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# La<sub>x</sub>Sr<sub>1-x</sub>Co<sub>0.35</sub>Bi<sub>0.2</sub>Fe<sub>0.45</sub>O<sub>3-δ</sub> (x = 0.5 to 0.8): A new series of oxygen separation membrane

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## ARTICLE INFO

## Article history:

Received 24 August 2015

Received in revised form

20 December 2015

Accepted 6 January 2016

Available online 4 February 2016

## Keywords:

Perovskite membrane

Combustion synthesis

Oxygen separation

Mixed conductor

Permeation

## ABSTRACT

The present study aims to develop a series of novel perovskite based materials with a nominal composition of La<sub>x</sub>Sr<sub>1-x</sub>Bi<sub>0.2</sub>Co<sub>0.35</sub>Fe<sub>0.45</sub>O<sub>3-δ</sub> (x = 0.5 to 0.8) as oxygen separation membranes. The powder has been synthesized by a soft chemical alanine assisted combustion method. X-ray diffractograms of calcined powders reveal orthorhombic perovskite structure. The optical properties measured by UV-VIS spectroscopy suggest that the variation of lanthanum concentration has mere effect in the electron density as well as band gap of the membranes. Total electrical conductivity as calculated is maximum for the composition with lowest lanthanum concentration (La = 0.5). The permeation flux as measured reveals that the flux generally decreases as the lanthanum concentration increases in the stoichiometry. A highest oxygen permeation flux of 0.23 ml/min/cm<sup>2</sup> has been achieved for the composition La<sub>0.5</sub>Sr<sub>0.5</sub>Bi<sub>0.2</sub>Co<sub>0.35</sub>Fe<sub>0.45</sub>O<sub>3-δ</sub> at 900 °C.

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## Introduction

Mixed ionic and electronic conducting (MIEC) oxide based membranes have drawn continuous research interest for their possible application as a dense membrane in separation and production of highly pure oxygen [1–4]. Conventional methods of high purity oxygen production like cryogenic distillation and pressure swing adsorption are seemed to be costly and energy intensive [5–7]. In this background, separation of pure oxygen from air using MIEC based ceramic membranes are now considered as one of the commercially viable method for oxygen production [8–10]. Apart from the oxygen permeation flux, the selectivity of the membrane is also very crucial factor for its successful industrialization. Dense ceramic membranes based on MIEC materials have the

capability to separate oxygen from air at elevated temperatures (>700 °C) with 100% selectivity [11].

MIEC oxides with ABO<sub>3</sub> type perovskite structure have plenty of scope to introduce various dopants both in their A and B-site [12]. In general, the A-site cations are alkaline, alkaline earth and lanthanide ions, while the B-site cations are mainly transition metal ions. The partial substitution in A-site with lower valent cation leads to the formation of oxygen vacancies and/or enhancement of oxidation state of B-site cation to maintain electro neutrality of the perovskite structure. The increase in oxygen vacancy helps in oxygen ion conductivity in the structure, while the electron hopping between B-site metal ions with multiple valency state results in electronic conduction [12]. Since the first report in 1980's by Teraoka et al. [13] on oxygen permeation through MIEC based La<sub>1-x</sub>Sr<sub>x</sub>Co<sub>1-y</sub>Fe<sub>y</sub>O<sub>3-δ</sub>, many studies have been published by varying different dopant concentration both in the A- and

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<http://dx.doi.org/10.1016/j.ijhydene.2016.01.021>

