Influence of CO2 on the oxygen permeation performance and the microstructure of perovskite-type 
(Ba0.5Sr0.5)(Co0.8Fe0.2)O3−δ membranes

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Received 5 October 2006; received in revised form 23 January 2007; accepted 24 January 2007
Available online 1 February 2007

Abstract

The influence of CO2 on the oxygen permeation performance of perovskite-type (Ba0.5Sr0.5)(Co0.8Fe0.2)O3−δ (BSCF) membranes under different experimental conditions is presented. First, pure CO2 was applied as the sweep gas at 875 °C yielding an immediate cessation of the oxygen permeation. In order to probe the reversibility of this stagnancy, several cycles of changing the sweep gas between helium and CO2 were conducted. The analysis of the microstructure after permeation experiments were carried out by transmission electron microscopy (TEM), X-ray diffraction (XRD) as well as by scanning electron microscopy (SEM). It was found that both microstructure as well as oxygen permeation are recovered in a helium atmosphere. Additionally, long-time treatment with pure CO2 for 72 h on the permeate side and the concentration effect of CO2 in the sweep gas were accomplished showing that the perovskite structure is impaired only up to a depth of 50 μm. Further on, the impact of CO2 on the feed side was examined by adding certain amounts of CO2 to the feed air. It was found that the impact of CO2 on the oxygen permeation applied in the sweep gas is superior to that applied on the feed gas.

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Keywords: BSCF; Oxygen permeation; CO2; Carbonate; Perovskite

1. Introduction

Much importance has been attached in the past years to solid oxide membranes regarding their property to separate oxygen from air with infinite selectivity. Especially mixed ionic–electronic conductors (MIECs) with perovskite structure are of great interest for many industrial processes in which a constant supply or removal of oxygen to or from reaction mixtures is required [1]. Many promising applications of MIECs as cathode material in solid-oxide fuel cells as well as in the production of oxygen-enriched air and in the conversion of hydrocarbons to synthesis gas have been reported [2–5]. Major advantages of these membranes are unreached permselectivity and remarkable high oxygen fluxes in the range observed on microporous materials [1].

In the area of MIECs with perovskite structure, compositions of (Ba0.5–xSr1−x)(Co0.8Fe0.2)O3−δ are regarded as state-of-the-art materials in view of their high oxygen permeation fluxes. For prospective industrial applications not only high permeability but also sufficient phase stability is essential. This includes reasonable thermal next to chemical stability particularly in reducing gas atmospheres or atmospheres containing CO2. The poisoning effect of CO2 is related to the fact that earth alkali metals – included in the perovskite structure – tend to form carbonates. Wang et al. and McIntosh et al. found that BSCF exhibits good phase stability down to a pO2 of 2 × 10−5 atm [6,7]. Recently, Yan et al. have published results dealing with the effect of CO2 between 450 and 750 °C on the cell performance of solid oxide fuel cells (SOFCs) having electrodes of the same material [8]. They found a negative but reversible effect on the cell performance even if relatively low CO2 partial pressures were supplied to the cathode side. Generally, the effect of CO2 on the membrane performance needs to be examined since CO2 is contained in natural air as well it is a by-product of the synthesis gas production. Especially with
the advent of zero emissions plants in which oxygen permeating membranes are flushed with CO₂-containing exhaust gases, the demand for CO₂ capable membranes becomes more significant [9]. It has to be stressed that – depending on the potential application of perovskite membranes – either the feed side or the permeate side needs to be examined regarding the CO₂ stability. Therefore, several investigations concerning – inter alias – the effect of CO₂ on different materials with the perovskite-type structure have been published in recent years [10–16].

