

Modelling of diffusion and conductivity relaxation of oxide ceramics



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ABSTRACT

A two-dimensional square grain model has been applied to simulate simultaneously the diffusion process and relaxation of the dc conduction of polycrystalline oxide materials due to a sudden change of the oxygen partial pressure of the surrounding gas phase. The numerical calculations are performed by employing the finite element approach. The grains are squares of equal side length (average grain size) and the grain boundaries may consist of thin slabs of uniform thickness. An additional (space charge) layer adjacent to the grain boundary cores (thin slabs) either blocking (depletion layer) or highly conductive for electronic charge carriers may surround the grains. The electronic transport number of the mixed ionic-electronic conducting oxide ceramics may be close to unity (predominant electronic conduction). If the chemical diffusion coefficient of the neutral mobile component (oxygen) of the grain boundary core regions is assumed to be higher by many orders of magnitude than that in the bulk, the simulated relaxation curves for mass transport (diffusion) and dc conduction can deviate remarkably from each other. Deviations between the relaxation of mass transport and dc conduction are found in the case of considerably different electronic conductivities of grain boundary core regions, space charge layers, and bulk. On the contrary, the relaxation curves of mass transport and electronic conductivity are in perfect coincidence, when either effective medium diffusion occurs or the effective conductivity is unaffected by the individual conductivities of core regions and possible space charge layers, i.e. the grain boundary resistivity is negligible.

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1. Introduction

The oxygen exchange reaction of mixed ionic-electronic conducting ceramics with the surrounding atmosphere gives rise to a change of the oxygen nonstoichiometry of the solid oxide [1]. The variation of the nonstoichiometry is correlated with a change of various properties, such as the electrical conductivity, lattice expansion (chemical expansion), and colour (optical properties). A proper knowledge of the kinetics for the incorporation or release of oxygen into/from oxide ceramics is of fundamental relevance for the improvement of the electrochemical performance of cathode materials for solid oxide fuel cells (SOFCs) [2,3] as well as the optimization of the electrical properties of various electroceramic materials applied, e.g., as BaTiO₃ – based PTC (positive temperature coefficient) resistors [4], multilayer ceramic capacitors (MLCCs) [5], and ZnO – based varistors [6]. The kinetics of oxidation (uptake of oxygen from the gas phase) or reduction (release of oxygen into the gas phase) of mixed conducting oxide ceramics is determined by the rate of the surface exchange reaction and diffusion of oxygen through the polycrystalline material [7]. Phenomenological kinetic parameters, viz. the chemical surface

exchange coefficient and the chemical diffusion coefficient, are required in order to describe macroscopically the oxygen exchange process (alteration of the oxygen nonstoichiometry). Apart from transport processes at the surface and in the bulk, diffusion of oxygen along or across grain boundaries might likewise play a decisive role for the overall re-equilibration of ceramic materials with the surrounding gas phase [8–16]. Especially in the case of interfacially controlled electroceramics, such as PTCs and varistors, fast grain boundary diffusion is crucial for re-oxidation processes necessary for the formation of Schottky barriers at the grain boundaries [4].

The phenomenological parameters (chemical surface exchange coefficient and chemical diffusion coefficient) are usually determined by an instantaneous change of the oxygen partial pressure (activity) in the gas phase, leading to the oxygen exchange reaction with the solid oxide until the new equilibrium oxygen activity is attained throughout the polycrystalline material. This relaxation process can be investigated experimentally by, e.g., time dependent measurements of the sample mass, lattice expansion (lattice parameters), and colour change employing thermogravimetry [17,18], dilatometry [18] (in-situ high temperature XRD [18,19]), and optical (transmission) spectroscopy [18,20,21], respectively. In addition, conductivity relaxation experiments, where the electrical conductivity is measured as a function of time,

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represent a powerful technique for the determination of the chemical surface exchange coefficient and the chemical diffusion coefficient [22–26]. Furthermore, it is worth mentioning that electrochemical methods, such as impedance spectroscopy [27] and emf-measurements [28], have been performed in order to study the surface exchange reaction and diffusion of oxygen in mixed conducting oxides.

It is the aim of this contribution to provide a two-dimensional finite element model suitable for the simultaneous simulation of diffusion (mass transport) and conductivity relaxation of a polycrystalline - predominantly electronically conducting - solid oxide. The microstructure is described by means of a square grain model, where the core regions of grain boundaries are thin homogeneous slabs. Additional blocking or highly conductive layers adjacent to the grain boundaries are introduced, taking account of space charge layers evolving at the grain boundaries. Assuming extremely fast transport of oxygen along core regions and slow diffusion into the grain interior, various cases with respect to the electronic conductivities of core regions, additional (space charge) layers, and the bulk are studied. Interestingly, the relaxation curves for mass transport and dc conduction deviate considerably from each other, if the electronic conductivities of grain boundary regions differ remarkably from those of the bulk. On the contrary, a perfect overlap of mass transport and conductivity relaxation curves is found, when the overall transport process of oxygen can be described by effective medium diffusion.

2. Theoretical aspects

The microstructure of the polycrystalline sample is described by means of a square grain model, as can be seen in Fig. 1. The grains are squares with equal side length of $d=0.1\ \mu\text{m}$ separated by thin slabs with a thickness of $\delta=0.5\ \text{nm}$. In addition, each grain (square) is surrounded by a layer of uniform thickness $w=10\ \text{nm}$. Hence, the grain boundaries of the polycrystalline material may consist of a core region, which is structurally different from the bulk (described by thin slabs in the present model), and an adjacent electrically active region which may deviate significantly from the grain interior with regard to the electrical properties, e.g., due to depletion layers with thickness $w=10\ \text{nm}$. The total thickness of the sample is $L=2.06\ \mu\text{m}$ (see Fig. 1).

