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Citation for published version (APA):

Di Felice, L., Middelkoop, V., Anzoletti, V., Snijkers, F., van Sint Annaland, M., & Gallucci, F. (2016). New high temperature sealing technique and permeability data for hollow fiber BSCF perovskite membranes. *Chemical Engineering and Processing : Process Intensification*, 107, 206-219. <https://doi.org/10.1016/j.cep.2014.12.004>

DOI:

[10.1016/j.cep.2014.12.004](https://doi.org/10.1016/j.cep.2014.12.004)

Document status and date:

Published: 01/09/2016

Document Version:

Author's version before peer-review

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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New high temperature sealing technique and permeability data for hollow fiber BSCF perovskite membranes

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Abstract

Oxygen permeation through BSCF perovskite hollow fiber membranes has been investigated in a laboratory scale reactor in a temperature range of 850-1000 °C at atmospheric pressure. An experimental study was conducted with particular focus on a new sealing technique which was found to provide fully gas-tight conditions with a 100% success rate for the 6 membranes reported in this work (and for 15 membranes in total). An overview of experimental tests on other sealants proposed in the literature is given. A new method for checking the sealing is suggested that allows detecting the possible leakages in all the parts of the membrane module. A loose-end reactor with a shell-and-tube layout is presented which allows accurate measurements of both gas leakages (if any) and product gas composition in a wide range of operating conditions (flow rates on both the permeate and feed side, O₂ feed partial pressure, temperature). Permeation fluxes were studied for BSCF membranes with different thicknesses (0.2 and 0.5 mm) using He as sweep gas. The O₂ flux increased with both increasing the O₂ driving force (i.e. the O₂ partial pressure difference through the dense ceramic layer) and the reactor temperature. Long term tests (600 h) have been carried out proving the high stability of both the membranes used and the newly proposed sealing technique. The presence of both O₂ bulk diffusion and surface exchange resistance is suggested to limit the permeation rate of the ceramic hollow fibres for the range of wall thicknesses investigated. Finally, LSCF capillaries have also been successfully sealed allowing to extend the use of the proposed gas tight sealing system to different compositions of hollow fibers perovskite membranes.

Keywords: O₂ Membrane, Sealing procedure, O₂ flux measurement, Membrane Module design

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1. Introduction

Perovskite membranes – with their rich defect chemistry, characteristic oxygen vacancies and electronic conductivity dynamics – have been studied for more than 20 years in the field of oxygen separation, as recently reviewed in the literature [1]. Although not yet implemented at industrial scale, an area of great interest for perovskite membranes is their integration in membrane reactors for high temperature syngas production, such as in the catalytic partial oxidation and autothermal reforming (ATR) of methane [2–8]. Hollow fiber membranes in particular can ensure a high surface area per unit volume compared to other configurations (planar or tubular) and can be produced with a small wall thickness (typically 0.1–0.5 mm), enhancing oxygen transport rates. The high reaction temperature (800 – 1000 °C) of an ATR perovskite membrane reactor allows effective membrane oxygen transport without any additional energy requirement; moreover, the reducing atmosphere of the permeate compartment provides a large oxygen potential gradient increasing the oxygen flux through the membrane. A complex reaction system takes place in the partial oxidation network as reported by Enger *et al* [9], in which the temperature profile along the reactor length is clearly the critical parameter affecting the reactor performance because of the highly exothermic (e.g. combustion reactions) or endothermic (CH₄ steam reforming) nature of the involved reactions. As oxygen permeation is strongly temperature dependent, hot- (or cold-) spots formation can produce runaway effects and has to be avoided.

