# $La_{0.2}Sr_{0.8}Fe_{0.8}Ta_{0.2}O_{3-\delta}$ based thin film membranes with surface modification for oxygen production

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## Abstract

High temperature dense ceramic membranes made from mixed ionic/electronic conducting perovskite ceramics represent a high potential as a reliable source for oxygen and syngas production. In this work, $La_{0.2}Sr_{0.8}Fe_{0.8}Ta_{0.2}O_{3-\delta}$ based thin film perovskite system was evaluated, addressing the effect of structural surface modification on oxygen permeation rates. Membranes with ~20 μm thick dense functional layer and varying surface area on permeate side were fabricated by a dip coating technique. Oxygen permeation was measured at temperatures between 800 and 1000 °C by using varying partial pressure of $O_2$ as a driving force. Maximum $O_2$ flux values of ~5.8 and ~8.7 $ml \cdot cm^{-2} \cdot min^{-1}$ were recorded for smooth and structured permeation surfaces, respectively. This indicates that the surface roughness, which corresponds to an increase in surface area at the permeate side; can lead to a significant improvement in oxygen permeation rates reaching ~50 % at 1000 $^{o}C$.

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## 1. Introduction

Many petrochemical processes, such as production of synthetic gas (syngas) by partial oxidation of methane, require a **steady** supply of pure oxygen. These processes would be very attractive from commercial and environmental point of view if the cost of the oxygen supply could be reduced. Dense oxygen separation membranes based on mixed oxygen ion and electron conducting (MIEC) materials **may result in** a cost effective alternative to cryogenic pure oxygen production [1-3]. **The considerable advantage of MIEC membranes lies in their ability to separate oxygen from air with a selectivity of 100%.** Furthermore, these membranes are operating at elevated temperatures (above 700 °C) and can be integrated directly into catalytic process reactors. **This would allow performing in one single step the oxygen separation and successive catalytic processes**.

During the last decade a large number of MIEC materials based on fluorite and perovskite structures have been synthesized and characterized [4]. However, due to this date, all of these materials basically share one common feature: the trade-off between oxygen flux and phase stability. One of the **accessible** solutions to this problem is the beneficial structural arrangement of membranes geometry in a way to reach higher oxygen flux rate and at the same time employing more stable phase compositions. This structural arrangement is based on the fact that slow transport kinetics in principle may be due to both contributions from bulk diffusion as well as reactions on membrane surfaces. This leads to two general strategies followed by numerous research groups [5-9]:

1. Decrease **the** membrane thickness below the critical thickness such that permeation rate is solely controlled by the surface exchange reactions.
2. If 1 is fulfilled, then increase the number of surface reaction sites by increasing the specific membrane surface area.

Based on these trends, **the high temperature oxygen** permeation membranes can be made using an asymmetric geometry which constitutes of a porous support layer of the same composition with a thin membrane layer on top which is surface structured **in such a way that the surface area where surface reactions take place is increased.**

In this study the perovskite membrane system with composition $La_{0.2}Sr_{0.8}Fe_{0.8}Ta_{0.2}O_{3-\delta}$ is evaluated. This perovskite system was chosen due to its promising apparent stability behaviour which was observed during temperature programmed reduction tests [10]. Dense ~20 µm thick membranes were prepared **on porous support** and deposition of a functional layer with pore former was done. After thermal treatment the pore former is removed leaving a highly porous structure with rough surface finish and thus increased surface area on permeate side where the oxygen oxidation reaction takes place. **The effect of this surface** modification on oxygen permeation rate is reported.

## 2. Experimental

### *2.1. Ceramic membrane preparation and characterization.*

MIEC membranes were prepared using $La_{0.2}Sr_{0.8}Fe_{0.8}Ta_{0.2}O_{3-\delta}$ (abbreviated in further text as LSFT2882) powder obtained from spray pyrolysis [10, 11]. Porous substrates were made by uniaxially pressing ~3 mm thick discs of LSFT2882 powder with 20 wt.% carbon black addition as a pore former. Dense functional layer deposition on porous substrates was performed by a dip coating technique using LSFT2882 powder suspension based on ethanol as a solvent. Sintering of membranes was done at 1230 °C for 2 hours. In the case of membranes with structural surface modification, a presintering step of the dense functional layer at 1100 °C was included prior to deposition of the LSFT2882 **powder** suspension with starch pore former on top.

