we assess the relative stabilities of one carbonate unit adsorbing on the ZrO_2 -terminated (100) surface as a function of tilt angle as shown in Fig. 4 (a)-(c). It is found that the parallel configuration exhibits the lowest energy compared to both the tilted or vertical counterparts. Then, we optimized the adsorption structure of four carbonate units on a single unit cell as depicted in Fig.4 (d). Although the adsorption of carbonate at the interface is a dynamic process, the co-adsorption structure calculated implies that the coverage of BZY surface can be very high or almost full, providing sufficient carbonate bridging species for protons to transfer. We also noticed that the interactions between carbonate affect the adsorption structure. Since the actual process is at high temperature, the equilibrium can be easily achieved and the adsorption structure with

the lowest energy would make the most contribution to the proton transfer process. In Fig.4 (a), the original parallel structure was achieved by geometry optimization, so the result again confirms that the parallel structure is the most stable and has the most contributions to proton transfer at the BZY/MC interface.

Fig.4 The optimized adsorption structures and relative energy

Now, we focus on the migration behavior of the H^+ with the assistance of MC. The H^+ migration along the Y-direction (“Path-3”) was used as an example for illustration purpose. Fig.5 shows the pathway considered and energy barriers calculated for H^+ migration, where

(a) and (b) are the side and top view, respectively, and (c) is the energetics calculated for each migration step. The pathway consists of four individual steps: $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$. Step I ($1 \rightarrow 2$) is the H^+ rotation around an O of the ZrO_2 -terminated surface; step II ($2 \rightarrow 3$) is the H^+ transfer from surface to CO_3^{2-} , step III ($3 \rightarrow 4$) is H^+ rotation around an O of CO_3^{2-} , and finally, step IV ($4 \rightarrow 1$) is H^+ transfer from CO_3^{2-} back to surface. It is interesting to see that during the whole process of H^+ migration, CO_3^{2-} links position “2” to “1” like a bridge lying above the hollow site. Fig.5 (c) displays that energy barriers for step I, II, III and IV are 0.326, 0.281, 0.332, and 0.061 eV, respectively. The highest energy barrier is 0.332 eV, suggesting that the step-III of H^+ rotation around O in CO_3^{2-} is the rate-limiting step, whereas H^+ transfer between surface and CO_3^{2-} is relatively easy with a low energy barrier. The energy barrier of 0.332 eV for H^+ migration is in excellent agreement with 0.33 eV obtained from the conductivity measurement of a BZY-MC composite [11]. Compared to the results shown in Fig.3, the presence of CO_3^{2-} on the surface of $BaZrO_3$ has significantly reduced the energy barrier for H^+ migration from 0.567 eV to 0.332 eV. Overall, the calculations confirm that MC provides an alternative easy pathway for protons to travel along the surface of BZY. The observed enhanced proton conductivity in BZY/MC composite is, therefore, the result of a facile proton exchange between BZY and MC phase along the interface.

Fig.5 Migration pathways and energy profiles (c) for proton migration along Y direction with the aid of molten carbonate (MC), (a) is side view and (b) is top view. The migration pathways are marked with arrows

IV. Conclusion

In summary, we have for the first time studied proton migration at the interface of BaZr(Y)O₃ and molten carbonate by density functional theory calculations. Proton migration along the ZrO₂-terminated (100) surface of BaZrO₃ favors a curved path with an energy barrier of 0.567 eV. In the presence of carbonate-ion, the energy barrier is significantly reduced to 0.332 eV, which is in excellent agreement with 0.33 eV of activation energy observed in conductivity measurement. The rate-determining step is the proton transfer with the absence of MC, whereas it becomes the proton rotation around oxygen in carbonate-ion in the presence of MC. In addition, the effect of Y-doping on the energy barrier for proton migration on surface is insignificant (0.567 eV for BZ surface vs 0.533 eV for BZY surface). Overall, the enhanced proton conductivity in BZY-MC composite electrolyte is attributed to the facile interfacial proton exchange between BZY and MC phase.

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