

# Molecular dynamics simulations of yttria-stabilized zirconia

H.W. Brinkman<sup>a</sup>, W.J. Briels<sup>b</sup>, H. Verweij<sup>a</sup>

<sup>a</sup> Department of Inorganic Materials Science, Faculty of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

<sup>b</sup> Department of Chemical Physics, Faculty of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Received 13 April 1995; in final form 8 September 1995

## Abstract

Oxygen diffusion in the oxygen ionic conductor yttria-stabilized zirconia is investigated by means of the molecular dynamics simulation technique. Oxygen ions migrate by means of a discrete hopping process, mainly between neighbouring tetrahedral sites. Diffusion appears to occur in a short time and a long time regime. Only when the oxygen ions have moved over distances much larger than the characteristic distances of the underlying crystal structure, a linear relation is found between the mean square displacement and time. The oxygen tracer diffusion coefficient, obtained from this long time regime, is  $1.86 \times 10^{-6}$  and  $3.23 \times 10^{-6}$  cm<sup>2</sup>/s at 1759 and 2057 K, respectively. The ionic conductivity, calculated from the tracer diffusion coefficient, agrees well with experimental values.

## 1. Introduction

The molecular dynamics (MD) technique is used to study the diffusion of oxygen ions in yttria-stabilized zirconia (YSZ). This material is well known as an oxygen ionic conductor at elevated temperatures and is applied in oxygen sensors and in solid oxide fuel cells. At room temperature undoped zirconia (ZrO<sub>2</sub>) has a monoclinic structure; doping with more than 17 mol% YO<sub>1.5</sub> (or about 9 mol% Y<sub>2</sub>O<sub>3</sub>) stabilizes the cubic fluorite structure at room temperature. The Zr<sup>4+</sup> and Y<sup>3+</sup> ions form an FCC lattice in which most of the tetrahedral positions are occupied by O<sup>2-</sup> ions. The substitution of Zr<sup>4+</sup> by Y<sup>3+</sup> causes the formation of oxygen vacancies (equal to half the amount of Y<sup>3+</sup> ions) to maintain electrical neutrality. These oxygen vacancies are mobile at high temperatures and give rise to oxygen ionic conductivity. The octahedral sites are not occupied.

Although YSZ is a material widely applied in

inorganic materials science, only one research group [1,2] has performed MD simulations with this material. Three compositions (ZrO<sub>2</sub>)<sub>1-x</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>x</sub> with  $x = 0.0485$ , 0.102 and 0.227 at 1800°C were investigated. The oxygen tracer diffusion coefficient has a maximum at  $x = 0.102$ , in accordance with experimental measurements.

In this Letter an MD investigation of oxygen diffusion in (ZrO<sub>2</sub>)<sub>0.92</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>0.08</sub> at 1759 and 2057 K is discussed. Compared to Shimojo et al.'s results [1], our simulation time is much longer, which turns out to be crucial if one wants to calculate diffusion coefficients. An extended investigation is published elsewhere [3].

## 2. Details of the simulation

Constant ( $N$ ,  $V$ ,  $E$ ) MD simulations have been performed using the GROMOS package [4] on a

Table 1  
Interionic potential parameters

$i-j$	$A_{ij}$ (kJ/mol)	$\rho_{ij}$ (nm)	$C_{ij}$ (kJ nm <sup>6</sup> /mol)	Ref.
Zr–Zr	0	1	0	–
Zr–Y	0	1	0	–
Y–Y	0	1	0	–
Zr–O	$9.512 \times 10^4$	0.0376	0	[6]
Y–O	$12.978 \times 10^4$	0.03491	0	[5]
O–O	$2.196 \times 10^6$	0.0149	$2.691 \times 10^{-3}$	[6]

Challenge L computer. The GROMOS code has been adjusted to calculate Coulombic interactions using the Ewald transformation. The equations of motion were integrated by a leap-frog algorithm; periodic boundary conditions were applied. Short range interactions between the ions were represented by Born–Mayer–Buckingham pair potentials,

$$V_{ij}(r_{ij}) = A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6. \quad (1)$$

Parameters were obtained from Refs. [5,6] and are given in Table 1. For the cation–cation interactions only Coulombic interactions were assumed. It was assumed that the YSZ system is fully ionic; the ionic charges were chosen to be 4+, 3+ and 2– for Zr, Y and O, respectively.

