



Design and optimization of porous ceramic supports for asymmetric ceria-based oxygen transport membranes



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ABSTRACT

The microstructure, mechanical properties and gas permeability of porous supports of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95-\delta}$ (CGO) were investigated as a function of sintering temperature and volume fraction of pore former for use in planar asymmetric oxygen transport membranes (OTMs). With increasing the pore former content from 11 vol% to 16 vol%, the gas permeabilities increased by a factor of 5 when support tapes were sintered to comparable densities. The improved permeabilities were due to a more favourable microstructure with larger interconnected pores at a porosity of 45% and a fracture strength of 47 ± 2 MPa ($m=7$). The achieved gas permeability of $2.25 \times 10^{-15} \text{ m}^2$ for a 0.4 mm thick support will not limit the gas transport for oxygen production but in partial oxidation of methane to syngas at higher oxygen fluxes. For integration of the CGO support layer into a flat, asymmetric CGO membrane, the sintering activity of the CGO membrane was reduced by Fe_2O_3 addition (replacing Co_3O_4 as sintering additive).

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1. Introduction

Oxygen transport membranes (OTMs) based on mixed ionic electronic conducting oxides (MIEC) are ceramic devices which can be used to extract pure oxygen from air and supply the oxygen into combustion processes or chemical reactions to improve process efficiencies [1–3]. Recently, thin film oxygen transport membranes based on chemically very stable materials, such as gadolinium doped ceria ($\text{Ce}_{0.1}\text{Gd}_{0.9}\text{O}_{1.95-\delta}$, CGO), have been shown to be able to sustain high fluxes of more than $10 \text{ Nml min}^{-1} \text{ cm}^{-2}$. CGO is a very chemically stable material and it should be possible to use the material in asymmetric OTMs for the direct integration into membrane reactors operating under harsh conditions (temperatures above $750 \text{ }^\circ\text{C}$ and reducing and aggressive gases), such as for syngas production [4–6] and oxidative coupling of methane (OCM) [7].

One of the drawbacks in utilizing single phase, mixed conducting CGO as a membrane material for OTMs is the limiting electronic conductivity at temperatures below $750 \text{ }^\circ\text{C}$ and at relatively high oxygen partial pressures [8,9]. For this reason, membranes based on CGO can only reach the flux targets required

for economical competitiveness if a couple of requirements are fulfilled: (1) a membrane layer thickness well below $50 \text{ }\mu\text{m}$, which can be realized by the deposition of the dense membrane layer on a porous, mechanically strong supporting ceramic structure, resulting in a so called asymmetric thin film membrane, (2) very reducing conditions ($p\text{O}_2 < 10^{-12} \text{ atm}$) on one side of the membrane (“fuel side”) to enhance the electronic conductivity of the material (by reduction of Ce^{4+} to Ce^{3+} ions in the fluorite structure) and (3) a large applied driving force during membrane operation (large $\Delta p\text{O}_2$ between the fuel and air side). Asymmetric CGO membranes were therefore first tested for applications that fulfil these requirements. In laboratory scale tests, a high oxygen flux of $16 \text{ Nml cm}^{-2} \text{ min}^{-1}$ at $900 \text{ }^\circ\text{C}$ was obtained for a $30 \text{ }\mu\text{m}$ thick CGO membrane on a porous Ni-YSZ support, which was operated under conditions relevant for syngas production [4,5]. Additional requirements for the asymmetric membrane architecture are determined by the properties and fabrication methods of the catalytic layers and the porous ceramic support. For example, in the case of the planar, asymmetric CGO membranes investigated for syngas production [4], the membrane consisted of a tape casted, thick porous Ni-YSZ support and an active Ni-YSZ catalyst layer, which were laminated together with a thin CGO membrane layer and subsequently co-sintered at a relatively high temperature of about $1300 \text{ }^\circ\text{C}$ (see Fig. 1a).