Phase purity after thermal treatment of LSFT2882 membranes was checked by means of X-ray diffraction using Bruker D8 diffractometer. Microstructures of processed membranes were observed on a Hitachi S3500N scanning electron microscope (SEM).

**Further details on the fabrication of gas-tight membranes as well as experimental techniques related to the LSFT2882 phase characterization were published elsewhere** [12].

### *2.2. Oxygen permeation measurements*

Oxygen flux measurement was performed by gas chromatography technique as a function of oxygen partial pressure. Disk shaped membranes were sealed as shown in Fig. 1 using gold as the sealing material (Fig. 1a). **The active membrane area after sealing was 1.1 cm$^2$. Variation in oxygen partial pressure at permeate (secondary) side was established by sweeping helium gas at different flow rates (50 – 860 ml/min). In order to extend the oxygen partial pressure range, mixing of helium gas with pure oxygen was performed too**. A constant flow of pure oxygen **(100 ml/min)** was supplied on the primary side during all experiments (Fig. 1b). **The total pressure on both sides was set to atmospheric pressure. Reference thermocouples (Fig. 1a) were located within both gas inlets, close to the membrane.**

Measurements were carried out between 800 and 1000 ºC leaving 4-6 hours for stabilization at each measurement condition. Oxygen concentration in sweep gas was determined by a Varian Micro–GC CP4900 gas chromatographer with argon as a carrier gas and performing the calibration with oxygen reference gases. **The possible leakages between primary- and secondary side were controlled by monitoring (gas chromatograph) whether He entered the oxygen exhaust gas on the primary side.**

## 3. Results

### *3.1. Sample preparation*

**The** XRD analysis showed formation of single-phase perovskite structure for all membrane samples after sintering cycle at 1230 °C. Detailed overview of phase evolution as a function of temperature is given elsewhere [12]. SEM micrographs of LSFT2882 membranes with smooth surface are shown in Fig. 2. Deposition by dip coating of colloidal LSFT2882 suspension on porous substrate resulted in ~ 20 µm thick and dense functional layer (Fig. 2a) with smooth surface finish on permeate (secondary) side (Fig. 2b). No voids/pores within dense layer or delamination defects between structural support and functional dense layer were observed. Microstructure of LSFT2882 membranes with rough surface modification on permeate side is shown in Fig. 3. Deposition of colloidal LSFT2882 suspension with pore former on top of presintered dense functional layer resulted in formation of 10-30 µm thick porous functional layer (Fig. 3a) exhibit a high roughness (Fig. 3b). **The grain sizes of LSFT2882 phase within both functional layers after final thermal treatment cycle (inclusions in Fig. 2b-3b) were within submicron range.**

### *3.2. Flux measurement*

**The He leakage check of membrane samples showed no trace of He permeating throughout the dense thin layer confirming that the membrane is gas tight.** Figure 4 demonstrates oxygen flux values as a function of oxygen partial pressure between 800 and 1000 ºC obtained for LSFT2882 membrane with smooth surface finish on permeate (secondary) side. Oxygen flux increased with temperature and difference in oxygen partial pressure (driving force) between primary and secondary side. A linear tendency was observed at 900 ºC and above at oxygen partial pressures down to 0.006 atm at the permeate side. Highest oxygen flux observed was ~5.8 $ml \cdot min^{-1} \cdot cm^{-2}$ obtained at 1000 ºC and oxygen partial pressure at 0.006 atm. Due to experimental setup with helium as a sweep gas and maximum gas flow rate of 860 ml/min, further decrease in oxygen partial pressure on secondary side was not possible. Steady state oxygen flux values within ~1.2 $ml \cdot min^{-1} \cdot cm^{-2}$ were reached at 800 ºC and oxygen partial pressures below 0.03 atm. No short term deviation in LSFT2882 membrane flux was observed by re-measuring several conditions at 1000 ºC after 12 days of membrane operation.

Figure 5 compares the performance at 1000 ºC of LSFT2882 membranes with smooth and rough surfaces on the secondary side. Increase by ~50 % in oxygen flux values within the whole range of oxygen partial pressures is observed for LSFT2882 membrane with rough surface finish. In this case the highest oxygen flux values up to ~8.7 $ml \cdot min^{-1} \cdot cm^{-2}$ were reached at oxygen partial pressure of ~0.01 atm on the permeate side.

