

Oxygen ion diffusivity in strained yttria stabilized zirconia: where is the fastest strain?

Akihiro Kushima and Bilge Yildiz*

Received 8th January 2010, Accepted 9th March 2010

First published as an Advance Article on the web 29th April 2010

DOI: 10.1039/c000259c

We present the mechanism and the extent of increase in the oxygen anion diffusivity in Y_2O_3 stabilized ZrO_2 (YSZ) under biaxial lattice strain. The oxygen vacancy migration paths and barriers in YSZ as a function of lattice strain was assessed computationally using density functional theory (DFT) and nudged elastic band (NEB) method. Two competing and non-linear processes acting in parallel were identified to alter the migration barrier upon applied strain: (1) the change in the space, or electronic density, along the migration path, and (2) the change in the strength of the interatomic bonds between the migrating oxygen and the nearest neighbor cations that keep the oxygen from migrating. The increase of the migration space and the weakening of the local oxygen–cation bonds correspond to a decrease of the migration barrier, and *vice versa*. The contribution of the bond strength to the changes in the migration barrier is more significant than that of the opening of migration space in strained YSZ. A database of migration barrier energies as a function of lattice strain for a set of representative defect distributions in the vicinity of the migration path in YSZ was constructed. This database was used in kinetic Monte Carlo (KMC) simulations to estimate the effective oxygen diffusivity in strained YSZ. The oxygen diffusivity exhibits an exponential increase up to a critical value of tensile strain, or the *fastest strain*. This increase is more significant at the lower temperatures. At the strain states higher than the critical strain, the diffusivity decreases. This is attributed to the local relaxations at large strain states beyond a limit of elastic bond strain, resulting in the strengthening of the local oxygen–cation bonds that increases the migration barrier. The highest enhancement of diffusivity in 9%-YSZ compared to its unstrained state is 6.8×10^3 times at 4% strain and at 400 K. The results indicate that inducing an optimal strain state by direct mechanical load or by creating a coherent hetero-interface with lattice mismatch can enable desirably high ionic conductivity in YSZ at reduced temperatures. The insights gained here particularly on the nonlinear and competing consequences of lattice strain on the local bonding structure and charge transport process are of importance for tuning the ionic transport properties in a variety of solid-state conducting material applications, including but not limited to fuel cells.

Introduction

There is much interest in decreasing the Solid Oxide Fuel Cell (SOFC) operating temperature to an intermediate-to-low temperature range to improve chemical and mechanical stability and reduce the cost. Enhancing the ionic transport in the electrolyte and cathode materials is a key for this purpose. Over the past several decades, developing new compositions with high ionic mobility at low temperatures has been the primary activity.¹ In recent years, however, nanoscale structures were shown as means for potentially increasing the transport properties in oxides of relevance to SOFCs.^{2–9} The importance of utilizing the favorable interface properties of nanoscale structures shifted the paradigm from developing new material compositions to tailoring nano-structures using existing materials for the above purpose.^{5,10} Among these, nanoscale hetero-layered oxides were suggested to enhance the ionic conductivity along the interfaces by orders of magnitude.^{5–9} The presence of an interface between

dissimilar oxides is commonly the source of charged mobile defects and local anisotropic distortions and strained interatomic bonds. These contribute to changes in the local electronic structure; formation, coordination and redistribution of charged defects; and mobility of defects in the vicinity of interfaces. Most recently, an eight orders of magnitude increase in ionic conductance was reported by Barriocanal *et al.*⁸ for 1–30 nm-thick yttria stabilized zirconia (YSZ) layers coherently “strained” between dielectric $SrTiO_3$ (STO) layers. The exact nature of the ionic vs. electronic conductance induced in the vicinity of the YSZ/STO interface remains debatable.¹¹ While these observations imply that the hetero-interfaces with controlled lattice-strain and defect-chemistry can play an important role in improving the ionic mobility, results to date remain phenomenological without systematic theoretical efforts. Beyond the SOFC materials domain, similar questions for the role of hetero-interfaces on the local bonding structure and the charge transport process are open for tuning the transport properties in a variety of solid-state conducting material applications.^{12–15} Systematic experimental and theoretical investigation of the role of local strain states on tuning the mechanism and magnitude of charge transfer properties in these materials is prone to pursuit.

Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA, 02139, USA. E-mail: byildiz@mit.edu; Tel: +617-324-4009

Two main mechanisms contribute to increase the ionic transport at the hetero-interface: (1) a favorable strain state at the interface to shift and/or change the symmetry of electron energy levels to provide for improved charge transfer¹⁶ and ion mobility,¹⁷ and (2) the alteration of the defect chemistry^{7,18} near the interface to enhance the density and distribution of desired charge carriers. To understand the underlying mechanism of oxygen anion transport in anion conducting ceramics, a significant number of theoretical studies using atomistic simulations based on both density functional theory (DFT) and empirical potentials have been conducted (examples related to this work in ref. 19–25). However, most of them are focused on the “bulk” or the “surface” ionic transport. Only few theoretical studies exist for the anion transport at hetero-interfaces, on specific cases, *i.e.* CaF₂/BaF₂, CeO₂/YSZ,²⁰ with no generalization of results. Of particular interest for this paper is the effect of lattice strain on the ionic conductivity in the YSZ, as may be encountered due to a lattice mismatch near the YSZ/STO interface. In probing the effect of strain on conductivity in YSZ, a number of experimental and simulation studies have been conducted in the past.^{21–24} Even though the past results imply a potential increase in the conductivity, the magnitude of increase was far lower than what was reported recently in ref. 8 for the YSZ/STO interface. Furthermore, the reported increases in magnitude of the enhancement are inconsistent among these past studies because of the differences in conditions, structures and methods that were considered. For example, results were based on examining either incoherent hetero-interfaces which cannot sustain large lattice strain,²¹ or low strain conditions,²⁴ or molecular dynamics simulation with empirical potentials^{23,24} which are not appropriate for interfaces, or phenomenological modeling using macroscopic elastic properties of the material.²² In essence, the mechanism by which a biaxial lattice strain alters the anion transport in the YSZ fluorite structure was not uncovered. Given these past inconsistencies and open questions, we adopt a first-principles-based approach in probing the mechanistic picture of the ionic conduction in strained YSZ. Our specific objectives are to elucidate the mechanism and to identify the possible extent of increase in the oxygen ion conductivity in YSZ due to a biaxial lattice strain.

In order to attain reliable results in probing the effect of strain on ionic transport in YSZ, it is important to consider a realistic representation of the defect structure, in particular the distribution of vacancies and dopant cations in YSZ. This is because the oxygen vacancy migration barrier, which can be altered by strain, depends strongly on the local defect distributions.²⁵ On the other hand, it is difficult to characterize experimentally the vacancy and cation distribution in YSZ at atomic resolution, therefore this type of information is not available from literature straightforwardly. In spite of the difficulties, past work on this topic provided useful insights on the vacancy–vacancy, vacancy–cation and cation–cation interactions, enabling a reasonable description of the defect structure in YSZ.

Here we provide a summary of defect–defect interactions that we considered for constructing the YSZ model. The final YSZ model used in our work should reasonably capture these reported defect–defect interactions. First of these interactions considered, namely the vacancy–cation interaction, determines the relative position of the vacancy with respect to the Zr and Y

in YSZ. In earlier studies for this interaction, there were contradicting experimental results; whether the vacancy is first nearest neighbor^{26–28} (1NN) or second nearest neighbor^{29–31} (2NN) to the Y cations. However, later experimental^{30–33} and theoretical^{34–40} studies indicated that the vacancy favors to bind to the host Zr cations, resulting in a configuration such that the vacancy is 1NN to the Zr and 2NN to the Y cations. Using DFT calculations, Bogicevic and Wolverton³⁷ showed that the local relaxation of atoms was responsible for the vacancy to favor the 2NN position to the Y cation; opposite to what is expected from the electrostatic interactions alone. The same trend was reported in doped CeO₂ when the dopant radius is larger than the host cation,⁴¹ as in YSZ. For the vacancy–vacancy and the cation–cation interactions, they concluded that the vacancies locate themselves as far away as possible from each other, and that the 1NN Y–Y pair configurations are slightly more favorable than the 2NN Y–Y pairs.^{36,38} More recent experimental work using selected area diffraction also indicated a random distribution of oxygen vacancies, maximizing the distance between them, in up to 10% yttria doped YSZ.⁴² Consistent with the findings of Bogicevic and Wolverton, theoretical results by Predith *et al.*⁴³ suggest even the existence of the ordering of the dopant cations (Y) in YSZ at high doping concentrations, and this cation ordering could exist locally in YSZ at the lower Y concentration range. Among these three types of defect–defect interactions, the vacancy–vacancy interaction is the strongest followed by the vacancy–cation interaction, and the cation–cation interaction is the weakest of the three.³⁶ Supporting the importance of the vacancy–vacancy interactions, it was shown recently that the vacancy distribution around the migration path could significantly impact the value of the migration barriers in YSZ.⁴⁴

