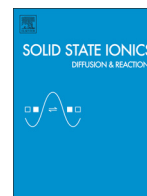




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Unusual properties of a model of an intergrain boundary in solid oxide ceramic electrolytes[☆]

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ABSTRACT

A simple model of an intergrain region of an oxide ceramic electrolyte is used for kinetic Monte Carlo (KMC) simulations of the charge and electric field distribution in the system consisted of the grain bulks and intergrain region. The activation energies of thermally activated particle transitions in the grain bulk and intergrain region alongside the medium dielectric constant were the parameters of the model. The influence of the charge distribution on the grain boundary resistance is discussed. The density gradient contribution to the free energy was taken into account; the modified Nernst–Planck–Poisson (NPP) equation was formulated and used for the analysis of the charge distribution in the vicinity of the intergrain region. The analytical solutions of the modified NPP equation are compared with the results of the KMC simulations. The parameters of yttria stabilized zirconia are used as reference values while the model is of a more general nature.

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1. Introduction

Ceramic electrolytes represent a class of technologically important materials that are widely used in energy storage and conversion devices, sensors, etc. [1–5]. At the same time, these electrolytes are very complicated objects for atomic-scale understanding of charge storage and transfer processes because of long range Coulomb interion interactions, highly defective crystalline structure and the important role that their electronic subsystems play in these processes. Probably, the only way to reliably predict their properties is the use of ab-initio wave function quantum mechanics calculations for generating force fields for further molecular dynamics (MD) simulations. However, this requires huge computational resources [6–9].

Density functional theory (DFT) methods although suffering from uncertainties arising from the approximations used [6–9] significantly reduce the computational requirements of quantum chemical calculations. These methods are widely used for investigating structural peculiarities of various crystalline materials and can be combined with MD simulations. Again, the latter are rather computer time consuming.

Yttria-stabilized zirconia (YSZ) is a widely investigated ceramic electrolyte. In the simplest versions the MD simulations of these systems are based on the rigid ion model when inter-ion interactions described by spherically symmetric potentials [10–13]. In these studies, the experimental findings that oxygen vacancies prefer to bind smaller zirconium

ions were reproduced and explained by elastic interactions stipulated by the difference between the zirconium and dopant ionic radii. The key problem of these methods is the parameterization of the interaction potentials. In part this problem is solved by using DFT that takes into account the high polarizability of oxygen ions [14–17]. Nevertheless, it can be difficult to properly represent long range Coulomb interactions that can lead to appearance of specific cooperative effects, especially when spatially non-homogeneous systems like electrode-electrolyte or intergrain regions are considered. Thus, simplified models that can elucidate some specific features of these complicated systems can be useful.

In this paper the results of kinetic Monte Carlo (KMC) simulations of a simple model of doped aliovalent oxide ceramics, containing grain and intergrain regions, are discussed. These results are compared with the analytical solutions of the modified Nernst–Planck–Poisson (NPP) equation. Although some numerical parameters of the model correspond to YSZ, the qualitative results may be of more general nature.

2. The model and simulation procedure

We have used the model of yttria stabilized zirconia (YSZ) suggested several years ago [18]. Based on this model, the authors were able to reproduce some basic properties of solid oxide fuel cells. The model consists of a quasi-one-dimensional sequence of enlarged crystalline cells, each of which contains two yttrium ions and, on average, a neutral oxygen vacancy that compensates the loss of the positive charge. The vacancy can exchange with a double charged negative oxygen ion in a nearest cell. Thus, it is enough to consider a neutral oxygen vacancy, an oxygen ion and a compensating positive charge per enlarged cell.

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The other oxygen ions and positive charges may not be explicitly taken into account. In dynamics it can happen that two oxygen vacancies or two oxygen ions occupy an enlarged cell simultaneously. Stronger concentration fluctuations are neglected. In fact, it is a lattice gas model with the possibility of double site occupation by oxygen ions or oxygen vacancies (Fig. 1). The fixed positively charged metal ions that ensure electrical neutrality of the system are not shown in the figure. This is opposite to the Kröger-Vink notation [19] where positively charged oxygen vacancies move on the background of negatively charged yttrium ions, but corresponds to the same physical situation. In the model the total number of oxygen ions is equal to the number of enlarged cells. Due to double site occupation, oxygen ions can pass ahead of each other thus avoiding problems of one-dimensional (single-file) diffusion, for which the square of the mean particle displacement is proportional to the square root of time instead of being proportional to time for two and larger spatial dimensions [20].

The lattice constant of the model is taken equal to $a = 0.737$ nm corresponding to 9.5% doping by yttrium in YSZ [18]. It is supposed that the host system creates the potential relief so that oxygen ions perform thermally activated jumps to vacant positions in the nearest lattice cells overcoming potential barriers

$$E_a = E_g + E_{gb}. \quad (1)$$

The total number of cells in the model is equal L ; $l \ll L$ cells belong to the intergrain region in the middle of the system. The distribution of the potential barriers is shown in Fig. 1b, where E_g and E_{gb} are the grain interior activation energy and the additional contribution in the intergrain region, respectively. In the other model the oxygen ion transitions from the grain bulks to the intergrain region are characterized by larger potential barriers $E_g + E_{gb}$, while the barriers inside the intergrain region are the same as in the bulks (the dashed lines in Fig. 1b).