## 3. Discussion

Deposition by dip coating LSFT2882 powder suspension on porous supports showed to produce dense, thin and defect free functional membrane layer with smooth surface finish on permeate side. The deposition of LSFT 2882 powder suspension with pore former on top of presintered dense functional layer resulted in rough surface finish layer with high surface area. The simplicity of the processing route chosen to obtain asymmetric membranes is only limited by requirement of clean processing environment to avoid the contamination of suspensions. **The use of LSFTa powder with small primary particles resulted in fine microstructure materials with grain size distribution below 1 µm within both functional layers.**

Asymmetric LSFT 2882 membranes with smooth surface finish reached oxygen fluxes up to 5.8 $ml\cdot min^{-1}\cdot cm^{-2}$ at 1000 ºC and no sign of oxygen flux deterioration was detected within 12 days of operation. Membranes with surface modification layer on oxygen permeate side showed ~50 % higher oxygen flux values compared with membrane without surface modification. The d**ifference in oxygen flux between these two membranes of identical composition at 1000 $^{o}$C points out the significance of surface exchange reactions with respect to the oxygen flux.** Observed oxygen flux enhancement is within the range reported by Kusaba et al. [13] for $La_{0.1}Sr_{0.9}Co_{0.9}Fe_{0.1}O_{3-\delta}$ and Figueiredo et al. [14] for $CaTi_{1-x}Fe_xO_{3-\delta}$ (x= 0.15, 0.20) perovskite systems. This ~50 % improvement was observed for these membranes at conditions where oxygen flux was basically governed by surface reactions and surface modifications were performed on the oxygen permeate side. In both investigations the authors observed that the rate was controlled by a combination of surface exchange on both primary and secondary side, however the primary side being less restrictive than the secondary side. According to Figueiredo et al. [14] the modification of both surfaces resulted in an overall permeation rate increase by 70 % compared to membranes with smooth surfaces. In case of asymmetric membrane geometry with porous support layer at the primary side (same as employed in this work) the modification of surface area is more or less obtained by the nature of the interface between membrane and porous support (Figs. 2-3).

## 4. Conclusions

Membranes with desired structural arrangement were successfully prepared by dip coating of porous substrates with $La_{0.2}Sr_{0.8}Fe_{0.8}Ta_{0.2}O_{3-\delta}$ powder suspensions and posterior thermal treatment. Prepared membranes of $La_{0.2}Sr_{0.8}Fe_{0.8}Ta_{0.2}O_{3-\delta}$ composition with ~20 µm thick dense layer reached ~5.8 $ml \cdot cm^{-2} \cdot min^{-1}$ oxygen flux rates at 1000 ºC and oxygen partial pressure ~0.006 atm on the secondary side and ~1 atm at the primary side. A high roughness corresponding to a large specific surface area on the secondary (permeate) side gave a ~50 % increase in oxygen permeation rate. This increase in oxygen flux rate indicates that for ~20 µm thick $La_{0.2}Sr_{0.8}Fe_{0.8}Ta_{0.2}O_{3-\delta}$ asymmetric membranes the surface exchange reactions on the permeate side may be considered as the main limiting factor for oxygen flux **at 1000 ºC**.

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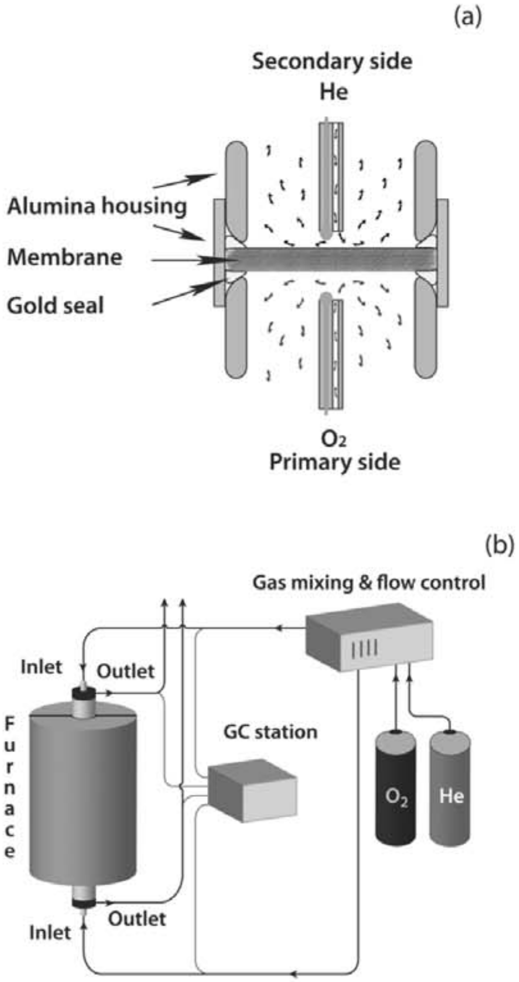

**Figure 1**. Experimental setup for the measurement of oxygen flux: (a) membrane fitting scheme and (b) gas supply and evaluation arrangement.

