



# Effect of cation substitution at the B site on the oxygen semi-permeation flux in $\text{La}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.7}\text{B}_{0.3}\text{O}_{3-\delta}$ dense perovskite membranes with B = Al, Co, Cu, Mg, Mn, Ni, Sn, Ti and Zn (part II)

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## H I G H L I G H T S

- The rate determining step of oxygen flux through the membranes is clearly determined.
- The kinetics of oxygen surface exchanges depend mainly on the B-site substitution.
- The oxygen bulk diffusion depends on the specific free volume.
- The value of the specific free volume depends mainly on the A-site substitution.

## A R T I C L E I N F O

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## A B S T R A C T

The aim of this paper is to provide insight into the effect of cation substitution at the B site on the oxygen semi-permeation performances. Particular attention is given here to identify the impact of cation substitution at the B site on oxygen diffusion and oxygen surface-exchange kinetics in the  $\text{La}_{0.5}\text{B}_{a_{0.5}}\text{Fe}_{0.7}\text{B}_{0.3}\text{O}_{3-\delta}$  perovskite membrane series with B = Al, Co, Cu, Mg, Mn, Ni, Sn, Ti and Zn.

This study clearly shows that the prediction of the oxygen semi-permeation performances of membrane materials from the nature of cation at the A or B sites in perovskite structure is quite complex. The cation substitution at the B-site has a low impact on the nature of rate-determining step and a significant impact on oxygen semi-permeation performances, contrary to the cation substitution at A-site. Unfortunately, it is not possible to establish a relevant trend about the effect of the nature of cation in the A or B sites in perovskite structure on oxygen diffusion and the oxygen surface-exchange kinetics.

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## 1. Introduction

The development of oxygen-transport membranes (OTMs) is of great interest for potential industrial applications, such as the partial oxidation of methane for syngas production, or oxyfuel combustion. One of the challenges for the development of OTMs is the selection of membrane materials with high oxygen permeation, good chemical stability under a reducing atmosphere and suitable mechanical properties under working conditions. Unfortunately, these properties are antagonists, and a compromise must be

achieved between performance and stability.

Recent studies [1,2] and our previous work [3] reported that the  $\text{La}_{1-x}\text{Ba}_x\text{FeO}_{3-\delta}$  perovskite membrane series correspond to an interesting compromise between oxygen semi-permeation and chemical stability. In contrast, the  $\text{Ba}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$  perovskite membrane series exhibits larger oxygen semi-permeation performances than those obtained with  $\text{La}_{1-x}\text{Ba}_x\text{FeO}_{3-\delta}$  perovskite membranes, but it does so with lower chemical stability and mechanical properties [4–7].

This study focuses on the effect of cation substitution at the site B on the oxygen semi-permeation flux and the rate-determining step. A large range of cation substitution at the B site in the  $\text{La}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.7}\text{B}_{0.3}\text{O}_{3-\delta}$  perovskite series (with B = Al, Co, Cu, Mg, Mn, Ni, Sn, Ti and Zn) is presented. These cations are usually

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reported as B-site dopant in the literature for the membrane materials [2,8,9]. The aim of this work is to provide a better understanding of the effect of the cation on the B site on the oxygen diffusion and surface-exchange kinetics through  $\text{La}_{1-x}\text{Ba}_x\text{FeBO}_{3-\delta}$  perovskite membranes.

## 2. Experimental

### 2.1. Powder synthesis

$\text{La}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.7}\text{B}_{0.3}\text{O}_{3-\delta}$  (with B = Al, Co, Cu, Mg, Mn, Sn, Ti and Zn) perovskite materials are synthesized using a solid–solid route. High-purity oxide and carbonate precursors, including  $\text{La}_2\text{O}_3$  (99.99%, Sigma–Aldrich),  $\text{Fe}_2\text{O}_3$  (99.5%, Alfa Aesar),  $\text{Co}_3\text{O}_4$  (99.7%, Alfa Aesar),  $\text{Al}_2\text{O}_3$  (99.9%, Alfa Aesar),  $\text{CuO}$  (99.7%, Alfa Aesar),  $\text{MgO}$  (99.5%, Alfa Aesar),  $\text{MnO}_2$  (99.9%, Alfa Aesar),  $\text{SnO}_2$  (99.9%, Alfa Aesar),  $\text{TiO}_2$  (99.9%, Alfa Aesar),  $\text{ZnO}$  (99.9%, Alfa Aesar) and  $\text{BaCO}_3$  (99.95%, Alfa Aesar) are mixed by attrition using 800- $\mu\text{m}$  zirconia balls in an ethanol media (600 rpm for 3 h).  $\text{La}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$  was synthesized by the nitrate-citrate route, as described elsewhere [10], to avoid the nickel oxide precursor ( $\text{NiO}$ ). All of the obtained powders are calcined at 1000 °C for 8 h, and the phase purity is confirmed with X-ray diffraction (Siemens D5000, Cu- $\text{K}_{\alpha 1}$ ). The calcined powders are ground by attrition milling (1000 rpm) to obtain a monomodal grain size of approximately 1–2  $\mu\text{m}$ .

