Available online at www.sciencedirect.com

ScienceDirect

Solid State Ionics 179 (2008) 1032 – 1035

SOLID STATE IONICS

www.elsevier.com/locate/ssi

Oxygen nonstoichiometry and exchange kinetics of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

Edith Bucher [a],*, Andreas Egger [a], Peter Ried [b], Werner Sitte [a], Peter Holtappels [b]

[a] Chair of Physical Chemistry, University of Leoben, Franz-Josef-Strasse 18, A-8700 Leoben, Austria
[b] Empa, Laboratory for High Performance Ceramics, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland

Received 18 June 2007; received in revised form 18 January 2008; accepted 24 January 2008

Abstract

The oxygen nonstoichiometry of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF5582) was investigated by thermogravimetry resulting in values of $2.40<(3-\delta)<2.57$ for the equilibrium oxygen content in the range $600 \leq T/°C \leq 900$ and $1E-4<pO_2/bar<0.4$. The oxygen exchange kinetics was studied by electrical conductivity relaxation as a function of temperature in the range $550 \leq T/°C \leq 725$ with chemical diffusion coefficients $1E-6<D_{chem}/cm^2\ s^{-1}<3E-5$ and surface exchange coefficients $2E-4<k_{chem}/cm\ s^{-1}<3E-3$. The activation energies of the kinetic parameters amount to $E_a(D_{chem})=86\pm8$ kJ mol^{-1} and $E_a(k_{chem})=64\pm12$ kJ mol^{-1}. Self-diffusion and surface exchange coefficients, as well as ionic conductivities are estimated.

Keywords: Perovskite oxide; BSCF; Oxygen nonstoichiometry; Oxygen exchange; Conductivity relaxation

1. Introduction

The mixed conducting perovskite-type oxides (La,Sr)(Co,Fe)$O_{3-\delta}$ have been widely investigated with respect to basic mass and charge transport properties as well as for application in solid oxide fuel cells (SOFCs) and oxygen permeable membranes. While $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ exhibits the highest oxygen permeability in this series [1], it has the disadvantage of undergoing a transition to the oxygen vacancy ordered brownmillerite structure at $T<800$ °C [2,3]. The perovskite phase can be stabilised by Ba-substitution leading to the composition of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF5582), which was proposed as a superior SOFC cathode material [4,5] and as a high-performance oxygen permeable membrane [6–9]. The cubic perovskite structure with disordered oxygen vacancies is maintained in BSCF5582 even at exceptionally high oxygen deficit ($0.3<\delta<0.8$ at $600<T/°C<900$) [7,9,10]. This clearly exceeds typical values of comparable perovskites, e.g. $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ with $0.15<\delta<0.40$ at 700–900 °C and $1E-4<pO_2/bar<1$ [11].

So far, the oxygen exchange properties of BSCF5582 have mainly been investigated by the permeation method [6–9], studying the steady-state oxygen permeation flux in a high pO_2 gradient, while investigations by non-steady-state methods close to equilibrium are scarce [12]. For potential application in intermediate temperature SOFC cathodes the dependence of the oxygen exchange properties on temperature and on oxygen partial pressure under operating conditions of the SOFC are of special interest. In a recent study we applied the conductivity relaxation method to investigate the oxygen partial pressure dependence of the chemical surface exchange coefficients (k_{chem}) and the chemical diffusion coefficients (D_{chem}) at 600 and 700 °C [13]. The present work will focus on the kinetic parameters as a function of T between 550 and 725 °C. In combination with thermogravimetric investigations of the oxygen nonstoichiometry as a function of T and pO_2 self-diffusion coefficients and oxygen exchange coefficients as well as ionic conductivities will be estimated.

2. Experimental

BSCF5582 powder was prepared by spray pyrolysis and characterised with regard to phase purity and elemental composition by XRD and ICP-AES, respectively [13].

The oxygen nonstoichiometry δ was investigated by use of a precision thermobalance (Setaram, TAG 2416) as a function of

---

* Corresponding author.
E-mail address: Edith.Bucher@mu-leoben.at (E. Bucher).

0167-2738/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ssi.2008.01.089

temperature and oxygen partial pressure. During isobaric experiments two temperature cycles were performed, heating from 20 to 900 °C and cooling back to 20 °C with rates of 1.3–5 K min^{-1}. Temperature ramps were chosen sufficiently low to obtain negligible thermal hystereses of δ (below ±0.004 in the range $600 \leq T/°C \leq 900$). Dynamic sequences were followed by dwell times of 1–2 h, where mass changes were usually below ±1 µg. Isothermal experiments were performed by equilibration of the sample at various oxygen partial pressures $1E-4 < pO_2/bar < 0.4$ until the corresponding mass signal was constant within ±1 µg. Sequentially, the pO_2 steps were performed from oxidising towards reducing atmospheres. Depending on T and pO_2, the required equilibration times between successive pO_2 steps were 1–24 h. Defined gas atmospheres were obtained by mixing Ar (5.0), O_2 (4.5), and Ar+1 vol.% O_2 using mass flow controllers (Mycrolis, FC2700). As a reference point the absolute oxygen nonstoichiometry was determined by equilibration of a sample at 700 °C and $pO_2=0.37$ bar and subsequent total reduction in a mixture of Ar (5.0) and Ar+3 vol.% H_2 at 900 °C. The oxygen partial pressure of the reducing Ar/H_2 atmosphere amounted to $pO_2=2.6E-21$ bar. The mass loss during reduction at 900 °C was monitored until the sample mass remained constant within ±1 µg for 24 h. XRD of the residue confirmed the total decomposition of the perovskite phase and showed characteristic reflections of Co/Fe.

