



New method to determine diffusion coefficients and surface rate constants in mixed ionic electronic conductors

C. Elschner*, M. Kusnezoff, S. Ziesche, A. Paepcke, A. Michaelis

Fraunhofer Institute for Ceramic Technologies and Systems, D-01277 Dresden, Germany

ARTICLE INFO

Article history:

Received 12 May 2010

Received in revised form 1 July 2010

Accepted 4 July 2010

Available online 13 July 2010

Keywords:

Permeation

Surface exchange

Chemical diffusion coefficient

Conductivity relaxation

Optimization

ABSTRACT

A new mathematical method to estimate diffusion coefficients (D) and surface rate constants (k) in mixed ionic electronic conductors has been developed. The so-called intersection line method neglects the dependency of D and k pairs on initial values like classical optimization programs do. The important advantages of the new developed method against classical optimization procedures in terms of independence of initial values and precision by finding the physically meaningful solution have been shown.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Mixed ionic electronic conduction is an interesting property observed especially in inorganic oxide materials. At elevated temperatures oxygen from the gas phase can be incorporated into mixed ionic electronic conductor (MIEC) material and moves via vacancy or interstitial mechanism. The oxygen ion shows a much lower bonding strength in the crystal lattice in comparison to the further cations, which are fixed in the lattice at these temperatures. Possible technical applications for this phenomenon are permeation membranes for oxygen separation, membrane-technology for partial oxidation of hydrocarbons in biogas-to-liquid or gas-to-liquid process used for fuel production or electrode materials for solid oxide fuel cells.

A typical way to characterize and compare these materials is to determine the diffusion coefficient and the surface rate constant. Both parameters are necessary to describe the oxygen flux in a detailed way.

The surface rate constant describes incorporation of oxygen into the near-surface layer of the bulk material and reverse. This process contains several steps like adsorption of molecular oxygen on the surface, splitting the molecule and electrochemical oxidation/reduction of atomic oxygen [1,2].

The diffusion coefficient describes the motion of oxygen ions through the bulk material [3–6], because of the complex interaction between these moving ions and the fixed lattice there are several definitions for diffusion coefficients in the literature [7–9].

To calculate the chemical diffusion coefficient and surface rate constant, conductivity relaxation experiments are usually used [10]. In these experiments the electrical conductivity of a MIEC sample is measured while the oxygen partial pressure in the surrounding atmosphere changes. In the beginning of the experiment the sample is in equilibrium with the surrounding atmosphere. After changes in oxygen partial pressure the sample relaxes to a new equilibrium and the concentration of mobile oxygen ions changes. By measuring the electric conductivity it is possible to record the time-dependent kinetics of this process. Often the change in the oxygen partial pressure will be realized as a step-function [11]. A new experimental setup recently developed by the authors use dynamic excitations, where the oxygen partial pressure in the atmosphere changes periodically [12]. In combination with these dynamic experiments we develop a new type of data analysis for calculation of diffusion coefficient and surface rate constant, which contains several benefits against classical optimization processes.

Further work in the field of diffusion modelling and diffusion coefficient and surface rate constant calculation by optimization processes is shown in [13–16].

This work is a continuation of our previous results [12] and focus on the mathematical possibilities to estimate D

* Corresponding author. Tel.: +49 351 463 34902.

E-mail addresses: chris.elschner@iapp.de, chriselsch@gmx.de (C. Elschner).

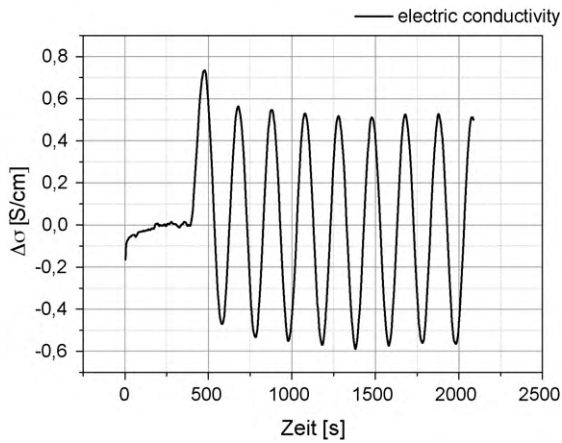


Fig. 1. The change of electrical conductivity $\Delta\sigma$ over time, while the oxygen partial pressure changes sinusoidal with a period of 200 s from 380 ppm to 1120 ppm at $T=950^\circ\text{C}$ in La_2NiO_4 .

and k values by the use of dynamic electrical conductivity experiments.