Already in 1995 Pei et al. described the chemical decomposition of Sr(Co1−xFeₓ)O₃−δ (SCF) hollow fibre membranes after partial oxidation of methane to synthesis gas. It was found that on the reaction side of the membrane the SCF tend to form strontium carbonate as well as a mixture of iron and cobalt oxides leading to membrane failures [10]. Tong et al. discovered the effect of CO₂ on the permeation performance of Ba(Co₀.₆₋₀.₄Zr₀.₂)O₃−δ (BCFZ) disc membranes when applied in the feed gas as well as in the sweep gas. Strong decrease of oxygen permeation flux was noticed for the case if the sweep gas contains CO₂. Otherwise no significant attenuation was found, if CO₂ was delivered on the feed side [11]. Similar results were found by Yi et al. after treatment of Sr₀.₉₅(Co₀.₅Fe₀.₅)O₃−δ with CO₂ and or H₂O containing atmospheres [12]. Homonnay et al. described the adsorption of CO₂ in the lattice of Sr(Co₀.₉₅Ca₀.₀₅)O₃−δ by Mössbauer spectroscopy. They found that CO₂ adsorption of about 4% occurs preferentially in Co-rich regions attributed to a lower coordination number of cobalt in the pristine material resulting in a separation of cobalt and iron pockets [13]. High-temperature in situ neutron powder diffraction on SCF ceramics in CO/CO₂ atmospheres were carried out by different groups while diffraction pattern of whole membrane profiles show no or even low contents of earth alkali carbonates but the formation of various oxides [14,15]. Very recently Yang et al. proposed the application of (La₀.₁Sr₀.₉)(Co₀.₅Fe₀.₅)O₃−δ (LSCF) to produce oxygen-enriched CO₂ via adsorption/desorption processes as it might be implemented in the oxyfuel process. High desorption efficiency and good reversibility of the sorption process was found if LSCF powder were treated by turns with O₂ and CO₂ [16].

Despite a few information is already available, a detailed examination of BSCF powders regarding CO₂-containing atmospheres is still lacking. Especially a profound investigation of the microstructure of BSCF membranes after poisoning with CO₂ has not been reported yet. Here, we present investigations concerning the influence of CO₂ on the oxygen permeation flux of BSCF disc membranes when applied in both the sweep as well as in the feed gas. Additionally, investigations of the microstructure after treatment with these atmospheres were carried out by (scanning) transmission electron microscopy (STEM, TEM) combined with electron energy-loss spectroscopy (EELS) involving electron-loss near-edge structures (ELNES), selected area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy (EDXS). Furthermore scanning electron microscopy (SEM) and X-ray diffraction (XRD) experiments were applied for analytical purposes.

2. Experimental

BSCF powders were synthesized via a combined citrate and EDTA complexing method according to Shao et al. Proper amounts of Ba(NO₃)₂, Sr(NO₃)₂, Co(NO₃)₂ and Fe(NO₃)₃ were dissolved in water and followed by the addition of citric acid, EDTA and NH₃ [17]. The reaction mixture was then heated under constant stirring to obtain a purple-coloured gel. Afterwards the gel was pre-calcined for 10 h at 350°C. The pre-calcined powders were grounded and finally fired for 10 h at 950°C to get the pure perovskite phase. The powders were then coldly pressed under 13 atm to prepare “green” membranes which were sintered at 1150°C with a dwelling time of 5 h.

To study the effect of CO₂ on the oxygen permeation, several permeation experiments were carried out on a self-made high-temperature permeation cell which is described in detail elsewhere [18]. Discs of BSCF (Ø = 16 mm, thickness = 1 mm) were sealed onto a ceramic tube with gold-paste (conducting paste, C5754, Heraeus) at 950°C for 2 h. After sealing, gas flow rates were delivered to the reactor by mass flow controllers (Bronckhorst Hi-Tech) and continuously read by an on-line gas chromatograph (Agilent Technologies, HP 6890, equipped with a Carboxen 1000 column). The feed side of the membrane was flushed either with pure air or with selected amounts of CO₂ (>99.95% purity) in air. On the permeate side pure helium or mixtures of helium with CO₂ were applied. The total flow rate on the feed side of the membrane was set to be 150 ml/min, the total flow rate on the permeate side to 30 ml/min or 140 ml/min, respectively. The absolute flow of the effluents rate was determined by using neon as an internal standardization. For that purpose the concentration of neon in effluents was measured. Since the flow rate of neon is known, it is thus possible to calculate the total effluents flow rate. The permeation flux through the membrane could then be calculated by the fraction O₂ in the effluents and the determination of the effective permeation area of the membrane which was 0.75 cm². The leakage was evaluated by measuring the amount N₂ in the effluents stream. After permeation experiments, the membranes were quenched to room temperature under indicated atmospheres.

In order to analyze the microstructure of membranes after permeation experiments, TEM was conducted at 200 kV with a JEOL JEM-2100F-UHR field-emission instrument equipped with a Gatan GIF 2001 energy filter and a 1k-CCD camera in order to obtain EEL spectra. EDXS was carried out by a light-element detector using the Clift–Lorimer quantification technique (INCA 200 TEM, Oxford Instruments). Specimens for TEM investigations were prepared as follows. First, pieces of 1 mm × 1 mm × 2 mm were cut out of the membrane followed by covering of the permeate side with a silicon single crystal using epoxy. Accordingly, the protected membrane pieces were polished on polymer embedded diamond lapping films down to 0.02 mm × 1 mm × 2 mm and glued onto a copper slot grid. Electron transparency was achieved by Ar⁺ ion sputtering at 3 kV under incident angles of 6° and 4° (Gatan, model 691 PIPS).