Despite the conceptual advantages due to the integration of reaction/separation and distributive oxygen feeding, the exploitation of perm-selective ceramic membranes for O₂ permeation is rather limited for a number of reasons. First of all, the problem of the high-temperature sealing between the membrane and the reactor module, which is of utmost importance to investigate the membrane permeability performance and to further carry out experimental tests of ATR using O₂ membranes in a safe and leak-free reactor. This aspect has been highlighted as an important improvement objective by recent reviews in the field [10–12] and as an essential step to allow for extensive commercial applications. However detailed discussion on this crucial aspect is often missing in the literature. Mostly, the

amount of leakage and the exact experimental procedure to measure and evaluate it are not well documented. The focus of this paper is thus to propose a new, simple and effective sealing procedure for high temperature gas-tight applications, which is needed for oxygen separation using perovskite membranes. Special emphasis will be given to the influence of both the selection of the laboratory-scale set-up configuration – a crucial aspect for the membrane to mechanically withstand thermal expansion and contraction – and the application of a leak-free sealing system, together with the implementation of a robust method for leakage detection. The new method for leakage detection allows to completely assess the presence for leakages in all the parts of the membrane module at the same time, thus it is suggested as a standard procedure for leak detection for O₂ selective membranes.

Characterization results and O₂ permeation experimental data through Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) will be reported. BSCF membranes have already been studied in literature and their stability under reaction conditions for syngas generation was pointed out in previous works [13][14][15]; this study shows that the sealing technique is reliable with high fluxes membranes under different conditions with pronounced chemical/thermal expansion and for long time. A study on membrane permeability as a function of key parameters such oxygen partial pressure and flow rate in the permeate and retentate, membrane thickness and reactor temperature is proposed in this paper in order to investigate the performance of O₂ transport through the membrane in a wide range of experimental conditions and up to 600 h operation at high temperature. The influence of key transport resistances (gas-solid mass transfer, bulk diffusion, and surface exchange) is preliminary discussed, although the derivation of flux permeation rate expressions is beyond the scope of this paper and will be investigated in a future work.

Finally, the gas-tight sealing technique proposed in this work will be applied to a La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) perovskite capillary in order to experimentally extend its viability to different perovskite compositions. In this way we proved our new sealing technique to high flux and low flux membranes, assessing the possibility to seal different types of membranes with the same procedure.

2. Experimental

2.1 Membrane preparation and characterisation

The gas-tight perovskite membranes used in this work were supplied by the Flemish Institute for Technological Research (VITO). The membranes were made in the form of capillaries (hollow fibres) from BSCF and LSCF mixed ionic-electronic conducting perovskite powders obtained from CerPoTech (Norway). The membranes were prepared using the spinning and phase inversion technique previously employed for the manufacture of both LSCF and BSCF perovskite membranes [16,17], but with an adjusted powder-polymer ratio of the spinning mixture. The geometry of membranes used is reported in Table 1; two different diameters and thicknesses of the BSCF membranes were obtained by changing the dimensions of the spinneret orifice.

The effects of the sealing method and high-temperature operation on the composition and structure of the membranes were investigated by using a combination of optical microscopy, electron-optical analytical and imaging techniques and X-ray diffraction (XRD). Cross-sectional images of the sealed samples were taken using a Zeiss SterEO Discovery.V12 microscope with 25x magnification. Element mapping was carried out using a JEOL JXA8530F in-lens Schottky Field Emission Gun Electron Probe Micro-Analyser (FEG-EPMA), with an operating voltage of 15 keV and a beam current of 10-30 nA and equipped with an energy dispersive spectrometer (EDS) and a wavelength-dispersive spectrometer (WDS). The former was used for point analysis to confirm elemental phases (not presented herein). The latter clearly resolves peak overlaps of neighbouring elements and was therefore used to quantitatively map constituent elements at locations of interest across the internal interfaces in the sample. XRD patterns of the crushed membrane samples were recorded with a Philips X'Pert diffractometer over a 2-theta range of 2–120° at a wavelength of 1.5405980 Å (Cu K-Alpha1 radiation).