A cubic MD simulation cell was chosen, consisting of  $3 \times 3 \times 3$  crystallographic unit cells (in the  $x$ ,  $y$  and  $z$  directions) containing a maximum of 324 ions. For the system  $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$  the MD cell contained 92  $\text{Zr}^{4+}$  ions, 16  $\text{Y}^{3+}$  ions and 208  $\text{O}^{2-}$  ions. According to experiments, the lattice parameter for the cubic YSZ unit cell increases slightly with temperature and yttria content. Therefore, the length of an MD cell was chosen to be 1.5633 nm at a temperature of 1759 K and 1.5678 nm at 2057 K. A cubic (FCC)  $\text{ZrO}_2$  cell was generated by positioning 108  $\text{Zr}^{4+}$  ions and 216  $\text{O}^{2-}$  ions at their regular lattice sites. Next, 16 of the  $\text{Zr}^{4+}$  ions were randomly substituted by  $\text{Y}^{3+}$  ions; 8 of the  $\text{O}^{2-}$  ions were randomly substituted by oxygen vacancies.

Velocities were attributed to the ions, and were re-scaled to an initial temperature of 1 K. In the equilibration stage of the simulation, the system was brought from 1 K to the desired simulation temperature using 5000 steps of 2 fs by weak coupling to an external temperature bath [7]. The systems appeared to be equilibrated already after 4 ps. The real simula-

tion run consisted of 500000 steps of 2 fs (total simulation time 1000 ps). Every 125 steps (every 0.25 ps) the positions of all ions in the system were recorded for 1000 ps. Due to periodic boundary conditions the positions of the ions were recorded with  $x$ ,  $y$  and  $z$  coordinates between 0 and the MD cell length. Every 2500 steps (every 5 ps) the kinetic, potential and total energies of the system were recorded for 1000 ps. For each run, the variation in total energy was not larger than 0.007%. During these runs the temperatures varied by approximately 3.2%.

### 3. Results and discussion

#### 3.1. Migration mechanism

The ion density distribution (i.e. the probability of finding ions in certain regions of the cell) for  $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$  at 1759 K over a 12.5 ps simulation time in the (110) face (slab width 0.01 nm) of a crystallographic unit cell is shown in Fig. 1. This face covers all box positions of interest: cube corners, face centers, tetrahedral and octahedral sites.

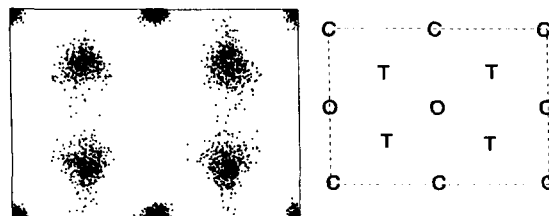


Fig. 1. Left: ion density distribution of the (110) face.  $\text{Zr}^{4+}$  and  $\text{Y}^{3+}$  are positioned at cube corners and (100) face centers;  $\text{O}^{2-}$  ions are positioned at tetrahedral sites. Right: cation sites (C), tetrahedral sites (T) and octahedral sites (O) in the (110) face.

Table 2

Number of oxygen ion jumps in different directions for  $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$  at 1759 K

Direction	Number of jumps	
[100]	2394	(35.1%)
[010]	2053	(30.1%)
[001]	2346	(34.3%)
$\langle 110 \rangle$	21	(0.3%)
$\langle 111 \rangle$	16	(0.2%)
total	6830	
diffusive	894	(13.1%)

Fig. 1 shows that the cations vibrate around their regular sites, that on average the anions tend to dwell in the region of their regular tetrahedral sites and that some of the anions migrate from one regular lattice site to another; so the migration process is a discrete hopping process and not a continuous liquid-like process. The octahedral sites remain vacant during almost the entire simulation. This indicates that octahedral sites hardly play a role in the diffusion process of oxygen ions in YSZ.

In Fig. 1 can be seen that anions migrate mainly in the [001] direction between regular lattice sites and not much in other directions. This is investigated further by looking at the numbers of jumps in the  $\langle 100 \rangle$  directions (to a neighbouring tetrahedral site), in the  $\langle 110 \rangle$  directions (to a tetrahedral site on ' $\sqrt{2}$  distance') and in the  $\langle 111 \rangle$  directions (to an octahedral site). In Table 2 the number of jumps are shown in each of these directions for  $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$  at 1759 K for a 200 ps simulation time. It is seen that almost all jumps occur in  $\langle 100 \rangle$  directions. The fractions of jumps in the [100], [010] and [001] directions are given separately in Table 2 and are almost equal, about 30–35%; this indicates that diffusion in the  $\langle 100 \rangle$  directions is rather isotropic. Similar results have been found by Shimojo et al. [2] for the system  $(\text{ZrO}_2)_{0.898}(\text{Y}_2\text{O}_3)_{0.102}$  at 2073 K.

