Performance of functional perovskite membranes for oxygen production

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Abstract
In this paper, the influence of composition, thickness, porous activation layers, and measurement conditions on the oxygen permeation rates of mixed ion electron conducting membranes is discussed. To this end, functional membranes, rather than pressed pellets, with an effective surface area of ~18 cm$^2$ and a thickness of ~200 µm with the compositions SrCo$_{0.8}$Fe$_{0.2}$O$_{3-δ}$, Sr$_{0.5}$Ba$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$, Sr$_{0.8}$La$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$, Ba$_{0.8}$La$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$, and Sr$_{0.4}$La$_{0.6}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ have been prepared and tested. The highest oxygen fluxes measured for the former two compounds under non-reducing conditions were ~13 Nml·cm$^{-2}$·min$^{-1}$. The coefficient of thermal expansion (CTE) was shown to be strongly dependent on the atmosphere. In a helium atmosphere, SrCo$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ and Sr$_{0.8}$La$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ show a negative CTE over a limited temperature range due to the phase transition from a brownmillerite to a perovskite phase. Membrane degradation due to kinetic demixing is an important issue in the long-term stability of Sr$_{0.5}$Ba$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$.

Keywords
Perovskite oxides, ceramic membranes, oxygen permeation, activation layer, coefficient of thermal expansion.
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1. Introduction

Dense ceramic materials exhibiting mixed ionic electronic conductivity can be used as a membrane material for the production of oxygen of very high purity and in partial oxidation reactions of hydrocarbons in membrane reactors. Such membrane systems hold the promise of being energy efficient in comparison with conventional technologies in both fields. Currently, the most promising membrane material for the production of oxygen is the family of perovskites with general formula ABO$_{3-\delta}$, where A is a mixture of alkaline and rare earth metals and B is a mixture of Co and Fe. The interest in the ionic and electronic conductivity of this family of compounds has grown since the publication of Teraoka in 1985 [1]. In a feasibility study Bredesen [2] has determined that for a commercially viable process a minimum oxygen flux of 10 Nml·cm$^{-2}$·min$^{-1}$ is required. To our best knowledge such a value has not been reported in the open literature as yet.

If the bulk transport through the membrane is the rate-determining step, the oxygen flux, $J$, is governed by the Wagner relation [3,4]:

$$J = \frac{RT \sigma_e \sigma_i}{16F^2(\sigma_e + \sigma_i)L} \ln \left( \frac{P_h}{P_l} \right)$$  \hspace{1cm} [1]

with: $R$ the gas constant, $T$ the temperature, $\sigma_e$ and $\sigma_i$ the electronic and ionic conductivities respectively, $F$ the Faraday constant, $L$ the thickness of the membrane, $p_h$ and $p_l$ the partial oxygen pressures on the feed and permeate sides, respectively. The validity of this relation is limited, as it does not take into account the dependencies of the conductivities on temperature and partial oxygen pressures in an explicit way. From the published data a clear trend can be observed between the membrane composition and the oxygen permeability. The perovskites ABO$_{3-\delta}$ with the highest oxygen permeability are those where the A-cation is an alkaline earth metal with a small amount of lanthanum allowed and where the B-cation is cobalt with about 20% iron. We have therefore selected the compounds SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ [1,5,6], Sr$_{0.5}$Ba$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ [7], Sr$_{0.5}$La$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ [8], and Ba$_{0.8}$La$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ [9]. These compounds will be compared with the more extensively studied compound Sr$_{0.4}$La$_{0.6}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ [10-12]. The influence of the temperature, the membrane thickness, and the oxygen partial pressure on the feed side on oxygen flux will be studied using 200 µm thick dense membranes and 6 µm thick dense layers on 200 µm thick porous supports.

If the surface reactions are rate determining, the oxygen flux is usually described by the following relation [13]:

$$J = c_i k \left( \sqrt{\frac{p_h}{p_0}} - \sqrt{\frac{p_l}{p_0}} \right)$$  \hspace{1cm} [2]