The model is a quasi-one-dimensional; it is supposed that the ions concentrations and charge are homogeneously distributed in plains perpendicular to the axis along the cells sequence with charge density $\sigma_j = -2c(j)e/a^2$, $c(j) = z(j)-1$ where $z(j) = 0, 1$ or 2 and is the number of oxygen ions in j -th lattice cell (occupation number), e is the elementary charge, $c(j)$ characterizes the excess charge in j -th lattice cell. j numerates the lattice cells and the corresponding plains as well. Thus the

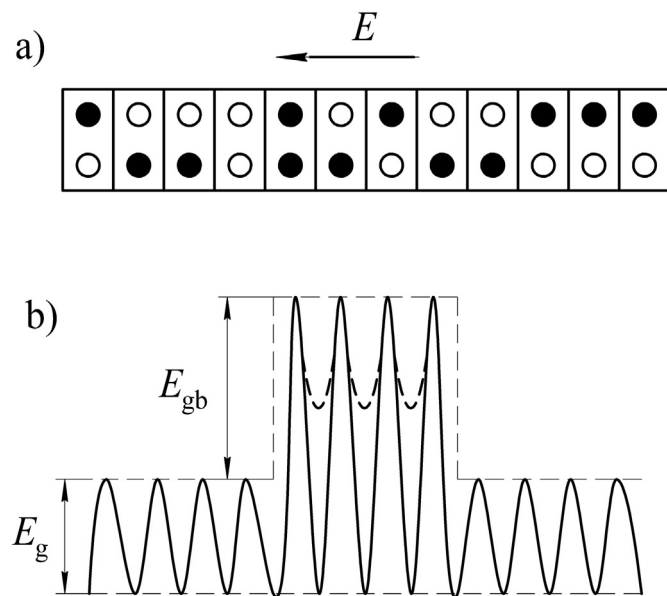


Fig. 1. A quasi-one-dimensional model for KMC simulation. a) Oxygen ions are represented by full circles, oxygen vacancies by open circles. b) The distribution of the activation barriers. E_g is the barrier height in the grain interior, E_{gb} is the additional contribution to the barrier height in the intergrain region.

potential barrier to be overcome by an oxygen ion for transition from j -th lattice cell to a nearest neighbor l -th cell has to be calculated as follows

$$E_{ajl} = E_a + E_{cjl}, \quad E_{cjl} = \beta_{jl}(U + E_j) + E_{sj}/2, \quad (2)$$

$$U = 2eEa, \quad E_j = \Delta E \left(\sum_{i=j+1}^{L/2} c(i) - \sum_{i=-(L/2-1)}^{-j-1} c(i) \right), \quad (3)$$

$$E_{sj} = \Delta E(c(j)-1), \quad \Delta E = 2e^2/(\epsilon\epsilon_0 a), \quad \beta_{jl} = \pm 1/2, \quad (4)$$

where U is the contribution of the external electric field E applied to the system, E_j is the contribution of Coulomb interaction of the oxygen ion in cell j with all the charged plains except plain j , and E_{sj} is the contribution of the interaction with the ions in the same plain, ϵ_0 is the electric constant, ϵ the dielectric constant. L is the number of cells in the system. The upper/bottom sign for β_{jl} is taken for the oxygen ion transitions to the nearest right/left cell that is chosen at random. Its absolute value $1/2$ corresponds to the assumption that the saddle point on the host system potential energy surface lies in the middle of the distance between the centers of neighboring crystalline cells. The transition is enabled if the occupation number of the destination cell is equal 0 or 1.

To perform KMC simulations the probability of an oxygen ion transition from j -th lattice cell to a nearest neighbor l -th cell is calculated according to the expression

$$w_{jl} = \exp(-E_{ajl}/k_B T), \quad (5)$$

where k_B is the Boltzmann constant, T is the absolute temperature.

An oxygen ion and its nearest destination cell (left or right) are chosen at random. If the destination cell occupation number is less than 2, a random number p from the diapason $[0, 1]$ is generated, otherwise another ion is checked. If $w_{jl} \geq p$, the transition of the ion to the nearest neighbor cell is accepted.

Although the electric field 10^6 V/m = 1 V/ μ m looks very large on a macroscopic scale it is a weak field on a microscopic scale because $2eEa/k_B T$ at 1000 K is equal to 0.0171. Even an order of magnitude larger field can be considered as a weak field.

It is necessary to note that the dielectric constant is a complicated material characteristic for systems like ionic crystals that depends on the characteristic spatial scale [21]. On nanometer scale it can considerably differ from its macroscopic value. For example, it was shown [22] that the dielectric constant obtained from the experimental values of the capacitance of the double layer in YSZ within the Gouy–Chapman theory varies from several tens to several hundred with temperature rise. This can be explained by high mobility of charged defects and high polarizability of oxygen ions. Furthermore, the difference of cation ionic sizes in doped compounds results in elastic interactions, which compete with Coulomb forces [14–17] decreasing their influence. It was shown that partial charges considerably improve the results of the rigid ion model ([23], p. 54). All these effects can roughly be taken into account by an increased value of the dielectric constant.

The electric conductivity activation energy in YSZ is around 0.8–1.0 eV [11,24]. However, with this value of E_g the transition probabilities are small, and to provide good statistics the required computer simulation time is rather large. In order to minimize the computation time [25] smaller values of E_g (0.2–0.4 eV) ensuring the transition probabilities less than 1 were used. Afterwards, the results can be recalculated to the required value of E_g . A particle leaving the system through the right boundary appears on the left side and vice versa, maintaining charge neutrality and constant number of mobile particles. The numbers of ions passing through the left and the right boundaries of the system are different because of an external field applied. A quite strong external field $E = 10^6$ or 10^7 V/m was used to ensure good statistics. Time is measured in Monte Carlo steps (MCS), and one MCS means that the number of trails to move oxygen ions is equal to the number of

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