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Feature article

Shaping of 3YSZ porous substrates for oxygen separation membranes

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ABSTRACT

In recent years, asymmetric membranes based on mixed ionic-electronic conductors (MIEC) have gained importance in practical gas separations. MIEC ceramic materials show high-energy efficiency and high-temperature resistance, which allows direct integration in industrial processes. Thin layers are supported on porous substrates that provide mechanical strength. In the asymmetric membrane manufacture, the control of support porosity and microstructure is crucial. Colloidal processing is an interesting method that allows controlling the final microstructure in both surfaces and bulk, with high reproducibility. Here, the development of asymmetric membranes with a top functional layer made of $Ce_{0.8}Gd_{0.2}O_{1.9}/Ni_2FeO_4$ composite is presented and aims to maximize oxygen permeation and membrane robustness. The porous substrate is prepared by slip casting while the functional layers by screen-printing. The effect of pore former volume and particle morphology were studied. The combination of spherical and flake-like PMMA particles enabled to generate open porosity suitable for fast gas transport.

1. Introduction

Oxygen production has high impact in several industries due to both its use as a reagent in chemical processes and its use to provide a more efficient combustion in thermal processes. Therefore, there is a need to efficiently produce high-purity oxygen at different scales. The main way to obtain oxygen is by cryogenic distillation of air [1]. However, this process presents important drawbacks related to the high energy requirements and large plant size. One of the alternatives is the use of gas-separation ceramics membranes, which allows the selective permeation of the oxygen by diffusion through the ceramic oxide lattice. Among other advantages, ceramic membranes allow the *in situ* O_2 production at small-to-medium scale where other technologies such as the cryogenic are not economically feasible. This kind of membranes should present both ionic and electronic conductivity [2,3], since oxygen permeates thanks to the presence of oxygen vacancies in the crystalline lattice driven by the oxygen pressure gradient across the membrane, and a counter-diffusion of electrons occurs to balance the charge at both sides of the membrane. In contrast to the difficulty to find a single materials with high thermo-chemical stability and proper mixed ionic-electronic conduction, dual-phase composite materials have enabled reaching promising results [4]. In this paper, a combination of a spinel Ni_2FeO_4 (NFO) and a fluorite $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO) is used, obtaining a stable composite material able to permeate oxygen [5,6]. NFO spinel could present both n-type and p-type electronic conductivity depending on the different synthesis techniques and crystal sizes. The n-type behavior has been attributed to the presence of Fe^{2+}, which enables the electron hopping from Fe^{2+} to Fe^{3+}. The p-type behavior has been related to the presence of Ni^{3+} and hole hopping from Ni^{3+} to Ni^{2+}. The last can be assigned to the deficiency or excess in Ni, because a Ni excess corresponds to Fe^{3+} deficiency compensated with Ni^{3+} (p-type) while a Ni deficiency corresponds to a Fe^{2+} compensation (n-type) [7]. On the other hand, the CGO present high ionic conductivity and stability [8,9] and together with NFO generates a composite material with high O_2 permeation features but due to the presence of two phases, the influence of the grain boundary is relevant.

When the oxygen flux is determined by the transport through the membrane bulk, the flux at the steady state through membrane can be describe by the Wagner equation:

$$j_{O_2} = \frac{RT}{16F^2}\sigma_{amb}\frac{1}{L}ln\frac{p'_{O_2}}{p''_{O_2}} \quad (1)$$

where R is the gas constant (J/Kmol), T is the temperature (K), F is the Faraday constant (C/mol), σ_{amb} is the ambipolar conductivity, L is the membrane thickness (m) and p'_{O2} and p''_{O2} are the oxygen partial pressure at both membrane sides. Note that, for a sufficiently thin membrane, the permeation can be limited by other phenom-

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ena such as oxygen surface gas-solid exchange, gas transport in the porous substrate and gas transport in the open gas chambers.

According to the Wagner Eq. (1), a membrane should be as thin as possible in order to optimize the permeation flux. In this sense, asymmetric membranes allow reaching thin layers of the separation membrane with high mechanical properties without decreasing their flux properties [10,11]. These membranes are constituted by a dense layer of MIEC material/composite deposited on a porous substrate [12]. There is a wide range of techniques that allows preparing thin layers on different substrates [13–15]. The choice of the technique must be in accordance with the characteristics of both the layer and the substrate. For asymmetric membranes, suspension-spraying and screen-printing processes allow the deposition of the membrane layer with controller thickness with high reproducibility and superficial quality on plane substrate of different areas.

