Processing and oxygen permeation studies of asymmetric multilayer Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_3$ membranes

A.V. Kovalevsky$^{a,b,*}$, A.A. Yaremchenko$^b$, V.A. Kolotygin$^b$, A.L. Shaula$^{b,c}$, V.V. Kharton$^b$, F.M.M. Snijkers$^a$, A. Buekenhoudt$^a$, J.R. Frade$^b$, E.N. Naumovich$^b$

$^a$ FVITO NV, Boeretang 200, B-2400 Mol, Belgium
$^b$ Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
$^c$ Department of Mechanical Engineering, SEG-CEMU, University of Coimbra, P-3030-788 Coimbra, Portugal

**Article Info**

Article history:
Received 30 April 2011
Received in revised form 21 June 2011
Accepted 22 June 2011
Available online 29 June 2011

**Keywords:**
Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_3$, Ceramic membranes, Membrane separation, Oxygen permeation, Surface activation

**Abstract**

The oxygen transport studies of dense Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_3$$^{−δ}$ (BSCF) ceramic membranes, prepared via glycine–nitrate route, demonstrated that the permeation rate is predominantly controlled by surface exchange kinetics when the membrane thickness is smaller than 1.00 mm. In order to improve oxygen exchange, an asymmetric membrane concept including two porous and one dense layer was implemented. The amount of graphite as a pore-forming additive, powder compaction and sintering conditions were optimized to produce three-layer membranes having appropriate mechanical strength and microstructure. Comparison of the data on oxygen permeation through three-layer and dense 1.00 mm thick symmetric membranes indicated that a moderate improvement of the overall performance was achieved due to asymmetric architecture. The oxygen fluxes through membrane with 170 μm thick dense and porous layers with thicknesses of 1.05 mm and 100 μm at 1173 K were found to be 1.5–1.8 times higher than those for a 1.00 mm thick symmetric membrane. The variation of oxygen flux changes with pressure and the values of the activation energies for oxygen permeation suggest significant gas diffusion limitations in the porous layers, whilst the role of other factors is still significant. Microstructure of the porous layers requires further optimization for successful application of the oxygen exchange catalysts.

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1. Introduction

At present time, high-temperature oxygen separation technologies based on mixed ionic and electronic conducting membranes (MIEC) receive considerable attention due to a number of important advantages over polymer-based membranes and industrial-scale state-of-the-art methods like pressure swing adsorption and cryogenic distillation [1−5]. In combination with the search for novel advanced materials, research efforts are also aimed at optimization of the membrane architecture, both for kinetic stability and total productivity reasons. In particular, an asymmetric concept comprising thin dense layer applied on a porous support offers improvement in oxygen permeation flux, at the same time providing sufficient thermomechanical stability of the membrane structure (Refs. [1,4,6−8] and references therein). Depending upon thickness of the gas-tight layer in such membranes, the performance-determining factors may be associated with bulk ambipolar conductivity, surface exchange, and/or gaseous oxygen diffusion in the porous layers.

At the same time, the asymmetric concept brings new compatibility issues into the membrane fabrication process. At the conditions of high temperature and oxygen chemical potential gradients the difference in expansion behavior between thin dense layer and porous support can generate stresses leading to formation of cracks and mechanical instability of the whole system. Using the support and dense layer consisted of the same material, one can ensure the chemical and mechanical stability of asymmetric membrane structure (Ref. [1] and references therein). However, in this case a technological problem is related to the densification of the thin film whilst maintaining the porous structure of the support. The latter requires additional efforts to be focused on the materials processing route, what composed one of the targets of the present work.

Due to the high level of ionic transport [9−12], in the present work the perovskite-type Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_3$$^{−δ}$ (BSCF) mixed conductor was chosen as a material for the planar asymmetric
membranes for oxygen separation from gas mixtures. According to the literature data, the membrane thickness ($d$) dependencies of the permeation fluxes through flat BSCF membranes showed that the permeation is, at least partially, limited by surface exchange kinetics. In particular, a deviation from the linear dependence of the permeate flux on inverse thickness of the membrane was demonstrated for $d = 1–2$ mm [12–15]. On the contrary, Wagner behavior of the permeation fluxes with change of oxygen chemical potential gradient was observed for BSCF tubular membranes with $d = 1.0$ mm at 1023–1173 K [16,17]. The membrane concept, implemented in present work, includes a thin dense layer supported by relatively thick porous one and covered with an additional thin porous layer. In this configuration, a thick porous support is supposed to provide additional mechanical strength to the whole system, whilst thin porous film may contribute to the activation of the dense layer due to development of the surface area. To our best knowledge, the described concept implemented via optimization of the material processing route and three-stage uni-axial compaction procedure, followed by sintering, was not yet applied to BSCF, one of the best mixed conductors.