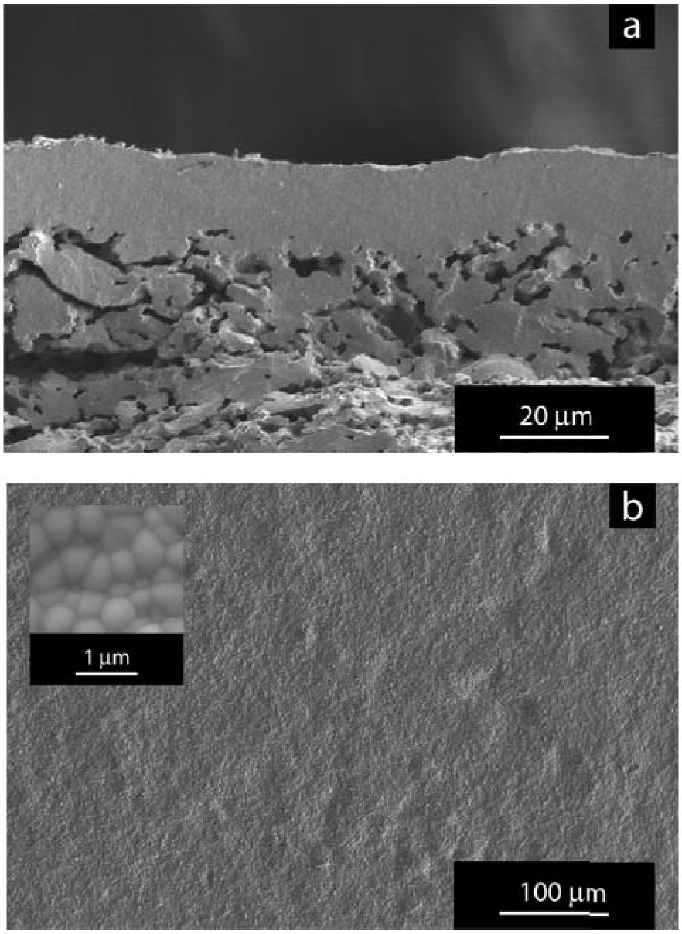

**Figure 2**. SEM micrographs corresponding to dense functional layer zone of asymmetric LSFT2882 membranes with smooth surface: (a) cross section and (b) top view with local magnification.

