



# Measurement of chemical diffusion coefficient and surface exchange on mixed ionic electronic conductors using periodical $pO_2$ oscillations

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## ABSTRACT

A new method for estimation of transport parameters in mixed ionic electronic conductors (MIEC) is proposed. Microscopic diffusion and surface exchange coefficients have been obtained with a dynamic conductivity analysis. The estimation of diffusion coefficient of interstitial oxygen and the surface exchange coefficient for well known compositions  $La_2NiO_4$  and  $La_2CuO_4$  shows very good agreement with SIMS data reported in the literature.

The novel characterization turns out to be a time saving method which allows the precise estimation of diffusion and surface exchange coefficients in mixed conductors.

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## 1. Introduction

Oxygen separation by ceramic permeation membranes is one of the best possibilities to produce relatively pure oxygen for combustion, gasification and other technical and chemical processes. The principle of oxygen separation in the dense ceramic membrane is based on conversion of the differential oxygen partial pressure over the membrane into oxygen flux.

The difference of the oxygen partial pressure across the ceramic membrane results in the electrochemical potential difference which is a driving force for the oxygen transport. The transfer of oxygen from oxygen rich to oxygen poor side of the membrane is an electrochemical process including following steps:

- (i) oxygen reduction on the membrane side exposed to higher  $pO_2$  (cathode side),
- (ii) oxygen transport through the membrane,
- (iii) oxidation of  $O^{2-}$  ions on the membrane surface exposed to lower  $pO_2$  (anode side).

The typical materials used for membrane manufacturing are mixed ionic electronic conductors (MIEC) or dual phase composites with a high ionic and electronic conductivity. The average electrochemical potential difference caused by pressure difference (5–20 atm) over the membrane is rather low (30–80 mV). Therefore

only membranes with negligible losses lead to considerable oxygen flux. The specific oxygen flux of ca.  $3 \text{ ml cm}^{-2} \text{ min}^{-1}$  is often treated as a common goal for permeation rate and corresponds to a current density of about  $0.8 \text{ A/cm}^2$ . To realize this flux the area specific resistance (ASR) of ceramic membrane in the range of  $90 \text{ m}\Omega \text{ cm}^2$  should be realized. This value is two times lower than the area specific resistance (ASR) of the best known semi-commercial anode supported cells [1] and is a big challenge for undergoing membrane material development.

The permeation flux across MIEC is determined by the concentration gradient of oxygen ions in the material, the ionic conductivity and the surface exchange rate on the surface. The two latter properties define the critical thickness of dense membrane ( $L_c$ ), firstly introduced by Steele [2] to describe the process of oxygen transport in materials usually used as cathodes for solid oxide fuel cells and permeation membranes:

$$L_c = \frac{D}{k} \quad (1)$$

with  $D$  – diffusion coefficient and  $k$  – surface rate constant.

The critical thickness defines the limit where the surface kinetics overtakes the control over the permeation rate. This parameter is very important for the technical design of the membrane. Different methods for the estimation of  $D$  and  $k$  values are known from the literature.

The isotope exchange depth profile measurement (IEDP) is often used to estimate the surface exchange and oxygen tracer diffusion coefficient. The method was firstly introduced by Steele and Kilner [3,4] in 1981–1992 and is a reference technique for determining the

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transport properties of oxygen in ionic conductors. The experimental basis for estimation of  $D$  and  $k$  is the measurement of oxygen isotope ( $O^{18}$ ) diffusion profile by secondary-ion mass spectroscopy (SIMS). The fitting of diffusion profile using theoretically obtained equation [3,4] yields the tracer diffusion coefficient and surface exchange rate. The relative uncertainty of the determined values for  $D$  and  $k$  using this method is in the range of 50%. The equipment and apparatus effort for the determination of  $D$  and  $k$  is rather high. The obtained values describe the diffusion of oxygen in the absence of the oxygen concentration gradients and differ from the chemical diffusion and surface exchange coefficients, which are actually responsible for oxygen transport. For the calculation of oxygen flux across the membrane made of material with estimated tracer diffusion and oxygen exchange coefficients additional data such as oxygen stoichiometry are needed.

In relaxation methods the time-dependent response of a physical property of the solid oxide e.g., mass [5] or electrical conductivity after imposing a stepwise change of the oxygen partial pressure in the ambient, is monitored. In general, the oxygen partial pressure in relaxation experiments is changed by switching between two gas flows with different oxygen partial pressures. The information about oxygen diffusion and surface exchange is obtained by fitting the relaxation curves with mathematical expression given by Crank [9]. Although the most evident way to obtain information about oxygen diffusion and surface exchange is to measure mass change of the sample [5], the measurement of electrical conductivity has the advantage of less apparatus effort [6–8]. The necessary requirement for conductivity relaxation (CR) is the correlation of ionic and electronic defect concentrations. Obviously it is fulfilled via the charge neutrality requirement. The chemical diffusion coefficient  $D$  and surface exchange rate  $k$  are usually determined by fitting the theoretical curve to the time-dependent experimental data. The disadvantage of this approach is that bulk diffusion and surface kinetics cannot be distinguished easily and are affected by flush time.

