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Ken Suzuki, Momoji Kubo, Yasunori Oumi, Ryuji Miura, Hiromitsu Takaba, Adil Fahmi, Abhijit Chatterjee, Kazuo Teraishi, and Akira Miyamoto[a]

Department of Molecular Chemistry & Engineering, Faculty of Engineering, Tohoku University, Aoba-ku, Sendai 980-77, Japan

The application of strain to yttria-stabilized zirconia (YSZ), which can be realized by sandwiching a thin YSZ film epitaxially between layers of a material with larger lattice constants, is proposed as a means to enhance oxygen ion mobility. The possible mechanism of such an enhancement was investigated by molecular dynamics using a CeO_2–YSZ superlattice. The calculated diffusion coefficient of oxygen ions in the superlattice is some 1.7 times higher than in YSZ alone due to a decreased activation barrier from the strain of the YSZ structure. © *1998 American Institute of Physics.* [S0003-6951(98)02137-8]

Considerable attention has been focused on cubic yttria-stabilized zirconia (YSZ), $(Y_2O_3)_c(ZrO_2)_{1-c}$, due, in part, to its industrial application in fuel cells, sensors, catalysts, and ceramics.[1-3] Key to these applications is the high mobility of oxygen ions which the material supports, any enhancement of which will improve the material's performance. Many studies have pursued the synthesis of YSZ-based materials with high oxygen ion diffusion and the effects of yttria concentration and temperature on oxygen ion mobility have been well studied experimentally. The diffusion coefficient of oxygen ions reaches a maximum at a yttria concentration of $c = 0.08$–0.10. Molecular dynamics (MD) simulations of ion diffusion in YSZ (Refs. 4–6) have also been reported.

We propose here a different approach to enhancing the oxygen ion diffusion in YSZ and its evaluation by MD simulations (Fig. 1). By sandwiching a strained YSZ layer between a material having larger lattice constants than that of YSZ, we propose that the oxygen ion diffusion in YSZ will be enhanced. Epitaxial growth of YSZ on a material with larger lattice constants will result in expansion of the YSZ lattice constants, together with some change in the local Zr–Zr, Zr–Y, and Y–Y distances. Such structural changes may lower the activation barrier for oxygen ion diffusion, potentially leading to an increased diffusion rate. Recent progress in experimental techniques for achieving epitaxial growth of metal oxides,[7] such as laser molecular beam epitaxy and chemical vapor deposition, may permit the construction of such strained YSZ superlattices.

The MD calculations were performed using the MX-DORTO program developed by Kawamura.[8] The Verlet algorithm was used for integrating the equations of motion, while the Ewald method was applied for calculating electrostatic interactions under three-dimensional periodic boundary conditions.[9] The temperature and pressure were controlled by scaling the atom velocities and unit cell parameters, respectively. Although this will not lead to an accurate ensemble, the MD shows qualitatively the right behavior. A

tensor is constructed for variable cell shape MD. The calculations were performed for 50 000 steps with a time step of 2.0×10^{-15} s. All simulations were performed at 1800 °C, as in previous works.[4-6] A two-body form for the interatomic potential given in Eq. (1) was used for all calculations. In Eq. (1), the first and second terms refer to Coulomb and exchange repulsion interactions, respectively,

$$U(r_{ij}) = Z_i Z_j e^2 / r_{ij} + f_0(b_i + b_j)$$
$$\times \exp[(a_i + a_j - r_{ij})/(b_i + b_j)], \qquad (1)$$

where Z_i is the atomic charge, e is the elementary electric charge, r_{ij} is the interatomic distance, and f_0 is a constant. The parameters a and b in Eq. (1) represent the size and stiffness, respectively. The potential parameters were adjusted (Table I) so as to reproduce the lattice constants and the thermal expansion coefficients of YSZ (10 mol % Y_2O_3), Y_2O_3, and CeO_2 crystals. The dynamical features of the oxygen ion diffusion process were investigated using the three-dimensional visualization programs MOMOVIE and RYUGA.[10]

MD simulations were carried out for four different concentrations of Y_2O_3 in YSZ: 4.85, 10.2, 16.1, and 22.7 mol % Y_2O_3. Figure 2(a) shows the trajectories of O, Zr, and Y ions in YSZ at 10.2 mol % of Y_2O_3. The cations of the YSZ structure (Zr and Y ions) maintain the face-central-cubic (fcc) arrangement and the oxygen ions are distributed over the tetrahedral sites formed by four neighboring cations
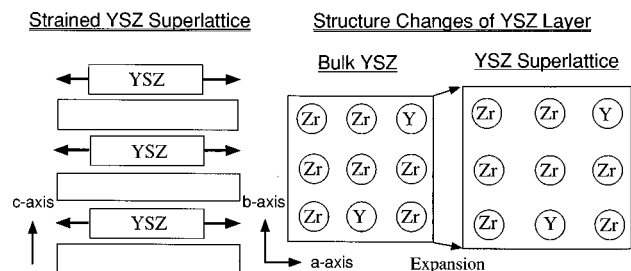

FIG. 1. Schematic concept for enhancing the oxygen ion diffusivity in YSZ: sandwiching YSZ between materials that have larger lattice parameters leads to a positive strain and increase in the YSZ lattice parameters. It is proposed to increase oxygen ion diffusivity.

