Mixed conducting membranes with an oxygen flux higher than 10 ml·cm⁻¹·min⁻¹

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Abstract
In this paper we discuss the influence of composition, measurement conditions, and membrane thickness on the oxygen permeability of the cobalt-iron perovskites.

From $\text{Sr}_{0.4}\text{La}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, $\text{Sr}_{0.8}\text{La}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, and $\text{Ba}_{0.8}\text{La}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, we have prepared membranes with a surface area of $\sim25$ cm$^2$ and with a thickness of $\sim200\mu$m. Under the optimal, but non-reducing, conditions we measured an oxygen flux of $\sim13$ ml·cm$^{-1}$·min$^{-1}$ for both SCF and SBCF. The oxygen production rate was over 200 ml·min$^{-1}$. The coefficient of thermal expansion (CTE) of SCF is shown to be strongly dependent on the atmosphere. The CTE of SCF is negative over a limited temperature range when heated in helium. This has been attributed to the brownmillerite to perovskite phase transformation.
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1. INTRODUCTION

Dense ceramic materials exhibiting mixed-ionic and electronic conductivity can be used in membranes for the production of oxygen of very high purity. Such a membrane system holds the promise of being energy efficient in comparison with cryogenic distillation and especially pressure swing adsorption techniques. Further, it will allow for a continuous production of oxygen. The highest energy efficiency is expected for the cogeneration of oxygen and electricity. Currently, the most promising membrane material is the perovskite with general formula \((\text{Sr/Ba/La})(\text{Co/Fe})\text{O}_{3-\delta}\). The interest in the ionic and electronic conductivity of this family of compounds has grown since the publication of Teraoka in 1985 [1], and from that time a large number of papers has been published. In a feasibility study, Bredesen [2] has determined that for a commercially viable process a minimum oxygen flux of \(10\ \text{ml·cm}^{-1}·\text{min}^{-1}\) is required. To our best knowledge such a value has not been reported in the open literature as of yet. Our main aim was to prepare a membrane that could surpass this value and produce about \(200\ \text{ml·min}^{-1}\ \text{O}_2\). To this end we have selected the most promising materials, prepared relatively thin (~200 µm) and large (~25 cm² surface area) membranes, and adjusted the measurement conditions. In this short paper we present some preliminary results.
2. EXPERIMENTAL

The perovskite powders with composition $\text{Sr}_{0.4}\text{La}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (SLC2F), $\text{Sr}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCF), $\text{Sr}_{0.8}\text{Ba}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SBCF), $\text{Sr}_{0.8}\text{La}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SLCF), and $\text{Ba}_{0.8}\text{La}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BLCF) were purchased from Praxair Speciality Products. Dense membranes with a thickness of about 200µm and a surface area of ~25cm$^2$ were prepared by tape casting, followed by a calcination step at ~1100°C. SEM micrographs showed that the remaining porosity (~5%) was present in the form of closed cavities, and that the voids were not interconnected.

The oxygen fluxes through the membranes were determined using an in-house developed testing rig. A mixture of $\text{O}_2/N_2$ was supplied on the membrane feed side. The oxygen partial pressure ($p\text{O}_2$) was controlled to be 0.1, 0.2, 0.5, or 1 bar. Helium was used as a sweep gas on the permeate side. The feed gas and sweep gas stream were operated in counter current mode. The effective membrane surface area was ~18cm$^2$. The oxygen and nitrogen contents in the permeate stream were determined with a Varian Star 3600CX series gas chromatograph. The oxygen fluxes were calculated from these values and the relevant sweep rate. Correction for leakage along the golden seals was based on Knudsen diffusion.

The coefficient of thermal expansion (CTE) of SCF was measured in pure helium, with a $p\text{O}_2$ of ~10$^{-5}$ bar, and in air, using a Netzsch Dilatometer 402E in the temperature range 20 ≤ $T/°C$ ≤ 1000.
3. RESULTS AND DISCUSSION

In Figure 3.1, we present the oxygen fluxes through the dense 200µm thick membrane made from the different perovskites between 800°C and 900°C, with a pO$_2$ of 0.21bar. The flux increases in the following order: SLC2F < BLCF ~ SLCF < SBCF ~ SCF. This order is in agreement with earlier work. Teraoka [1] reported that the oxygen flux decreases upon the addition of lanthanum to SCF. The similar permeabilities of SBCF and SCF are consistent with the data reported by Shao [3]. The change in the observed oxygen fluxes as a result of the incorporation of La in the perovskites is much larger than that of the partial substitution of Sr by Ba.

