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The strain effect on colossal oxygen ionic conductivity in nanoscale zirconia electrolytes: a first-principlesbased study

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Density functional theory calculations and first-principles molecular dynamics (MD) simulations have been performed to examine the strain effect on the colossal oxygen ionic conductivity in selected sandwich structures of zirconia electrolytes. For the KTaO₃/YSZ/KTaO₃ sandwich structure with 9.7% lattice mismatch, transition state calculations indicate that the strain effect changes the oxygen migration pathways from straight line into zigzag form and reduces the energy barrier by 0.2 eV. On the basis of our computational results, a possible oxygen ion diffusion highway is suggested. By finite-temperature MD simulations, an activation barrier of 0.33 eV is obtained, corresponding to an oxygen ionic conductivity which is 6.4×10^7 times higher than that of the unstrained bulk zirconia at 500 K. A nearly linear relationship is identified between the energy barrier and the lattice mismatch in the sandwich structures.

Introduction

Solid oxide fuel cells (SOFCs) are considered to be promising non-polluting technology for the substitution of fossil fuels and have attracted much attention because of their high conversion efficiency from chemical energy into electrical energy.^{1–10} Currently, the most commonly used electrolyte in SOFCs is yttria-stabilized zirconia (YSZ). However, since YSZ suffers from poor oxygen ionic conductivity at room temperature, the SOFCs can now only work at high temperatures ranging from 800 to 1000 °C, and their commercialization is thus severely hindered.¹¹

To improve the operational safety and thermal stability of SOFCs, much effort has been made to lower the operating temperature down to intermediate or even room temperature without sacrificing the ionic conductivity of the electrolyte and the power density. Two main approaches have been proposed to improve the SOFC performance at intermediate temperature.¹² One is to introduce novel electrolyte materials $AO_2-M_2O_3$ by optimizing the type and amount of doped M_2O_3 , in order to obtain higher ionic conductivity (the doping effect),¹³⁻¹⁷ and in

general this effect could increase the oxygen-ion conductivity by less than one order of magnitude.¹⁸ The other attempts to increase the density of grain boundaries by reducing samples from micro to nano-crystalline.^{19,20} Nevertheless, both approaches so far could not obtain a satisfactory enhancement of ionic conductivity, making it challenging to bring the SOFC operating temperature down to near the ambient conditions.

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To achieve a higher conductivity level, researchers have turned their attention to create specific hetero-interfaces by employing epitaxial thin-films. Recently, an eight orders of magnitude increase in oxygen ionic conductivity was reported by Garcia-Barriocanal et al. in a sandwich structure, the YSZ/ strontium titanate (STO) epitaxial heterostructure on the STO substrate (STO/YSZ/STO).²¹ Questions have been subsequently raised about which are the true (or dominant) charge carriers in the materials: ionic charge carriers in YSZ or electronic charge carriers in SrTiO₃?^{22,23} The evidence is currently in favour of the electronic character, which is verified in most recent tracer diffusion experiments and finite element simulations of YSZ thin films on various substrates.²⁴ First-principles-based,²⁵ empirical pair-potentials-based²⁶ molecular dynamics (MD) and even kinetic Monte Carlo simulations²⁷ indicate that the ionic conductivity enhancement is about 10⁴-10⁶ in modeled electrolytes. Besides that the specific hetero-interfaces with lattice mismatch can promote the oxygen ion migration effectively (the strain effect),^{21,28} the accumulation of the oxygen ions next to the interface area is believed to improve the ionic

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conductivity (the space-charge effect). The space charge layers influence the fast diffusion paths in polycrystalline materials with grain boundaries,²⁹ and this effect could increase the oxygen-ion conductivity by 10² in halide-based thin layers³⁰ or by less than one order of magnitude estimated in the STO/YSZ/STO heterostructure.²⁶ Obviously, the enhancements of ionic conductivity from both the doping effect and the space-charge effect are relatively smaller than that from the strain effect. In this article, therefore, we just aim at exploring the microscopic insight into the latter effect on the oxygen ionic conductivity in nanoscale zirconia electrolytes.