In this study, we considered only the strain state in the bulk to provide for improved ionic mobility in YSZ and did not include an interface explicitly as in Barriocanal's work.⁸ Therefore, the model in this paper excludes the effect of altered defect chemistry near the interfaces of YSZ as a source of increase in oxygen diffusivity. In the following sections, we describe the simulation approach to calculate the oxygen vacancy migration path and energy barriers. We report the energetically favorable distributions of oxygen vacancies and Y cations in the YSZ model structure to enable a realistic representation of YSZ in this study. The mechanism by which the lattice strain increases or decreases the anion transport in YSZ are discussed. Because the vacancy migration barrier depends on the local defect configurations, a database of migration barrier energies as a function of lattice strain for a set of representative defect distributions in the vicinity of the migration path are constructed and presented. Finally, the effective tracer diffusivity of oxygen in YSZ at different strain states is presented and interpreted in comparison to the recent results reported for the YSZ/STO interface.⁸

Simulation approach

The YSZ model was established to capture the charged defect interactions and the defect distribution in the bulk YSZ, as summarized in the Introduction. Upon identifying the stable vacancy–cation distribution, the effect of the biaxial lattice strain in the *xy*-plane on the migration barrier and on the

effective vacancy diffusivity were calculated and interpreted. We used first-principles-based simulations to directly and accurately probe the atomistic-scale nature of the vacancy migration in the presence of lattice strain. The kinetic Monte Carlo (KMC) method was used for calculating the effective diffusivities.

The first principles calculations for identifying the energies were performed by the Vienna *ab initio* simulation package (VASP),^{45,46} employing density functional theory (DFT) using a plane-wave basis set. Projector-augmented wave (PAW) method^{47,48} with plane waves up to the energy cutoff at 400 eV was used and the exchange–correlation energy was evaluated by the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) function.⁴⁹ Y, Zr and O atoms were described by 11 (4s²4p⁶5s²4d¹), 12 (4s²4p⁶5s²4d²), and 6 (2s²2p⁴) valence electrons, respectively. The Γ point in the Brillouin zone was selected in the calculation. We confirmed the energy convergence by comparing the energy obtained from each of the k -point meshes of $3 \times 3 \times 3$, $5 \times 5 \times 5$ and $7 \times 7 \times 7$. The calculated energies are within 0.6% error compared to the energy obtained using only the Γ point. The same condition was applied to all of the simulations in this study unless stated otherwise.

YSZ has the fluorite crystal structure with the cations (Y³⁺, Zr⁴⁺) occupying the FCC lattice sites and the O²⁻ ions occupying the tetragonal sites. For every two Y atoms, one oxygen vacancy is created to satisfy charge neutrality. The oxygen vacancy migrates by hopping to the adjacent tetragonal site as schematically illustrated in Fig. 1. The migration barrier depends on the neighboring atoms 1–6 in the figure.²⁵ The surrounding cations within a larger cutoff radius to the migration path must also be accounted for in order to accurately quantify the effect of the strain on the migration barrier.⁵⁰ However, this leads to an impractical number of patterns (well above 10 000 configurations just by including the next nearest neighbor cations to the migration path) to be handled by the DFT simulation. Therefore, we selected a subset of defect structure patterns near the migration path, forming a database of migration paths and barriers. This database serves as input for the KMC calculations in estimating the effective diffusivity as a function of lattice strain and temperature. In constructing this database, first, we considered only two combinations of atoms at the sites 3 and 4, as Zr–Zr and Zr–Y, in the migration path shown in Fig. 1. The migration barrier through the Y–Y pair was found to be significantly higher than these two combinations, and this makes the Y–Y pair unlikely on a vacancy migration path. This selection was also validated by the work of Car *et al.*,⁵⁰ which implied the

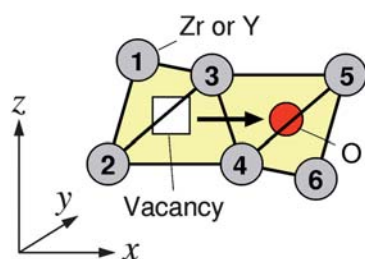


Fig. 1 Migration path of the oxygen vacancy. Positions 1–6 are occupied by the cations Zr or Y.

Zr–Zr and Zr–Y subset at sites 3 and 4 to be sufficient to capture the quantitative trends in ionic conductivity in YSZ as a function of Y₂O₃ doping concentration. Second, we considered the defect configurations outside of the first neighbor cations to the migration path to affect the barrier. The particularly important impact of the vacancy interactions on the migration barrier was recently reported by Pietrucci *et al.*⁴⁴ Therefore, in creating the migration path and barrier database, we varied the relative positions of the Y cations and the vacancies with respect to the initial and final positions of the vacancy on the migration path. The details of the migration path configurations in this database are provided in the following section. For each migration path configuration, nudged elastic band (NEB) method⁵¹ was used to find the vacancy migration barrier as a function of biaxial strain on the xy -plane. Given that the vacancy migration path in YSZ is rather simple with single hops between the adjacent tetragonal sites, the saddle point is expected near the midst of the migration path.^{25,50} Three images between the initial and the final states were taken in the simulations. Here we used the climbing image NEB method⁵² to calculate not only the minimum energy path but also the transition state configuration at the saddle point. The method drives the image with the highest energy up to the saddle point, by maximizing its energy along the band connected to the image and minimizing in all other directions. This way, the method allows us to accurately calculate the saddle point energy and configuration with a small number of images needed in the calculation. The NEB simulations were conducted with fixed lattice vectors.

The database created for the migration barrier values at different lattice strains and the defect configurations was provided as input for kinetic Monte Carlo (KMC) simulations. KMC calculations were performed to quantify the effective diffusivity of oxygen in YSZ as a function of strain and temperature. The diffusivity calculated in this work is the oxygen tracer diffusion constant. We expect that the lattice strain has a similar order of magnitude impact on the mobility of an oxygen ion in both the chemical and the tracer diffusion constants, especially in the range of low vacancy concentrations.⁵³ In the simulation model, oxygen atoms were assumed to hop to the nearest neighbor site on the oxygen sublattice through the path shown in Fig. 1. The rate of hops in the migration paths were obtained by the Boltzman relationship as,

$$v_{AB} = \nu_0 \exp\left(\frac{-E_{AB}}{k_B T}\right) \quad (1)$$

where E_{AB} , found by the DFT-NEB simulations, denotes the migration barrier across the A–B cation pair at sites 3 and 4 in Fig. 1. The attempt frequency was fixed at $\nu_0 = 10^{13} \text{ s}^{-1}$, which is appropriate for most metal oxide systems.⁵⁰ The periodic boundary conditions were applied to all three dimensions of the simulation cell. The vacancy diffusivity, D_v was extracted from mean square displacement $\langle R^2 \rangle$ calculated in the KMC simulation using the Einstein relation,

$$\langle R^2 \rangle = 6D_v t. \quad (2)$$

The oxygen diffusivity D_O was then obtained using D_v considering the balance between the fluxes of oxygen atoms and vacancies as,

$$D_O = \frac{c_v}{1 - c_v} D_v \quad (3)$$

where c_v is the vacancy concentration fraction. D_v exponentially depends on the effective barrier for oxygen vacancy migration, E_{eff} , as,

$$D_v = d_v^0 \exp\left(-\frac{E_{\text{eff}}}{k_B T}\right) \quad (4)$$

where, d_v^0 is a constant. At small values of c_v , D_0 scales almost linearly with c_v . On the other hand, the change in the migration barrier, E_{eff} , contributes exponentially to D_v and D_0 .

Results and discussion

This section consists of five sub-sections, I–V. Sub-sections I–II demonstrate that the YSZ model in this work captures the reported vacancy and cation interactions in stabilizing the cubic structure in YSZ. The results in I and II are important for obtaining reliable values of the energy barriers for vacancy migration in YSZ. Sub-section III reports the effect of defect configurations in the vicinity of the migrating vacancy on the migration energy barrier. This proves that, in order to assess the effect of strain on migration barriers, one must consider a realistic subset of defect configurations in YSZ, and we report these in sub-section IV. Sub-section IV in particular illustrates the mechanism by which strain alters the diffusion barriers for oxygen vacancies in YSZ. Finally sub-section V quantifies the effective increase in oxygen tracer diffusivity as a function of biaxial lattice strain, based on the subset of defect configurations considered in this work for YSZ.