2.2 Setup configuration

Mechanical resistance of hollow fibre perovskite membranes can be strongly affected by the selected reactor configuration, where free thermal expansion of the different materials is one of the main engineering aspects that have to be taken into account during the

module design process. Several configurations have been developed in this work as reported in Figure 1, Two fixed-ends configurations (Figure 1 A, B) – most commonly suggested in the literature – have been found to be inadequate causing membranes to break often during heat treatment, probably because of different thermal expansion of the perovskite material and the rest of the reactor module. The key to a suitable reactor layout is the presence of one loose-end (or finger-like configuration) which allows free longitudinal membrane thermal expansion/contraction during heating/cooling cycles (Figure 1C). In this case, the inlet gas is fed from the bottom of a 99.7% Al_2O_3 capillary (1 mm inner – 1.6 mm outer diameter, 500 mm length) placed inside an outer (co-axial) 99.7% Al_2O_3 tube (3 mm inner-6 mm outer diameter). At the end of this tube (about 400 mm long) the membrane is housed and in turn connected to an Al_2O_3 cap (3 mm inner-6 mm outer diameter, 15 mm length) at the other end. Both edges of the membranes are sealed following the procedure described in the next section. The fact that the reactor is loose at one end and that the inlet and outlet of the reactor are located at the bottom, are both key factors in accommodating the mechanical stress that is generated in the jointed sections during thermal cycling. This configuration has been further improved with a shell-and-tube configuration which consists of three coaxial tubes as shown in Figure 1D. An outer shell (stainless steel T-310, 25.4 mm outer, 21 mm inner diameter) was placed, in which air, N_2 and O_2 were (co)-fed in order to check the influence of O_2 partial pressure and flow rate on the feed side of the membrane.

The outlet gas composition from both the core (permeate) and the shell (retentate) side of the reactor were connected with a GMS815P analyser (SICK) equipped with a module OXOR-P for O_2 measurement and a module, THERMOR, to measure H_2 which was calibrated and used for helium detection. In each test N_2 or He – present at a fixed and known molar flow rate on the retentate and permeate side, respectively – provided a reference flow to evaluate the absolute yield of the reaction products. A Varian Micro GC CP-4900 was also connected to the set-up; it was equipped with a molsieve column ($\text{M5A}^{\text{H}}\text{BF}$, 10m) capable of detecting both O_2 and N_2 concentrations. Cross-checking both measurements with the analyser and the micro-GC gives a precise estimation of possible leakage and an exact measurement of oxygen permeation.

The final piping and instrumentation diagram for the set-up used in this work is shown in Figure 2. The setup allows for an easy change in flow direction enabling us to study both co-current and counter-current configurations.

2.3 The sealing system and procedure

Using the configuration shown in Figure 1D, the perovskite membrane was connected to Al_2O_3 (99.7%) tubes by a suitable high temperature gas-tight sealant. Although this is one of the main barriers limiting engineering and scale-up aspects of perovskite membrane reactors, detailed information on the performance of high temperature sealings are still rarely reported in the literature. It is well known that the seal should meet certain requirements such as good wettability, suitable viscosity and rigidity, chemical inertia and compatibility of the thermal expansion coefficient [18]. A number of seals have been proposed in the literature but the description of the choice of the material, the sealing application technique, performance, success rate and durability are often omitted.

Ceramic seals (Aremco Ceramabond) have been used [19] which resulted in leakage from the permeate to the shell (retentate) side of the packed-bed membrane reactor, affecting the final reactor performance. Other leakages (not well specified) were found when using another type of ceramic sealant (Sauereisen) [20].

Gold and silver pastes are often used because of their chemical inertness and durability at high temperature. O_2 leakages in the range of 2-5% [21–23] have been detected by using gold paste; an error of 10% is claimed due to leakage detection by other authors [24]. An impermeable gold coating layer of about 270 nm length has been applied on hollow fiber membranes to avoid the use of additional high temperature sealants [25].