It is observed during analysis of the simulation data that some of the anions that migrate to a neighbouring tetrahedral site, migrate back to the original tetrahedral site a few time steps later. These migrations will not contribute to the diffusion process and are further referred to as non-diffusive migrations. In Ref. [3] we have found that within the range of 3.85 to 16.13 mol%  $\text{Y}_2\text{O}_3$  dopant at 1759 K, the system

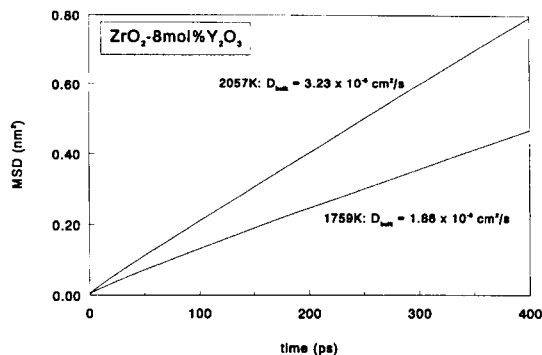


Fig. 2. Mean square displacement (MSD) of oxygen ions in  $\text{ZrO}_2$ -8 mol%  $\text{Y}_2\text{O}_3$  as a function of time for two temperatures.

with 8.00 mol%  $\text{Y}_2\text{O}_3$  has the largest number of diffusive jumps. This is in agreement with literature where a maximum in ionic conductivity is observed for YSZ with about 8–10 mol% yttria.

### 3.2. Diffusion coefficient

Fig. 2 shows the mean square displacement (MSD) of oxygen ions as a function of time at two temperatures. The MSD of  $\text{Zr}^{4+}$  and  $\text{Y}^{3+}$  (not given in the figure) remains constant, while the MSD of the oxygen ions increases with time. This is another indication of the fact that oxygen ions migrate to other lattice sites while cations do not migrate and

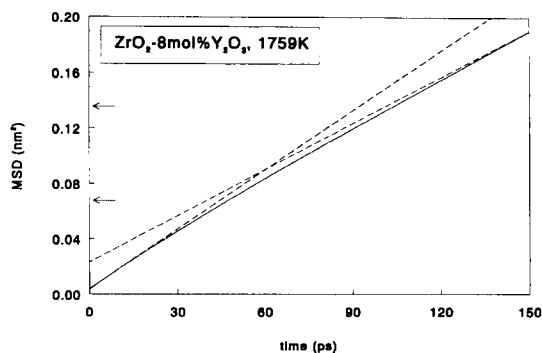


Fig. 3. Mean square displacement (MSD) of oxygen ions in  $\text{ZrO}_2$ -8 mol%  $\text{Y}_2\text{O}_3$  as a function of time at 1759 K. Dashed lines indicate the slope of the curves in the beginning (3–15 ps) and at the end (time  $\rightarrow \infty$ ). Arrows indicate the squared distances between two nearest neighbour tetrahedral sites and next-nearest neighbour sites.

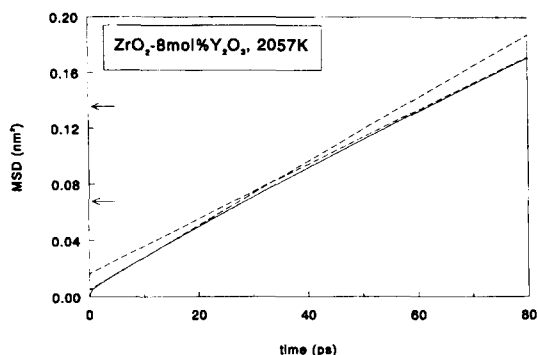


Fig. 4. Mean square displacement (MSD) of oxygen ions in  $\text{ZrO}_2$ -8 mol%  $\text{Y}_2\text{O}_3$  as a function of time at 2057 K. Dashed lines indicate the slope of the curves in the beginning (3–15 ps) and at the end (time  $\rightarrow \infty$ ). Arrows indicate the squared distances between two nearest neighbour tetrahedral sites and next-nearest neighbour sites.

only vibrate around their regular lattice sites, as has already been observed in Fig. 1. The MSD of oxygen ions as a function of time displays several regimes as can be seen in Figs. 2–4. Within the first fraction of a picosecond the vibrational movement around the regular lattice sites determines the MSD. Next, a non-linear relation is found between MSD and time. At MSD values larger than about  $0.16 \text{ nm}^2$  a linear relation is observed between MSD and time.

The oxygen tracer diffusion coefficient  $D(t)$  is related to the MSD of an oxygen particle in time  $t$  via [8]

$$\begin{aligned} \text{MSD}(t) &= \frac{1}{N} \sum_{n=1}^N \langle [r_n(t_0 + t) - r_n(t_0)]^2 \rangle \\ &= B + 6D(t)|t|. \end{aligned} \quad (2)$$

The brackets  $\langle \rangle$  are to be understood as an average over all time origins  $t_0$  within the simulation run; summation occurs over all  $N$  oxygen ions to obtain a statistical accuracy as good as possible. This relation is known as the Einstein relation; the (bulk) tracer diffusion coefficient  $D_{\text{bulk}}$  is obtained when time goes to infinity.