The requirements of the porous support respect to the MIEC layer are that they should present chemical compatibility, similar thermal expansion coefficient, good gas permeation and excellent mechanical properties under operation conditions [16]. In this sense, 3 mol% Yttria stabilized Zirconium (3YSZ) meets the requirements as substrate, due to it high chemical stability and high mechanical properties. As for the layer deposition, there are numerous processing routes to obtain porous 3YSZ substrate. In the recent years, substrate processing of asymmetric membranes has been focused in tape casting [17,18], freeze casting [19,20], pressing [21,22] and extrusion processing [23,24], while slip casting has been received less attention [25,26]. In previous works on membrane manufacture by slip casting, the porosity in the substrate was induced by careful control of (i) the particle size during processing and (ii) the thermal treatment. However, the use of pore-former particles enables to tailor the porosity and sinter the substrate at higher temperatures without much porosity loss, what in turn increases the membrane mechanical properties. On the other hand, slip casting is one of the most common industrial methods for ceramic processing that provides high dispersion degree of ceramic phases and accurate control of the microstructure in cast porous materials [27,28]. Slip casting is a simple, industrially and economically viable shaping technique and allows obtaining complex geometries/morphologies than other processing techniques. In addition, the colloidal processing implies the formation of suspensions in aqueous media, which is a drawback in the case of both non-oxide ceramic and metal particles, due to the elevated reactivity of these materials with the suspension media. From an electrochemical point of view, water is one of the more complex liquid media to work with. It has a very high polar moment, which requires careful control of the conditions of the suspensions [29,30].

The present work focuses on the development of asymmetric membranes by different processing methods with a top functional layer made of the $Ce_{0.8}Gd_{0.2}O_{1.9}/Ni_2FeO_4$/(CGO-NFO) dual-phase material with the aim to maximize oxygen permeation and membrane robustness under harsh operation conditions, *i.e.* high temperature, important pressure gradient across the membrane and high CO_2 concentrations. In this case, the porous substrate of the membrane is prepared by slip casting while the functional layer by screen-printing.

2. Materials and methodology

The membrane substrates were prepared using a commercial 3YSZ powder (TZ-3YS-E, TOSOH Corporation, Japan) with 90 nm of average particle size, a specific surface area of 7.30 m^2/g and 6.05 g/cm^3 of density. A micrograph of the as received powders is present in Fig. 1. As can be observed, the 3YSZ powder is formed by agglomerates of nanometric particles.

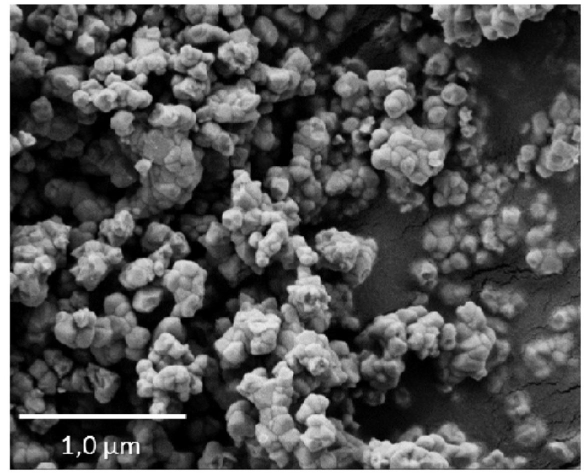

Fig. 1. Micrograph of the 3YSZ powder as received.

Table 1
Morphological characteristics of the PMMA particles.

Code	Size dv50 (μm)	Morphology	Reference
S-006	6.0	Spherical	MX-500, Esprix (USA)
S-020	20	Spherical	MX-2000, Esprix (USA)
S-050	50	Spherical	Altuglass BS100, Arkema (France)
F-150	150	Flakes	Porlat K85, Zschimmer & Schwarz (Germany)

The characterization of the colloidal properties of the 3YSZ comprised the zeta potential measurement as a function of pH and was performed using a suspension with a solid content of 0.1 g/L in 10^{-2} M KCl, using HTMA and HNO_3 to adjust the pH. Measurements were carry out using a Zetasizer Nano ZS (Malvern, UK).

In order to introduce porosity in the microstructure of the final body, different polymethylmethacrylate (PMMA) powders were added to the 3YSZ slurries. Table 1 presents the characteristics of the pore formers used in the slurries, and Fig. 2 shows the corresponding SEM micrographs.

To measure the rheology, a Haake Mars rheometer (Thermo Scientific, Germany) with a double-cone plate fix of 60 mm of diameter and angle of 2° (DC60/2°) was used. Tests were performed in a control rate mode (CR) shearing from 0 to 1000 s^{-1} in 2 min, dwelling at 1000 s^{-1} for 1 min and shearing down to 0 s^{-1} in 2 min and control stress from 0 to 6 Pa in 2 min and down to 0 Pa in the same time. All tests were done at a constant temperature of 23 ± 0.5 °C. The applied high-shear rates during up-ramps are enough to achieve a reproducible suspension microstructure, dependent only on the suspension composition, but not on the slurry preparation history [31]. The flow curves were fitted using the Cross model (Eq. (2)), which describes the pseudoplastic behavior.

$$\eta = \eta_\infty \frac{\eta_0 - \eta_\infty}{1 + (C\Upsilon)^n} \quad (2)$$

where η_0 and η_∞ are the extrapolation of the viscosity to zero and infinity respectively, C is a time constant and n is the rate constant, and it is a parameter which is related with the dependence of viscosity on the shear rate. The Cross model describes the limit behavior of the standing suspension and at infinite shear rate, therefore not only gives information about suspension viscosity but about its stability.

For the MIEC membrane layers, a combination of $Ce_{0.8}Gd_{0.2}O_{1.9}$ and Ni_2FeO_4 (CGO-NFO) was prepared by solid state reaction method, comprising the sintering of the ball-milled single oxides at 1250 °C followed by further ball milling. The particle size of the