The present work was mainly concentrated on the processing and oxygen permeation studies of BSCF-based three-layer asymmetric flat membranes in order to assess effects related to the membrane architecture. According to the literature data, the grain size may significantly affect the permeation rates through BSCF membranes; however, the results are often contradictory [18–20]. In particular, cases, a chosen synthesis method may affect the relationship between transport and oxygen exchange properties even for similar materials, due to a specific grain size range. Efficiency of the implementation of asymmetric concept strongly depends on the factors limiting the oxygen permeation process. Therefore, in addition to BSCF, SrCo0.8Fe0.2O3 (SCF), demonstrating one of the highest levels of ionic transport, was also prepared via glycine–nitrate route. Both materials were characterized together with respect to the transport properties and stability, in order to compare with the data already known in the literature and, thus, to distinguish the effect of preparation method and membrane configuration impact, what is of especially high importance for the materials possessing high permeation rates.

## 2. Experimental

BSCF and SCF powders were synthesized via the glycine–nitrate process (GNP), a self-combustion technique using nitrates of metal components as an oxidant and glycine as a fuel and chelating agent [21]. SEM inspection of the powder after subsequent annealing at 1173 K for 2 h for removing organic residues shows, however, a high agglomeration of the particles. In order to decrease agglomeration and to provide easier densification of the ceramics during sintering, the powder was subjected to ball milling. The conditions for fabrication of asymmetric membranes are described in Section 3.3. The same conditions of powder preparation, compaction and sintering were used for the production of dense 0.58–2.67 mm thick symmetric membranes, also studied for the sake of comparative analysis and estimation of the surface exchange limitations.

The characterization included X-ray diffraction (XRD) analysis, scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM/EDS), picometry, gas-tightness control, mercury intrusion porosimetry, thermogravimetry, nitrogen permeation, total conductivity and Seebeck coefficient vs. $p(O_2)$ measurements, Vickers hardness tests and determination of the steady-state oxygen permeation fluxes; description of the experimental procedures and equipment can be found elsewhere (Refs. [8,22–25] and references cited). Nitrogen permeability of the BSCF porous membranes having various porosities was estimated using Veletrog gas filtration installation, equipped with Amatfilter TPA025 module for sealing of the flat membranes and a digital mass-flow meter to measure the nitrogen flux through membrane under nitrogen pressure drop from 2.5 to 1 atm. Vickers hardness was measured at room temperature on a Wilson-Wolpert Vickers microhardness tester Tukon 2100B with load pressure up to 0.5 kg.

For all membranes studied in this work, zero level of physical leakages was confirmed under a total pressure gradient of 2–4 atm. Two techniques were used for the determination of steady-state oxygen permeation fluxes at 973–1223 K (Fig. 1). In all cases, the oxygen partial pressure at the membrane feed side ($p_2$) was equal to 21.2 kPa (air), the membrane surface with thin porous layer operated as permeate side exposed to oxygen partial pressure $p_1$. The permeation measurements, described elsewhere ([23] and references therein) and referred to as Method 1, were performed using electrochemical cells made of yttria-stabilized zirconia and equipped with an oxygen pump and a sensor. For this technique, the transport of oxygen through the membrane and, then, through

![Fig. 1. Schematic drawings of the setups used for oxygen permeation studies.](image-url)
internal space of the solid-electrolyte cells is only driven by the oxygen chemical potential gradient created by the electrochemical pump; no sweep gas is supplied onto the membrane surface, whilst the permeate-side gas phase contains only oxygen and traces of nitrogen remaining after sealing. For comparison, another series of measurements were performed under air/Ar gradients, supplying the sweep gas mixtures onto the membrane permeate side (Method 2). The experimental setup, comprising a dense membrane disk hermetically sealed onto YSZ tube and two YSZ sensors at the inlet and outlet of the system, was described in Ref. [24].

3. Results and discussion

3.1. General characterization

XRD analysis confirmed the formation of single-phase cubic perovskite-type structure for the BSCF and SCF ceramics after sintering, with the lattice parameters of 0.3987 ± 0.0001 nm and 0.3865 ± 0.0001 nm (space group: Pm3m), respectively, in agreement with the literature data [9,26]. Typical SEM micrograph of the sintered and fractured BSCF membrane is shown in Fig. 2A
and indicates a formation of dense ceramics under the selected sintering conditions. If assuming that the equilibrium oxygen nonstoichiometry $\delta$ of BSCF at room temperature in air is $\sim$ 0.33 [12,27], the density of obtained ceramics is close to 93% of theoretical.

Fig. 3 presents the oxygen nonstoichiometry data for BSCF and SCF in air, calculated from the results of thermogravimetric analysis. In accordance with Ref. [28], the oxygen nonstoichiometry of BSCF is higher than for SCF, due to an increased average metal–oxygen bond distance leading to a weaker oxygen bonding. The results, obtained in present work, are generally in good agreement with the thermogravimetric data in literature [28,29], reflecting the main tendencies of nonstoichiometry changes with temperature, characteristic for these materials. Despite the significant difference with the oxygen content in BSCF, calculated from neutron diffraction at $p(O_2)$ = 101.3 kPa [28], the slopes of the $(3-\delta)$ vs. $T$ curves are similar for both measurements.