Interestingly, to provide a timely theoretical understanding of the origin of the huge ionic conductivity, Pennycook et al. employed a simplified model merely considering the strained zirconia with a built-in supply of O vacancies instead of the STO/YSZ/STO sandwich structure, and the strain corresponds to 8% lattice-mismatch between STO and YSZ.25 From firstprinciples finite-temperature MD simulations, they obtained an ionic conductivity enhancement that agrees well with the experimental observation. This result indicates that the lattice-mismatchderived strain plays a critical role in enhancing the ionic conductivity of the STO/YSZ/STO sandwich structure. One may naturally ask: (1) if we substitute STO with another perovskite oxide (ABO) so that the resulting sandwich structure ABO/YSZ/ABO produces an even greater strain, would it lead to a further enhancement in the ionic conductivity? (2) What is the general relation between the strain and the ionic conductivity? In addition, possible migration routes of the oxygen ions in YSZ under strain should be explored in theory.

To address the above problems, we performed comprehensive first-principles-based calculations to investigate the strain effect on the oxygen ionic conductivity in selected ABO/YSZ/ ABO sandwich structures. Our results indicate that increasing strain would lead to ionic conductivity enhancement and the strain is linearly correlated with the activation barrier of the oxygen ion migration.

Details of models and calculations

We followed the work of Pennycook et al.25 to construct the ABO/YSZ/ABO sandwich structures. To obtain a greater strain in the sandwich structure, the selected ABO should have a greater lattice-mismatch between YSZ and ABO than between YSZ and STO. To this end, we have considered a large family of transitionmetal oxides of the perovskite structures. Since zirconia has a cubic structure, the selected perovskite structure should also be cubic, and the structure of the cubic phase should be stable at room temperature, as the cubic phase is typically a hightemperature phase for perovskites. Moreover, the chosen perovskite requires a big energy gap to prevent electronic transport, because electron conduction reduces the electrical energy conversion efficiency and does harm to the SOFC system. With the above reasons in mind, cubic KTaO₃ (KTO) with an energy gap of 3.79 eV and a lattice constant of 3.98 Å would be a good choice. The lattice mismatch between KTO and YSZ is 9.7%, in comparison with 8.0% between STO and YSZ.

All first-principles calculations and MD simulations were carried out using the Vienna *Ab initio* Simulation Package.³¹ We applied density-functional theory (DFT) in the generalized gradient approximation parameterized by the Perdew–Burke–Ernzerhof function,³² along with a plane-wave basis set to describe the interaction between the valence electrons and the ion cores. Sandwich structures were built for optimizing the interior YSZ thickness, which was then used to examine the atomic motion in strained YSZ, and to be the starting point for the MD simulations.

In the optimization, the structural relaxations without symmetry constraints were carried out until the Hellmann–Feynman force on each atom reduces by less than 10^{-2} eV Å⁻¹, while self-consistent procedures were done with a convergence criterion of 10^{-5} eV in energy, and the cutoff energy of 400 eV was found to be good enough for numerical convergence with an $8 \times 8 \times 8$ Monkhorst–Pack *k*-mesh grid. A climbing-image nudged elastic band (cNEB) method^{33,34} was used to locate the transition states (TS) of oxygen hopping.

As for the MD simulation, the Car–Parrinello MD simulation is a powerful technique to study the microscopic nature of atomic motion in crystals. The diffusion constants of oxygen ions can be analyzed microscopically with the structural information. The Nosé algorithm was applied to control the temperature. A supercell composed of three unit cells in the two lateral directions and two optimized unit cells in thickness was used. Only the Γ point in k space was included in bulk MD simulations. An atomic motion time step of 3.6 femtoseconds was used so that no atom could travel further than 0.1 Å per time step. The computed systems were cooled from 2200 K to 0 K at a rate of -2 K per step. The simulations of diffusion were performed up to 2000 steps, and a total simulation time of 7 picoseconds was found to be long enough to accurately determine the diffusivity.

Results and discussion

Transition state search for oxygen ion hopping routes

In Fig. 1a, we present the optimized structure of cubic bulk zirconia with a lattice constant of 5.129 Å at 0 K, which is very close to the experimental values of 5.090 $\text{\AA}^{35}_{,35}$ 5.11 $\text{\AA}^{36}_{,35}$ and a theoretical value of 5.106 Å.37 In YSZ, the addition of yttrium atoms replaces some of the Zr ions in the zirconia lattice and produces oxygen vacancies, which permit YSZ to conduct oxygen ions. To avoid any correlation effect between the vacancy and other defects, we followed the method of Hirschfeld and Lustfeld³⁷ to simplify YSZ as a pure zirconia with only one vacancy in the unit cell. There are three possible pathways for direct oxygen ion migration in zirconia and only the first nearest neighbor hopping (route R_0 in Fig. 1) from one tetrahedron to a neighboring one needs to be considered. The calculated energy barrier for this pathway is 1.66 eV, which is so high that it makes O hopping very difficult. This would be the reason why the working temperature of the zirconia-based electrolyte in SOFCs has to be no less than 800 °C.



