

## TITLE

Mechanical Stress Effect on Oxygen Ion Mobility in 8 mol%-Yttria-Stabilized Zirconia Electrolyte

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## ABSTRACT

In the present study, the effect of mechanical tensile stress on oxygen mobility in 8 mol% yttria-stabilized zirconia (8YSZ) was investigated. The experimental results show that the ionic conductivity increases with stress and saturates. The maximum improvement in the conductivity was about 18 % observed at 973 K. The simulation results show that the diffusion coefficient increases with stress and decreases with excessive stress. The maximum improvement was about 40 % observed at 973 K. The improvement was larger at lower temperatures in both the experiment and the simulation. The strain caused by the stress is considered to have caused the gradient in the potential energies of the neighbouring oxygen sites, especially around the yttrium ions, which probably facilitated the migration of the oxygen ions.

## KEY WORDS

Ionic conductivity, Residual stress, ZrO<sub>2</sub>, Fuel cells

## INTRODUCTION

Fuel cells are attractive as a way to solve global energy and environmental problems. Among the various fuel cells, the solid oxide fuel cell (SOFC) has the highest efficiency so there are high expectations for its applications, such as a source for distributed household power and vehicular auxiliary power. A lot of research has been conducted to improve the cell performance. The unit cell of the SOFC has a layered structure consisting of an anode, electrolyte, and cathode. Because the conductivity of oxygen ions in the electrolyte has a significant effect on the cell performance, many kinds of electrolyte materials with high ionic conductivity have been developed [1,2]. Zirconia-based materials, e.g., yttria-stabilized zirconia (YSZ), are common electrolytes for SOFCs at present.

Due to differences in the thermal expansion and reduction shrinkage of each material in the layered unit cell, residual stress and thermal stress occur. Several researchers [3,4] have reported that the internal stress possibly reaches to hundreds of MPa, which could degrade the materials and cause a fatal fracture of the cell. In addition, such a huge mechanical stress could also exert influence on the power generation of the SOFC during operation, but the effect of the mechanical stress on the cell performance and the ionic conductivity of the electrolyte have not been clarified.

The ionic conductivity of the electrolyte is attributed to the mobility of the oxygen ions. The migration of the oxygen ions in the YSZ electrolytes has been mechanically observed in the measurement of internal friction [5-7], where the mechanical strain excites the oxygen ion to migrate. The oxygen migration in the YSZ electrolytes has also been observed in the mechanical anelastic behaviour at room temperature [8], where the strain increases with time under a constant stress. Our previous study showed that the tensile stress could increase the conductivity at a relatively low temperature [9] while the decrease of the ionic conductivity by compressive stress was observed in the Ref. [10]. In addition, a molecular dynamics

simulation (MD) showed that the expansive strain induced in the YSZ could facilitate the diffusion of the oxygen ions [11]. These studies suggest that the effect of mechanical stress on ionic conductivity as well as cell performance should be considered..

In the present study, the effect of tensile stress on the mobility of the oxygen ions in 8 mol% yttria-stabilized zirconia (8YSZ) was investigated. In our experiment, impedance analysis was conducted with mechanically tensioned 8YSZ polycrystalline specimens to examine the tensile stress effect on the conductivity of the oxygen ions. By using an MD simulation, the movement of the oxygen ions with time was calculated under various tensile stress conditions and the stress effect on the self-diffusion coefficient was determined. Based on the results of both the experiment and the simulation, the effect of mechanical stress on oxygen mobility was discussed.

## EXPERIMENTAL PROCEDURE

The effect of tensile stress on the conductivity of the oxygen ions in 8 mol%-yttria-stabilized zirconia (8YSZ) was experimentally investigated. Polycrystalline specimens were prepared from 8YSZ powders (TZ-8Y, Tosol) by the solid-state reaction method. The prepared specimens were cut to a dog-bone shape by a diamond saw for the tensile test. Figure 1 shows the experimental setup used in the present study. After a specimen was hung on alumina jigs, the temperature of the specimen was raised by an infrared furnace (E410-P, Ulvac) and was held at a test temperature. At the test temperature, the specimen was tensioned by a universal material testing machine (4444, Instron). While the tensile load was held at a certain level, the impedance was measured in air by an electrochemical impedance meter (3532-80, Hioki). Then, the conductivity of the oxygen ions was derived from the impedance, and the effect of the tensile stress on the ionic conductivity was investigated.

Both the width and thickness of each specimen were about 1.9 mm. The span of the straight part of the specimen was about 15 mm. The platinum paste were put on the specimen as electrodes, on which the

platinum wires were wound for the impedance measurement. The test temperature ranged from 973 to 1273K. The applied tensile stress was elastic and smaller than 6.0 MPa, where the possible minimum stress was 0.41 MPa with the present experimental setup. The frequency used for the impedance measurement was from 4.0 Hz to 1.0 M Hz and the applied voltage was 1.0 V.