I. Defect structure in YSZ: oxygen vacancy and yttrium distribution

To determine the favorable location of vacancies with respect to the Y cations in the YSZ model, we tested a number of defect configurations. These models constitute 30 Zr, 2 Y and 63 O atoms, corresponding to a low doping ratio, 3% Y_2O_3 , allowing only one vacancy in the simulation cell, in order to eliminate the vacancy–vacancy interaction in this part of the simulations. At this low Y_2O_3 doping, the YSZ oxygen sublattice cannot keep its cubic structure.³⁴ Therefore, only in this part of the simulations, the atoms beyond the second neighbor oxygen shell to Y cations and beyond the third neighbor oxygen shell to the vacancy were fixed to retain the cubic phase.³⁴ The comparison of the energies for the different YSZ models and defect configurations is presented in Fig. 2. The energies are shifted such that the lowest energy found is zero. The results show that the total energy can vary by up to 0.5 eV when the Y cation is located at the third or first neighbor site to the vacancy, instead of the second. This result is consistent with the prior reports on cation–vacancy interactions in YSZ, as discussed in the Introduction. Since this large energy difference arises from local configuration differences, the result suggests that the cation configuration surrounding the diffusion path of the oxygen–vacancy pair should be taken into account for accurate evaluation of the migration barriers.

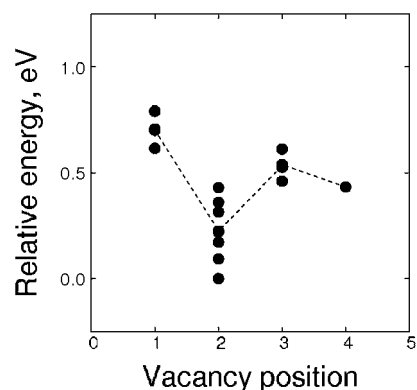


Fig. 2 Energy as a function of the neighboring location of the oxygen vacancy with respect to the Y cations in YSZ. The energies were calculated for different cation/vacancy distributions, and plotted such that the lowest energy found is zero.

II. Distortion from the cubic lattice sites in YSZ

The atoms are not stabilized at the exact fluorite structure lattice centers in YSZ, and large displacements of the cations and the anions from the fluorite lattice sites are present.^{55–57} This is in part due to the relaxation of the nearest neighbor oxygen anions and cations towards and away from the vacancy, respectively.³² For an acceptable YSZ structure in this study, it is important to capture this deviation quantitatively consistently with past experimental and simulation reports. For this purpose, we evaluated the dependence of the atomic displacements from the ideal fluorite lattice sites on the local defect structures in a set of candidate YSZ models. The fully relaxed structure of the models constituted 9% Y_2O_3 doped YSZ, made of 26 Zr, 6 Y and 61 O atoms in the simulation cell. The relaxation of the atoms were not constrained in this and the following simulations because the cubic structure is stable in the 9% Y_2O_3 doped YSZ, as long as

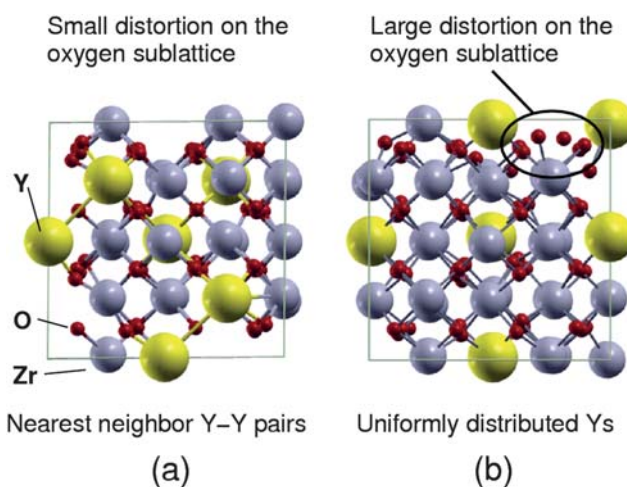


Fig. 3 Fully relaxed atomic configurations of the 9% yttria doped zirconia with (a) nearest neighbor Y–Y pairs, and (b) uniformly distributed Y. Yellow, gray and red spheres indicate Y, Zr and O ions. Large distortion of the oxygen anion sublattice is evident when Y cations are uniformly spread in the YSZ without any short-range ordering of the Y cations.

the vacancies and dopant cations are distributed to enable the stability. Fig. 3 shows the relaxed atomic configurations for two models of YSZ. The first one (Fig. 3(a)) has first nearest neighbor (1NN) Y–Y pairs and the second one (Fig. 3(b)) has a uniform distribution of Y cations in the cell. In both models, the vacancies were placed as far away as possible from each other and located second nearest neighbor (2NN) to Y cations if allowed by the available space. The first model retains an overall cubic structure with oxygen anions displaced by 0.1–0.27 Å from the ideal fluorite lattice sites. The extent of the displacements calculated here is well within the experimentally measured value of $\sim 0.36 \text{ \AA}$ ²⁸ and prior simulation results of 0.20–0.31 Å.³⁴ On the other hand, the second model shows large distortions, exemplified at the circled region in Fig. 3(b), and has 1.2 eV higher energy compared to the first one. This difference arises due to local configuration differences, and thus, can affect the vacancy migration barrier in YSZ which ranges from 0.2 to 1.4 eV.²⁵ The lack of stability of the cubic oxygen sublattice in the second model is due to the limited available space to accommodate the relative positions of the vacancy and Y cations at the favorable distances when the Y atoms are distributed uniformly into the model. In the circled region in Fig. 3(b), a vacancy is located at the 1NN position to the Y cations. This is because the 2NN position for the vacancy is not available to all the Y atoms when the Y atoms are distributed uniformly in the model. The restriction of some vacancies to the unfavorable 1NN positions with respect to the Y in YSZ destabilizes the cubic phase. On the contrary, the first model configuration with the Y–Y pairs introduces more space for the vacancies to be placed at the 2NN positions with respect to the Y cations. This enables more stability on the cubic oxygen sublattice. This result is consistent with the locally ordered nature of Y cations in YSZ at high concentrations of Y_2O_3 , as found by Predith *et al.*,⁴³ even if the YSZ has only 9% Y_2O_3 , here. While the effect of Y–Y pairing on the migration barrier in a cubic YSZ is small compared to that of the vacancy–vacancy and vacancy–cation interactions,³⁶ it is important to consider it to enable a stabilized cubic fluorite structure of YSZ in the model.

III. Vacancy migration barriers in YSZ: effect of the local defect structure

As implied in the previous section, the local defect structure around the oxygen vacancy migration path in YSZ affects the stability of the structure and the migration barrier,⁵⁴ and this in turn can determine the favorable paths for vacancy to migrate through. To illustrate this, we present the differences in the migration barrier in a model with 1NN Y–Y pairs, which lower the energy and enable the stabilization of cubic phase. The consequent migration paths considered were $A \rightarrow B \rightarrow C$ in Fig. 4(a). All six nearest neighbor cations (1–6 as shown in Fig. 1) are the same, Zr, for each migration step in $A \rightarrow B \rightarrow C$. On the other hand, the distribution of vacancies and Y cations near $A \rightarrow B$ and $B \rightarrow C$ differ beyond the nearest neighbor cations. This enables to investigate the variation of the migration barrier as a function of the defect structure near the migration path beyond the nearest neighbor cations. Fig. 4(b) shows the relative energy in the NEB trajectories for the migration through $A \rightarrow B \rightarrow C$. The resulting migration barriers range from 0.55 to 0.95 eV, even

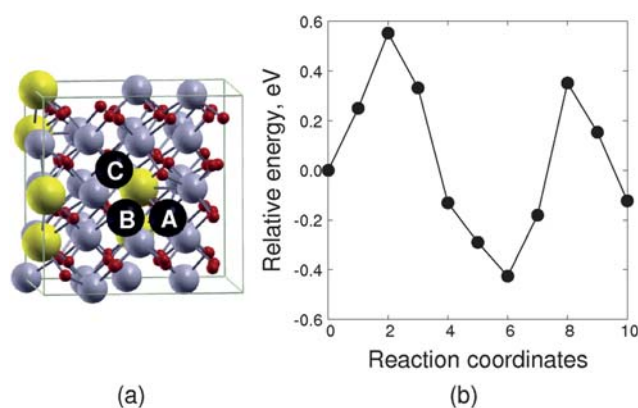


Fig. 4 (a) The vacancy positions and local structure considered for the vacancy migration path, $A \rightarrow B \rightarrow C$. Large black spheres indicate positions of the vacancies. Yellow, gray and red spheres indicate Y, Zr and O ions. Numbers of Y cations at the second nearest neighbor position to the vacancy is two at sites A and B, and one at site C. (b) NEB barriers calculated along the $A \rightarrow B$ and $B \rightarrow C$ paths. The variation in the migration barrier is clear in (b), even though all the six nearest neighbor cations in the migration path are Zr. The difference in barriers is due to the dissimilar vacancy and Y distribution near the $A \rightarrow B$ and $B \rightarrow C$ paths beyond the nearest neighbor cations.

though all the cations in the nearest neighbor position to the migration path are the same. This significant difference exemplified in the migration barriers in $A \rightarrow B \rightarrow C$ indicates that it is important to systematically take into account the longer-range interactions between the migrating vacancy and its surrounding cations and vacancies in YSZ.

