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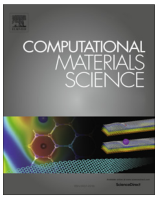

Modelling of surface exchange reaction, oxygen diffusion, and conductivity relaxation of solid oxides: Application to the van der Pauw method on disk-shaped samples

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ABSTRACT

The surface exchange reaction and diffusion of oxygen through oxide ceramic samples as well as the relaxation of the dc conductivity upon an instantaneous change of the oxygen activity in the surrounding atmosphere have been modelled simultaneously by means of the finite element method. The simulations of conductivity relaxation curves are valid for mixed ionic–electronic conducting disk-shaped (cylindrical) samples with predominant electronic conduction, employing a four-point dc method in van der Pauw geometry. Numerical results, based on a three-dimensional finite element model, are compared with the pertinent analytical solutions to the diffusion equations. Interestingly, in the case of diffusion-controlled kinetics the relaxation curves for the total amount of exchanged oxygen (mass transport) deviate remarkably from those for the normalized conductivity (conductivity relaxation). Constraints for the accuracy of the determination of chemical diffusion coefficients and surface exchange coefficients in terms of sample geometry (diameter and thickness) have been elaborated. Basically, identical relaxation curves for mass transport and dc conduction are anticipated, when the transport processes can be assumed to be one-dimensional, which is fulfilled for disk-shaped samples with a ratio of diameter/thickness being higher than 4.

1. Introduction

A detailed knowledge of oxygen exchange processes between a gas phase and oxide ceramics is of fundamental interest as well as technological relevance [1,2]. If the oxygen activity of the surrounding atmosphere is altered, oxygen will be incorporated into (oxidation) or released from (reduction) the mixed ionic-electronic conducting sample, leading to a change of the oxygen nonstoichiometry. Basically, the kinetics of this re-equilibration process is governed by a surface exchange reaction and diffusion of oxygen through the solid oxide. The surface exchange reaction can be described phenomenologically by means of a chemical surface exchange coefficient, while the transport of oxygen through the solid sample is determined by the chemical diffusion coefficient. It is worthwhile mentioning that grain boundaries might play an important role with respect to these transport processes [3–9].

The sound understanding of oxygen exchange processes is an essential prerequisite for the development of novel cathode materials for solid oxide fuel cells. The area specific resistance of state-of-the-art cathodes, such as $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, is governed by surface exchange reactions as well as diffusion of oxygen through the lattice of the perovskite-type compounds [10–12]. Moreover, the re-oxidation of electroceramic materials, e.g. doped $BaTiO_3$ and ZnO, is of high technological importance for the production of PTC (positive temperature coefficient) resistors, multilayer ceramic capacitors (MLCCs), and ZnO-based varistors. It is worth mentioning that fast grain boundary diffusion is crucial for the re-oxidation processes of grain boundary regions in donor doped barium titanate [13–16].

The experimental determination of the phenomenological kinetic parameters, i.e. chemical diffusion coefficient and surface exchange coefficient, is a necessary requirement to gain a deeper understanding of the transport mechanisms in oxide ceramics. Various experimental methods are available for this purpose, such as thermogravimetry [17], carrier gas coulometry [18], impedance spectroscopy [19], emf-measurements [20], and conductivity relaxation experiments [21–23]. In the case of conductivity relaxation experiments the van der Pauw technique has been introduced [24]. This method is a powerful tool for accurate four-point dc measurements of the electrical conductivity on homogeneous samples of uniform thickness and arbitrary shape.

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It is the aim of this contribution to present a three-dimensional finite element model in order to calculate conductivity relaxation curves for disk-shaped (cylindrical) samples with four peripheral line contacts in van der Pauw geometry. Mass transport, owing to surface exchange reaction and diffusion of oxygen, is coupled with dc conduction. The finite element simulations refer to mixed ionic-electronic conducting materials with predominant electronic conduction. The numerical results are compared with analytical solutions to the diffusion equations. Especially in the case of diffusion-controlled kinetics, the relaxation curves for mass transport and dc conduction may differ considerably, which is discussed in detail with respect to possible constraints for the determination of chemical diffusion coefficients and surface exchange coefficients from conductivity relaxation experiments.

