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Perovskite foams used in combination with dense ceramic membranes for oxygen transport membrane applications

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ABSTRACT

The future industrial implementation of membranes for oxygen transport requires new designs to increase oxygen semi-permeation, together with robust performance under operating conditions. This work describes the development of innovative membrane designs based on perovskite foams with a very large porosity (above 90%) supporting thin dense perovskite membranes (thickness of 50–100 μm). The preparation of such foam-supported membranes is described in this paper. The performances in terms of oxygen semi-permeation are also measured and compared with the best results reported in the literature up to date.

1. Introduction

Recent works show that dense membranes with a low thickness and gastight are required to obtain suitable oxygen semi-permeation for potential use in oxygen transport applications. Several membrane designs have been reported in the literature [1–7]. All are based on asymmetric devices combining a dense membrane and a porous support.

Usually, the methods used for the fabrication of porous supports lead to a moderate porosity (30–50 vol%), then limiting the oxygen diffusion through the support. The solution suggested in this paper is to use perovskite foam supports with a large porosity (i.e. above 90%) in order not to limit the kinetics of oxygen gas diffusion to the supported dense membrane (Fig. 1).

Such porous foam supports can also provide several additional advantages:

- Provide suitable mechanical properties,
- Not to limit the gas diffusion in the vicinity of the dense membrane surface in contact with the foam support,
- Improve the exchange surface between the gas and the membrane.

Following this strategy, Zhang et al. [1] and He et al. [2,3] reported the preparation of asymmetric membranes (i.e. $Zr_{0.64}Y_{0.16}0_{2-\delta}$ – $La_{0.8}Sr_{0.2}Fe_{0.5}Cr_{0.5}O_{3-\delta}$ composite) using the tape casting process associated with the phase inversion method (Fig. 1). This method makes it possible the fabrication of a continuous structure consisting in a thin dense layer, ranging from 25 to 75 μm in thickness, attached to a porous support. The porosity of the support is quite high (40–50 vol%), with a microchannel structure (20–50 μm diameter) oriented perpendicular to the surface of the membrane. Recently, the impact of such a microchannel structured support on the oxygen semi-permeation of membranes was investigated by Shao et al. [4]. They demonstrated that the superior performances of these membranes can be mostly attributed to the aligned microchannel structure that provides fast pathways for oxygen molecular diffusion up to the thin dense membrane, unlike the usual tortuous pore network structures.

The results of Shao et al. suggested that the porous microchannel structure could be even more efficient if its porosity was significantly larger than that reported by the authors (*i.e.,* 40–50 vol%). Indeed, it could promote oxygen molecular diffusion through the support pores. In this respect, the present paper is therefore focused on the development and performance of asymmetric membranes based on perovskite foam support with a porosity above 90 vol% and a high connectivity of the pores.

Many robust methods have been reported in the literature for the manufacturing of ceramic foams [8]. One of the most common methods relies on the use of a polymeric template (*i.e.,* isolated porogens or sponges with 3D cellular networks). In the case of a polymeric sponge which is first soaked into a ceramic suspension usually containing binders. The excess of suspension is then evacuated, for instance by centrifugation, and a coating is obtained on the struts of the polymeric foam. The coating thickness depends on the surface tension and viscosity (*i.e.,* the formulation) of the initial suspension. Finally, after

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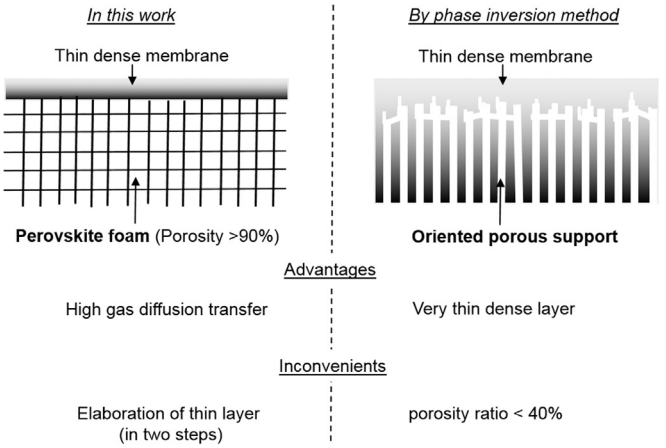

Fig. 1. New designs of asymmetric membrane, a) a perovskite foam support covered with a thin dense film (this work) and, b) with phase inversion method as recently reported by Zhang et al. [1] or He et al. [2,3].

drying, the ceramic-coated template is pyrolyed into a ceramic foam with a high pore connectivity. The pores' average size and porous volume can be chosen upstream of the process through the choice of the template. This method has the advantages of both being easy to implement for a wide range of ceramics and of being quite inexpensive.