where $c_i$ is the oxide ion density and $k$ the surface exchange coefficient, and $p_0$ is standard pressure. The reader is referred to ref [14] for an in-depth theoretical treatment of the surface kinetics and the resulting flux relations. Deng [15] has shown, on a theoretical basis, that the oxygen flux can be enhanced by the application of porous activation layers on either side of the membrane. Lee et al. [5] have confirmed this experimentally using ~1 mm thick SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ discs. Here, 200 µm thick dense Sr$_{0.4}$La$_{0.6}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ membranes with 10 µm thick porous activation layers on the feed and/or permeate side will be compared with a similar membrane without activation layers.
For building a membrane reactor, the oxygen fluxes are not the only parameter that determine success. As mentioned before, thin membranes are supported on a thicker porous support. Depending on the strength required this might be the same or a completely different material. Also, the ceramic membranes have to be connected to a module, manifolding etc. which consists most likely of steel. Further the membrane has to withstand start up and shut down procedures. In all these instances the coefficient of thermal expansion (CTE) is one of the key parameters. In the optimal case the CTE of a certain composition should be constant with temperature and gas atmosphere, and comparable to that of the construction materials, e.g. steel. Dilatometry was used to study the dependency of the CTE on temperature, composition and atmosphere.

Further, we present pre- and post-test Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analyses to study the porosity and the changes in surface morphology and composition of the tested membranes.
2. Experimental

The perovskite powders with composition SrCo$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (SCF), Sr$_{0.5}$Ba$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (SBCF), Sr$_{0.4}$La$_{0.6}$Co$_{0.2}$Fe$_{0.2}$O$_{3-δ}$ (SLCF), Ba$_{0.8}$La$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (BLCF), and Sr$_{0.8}$La$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (SLC2F) were purchased from Praxair Specialty Products. Dense membranes of ~200 µm thick were prepared by tape casting the perovskite in a polyvinyl butyral (PVB) binder system, with ethanol and toluene as solvents. These “green” tapes were sintered between 1300 and 1425 K for 1 to 8 h. Thin, ~10 µm, activation layers of SLC2F were prepared by screen printing a paste of the perovskite and ethyl cellulose on a sintered tape, followed by a sinter step at 1375 K for 1 h. Porous SLC2F supports were prepared analogous to the dense membranes, with carbon added to provide the porosity. A thin, ~6 µm, dense top layer was screen printed on the “green” porous support, followed by co-sintering at 1375 K. Qualitative information on the presence of continuous porosity in calcined supports or membranes was obtained by testing with ethanol. The sample was placed on a bed of filtration paper that was drenched with ethanol. The appearance of ethanol on the topside was taken as a sign for the presence of continuous porosity. Further information on the porosity and the surface morphology was obtained by pre- and post-test analyses of the membrane surfaces and cross section by means of scanning electron microscopy using a Jeol 6330F SEM equipped with a Noran Voyager EDX. The EDX data were collected to obtain a qualitative view of possible fluctuations in the composition.

X-ray diffraction patterns (XRD) were collected on a Bruker D8 Advance equipped with a Sol-X energy dispersive detector operating in Bragg-Brentano geometry in the angular range \(10° \leq 2\theta \leq 100°\) with a step size of 0.01 °2θ. XRD patterns were analysed by the Rietveld method [16], as implemented in the GSAS program suite [17]. The cell parameter, peak width and density are the most important results for this part.

The CTE of the compounds were measured under a gentle flow of helium with a pO$_2$ of ~$10^{-5}$ bar. The first set of measurements was performed using a Netzsch Dilatometer 402C, in the temperature range \(300 \leq T/K \leq 1275\). To study the influence of the pO$_2$, the CTE of SCF was also measured on a Netzsch Dilatometer 402E in He and stagnant air. In all cases, dense rods were successively heated and cooled three times at 5 K·min$^{-1}$. The data collected on heating and cooling during the second and third run were overlying.

The oxygen fluxes through the membranes were determined using an in-house developed measurement set up in the temperature range \(975 \leq T/K \leq 1275\) [12]. The dimensions of the used membranes were ~5 x 5 cm$^2$. The feed gas consisted of a mixture of O$_2$/N$_2$ with an oxygen partial pressure, pO$_2$(feed), of 0.10, 0.21, 0.50, or 1.00 bar and a flow rate of 500 NmL·min$^{-1}$. A flow of 600 NmL·min$^{-1}$ of helium was used as a sweep gas. These flows were required to accommodate the highest production rate of oxygen observed in the current investigations (> 200 ml/min). The feed and permeate flows were counter current. Gold is used as sealant between the membrane and the Al$_2$O$_3$ housing. The seal was airtight after heating at 1275 K. The oxygen fluxes were measured starting from the highest temperature at constant pO$_2$(feed), starting at 0.21 bar, subsequently at 0.50 and 1.00 bar and finally at 0.10 bar and calculated from the oxygen content in the permeate stream, which was measured with a gas chromatograph (Perkin Elmer AutoSystem XL). The oxygen fluxes were corrected for leakage, which was in all cases less than 5%. A typical on stream time of a membrane was about three weeks. The influence of time on the oxygen fluxes [6,18] was not taken into account during the current experiments.