The horizontal arrows in Figs. 3 and 4 at MSD values of  $0.068$  and  $0.136 \text{ nm}^2$  correspond to the (squared) nearest- and next-nearest distance, respectively, between two tetrahedral sites. It is seen that only when the ions have moved over distances much larger than these characteristic distances, a linear

relation between MSD and time is found. The bulk oxygen tracer diffusion coefficients are calculated from the MSD versus time curves according to Eq. (2). Both MSD versus time curves are fitted to a straight line between 150 and 400 ps. For the simulation at 1759 K,  $D_{\text{bulk}}$  is  $1.86 \times 10^{-6} \text{ cm}^2/\text{s}$ ; at 2057 K  $D_{\text{bulk}}$  is  $3.23 \times 10^{-6} \text{ cm}^2/\text{s}$ . In Fig. 2 it is seen that anions move faster with rising temperature. At the lower temperature it takes longer for the system to reach the ‘bulk’ regime than at the higher temperature; in Fig. 3 (1759 K) the ‘transition time’ is around 60 ps whereas in Fig. 4 (2057 K) this time is around 35 ps.

For comparison with Shimojo et al. [1], estimates of a ‘short time diffusion constant’ are given by fitting the MSD versus time curves between 3 and 15 ps to a straight line. These fits are given as dotted lines in Figs. 3 and 4. For the simulation at 1759 K,  $D_{\text{short}}$  is  $2.38 \times 10^{-6} \text{ cm}^2/\text{s}$ ; at 2057 K  $D_{\text{short}}$  is  $3.80 \times 10^{-6} \text{ cm}^2/\text{s}$ . Notice that these ‘short time diffusion constants’ are 18–28% larger than the ‘bulk’ diffusion constants. In their investigation, Shimojo et al. [1] only observe the first, short time regime. Their total correlation time is 30 ps, which is much too short to observe a transition to ‘bulk’ behaviour. From Fig. 6 in Ref. [1] an oxygen tracer diffusion coefficient of  $3.6 \times 10^{-6} \text{ cm}^2/\text{s}$  is found at  $1800^\circ\text{C}$ , which compares well to our value for  $D_{\text{short}}$  at 2057 K.

The oxygen tracer diffusion coefficient  $D$  can be transformed to the dc oxygen ionic conductivity ( $\sigma$ ) via the Nernst–Einstein relation (see e.g. Ref. [9]),

$$\sigma = \frac{H_R N (ze)^2 D}{k_B T}. \quad (3)$$

Here  $H_R$  is the Haven ratio. For vacancy diffusion in an FCC structure,  $H_R$  is equal to the tracer correlation factor  $f$ . At low defect concentrations (in our system the oxygen vacancy concentration is 3.7% of the total number of anion sites)  $f$  is 0.7815 [9].  $N$  is the concentration of the mobile ions,  $ze$  is their charge,  $k_B$  is Boltzmann’s constant and  $T$  is the temperature. For  $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$  the ionic conductivity calculated by Eq. (3) is  $0.3$  and  $0.5 \text{ } \Omega^{-1} \text{ cm}^{-1}$  at 1759 and 2057 K, respectively, using the  $D_{\text{bulk}}$  values given in Fig. 2. Compared to the experimental values for  $(\text{ZrO}_2)_{0.91}(\text{Y}_2\text{O}_3)_{0.09}$  (about 0.9

$\Omega^{-1} \text{ cm}^{-1}$  at 1759 K and  $1.9 \Omega^{-1} \text{ cm}^{-1}$  at 2057 K [10]), these values differ by a factor of 3–4.

#### 4. Conclusions

The results presented here show that oxygen diffusion in  $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$  occurs by means of a discrete hopping mechanism, mainly in  $\langle 100 \rangle$  directions. Our results clearly show a transition from a short time to a long time diffusion regime. This transition occurs when the displacements of the oxygen ions are roughly equal to the characteristic distances of the underlying crystal structure. In the past this has not been realized well enough. The ‘bulk’ oxygen tracer diffusion coefficient, obtained from the long time regime, is  $1.86 \times 10^{-6}$  and  $3.23 \times 10^{-6} \text{ cm}^2/\text{s}$  at 1759 and 2057 K, respectively. The ionic conductivities, calculated from these diffusion coefficients, differ only by a factor of 3–4 from experimental values.

#### Acknowledgements

This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with

financial aid from the Netherlands Organization for Scientific Research (NWO).

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