SOLID STATE IONICS
DIFFUSION & REACTIONS

Molecular dynamics simulation of oxygen diffusion in cubic yttria-stabilized zirconia: Effects of temperature and composition

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ABSTRACT

Diffusion of oxygen ions in yttria-stabilized zirconia was studied using constant-volume molecular dynamics simulations for temperatures ranging from 1000 K to 2000 K and for varied compositions between 4 and 12 mol% Y_2O_3. Non-monotonic dependence of diffusion coefficients on yttria content was observed with a maximum at 5–7 mol%. With increasing temperature the position of diffusion maximum was drifting towards higher Y_2O_3 content. The highest oxygen diffusion coefficients were obtained for Y_2O_3 concentrations close to the limit of cubic phase stability region. Diffusion activation energies increased monotonically with increasing concentration of the dopant.

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1. Introduction

Yttria-stabilized zirconia (YSZ) is one of the most important engineering ceramic materials with a wide variety of actual and potential applications. Because of its ability to conduct oxygen ions YSZ is often the material of choice for designing high-temperature solid-oxide fuel cells. The ion conduction in YSZ is the result of substitution of Zr^{4+} ions in the cation sub-lattice of ZrO_2 by Y^{3+} ions, which stabilizes the eight-coordinate fluorite-type cubic structure and creates vacancies in the anion sub-lattice. For low dopant concentrations the oxygen ion conductivity in YSZ increases with increasing number of vacancies. However, the addition of Y^{3+} ions also increases the migration energy for O^{2-} anions crossing a Y–Y or Y–Zr edge. This effect decreases the mobility in the anion sub-lattice and with increasing concentration of yttrium gradually might override the increase in the number of vacancies, causing the ion conductivity to pass through a maximum. In experimental studies this maximum is usually observed between 7 and 10 mol% Y_2O_3 [1–6]. Temperature is another important factor influencing the position of oxygen conductivity maximum. At higher temperatures the mobility in the anion sub-lattice increases, while the migration barriers are not affected by temperature. Thus, in high-

temperature studies the conductivity maximum can be observed at higher yttrium contents [6].

Significant discrepancies between the oxygen diffusivities or conductivities obtained by different experimental techniques and the demand for atomic-level insight into the mechanisms of ionic diffusion have spurred the interest in computer simulation studies of oxygen conduction. However, up to date only a limited number of simulation studies were devoted to the combined effects of temperature and YSZ composition. The pioneering work of Okazaki et al. [7] demonstrated the existence of oxygen diffusion maximum near 10 mol% Y_2O_3 by Molecular Dynamics (MD) simulations. In an in-depth study by Li and Hafskjold [8] the effects of composition and temperature on the diffusion of oxygen anions have received more attention. Depending on the set of parameters used for intermolecular potentials in MD simulations, the strongest oxygen diffusion was observed between 8 and 11 mol% Y_2O_3 at 900 K. The location of diffusion maximum was also influenced by the distribution of dopant cations in the crystalline structure. For higher temperatures (1200 K and 1500 K) the diffusivity showed a weak maximum at 11–15 mol% Y_2O_3 or even increased monotonically for YSZ samples containing up to 20 mol% Y_2O_3. Suzuki et al. [9] observed the highest oxygen diffusion near 10 mol% Y_2O_3 in MD simulations of bulk YSZ, but systems with lower concentrations of the dopant were not investigated in detail. In the computational study by Yamamura and co-workers [10] the highest values of oxygen diffusion coefficients were obtained for YSZ8 at 1273 K. In general, the early simulation studies provided sufficient level of detail for neither

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temperature nor YSZ composition, thus complicating the determination of the exact position of diffusion maximum and precluding the analysis of its sensitivity to temperature. With increasing availability of computational resources these shortcomings were addressed in subsequent studies.

In an MD simulation study by Sawaguchi and Ogawa [11] the position of the maximum was determined to be near 7.5 mol% Y_2O_3 at 973 K, 9.0 mol% at 1800 K, and at 11–14 mol% above 2000 K. In the work of Kilo et al. [12] oxygen diffusivity was shown to have a maximum at 10 mol% Y_2O_3 at 973 K with the highest diffusion coefficient value being obtained for 11 mol% Y_2O_3. Simulations for higher temperatures were said to have been carried out, but were not reported in detail. Performing an MD study in a wide temperature range, Arima et al. [13] observed the highest oxygen diffusivities either at 8 mol% Y_2O_3 (1200 K, 1400 K, 1600 K, 2000 K) or slightly above 10 mol% (1000 K, 1800 K). The apparent lack of systematicity in these data can be attributed to small system size and short simulation times. Cheng and co-workers [14] located a diffusion maximum for YSZ8 at 1273. However, the influence of temperature on the position of the diffusion maximum has not been determined despite the availability of simulation data for other temperatures.