Fig. 1 Simulation models of (a) unstrained zirconia, (b) top-view and (c) sideview of zirconia with 9.7% strain. The expansive strain is in the *x*-*y* plane. Open circles stand for oxygen vacancies, and green and red spheres for Zr and O atoms, respectively.

Then we study the oxygen ion migration in strained zirconia with 9.7% lattice mismatch by KTO. Geometric structures based on the simplified model of Pennycook *et al.*²⁵ were optimized before and after O hopping in transition state calculations. Our results showed that the O ions in the unstrained zirconia are located in straight lines, in contrast, the O ions in the strained zirconia deviate from their original positions and are distributed in zigzag forms (see Fig. 1).

Surveying all the O hopping pathways, we have found 8 possible routes in 9.7%-strained ZrO_2 as shown in Fig. 1 (routes R_1-R_8). These routes can be classified into three groups according to the energy barriers: 1.42 and 1.44 eV for R_3 and R_6 ; 4.06, 4.13, 4.48, and 4.54 eV for R_1 , R_2 , R_4 , and R_8 ; as well as 7.67 and 8.09 eV for R_5 and R_7 , respectively. Obviously, the energy barriers for the latter two groups are too high for O ion migration.

The appearance of the oxygen zigzag distribution breaks the original zirconia symmetry and changes the O hopping pathways from isotropic in unstrained zirconia to anisotropic in strained zirconia. When zirconia is 9.7% strained by KTO, the energy barrier of O hopping to a neighboring vacancy drops from 1.66 eV (R₀) to 1.42 eV (R₃) or 1.44 eV (R₆), which is lowered by about 0.22-0.24 eV. In a recent experimental study,³⁸ a decrease in energy barrier by 0.14 eV was reported when the layer thickness is reduced from 200 nm down to 24 nm. Thus, the strain effect is more effective than the thickness effect in improving the oxygen ionic conductivity. We suggest " R_3 - R_6 - R_3 - R_6 ..." to be the possible oxygen ion diffusion highway in the strained zirconia, with energy barriers of 1.42-1.44-1.42-1.44... eV, which has a great advantage over the oxygen diffusion route in unstrained zirconia (R₀-R₀...; 1.66-1.66... eV). It should be noted here that the reported oxygen ion diffusion highway is located in the interior of the strained zirconia and please refer to a pioneering study that employed a similar DFT/NEB method to provide a systematic mechanistic explanation of the biaxial lattice strain effect in the YSZ, which is actually much more complicated in terms of the oxygen vacancy migration.²⁷ To fully understand the atomic mechanism of the oxygen ionic conductivity at the interfaceregions of the sandwich structure, a much bigger supercell with several fully-relaxed layers of ABO and YSZ should be used, however, the computational demands of first-principles calculation are extremely high. Although the static atomistic simulations based on empirical pair-potentials are claimed to be capable of handling such larger structural models,²⁶ the accurate description of the electronic charge carriers in the electrolytes is hard to achieve, especially at a microscopic level to search the oxygen migration paths. Without very expensive computations aiming at reproducing the real experimental observations by considering the doping and space-charge effects and vacancy-vacancy interactions all together, the oxygen ion diffusion highway and the reduced energy barrier by about 0.2 eV obtained in the present work would be meaningful to clearly elucidate the strain effect on colossal oxygen ionic conductivity.

Molecular dynamics simulations

In order to take into account the temperature effect on the oxygen ionic conductivity, we performed first-principles finitetemperature MD simulation. To test the accuracy of our method, we first repeated the previous work of Pennycook et al.²⁵ on the STO/YSZ/STO sandwich structure (8.0% lattice mismatch) and obtained an activation barrier of 0.45 eV, which agrees well with the reported value of 0.4 \pm 0.1 eV.²⁵ We then proceeded to replace SrTiO₃ by KTaO₃ with 9.7% lattice mismatch and expected that this would lead to an even larger enhancement in oxygen ionic conductivity. The oxygen ion mobility is obtained by calculating the mean square displacement (MSD) of the oxygen ions at different temperatures, ranging from 1000 to 2500 K. The MSDs are plotted as a function of simulation time in Fig. 2. For each given temperature, the MSD displays almost linear time dependence, implying that the oxygen ions diffuse with time at a nearly constant rate. For each given simulation time, the MSD increases with increasing temperature, indicating that the oxygen ions diffuse faster with elevated temperature. By comparison, the MSD of