Silver paste has been used by Wang *et al.* [26], which found a “small” (unspecified) leakage at high temperature, and by Leo *et al.* [27], who claim gas tightness verified by the absence of N_2 gas in the permeate. It is worth mentioning here that the absence of feed gas traces (N_2) on the permeate side does not (completely) prove gas-tightness conditions, as will be discussed later in this work. An oxygen purity of 99.96% has been found on the permeate side of the membrane reactor – by using a combined ceramic/silver sealing technique – in which the retentate (corresponding to the shell side of the membrane reactor) is at elevated pressure (10 bar) [28].

The use of glass sealants is limited by their known reactivity at high temperature; some authors presented ceramic-glass composites as high temperature seals for perovskite membranes [18] reporting leak-tight conditions; as will be shown, the proposed procedure

has been pursued in this work but the resulting sealing was not found to be gas-tight at our conditions.

These categories of sealants – glass, ceramic and noble metals, and some combinations of those – have been tested in this work as summarized in Table 2, which also reports the adopted curing procedures. Glass powders have been pre-mixed with ethanol to obtain a viscous paste with optimal wettability properties before use.

2.4 Leakage detection

An appropriate leak detection method is crucial to investigate the performance of a sealing system. A commonly adopted procedure is to measure the amount of N₂ at the permeate side, where only sweep (often He or Ar) and permeating oxygen should be present [29]. This allows for subtracting the contribution of the molecular oxygen flux caused by leakage, as commonly proposed [30,31]. However, if a set-up configuration such as the one presented in this work is used, the size of the leak detected by this method is intrinsically low because the permeate side is usually slightly over-pressurized relative to the retentate side – which in general is an outer shell or the open air at 1 bar. Therefore the main leak is expected to be in the opposite direction, namely from the permeate to the retentate, depending on the extent of pressure drop on the permeate side (and not only on the performance of the sealant itself). In any case, mass balances for both the retentate and the permeate side should be used to be able to assess the extent of leakage.

In this work, leaks were monitored on both sides of the membrane by measuring both the amount of nitrogen on the permeate side (by GC analysis) and the amount of helium on the retentate side (THERMOR analysis), with an accuracy of 0.1% in the flow. These values were also cross-checked with both the flow rate measurements in the retentate and permeate.

3. Results and discussion

3.1 Sealant selection

Among the different sealing options reported in the literature, ceramic (Aremco Ceramabond 503, Cotronics 940 HT), glass (Schott 8252) and noble metals (MaTeCK gold conducting paste #902904) have been tested in this work, as reported in Table 2 together with the adopted curing procedures.

Figure 3A shows a LSCF perovskite membrane sealed with the ceramic Aremco Ceramabond; the membrane does not show any evident cracks, while small bubbles can be observed in the sealing supporting the hypothesis that the ceramic sealant is (slightly) porous. A leak has been detected when both ceramic sealants were used; as expected and explained above, the leakage from the permeate to the retentate has been found to be more significant (10-30% of the permeate flow rate) than the amount of nitrogen measured in the permeate (often below 5%). It is worth mentioning that this level of leakage is also obtained when the ceramic sealant is used to connect impermeable ceramic tubes.

The SCHOTT 8252 option has been found to be gas-tight when sealing two different Al_2O_3 tubes; however, this system failed to be leak-free when a hollow fibre membrane was connected instead of an Al_2O_3 tube. An optical microscopy image of a SCHOTT 8252 sealed membrane is provided in Figure 3B, showing transverse crack lines in the membrane wall. As reported in the literature, this can be due to chemical interaction between glass and perovskite [18] or to differences in thermal expansion. It is also likely that some of the cracks may be associated with the specimen preparation for further analyses by EPMA.

Different combinations of glass sealing-membrane powder- NaAlO_2 physically mixed were tested in this work as suggested by Qi *et al.* [18] adding up to 70 wt% of LSCF or BSCF powders (from Treibacher Industrie AG), glass-ceramic mixtures were used as an attempt to overcome the problem of chemical interaction and different thermal expansion coefficients at the interface between the glass sealant and the membrane. An overview of those combinations is also shown in Table 2; however the resulting sealing was found to fail in gas-tightness tests under our experimental conditions.