Devanathan et al. [15] emphasized the discovery of diffusion maximum at 8 mol% Y_2O_3. A more detailed analysis of their simulation data reveals the fact that at 1125 K oxygen diffusivities for YSZ6 and YSZ8 are almost equal, with the diffusion coefficient for YSZ6 possibly being even higher than that for YSZ8. On the other hand, above 2000 K YSZ10 appears to show higher oxygen diffusion than both YSZ6 and YSZ8. Therefore, YSZ8 displays the highest oxygen diffusion only in about a half of the whole temperature range considered. The data obtained by Araki and Arai [16] from MD simulations using the Buckingham potential with two different sets of parameters indicate that below 1500 K the oxygen diffusion coefficient for YSZ4 is greater than that for YSZ8. The diffusion coefficients for these two samples become equal around 1600 K, while for higher temperatures the latter sample demonstrates higher oxygen diffusion. Marrocchelli et al. [17] observed the highest oxygen diffusion coefficients near 6.4 (1250 K) and 8.7 (1670 K) mol% Y_2O_3 in MD simulations with ab initio-parameterized polarizable interaction potentials. Lau and Dunlap [18] found no temperature influence on the position of oxygen diffusion maximum, reporting the highest oxygen conductivities for YSZ8 crystals at 800 K, 1000 K, and 1200 K. Unfortunately, the determination of the exact location of diffusion maximum at these temperatures is hindered by the lack of data for lower (ca. 7 mol%) content of Y_2O_3, while for higher temperatures (1400 K and above) no data is available. Finally, Chang et al. [19] reported a diffusion maximum at 7 mol% Y_2O_3 at 1273 K.

In recent years MD studies were supplemented by Kinetic Monte Carlo (KMC) simulations. In an extensive multiscale study [20] KMC simulation reproduced both primary trends observed in experimental studies: the existence of oxygen diffusivity maximum (found between 7 and 11 mol% Y_2O_3 for 1000–2200 K) and the shift of its position towards higher yttria content with increasing temperature. Pornprasertsuk et al. studied oxygen diffusion in YSZ using KMC [21]. In the low-temperature region (750–1200 K) the highest diffusion coefficients were obtained between 7 and 8 mol% Y_2O_3, while at higher temperatures (1350–1500 K) the maximum shifted to 8–9 mol%. The authors noted that KMC simulation data should in fact correspond to higher experimental temperatures due to underestimation of migration barriers in their DFT calculations. In a KMC study by Lee and co-workers [22] the maximum of oxygen conductivity was found near 8 mol% Y_2O_3.

The goal of the present work is to produce a detailed dependence of oxygen diffusion on YSZ composition in the temperature range relevant for engineering applications based on oxygen ion conduction. Different parameterizations of interaction potentials will be used to compensate for the model-dependence of computed diffusion coefficients. Special attention will be paid to the influence of temperature and composition on the location of diffusion maximum and to the dependence of diffusion activation energy on composition.

2. Simulation details

Molecular simulation studies of ionic diffusion typically make use of either the constant-pressure (NpT) or constant-volume (NVT) molecular dynamics technique. In constant-pressure MD studies the volume of the basic cell is noticeably fluctuating during the simulation. The magnitude of these fluctuations may sometimes be as large as several percent of the average cell length. While for the easily compressible fluid phases the use of this approach is justified, for solids such volume changes appear to be very large and may occasionally result in unrealistic behavior of the simulated system. Furthermore, from a technical point of view the calculation of diffusion coefficients via the Einstein relation assumes that the coordinates of particles are changing only due to diffusion, not due to the rescaling of coordinates during volume changes. Therefore, though both NVT and NpT techniques should theoretically yield identical results for diffusion in the limit of an infinitely large system, for nanometer-sized fragments of bulk ionic conductors typically used in simulation studies the results obtained by the two MD techniques may be significantly different.

In this work NVT molecular dynamics simulations were carried out for a system of $5 \times 5 \times 5$ unit cells containing from 1481 (YSZ4) to 1446 (YSZ12) ions (Table 1). The initial structure was created by substituting a number of Zr^{4+} cations chosen at random in an ideal ZrO_2 cubic lattice by Y^{3+} cations. Vacancies in the anionic sub-lattice were created by removing oxygen ions from random positions. The number of created vacancies was equal to a half of the number of Y^{3+} cations, as required by the electroneutrality condition. Since the computed properties of simulated YSZ samples can be affected by the distribution of Y^{3+} cations, this potential problem was addressed by running a series of MD test simulations at intermediate temperature (1500 K) using several different cation distributions for each YSZ composition. While the values of diffusion coefficients obtained for various distributions of cations may differ significantly from each other, the data averaged for up to 20 random cation distributions appear to be completely consistent with the single-configuration data on the dependence of diffusion on Y_2O_3 concentration presented in this work. However, a detailed simulation study of cation distribution effects is clearly desirable to evaluate their role with more precision and confidence.

The formula introduced by Terblanche [23] was used to calculate the lattice parameters for different temperatures and YSZ compositions:

$$l = 5.1208 + 0.00231y + 4.6468 \cdot 10^{-5}(T-273) + 7.6613 \cdot 10^{-9}(T-273) \quad (1)$$

where l is the size of the cubic YSZ unit lattice, T is the temperature and y is the mole percentage of Y_2O_3. Though this formula was initially derived for temperatures from ambient to 1270 K, later it was confirmed to be valid at least up to 1473 K [24]. Since no anomalies were observed

Table 1
Details of simulated systems.

YSZ sample	Exact Y_2O_3 content, mol%	Cell size, nm[a]	Number of ions in simulation cell		
			Zr^{4+}	Y^{3+}	O^{2-}
YSZ4	3.95	2.5935	462	38	981
YSZ5	5.04	2.5947	452	48	976
YSZ6	5.93	2.5958	444	56	972
YSZ7	7.07	2.5970	434	66	967
YSZ8	7.99	2.5981	426	74	963
YSZ9	8.93	2.5993	418	82	959
YSZ10	9.89	2.6005	410	90	955
YSZ12	12.11	2.6028	392	108	946

[a] The length of cubic simulation cell varies with temperature. The values given in the table correspond to 1500 K.