Temperature dependencies of the total conductivity of BSCF and SCF ceramics in air are presented in Fig. 4. The materials, prepared in present work, demonstrate similar absolute values and trends of the conductivity behavior with temperature and composition of A-sublattice if compared to the literature data [12,26,30]. Under oxidizing conditions, the total conductivity of BSCF and SCF at 973–1223 K decreases with reducing partial oxygen pressure, whilst the Seebeck coefficient has a positive sign and increases at $p(O_2)$ $> 10^3$ Pa (Fig. 5). This confirms that p-type electronic transport dominates under these conditions [12,26,30]. The Seebeck coefficient of BSCF passes through a maximum at $p(O_2) \sim 10^2–10^3$ Pa, for SCF the corresponding maximum is shifted to the lower oxygen partial pressure. The latter is characteristic for the start of transition from dominant p- to n-type regime. In the case of BSCF, having higher oxygen nonstoichiometry,
correspondingly, the transition occurs at higher oxygen partial pressures. The higher sensitivity of the Seebeck coefficient to different electronic transitions in mixed conductor, if compared to the total conductivity, accounts for the choice of this method for characterization of materials, prepared in present work. At 973–1223 K and oxygen partial pressures below 1–10 Pa the electrical properties become almost \( p(O_2) \) independent (Fig. 6). In the case of SCF such behavior is attributed to the formation of the ordered brownmillerite phase [28, 29], whilst for BSCF, for which perovskite–brownmillerite transition was not observed in the discussed conditions [28], this may be related to small changes of the oxygen nonstoichiometry under reduced oxygen partial pressures.

Table 1 lists the approximate stability boundaries for SCF and BSCF at reduced oxygen chemical potentials, evaluated from data on the total conductivity vs. \( p(O_2) \) dependencies, the literature data on strontium ferrite, cobalt and iron oxides is added for comparison [31–33]. The oxygen pressure corresponding to a dramatic conductivity drop caused by the phase decomposition was considered as stability limit at a given temperature (Fig. 7), in agreement with XRD. As expected, the decomposition of BSCF occurs at oxygen chemical potentials close to the CoO/Co boundary (Table 1). BSCF and SCF demonstrate similar values of low-\( p(O_2) \) stability at 1023–1223 K, suggesting the same mechanisms of decomposition, which, in the case of SCF, takes place via the formation of Ruddlesden–Popper \( \text{Sr}_{3n+1} \text{(Co,Fe)}_n \text{O}_{3n+2} \) phase and CoO [34].

3.2. Oxygen permeation-limiting factors for dense symmetric BSCF membranes

The permeation fluxes through symmetric BSCF ceramic membranes are higher than that for SCF, fabricated and studied in the same conditions (Fig. 8). The latter, again, agrees with the literature data, together with the obtained absolute values of \( j(O_2) \) [9, 13, 14, 16–18, 20]. The difference in oxygen permeation fluxes through BSCF and SCF membranes increases with temperature decrease [9, 11]. In combination with the data on oxygen nonstoichiometry, electrical conductivity and Seebeck coefficient it can be concluded that BSCF and SCF, prepared in present work using glycine–nitrate route, show the similar transport and electrical properties to those already described in the literature. Therefore, the effect of asymmetric configuration, studied in this work, can be considered as a general approach for improvement of the oxygen fluxes through BSCF membranes, not a consequence of a particular preparation method.

Fig. 9A and B presents the dependencies of the permeation fluxes on the oxygen partial pressure drop measured by Method 1 at 1123–1223 K for BSCF membranes having various thicknesses. At \( d \leq 1.00 \) mm the fluxes become almost thickness-independent,
Table 1
Low-oxygen phase stability boundaries of the selected cobalt- and iron-containing materials.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Low-oxygen phase stability boundary (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1223</td>
<td>4.7 × 10⁻⁷</td>
</tr>
<tr>
<td>1173</td>
<td>5.3 × 10⁻⁸</td>
</tr>
<tr>
<td>1223</td>
<td>4.4 × 10⁻⁸</td>
</tr>
<tr>
<td>1023</td>
<td>3.1 × 10⁻¹⁰</td>
</tr>
<tr>
<td>973</td>
<td>1.3 × 10⁻¹¹</td>
</tr>
<tr>
<td>973</td>
<td>6.5 × 10⁻¹¹</td>
</tr>
</tbody>
</table>

although ~1.7 increase in \(j(\text{O}_2)\) in similar conditions can be expected if decreasing the membrane thickness from 1.00 mm to 0.58 mm and considering bulk diffusion-limited behavior. The latter unambiguously shows that the permeation through BSCF dense symmetric membranes, fabricated using glycate–nitrare route, is limited predominantly by the surface exchange kinetics, when the thickness is smaller than 1.00 mm. The factors limiting the permeation process can be also analyzed in terms of specific oxygen permeability \(j(\text{O}_2)\) [35]:

\[
j(\text{O}_2) = j \times d \times \left[ \ln \left( \frac{p_2}{p_1} \right) \right]^{-1}
\]