2. Experimental

The detailed experimental setup for conductivity relaxation measurements within $p\text{O}_2$ -oscillations is described elsewhere [12]. La_2NiO_4 was used as test material to check the possibilities of the new method. The electrical conductivity of a La_2NiO_4 MIEC sample (15 mm \times 4.5 mm \times 1.5 mm) was measured by four point setup, while an applied atmosphere was flowing along the sample, as carrier gas N_2 8 l/h was used. To control the oxygen partial pressure in the carrier gas we employed an electrochemical cell from Fa. Zirox, Germany. The electrochemical cell works as an oxygen pump which produces a sinusoidal change of the oxygen partial pressure in the flowing gas. The oxygen partial pressure changes from 380 ppm to 1120 ppm by periodic oscillations. As a consequence of changing oxygen partial pressure in the surrounding atmosphere, the oxygen concentration in the MIEC changes, too. Because of the interrelationship between oxygen concentration and electrical conductivity, the sinusoidal oscillations can be measured via electrical four point measurement. In Fig. 1a typical measurement can be seen, after a setting time the electrical conductivity oscillates nearly sinusoidal. Comparison of the amplitude at maximum and minimum indicates a slightly non-linear behaviour. The non-linearity results from oxygen exchange process [12] and can be confirmed by the measurement of equilibrium values of electrical conductivity at different oxygen partial pressures, see Fig. 2.

3. Mathematical description

To describe the physical processes in detail a two-dimensional numerical model based on a finite element code was developed. The FEM-model works on a commercial software code FlexPDE5 from PDE Solutions Inc., 2120 Spruce Way, Antioch, CA 94509, USA. The model estimates the distribution of oxygen in the MIEC sample by solving the diffusion equation [17]

$$\frac{\partial c(x, y, t)}{\partial t} = D^\delta \left(\frac{\partial^2 c(x, y, t)}{\partial x^2} + \frac{\partial^2 c(x, y, t)}{\partial y^2} \right), \quad (1)$$

using the known boundary conditions for surface exchange [1]

$$-D^\delta \vec{\nabla}_n(c(x, y, t)) = k^\delta (c_{\text{surface}}(p\text{O}_2) - c(x, y, t)). \quad (2)$$

Here $c(x, y, t)$ is the time-dependent oxygen concentration, D^δ the chemical diffusion coefficient and k^δ the surface rate constant. The

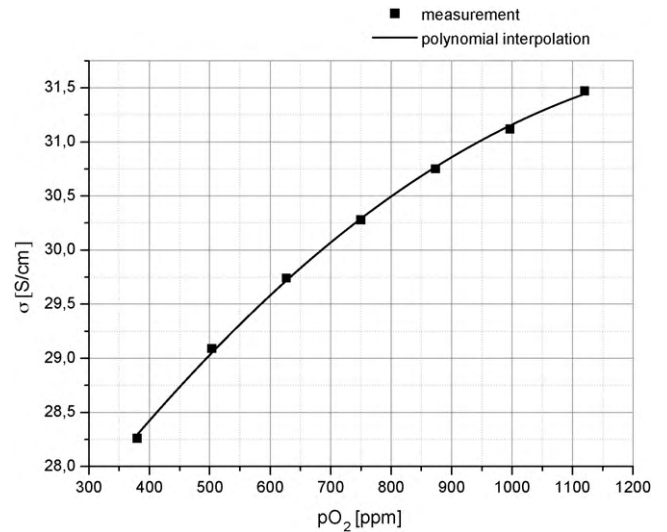


Fig. 2. Equilibrium values of electrical conductivity versus oxygen partial pressure at $T=950^\circ\text{C}$ in La_2NiO_4 .

periodic sinusoidal oxygen exchange at the surface is given by

$$c_{\text{surface}}(p\text{O}_2) = A \sin(\omega t) + B \sin^2(\omega t) \quad (3)$$

with A and B as fitting parameter from thermogravimetric measurements [12]. All noticed non-linear effects can be modelled in this approach. As mentioned above the non-linearity is weak, because of this the constant A is much larger than B .

The solution of Eq. (1) gives the detailed distribution of oxygen in the MIEC at every time step. The local electrical conductivity of the sample is assumed to be proportional to the oxygen concentration

$$\sigma_{\text{local}}(x, y, t) \propto c(x, y, t) \quad (4)$$

To reach values consistent with the results of conductivity measurement, the local electrical conductivity must be integrated over the cross-section of the sample.

$$\sigma(t) = C \iint \sigma_{\text{local}}(x, y, t) dx dy \quad (5)$$

with C as normalization factor.

4. Results: estimation of diffusion coefficients and surface rate constants

Eqs. (1)–(5) are used to describe the diffusion and surface exchange process. The standard procedure to determine the unknown parameters D^δ and k^δ is an optimization task. By screening the (D^δ, k^δ) pairs the minimization of the misfit between mathematical model and measurement must be obtained and the correct values for both parameters have to be found. The result of the optimization process gives the (D^δ, k^δ) values which show the best coincidence between the mathematical model and the measurement data.

The advantage of this special optimization problem is that it is two dimensional. Therefore it is possible to plot the error data for different D^δ and k^δ values graphically and interpret this error-landscape in a simple manner, see Fig. 3. This plot is given for several solutions of Eq. (1) with different (D^δ, k^δ) pairs.

In general each optimization program can be used to find the global minimum in such an error-landscape. A well known, but often neglected problem is the dependence of the fit results on the initial values. An optimization program converges often only to the global minimum when the initial value is close to the unknown destination point. Local minima inhibit a successful optimization

Download English Version:

<https://daneshyari.com/en/article/636279>

Download Persian Version:

<https://daneshyari.com/article/636279>

[Daneshyari.com](https://daneshyari.com)