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3. Results

Flat self-supporting functional membranes with dimensions of ~5 x 5 cm² and a thickness of ~200 µm were prepared. The relative densities of these dense membranes are given in Table 3.1. Ethanol tests and SEM micrographs of cross sections of the membranes showed the presence of closed porosity but no continuous porosity was observed in the dense membranes. A SEM micrograph of the cross-section of the SLC2F membrane with porous activation layers on both the feed and permeate sides is given in Figure 3.1a. The two porous (~35%) activation layers are clearly visible in the main figure and the closed porosity in the dense part is visible in the inset. Figure 3.1b shows a ~6µm thick SLC2F membrane on a ~200 µm thick porous support that has a density of ~88%. Ethanol tests showed that the porosity of the support was continuous.

Table 3.1: The cell parameter (a), the cell volume (V), the X-ray density (Dₓ), the full width at halve maximum (FWHM) of the (110) reflection of the various perovskites tested in this study, and the relative density of the gastight membranes (D₉₁%

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>V (Å³)</th>
<th>Dₓ (g/cm³)</th>
<th>FWHM (110) °2θ</th>
<th>D₉₁ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCo₀.8Fe₀.2O₃₋δ</td>
<td>3.86889(2)</td>
<td>57.911(1)</td>
<td>5.56</td>
<td>0.06</td>
<td>94.2</td>
</tr>
<tr>
<td>Sr₀.5Ba₀.5Co₀.8Fe₀.2O₃₋δ</td>
<td>3.98808(3)</td>
<td>63.429(1)</td>
<td>5.73</td>
<td>0.07</td>
<td>89.7</td>
</tr>
<tr>
<td>Sr₀.8La₀.2Co₀.8Fe₀.2O₃₋δ</td>
<td>3.84310(3)</td>
<td>56.760(1)</td>
<td>5.97</td>
<td>0.06</td>
<td>97.9</td>
</tr>
<tr>
<td>Ba₀.8La₀.2Co₀.8Fe₀.2O₃₋δ</td>
<td>3.99289(5)</td>
<td>63.659(2)</td>
<td>6.36</td>
<td>0.13</td>
<td>91.3</td>
</tr>
</tbody>
</table>

Analyses of the X-ray diffraction patterns after calcinations proved that all compositions are single phase and adopt the cubic perovskite structure with space group Pm-3m. Table 3.1 shows the results of the Rietveld refinements. The compound SLC2F was used as a well-known reference compound [10-12] and was therefore not characterized in detail. The values for the lattice parameters are in agreement with those previously reported [4,6,19]. The full width at half maximum (FWHM) of the (110) reflection located at ~32 °2θ, was close to the instrumental resolution (~0.05 °2θ). Only BLCF showed a significantly broadened peak.

The CTE for the four compounds in flowing helium, pO₂ ~ 10⁻⁵ bar, are presented in Figure 3.2a. The barium containing compounds have a more or less constant value of ~17 x 10⁻⁶ K⁻¹ (BLCF) and ~18 x 10⁻⁶ K⁻¹ (SBCF) and are comparable with those reported before [20,21]. Those compounds containing no barium have a negative CTE over a limited temperature range.
centred around ~975K (SCF) and ~1100K (SLCF). This dip is not observed when the CTE of SCF is measured in air (see Figure 3.2b). Further, the CTE is significantly higher and shows an increase at ~725K.

Figure 3.2  The CTE as a function of temperature measured during heating of (a) SCF, SBCF, SLCF, and BLCF in flowing He, and (b) SCF in flowing He, on two different dilatometers, and in stagnant air

Figure 3.3 shows the oxygen fluxes through the dense 200 µm thick membranes between 1075 K and 1175 K. The flux increases on going from SLC2F < BLCF ~ SLCF < SCF ~ SBCF; with the replacement of strontium with barium having little effect. This observation confirms the order published by Teraoka [1] and Shao [7]. The absolute value obtained for SLC2F is in perfect agreement with the data published on a similar membrane [12]. The influence of the feed gas composition in an extended temperature range for SCF, SBCF and SLCF is presented in Figure 3.4. At 975 K, the oxygen flux through SBCF is about twice that of SCF, whereas they are very similar at 1275 K.
Figure 3.3  The oxygen flux as a function of temperature of SCF, SBCF, SLCF, BLCF, and SLC2F with $p_{O_2}(\text{feed}) = 0.21$ bar and flowing He on the permeate side