We evaluated a subset of defect configurations near the migration path to form a representative database of migration barriers in YSZ. The five different configurations, models A–E, that yield ten forward and backward jump barriers considered here are shown in Fig. 5. This subset aims to capture the isolated

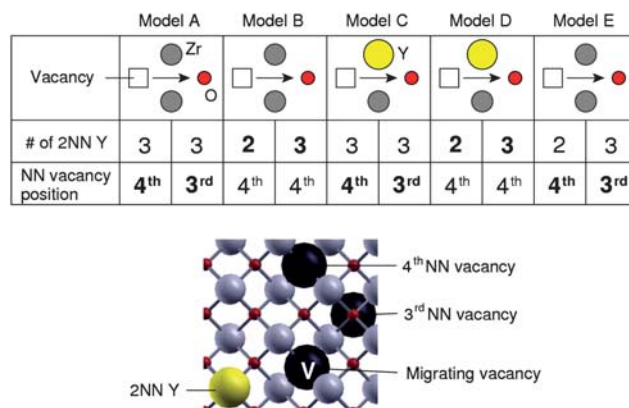


Fig. 5 Models A–E with varying defect configurations surrounding the migration path. “# of 2NNY” denotes the number of second nearest neighbor Y cations to the vacancy positions. “NN vacancy position” denotes that the nearest neighbor vacancy to the migrating vacancy is located at n -th nearest neighbor position on the anion sublattice (n -th = 3rd or 4th in these models). Lower panel indicates the 2NN Y position, and the 3rd and 4th nearest neighbor vacancies on the anion sublattice with respect to the migrating vacancy V.

and coupled effects of vacancy–vacancy and vacancy–cation interactions in the local environment around the migration path. The vacancy–vacancy interaction is considered up to the fourth nearest neighbor on the anion sublattice, which was the maximum that could be accommodated in our $2 \times 2 \times 2$ unit cell model when the nearest neighbor vacancy pairs are avoided. The cation–vacancy interaction was taken up to the second nearest neighbor. First, for considering the effect of the nearest neighbor cations in the migration path (sites 1–6 in Fig. 1), we only included the variation of the bridging cation pairs (sites 3 and 4 in Fig. 1). This was shown to be the most important contribution to the vacancy migration in YSZ⁵⁰ when the long-range interactions were not considered. In models A, B, and E, the vacancy migrates through the Zr–Zr cation pair, and in models C and D, through the Zr–Y cation pair in the midst of the path. All the other cation sites closest to the migration path (sites 1, 2, 5 and 6 in Fig. 1) are Zr. The path through Y–Y pair was excluded from the simulations since it has a much higher migration barrier compared to the Zr–Zr and Zr–Y pairs,^{25,50,54} making it significantly less likely to migrate through the Y–Y cation pair. Second, for vacancy–vacancy interaction, models A and C consider the position of nearest neighbor vacancies, denoted as “NN vacancy position” in Fig. 5, to the initial and the final position of the migrating vacancy. The distance between the migrating vacancy and the nearest neighbor vacancy changes from the fourth to the third on the anion sublattice upon migrating from the initial to the final position (and *vice versa* in the backward migration). # of 2NN Y are the same in models A and C. Third, for vacancy–cation interaction beyond the nearest neighbor cations, models B and D consider the number of Y cations that are at the second nearest neighbor (2NN) position with respect to the initial and the final state of the vacancy. This is denoted as “# of 2NN Y” in Fig. 5. The number of 2NN Y cations changes from two to three upon migrating from the initial to the final state (and *vice versa* in the backward migration). Lastly, in model E, both the number of 2NN Y cations and the distance to the nearest vacancies at the initial and the final state were varied. The former changes from three to two and the latter from the fourth to the third nearest neighbor (and *vice versa* in the backward migration).

In creating the database of migration paths and barriers, a model to represent a symmetric defect configuration around the initial and final states of the migrating vacancy was not possible. This is because of the computational limitation in the simulation cell size used in our DFT/NEB calculations. In computing the effective diffusivity in the following sections, we will show that we represented the barrier for a symmetric migration path to be the average of the barriers from models A–E.

A simulation unit cell of $2 \times 2 \times 2$ dimensions, containing 26 Zr, 6 Y and 61 O atoms corresponding to a 9% yttria doped zirconia was used in the calculation of the migration energy barriers for each of the models A–E described in Fig. 5. The oxygen vacancies and the Y cations were distributed in the cell satisfying the defect interactions discussed in the previous sections. Atomic configurations and the cell vectors were fully relaxed such that the total energy was minimized and the net stress acting on the cell was zero. The migration barriers for each model path were calculated using the climbing NEB technique. The calculated barriers for each path (A–E) are shown in Fig. 6. The energy values are relative to the initial state configuration.

The reaction coordinate of each NEB image was normalized with respect to the distance between the initial and the final state of the vacancy. The oxygen vacancy migration process requires climbing over the highest energy (the saddle point) between the initial and the final state. \vec{E}_B and \overleftarrow{E}_B in Fig. 6 are the migration barriers for the forward and the backward jumps, respectively, corresponding to the migration from the initial to the final positions of the vacancy shown in Fig. 5, and *vice versa*.

As a result, the migration configurations in models C and D have higher barrier than those in models A, B and E. This is primarily because of the difficulty in passing through the Zr–Y pair compared to that through Zr–Zr pair. The forward jump barrier is higher than the backward jump barrier for models A and C, and lower for models B and D. For models A and C, this is because the distance from the migrating vacancy to the nearest neighbor vacancy is shorter at the final state, making it more difficult for the migrating vacancy to approach to the final state, primarily due the electrostatic interaction of vacancies. For models B and D, the number of Y cations at the second nearest neighbor position to the migrating vacancy is larger at the final state, making this final state energetically more favorable, and thus the reduced migration barrier in the forward migration. In model E, the forward jump barrier is higher than the backward one. Considering the vacancy–cation interactions, the final state in model E is energetically more favorable than the initial state because of the presence of a larger number of 2NN Y cations to the migrating vacancy at the final state. This suggests the migration barrier for the forward jump to be lower than the backward one. However, the result shows the opposite behavior, because the migrating vacancy is actually getting closer to its nearest neighbor vacancy at its final state. This indicates that the vacancy–vacancy interaction dominates the vacancy–cation interaction in determining the energy barriers in model E. All implications related to the defect–defect interactions leading to the resulting migration barriers in models A–E in the unstrained state of YSZ are consistent with those suggested by previous

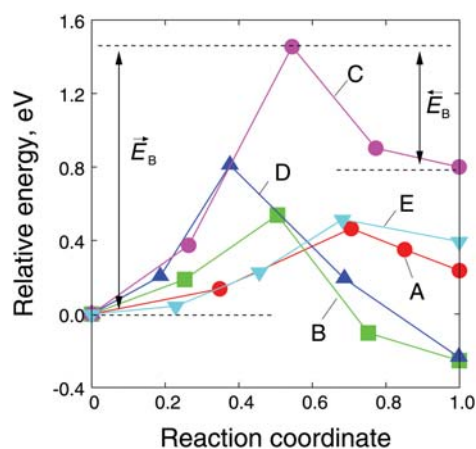


Fig. 6 NEB paths and the corresponding energies in the migration path calculated for models A–E. The relative energy and the coordinates are normalized with respect to the initial energy, and the distance between the initial and the final state, respectively. The saddle point energy is the highest energy state between the initial and the final states, and \vec{E}_B and \overleftarrow{E}_B stand for barriers in the forward and the backward jumps, respectively.

reports by Bogicevic *et al.*³⁶ Therefore, the results presented here enable a reasonable model of YSZ for assessing the effect of biaxial lattice strain on the ionic mobility.