where \(p_2\) and \(p_1\) are the oxygen partial pressures at the membrane feed and permeate sides, respectively. Since the quantity \(j(\text{O}_2)\) is proportional to \(j \times d\), the specific permeability should be independent on the membrane thickness if the surface limitations are negligible. According to Fig. 9C and D, the oxygen permeability of BSCF membranes depends on the thickness even in the range of 1.00–2.67 mm, decreasing with reducing \(d\). In combination with the thickness dependence of the oxygen permeation fluxes (Figs. 9A, 9B and 10) these observations indicate that the oxygen permeation process through BSCF membranes, fabricated in the present work, is limited by both oxygen bulk diffusion and surface reactions for \(d = 1.00–2.67\) mm. The difference between fluxes through membranes having different thicknesses at fixed oxygen partial pressure drop becomes larger at temperatures below 1123 K (Fig. 10), due to the fact that, typically, for perovskite-type oxides, and for BSCF, in particular, \(E_a\) for bulk diffusion is lower than that for the oxygen exchange [9,36–38]. Since the role of oxygen exchange kinetics increases when decreasing the membrane thickness, the latter also explains an increase in activation energy \((E_a)\) of the permeation flux for thinner (1.00 mm) membrane compared to the thicker one (2.67 mm) (Table 2). The obtained results are in agreement with literature data on oxygen permeation-limiting factors for the dense flat BSCF membranes [12–15]; an insignificant difference in the thickness range for predominant limitation by the surface exchange kinetics apparently relates to the different microstructure of the tested BSCF membranes.

The relative roles of the bulk ambipolar transport and surface exchange may be estimated decomposing the overall driving force.
Table 2
Activation energies for various parameters of oxygen transport through BSCF membranes.

<table>
<thead>
<tr>
<th>Parameter*</th>
<th>Membrane</th>
<th>( \frac{p_2}{p_1} ) (Pa)</th>
<th>T (K)</th>
<th>( E_a ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{(k_{ex}^f \times k_{ex}^p)}{(k_{ex}^f + k_{ex}^p)} )</td>
<td>No layers</td>
<td>21,223/8500</td>
<td>1073–1223</td>
<td>59.7 ± 0.6</td>
</tr>
<tr>
<td>( j )</td>
<td>No layers</td>
<td>21,223/8500</td>
<td>1073–1223</td>
<td>59.7 ± 0.6</td>
</tr>
<tr>
<td>( p )</td>
<td>No layers</td>
<td>21,223/8500</td>
<td>1073–1223</td>
<td>59.7 ± 0.6</td>
</tr>
<tr>
<td>( k_1 )</td>
<td>3L-170-100 OP – Method 1</td>
<td>21,223/13,400</td>
<td>1073–1223</td>
<td>59.7 ± 0.6</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>3L-170-100 OP – Method 2</td>
<td>973–1223</td>
<td>59.7 ± 0.6</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated by model: \( Y = (Y_0/T_0)exp(–E_a/RT) \).

expressed as \( \ln(p_2/p_1) \), into three contributions associated with membrane bulk and surfaces; a detailed description of the corresponding model can be found elsewhere [39]:

\[
\ln(p_2/p_1) = \frac{16\sigma_{amb}^2}{RT_{amb}^2} d + \left[ (k_{ex}^f)^{-1} + (k_{ex}^p)^{-1} \right]^{-1} \times (d + d_s) \tag{2}
\]

where \( \sigma_{amb} \) is the ambipolar conductivity, \( d_s \) is the critical thickness, \( k_{ex} \) is the exchange coefficient, and the superscripts \( f \) and \( p \) denote the feed- and permeate sides, respectively. Examples of fitting of the \( \ln(p_2/p_1) \) vs. \( d \) data at 1073 K and 1123 K, and obtained results are shown in Fig. 11. The slope of \( \log((k_{ex}^f \times k_{ex}^p)/(k_{ex}^f + k_{ex}^p)) \) vs. \( \log(p_2/p_1) \) is close to 1/4: various oxygen exchange mechanisms which may correspond to this value are described in [40]. In particular, for cathodic oxygen reaction the slope of the cathode resistance as a function of oxygen partial pressure close to 1/4 may indicate that atomic oxygen is involved in the rate determining step [41]. Whatever the mechanism of the oxygen exchange reaction, the surface exchange rate decreases with \( p(O_2) \), similar trend is typical for most perovskite-type mixed conductors under oxidizing conditions [5].

The activation energy of the surface exchange rate \( (k_{ex}^f \times k_{ex}^p)/(k_{ex}^f + k_{ex}^p) \), calculated from the thickness dependence of the oxygen permeation flux (Table 2), is close to that obtained using conductivity relaxation technique at 828–998 K (64 ± 12 kJ/mol) for BSCF, prepared via spray pyrolysis [27]. However, depending on the preparation route and measurement method, the literature data for \( E_a \) of the surface exchange vary in the wide range of 64–160 kJ/mol.

![Fig. 10. Oxygen permeation fluxes through dense BSCF ceramics membranes vs. reciprocal membrane thickness under fixed oxygen partial pressure gradient (Method 1).](image)

![Fig. 11. (A) Example illustrating the fitting of oxygen permeation data under fixed \( p(O_2) \) gradient; (B) dependence of \( k_{ex} \) on \( p(O_2) \) gradient; (C) temperature dependence of \( k_{ex} \) at fixed \( p(O_2) \) gradient.](image)
Table 3
Abbreviations and properties of gas-tight and porous BSCF ceramics.