Fig. 2 MSDs of oxygen ions during MD simulations at various temperatures. Inset: Arrhenius plot of the diffusivity coefficient from the strained MSDs (Å² ps⁻¹). The linear fit shown in green yields an energy barrier of 0.33 ± 0.1 eV. Right panels: Snapshots of the strained O sublattice at 1000 K with complete disorder, in contrast to the unstrained zirconia in which most O atoms simply oscillate on the cubic-fluorite positions. O atoms are shown as small red balls, and Zr atoms as big green balls. The 9.7% expansive strain is in the plane of the page.

O ions in unstrained zirconia is very small on the same time scale even at 2500 K.

The oxygen ion migration can be further described by the height of the energy barrier. Oxygen diffusivity can be calculated from the MSDs using the Einstein relation $\langle r^2 \rangle = 6Dt$, in which $\langle r^2 \rangle$ is the MSD of the oxygen ions, D is the diffusivity coefficient, and t is the simulation time. The energy barrier $E_{\rm b}$ is obtained by fitting the Arrhenius plot (the inset in Fig. 2) to the expression $D = D_0 \exp(-E_{\rm b}/kT)$, where D_0 is the pre-exponential factor, k is the Boltzmann constant, and T is the temperature. As expected from the simplified model, the activation barrier for KTO/YSZ/KTO (9.7% lattice mismatch) is 0.33 eV, which is smaller than 0.45 eV for STO/YSZ/STO (8.0% lattice mismatch). Lower activation barrier means easier oxygen ion migration and more frequent O hopping in the zirconia sublattice. Following the treatment of Pennycook et al.,25 we estimated the oxygen ionic conductivity for KTO-strained zirconia to be 6.4 imes 10^7 times higher than that of the unstrained bulk zirconia at 500 K, which is about 18 times larger than the estimated enhancement (3.6×10^6 times) for STO-strained zirconia. Based on our theoretical findings, we expect that KTO/YSZ/KTO sandwich structure is a very promising material for intermediate temperature and even room temperature electrolytes. We are looking forward to experimental confirmation in the near future. Snapshots of MD simulations of unstrained ZrO2 at 2500 K and the 9.7% strained structure at 1000 K are also shown in Fig. 2. The structure of unstrained cubic ZrO₂ at a very high temperature of 2500 K indicates that most O ions still display relatively localized oscillations around the cubic-fluorite tetrahedral positions, while 9.7% strain results in a completely random O sublattice at a low temperature of 1000 K.

Our result confirms that the lattice-mismatch-derived strain plays a critical role in enhancing the ionic conductivity of the ABO-strained ZrO₂ structure. Although we have chosen KTaO₃ as a prototype to provide strain in the ABO/YSZ/ABO structure and achieved giant enhancement in the oxygen ionic conductivity, this recipe would be general and workable for other perovskites or even non-perovskites if they meet the requirements mentioned in the Details of models and calculations section. This drives us to explore other epitaxially grown sandwich structures, such as Al₂O₃/YSZ/Al₂O₃. As shown in Fig. 3, the calculated activation barrier for Al₂O₃-strained ZrO₂ (4.0% lattice mismatch) is 0.64 eV, corresponding to an oxygen ionic conductivity 4.4×10^4 times higher than that of unstrained zirconia at 500 K. Moreover, a nearly linear relationship is revealed in Fig. 3 between the activation barrier and the lattice mismatch in the ABO/YSZ/ABO sandwich structures. This would provide a useful guideline to search for a new sandwich structure with even greater oxygen ionic conductivity.

Further exploration of the role of strain

In both the calculations on STO-strained zirconia by Pennycook *et al.* and our calculations on KTO or Al_2O_3 -strained zirconia, the thickness of zirconia was chosen to be 1 nm, which is the experimental value for YSZ in STO/YSZ/STO and corresponds to two unit cells. To further reduce the energy barrier, we could in



Fig. 3 Energy barriers of zirconia with different strains. Unstrained zirconia is in red, Al_2O_3 -strained 1 nm zirconia in green, $SrTiO_3$ -strained 1 nm zirconia in dark blue, $KTaO_3$ -strained 1 nm zirconia in light blue, and $KTaO_3$ -strained 0.5 nm zirconia in pink.

principle cut the thickness of YSZ to 0.5 nm, which corresponds to one unit cell. Our MD simulations show that the activation barrier decreases to 0.29 eV, which is the lowest value ever reported to date. The oxygen ionic conductivity for KTOstrained 0.5 nm thick zirconia is thus 1.4×10^8 times higher than that of unstrained zirconia at 500 K, which is twice as large as that for KTO-strained 1 nm thick zirconia. This result indicates that the oxygen ionic conductivity is highly sensitive both to the strain and to the layer thickness of YSZ when the thickness is reduced to very few unit cells.