IV. Migration barrier as a function of biaxial lattice strain

In assessing the role of the biaxial xy -plane lattice strain on the oxygen vacancy transport, we investigated the corresponding changes in the migration barriers, and the underlying reasons for these changes on models A–E in Fig. 5. The xy -plane strains considered here were 0.00, 0.02, 0.04, 0.06 and 0.08. The range of strain considered in this study is far above the experimentally measured fracture strain of a single-crystal YSZ that is less than 0.5%.⁵⁸ However, large strain in brittle ceramics could be achieved by creating coherent hetero-interfaces at the nanoscale. A maximum 7% tensile lattice strain was suggested to exist in the YSZ thin film interfaces coherently strained between STO layers due to the mismatch between STO and YSZ.⁸ On the other hand, ability of thin-film (10–30 nm) YSZ to sustain this large tensile strain is unclear. We considered only tensile strain to increase the interatomic distances in YSZ, allowing more space for the oxygen migration. Results for model A are shown in Fig. 7. The migration barrier monotonically reduces with the increase in the biaxial lattice strain. The barrier in the forward jump decreases from 0.47 eV at $\varepsilon = 0.00$ to 0.07 eV at $\varepsilon = 0.04$, suggesting a significant enhancement of the vacancy diffusivity through this path under strain. Beyond this strain level, the vacancy was not stable at the initial site and favored to form at the defined final site in model A, with no barrier in the suggested transition path. This result implies that the defect interactions influencing the stability and energetics can also change with the strain state of YSZ. While not explicitly included in our DFT calculations, we implicitly took into account the effect of the strain on the stable defect configurations in the KMC simulations, as explained in the following section. We considered both the forward and the backward migration barriers, and the system has a higher probability of taking the lower energy migration paths favoring the more stable structures.

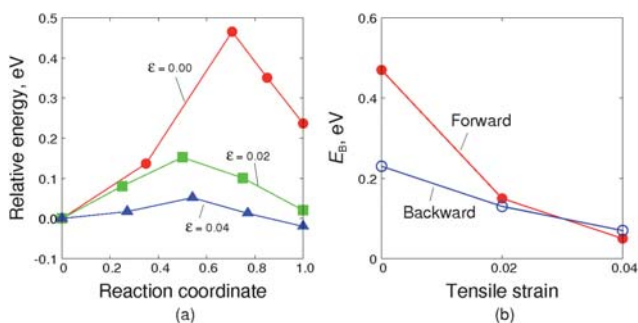


Fig. 7 (a) NEB paths and the corresponding energies in the migration path calculated for model A. The relative energy and the migration coordinates are normalized with respect to the initial energy, and the distance between the initial and the final state, respectively. The saddle point energy is the highest energy state between the initial and the final states. (b) The vacancy migration barrier, E_B , as a function of biaxial lattice strain. The filled circles and the open circles indicate forward and backward jump, respectively. The barrier decrease as the strain increases in the migration path in model A.

The picture is not as straight-forward in models B–E as in model A that shows a monotonic reduction in the migration barrier with strain. Depending on the extent of the lattice strain, the consequent barrier either decreases or increases in the configurations represented by models B–E, as shown in Fig. 8. The lack of a straight-forward trend in the magnitude of migration barrier as a function of lattice strain suggests that there is more than one mechanism acting simultaneously upon strain in YSZ. Here, we explain the competing effects of strain on the vacancy migration barrier in YSZ from an atomistic and electronic perspective. The oxygen vacancy migration process involves bond-breaking and bond-making between the migrating oxygen and the surrounding cations. Therefore, we investigated the changes in the electronic density distribution of the valence electrons describing the Zr, Y and O atoms near the migration path to explain the local effects of strain in YSZ. We focused on the two planes in the migration path as shown in Fig. 9. The charge distribution on the “oxygen plane” in Fig. 9 correlates to the “space available” for the oxygen, denoted as O, to migrate along the prescribed path. The migration space is also related to the cation–cation distance midst the migration path. On the other hand, the “bonding plane” in Fig. 9 shows a measure of the “bonding strength” between the oxygen and the nearest cations at the initial site, quantified in terms of the oxygen–cation “bond thickness”. It is this set of bonds, shown between the oxygen denoted as O and the cation denoted as C, which are broken in the initiation of oxygen diffusion. Both the migration space and the bond strength change when YSZ is subjected to biaxial strain. Fig. 10 illustrates an example in which the increase in strain increases the open space, and also increases the O–C bonding strength to the extent of local inelastic relaxation near the initial state of oxygen. In this case, the lattice strain is beyond just

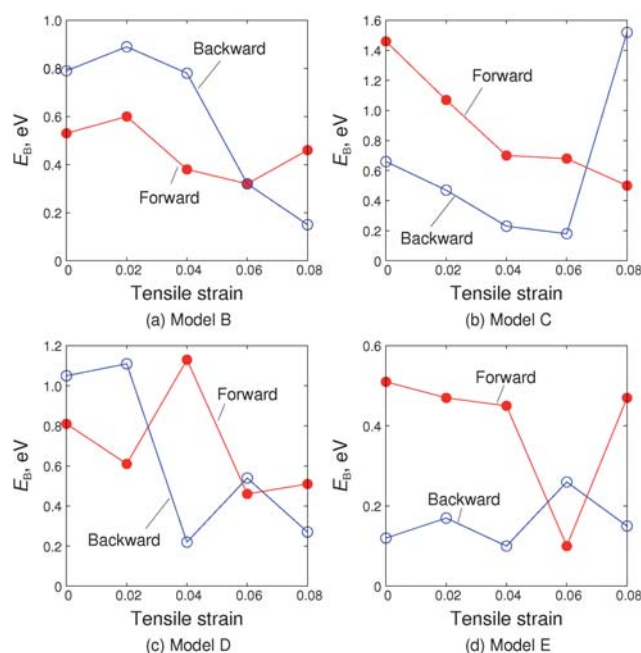


Fig. 8 The vacancy migration barrier, E_B , as a function of biaxial lattice strain for models B–E (in a–d). The filled circles and the open circles indicate the forward and the backward jump barriers, respectively.

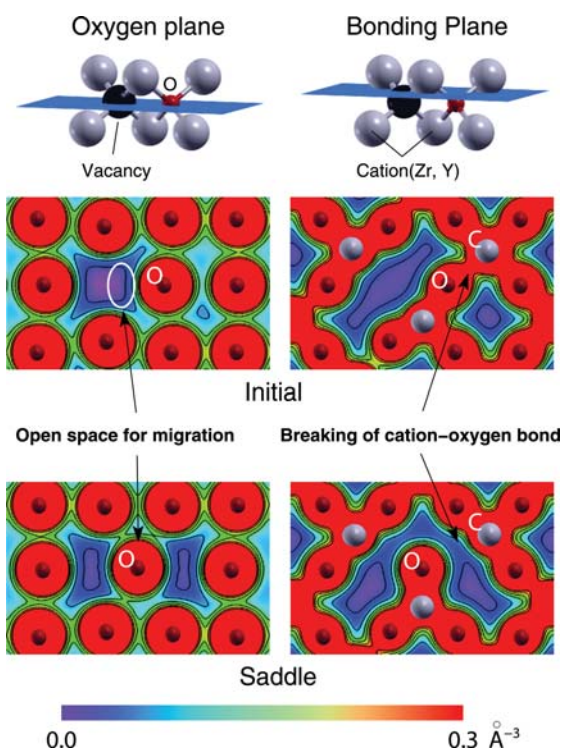


Fig. 9 The electronic density distribution on the “oxygen plane” and the “bonding plane” at the initial and the saddle states. The migrating oxygen, O, moves towards the open migration space, and the bond between oxygen O and cation C breaks in the migration.

elastically extending the oxygen–cation bond length; the oxygen, O, was actually attracted towards the cation C and broke its bond from the opposite cation upon *local relaxation* of atoms. As a result, a stronger binding of O to C arises, shown with the thicker O–C bond in Fig. 10. These two consequences of strain act oppositely on the migration barrier – the former (opening of migration space) favors the migration and the latter (local inelastic relaxations near the oxygen) inhibits the migration.