<table>
<thead>
<tr>
<th>Sample abbreviation</th>
<th>Additives</th>
<th>Compaction pressure (MPa)</th>
<th>Shrinkage in thickness (%)</th>
<th>( \rho_{\text{exp}}/\rho_{\text{theor}} ) * (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-150</td>
<td>–</td>
<td>150</td>
<td>33.5</td>
<td>84.7</td>
</tr>
<tr>
<td>BD2-100</td>
<td>–</td>
<td>100</td>
<td>26.3</td>
<td>–</td>
</tr>
<tr>
<td>BD2-150</td>
<td>–</td>
<td>150</td>
<td>23.6</td>
<td>88.6</td>
</tr>
<tr>
<td>BD3-150</td>
<td>–</td>
<td>150</td>
<td>22.4</td>
<td>89.9</td>
</tr>
<tr>
<td>BD3-200</td>
<td>–</td>
<td>200</td>
<td>22.2</td>
<td>–</td>
</tr>
<tr>
<td>BD3-250</td>
<td>–</td>
<td>250</td>
<td>21.8</td>
<td>91.6</td>
</tr>
<tr>
<td>BD3-300</td>
<td>–</td>
<td>300</td>
<td>21.5</td>
<td>92.8</td>
</tr>
<tr>
<td>BD4-300</td>
<td>–</td>
<td>300</td>
<td>–</td>
<td>88.5</td>
</tr>
<tr>
<td>BDG35-150</td>
<td>35</td>
<td>150</td>
<td>–</td>
<td>34.0</td>
</tr>
<tr>
<td>BDG35-300</td>
<td>35</td>
<td>300</td>
<td>–</td>
<td>39.6</td>
</tr>
<tr>
<td>BDG27-300</td>
<td>27</td>
<td>175</td>
<td>29.3</td>
<td>–</td>
</tr>
<tr>
<td>BDG27-300</td>
<td>27</td>
<td>300</td>
<td>25.9</td>
<td>53.7</td>
</tr>
<tr>
<td>BDG20-300</td>
<td>20</td>
<td>300</td>
<td>23.1</td>
<td>60.0</td>
</tr>
<tr>
<td>BDG10-300</td>
<td>10</td>
<td>300</td>
<td>22.2</td>
<td>65.8</td>
</tr>
</tbody>
</table>

* Experimental density \( \rho_{\text{exp}} \) was measured by Archimedean method; theoretical density \( \rho_{\text{theor}} \) was calculated from the results of XRD analysis.

at 650–1173 K [27,38,42,43]. Apparently, in the case of BSCF the ceramics microstructure may have a significant effect on the surface exchange kinetics. At the same time, the values of the activation energy for oxygen permeation flux through dense symmetric BSCF membranes at various oxygen partial pressure gradients in the literature normally range from 25 to 50 kJ/mol [9,20,36,38,43,44] at 973–1223 K for 1.0–2.0 mm thick samples, in good agreement with the values, obtained in present work (Table 2). However, for thinner hollow fiber \( (d=0.25 \text{ mm}) \) and capillary \( (d=0.40 \text{ mm}) \) membranes noticeably higher activation energies of 80–120 kJ/mol at 1073–1223 K were also observed [45,46].

3.3. Processing of BSCF ceramics and fabrication of asymmetric membranes

After ball-milling BSCF powder showed unexpectedly poor compacting ability and, in order to facilitate compaction procedure, additions of various amounts of Degalan P24 as a binder \( (1–4 \text{ wt.\%}) \) were tested. The abbreviations and properties of BSCF ceramic samples, prepared from the powder containing Degalan P24, are listed in Table 3. Optimal concentration of the binder was found to be \( \sim 3 \text{ wt.\%} \). Increase of the compaction pressure and the amount of the binder in the range below \( \sim 3 \text{ wt.\%} \) resulted in lower shrinkage and higher density of BSCF ceramics. However, at pressures above 300 MPa a formation of large defects and cracks in green samples was observed, whatever the binder concentration. Therefore, in further fabrication of asymmetric BSCF membranes, the compaction pressure of 300 MPa was used.

According to the results, presented in Fig. 12, sintering time has almost no influence on the density of BSCF ceramics, maximum densification was observed after annealing at 1385–1395 K for \( \sim 5 \text{ h} \). Further increase in sintering temperature results in significant decrease of \( \rho_{\text{exp}} \), apparently due to the fast grain growth. So, since obtaining a perfect thin dense layer in the asymmetric membrane configuration is more difficult than optimizing the porosity and mechanical strength of support layer, the sintering conditions for porous BSCF ceramics were also selected to be 1385–1395 K for 5 h.