## SIMULATION PROCESS

The effect of tensile stress on the diffusion of the oxygen ions in 8YSZ was investigated by MD simulation. The fluorite crystal structure of 8YSZ was modelled by using an MD program (Materials Explorer 5.0, Fujitsu). The MD cell was prepared in the following process. The original model consisted of  $5 \times 5 \times 5$  unit cells with 25.978-Å side lengths [12,13], containing 500 ions. The original model was kept at 300 K for 30 ps ( $0.5 \text{ fs} \times 60,000$  steps) and sequentially kept at a simulation temperature for 100 ps ( $0.5 \text{ fs} \times 200,000$  steps). During this process, the cell shape was kept cubic. From pair correlation functions, the structure of the MD model prepared through this process was confirmed to be consistent with that in the other studies [13-15]. Then, tensile stress along the  $\langle 111 \rangle$  crystal axis was applied to the MD model.

The simulation was carried out by the Gear's integration method. The Born-Mayer-Huggins interatomic potential was used with the parameters reported in the Ref. [13]. The temperature was controlled by the velocity scaling method, and the Coulomb interaction was calculated by the Edward method. The applied stress was from 0 Pa to 3.8 GPa. The periodic boundary condition was considered, and the shape of the MD cell was assumed to be deformable during the tensile stress loading. The simulation temperature was ranged from 973 to 2000 K, which is from 0.326 to 0.669 K when normalized by the melting point (2988 K). The number of atoms, the temperature, and the pressure were kept constant during the simulation (NTP ensemble).

## RESULTS AND DISCUSSION

### Experimental Results and Discussion

Figure 2 shows the Cole-Cole plots of the impedance and an Arrhenius plot of the ionic conductivity of measured under 0.41 MPa of tensile stress. The conductivity measured at 1273 K with the minimum stress of 0.41 MPa was 0.156 S/cm, which almost agreed with the ones measured without stress in the other studies [1, 9, 16]. In Fig. 2(b), the conductivity with 0.41 MPa slightly higher than the one measured without stress in the Ref. [9], in which the specimen was prepared in the same way as the present study, but they show the same trend. As the conductivity obviously follows a thermally- activated process, the activation energy for the ionic conduction  $\Delta H_c$  was obtained according to the following equation [6,17]:

$$\sigma T = A \exp(-\Delta H_c / RT) \quad (1),$$

where  $\sigma$  is ionic conductivity,  $A$  is the pre-exponential factor,  $R$  is the gas constant, and  $T$  is temperature. The activation energy of the conductivity  $\Delta H_c$  with 0.41 MPa was about 0.80 eV, which is equal to the values obtained in other studies measured without stress. [6,9,16,17]

Figure 3(a) shows Cole-Cole plots of the impedance measured at 973 K with various stresses. The impedance obviously varies with the stress. Figure 3(b) shows the change of the conductivity with the stress, where the conductivity was normalised by the one measured with 0.41 MPa. At any temperature, the impedance increases with the stress and saturates. The improvement of the conductivity was large at the lowest temperature 973 K, and its maximum was about 18 %. The same trend was obtained in the case of the sequential reloading (Fig. 3(c)) because the deformation caused by the stress was elastic. The activation energy  $\Delta H_c$  is almost constant at about 0.80 eV regardless of the applied stress, which implies that there is no change in the fundamental mechanism of the ionic conduction.

In the fluorite structure of 8YSZ, an oxygen ion is located inside a tetrahedron of four cations (Fig. 4), so the potential energy of the oxygen site is determined by those cations [5]. The oxygen ion migrates to its neighbouring site in the other tetrahedron, mostly in the  $\langle 100 \rangle$  direction. Applying stress causes

different strains in the two tetrahedrons depending on the existence of the oxygen ion, which results in differences between the potential energies of the neighbouring oxygen sites [5]. Thus, the gradient of the potential energies produced by the stress could facilitate the migration of the oxygen ions and improve ionic conductivity. Furthermore, the gradient of the potential energies could become larger when one or more zirconium ions around the oxygen ion are substituted by the yttrium ions, thus the oxygen migrations near the yttrium ions can be further facilitated by the applied stress, which will be seen in the MD simulation results.

#### Simulation Results and Discussion

The movement of each type of ions was evaluated by the mean square displacement  $L_{\text{MSD}}$  calculated by [18]

$$L_{\text{MSD}} = (1/N) \sum [r(t) - r(0)]^2 \quad (i = 1 \sim N) \quad (2),$$

where  $r$  is displacement of each ion,  $N$  is a number of ion, and  $t$  is time. Figure 5(a) shows the mean square displacement of the oxygen ions calculated under a no stress condition. The oxygen ions move with time whereas the displacement of the cations is quite small; for instance, at 1273 K, the final displacements of the oxygen ion and the cations after 100 ps are 0.25 and 0.001 nm<sup>2</sup>, respectively. The displacement of the oxygen ion was larger at higher temperatures. Figure 5(b) shows an Arrhenius plot of the self-diffusion coefficient of the oxygen ions  $D_{(\text{O})}$  derived from the slope of Fig. 5(a) according to the following equation:

$$D_{(\text{O})} = L_{\text{MSD}(\text{O})} / 6t \quad (3),$$

where the simulation time from 20 to 100 ps was considered. The self-diffusion process was a thermally-activated one. The activation energy for the ionic diffusion  $\Delta H_{\text{d}}$  was obtained from the slope of Fig. 5(b) according to the following equation [17]:

$$D_{(\text{O})} = B \exp(-\Delta H_{\text{d}} / RT) \quad (4),$$

where B is the pre-exponential factor. The activation energy was 0.43 eV, which is consistent with other MD studies [12,13], has the same order of magnitude of  $\Delta H_c$  obtained from the impedance measurement. It has been generally considered that both the conductivity and the diffusion coefficient are similarly attributed to the same phenomenon, i.e., the oxygen migration [6, 12,13].

Figure 6 shows the mean square displacement of the oxygen ion at 1273 K with various tensile stresses. The displacement of the oxygen ion is obviously affected by the stress. Figure 6(b) shows the change of  $D_{(O)}$  at 1273 K with stress, where the coefficient is normalised by the  $D_{(O)}$  without stress. The diffusion coefficient at 1273 K increases by maximum of 22 % with 0.038 MPa but decreases with excessive stress, i.e., more than 0.38 MPa. It increases by maximum of 40 % at 973 K but merely 4 % at 2000 K. It should be also noted here that the distances between Zr and O ions were 0.208 nm without stress, which is consistent with the other simulations [12,13] and also the experimental values in Ref. [19], and it was almost constant at 0.208 nm up to 0.38 MPa, but showed slightly smaller values 0.207 nm with 38 MPa and 380 MPa.

Figure 7 shows one layer parallel to (100) taken out from the MD model with the diffusion paths of the oxygen, zirconium, and yttrium ions during the simulation time (100 ps) with/without stress. Regardless of the stress, the oxygen ions migrate a long distance in the  $\langle 100 \rangle$  directions whereas the cations only thermally vibrates around their original positions. In addition, as is well known, it is seen that the oxygen ions migrate mostly between the zirconium ions but rarely between the yttrium ions or between the zirconium ion and the yttrium ion due to the larger ionic radius of the yttrium ion [2,16]. Comparison of Figs. 7(a) and 7(b) shows, however, that applying stress allows the oxygen ions to migrate through some of the paths between the yttrium ion and zirconium ion (as shown with dashed circles in Fig. 7(b)), which obviously results in further migration of the oxygen ions. As for the oxygen migration at 1273 K in the  $\langle 100 \rangle$  direction, there were 15 possible paths between the yttrium ion and the zirconium ion in the whole MD model without stress while 24 possible paths appeared with the stress of 0.38 MPa, when  $D_{(O)}$

showed its maximum (Fig. 6(b)). This could be because the stress causes the difference in the potential energy in the oxygen sites and contributes to the promotion of the oxygen migration, especially around the yttrium ions, as explained in Fig. 4. The stress works on the oxygen migration more effectively at lower temperatures probably because the oxygen ion is normally associated with the yttrium ion at lower temperatures due to the charge neutrality [16].

## CONCLUSION

In the present study, the effect of mechanical tensile stress on oxygen mobility in 8 mol% yttria-stabilized zirconia (8YSZ) was investigated. An impedance analysis with mechanically tensioned 8YSZ specimens was conducted in an experiment, and the stress effect on the ionic conductivity of the oxygen ion was examined. In a simulation, the mean square displacement was calculated with various stresses and the stress effect on the self-diffusion coefficient of the oxygen ions was examined.

The experimental results show that the ionic conductivity increases with stress and saturates. The maximum improvement in the conductivity was about 18 % observed at 973 K. The simulation results show that the diffusion coefficient increases with stress and decreases with excessive stress. The maximum improvement was about 40 % observed at 973 K. The improvement was larger at lower temperatures in both the experiment and the simulation. The strain caused by the stress is considered to have caused the gradient in the potential energies of the neighbouring oxygen sites, especially around the yttrium ions, which probably facilitated the migration of the oxygen ions.

The present results imply the importance of considering mechanical stress in the electrolyte of solid oxide fuel cells and also a possibility of improving the power performance by using the stress effect.

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## CAPTIONS

Figure 1 Experimental setup

Figure 2 Temperature dependence of ionic conductivity

(a) Measured with 0.41 MPa (b) Arrhenius plot

Figure 3 Stress effect on ionic conductivity

(a) Measured at 973 K (b) Normalised by value measured with 0.41 MPa (c) Reloading case

Figure 4 Oxygen site in tetrahedron of cations

Figure 5 Temperature dependence of diffusion of oxygen ions without stress

(a) Mean square displacement (b) Self-diffusion coefficient

Figure 6 Stress effect on diffusion of oxygen ion at 1273 K

(a) Mean square displacement (b) Normalised self-diffusion coefficient

Figure 7 Diffusion path at 1273 K during simulation

(a) Without stress (b) With stress of 0.38 MPa in the  $\langle 111 \rangle$  direction