A specific illustration of these competing consequences of biaxial strain in YSZ represented by model E is shown in Fig. 11. The resulting change in the migration space was quantified as the distance between the cations midst the migration path, $\Delta(\text{Zr–Zr})$ in this configuration. The bond O–C in Fig. 11(b) is one of the oxygen–zirconium bonds that break upon the migration of oxygen. The large reduction in the forward migration barrier from 0.51 eV at $\epsilon = 0.00$ to 0.10 eV at $\epsilon = 0.06$ as shown in Fig. 8(d) corresponds to the increase in the $\Delta(\text{Zr–Zr})$ distance (shown in Fig. 11(a)) and the weakening of the O–C bond (shown in Fig. 11(b)). On the other hand, this trend is not monotonic. At higher strain, $\epsilon = 0.08$, the cation–cation distance decreases and the oxygen–zirconium bond strengthens again, resulting in a significant increase of the migration barrier from 0.10 eV at $\epsilon = 0.06$ to 0.47 eV at $\epsilon = 0.08$. At this strain, the local relaxation of the atoms particularly re-strengthens the oxygen–zirconium bond at the initial site of the oxygen, also affecting the migration space. If assumed independent, the oxygen–cation bond strength is more strongly correlated to this large increase in the barrier at large strain seen in Fig. 8(d). The increase in the cation–oxygen bond strength is evident at $\epsilon = 0.08$ in Fig. 11(b), but a very small

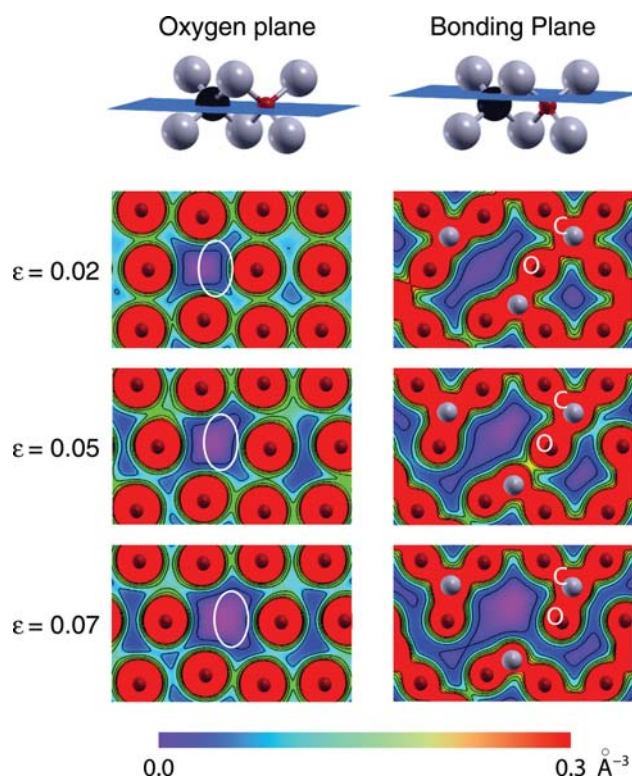


Fig. 10 Change in the electronic density distribution on the oxygen plane and the bonding plane under biaxial lattice strain, ϵ , from 0.00 to 0.07. Gray and red spheres represent Zr and O atoms, respectively.

change occurs in the $\Delta(\text{Zr–Zr})$ in Fig. 11(a). While we present this set of results explicitly for the model E, the same qualitative correlation of the competing effects of the migration space and the cation–oxygen bond strength governed the migration barrier changes with strain consistently also in the other models A–D.

V. Effective oxygen diffusivity as a function of biaxial lattice strain

Models A–E constituted the database of the migration paths and barriers as a function of the biaxial strain in YSZ. Using this database to govern the overall oxygen diffusion, the macroscopic oxygen diffusivity in the bulk of YSZ was estimated by KMC simulations as described in the Simulation Approach section. A $15 \times 15 \times 15$ simulation cell of 8% yttria doped zirconia was used, consistent with the doping ratio in YSZ reported in the Ref. 8 for the YSZ/STO heterolayers. Y cations and vacancies were distributed randomly in the KMC simulation cell. At a first sight, this configuration contradicts with the implications for the presence of 1NN Y–Y pairs in YSZ as discussed in Introduction. On the other hand, the rules in selecting the diffusion barriers in the KMC simulations were taken consistently with the local defect configurations, including the effect of Y–Y pairs as evaluated in the DFT-NEB calculations in this work. Therefore, we considered this model in KMC to be reasonable for assessing the overall oxygen diffusivity in YSZ. Supporting this approach, past DFT and KMC studies of oxygen diffusivity in YSZ with randomly distributed Y atoms and vacancies were shown to give

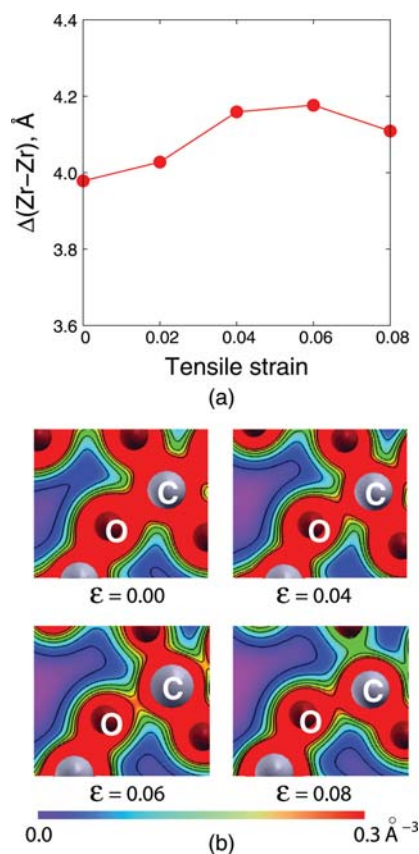


Fig. 11 (a) Change in the cation–cation distance, $\Delta(\text{Zr-Zr})$, and (b) the bond thickness (strength) for O–C in the migration under biaxial lattice strain from 0.00 to 0.08 for the forward jump in model E (see also Fig. 8(d)). Increase in the migration space $\Delta(\text{Zr-Zr})$, and the weakening of the O–C bond correspond to the decrease of the migration barrier in Fig. 8(d), and *vice versa*. Large gray spheres and small red spheres are Zr and O atoms, respectively. The isoline interval is 0.5 \AA^{-3} .

the correct yttria doping ratio for the maximum oxygen diffusivity.^{25,50}

The effect of the local defect environment around the migration path on the barriers input to the KMC simulations was taken into account as follows:

Definitions. \vec{E}_α and \overleftarrow{E}_α are the forward and backward jump energy barriers in each model α ($\alpha = \text{A, B, C, D, E}$), respectively. r_v^i and r_v^f stand for the distance of the first nearest neighbor (1NN) vacancy to the migrating vacancy at the initial and final state, respectively. n_Y^i , and n_Y^f are the number of second nearest neighbor (2NN) Y cations to the migrating vacancy at the initial and final state, respectively.

Rules. The rules in determining the energy barrier for each hop in the KMC simulations treat the local defect configurations in a coarse grained fashion, based on the models A–E (Fig. 5) assumed to govern the oxygen vacancy diffusion in YSZ. In models A and C, the vacancy forward hopping (from initial to final state) results in a decrease of the 1NN vacancy distance to the migrating vacancy, that is $r_v^i > r_v^f$. Then, in the KMC simulation, \vec{E}_α and \overleftarrow{E}_α ($\alpha = \text{A, C}$) are chosen for the cases of $r_v^i > r_v^f$,

and $r_v^i < r_v^f$, respectively. In models B and D, the vacancy forward hopping (from initial to final state) results in an increase in the number of 2NN Y to the migrating vacancy, that is $n_Y^i < n_Y^f$. Then, in the KMC simulation, \vec{E}_α and \overleftarrow{E}_α ($\alpha = \text{B, D}$) are chosen for the cases of $n_Y^i < n_Y^f$ and $n_Y^i > n_Y^f$, respectively. The explicit definition of the rules implemented in the KMC simulations is as follows:

(1) For the vacancy migration through a Zr–Zr pair midst the migration path, we select the barrier among \vec{E}_A , \overleftarrow{E}_A , \vec{E}_B and \overleftarrow{E}_B according to the following criteria:

- If $r_v^i > r_v^f$, select \vec{E}_A ; and if $r_v^i < r_v^f$, select \overleftarrow{E}_A .
- If $r_v^i = r_v^f$ and $n_Y^i > n_Y^f$, select \vec{E}_B ; or if $r_v^i = r_v^f$ and $n_Y^i < n_Y^f$, select \overleftarrow{E}_B .
- If $r_v^i = r_v^f$ and $n_Y^i = n_Y^f$, randomly choose barriers from \vec{E}_A , \overleftarrow{E}_A , \vec{E}_B , and \overleftarrow{E}_B .