### 2.2. Shaping using the tape-casting process, firing and density measurements

Tape casting is used to obtain thin green sheets (150  $\mu\text{m}$  thick). Then, the green sheets are thermo-laminated at 60 °C under 50 MPa and fired to obtain a relative density of more than 95% and a thickness of 1 mm. The sintering conditions for the membrane materials are listed in Table 1. More details concerning sample shaping are provided in previous studies [10,11]. The density of the sintered membranes is measured using the Archimedes method, and the grain size is evaluated from observations obtained by scanning electron microscopy (SEM, Cambridge Instruments).

### 2.3. Oxygen surface-exchange and semi-permeation measurements

The oxygen semi-permeation and oxygen activity at the membrane surface are measured using a homemade apparatus, described in previous studies [12,13]. The oxygen-permeation measurement is performed on two membrane samples for each membrane material to ensure reproducibility. The dense membrane is sealed between two alumina tubes using gold rings [14]. The measurements are performed at a temperature ranging from 980 to 600 °C with an interval of 25 °C with an air/argon atmosphere gradient. The originality of the device is the presence of metallic electrodes and tips on the surface membrane. This system

of electrodes and tips makes possible the determination of the oxygen surface activities and of the oxygen chemical potential drop through and at the membrane surfaces. Then, the oxygen chemical potential through the membrane is evaluated, as previously described by Geffroy et al. [12].

The determination of the oxygen chemical potential drop makes it possible to calculate a new criterion introduced by Geffroy et al. [13],  $B_c$ , which is defined in Eq. (1):

$$B_c = \frac{\Delta\mu_{\text{O}_2}^{\text{surface}}}{\Delta\mu_{\text{O}_2}^{\text{bulk}}}, \quad (1)$$

where  $\Delta\mu_{\text{O}_2}^{\text{surface(lean)}} = \mu_{\text{O}_2}^{\text{surf(lean)}} - \mu_{\text{O}_2}^{\text{gas(lean)}}$  and  $\Delta\mu_{\text{O}_2}^{\text{bulk}} = \mu_{\text{O}_2}^{\text{surf(rich)}} - \mu_{\text{O}_2}^{\text{surf(lean)}}$ .  $\Delta\mu_{\text{O}_2}^{\text{surface(rich)}} = \mu_{\text{O}_2}^{\text{gas(rich)}} - \mu_{\text{O}_2}^{\text{surf(rich)}}$ .

According to Eq. (1), three cases can be considered:

- when  $B_c > 1$ , the oxygen flux is governed by oxygen surface exchange.
- when  $B_c < 1$ , the oxygen flux is governed by oxygen diffusion.
- when  $B_c \approx 1$ , a mixed regime is present in which the oxygen flux is governed by both oxygen diffusion and surface exchange.

The value of  $B_c$  is characteristic of the rate-determining step of the oxygen semi-permeation flux through the membrane.

### 2.4. Thermogravimetric analysis

Thermogravimetric analyses of 300-mg powder samples are performed from room temperature to 1000 °C under air ( $P_{\text{O}_2} = 0.21$  atm), using a differential thermogravimetric analyzer (LABSYS, Setaram). The samples are heated and cooled at 2 °C/min.

### 2.5. Electrical-conductivity measurement

The electrical conductivity is evaluated by a four-probe device from room temperature to 1000 °C under air. The bar samples are obtained by laminating rectangular tape-casted punched units and sintered using similar conditions, as reported in Table 1. After sintering, the bar samples have approximate dimensions of 1 × 2.5 × 24 mm<sup>3</sup>. Both ends of the bar sample were coated by platinum electrodes. Two additional platinum electrodes were placed 5–8 mm from each end of the bar. The platinum electrodes were prepared via platinum-ink coating (Pt paste Ferro 6402, CDS), and the samples were heated to 1000 °C in air to obtain cohesive and porous platinum electrodes.

**Table 1**  
Sintering conditions and chemical compositions of the membrane materials.

Membrane materials	Acronym	Sintering conditions	Mean grain size ( $\mu\text{m}$ )	Density of starting powders (pycnometer, $\text{g cm}^{-3}$ )	Relative density of sintered membranes
$\text{La}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.7}\text{Al}_{0.3}\text{O}_{3-\delta}$	LBFAl	1250 °C, 1 h, air	0.5–1	5.34	95%
$\text{La}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.7}\text{Co}_{0.3}\text{O}_{3-\delta}$	LBFCo	1150 °C, 4 h, air	1–2	6.06	>95%
$\text{La}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.7}\text{Cu}_{0.3}\text{O}_{3-\delta}$	LBFCu	1150 °C, 1 h, air	1–2	5.40	95%
$\text{La}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.7}\text{Mg}_{0.3}\text{O}_{3-\delta}$	LBFMg	1475 °C, 4 h, air	0.5–4	4.99	94%
$\text{La}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.7}\text{Mn}_{0.3}\text{O}_{3-\delta}$	LBFMn	1325 °C, 1 h, air		5.61	>95%
$\text{La}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$	LBFNi	1350 °C, 1 h, air	3–7	5.99	>95%
$\text{La}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.7}\text{Sn}_{0.3}\text{O}_{3-\delta}$	LBFSn	1225 °C, 1 h, air	0.5–1	5.83	95%
$\text{La}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.7}\text{Ti}_{0.3}\text{O}_{3-\delta}$	LBFTi	1450 °C, 1 h, air	1–4	5.36	>95%
$\text{La}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.7}\text{Zn}_{0.3}\text{O}_{3-\delta}$	LBFZn	1250 °C, 1 h, air	1–2	5.58	95%

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