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# Improvement of oxygen flux through perovskite membranes using a coating of ultra-divided particles

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## HIGHLIGHTS

- Improvement of the oxygen semi-permeation performances.
- Increasing the kinetic surface exchanges by a coating of ultra-divided particles.
- Dependence of nature and microstructure of membrane surfaces on the oxygen flux.
- Development of optimal design from  $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.7}\text{Ga}_{0.3}\text{O}_{3-\delta}$  /  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Ga}_{0.2}\text{O}_{3-\delta}$  perovskite membranes.
- Identification of rate determining step evolution in relation with the membrane design.

## ARTICLE INFO

## Article history:

Received 1 June 2016

Received in revised form

6 September 2016

Accepted 15 September 2016

Available online 16 September 2016

## Keywords:

Perovskite ceramic membrane

Mixed conductor

Oxygen semi-permeation

Surface exchange mechanism

Bulk diffusion

Coating

## ABSTRACT

In the last decades, numerous mixed ionic and electronic conducting materials with a perovskite structure have been investigated for their potential applications as membrane materials for oxygen separation applications. This work shows that significant improvement of electrochemical properties of two perovskite materials,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$  (LSFCo<sub>6482</sub>) and  $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.7}\text{Ga}_{0.3}\text{O}_{3-\delta}$  (LSFG<sub>5573</sub>) is obtained using ultra-divided particles perovskite coating. This coating is obtained by dip-coating thanks to a derived sol-gel synthesis route. The ultra-divided particles have a grain size distribution from 300 to 500 nm. The oxygen flux measured using a specific setup shows that the oxygen surface exchange kinetics and bulk diffusion coefficient depend on the microstructure and the chemical composition of the coating material. The relation established between chemical formulation, microstructure, and oxygen flux were used to design optimized membranes.

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## 1. Introduction

Mixed conducting materials are of great interest because they find many potential industrial applications such as electrode in solid oxide fuel cell (SOFC), for energy conversion. These technologies are commonly based on anionic oxygen transport through a ceramic membrane. Nowadays even if many mixed conducting materials have been studied in the literature (Geffroy et al., 2013; Sunsaro et al., 2008), none of them meets all the criteria for industrial applications. The goal is to find the best compromise between oxygen semi-permeation flux, chemical stability, mechanical properties, and membrane cost. The main difficulty is

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the interdependence of all those properties. If the oxygen flux is limited by bulk diffusion, one solution to improve the oxygen permeation rate is to decrease the membrane thickness down to several microns. This requires a porous support to sustain the membrane with a huge impact on overall cost per square meter of membrane (Watanabe et al., 2010).

If the oxygen flux is limited by surface exchange kinetics, the microstructure and the chemistry of membrane surface have usually a large impact on the oxygen flux through the membrane (Xu and Thomson, 1999). In the literature, numerous solutions have been reported, as the coating of porous layer applied by painting, screen printing, spin-coating, dip-coating, electro-deposition (Bouwmeester et al., 1994; Deng et al., 1994)... For instance, Hayamizu et al. (2014) have reported an increase of oxygen flux by a factor of 3.6 using a porous coating of 6.5 μm thickness and 0.9 μm particle size.

Today the state of the art considering porous coating is mainly the grain size in the range of a few microns. Very few publications deal with coating having submicron particles and the impact of the microstructure of the coating is not yet well understood (Kida et al., 2015; Lee et al., 2003).

As mentioned above the limiting step of oxygen permeation through the membrane will drive the membrane performance optimization. In recent works, Valentin et al. (2010) introduce the  $B_c$  coefficient, which leads to the identification of the rate determining step of oxygen transport through the membrane. So three cases are considered: if  $B_c \gg 1$ , the oxygen flux is governed by oxygen surface exchange, if  $B_c \ll 1$  the oxygen flux is governed by oxygen diffusion, and if  $B_c = 1$ , the oxygen flux is governed by both oxygen diffusion and surface exchanges. The last case is called mixed regime.

Reichmann et al. show that the bulk diffusion coefficient increases with the grain size whereas the surface exchange kinetics increases when the grain size decreases (Reichmann et al., 2016). In this way, we assume that the optimum membrane architecture and microstructure, would be with large grains ( $> 1 \mu\text{m}$ ) in the bulk and small grains ( $\sim 100 \text{ nm}$ ) at the membrane surface, as shown on Fig. 1.

Then, this paper is focused on the impact of membrane chemical composition and nanostructured porous coating on the surface exchange kinetics at both sides of the membrane. Several coating microstructures are tested on two membranes  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$  (LSFCo<sub>6482</sub>) and  $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.7}\text{Ga}_{0.3}\text{O}_{3-\delta}$  (LSFG<sub>5573</sub>) selected because the limiting steps for oxygen permeation are respectively surface and a mix surface/bulk (Ge et al., 2009).