Table 4
Results of mercury intrusion porosimetry studies for porous BSCF ceramics.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average pore diameter (( \mu \text{m} ))</th>
<th>Open porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDG35-300</td>
<td>19.8</td>
<td>68.2</td>
</tr>
<tr>
<td>BDG27-300</td>
<td>4.2</td>
<td>49.2</td>
</tr>
<tr>
<td>BDG10-300</td>
<td>3.5</td>
<td>33.0</td>
</tr>
</tbody>
</table>
In order to provide an adequate porosity of supports, graphite was used as a pore-forming agent. Sintered porous BSCF ceramic samples were characterized separately to find an optimal amount of graphite to be used in fabrication of the thin porous layers in asymmetric configuration. The graphite content was varied in the range from 10 to 35 wt.% (Table 3), for facilitating of the compacting ability Degalan P24 binder (4 wt.%) was also added to the powder. As expected, the relative density of the ceramics decreases with addition of graphite (Fig. 2 and Table 3), the shrinkage of porous samples after sintering is relatively close to that of the dense membranes, indicating a good possibility to avoid delamination of the layers in asymmetric membrane structure. Variation in graphite content in green samples before sintering in the range from 10 to 35 wt.% allows the fabrication of BSCF ceramics with density from 34 to 60% of theoretical, calculated from the results of Archimedes method and XRD analysis.

The results of mercury intrusion porosimetry for the porous ceramics, fabricated from BSCF powder, containing 10–35 wt.% of graphite before compacting and sintering steps, are presented in Fig. 13 and Table 4. For all studied samples the dependence of weight normalized intrusion volume on pore size shows rather monomodal behavior, with average pore diameter varied from 3.5 to 19.8 μm. It is necessary to note that magnitude of the open porosity determined by mercury intrusion porosimetry (Table 4) is close to the \((1 - \rho_{\text{exp}}/\rho_{\text{theor}})\) value, calculated from Archimedes method and XRD results (Table 3). In fact, both methods refer to the determination of fraction of the total volume, in which fluid

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**Fig. 14.** Dependence of the nitrogen permeation flux through porous BSCF ceramic membranes on nitrogen inlet pressure \((p_{in})\) at 300 K.

**Fig. 15.** Optical micrographs of the typical indents on the ceramics surface after Vickers hardness tests: dense layer of 2L-170 membrane (A), BD-300 (B), BDG10-300 (C) and BDG27-300 (D).
flow is effectively taking place. However, the difference between these two methods increases with an increase in porosity above ~50%. Apparently, the latter indicates a formation of the complex pore structure with significant difference in saturation with water and mercury intrusion, or, most likely, a lower reproducibility of the porous structure during fabrication procedure in the case of high porosities. Though increasing graphite content up to 35 wt.% leads to a significant increase in open porosity, the rather insufficient mechanical strength limits the possibility of using such kind of porous supports in the asymmetric configuration. Apparently, this abrupt decrease in strength is associated with preferable formation of excessively large pores (Table 4 and Fig. 13) if compared with increasing the number of pores and their tortuosity. At the same time, the increase of graphite content in a green sample from

Fig. 16. Dependence of oxygen permeation fluxes through selected three-layer BSCF ceramic membranes on oxygen partial pressure gradient. The solid and dashed lines correspond to the fit using Eq. (2).

Fig. 17. Dependence of oxygen permeation fluxes through selected three-layer BSCF ceramics membranes on oxygen partial pressure gradient (Method 2).

Fig. 18. Dependence of oxygen permeation fluxes through selected three-layer BSCF ceramics membranes, modified with Ag and PrOₓ, on oxygen partial pressure gradient at 1223 K (A) and 1123 K (B) (Method 1). 10 to 27 wt.% leads to an insignificant increase of the average pore diameter (Table 4).

The results of nitrogen permeability tests of the porous ceramic membranes, fabricated from powder containing 10 and 27 wt.% of graphite, are shown in Fig. 14. Though the values, obtained for BDG10-300 membrane, are comparable to the oxygen permeation fluxes through BSCF membranes in operation conditions, further increase in the permeability of support is favorable in order to avoid gas diffusion limitations in the pores. At the same time, nitrogen flux through BDG27-300 is several orders of magnitude higher, providing additional space for diffusion of gas species as well as for the incorporation of surface activation species for further increase in performance. Thus, considering sufficient mechanical strength, porosity and the results of nitrogen permeability tests, the selected amount of graphite addition to obtain porous layers in asymmetric membrane configuration corresponds to ~27 wt%.

The flat three-layer asymmetric membranes were fabricated by a three-stage uni-axial compaction procedure. Calculated amount of BSCF powder, containing 4 wt.% of Degalan P24 and 27 wt.% of graphite, was placed into a mold and compacted at 100 MPa to form the thick porous support layer. Then a fixed amount of BSCF, containing 3 wt.% of the binder was added on the top of the first compact, flattened and compacted again at 100 MPa. In this way a green precursor for a thin dense layer was formed. At the final stage, in order to provide the formation of a second thin porous layer, a calculated amount of the powder similar to that in the first case was added into the mold, accurately flattened and the whole structure was then compacted at 300 MPa to form a three-layer asymmetric membrane. Thus prepared green membranes were sintered at 1393 K for 5 h, using heating/cooling rates as slow as 1–2 K/min, in order to suppress possible formation of micro-cracks and bending. After sintering, the thicknesses of the thick porous support, of the dense layer and of the thin porous layer were 1.05 mm (fixed), 170 μm (fixed) and 30–300 μm (varied), respectively. A SEM micro-
graph of three-layer asymmetric membrane with the 60 µm thick
thin porous layer is shown in Fig. 2F.