![Figure 3.1](image.png)

Figure 3.1 The oxygen fluxes of SLC2F, SCF, SBCF, SLCF, BLCF as a function of temperature (feed pO$_2$ = 0.21 bar)

The influence of the feed gas composition on the oxygen flux for the two materials with the highest oxygen fluxes, SCF and SBCF, is presented in Figure 3.2. The oxygen fluxes increase with increasing pO$_2$ over the full temperature range for both compositions. The differences are however smaller at low temperatures than at high temperatures. There is a trend for the oxygen flux to become less dependent on the temperature when the pO$_2$ is low and when the temperature is high. The highest oxygen flux we have measured is 13.3 ml·cm$^{-1}$·min$^{-1}$ for SBCF at T = 1000°C and pO$_2$ = 1bar. The flux for SCF is only slighter lower at 12.9 ml·cm$^{-1}$·min$^{-1}$ under similar conditions. These values are much higher than previously reported in the open literature, where common oxygen fluxes are of the order of 1 ml·cm$^{-1}$·min$^{-1}$ [1,4]. However, the comparison with literature data is complicated due to differences in experimental procedures. Our measurements are distinct from earlier reports because of the use of a much greater effective membrane surface area, ~18 cm$^2$ vs. ~1cm$^2$; thinner membranes, ~200µm vs. ~1mm; and a relatively high pO$_2$ and temperature. The measured high oxygen fluxes, compared with the literature values can partly be attributed to the process conditions, e.g. to the high temperature and high pO$_2$. The maximum temperature that we have used is indeed well above what seems to be desirable from a technical point of view. However, the main reason for our high fluxes can be found in the application of thin membranes.
The coefficients of thermal expansion (CTE) for SCF in helium and in air are presented in Figure 3.3. Under helium ($pO_2 \sim 10^{-5}$ bar), the CTE is negative over a limited temperature range, reaching a minimum at ~700°C. This dip is not observed when the same experiment is performed in air ($pO_2 = 0.21$ bar). However, under these conditions a sudden increase in the CTE is observed at ~500°C. In the whole temperature region studied, the CTE is significantly higher in air than in helium. The occurrence of major changes in the CTE of SCF with temperature and $pO_2$, shows that an average value over a large temperature range (see e.g. Petric [5]) has severely limited usability. The dependence of the CTE on the $pO_2$ is easily understood once the influence of the vacancy concentration on the cell parameters is appreciated. The primitive unit cell volumes for the compounds SrCo$_{0.1}$Fe$_{0.9}$O$_{3-\delta}$ have been determined at room temperature. The smallest cell volume, 56.90 Å$^3$, is found for $\delta = 0$ [6], and it increases to 57.0 Å$^3$ ($\delta = 1/8$), 57.6 ($\delta = 1/4$) to 61.0 ($\delta = 1/2$) [7]. The primitive unit cell of the brownmillerite phase ($\delta = 1/2$) is about 6% larger than that of the perovskite phase. SCF has the brownmillerite structure in $pO_2 = 10^{-5}$ bar at temperatures below ~700°C. At higher temperatures, the vacancy ordering melts and a transition to the perovskite structure occurs [8]. This is consistent with our measurements of the CTE in helium. At low temperatures, a relatively large primitive unit cell expands with temperature. At ~600°C the transition to the perovskite with the much smaller cell sets in and a shrinkage is observed. This transition completes on further heating, and the cell expands again.

Figure 3.3 The coefficient of thermal expansion of SCF versus temperature in air and in helium
4. CONCLUSION

We have successfully prepared two different perovskite membranes with high oxygen fluxes of \(~13 \text{ mI cm}^{-1} \text{ min}^{-1}\). It was proved to be possible to separate oxygen from air at a rate of \(213 \text{ mI min}^{-1}\) using these membranes and our testing rig. To our best knowledge, such high values have not been published in the open literature before. The dilatometric measurements show clearly that the coefficient of thermal expansion is strongly dependent on the atmosphere and temperature. This implies that the use of an average value over a large temperature region is prone to yield the wrong conclusion in the assessment of technical feasibility.
REFERENCES


APPENDIX A  POSTER

Mixed conducting membranes with an oxygen flux higher than 10 ml-cm\(^{-2}\)-min\(^{-1}\)

Background
An economically viable market introduction of pervoskite membranes for the on-site stand-alone oxygen production in an energy effective manner requires an oxygen flux of over 10 ml-cm\(^{-2}\)-min\(^{-1}\)


Objective
Obtain a membrane that produces more than 200 ml min\(^{-1}\) O\(_2\) with a flux of more than 10 ml cm\(^{-2}\)-min\(^{-1}\).

Membrane characteristics
Effective Surface area = 18 cm\(^{2}\)
Thickness = 200µm
Materials: Sr\(_{0.8}\)La\(_{0.2}\)Co\(_{0.5}\)Fe\(_{0.5}\)O\(_{3}\) (SLC2F),
Ba\(_{0.5}\)La\(_{0.5}\)Co\(_{0.5}\)Fe\(_{0.5}\)O\(_{3}\) (BLCF), SrCo\(_{0.8}\)Fe\(_{0.2}\)O\(_{3}\) (SCF),
Sr\(_{2}\)Ba\(_{0.8}\)Co\(_{0.5}\)Fe\(_{0.5}\)O\(_{3}\) (SBCF), and
Sr\(_{1.5}\)Ba\(_{0.5}\)Co\(_{0.5}\)Fe\(_{0.5}\)O\(_{3}\) (SLCF)
Preparation method: Tape casting followed by calcination at \(\approx 1100^\circ\)C

Results
SCF and SBCF show the highest O\(_2\) fluxes.
Substitution with La reduces these fluxes.
Flux target has been reached under favourable measurement conditions.

Vision
Similar fluxes at lower temperatures.
Scaled-down membranes with geometry of full-size module (\(\approx 100\) m\(^2\)-hr\(^{-1}\) O\(_2\)).
Materials development for partial oxidation membrane reactors.

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