Additionally, SEM combined with EDXS as well as XRD were conducted on both surfaces and on fracture surfaces. SEM
studies were carried out on a JEOL JSM-6700F field-emission instrument using a secondary electron detector (SE) at an accelerating voltage of 2 kV. EDX spectra were obtained at an accelerating voltage of 15 kV using a light-element detector (INCA 300, Oxford Instruments). To determine the crystal structure of membrane surfaces, XRD were conducted with monochromated Cu Kα1 radiation in the range of 20–90° 2θ at room temperature (Philips X’Pert-PW1710). Light reflection microscopy was made on polished cross-sections of specimen prepared for TEM (Leitz Orthoplan equipped with a phototube and a Nikon D50 digital camera).

3. Results and discussion

Fig. 1 shows the oxygen permeation of a BSCF membrane while swept in periodic cycles by helium and CO2 at 875 °C. If helium is used as the sweep gas, permeation fluxes of 1.9 ml/min/cm² are obtained which are in the same order of magnitude as reported earlier, e.g. by Shao et al. [17]. Changing the sweep gas to CO2 causes an immediate stagnancy of the oxygen permeation. However, if the sweep gas is shifted back to pure helium the virgin oxygen permeation flux or even higher values are be obtained. This reversibility is in good agreement with data published for BCFZ by Tong et al. [11]. Fig. 2a shows a sketch of the chemical potential gradient of oxygen across the perovskite membrane. The marked area indicates the particular area of investigation by secondary electron SEM micrographs of membrane fracture surfaces as displayed in Fig. 2b–d.

In Fig. 2b the fracture surface of a membrane when stopped in a CO2 atmosphere (after a treatment time for 100 min) is displayed. Three areas with different chemical compositions (cf. Table 1) and morphologies have been assigned. Decomposition of the perovskite structure (i) occurs up to a depth of 40 μm, as indicated by the morphology as well as by EDXS because the pure perovskite stoichiometry is found so far. The decomposed layer itself is separated into two basically distinct areas assigned with (ii) and (iii). Layer (ii), which abuts on the pure perovskite phase, exhibits a plate-like morphology as well as a different stoichiometry (cf. Table 1) and is restricted to a thickness of approximately 25 μm. EDXS analysis give raise to the assumption that a mixture of carbonates as well mixed-oxides are present in this layer. Also, a gradient of the carbonate formation can be concluded because a diminution of the carbon content in this layer from 21 at.% (close to the surface film (iii)) down to 15 at.% (close to the bulk (i)) is observed. At the very edge of the permeate side, a film exhibiting a thickness of 5 μm is labelled as layer (iii). Since this film contains almost no iron and cobalt it is assumed that only a mixed strontium-enriched carbonate (Ba0.4Sr1−x)CO3 is present. The particular enrichment of strontium can be attributed to the fact that the mixing enthalpy of (Ba0.4Sr1−x)CO3 solid solutions reaches a maximum if x = 0.35 as described by Kiselva et al. [20].

Further on, the elemental distribution at the permeate side of the membrane is visualised by EDXS in Fig. 3a, emphasizing the above-explained phase formations. In order to confirm the formation of a carbonate top layer, XRD measurements of the permeate surface were conducted. XRD pattern clearly indicate the formation of the mixed carbonate with an excess of strontium as mentioned above. Kiselva et al. examined the variation in lattice constants of various (Ba,Sr)CO3 stoichiometries. Using these parameters, it is found that applying an orthorhombic cell (a = 6.2262; b = 5.1957; c = 8.6190) which is related to (Ba0.4Sr0.6)CO3 fits very well to the XRD pattern in Fig. 4c and d. This finding underlines the enrichment of strontium in the carbonate, as indicated by EDXS. XRD pattern show several additional reflections, which are not identified but further discussed below.