In order to assess the mechanical strength of asymmetric
membranes, including dense and porous BSCF layers, two-layer
asymmetric membranes were also fabricated by finalizing the
compaction procedure at 300 MPa on the second stage. Selected
three-layer membranes were activated by deposition of Ag and
PrO$_x$ into thin porous layers, the activation procedure was similar
to that described elsewhere [47]. Corresponding abbreviations of the asymmetric membranes fabricated in present work are listed in Table 5.

Micro-indentation tests of the dense BSCF ceramics and the surface of the dense layer of two-layer asymmetric membrane showed similar results, typical indents are presented in Fig. 15. Corresponding values of Vickers hardness vary in the range of 4.5–4.7 GPa, within the limits of experimental error. As expected, the mechanical strength of porous BSCF ceramics is significantly lower and decreases with an increase in porosity (Table 6). Thus, the selected approach allows to fabricate asymmetric membrane structures without creation of any noticeable stresses on the boundary between dense and porous layers.

3.4. Oxygen transport through asymmetric three-layer BSCF membranes

Comparison of the data on oxygen permeation fluxes through dense 1.00 mm thick symmetric BSCF and 3L-170-100 membranes, measured by Method 1, indicates that only a moderate improvement of the overall membrane performance was achieved by the implementation of asymmetric concept including three-layer structure (Figs. 9 and 16). For instance, the oxygen fluxes through 3L-170-100 membrane at 1173 K were only ~1.5–1.8 times higher than those for a 1.00 mm thick symmetric membrane, although one could expect a 5–6 times increase, if the surface limitations would be avoided. Apparently, the formation of three-layer membranes leads to an appearance of additional permeation-limiting factor, namely gas diffusion in the porous layers. In case of using Method 2, when a flowing Ar–O$_2$ mixture is supplied at the permeate-side surface, the oxygen fluxes drastically increase (Fig. 16). Since the feed-side surface of asymmetric membrane during measurement was exposed to a static air atmosphere in both methods, supplying sweep gas onto the permeate side leads to a faster oxygen removal from the pores, indicating that the oxygen transport through fabricated asymmetric membranes is essentially governed by the molecular oxygen diffusion in the pores of the thin layer on the permeate side.

Another confirmation of the critical role of the gaseous O$_2$ diffusion in pores as a transport-determining parameter arises from the linear dependence of the flux on $(p_2 - p_1)$ (Fig. 16). In this case, the oxygen flux may be expressed as:

$$j = k_1(p_2 - p_1) + k_2$$

where $k_1$ and $k_2$ are the constants. For a porous membrane, $k_1$ corresponds to the gas permeability [48], whereas $k_2$ accumulates experimental errors. For a multilayer membrane, the model is approximate, with the latter term accumulating deviations associated, in particular, with the presence of multiple parallel and serial steps affecting oxygen transfer. Nonetheless, this model shows a good agreement with data obtained for asymmetric three-layer BSCF membranes; corresponding linear regression parameters are listed in Table 7. The correlation is better for 3L-170-100 membrane, because of the absence of flushing of the porous layer at the permeate side with sweep gas and corresponding slower gas diffusion. Faster diffusion in the porous layer due to the sweep gas flow explains higher $k_1$ values obtained for 3L-170-30 membrane, characterized by Method 2. For the membranes, measured in similar experimental setup, the fluxes decrease with an increase of the thickness of the porous layer at permeate side (Fig. 17), again confirming a significant contribution of oxygen diffusion through porous layer to the total permeation rate.

The activation energies of the oxygen permeation flux through asymmetric membranes, measured by Method 1, vary in the range of 28–37 kJ/mol at 1023–1223 K and are noticeably lower than that for symmetric dense membranes (Table 2). Taking into account a moderate increase of the oxygen permeation rate due to implementation of the asymmetric concept, one can conclude that the presence of porous layers facilitates the oxygen surface exchange. However, the obtained $E_a$ values for the oxygen permeation through three-layer BSCF membranes are significantly higher than those characteristic for diffusion in gases, indicating that, besides O$_2$ diffusion in pores, other factors still play an important role as permeation-limiting steps. The latter assumption is in good agreement with an increase in activation energy up to 43 kJ/mol, observed for 3L-170–30 membrane, characterized by Method 2, which provides faster oxygen diffusion in pores (Table 2). It is interesting to note that the activation energies, calculated for $k_1$ of 3L-170–30 membrane, measured by Method 2, and $(k_{ex} \times k_{pa})/(k_{ex} + k_{pa})$ parameters are similar. Though the coincidence might be fortuitous, a possible explanation may include diffusion of an oxygen molecule to a reaction site on the surface as a slowest step of the surface exchange reaction.