A different technique was studied in this work to avoid chemical interaction between the glass sealant and the perovskite membrane. A (thin) layer of an inert material (gold paste), 20 mm in length and with a thickness of 0.02-0.04 mm, was applied to both membrane edges – aimed at protecting the membrane surface from reaction. This has been dried 1 h at room temperature and then placed in an oven for the curing procedure (heating up to 1000 °C at a rate of 2 °C/min, 1 h dwell, then cooling down to room temperature at the same rate, see Figure 4 for an image of the coated membranes with different length). The second step of the sealing procedure consisted of applying the glass seal (SCHOTT 8252) on top of the gold paste, thereby bonding the membrane into the alumina tubes until the final cure

and strength of the joint was obtained by heating the sample to 1020 °C at a rate of 2 °C/min, holding for 1 h dwell and cooling it down to the desired operating temperature.

Optical microscope images of this sealing system are shown in Figure 5 in which the LSCF membrane was used. The gold layer has been found to successfully protect the perovskite capillary. This was also confirmed by EPMA mapping (Figure 6) of the interfaces between the components in the joint (alumina, sealant, gold, membrane) where no diffusion or local chemical inhomogeneity was found. Although Figure 6 shows cracks through the membrane wall the gold coating provided a uniform layer which ensured the gas-tightness of the system.

Subsequent permeation measurements were performed by making use of this sealing technique; additionally, all the membranes sealed with this procedure in this work (6 in total, 3 LSCF and 3 BSCF) were successfully sealed and tested making the success rate of this procedure 100%.

For both the BSCF_1 and BSCF_2 samples, elemental information obtained from the SEM/WDS analyses of the interfacial regions between the membrane and the sealant shows no migration/diffusion of elements (Figure 7) except at the places where the gold coating is unintentionally scraped off (as can be seen in the close-up shown in Figure 7B). The XRD patterns (Figure 8) confirmed a cubic perovskite structure for both post operation samples, BSCF_1 and BSCF_2 corresponding to a phase pure pre-operation sample (an unused membrane) with evidence of phases such as cobalt oxide, tricobalt tetraoxide and strontium carbon oxide (outside the sealed zone of the membrane).

3.2 Permeability tests

Oxygen permeation data were collected while continuously monitoring sealing performance through leakages detection; the obtained (leak free) results are presented below.

3.2.1 BSCF membranes

A first batch of permeability tests was carried out at $850 < T < 1000$ °C for the membrane BSCF_1 (see Table 1), in which the He flow rate in the sweep side was varied from 50 to 350 Sml/min in order to investigate the influence of the O₂ partial pressure in the permeate side; the air flow rate in the shell was kept constant at 500 Sml/min. After about 40 h, the system was still fully gas-tight and was then cooled down with a ramp of 2 °C/min. Once at room

temperature, a new leak test was carried out and leakages were found on both edges of the membrane at the interface between the glass and the gold – suggesting that thermal expansion can play a role when wide temperature ramps are performed. It is worth mentioning here that this has not been considered as a major issue because: 1) the membranes never broke during these heating cycles; 2) by simply re-applying a layer of glass sealant on top of the previous layer and re-curing following the same procedure previously described, the system recovered gas-tightness properties. A second run of 30 h was therefore carried out with the same membrane. Although this procedure is suitable for lab-scale tests, further investigation on sealing development is necessary to bring such a sealing to a commercial application.

The obtained O_2 permeation fluxes as a function of the He flow rate at different temperatures for the membrane BSCF_1 are shown in Figure 9. It is evident that the O_2 permeation rate increases with increasing temperature – according to the Wagner theory [1] – and with increasing the sweep flow rate as an effect of decreased oxygen pressure at the permeate side. It should also be considered that gas phase polarization is reduced when the gas volume streams are increased. The maximum permeation rate obtained (1000 °C and 350 Sml/min He) has been found to be 5.7 Sml/min, which is relatively high compared to other membrane compositions as reported in literature [1,32].