It has been shown by ten Elshof et al. [6] that transformation of the time-dependent response of the electrical conductivity to the frequency domain can yield information regarding the nature of the rate-determining step in the re-equilibration process after an abrupt change of the oxygen partial pressure in the ambient. In conductivity relaxation and dynamic thermogravimetric experiments a flush-time correction is needed if the relaxation time approaches the flush time of the reactor volume [10,11]. The flush times encountered in dynamic thermogravimetric experiments are usually large due to the inherently large reactor volumes and therefore the CR method allows more reliable estimation of  $D$  and  $k$ . Fourier transformation of the CR response data presents clear insight into the limitations of the analysis and allows the determination of  $D$  and  $k$  using the equivalent circuits well known from impedance spectroscopy. It can also easily provide estimates of uncertainty for the obtained parameters,  $D$  and  $k$ . The presence of ‘flushing problems’ are indicated by presence of the high-frequency inductive loop in the impedance plot. Also other distortions, e.g. due to the data acquisition system, will become evident in the frequency domain presentation [11]. Thus the accuracy of extracted data can be essentially increased. However the fitting of measured impedance spectra by equivalent circuit implies assumption that the equivalent circuit perfectly mirror the processes in mixed conductor. Usually the one-dimensional simulation of oxygen transport is used to obtain the analytical expression for equivalent circuit. This simulation is a simplification of real geometries and effects and has an impact on accuracy for  $D$  and  $k$  determination.

The conductivity relaxation combined with the  $pO_2$ -measurements in the gas phase has been applied by Preis et al. [12] and includes the possibility for coulometric analysis of oxygen content in the carrier gas. Using this method the direct correlation

to oxygen depletion from the sample and the complementary proof of the data obtained from conductivity relaxation is done.

Generally only the order of magnitude for absolute values of the chemical diffusion and surface exchange coefficients can be obtained using the CR technique. The  $D$  and  $k$  values estimated from CR are often in poor agreement with values obtained from SIMS measurements due to high uncertainty of estimated of chemical diffusion coefficients and oxygen stoichiometry of material needed for reverse calculation of tracer diffusion coefficient. Nevertheless CR can be effectively used for reliable comparison of material properties using the same measurement procedure and the samples with the similar geometry and microstructure (grain size and porosity). For the estimation of the magnitude of the ionic conductivity and polarization resistance the additional data has to be measured similar to IEDP [13]. To avoid these restrictions novel methods and experimental setups for measurement of  $D$  and  $k$  are regularly reported.

Diethelm et al. [14] and Lade and Jacobsen [15] have used a special cell geometry and impedance spectroscopy for determination of the diffusion coefficient and surface exchange rate constant. These methods need hermetic seals and are, however, restricted in temperature range due to inherent limitations set forth by the used sealing glasses.

Direct measurement of surface polarization resistance has been tried by Hendriksen et al. [16]. This has been done by changing the  $pO_2$  in the gas phase and a potentiometric measurement of the difference of the thermodynamic potential ( $\Delta\mu_{O_2}$ ) between gas phase and MIEC surface [16]. In this case the potential difference and oxygen flux ( $J_{O_2}$ ) throughout the membrane are measured simultaneously as a function of oxygen partial pressure. The polarization resistance is calculated from the slope of  $U-J_{O_2}$  curve. The difficulty of this method is that measured potential difference on the cone probe is  $<0.5$  mV. The polarization resistance values obtained by this technique are very small ( $90\text{--}300 \mu\Omega \text{ cm}^2$ ) which is in contradiction with observed polarization losses.

Pressure modulation and Frequency-Domain Analysis is another way to obtain the transport parameters [17]. The air pressure modulation has been done in the frequency range  $0.001\text{--}50$  Hz. The sinusoidal conductivity change is used to evaluate the chemical diffusion and the surface exchange coefficients. At the current status the method cannot be used for the evaluation of potential MIEC materials due to very low amplitude of induced  $pO_2$  oscillations [17].

In our work a novel technique for better estimation of chemical diffusion and surface exchange coefficients is proposed. The measurement principle is based on analysis of periodical conductivity oscillations induced by periodical change of the oxygen partial pressure surrounding the sample. The resulting conductivity oscillation has been fitted by 2D simulation of oxygen defect concentration distribution in the sample taking into consideration their real lateral dimensions.

## 2. Experimental

### 2.1. Powder preparation and sample fabrication

$La_2NiO_4$  and  $La_2CuO_4$  powders were prepared by mixing the raw materials of  $La(OH)_3$ , NiO or CuO (99.9% purity). The mixtures were milled with ethanol in a zirconia ball mill for 24 h. After drying the mixtures were heated and annealed in air at  $1200^\circ\text{C } 3K'/10 \text{ h}/3K'$  in alumina crucibles. After cooling to room temperature the products were milled again and small amounts of a polyvinyl alcohol-water solution were added to the milled powders to enhance their compressibilities. The prepared powders were pressed in pellets with a diameter of 25 mm and finally sintered in air ( $La_2NiO_4$ :  $1350^\circ\text{C}$

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