(2) For the vacancy migration through a Zr–Y pair midst the migration path, we select the barrier among \vec{E}_C , \overleftarrow{E}_C , \vec{E}_D and \overleftarrow{E}_D according to the following criteria:

- If $r_v^i > r_v^f$, select \vec{E}_C ; if $r_v^i < r_v^f$, select \overleftarrow{E}_C .
- If $r_v^i = r_v^f$ and $n_Y^i > n_Y^f$, select \vec{E}_D ; or if $r_v^i = r_v^f$ and $n_Y^i < n_Y^f$, select \overleftarrow{E}_D .
- If $r_v^i = r_v^f$ and $n_Y^i = n_Y^f$, randomly choose barriers from \vec{E}_C , \overleftarrow{E}_C , \vec{E}_D and \overleftarrow{E}_D .

(3) Vacancy migration through Y–Y pair is prohibited.

When $r_v^i = r_v^f$ and $n_Y^i = n_Y^f$, the migration path is surrounded by a symmetric distribution of defects. This case was not possible to account for in the DFT-NEB calculations due to the computational limitations on the simulation size. We assumed such a symmetric path to be governed by a migration barrier that is the average of the barriers from the non-symmetric models represented in A–E here. Therefore, the random selections among the entire set of \vec{E}_α and \overleftarrow{E}_α (for $\alpha = \text{A, B, C, D, E}$) during the 10^8 KMC steps should provide sufficient statistics to represent the average migration barrier for the symmetric path, $r_v^i = r_v^f$ and $n_Y^i = n_Y^f$. Moreover, the probability of having symmetric path in the KMC runs was less than 3%. Therefore, the error that may arise due to selecting an average migration barrier for the symmetric configuration is expected to have little significance on the effective diffusivity.

As seen from the rules above, the energy barrier for each hop in the KMC simulations was chosen based on a coarse grained treatment of the local defect configurations around the migrating vacancy. We believe this approach gives a reasonable result, particularly based on the validity of the models A–E (Fig. 5) to govern the oxygen vacancy diffusion in YSZ. On the other hand, the reader can refer to a more accurate treatment of the diffusion barriers in KMC simulations using the cluster expansion method,^{43,59} which can account for the energy deviations due to the local atomic structures around each hop. In that case, the KMC model itself has to take into account the stable distributions of vacancies and cations (as in subsections I and II), rather than a random distribution, making the task exhaustive.

The KMC simulations were performed as a function of temperature ranging as 400, 600, 800 and 1000 K, and of biaxial strain ranging as 0.00, 0.02, 0.04, 0.06 and 0.08. Ten simulations with different distributions of dopant cations and vacancies were conducted for each temperature and strain state. The resulting strain dependence of the effective oxygen tracer diffusivity D_O is shown in Fig. 12. y -axis in the figure is on a relative scale with

respect to the oxygen diffusivity, D_0^0 at $\varepsilon = 0.00$ for the lowest temperature simulated, 400 K. The reported results show the average values and the error bars over the ten simulations. The result is not a simple monotonic increase of diffusivity with increasing strain in the entire range considered. The oxygen diffusivity exhibits an exponential increase up to a critical value, 4% of tensile strain. This increase is more significant at the lower temperatures. The maximum enhancement in diffusivity compared to the unstrained state in YSZ is 6.8×10^3 times higher at 4% strain and at 400 K. At the higher strain states, the diffusivity decreases. This is attributed to the local relaxations beyond a limit of elastic bond strain, resulting in the strengthening of the local oxygen–cation bonds that increases the migration barrier.

Our first-principles-based simulation results indicate that a biaxial strain in YSZ induced by a lattice-mismatch coherent interface can significantly increase the diffusivity up to a critical strain state, and worsen it beyond that strain state. One could view this critical strain state as the optimal strain to induce in the material to attain the maximum benefit of the biaxial lattice strain on the oxygen diffusivity. We note that a recent prediction by Schichtel *et al.*²² using a model based on the elastic properties of YSZ estimated 2.5 orders of magnitude increase in the ionic conductivity of YSZ at 7% strain at 573 K. The model of Schichtel *et al.* relies on the isotropic pressure induced by the strain to enhance the diffusivity, and does not take into account the competing relaxations at these large tensile strain states in YSZ. Therefore, it cannot capture the local bond-strength changes that may mitigate the diffusivity at large strain values. In spite of the differences in our and Schichtel's model, the magnitude of the maximum increase in the oxygen diffusivity in strained YSZ predicted by these models range from 2.5 to 3.8 orders of magnitude. Therefore, the lattice strain (elastic and inelastic) alone cannot explain the eight orders of magnitude increase of ionic conductivity in YSZ reported by Barriocanal *et al.*⁸ These results do not take into account the space-charge

effects in altering the anion concentrations near the YSZ interface. On the other hand, the contribution to the increase in the anion diffusivity due to a possible space-charge-induced increase in the vacancy concentration is almost linear at low concentration of vacancies (see eqn (3)) as in the 9% Y_2O_3 doped YSZ. Therefore, this contribution is expected to be small compared to the exponential increase found here due to the applied biaxial lattice strain.⁶⁰

Conclusion

This work provides a mechanistic and systematic assessment of the effect of biaxial lattice strain on the oxygen diffusivity in YSZ, independently from the defect chemistry near a hetero-interface with a dissimilar oxide, *e.g.* YSZ/STO as reported by Barriocanal *et al.*⁸ Using DFT/NEB simulations, we uncovered the underlying microscopic mechanism by which the biaxial tensile strain acts on the oxygen vacancy transport in YSZ. The migration barrier correlates fundamentally with two competing processes acting in parallel in the presence of lattice strain: (1) the migration space, quantified as the cation–cation distance midst the migration path for the oxygen, and (2) the strength of the bond between the oxygen and the nearest cation preventing the oxygen from migrating. Increasing of the migration space and weakening of the oxygen–cation bond contribute to the decrease of the vacancy migration barrier, and *vice versa*. In assessing the effective diffusivity as a function of strain in YSZ, we constructed a data base of migration paths and barriers to account for the important effects of local distributions of vacancies and dopant cations near the migration path. KMC simulations using this database showed that the macroscopic oxygen diffusivity increases exponentially in YSZ up to a critical value of biaxial tensile strain, with a more significant impact at the lower temperatures. Beyond this critical value, the strain state in YSZ worsens the diffusivity due to the local relaxations that strengthen the oxygen–cation bond at the initiation of migration. One could view this critical strain state as the optimal strain, or the *fastest strain*, to attain the highest benefit of the biaxial lattice strain on the oxygen diffusivity in the material system. The maximum enhancement in diffusivity in YSZ was 6.8×10^3 times higher at 4% strain and temperature of 400 K. This is a significant and desirable increase. Nevertheless, it is far below the eight orders of magnitude increase reported by Barriocanal *et al.* for the thin-film YSZ layers coherently strained between STO layers.⁸ Therefore, we believe that the lattice strain alone cannot be responsible for the colossally high ionic conductivity suggested to occur in YSZ in ref. 8. Nevertheless, given our results, controlling the lattice strain by direct mechanical load or by creating a coherent hetero-interface to induce an optimal strain state can enable desirably high ionic conductivity at reduced temperatures in the fluorite material, the YSZ in this case.

The insights gained here for the role of lattice strain on the local bonding structure and ionic charge transport process are of importance for modulating the transport properties in a variety of solid state conducting material applications, beyond the specific SOFC electrolyte material studied in this work. Interesting examples may extend to Li-ion batteries, oxygen gas sensors, semi-conductors and photovoltaics. We believe that the mechanistic results obtained in this study, particularly on the

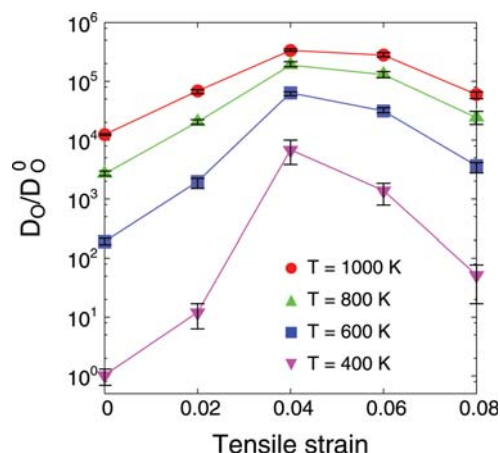


Fig. 12 The relative enhancement of the oxygen diffusivity calculated by the kinetic Monte Carlo simulations at different temperatures and strain states. D_0^0 is the oxygen diffusivity at $\varepsilon = 0.00$ at 400 K. The diffusivity increases exponentially with strain, and shows a maximum at (or near) $\varepsilon = 0.04$ followed by a decrease at higher strains. The increase in diffusivity is more significant at lower temperatures.

non-linear and competing consequences of strain on the bonding structure in the vicinity of the ionic carrier species, provides insights for creating functional strained nano-structures for ionic and electronic conducting devices, including but not limited to SOFCs.