Additional tests were carried out with the same membrane under experimental conditions, where 1) the permeate (tube side) was pressurized to check for He leakages to the retentate (shell side) at more severe conditions; 2) the air flow rate in the feed was varied to investigate the effect of O_2 mass transfer limitations in the shell side and 3) different N_2/O_2 mixtures were used – instead of air – to investigate the influence of the O_2 partial pressure on the permeation rate. Results are shown in Figure 10A-B-C respectively; no He is detected in the retentate side of the membrane proving that the sealing system keeps gas-tightness operation even at moderate pressures.

Longer tests were carried out for the membrane BSCF_2 (effective length equivalent to BSCF_1), which was operated for more than 600 h before the test was stopped while the membrane exhibited the same permselectivity and permeation flux, and the sealing still was found to be gas tight. Stability and permeation tests have been carried out over a wider range of experimental conditions for this membrane, where the He sweep flow rate was varied from 50 to 700 Sml/min and the air flow rate from 500 to 2100 Sml/min. The gas-

tightness of the sealing system was continuously monitored and no leaks were found in this broad range of investigated operating conditions.

The detected O_2 flow rate in the permeate side at the same operating conditions (100 Sml/min He, 500 Sml/min air, 950 °C) at different times of the experiment is plotted in Figure 11, for the sake of comparison together with the temperature to which the membrane was exposed in the experiments. An initial activation time of about 50 h is observed at the beginning of the test, before a steady state is reached; this increasing behaviour may be related to the self-adjustment of crystal lattice under permeation conditions [33]. A slightly lower O_2 permeation is found in the range 100-150, 300-320 and 490-510 h, i.e. after a step at low temperature ($T < 900^\circ\text{C}$), but a time step of 2-3 h at 1000 °C allows the membrane to reactivate as shown at 150-170 h and 330-340 h. A temperature dependency of O_2 permeation has been observed by other authors when Ba-based perovskite membranes were used, which can be ascribed to carbonates formation (due to CO_2 impurities in the feed/sweep gases even at ppm levels) or to phase transitions and surface segregation [5,34].

Gas-solid mass transfer limitations in the retentate can affect permeation results, as shown in Figure 12 where permeation curves are reported for the different air flow rates of 450 and 2000 Sml/min; as a matter of fact, for operating conditions most prone to be influenced by bulk-to-wall mass transfer (i.e. $T=1000^\circ\text{C}$ and $He=700$ Sml/min, where the highest oxygen fluxes were measured) no significant changes in the permeation fluxes were observed only at air flow rates above 1500 Sml/min.

The results for the O_2 permeation rate as a function of the sweep flow rate and temperature obtained with the BSCF_2 membrane are summarized in Figure 13A – analogous to Figure 9 for BSCF_1 – and B, where the permeation rate shown as a function of the temperature instead of sweep flow rate. The observed constant slope in the Arrhenius plot (Figure 14) indicates that a single activation energy can be used to describe the temperature dependency of the oxygen permeation rate over the entire large investigated temperature range at different helium flow rates (i.e., O_2 partial pressure in the permeate side), as also observed by other researchers with a BCFZ membrane [35].

When compared to the permeation rates of the thinner BSCF_1 membrane, the decrease in the oxygen flux for BSCF_2 is not linearly proportional to the increase in membrane thickness (Figure 15), as the Wagner theory would predict assuming that O_2 bulk diffusion is

the only rate limiting step. As a consequence, it is suggested that both bulk diffusion and surface exchange kinetics contribute to limit the O₂ permeation rate within the investigated experimental conditions for a ceramic hollow fibre membrane with a thickness of 0.2 – 0.5 mm. This is in agreement with the work by Schiestel *et al.* [23] with slightly thinner membrane walls (0.175 mm), while bulk diffusion was found to be the rate limiting step when thicker membranes were used [36][37][38]