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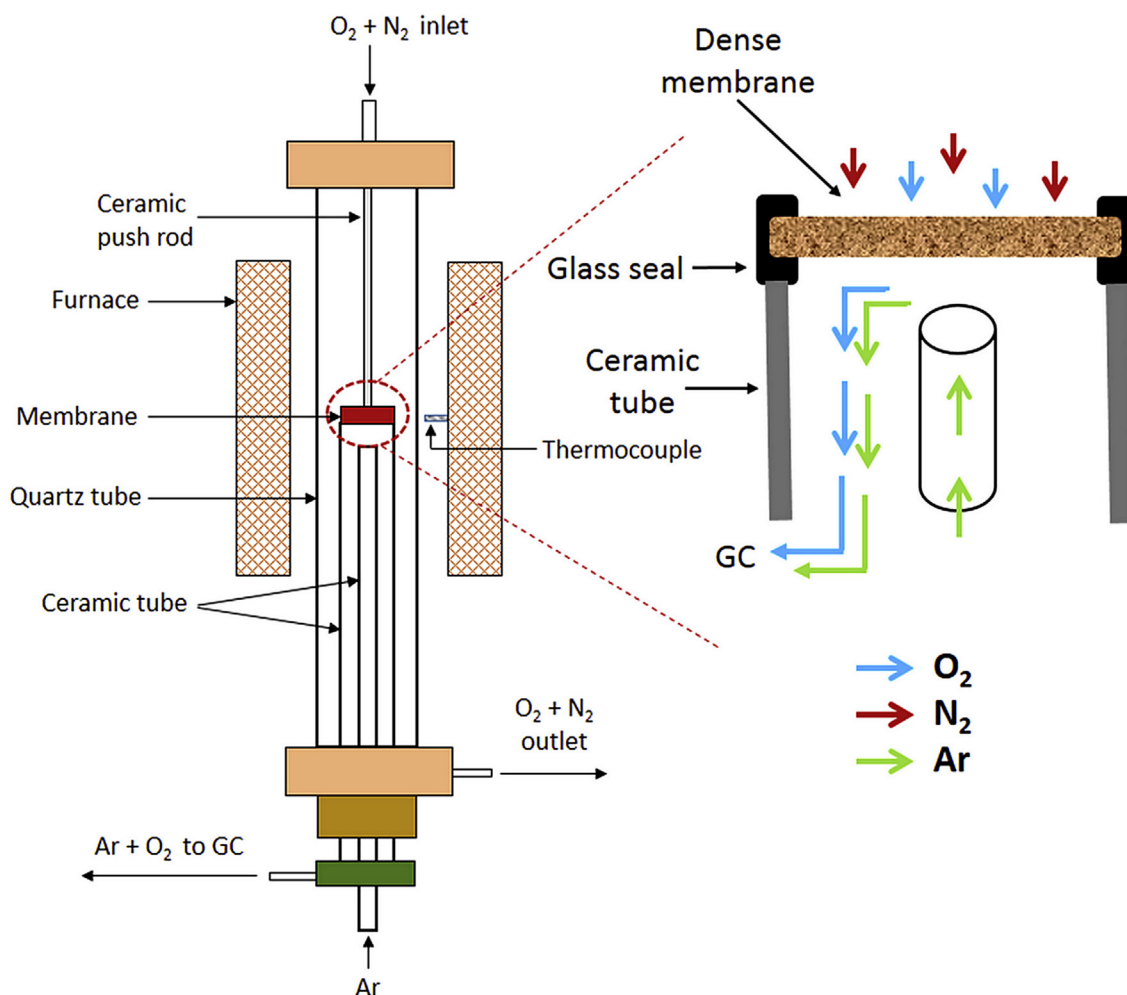
**Table 1 – Sample identification codes of LSBCF compositions.**

La doping (mol %)	Composition	Sample ID	Crystallite size of calcined powder (700 °C) (nm)
50	$\text{La}_{0.5}\text{Sr}_{0.5}\text{Bi}_{0.2}\text{Co}_{0.35}\text{Fe}_{0.45}\text{O}_{3-\delta}$	L5	14.7
60	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Bi}_{0.2}\text{Co}_{0.35}\text{Fe}_{0.45}\text{O}_{3-\delta}$	L6	15.0
70	$\text{La}_{0.7}\text{Sr}_{0.3}\text{Bi}_{0.2}\text{Co}_{0.35}\text{Fe}_{0.45}\text{O}_{3-\delta}$	L7	15.2
80	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Bi}_{0.2}\text{Co}_{0.35}\text{Fe}_{0.45}\text{O}_{3-\delta}$	L8	15.6

B-site of the perovskite [8,12,14–17]. Teraoka et al. [13] observed that the oxygen flux increases by substituting  $\text{Sr}^{2+}$  for  $\text{La}^{3+}$  at the A-site and  $\text{Co}^{3+}$  for  $\text{Fe}^{3+}$  at the B-site. Thermodynamic approach using an Ellingham diagram shows that the smaller  $\text{La}^{3+}$  ion ( $r = 136$  pm) improves tolerance against  $\text{CO}_2$  as compared to the bigger  $\text{Sr}^{2+}$  ion ( $r = 144$  pm) [18]. Few studies also revealed that a small amount of iron in the structure is helpful for long term stability of the perovskite [19]. Similarly, presence of bismuth may significantly improve

the oxygen permeability and stability of the membrane at elevated temperature [20–25]. Sunarso et al. [20] in his study showed large improvement of oxygen permeation and phase stability by Bi-doping in  $\text{BaSc}_{0.1}\text{Co}_{0.9}\text{O}_{3-\delta}$  perovskite. Similarly, Li et al. [21] reported that the oxygen permeation flux increases with the increasing bismuth content in  $\text{Sr}_{10-n/2}\text{Bi}_n\text{Fe}_{20}\text{O}_m$  and  $\text{Sr}_{1-x}\text{Bi}_x\text{FeO}_3$  systems. Shao et al. [22] also reported that oxygen flux increases with the addition of bismuth in  $\text{BaCoO}_{3-\delta}$ . But lowering of bismuth content is absolutely necessary because of the large thermal expansion coefficient of bismuth doped  $\text{BaCoO}_{3-\delta}$  material. Again, during selection of such multi component perovskites containing costly and toxic metals, a number of parameters such as their commercial viability, cost and toxicity has to be considered while optimizing membrane performance [8,26].

In the present work attempt has been made, for the first time, to synthesize a novel composition;  $\text{La}_x\text{Sr}_{1-x}\text{Co}_{0.35}\text{Bi}_{0.2}\text{Fe}_{0.45}\text{O}_{3-\delta}$  ( $x = 0.5–0.8$ ) (henceforth referred as LSBCF) perovskite by aqueous based combustion method using alanine as a chelating agent. The effect of lanthanum concentration on the physico-chemical and permeation properties of LSBCF have been studied in detail. The stability of the synthesized membranes has also been studied and discussed.

**Fig. 1 – Schematic representation of high temperature oxygen permeation set up.**

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