As already noted, the oxygen permeation flux is totally recovered, when the sweep gas is shifted to helium. It might be assumed, that the recovering of the oxygen permeation flux is accompanied by a reconstruction of the perovskite phase. This presumption was proven by SEM, EDXS and XRD on a membrane that has been treated first for 100 min with pure CO2 as sweep gas followed by a substitution with helium for 100 min like the alternating cycle displayed in Fig. 1. Fig. 2c shows that the plate-like morphology of the intermediate layer (ii) in Fig. 2b is completely vanished, whereas the very edge of the membrane exhibits a slight deviation from the dense structure of layer (i). Additionally, a minor enrichment of carbon – compared to the pure perovskite – is present (cf. Table 1). This circumstance gives raise the assumption that a little amount of carbonate remains in this layer, which is therefore labelled as (i*)

The elemental distribution by EDXS in Fig. 3b shows an homogenous distribution off all four cations underlying the fact, that only a poor amount of the carbonates resides in layer (i*). XRD pattern of the recovered membrane in Fig. 4b emphasizes the assertion that only small amounts of the carbonate phase exist since only reflections that are related to the perovskite structure in Fig. 4a can be found.

In order to study the mechanism of decomposition of the perovskite phase, a long-time permeation experiment was conducted in which the permeate side had been exposed to CO2 for 4320 min. No visible increase of the surface film (iii) could be observed (cf. Fig. 2d) and no significant change in its chemical composition is found for the long-time treatment. Only a more accented separation of layers (ii) and (iii) is observed as displayed by Fig. 3c. It shows a well-defined boundary between
Fig. 2. (a) Sketch clarifying the mechanism of oxygen permeation through the membrane. (b–d) SEM micrographs showing the permeate side of the membrane when permeation was stopped after a treatment (b) for 100 min with pure CO$_2$ as sweep gas, (c) after recovering for 100 min with pure helium as sweep gas and (d) for 4320 min with CO$_2$ as sweep gas.

layers (ii) and (iii) as indicated by the distribution of iron and cobalt. The intermediate layer (ii) shows a slight expansion (app. $10^{-3}$.m) as shown in Fig. 2d. Quantitative analysis of the chemical composition inside this layer is found to follow the same trend as the intermediate layer obtained in the short-time CO$_2$ treatment, exhibiting a monotonic diminution of the carbonate content. XRD pattern of long-time CO$_2$ treated membranes indicate a similar XRD pattern as for the short-time treated (cf. Fig. 4c and d). Obviously, a decrease of the carbonate reflections is found while the reflections for the unknown phase

Table 1
Summary of the elemental distribution of Ba, Sr, Co, Fe, O and C obtained by EDXS at fracture surfaces of membranes after treatment with CO$_2$ (100 min), CO$_2$ (4320 min) and recovering with helium (100 min)

<table>
<thead>
<tr>
<th></th>
<th>Stopped in CO$_2$, after 100 min</th>
<th>Stopped in CO$_2$, after 4320 min</th>
<th>Stopped in helium, after 100 min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 µm$^a$</td>
<td>5 µm$^a$</td>
<td>20 µm$^a$</td>
</tr>
<tr>
<td>Ba (at.%)</td>
<td>5.9</td>
<td>4.5</td>
<td>7.0</td>
</tr>
<tr>
<td>Sr (at.%)</td>
<td>7.8</td>
<td>4.9</td>
<td>6.9</td>
</tr>
<tr>
<td>Co (at.%)</td>
<td>0.6</td>
<td>5.7</td>
<td>10.9</td>
</tr>
<tr>
<td>Fe (at.%)</td>
<td>0.6</td>
<td>1.2</td>
<td>2.9</td>
</tr>
<tr>
<td>O (at.%)</td>
<td>58.1</td>
<td>62.5</td>
<td>58.2</td>
</tr>
<tr>
<td>C (at.%)</td>
<td>26.8</td>
<td>21.2</td>
<td>14.1</td>
</tr>
</tbody>
</table>

The standard deviation for quantification data of Ba, Sr, Co, Fe is assumed to be $\pm 12\%$, according to [19]. Quantifications for carbon demonstrate only trends.

$^a$ Distance to edge of permeate side.
increase. Considering that the carbonate layer thickness does not change significantly, the increase of the reflections related to the unknown phase might be due to proceeding crystallisation of this phase. Hence, the formation of the unknown phase in layer (ii) occurs slower than the formation of the carbonate. This phenomenon can be explained as follows: first, strontium and barium form the carbonate, when CO₂ is applied. The moiety of the cations forms a second crystalline phase, with slower kinetics. Due to that reason the crystallinity of this phase can then be detected by XRD with higher intensity, if a longer reaction period is applied.