3.2.2 LSCF membranes

A last batch of combined sealing technique resistance – permeability tests was carried out for the membrane LSCF_1 at $850 < T < 950$ °C, where the He flow rate in the sweep side and the air flow rate in the retentate side have been kept constant at 100 Sml/min and 500 Sml/min, respectively, see Figure 16. Due to the low O₂ permeation rate detected, no effects have been found varying the air flow rate in the range 300-700 Sml/min. A leak test was again carried out by increasing the total pressure in the (He) sweep side up to 1.3 bars by verifying that the helium concentration in the retentate (shell) was below the detection limits of the THERMOR analyzer, confirming the consistency of the proposed sealing technique. An evident activation is observed at 950°C, where the O₂ flux increases disproportionately compared to the trend observed at lower temperature; however, due to the low permeation rates obtained with this membrane composition – in agreement with literature data [36] – this membrane composition has not been further investigated, although its deployment allowed to extend the use of the proposed gas tight sealing system to different families of hollow fibers perovskite membranes.

4. Conclusions

Although a number of works have been published on perovskite dense membranes for O₂ separation, few of them are focused on crucial engineering aspects such as the choice of the reactor configuration and the selection of the sealing, as addressed in this work. Moreover, most of the sealings proposed in the literature are not gas-tight, as discussed in this paper.

Both the set-up configuration and the sealing have been optimized in order to test BSCF and LSCF hollow fibre perovskite membranes for oxygen separation. A shell-and-tube reactor with a finger-like membrane arrangement is proposed, which allows free thermal expansion of the membrane; with this layout, membranes can withstand thermal cycles in

the range 20-1000°C. A new sealing technique consisting of an inert gold layer applied between the membrane and the glass sealant is developed and it is shown that this produces gas-tight conditions for over 600 h; during this time period, leakages have been continuously monitored and found to be absent in both the shell and the tube side of the membrane.

The BSCF hollow fiber perovskite membranes showed higher permeation rates and have been tested for different thicknesses over a wide range of experimental conditions; both surface exchange and bulk diffusion were supposed to be rate limiting for the adopted membrane thickness range of 0.2-0.5 mm. A quantitative description of the O₂ flux permeation rate will be developed in a future work and the results will be used for the development of an ATR reactor using O₂ selective membranes for integrated air separation.

Acknowledgements

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° NMP3-LA-2011-262840 (DEMCAMER project). The technical support of Joris Garenfield is gratefully acknowledged. The authors gratefully acknowledge the Hercules Foundation (project ZW09-09) for providing access to the FEG-EPMA at MTM-KU Leuven

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Table 1: Composition, nomenclature, size and thickness of membranes used

Composition	Name	Length (mm)	Outer diameter (mm)	Thickness (mm)
$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$	BSCF_1	110	2.7	0.2
	BSCF_2	100	3.5	0.5
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$	LSCF_1	50	2.7	0.2

Table 2: Properties, curing procedures and adopted combination of sealants

Brand/Item	Type	Features			Curing procedure
Schott 8252	Glass powder	+ high temperature + gas tight - reactive			2°C/min to 1020°C, 1h dwell
Aremco Ceramabond 503	Ceramic paste	- not gas tight			90°C, 260°C, 370°C for 1h each (dwell)
Cotronics 940HT		- not gas tight			90°C for 15min (dwell)
MaTeck #902904	Gold paste	+ Inert + high melting temperature (1065 °C)			2°C/min to 1000°C, 1h dwell
Combination	Mixing method	Proportions of the sealants used			
Aremco Ceramabond 503	Physical mix	30	50	70	2°C/min to 1100°C, 1h dwell
Schott 8252		70	50	30	
Glass	Physical mix	30	50	70	2°C/min to 1100°C, 1h dwell
Membrane powder		70	50	30	
NaAlO_2		0	0	0	
Schott 8252	1)Coating of gold paste	About 0.2 g of gold per membrane			1) 2°C/min to 1020°C, 1h dwell
MaTeck #902904	2) application of glass seal				2) 2°C/min to 1000°C, 1h dwell

Figure 1: Setup configurations investigated throughout this work: horizontal and vertical two fixed-ends configuration (A, B), one loose-end (C), one loose-end with an external shell (D).