The temperature dependences of the kinetic parameters (D_{chem} and k_{chem}) were investigated by dc conductivity relaxation experiments as a function of temperature ($550 \leq T/°C \leq 725$). During cooling from 700 to 550 °C experiments were performed at constant temperatures in intervals of 50 K. Subsequently, a heating run was performed with experiments in intervals of 25 K, from 550 up to 725 °C. Results obtained upon cooling were in good agreement with those obtained upon heating. Small oxidation and reduction steps between $pO_{2,Hi}=2.1E-2$ bar and $pO_{2,Lo}=9.0E-3$ bar were alternately applied to study the oxygen exchange kinetics close to equilibrium. Usually, a sequence of 2–3 reduction/oxidation cycles was performed at each T. Intermittent to successive pO_2 steps, the sample signal was monitored to ensure that complete equilibrium with the gas phase was obtained. The minimum factor of equilibration time relative to the duration of the experiment was 3. During the equilibration intervals between successive experiments the normalised electronic conductivity remained constant within ±1%. Oxygen partial pressures were adjusted by mixtures of O_2 (4.5) and Ar+1 vol.%O_2 using mass flow controllers (Hastings, HFC 302). Fast pO_2 steps were realised by switching between two continuous gas streams with flow rates of 1.6 l h^{-1}. The experimental relaxation curves of a dense disc shaped sample (thickness 0.760 mm) with 4 point-contacts in van der Pauw geometry [14] were monitored via the voltage response at constant dc current with a combined high-impedance multimeter and power source (Keithley, 2400). The transient response of the gas phase (finite flush time of the reactor) was separately determined in a series of experiments with the empty reactor using the *in-situ* oxygen sensor described below. An average flush time $\tau=4.8\pm0.5$ s was obtained, where reduction experiments were usually slightly faster than oxidation experiments with a difference of approximately 0.5 s. The normalised electronic conductivity was analysed by nonlinear least squares fits to the solution function of the appropriate diffusion equations, taking into account the finite flush time of the reactor [15,16], using a constant $\tau=5$ s.

For *in-situ* measurements of the oxygen partial pressure in both thermogravimetry and conductivity relaxation experiments potentiometric oxygen sensors with Ir/IrO_2 reference (Setnag) were applied. Estimated experimental errors $\Delta T=\pm0.5$ K, $\Delta pO_2=\pm2\%$, and $\Delta\delta=\pm0.007$, and propagated errors are given as one standard deviation.

3. Results and discussion

3.1. Oxygen nonstoichiometry

The oxygen deficit of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ is given as a function of T and pO_2 in Fig. 1. Isothermal experiments at 700–900 °C and intersections of isobaric experiments at 600–900 °C are in good agreement with each other. The oxygen nonstoichiometry increases continuously with increasing temperature and decreasing pO_2. No evidence for a transition to an ordered brownmillerite structure ($ABO_{2.5}$) at $\delta \rightarrow 0.5$ was observed.

In literature few studies on the oxygen nonstoichiometry of BSCF5582 are available. While trends in δ vs. pO_2 and vs. T are similar, discrepancies on the absolute values of δ are found. For example, data obtained at 700 °C by thermogravimetry range from $\delta=0.26$ ($pO_2=0.21$ bar) [7] and $\delta=0.34$ ($pO_2=1.0$ bar) [10] to $\delta=0.68$ (0.21 bar) [9]. Vente et al. [9] also reported values determined by *in-situ* neutron diffraction at 700 °C, e.g. $\delta=0.69$ ($pO_2=1.0$ bar). The oxygen nonstoichiometry as determined in the present study at 700 °C, $\delta=0.46$ ($pO_2=0.21$ bar), Fig. 1, is between the upper and lower limits of currently available literature data.

The thermodynamic factor of oxygen γ_O [17] was obtained according to

$$\gamma_O = \frac{1}{2}\left(\frac{\partial \ln pO_2}{\partial \ln(3-\delta)}\right)_T \tag{1}$$

by linear regression. With good linear correlation of ln pO_2 vs. ln $(3-\delta)$ ($R^2>0.98$), γ_O was assumed constant over the pO_2

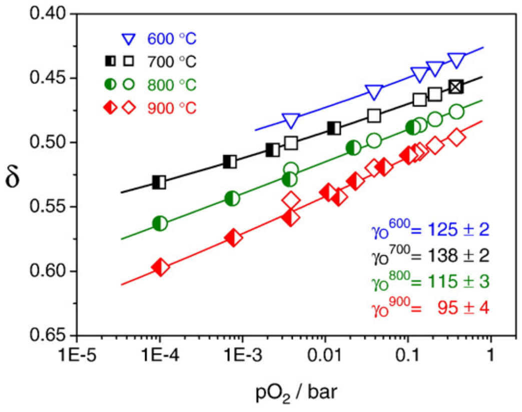

Fig. 1. Oxygen nonstoichiometry δ and thermodynamic factor of oxygen γ_O (Eq. (1)) of BSCF5582 at 600–900 °C. Results from isotherms (half filled symbols) are compared with isobars (open symbols). The reference point (☒) was obtained by total reduction in Ar–H_2. The experimental error is estimated to $\delta\pm0.007$. Lines are a guide to the eye.