As already mentioned, no significant increase in the thickness of the decomposed layer is observed. This fact can be attributed to the above assumed mechanism of the
decomposition, regarding a fast formation of the carbonate top layer. This layer can be appreciated as a protective layer regarding the carbonate formation. Gomes and Dekeyser refer this case, if the reaction product builds up a layer between the reactants, to tarnishing reactions [21]. If the reaction product forms a compact, non-porous layer, the reaction rate is limited by transport phenomena through the product layer. Since the thickness of the carbonate is restricted to $5 \mu m$ even after long-time treatment, it can be therefore concluded that a dense carbonate layer is formed. This layer causes an immense decrease of the CO$_2$ transport to the buried perovskite surface resulting in a stagnancy of the carbonate formation.

In order to get a more detailed understanding of the microstructure of layer (ii), TEM investigations were conducted at the boundary to layer (iii). Fig. 5a shows a bright-field micrograph of layer (ii). The plate-like morphology found by SEM and light microscopy (cf. Fig. 6) in this layer can be confirmed even by TEM. Elemental distributions acquired by EDXS, clearly indicate the presence of two distinct phases (cf. Fig. 7). The first can be attributed to the plate-like morphology being a mixed oxide $(\mathrm{Ba, Sr})_x(\mathrm{Co, Fe})_y\mathrm{O}_z$ – thus containing all four cations – with complex structure. The second occurs complementary between the plate-like parts and can be related to the above-mentioned strontium-enriched carbonate. SAED of the marked circular area indicates the occurrence of carbonate single crystals next to single crystals of the mixed oxide (cf. Fig. 5a and b).

As already mentioned, several non-carbonate reflections were investigated in the XRD pattern in Fig. 4c and d which cannot be explained by already known phases. Despite the fact a phase attribution is lacking, unindexed $d$-values in the XRD pattern can be found in SAED of Fig. 5b, by converting them according to the Bragg equation ($d = 0.4095, 0.4014, 0.3202, 0.3017, 0.2601, 0.2580, 0.2181, 0.2008$ nm). Furthermore, a large unit cell is assumed as because of $d$-values found in the SAED. This can be concluded since at least one cell parameter has a minimum size of $1.2$ nm.

Additionally, O-K ELNES were used to confirm the local chemical environment around oxygen atoms. The spectra have been acquired with a small spectrometer entrance aperture to obtain solely information from forwarded scattered electrons that suffered just small transversal momentum transfers. Thus, primarily dipole selection rules apply, and the O-K ELNES probes transitions from O 1s core levels into unoccupied final states of p character that are centered on the oxygen atom. Therefore, the spectra of Fig. 5c reflect on O 2p bands that may hybridize with the metal 3d and higher energy orbitals. In Fig. 5c, the O-K near-edge fine-structure of area 1 clearly indicates the presence of a carbonate bonding [22] with two pronounced peaks, whereas a first small peak at $\sim 535$ eV is followed by an intensive peak at $\sim 541$ eV exhibiting a shoulder-like structure towards higher energies. The spectrum of the complex oxide, $(\mathrm{Ba, Sr})_x(\mathrm{Co, Fe})_y\mathrm{O}_z$, from area 2 shows a leading, relatively narrow peak at $\sim 532$ eV. This leading peak reflects that the $t_{2g}$ states $(d_{xy}, d_{xz},$ and $d_{yz}$ orbitals) of cobalt and iron are hybridized with the unoccupied oxygen 2p states via 2p–3d interactions, as it is often observed in complex oxides [23]. Further on, a broad peak has a maximum at $\sim 543$ eV with two clearly resolved peaks in the left shoulder: at $\sim 537$ and $\sim 541$ eV, respectively. The peak at $\sim 543$ eV refers to excitations of O 2p electrons into unoccupied $(\mathrm{Co, Fe}) e_g$ states $(d_{z^2}, d_{z^2-y^2}$ orbitals). The extra features at
∼537 and ∼541 eV can be attributed to additional interactions of the oxygen ligand with ns and np states of barium and strontium cations [22]. All these characteristics of the O-K ELNES show some structural relationship to perovskites (ABO$_3$) with octahedral coordination of the B-site cation (here cobalt and iron) to oxygen.

To a minor extent, cobalt oxide with rocksalt structure is eminent in the intermediate layer. Fig. 8 shows a TEM bright-field micrograph accompanied with an SAED of this oxide. Additionally, the presence of pure cobalt oxide was proven by EDXS.