Figure 2: P&ID of the setup

Figure 3: Optical micrographs of the cross sections of perovskite membranes sealed with
 A) Aremco Ceramabond and B) SCHOTT glass sealant 8252; 1: Al₂O₃ tubes, 2: Aremco seal, 3:
 membrane wall, 4: glass seal 8252

Figure 4: gold coated BSCF hollow fiber membranes of different lengths

Figure 5: Optical micrographs of the cross sections of perovskite membranes sealed with gold coating + SCHOTT glass sealant 8252; 1: Al_2O_3 tubes, 2: glass seal 8252; 3: membrane wall, 4: MaTeck gold coating

Figure 6: Post-operation WDS elemental maps acquired at the representative locations in a glass-sealed gold-coated LSCF membrane, 1) Al_2O_3 tube, 2) glass seal (Ca, Si, Mg, O), 3) gold layer and 4) membrane wall (La, Sr, Co, Fe, O). Scale bar for all images is 100 μm .

A

Figure 7: Post-operation optical microscopy image (top left), SEM micrograph (top right) and WDS mapping (bottom) acquired at the representative interface regions of a glass-sealed gold-coated BSCF_1 (A) and BSCF_2 (B) membranes, showing the elemental distribution of 1) Al₂O₃ tube, 2) glass seal (Ca, Si, Mg, O), 3) gold layer and 4) membrane wall (Ba, Sr, Co, Fe, O). Scale bar for WDS images in (A) 50 μ m, in (B) 100 μ m.

Figure 8: Pre- and post-operation XRD patterns of BSCF membranes showing a cubic perovskite structure. Low intensity peaks in the post-operation samples are assigned to cobalt oxide, tricobalt tetraoxide and strontium carbon oxide phases (compare all the peak positions in the peak list). The XRD patterns are shown here split in two 2-theta ranges, 20-60° (top) and 60-80° (bottom).

Figure 9: Permeation fluxes as a function of helium flow rates for a BSCF hollow fiber membrane with 0.2 mm thickness (BSCF_1) and 62 mm effective (non-coated) length.

Figure 10: Influence of gas overpressure in the permeate (A), oxygen content in the retentate (B) and air flow rate in the retentate (C) on oxygen permeation flux (J_{O_2}) for a BSCF hollow fiber membrane with 0.2 mm thickness (BSCF_1). Conditions: He = 100 ml/min, $T = 900^\circ\text{C}$, membrane BSCF_1

Figure 11: Permeating O_2 flow rate in the outlet of the BSCF perovskite membrane reactor with 0.5 mm thickness (BSCF_2), permeate side. He flow: 100 Sml/min, Air flow = 500 Sml/min

Figure 12: Permeation fluxes for a BSCF hollow fiber membrane with 0.5 mm thickness

(BSCF_2) as a function of helium flow rates for two different air flow rates: (•) 450 Sml/min, (▪) 2000 Sml/min, $T = 950^{\circ}\text{C}$.

Figure 13: Permeation fluxes for a BSCF hollow fiber membrane with 0.5 mm thickness (BSCF_2) as a function of helium flow rates (A) and temperature (B)

Figure 14: Arrhenius plot for a BSCF hollow fiber membrane with 0.5 mm thickness (BSCF_2), air flow (retentate) 2000 Sml/min

Figure 15: O₂ permeation flux for BSCF hollow fiber membrane with different thicknesses: •: 0.2 mm (BSCF_1), ▣: 0.5 mm (BSCF_2), T= 850 °C (A), 925 °C (B) and 950 °C (C)

Figure 16: Permeation data of LSCF_1 membrane, He flow 100 ml/min, as a function of temperature