Acknowledgements

We thank the Nuclear Regulatory Commission for financial support, and the National Science Foundation for computational support through the TeraGrid Advanced Support Program under Grant No. TG-ASC090058.

References

- J. C. Boivin and G. Mairesse, *Chem. Mater.*, 1998, **10**, 2870.
- T. Suzuki, I. Kosacki and H. U. Anderson, *Solid State Ionics*, 2002, **151**, 111.
- I. Kosacki, C. M. Rouleau, P. J. Becher, J. Bentley and D. H. Lowndes, *Solid State Ionics*, 2005, **176**, 1319.
- J. H. Shim, C.-C. Chao, H. Huang and F. B. Prinz, *Chem. Mater.*, 2007, **19**, 3850.
- J. Maier, *Nat. Mater.*, 2005, **4**, 805.
- N. Sata, K. Eberman, K. Eberl and J. Maier, *Nature*, 2000, **408**, 946.
- X. X. Guo, I. Matei, J.-S. Lee and J. Maier, *Appl. Phys. Lett.*, 2007, **91**, 103102.
- J. G. Barriocanal, A. R. Calzada, M. Varela, Z. Sefrioui, E. Iborra, C. Leon, S. J. Pennycook and J. Santamaria, *Science*, 2008, **321**, 676.
- S. Ramanathan, *J. Vac. Sci. Technol., A*, 2009, **27**, 1126.
- A. J. Jacobson, *Chem. Mater.*, 2010, **22**, 660.
- X. Guo, *Science*, 2009, **324**, 465; J. G. Barriocanal, A. R. Calzada, M. Varela, Z. Sefrioui, E. Iborra, C. Leon, S. J. Pennycook and J. Santamaria, *Science*, 2009, **324**, 465.
- M. P. O'Callaghan, A. S. Powell, J. J. Titman, G. Z. Chen and E. J. Cussen, *Chem. Mater.*, 2008, **20**, 2360.
- Y. Hoshina, K. Iwasaki, A. Yamada and M. Konagai, *Jpn. J. Appl. Phys.*, 2009, **48**, 04C125.
- J. Munguía, G. Bremond, J. M. Bluet, J. M. Hartmann and M. Mermoux, *Appl. Phys. Lett.*, 2008, **93**, 102101.
- V. R. D'Costa, Y.-Y. Fang, J. Tolle, J. Kouvetakis and J. Menéndez, *Phys. Rev. Lett.*, 2009, **102**, 107403.
- M. Mavrikakis, P. Stoltze and J. K. Nørskov, *Catal. Lett.*, 2000, **64**, 101.
- J. Kilner, *Nat. Mater.*, 2008, **7**, 838.
- J. Maier, *Prog. Solid State Chem.*, 1995, **23**, 171.
- A. K. Ivanov-Shitz, *Crystallogr. Rep.*, 2007, **52**, 129.
- D. C. Sayle, J. A. Doig, S. C. Parker and G. W. Watson, *Chem. Commun.*, 2003, 1804.
- C. Korte, A. Peters, J. Janek, D. Hesse and N. Zakharov, *Phys. Chem. Chem. Phys.*, 2008, **10**, 4623.
- N. Schichtel, C. Korte, D. Hesse and J. Janek, *Phys. Chem. Chem. Phys.*, 2009, **11**, 3043.
- K. Suzuki, M. Kubo, Y. Oumi, R. Miura, H. Takaba, A. Fahmi, A. Chatterjee, K. Teraishi and A. Miyamoto, *Appl. Phys. Lett.*, 1998, **73**, 1502.
- W. Araki, Y. Imai and T. Adachi, *J. Eur. Ceram. Soc.*, 2009, **29**, 2275.
- R. Pornprasertsuk, P. Ramanarayanan, C. B. Musgrave and F. B. J. Prinz, *J. Appl. Phys.*, 2005, **98**, 103513.
- W. L. Roth, R. Wong, A. I. Goldman, E. Canova, Y. H. Kao and B. Dunn, *Solid State Ionics*, 1986, **18–19**, 1115; H. Morikawa, Y. Shimizugawa, F. Marumo, T. Harasawa, H. Ikawa, K. Tohji and Y. Udagawa, *J. Ceram. Soc. Jpn*, 1988, **96**, 253; M. H. Tuilier, J. Dexpert-Ghys, H. Dexpert and P. Lagarde, *J. Solid State Chem.*, 1987, **69**, 153.
- M. Weller, *Z. Metallkd.*, 1993, **84**, 6.
- D. Steele and B. E. F. Fender, *J. Phys. C: Solid State Phys.*, 1974, **7**, 1.
- B. W. Veal, A. G. McKale, A. P. Paulikas, S. J. Rothman and L. J. Nowicki, *Physica B+C*, 1988, **150**, 234; D. Komyoji, A. Yoshiasa, T. Moriga, S. Emura, F. Kanamaru and K. Koto, *Solid State Ionics*, 1992, **50**, 291.
- C. R. A. Catlow, A. V. Chadwick, G. N. Greaves and L. M. Moroney, *J. Am. Ceram. Soc.*, 1986, **69**, 272.
- P. Li and J. E. Penner-Hahn, *Phys. Rev. B: Condens. Matter*, 1993, **48**, 10063; P. Li and J. E. Penner-Hahn, *Phys. Rev. B: Condens. Matter*, 1993, **48**, 10074; P. Li and J. E. Penner-Hahn, *Phys. Rev. B: Condens. Matter*, 1993, **48**, 10082.
- J. P. Goff, W. Hayes, S. Hull, M. T. Hutchings and K. N. Clausen, *Phys. Rev. B*, 1999, **59**, 14202.
- K. Kawata, H. Maekawa, T. Nemoto and T. Yamamura, *Solid State Ionics*, 2006, **177**, 1687.
- G. Stapper, M. Bernasconi, N. Nicoloso and M. Parrinello, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 797.
- A. Bogicevic, C. Wolverton, G. M. Crosbie and E. B. Stechel, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **64**, 014106.
- A. Bogicevic and C. Wolverton, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2003, **67**, 024106.
- A. Bogicevic and C. Wolverton, *Europhys. Lett.*, 2001, **56**, 393.
- X. Xia, R. Oldman and R. Catlow, *Chem. Mater.*, 2009, **21**, 3576.
- M. Sakib Khan, M. Saiful Islam and D. R. Bates, *J. Mater. Chem.*, 1998, **8**, 2299.
- M. O. Zacate, L. Minervini, D. J. Bradfield, R. W. Grimes and K. E. Sickafus, *Solid State Ionics*, 2000, **128**, 243.
- D. A. Andersson, S. I. Simak, N. V. Skorodumova, I. A. Abrikosov and B. Johansson, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 3518.
- S. Garcia-Martin, D. P. Fagg and J. T. S. Irvine, *Chem. Mater.*, 2008, **20**, 5933.
- A. Predith, G. Ceder, C. Wolverton, K. Persson and T. Mueller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **77**, 144104.
- F. Pietrucci, M. Bernasconi, A. Laio and M. Parrinello, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 094301.
- G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter*, 1993, **47**, 558.
- G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter*, 1996, **54**, 11169.
- P. E. Blöchl, *Phys. Rev. B: Condens. Matter*, 1994, **50**, 17953.
- G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758.
- J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- R. Krishnamurthy, Y.-G. Yoon, D. J. Srolovitz and R. Car, *J. Am. Ceram. Soc.*, 2004, **87**, 1821.
- G. Mills and H. Jónsson, *Phys. Rev. Lett.*, 1994, **72**, 1124.
- G. Henkelman, B. P. Uberuaga and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9901.
- A. Van der Ven, G. Ceder, M. Asta and P. D. Tepesch, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **64**, 184307.
- M. Martin, *J. Electroceram.*, 2006, **17**, 765.
- F. Frey, H. Boysen and I. K. Bischoff, *Z. Kristallogr.*, 2005, **220**, 1017.
- D. N. Argyriou, M. M. Elcombe and A. C. Larson, *J. Phys. Chem. Solids*, 1996, **57**, 183.
- N. Ishizawa, Y. Matsushima, M. Hayashi and M. Ueki, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1999, **55**, 726.
- D. Baiter, M. Bartsch, B. Baufeld, A. Tikhonovsky, M. Rühle and U. Messerschmidt, *J. Am. Ceram. Soc.*, 2001, **84**, 1755.
- A. Van der Ven, J. C. Thomas, Q. C. Xu, B. Swoboda and D. Morgan, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 104306.
- A. Kushima and B. Yildiz, *ECS Trans.*, 2009, **25**, 1599.