In the case of mixed ionic-electronic conducting oxide ceramics an instantaneous change of the oxygen partial pressure of the surrounding gas phase (diffusion source) gives rise to a chemical

diffusion process of oxygen in the solid polycrystalline sample which is accompanied by a stoichiometry change leading to a variation of the electronic conductivity with time until the sample has attained a new oxygen activity in equilibrium with the gas phase (relaxation process). The diffusion equations for the bulk and grain boundary (core) regions read

$$\frac{\partial c}{\partial t} = \bar{D}\nabla^2 c \quad (1a)$$

and

$$\frac{\partial c'}{\partial t} = \bar{D}'\nabla^2 c' \quad (1b)$$

with \bar{D} , \bar{D}' , c , and c' denoting the spatially invariant chemical diffusion coefficients of oxygen and the concentrations of the diffusing neutral component (oxygen nonstoichiometry) in the bulk and grain boundary regions, respectively. The oxygen exchange reaction at the surface of the sample ($x=0$) can be described phenomenologically by introducing surface exchange coefficients \tilde{k} and \tilde{k}' for bulk and grain boundaries (core regions), respectively, resulting in boundary conditions for mass transfer, i.e. $\bar{D}\partial c/\partial x = \tilde{k}(c - c_\infty)$ and $\bar{D}'\partial c'/\partial x = \tilde{k}'(c' - c'_\infty)$ at $x=0$. The quantities c_∞ and c'_∞ are the new equilibrium concentrations for $t \rightarrow \infty$ of the diffusant (oxygen nonstoichiometry) in bulk and grain boundary regions. However, for the sake of simplicity the surface at $x=0$ may be in equilibrium with the surrounding gas phase ($\tilde{k}, \tilde{k}' \rightarrow \infty$), leading to the boundary conditions at $x=0$ ($t \geq 0$): $c = c_\infty$ and $c' = c'_\infty$ (constant source). The boundary conditions at the remaining surfaces ($x=L$ and $y = \pm L/2$), which are assumed to be diffusion barriers, are given by $\partial c/\partial x = \partial c'/\partial x = 0$ ($x=L$) and $\partial c/\partial y = \partial c'/\partial y = 0$ ($y = \pm L/2$). The continuity of diffusant concentration and flux at the grain boundary/grain interface can be expressed as $c' = sc$ and $\bar{D}\partial c/\partial n = \bar{D}'\partial c'/\partial n$ ($\partial/\partial n$ is the normal derivative). The segregation factor can be correlated to the chemical capacitances, $(\partial\mu/\partial c)^{-1}$, of bulk and grain boundaries, i.e. $s = (\partial\mu/\partial c)/(\partial\mu/\partial c')$ [29].

The electric potential at the electrodes necessary for the determination of the conductivity as a function of time is kept constant, i.e. $\phi=0.02\ \text{V}$ at $y=L/2$ and $\phi=0$ at $y=-L/2$. The remaining surfaces at $x=0$ and $x=L$ may be electrically insulating. The electronic current density is given by $j = \sigma_e/e\nabla\tilde{\mu}_e \approx -\sigma_e\nabla\phi$, where σ_e and $\tilde{\mu}_e$ are the electronic conductivity and the electrochemical potential of electrons, respectively. It is assumed that (i) the electronic transport number of the mixed conductor may be almost unity, $t_e \approx 1$, and (ii) any polarization processes, affecting the

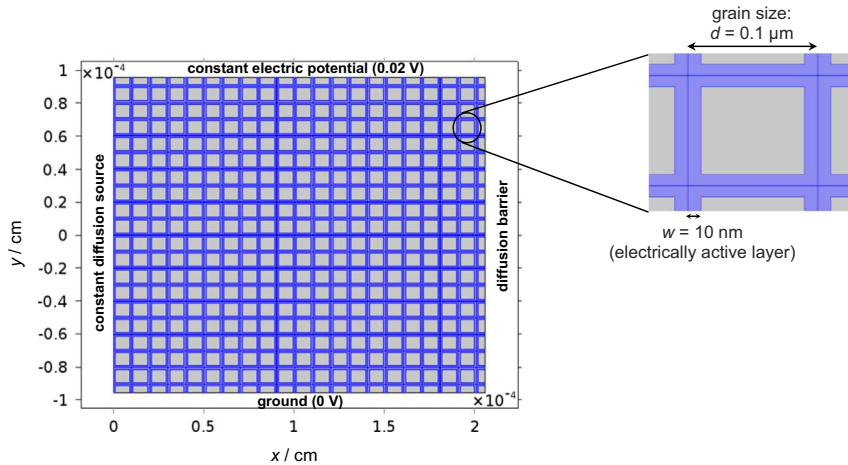


Fig. 1. Two-dimensional square grain model for the microstructure of a polycrystalline material (oxide ceramics). The squares of equal side length, $d=0.1\ \mu\text{m}$, represent the grains, the grain boundary core regions are slabs of uniform thickness, $\delta=0.5\ \text{nm}$, and additional blocking or highly conductive layers with a width of $w=10\ \text{nm}$ surround each grain (see magnification). Thickness of the sample: $L=2.06\ \mu\text{m}$.

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