## 2. Experimental

### 2.1. Perovskite powder synthesis and membrane manufacturing

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}$  (LSFCo<sub>6482</sub>) and  $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.7}\text{Ga}_{0.3}$  (LSFG<sub>5573</sub>) powders are synthesized, using a high temperature solid state reaction, from pure oxides and carbonate precursors:  $\text{La}_2\text{O}_3$  (99.99%, Alfa Aesar),  $\text{Fe}_2\text{O}_3$  (98%, Alfa Aesar),  $\text{Co}_3\text{O}_4$  (99.7%, Alfa Aesar),  $\text{Ga}_2\text{O}_3$  (99.99%, Sigma-Aldrich), and  $\text{SrCO}_3$  (99.9%, Sigma-Aldrich). Proper amounts of oxide and carbonate precursors are mixed and attrition-milled in ethanol media for 3 h at 600 rpm using zirconia balls ( $\Phi_{\text{balls}} = 800 \mu\text{m}$ ). Then, the mixture is separated from the balls, dried, and calcined at  $1100^\circ\text{C}$  for 5 h to obtain the final perovskite phase. The calcined powder is attrition-milled again into ethanol to obtain the desired monomodal grain size distribution centered on  $1 \mu\text{m}$ . The size distribution is measured using a laser granulometer (Horiba LA950).

Perovskite membranes are produced by tape casting process (Chartier, 1994). A slurry of the perovskite powder is elaborated from an organic solvent, a binder, a plasticizer, and a phosphate ester type dispersant. Plasticizer and binder are added to adjust slurry rheological behavior for tape casting. After casting, the green tape of  $150 \mu\text{m}$  thickness is dried and cut into 30 mm diameter disks. Those disks are stacked and thermo-laminated at  $70^\circ\text{C}$  under a pressure of 50 MPa, debinded and sintered to obtain a relative density more than 95% and a membrane thickness of about 1 mm.

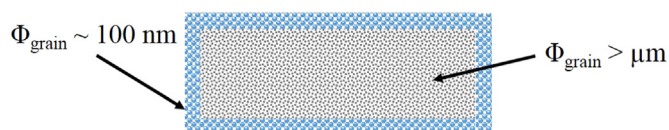


Fig. 1. Optimum membrane architecture according to previous work (Reichmann et al., 2016).

### 2.2. Perovskite sol preparation and coating manufacturing

The synthesis route of an ultra-divided perovskite has recently been reported by Vivet et al. (2014). The perovskite sol is prepared into a mixture of absolute ethanol, ammonia, and a surfactant. In parallel, a mixture of nitrate precursors ( $\text{Sr}(\text{NO}_3)_2$  ( $\geq 99.0\%$ , Sigma-Aldrich),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (98+%, Alfa Aesar),  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.9%, Alfa Aesar),  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (99.9%, Alfa Aesar) and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98.0–102.0%, Alfa Aesar)) is solved according to the stoichiometry desired into demineralized water. This last solution is added drop by drop in the first one. Finally, the mixture is refluxed 1 h at  $70^\circ\text{C}$ . The final solution becomes clear and the sol cooled down at room temperature to obtain a gel.

A coating of ultra-divided particles is performed on a dense membrane by dip-coating using the sol presented in previous section (Baque and Serquis, 2007). The dense membrane is dropped into the perovskite sol and removed with a constant speed of 10 mm/s. Then, the membrane is dried at room temperature to remove slowly the solvent and obtain a gel. The perovskite phase is obtained after calcination at  $1100^\circ\text{C}$  under air for 2 h (heating rate is  $1^\circ\text{C}/\text{min}$ ).

### 2.3. Chemical analysis and microstructure characterizations

The powder synthesized by solid state reaction and the one obtained by sol are both calcined at  $1100^\circ\text{C}$  for 5 h and 2 h respectively. The formation of a perovskite phase is confirmed by X-ray diffraction (Siemens D5000,  $\text{Cu-K}\alpha_1$ ). The density of the sintered membrane is determined by Archimedes method and the chemical composition of each batch by inductively coupled plasma atomic emission spectrometer (ICP-AES).

Mean grain size of the membrane and of the coating are measured by image analysis using Scanning Electron Microscopy (SEM, Cambridge Stereoscan 260).

### 2.4. Oxygen semi-permeation and surface exchange kinetics measurements

The oxygen semi-permeation and the oxygen activity at the membrane surfaces were measured using a homemade setup described in previous work and presented on Fig. 2. The membrane is sealed between two alumina tubes thanks to gold rings (done at  $980^\circ\text{C}$ ) (Vivet et al., 2011). The membrane separates two chambers, one where synthetic air is injected (oxygen rich atmosphere,

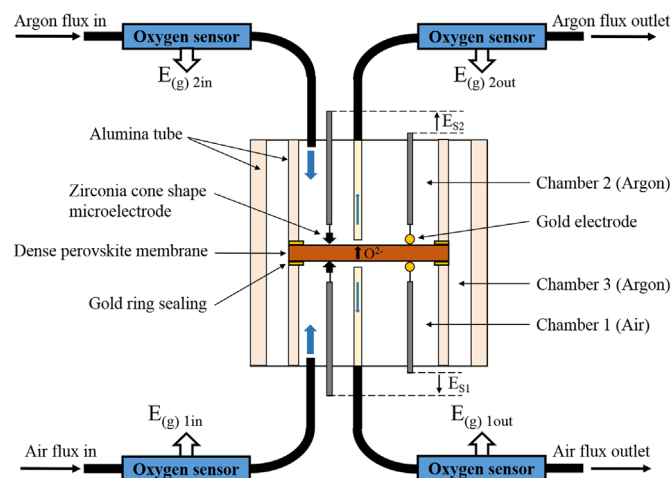


Fig. 2. Scheme of the homemade experimental setup used to determine oxygen semi-permeation flux and oxygen activities at membrane surfaces (Geffroy et al., 2013).

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