To shed light on the role of the interface, a sandwich structure composed of three unit cells in the two lateral directions and two optimized unit cells in the transverse direction of KTO was used in our calculations. In this situation, the spacecharge effect has been automatically taken into account. The zigzag distribution of O ions in strained zirconia is still energetically favorable in the sandwich structure. Then, the annealing of the real KTO/1-nm-YSZ/KTO sandwich structure from 1200 K down to 270 K was simulated. Experimentally, as the conductance of the sandwich structure exhibits virtually no dependence on the thickness of the YSZ layer when its width is on the scale of tens of nanometers, the authors inferred that colossal conduction occurs primarily in the near-interface region,²¹ but so far no direct theoretical evidence has been reported to support this. As shown in Fig. 4a and b, we classified the oxygen ions in the KTO/1-nm-YSZ/KTO structure into nine regions (from A to I), and then determined the activity levels of oxygen ions from the oxygen MSDs during MD simulation at 270 K. The oxygen MSD of region A is zero, since these atoms are fixed. Obviously, the oxygen MSDs on D and G regions of the YSZ-KTO interface are higher than those of regions E and F which are the interior parts of ZrO2. This is direct proof for the statement that colossal conduction occurs primarily in the near-interface regions, which can be partly regarded as the space-charge effect. Moreover, the difference of MSDs between the interface (D and G) and inside of YSZ (E and F) is not so



Fig. 4 (a) MSDs of oxygen atoms in different regions of the KTO/1-nm-YSZ/KTO at 270 K. The peaks of D and G indicate that there are high-speed oxygen diffusion channels at the interfacial regions. (b) Snapshots of the sandwich structure from MD simulations at 270 K. Zr atoms are shown as green balls, O in small red, Y in gray, K in big purple, and Ta in blue.

huge suggesting that the space-charge effect or the interfacial effect is not the primary factor for the colossal oxygen ionic conductivity, which is consistent with the findings in previous studies.^{26,29,30}

Conclusions

In this paper, we have performed first-principles-based TS calculations and MD simulations to explore the strain effect on colossal oxygen ionic conductivity in zirconia electrolytes. The results we have obtained can be summarized as follows.

From TS calculations on the O ion migration pathways in zirconia electrolytes with one vacancy, we found that the strain effect changes the oxygen migration routes from straight lines into zigzag forms and reduced the energy barriers by about 0.2 eV. Based on the calculated energy barriers, we suggest a possible oxygen ion diffusion highway in strained zirconia, with energy barriers of about 1.4 eV, which is obviously more favorable than the oxygen diffusion route in unstrained zirconia.

By first-principles finite-temperature MD simulations, we obtained the activation barrier for 9.7%-strained zirconia by KTO to be 0.33 eV, which is smaller than 0.45 eV for 8.0%-strained zirconia by STO. The estimated oxygen ionic conductivity for KTO-strained zirconia is 6.4×10^7 times higher than that of the unstrained bulk zirconia at 500 K, and is about 18 times larger than the oxygen ionic conductivity for STO-strained zirconia.

To examine the general relation between the strain and the oxygen ionic conductivity, we have further investigated Al_2O_3 -strained zirconia (4.0% lattice mismatch) through MD simulations. The calculated activation barrier is 0.64 eV, which corresponds to an enhancement in the oxygen ionic conductivity by 4.4 \times 10⁴ times in comparison with the unstrained bulk zirconia at 500 K. By correlating the energy barrier with the lattice mismatch, a nearly linear relationship is identified between the energy barrier and the lattice mismatch.

By classifying the oxygen ions in the KTO/YSZ/KTO structure into different regions and examining the activity levels of oxygen ions from the oxygen MSDs during MD simulation at 270 K, we found that the oxygen MSDs on the YSZ–KTO interface regions are remarkably higher than those on the interior regions of zirconia, which provides evident proof for colossal conduction occurring primarily in the near-interface regions.

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