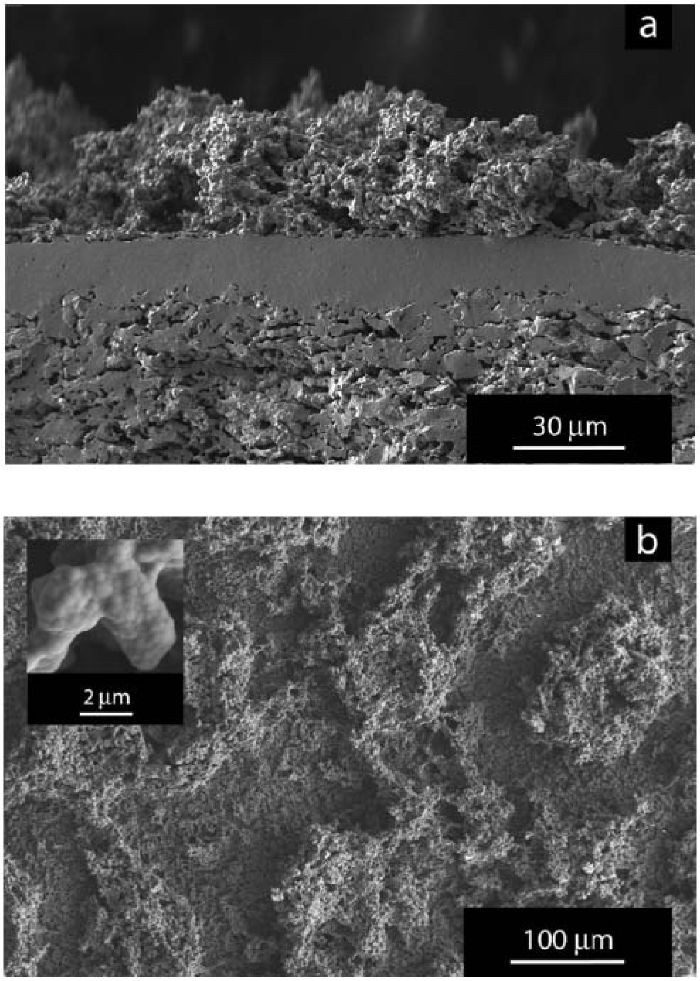

**Figure 3**. SEM micrographs corresponding to dense functional layer zone of asymmetric LSFT2882 membranes with rough surface modification: (a) cross section and (b) top view with local magnification.

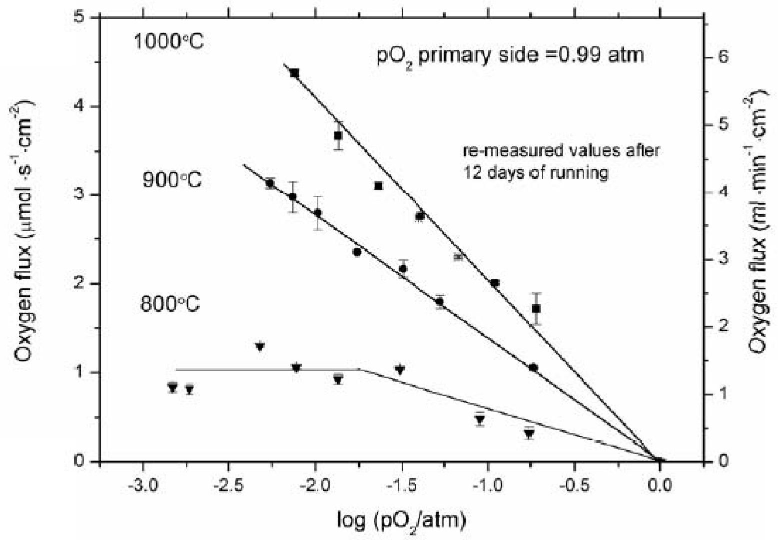

**Figure 4**. Oxygen fluxes as a function of oxygen partial pressure measured at 800 – 1000 °C temperature range corresponding to LSFT2882 membrane with smooth surface on permeate side.

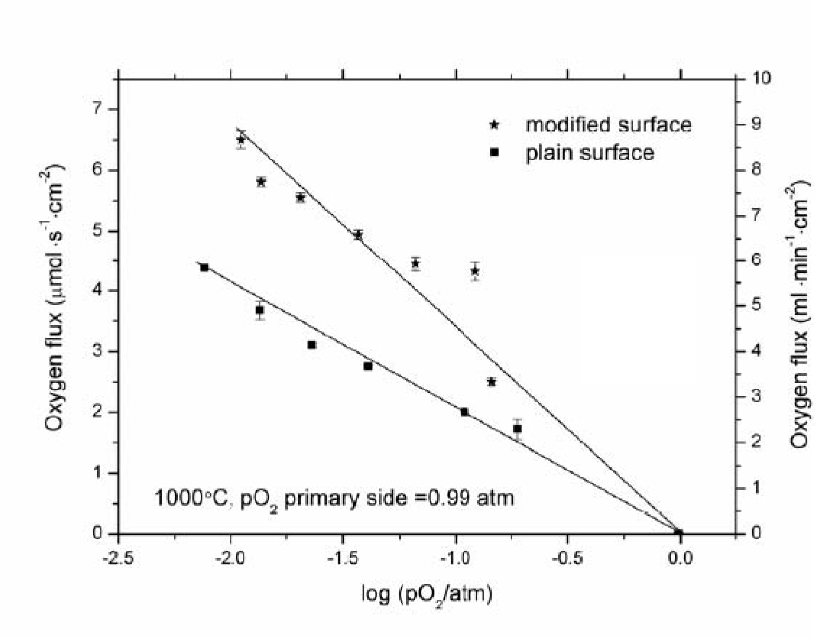

**Figure 5**. Oxygen fluxes as a function of oxygen partial pressure measured at 1000 °C corresponding to LSFT2882 membranes with smooth and rough surfaces on permeate side.