[a]Corresponding author. Electronic mail: miyamoto@aki.che.tohoku.ac.jp

TABLE I. The potential parameters of Zr, Ce, Y, and O ions.

Atom	Z_i	$a_i/\text{Å}$	$b_i/\text{Å}$
Zr	+2.4	1.227	0.070
Ce	+2.4	1.396	0.070
Y	+1.8	1.327	0.070
O	−1.2	1.503	0.075

and diffuse between well-defined sites in the [100], [010], and [001] directions. In order to investigate the effect of Y_2O_3 concentration on the oxygen ion diffusion, mean-square displacements (MSD) for all constituting ions were calculated at all dopant concentrations. The self-diffusion coefficient D of oxygen ions obtained from the slope of the MSD values has a maximum at 10.2 mol % of Y_2O_3 in the plot of D versus the dopant concentration, in agreement with experimental results[11] and previous MD simulations.[4] The oxygen ion diffusion in bulk YSZ at 9.1 mol % Y_2O_3 was simulated over the temperature range 800–1800 °C and the activation energy for oxygen ion diffusion was calculated from Arrhenius plots of D versus temperature. The activation energy obtained is 15 kcal/mol, in close agreement with the experimental value of 18 kcal/mol.[12]

Following this verification of the simulation procedures and interatomic potentials, a strained YSZ lattice was simulated to verify our concept of enhanced oxygen ion diffusion (Fig. 1) and to investigate the role of lattice strain on the YSZ structural dynamics. The strained YSZ structure was constructed with a Y_2O_3 concentration of 10.2 mol %, which gives the maximum oxygen ion diffusivity. The lattice constants a and b of YSZ at 10.2 mol % Y_2O_3 were expanded to 5.506 Å (strain=$\Delta a/a_0$=5.0%, with a_0=5.243 Å), while the lattice constant c was fixed at the original value of 5.243 Å; this is denoted YSZ with 5.0% strain. When YSZ epitaxially grows above a material having larger lattice constants than those of YSZ, the a and b parameters will elongate, whereas the c parameter is expected to contact slightly according to the Poisson's ratio. As reduction of the c parameter is relatively small, its value was not changed for the present simulations.

Figure 2(b) shows trajectories of O, Zr, and Y ions in the YSZ structure with 5.0% lateral strain. The oxygen ion diffusion in this structure is increased relative to that in the unstrained structure as shown in Fig. 2(a). The MSD values for oxygen ions in the structure with 0.0% and 5.0% strain are both plotted in Fig. 3. The diffusion coefficient of oxygen ions in the YSZ structure with 5.0% strain is about 2.7 times
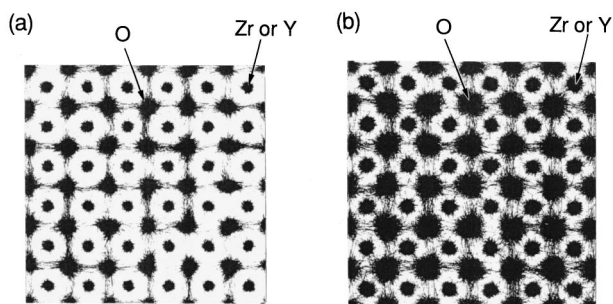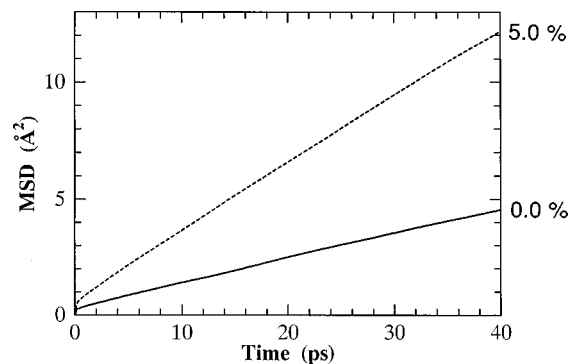
FIG. 3. Mean-square displacements (MSD) of oxygen ions in YSZ at 10.2 mol % Y_2O_3 with 0.0% and 5.0% strain.