Figure 3.4  The oxygen flux as a function of temperature of (a) SCF, (b) SBCF, and (c) SLCF with $p_{O_2}(\text{feed}) = 0.10, 0.21, 0.50, \text{ and } 1.00$ bar and flowing He on the permeate side

In Figure 3.5 shows the influence of a $\sim 10 \, \mu\text{m}$ porous ($\sim 35 \%$) layers deposited on a $\sim 200 \, \mu\text{m}$ SLC2F membrane on the oxygen flux. The coding indicates the location of the various layers and runs from the feed to the permeate side with “p” denoting the porous layer and “d” the dense layer. Figure 3.5 presents also the oxygen flux through a $\sim 6 \, \mu\text{m}$ dense layer deposited on
the permeate side of a ~200 μm porous (~12%) support (pd 2). The increase of the flux because of the use of activation layers is less than 20%. The application of these layers on the permeate side is more effective than on the feed side. This result confirms the observation by Lee [5] for SCF. In contrast to Lee [5], we find that one layer on the permeate side is more effective than one layer on either side. The increase of up to a factor of 3 achieved by using a thin supported membrane is larger than the increases due to the use of activation layers.

Figure 3.5  The oxygen flux as a function of temperature of SLC2F with \( pO_2(\text{feed}) = 0.21 \), and flowing He on the permeate side using membranes with no activation layers “d”, with a 10 μm thick activation layer on the feed side “pd”, on the permeate side “dp” with a layer on both sides “pdp” compared with that of a ~6 μm thick dense layer on a ~200 μm thick porous (12%) support “pd2”

Figure 3.6 and Figure 3.7 illustrate the type of changes in the surface structure of SBCF membranes that have occurred during the 3 weeks of testing. Figure 3.6 shows the presence of protuberances, of up to 10 μm in diameter, on the permeate surface. EDX analyses showed that these protuberances consisted mainly of cobalt and oxygen, whereas the overall composition of the membrane remained almost unchanged. Figure 3.7 shows one micrograph taken at a location far away (a) and one nearby (b) from the helium inlet on the permeate side. The surface far away from the helium inlet, where the \( pO_2 \) has been relatively high, is smooth and very similar to that on the feed side after the permeation experiment and to the surface before the test. Grain sizes range between 10 and 20 μm. The surface near the helium inlet, where the \( pO_2 \) has been relatively low, has become very rough, and the grain boundaries seem to be etched away. EDX analyses showed a significant enrichment of both strontium and barium near the helium inlet. A similar enrichment has also been observed for \( \text{Sr}_{0.4}\text{La}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta} \) [12] and \( \text{Sr}_{0.7}\text{La}_{0.3}\text{CoO}_{3-\delta} \) [22].
Figure 3.6  SEM micrograph of (a) a cross section of the SBCF membrane (the permeate side can be found on the left hand side), and (b) of the permeate surface, showing the presence of cobalt oxide protuberance from the surface on the permeate side

Figure 3.7  SEM micrograph of details of the surface on the permeate side of an SBCF membrane, (a) far away from the He inlet, and (b) near the He inlet after the measurement has been concluded.
4. Discussion

The analyses of the XRD patterns do not show any deviation from the ideal cubic perovskite structure. This confirms the literature data [4,6,19]. The observed cell parameters are consistent with ionic radii of the A-cation and the expected vacancy concentration. The narrow diffraction peaks indicate that the membranes consist of well-crystallized material. Only BLCF had a significantly higher FWHM, indicating a lower degree of crystallization.

The coefficient of thermal expansion in the current experiments is combination of “linear expansion” and “chemical expansion”. Depending on whether the sample has an oxygen stoichiometry deviating from equilibrium at a certain T and pO$_2$, oxygen uptake or release can result in supplemental shrinkage or expansion respectively. To unravel the two effects, neutron diffraction experiments on the four compositions as a function of both pO$_2$ and T are planned. Our current results show major changes in the CTE with temperature, composition, and oxygen partial pressure, indicating that an average value over a large temperature range (see e.g. [20,21]) has a severely limited usability. SCF has the brownmillerite structure ($\delta=0.5$) in pO$_2 = 10^{-5}$ bar at temperatures below $\sim 975$ K [19,23]. At higher temperatures, the vacancy ordering melts and a transition to the perovskite structure occurs. Concomitant with this phase transition, the volume of the primitive unit cell decreases and a negative CTE is observed. In air, the perovskite phase of SCF is stable over the whole temperature range under investigation [23] and no drop in CTE is observed. The increase at $\sim 725$ K is consistent with the literature for other perovskites containing cobalt and iron [21]. The barium containing compounds have a more or less constant CTE and we conclude that the brownmillerite structure is not formed under the current conditions. This may very well be the origin of the reported higher phase stability of BSCF compared to SCF [7].