Summarizing the above-presented results, the following circumstance can be concluded. If CO$_2$ is applied as the sweep gas, first a strontium-enriched carbonate is formed along a fast reaction pathway, resulting in an immediate stop of the oxygen permeation due the protective character of the carbonate. Second, the remaining cations form a new complex oxide, with large unit cell, in which the crystallisation increases with reaction time accompanied with the formation of cobalt oxide in rocksalt structure.

As discussed above, a complete vanishing of the oxygen permeation flux can be found, if helium is substituted by CO$_2$. Following, the concentration and time effect of CO$_2$ when applied either in the feed or in the sweep gas will be discussed. Fig. 9 shows the CO$_2$ concentration depending diminution of the oxygen permeation flux if supplied in the sweep gas and the associated oxygen partial pressure. Introducing 5% CO$_2$ in the sweep gas causes an attenuation of 17% after 2 min of CO$_2$ addition. This fact fits the assumption of fast kinetics regarding
the formation of the carbonate top layer. Following, the oxygen permeation flux declines down to 60% of the virgin flux already after a reaction time of 120 min and down to 50% after 460 min of CO2 supply. A this point a steady-state is reached since even an exposure time for more than 20 h did not cause a significant further decrease of the oxygen permeation flux.

A second experiment was conducted in which the CO2 concentration was set to 10% and 15% after a certain reaction time in order to examine whether the decrease of the oxygen permeation performance is simply due to time. Obviously, a strong acceleration of the descent emerges if the CO2 concentration is increased. Comparing the oxygen permeation under the influence of 5% CO2 with 10% CO2 in the sweep gas flux after 320 min one can see that a doubling of the CO2 content halves the oxygen permeation flux.

From the long-term experiment in which 5% CO2 was applied it can be concluded that the carbonate layer reaches an equilibrium thickness that still allows oxygen permeation even though with a reduced performance. That indicates a competition between two reactions. The first reaction, that stabilizes the perovskite phase, is supported by oxygen, as commonly known in literature [24]. The second reaction leading to the formation of the carbonate and the above mentioned oxides. Implying that no competition would take place the oxygen permeation flux would stop after a certain time in each applied CO2 concentration since a continuously increase of the carbonate would occur. Therefore, the relation between the amounts of oxygen compared to the amount of CO2 contained in the gas atmosphere seems to be the important factor that causes diminishing of oxygen permeation across the BSCF membrane.

Further proof for this supposition is shown in Fig. 10, in which the oxygen permeation flux is plotted versus the CO2 content in the feed air. Up to 10% CO2, the oxygen permeation flux decreases only down to 90%, whereas the oxygen permeation flux decreased down to 50%, if only 5% of CO2 was applied in the sweep gas. If the oxygen content on the feed side was increased to 15%, a relatively fast decrease of the oxygen permeation performance down to 78% within 120 min was observed. The concentration step from 10% to 15% CO2 can therefore be assumed to be the threshold at which the decomposition of the perovskite becomes significant. Further increase to 20% resulted in a fast reduction to 22% in the space of time of 120 min.

The effect of the temperature on the carbonate formation and hence the impact of the temperature on the oxygen permeation flux can be found elsewhere [25]. Feldhoff et al. reported the free enthalpy in dependence of the temperature. It can be seen that raising the temperature avails the formation of the mixed carbonate. Hence, one can conclude that lowering the temperature during would even lower the oxygen permeation because of the advanced carbonate formation.

4. Conclusion

The poisoning effect of CO2 on the oxygen permeation flux as well as on changes in the microstructure of BSCF membranes has been investigated. It has been shown, that using pure CO2 as sweep gas causes an immediate stop of the oxygen permeation flux but can be easily recovered by sweeping with pure helium. Examinations of the microstructure clearly indicate the decomposition of the perovskite structure up to a maximum depth of 40–50 μm, even when exposed to CO2 for more than 4300 min. The decomposed layer was found to be separated into two different phases, whereas the intermediate layer contains mainly a strontium-enriched mixed carbonate next to a novel mixed oxide, as indicated by SEM, XRD and TEM observations. Further, the concentration effect of CO2 in the gas exposed to the membrane was examined regarding their influence on the oxygen permeation. It was found that BSCF membranes are capable to sustain up to 10% CO2, if applied in the feed air. That leads to the assumption that if the O2:CO2 ratio falls not significantly below 2:1, BSCF membranes can be
operated in these environments without significant decrease in their performance at least for 120 min.

Acknowledgements

The authors greatly acknowledge the financial support by DFG grant no. FE 928/1-1 and fruitful discussions with Prof. Jürgen Caro.

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