larger than that without strain. The introduction of strain appears to enhance the oxygen ion diffusivity in YSZ. Moreover, Fig. 2 indicates that the mobilities of Zr and Y ions in YSZ with 5.0% strain also increase, although they do not migrate through the YSZ structure under the conditions simulated. The increased mobility of the Zr and Y ions may facilitate the greater diffusivity rate of the oxygen ions; in order to clarify the mechanism of enhanced oxygen ion mobility in the strained YSZ structure, we investigated the dynamical structural details in YSZ for the 5.0% and 0.0% strain cases. Figure 4 shows the Zr–Zr partial radial distribution functions (RDF) integrated over the 50 000 MD simulation steps. The first peak, at 3.6 Å, in the unstrained case, shifts to 3.7 Å when 5% lateral strain is applied. Similar shifts are observed for the second, third, and fourth peaks. Furthermore, all of the peaks are broadened in the strained case, indicative of increased vibrational amplitudes. As a direct consequence, the oxygen ions should more easily cross the midpoint of the Zr–Zr vectors when migrating towards a neighboring tetrahedral site. Previous works[1,2] have reported that the maximum barrier along the oxygen ion diffusion path is located at the center point between two cations (Zr–Zr, Zr–Y, and Y–Y). Our simulations confirm that larger average cation–cation distances and large vibrational amplitudes lead to a lowering of the barrier height, which enhances the oxygen ion diffusion.

CeO_2 is a suitable candidate for sandwiching the YSZ structure to introduce strain by expanding the a and b lattice parameters. Like YSZ, CeO_2 adopts the fluorite structure, with a lattice parameter of 5.411 Å, some 5.17% larger than that of the YSZ at 10 mol % Y_2O_3, 5.145 Å. Hence, YSZ is

FIG. 2. Trajectories of O, Zr, and Y ions in YSZ at 10.2 mol % Y_2O_3 (a) with no strain and (b) with 5.0% strain.
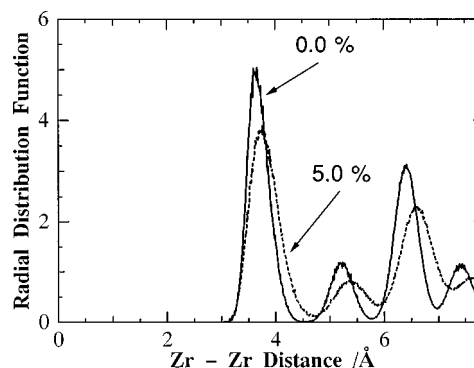
FIG. 4. Zr–Zr partial radial distribution functions in YSZ at 10.2 mol % Y_2O_3 (a) with no strain and (b) with 5.0% strain.
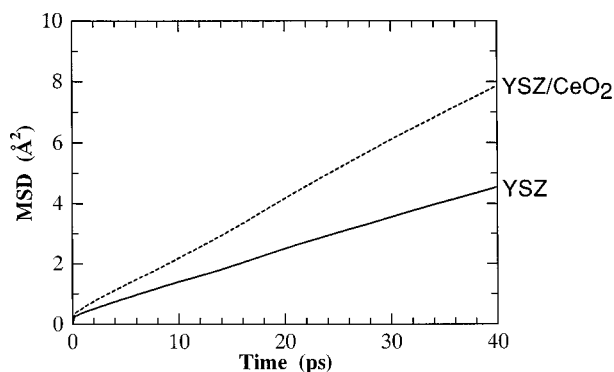
FIG. 5. Mean-square displacements of oxygen ions in the YSZ and YSZ/CeO$_2$ superlattice at 10.2 mol % Y$_2$O$_3$.

expected to grow epitaxially on CeO$_2$ and vice versa. We performed MD calculations on a superlattice comprising YSZ at 10.2 mol % Y$_2$O$_3$ (three layers) and CeO$_2$ (three layers) and compared the oxygen ion diffusivity for YSZ alone. The cell parameters of the superlattice model were optimized; the *a* and *b* parameters of the YSZ slab increase, and the *c* parameter decreases relative to the bulk. Figure 5 shows MSD values of the oxygen ions in the YSZ and YSZ/CeO$_2$ structures. The diffusion coefficient of the oxygen ions in the YSZ component of the YSZ/CeO$_2$ superlattice is surprisingly some 1.7 times larger than that in bulk YSZ. Hence, CeO$_2$ is indicated as a suitable material for

enhancing the oxygen ion diffusivity in YSZ. The depth profile of the oxygen ion MSD in the YSZ/CeO$_2$ system was also examined; the oxygen ions located in the middle region of the YSZ component are found to diffuse more rapidly than those at the YSZ/CeO$_2$ interface.

In conclusion, the oxygen ion diffusion in YSZ is enhanced significantly when YSZ is sandwiched between a material having larger lattice constants. A YSZ/CeO$_2$ strained superlattice is suggested as a potential candidate for enhancing the oxygen ion diffusion in this way.

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