The functional membranes prepared from SCF and SBCF have an oxygen flux about 13 Nml·cm$^{-2}$·min$^{-1}$ at 1275 K and a pO$_2$(feed) of 1 bar. These values are much higher than previously reported in the open literature, where common oxygen flux values are in the order of 1 Nml·cm$^{-2}$·min$^{-1}$ [1,4-8,11]. Part of the flux increase that we have achieved can be attributed to the measurement conditions, e.g. the high temperature, pO$_2$(feed) and sweep gas flow rate. The maximum temperature that we have used is indeed well above what seems to be desirable from a technological point of view. At first sight, the pO$_2$(feed) may appear to be too high as well. However, this value is very reasonable as the air feed pressure in a commercial full scale plant is expected to be about 15 bar, i.e. a pO$_2$(feed) of $\sim$3 bar. The main reason for our high oxygen fluxes can be found in the application of thin functional membranes.

The oxygen flux increases in the order SLC2F < BLCF < SLCF < SCF < SBCF, confirming the results of Teraoka [1] and Shao [7]. The absolute values of our oxygen fluxes for SLC2F are in good agreement with Chen [11] and Viitanen [12]. The high flux of BSCF at 975K compared to that of SCF can be attributed to the presence of a brownmillerite phase for SCF. In the brownmillerite phase the oxide vacancies are ordered and much less mobile than in the perovskite with disordered vacancies [6,24]. The incorporation of the trivalent lanthanum on the A-position leads to a lower oxide vacancy concentration and thus to lower oxygen fluxes.

The oxygen flux increases by a factor of $\sim 3$ on going from a dense 200 µm thick SLC2F membrane to a 6 µm thick supported membrane. This value is about one order of magnitude less than what can be estimated on basis of equation 1. The main reasons for this can be found in the limited porosity of the porous support and the formation of stagnant layers in the support, which was located on the feed side. Alternatively, the kinetics of the surface reaction might become the rate-limiting step. From Figure 3.5, it is also clear that the reduction of the thickness of an LSC2F membrane from $\sim$200 µm to $\sim$6 µm is much more efficient than the application of
porous activation layers. The relative increases of the fluxes are of the same order of magnitude as those reported by Lee et al. [5]. For both compounds the enhancement reduces with increasing temperature. This can be attributed to the different temperature dependencies of the bulk transport and the surface oxygen exchange process. In the case of SLC2F, the activation energy of the latter has been shown to be about double that of the former [8,11]. Our results show again that it will be very difficult to obtain the flux increase by two orders of magnitude that Lee et al. [5] predict on the basis of model calculations.

Our SEM micrographs show clearly that cation diffusion is an important issue for a membrane made from SBCF. The increased roughness that we observe near the He inlet has also been reported on the surface exposed to methane by Wang et al. [25]. This deterioration can be ascribed to kinetic demixing during oxygen transport [12,22,24]. The driving force for kinetic demixing is a difference in the self-diffusion coefficient for the elements present under the influence of a gradient of the chemical potential. This kinetic demixing has lead to an enrichment of the permeate side with strontium and barium. Strangely enough regions where etching has occurred coexists with regions where cobalt oxide particles grow out of the surface. This leads us to believe that also phase separation is an important issue for this class of compounds.
5. Conclusion

Functional membranes have successfully prepared using SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ and Sr$_{0.8}$Ba$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ with an oxygen flux of $\sim$13 Nml·cm$^{-2}$·min$^{-1}$. At 1275K, these compounds behave very similar. At lower temperatures, however, the oxygen flux of Sr$_{0.5}$Ba$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ is much higher than that of SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$. This has been attributed to the formation of a brownmillerite phase for the latter composition. The coefficient of thermal expansion is shown to be far from constant over the whole temperature range studied. SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ and Sr$_{0.8}$La$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ even show a negative CTE in a limited temperature range under oxygen lean conditions. This can be ascribed to the brownmillerite-perovskite order-disorder transition. Long term stability is a crucial parameter, regarding the observed kinetic demixing and phase separation, that has to be determined urgently.
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