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Oxygen equilibration kinetics of mixed-conducting perovskites BSCF, LSCF, and PSCF at 900 °C determined by electrical conductivity relaxation

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ABSTRACT

For an application of mixed ionic-electronic conducting (MIEC) perovskite oxides, e.g., as solid oxide fuel cell (SOFC) cathodes, as high-temperature gas sensors or as oxygen-transport membrane (OTM) materials, the kinetics of oxygen transport is of fundamental importance.

A common setup for the determination of the chemical diffusion coefficient D^δ and the surface exchange coefficient k^δ is the electrical conductivity relaxation (ECR) method where the conductivity response of an MIEC sample is measured after the ambient oxygen partial pressure pO_2 has been abruptly changed using different gas mixtures. In the present study, however, a closed tubular zirconia "oxygen pump" setup was used which facilitates precise pO_2 control in a closed sample space with a high resolution at temperatures above 700 °C in atmospheres ranging from pure oxygen continuously down to $pO_2 = 10^{-18}$ bar. Reasonably fast pO_2 changes enable an application of the ECR technique on MIEC oxides down to lower partial pressures not easily accessible with gas mixtures.

The oxygen transport parameters of dense ceramic bulk samples of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF), and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (PSCF) have been studied as a function of temperature (800 and 900 °C) in the range between $10^{-6} \leq pO_2/\text{bar} \leq 0.21$. The D^δ and k^δ values obtained for LSCF at 800 °C are in good agreement with values from literature, proving the usability of the setup for ECR measurements. For BSCF, LSCF, and PSCF, D^δ and k^δ values could be determined for the first time at 900 °C as a function of pO_2.

1. Introduction

Mixed ionic-electronic conducting (MIEC) perovskite-type oxides are very promising materials for a large variety of high-temperature applications, ranging from solid oxide fuel cell (SOFC) electrodes [e.g., 1–3], resistive-type gas sensors, [e.g., 4,5], to oxygen-transport membranes (OTMs) [e.g., 6,7] used for the separation of gaseous oxygen. In all of these applications it is of course a prerequisite that the material be stable under the operating conditions, and it should be compatible with other materials with which it is in direct contact — often a non-trivial task in view of the high operation temperatures [8]. Most obviously, however, the material should exhibit excellent oxygen transport properties under typical operating conditions regarding temperature (mostly in the range between $T = 600...900$ °C) and oxygen partial pressure pO_2.

Since the flexibility and stability of the ABO_3 perovskite structure with respect to cation substitution greatly facilitate custom-tailoring of material properties, a variety of efforts by many research groups, starting already three decades ago [9], has succeeded in deriving $(A,Sr)(Co,Fe)O_{3-\delta}$-based solid solutions (A = Ba, La, Pr…) that exhibit high oxygen vacancy concentrations, good ionic and electronic conductivities, and, therefore, show good oxygen transport properties. Amongst this class of materials, the chemical compositions $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) [e.g., 10–19], $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [e.g., 20–24] and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (PSCF) [e.g., 25–27] have been proposed for use in the above-listed applications. BSCF is a material with excellent oxygen ionic and electronic transport properties and, hence, in its cubic phase, a promising candidate for oxygen permeation membranes (the absence of CO_2, however, is a prerequisite as this leads to a fast decomposition [e.g., 28–31]). LSCF is well-known from SOFC research as a state-of-the-art mixed-conducting cathode material. PSCF has been considered by some research groups as an intermediate-temperature alternative to LSCF.

For the different applications mentioned above, oxygen partial pressures may typically range between, e.g., pure oxygen atmospheres and values as low as $pO_2 = 10^{-4}$ bar: OTMs operated in four-end

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mode [e.g., 32], i.e. with pressurized air on the feed side and flue gas recirculation on the permeate side, may encounter low-end values of $pO_2 \approx 50$ mbar, in three-end mode the vacuum pump on the permeate side may even lead to slightly lower pO_2 values of around 1 mbar — a further decrease in permeate pressure would in principle be preferable in view of oxygen permeation, but would also lead to an extraordinary increase in required pumping power. In SOFC application, a cathode overpotential of up to 200 mV can result in partial pressures as low as 10^{-4} bar (at 750 °C) at the MIEC surface.

Therefore, an investigation of the oxygen transport kinetics — namely the chemical diffusion coefficient D^δ and the surface exchange coefficient k^δ — is of interest not only in ambient air (or in even more oxidizing atmospheres), but for a much broader pO_2 range as these values determine the performance of the materials. In the case of a thin-film OTM made of LSCF, for instance, we could recently show [33] that oxygen surface excorporation at the low-pO_2 permeate side of the membrane becomes the rate-determining process for oxygen permeation across the membrane.

The kinetics of oxygen transport can be studied using electrical conductivity relaxation (ECR). This method involves monitoring of the transient conductivity exhibited by the MIEC, at fixed temperature, after an instantaneous change of the ambient pO_2. The chemical diffusion coefficient D^δ and the surface exchange coefficient k^δ are obtained from a single experiment by fitting the transient conductivity to the appropriate solution of Fick's second law [34] for given boundary conditions (determined by the sample dimensions and the setup characteristics).