2. Theoretical considerations

A finite element model for disk-shaped (cylindrical) samples has been developed in order to investigate the effect of three-dimensional diffusion on conductivity relaxation processes employing the van der Pauw method. In the case of oxide ceramics an instantaneous change of the oxygen partial pressure in the surrounding atmosphere gives rise to an oxygen exchange process. When a finite (short) time is required to flush the reactor, containing the sample, with new gas in order to attain a change of the oxygen partial pressure, the finite switching time (flush-time) should be taken into account, see e.g. Refs. [18,25]. For the sake of simplicity this situation is disregarded in the present approach, i.e. instantaneous oxygen partial pressure changes are assumed. The oxygen exchange kinetics is governed by chemical diffusion of oxygen in the sample as well as the surface exchange reaction. As the change of the oxygen nonstoichiometry owing to the oxygen exchange reaction is associated with a variation of the electronic conductivity, the measurement of the conductivity as a function of time is a valuable technique (conductivity relaxation experiment) for the determination of the chemical diffusion coefficient and the chemical surface exchange coefficient. A homogeneous disk-shaped sample (diameter: $2r_0 = 2.0$ cm and thickness: $L = 1.0$ cm) with four peripheral line-contacts (van der Pauw geometry) is shown in Fig. 1. Basically, the van der Pauw method is limited to thin homogeneous samples using four peripheral point contacts. An additional necessary requirement for this method is a singly connected surface with no holes (pore-free sample) [26]. However, employing peripheral line-contacts, as illustrated in Fig. 1, allows the application of this technique to thick (pore-free) samples of arbitrary uniform thickness. The electronic transport number of the mixed ionic-electronic conducting specimen may be almost equal to one, $t_e \approx 1$. Whereas the conductivity of the electronically conducting line-contacts is assumed as $\sigma_{\text{contact}} = 1000\ \text{S cm}^{-1}$, the conductivity of the sample may vary from $\sigma_0 = 10\ \text{S cm}^{-1}$ to $\sigma_\infty = 20\ \text{S cm}^{-1}$ during the conductivity relaxation. Any polarization processes at the electronic electrodes are disregard, since the specimen is predominantly electronically conducing ($t_e \approx 1$).

The diffusion of oxygen can be described by Fick's second law

$$\frac{\partial c}{\partial t} = \tilde{D}\nabla^2 c, \tag{1}$$

where $\tilde{D}$ and c are the chemical diffusion coefficient and the concentration of the diffusing species (mobile neutral component), respectively. In the case of small oxygen partial pressure steps (linear response) the boundary conditions for the surface exchange reaction read [27,28]

$$-\tilde{D}\frac{\partial c}{\partial r} = \tilde{k}(c - c_\infty); \quad r = r_0, \tag{2a}$$

$$\pm\tilde{D}\frac{\partial c}{\partial z} = \tilde{k}(c - c_\infty); \quad z = 0, L, \tag{2b}$$

with $\tilde{k}$ and c_∞ denoting the chemical surface exchange coefficient and the diffusant concentration for $t \to \infty$ (at the end of the relaxation process), respectively. The current density for $t_e \approx 1$ is given by

$$j = \frac{\sigma_e}{F}\,\text{grad}\,\tilde{\mu}_e, \tag{3}$$

where σ_e and $\tilde{\mu}_e$ refer to the electronic conductivity and the electrochemical potential of electronic charge carriers, respectively, and F is the Faraday constant. As polarization processes at the electrodes are assumed to be negligible, the transport processes owing to oxygen exchange are not affected by the conductivity measurement, i.e. $\text{grad}\,\tilde{\mu}_e \approx -F\text{grad}\,\phi$ (ϕ is the electric potential) is valid for the driving force of the electric current. The continuity equation for the current density can be written as

$$\nabla \cdot j = 0. \tag{4}$$

In the following, boundary conditions for dc conduction in van der Pauw geometry are introduced. The contacts R and S may be the current carrying electrodes, while contacts P and Q are probes for the voltage measurements. A constant current is fed through line-contact R

$$I_{RS} = \iint_{\text{contact R}} j\,dA = \text{const}; \quad \text{contact R} \tag{5a}$$

and

$$\tilde{\mu}_{e,S} = 0\ (\text{ground}, \phi_S = 0); \quad \text{contact S}. \tag{5b}$$

If the $p(O_2)$-steps are sufficiently small, a linear relation between the electronic conductivity and the oxygen nonstoichiometry

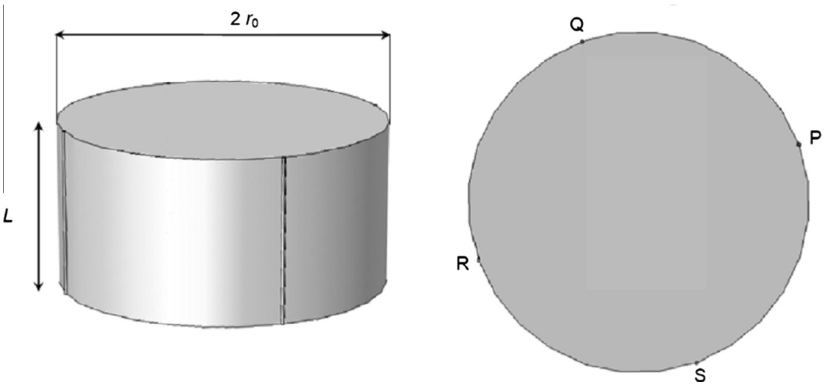

Fig. 1. Schematic view of a disk-shaped (cylindrical) sample with four peripheral line contacts (van der Pauw geometry).