For the dense membrane, one of our previous works [9,10] showed that the $La_xSr_{1-x}Fe_yGa_{1-y}O_{3-\delta}$ perovskite membranes correspond to the best compromise between a high oxygen permeation, a good chemical stability and suitable mechanical properties. These last material criteria are key parameters for industrial applications. In this respect, the dense membrane material investigated in this work is $La_{0.6}Sr_{0.4}Fe_{0.7}Ga_{0.3}O_{3-\delta}$ perovskite, corresponding to the composition having a high oxygen flux performance [9].

2. Experimental

2.1. Preparation of the perovskite foam

The method developed for the manufacturing of ceramic foams makes it possible to control the pore size in a fully open porosity structure [11–14]. The manufacturing technique requires the use upstream of the process of a polyurethane (PU) foam which is the organic template. The PU foam was impregnated in a controlled manner with the ceramic suspension to prevent the clogging of the pores. After soaking the PU foam in the ceramic suspension, the PU backbone was first pyrolyzed at a moderate temperature in air to eliminate the organics, followed by a high temperature treatment to obtain the ceramic replica with dense struts.

2.2. Elaboration of perovskite suspension suitable for dip-coating of PU foams

The formulation of a stable aqueous suspension for the elaboration of perovskite foams is based on the procedure developed by R. Faure for alumina [15]. The powder loading after optimization is fixed at 40 vol %. A dispersant based on PMMA, Darvan C (RT Vanderbilt Company Inc., US), is used to stabilize the suspension, thereby lowering its viscosity. A polyvinyl alcohol-based binder (PAF OPTAPIX 35, Zschimmer & Schwarz GmbH, Germany) is also used to provide sufficient cohesion to the coating obtained after impregnation.

Two additional agents have to be introduced to prepare an aqueous suspension adapted to the impregnation method:

– The first is linked to the low wetting of the PU foam by the aqueous suspension. The addition of a wetting agent (BYK 348, Byk Chemie GmbH) reduces the surface tension and increases the amount of the slurry deposited at the first impregnation.
– The second is linked to the formation of air bubbles during the impregnation of the suspension in the PU foams. An anti-foaming agent (Contraspum, Zschimmer & Schwarz GmbH) is used to limit the formation of these bubbles. Finally, the suspension formulation optimized for foam impregnation is presented in Table 1.

Table 1
Composition of the perovskite suspension for foam impregnation.

Function	Compound	wt%
Powder	Perovskite	70.0
Solvent	Water	16.4
Dispersing agent	Darvan C	1.4
Binder	Optapix PAF 35	8.6
Wetting agent	BYK 348	0.05
Anti-foaming agent	Contraspum	0.10

2.3. Impregnation method for preparation of the perovskite foam

The PU foam has a large open porosity above 94 vol% with an average channel size close to 1 mm diameter. The foam is impregnated by the perovskite suspension exploiting suction effects, with the PU foam initially compressed prior to the immersion in the suspension. This ensures that the pores of the foam are completely filled by the perovskite suspension. Then, the foam is compressed slightly to remove the excess suspension, and to obtain a homogenous distribution of the perovskite suspension onto the foam support. The pores of the impregnated foam support are then emptied using air flow at low pressure (a few bars). Finally, the foam is dried in open air at room temperature. To increase the amount of the material impregnated, the foam must be impregnated several times with a drying time (24 h at room temperature) between each impregnation step. The amount of the impregnated material is measured by weighing the PU foam support before and after the impregnation and drying.

2.4. Debinding and sintering of the perovskite foam

One of the critical steps for the development of foams is the removal of the organics, especially the PU template. The removal cycle of organics can defined on the base of TG-DTA analysis (Fig. 2).

The pyrolysis of the organic compounds starts at a temperature of 210 °C, corresponding to the removal of the dispersing agent and binder that are a part of the formulation of the ceramic suspension. The pyrolysis of polyurethane starts at a higher temperature, typically at 320 °C, and corresponds to a large weight loss (15 wt%). Above 475 °C, there is no weight loss, and the pyrolysis of the organics is completed. Then, the debinding treatment corresponds to the low heating rate,

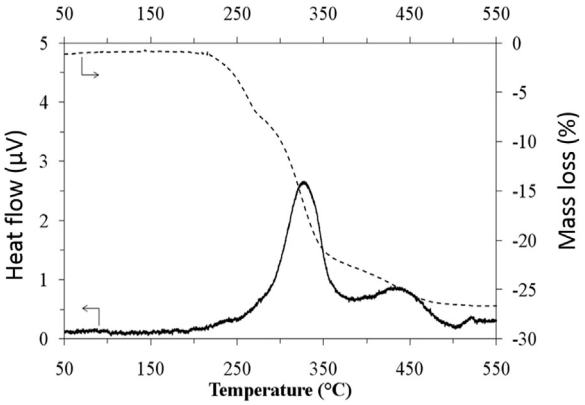

Fig. 2. DTA-TG analysis of impregnated polyurethane support.