Commonly, the (ideally instantaneous) pO_2 change in such an experiment is achieved by switching between two different gas streams with different pO_2 values. In the present study, the oxygen transport parameters of BSCF, LSCF, and PSCF are studied by means of ECR as a function of pO_2 in the range between $10^{-6} \le pO_2/\text{bar} \le 0.21$ at temperatures of 800 and 900 °C. Rather than using different gas streams with known pO_2, a coulometric oxygen titration setup is used, consisting of a custom-made closed tubular zirconia "oxygen pump" with Pt electrodes [35,36] to control the pO_2 over the sample and to enable well-defined step changes in the pO_2.

D^δ and k^δ values obtained for the above-mentioned materials are compared to values from the literature (if available); for BSCF, LSCF, and PSCF values could be determined for the first time at the very high temperature of 900 °C as a function of pO_2.

2. Experimental

2.1. Sample preparation

Commercially available MIEC oxide powder ($Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), Treibacher, Austria) as well as own powders prepared by spray pyrolysis ($La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (PSCF)) were used. XRD analyses confirmed all raw powders to be single-phase perovskite compositions.

From these powders, dense ceramic bulk samples were fabricated by uniaxial pressing at 10 kN/cm^2 and subsequent sintering. In the case of BSCF, sintering occurred for 12 h at 1000 °C, in the case of LSCF for 5 h at 1200 °C, while PSCF was sintered for 5 h at 1250 °C. The resulting dense pellets (SEM cross-sectional analyses showed densities of >95%) were subsequently cut by ultrasonic lapping and mechanically polished (P1200 emery paper).

For conductivity measurements all bulks were contacted with Pt wires using a frit-free Pt paste fired at 1050 °C for 1 h in ambient air. Owing to the fairly low electrical resistance of the MIEC bulk samples, electrical measurements were all carried out in 4-point technique. The resulting bar-shaped dense bulk samples had the following geometries: $10 \times 6 \times 1.2$ mm^3 for the BSCF sample, $10 \times 6 \times 1.1$ mm^3 for the LSCF sample, and $10 \times 6 \times 1.1$ mm^3 for the PSCF sample.

2.2. Measurement setup

An "oxygen pump" introduced by Beetz [35] for pO_2 control within the complete range between 10^{-18} bar and 1 bar at temperatures of approx. 700…1000 °C was recently modified [36] for the present investigations. It consists (Fig. 1) of a sealed zirconia (YSZ) tube (situated within a furnace) into which the electrically contacted sample is placed. By applying a voltage U_pump according to the well-known Nernst equation

$$U = \frac{RT}{4F} \ln \frac{pO_{2,\text{outside}}}{pO_{2,\text{inside}}} \tag{1}$$

between the large-area Pt-pasted electrodes on the inner and outer sides of the tube precise pO_2 control is achieved between sample chamber (volume ~38 cm^3) and outer gas compartment where a constant flow of pure oxygen is maintained. F is the Faraday constant, R the universal gas constant, T the absolute temperature, and $pO_{2,\text{outside}}$ and $pO_{2,\text{inside}}$ are the oxygen partial pressures outside and inside the sample chamber, respectively. The exact pO_2 values in the direct vicinity of the sample are furthermore monitored by a potentiometric Nernst probe (reference electrodes, cf. Fig. 1). The electronic setup to control pO_2 and measure the pump current is custom-made (IAM-WET); electrical measurements on bulk samples were carried out using an Agilent Micro Ohm Meter (34420 A).

This setup not only allows for coulometric titration measurements on powder samples, thus providing knowledge on the pO_2 stability limits [36,37] of MIEC compositions as $f(pO_2)$ down to 10^{-18} bar, but, as shown here, also allows for electrical conductivity measurements which facilitate determination of D^δ and k^δ values within a certain pO_2 range.

Conductivity relaxation measurements were performed on the dense ceramic MIEC bulk samples at pO_2 values in the range between 10^{-6} and 1 bar in not-too-large pO_2 steps (for LSCF one decade, for BSCF and PSCF approximately half a decade), thus remaining close to chemical equilibrium, at temperatures of 800 and 900 °C in order to determine D^δ and k^δ values as a function of temperature and pO_2.

One limitation of the setup is given by the speed of the oxygen pumping through the zirconia at around 10^{-1} bar pO_2 and above. Under such highly oxidizing conditions one-decade step changes in pO_2 may take up to several minutes, as the maximum amount of oxygen transported through the YSZ tube is limited by the inherent pumping capabilities of the setup [36]. Regarding sample oxygen exchange kinetics, these pumping times might be too long for parameter extraction. (This is discussed in more detail below.) Despite this limitation, however, the setup provides the possibility of precise measurements at oxygen partial pressure ranges not easily accessible using gas mixtures.

3. Results and discussion

3.1. Conductivity measurements as $f(pO_2,T)$

For the perovskite-oxide compositions investigated in this study oxygen exchange with the ambient gas phase at high temperatures occurs according to:

$$^1/_2 O_{2,\text{gas}} + V_O^{\bullet\bullet} \leftrightarrow O_O^x + 2h^\bullet \tag{2}$$

where O_O^x and $V_O^{\bullet\bullet}$ denote oxygen ions on the regular oxygen lattice sites and oxygen vacancies, respectively (in Kröger–Vink notation), and $h^\bullet$ holes. Due to the highly changeable oxygen non-stoichiometry the dominating (p-type) electronic conductivity is a function of ambient oxygen partial pressure pO_2 (and T) [37], as can be seen from Fig. 2 for the case of a dense ceramic LSCF sample at two different temperatures (800 and 900 °C). After each oxygen partial pressure change, a period of 4 h was allowed for the equilibration of the sample; after this period