The deposition of Ag and PrO$_x$ into thin porous layers of asymmetric membranes, fabricated in present work, mostly results in blocking of pores and corresponding decrease in the oxygen permeation fluxes (Fig. 18). Higher surface density of PrO$_x$ (Table 5) is responsible for the lower permeation rate through 3L-170-100–PrO$_x$ compared to 3L-170–60–Ag membrane. The activation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Microindentation place</th>
<th>Vickers hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2L-170</td>
<td>Surface of the dense layer</td>
<td>4.5 ± 0.6</td>
</tr>
<tr>
<td>BDG3-300</td>
<td>Surface</td>
<td>4.7 ± 0.6</td>
</tr>
<tr>
<td>BDG10-300</td>
<td>Surface</td>
<td>0.95 ± 0.09</td>
</tr>
<tr>
<td>BDG27-300</td>
<td>Surface</td>
<td>0.72 ± 0.05</td>
</tr>
</tbody>
</table>

Table 6
Results of Vickers hardness tests on dense and porous BSCF membranes.
Table 7
Parameters of the regression model (3) (95% confidence).

<table>
<thead>
<tr>
<th>Membrane/method</th>
<th>T (K)</th>
<th>$k_1 (10^{-12} \text{mol}/(\text{cm}^2 \times s \times Pa))$</th>
<th>$k_2 (10^{-12} \text{mol}/(\text{cm}^2 \times s))$</th>
<th>ρ</th>
</tr>
</thead>
<tbody>
<tr>
<td>3L-170-100</td>
<td>1223</td>
<td>$1.18 \pm 0.02$</td>
<td>$-0.18 \pm 0.13$</td>
<td>0.99996</td>
</tr>
<tr>
<td>Method 1</td>
<td>1173</td>
<td>$1.09 \pm 0.02$</td>
<td>$-0.17 \pm 0.16$</td>
<td>0.99993</td>
</tr>
<tr>
<td></td>
<td>1123</td>
<td>$1.00 \pm 0.03$</td>
<td>$-0.14 \pm 0.16$</td>
<td>0.99990</td>
</tr>
<tr>
<td></td>
<td>1073</td>
<td>$0.89 \pm 0.05$</td>
<td>$-0.14 \pm 0.26$</td>
<td>0.99885</td>
</tr>
<tr>
<td>3L-170-30</td>
<td>1223</td>
<td>$2.15 \pm 0.07$</td>
<td>$-0.91 \pm 1.1$</td>
<td>0.99895</td>
</tr>
<tr>
<td>Method 2</td>
<td>1123</td>
<td>$2.13 \pm 0.23$</td>
<td>$-12.0 \pm 3.6$</td>
<td>0.99834</td>
</tr>
<tr>
<td></td>
<td>1123</td>
<td>$1.70 \pm 0.12$</td>
<td>$-8.5 \pm 1.9$</td>
<td>0.99869</td>
</tr>
<tr>
<td></td>
<td>1073</td>
<td>$1.31 \pm 0.09$</td>
<td>$-5.5 \pm 1.4$</td>
<td>0.99885</td>
</tr>
<tr>
<td></td>
<td>1023</td>
<td>$1.00 \pm 0.06$</td>
<td>$-3.5 \pm 1.1$</td>
<td>0.99849</td>
</tr>
<tr>
<td></td>
<td>973</td>
<td>$0.73 \pm 0.04$</td>
<td>$-1.9 \pm 0.6$</td>
<td>0.99902</td>
</tr>
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</table>

4. Conclusions
The use of graphite as a pore-forming additive makes it possible to produce high-quality three-layer BSCF membranes by three-stage uniaxial compaction procedure. In tested asymmetric configuration the thicknesses of the thick porous support and the dense layer were fixed, whilst the thickness of the thin porous layer was varied from 30 to 300 μm. Comparison of the data on oxygen permeation fluxes through dense symmetric and three-layer membranes indicates that only a moderate improvement of the overall performance was achieved by the implementation of asymmetric concept. The activation energies of the oxygen permeation flux through asymmetric membranes, measured in the electrochemical cell without sweep gas flow, are noticeably lower than that for symmetric 1.00 mm thick dense membranes and vary in the range of 28–37 kJ/mol at 1023–1223 K. The formation of three-layer membranes leads to an appearance of important permeation-limiting factor, namely gas diffusion in the porous layers, however, other factors may also play an important role as permeation-limiting steps. Deposition of Ag and PrOx into thin porous layers of asymmetric membranes, fabricated in present work, mostly results in the blocking of pores and corresponding decrease in oxygen permeation fluxes. Further optimization of the porous layers is needed in order to accelerate gas diffusion and to provide a microstructure appropriate for the deposition of oxygen exchange catalysts.

Acknowledgements
This work was supported by the by the Belgian Federal Science Policy Foundation (FOD Science policy) and by the FCT, Portugal (Projects PTDC/CTM/64357/2006, SFRH/BD/45227/2008, SFRH/BPD/28913/2006 and SFRH/BPD/28629/2006). Experimental assistance of J.-P. Moreels, J.F.C. Cooymans, R. Kemps, W. Hendrix, M. Mertens, I. Thijs and W. Bouwen (VITO) is gratefully acknowledged.

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