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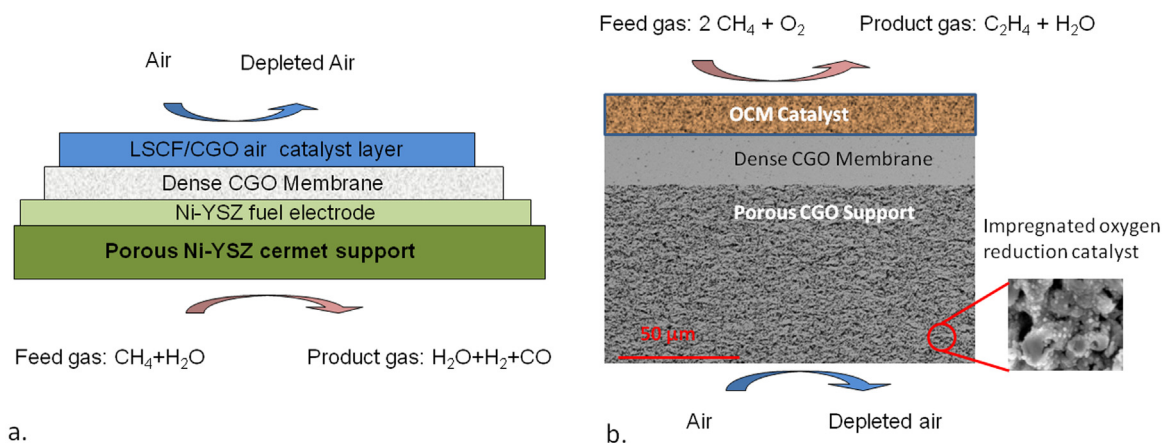


Fig. 1. Schematic of different asymmetric CGO membrane architectures tested for OTM applications: (a) Ni-YSZ supported membrane for syngas production on the permeate (fuel) side [4] and (b) porous ceramic supported membrane which allows catalyst flexibility by infiltration after firing [10]. On the air side of the membranes an additional oxygen reduction catalyst was applied for both asymmetric membrane types after co-firing of the multilayer (in case b, the air catalyst was $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ as described in [10]).

A porosity of more than 35%, required for gas transport through the support structure, was introduced into the 0.3 mm thick NiO-YSZ support by the volume change resulting from reducing the NiO to metallic nickel [11–14]. If such asymmetric CGO membranes should be used for further applications in membrane reactors, for example in OCM [7], the nickel catalyst in the Ni-YSZ supports (used for syngas application) needs to be replaced by a more suitable catalyst (e.g. $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$). Hence, for a flexible design the Ni-YSZ cermet support should be replaced entirely by a catalyst free (nickel free) porous ceramic material that could be used as a generic support for various catalysts/chemical reactions. A specific catalyst system as required for a specific chemical reaction can then be introduced into the sintered ceramic support structure by infiltration techniques [10]. Several support materials, such as 3YSZ, MgO and CGO were considered. Regardless of the selected material, the design of a new ceramic support requires a microstructure with

- Sufficient gas permeation and mechanical strength (both influenced by the porosity),
- a good thermomechanical and chemical match with the thin film CGO membrane layer, e.g. avoiding chemical reactions between the layers and minimization of thermal stresses.
- Tailored sintering behaviour (shrinkage) of the individual layers for co-sintering in an asymmetric structure.

We shall discuss these requirements in more detail below. With respect to requirement (a), a high gas permeability of a porous ceramic support structure should be achieved by creating sufficient open porosity in the range of 30–40% (after firing). Different approaches can be adopted to produce a support structure with sufficient porosity. One of the most suitable approaches is the use of a sacrificial pore former, especially if a co-firing of asymmetric porous-dense multilayers is considered. For this case the pore former, e.g. graphite, is added to the tape casting formulation and is subsequently removed during de-binding to produce the required pores. Corbin et al. [15] showed that graphite is an efficient pore forming agent that can be added in variable amounts to create porosities between 20% and 80% in tape-casted layers (of yttrium stabilized zirconia (YSZ)) without a significant change in the total shrinkage during sintering. To ensure good gas permeability through a porous membrane support and sufficient mechanical strength, the open porosity should usually be in the range of 35–50% depending on the thickness and microstructure of the support structure (at thicknesses of 0.5–1.5 mm). The oxygen flux through an asymmetric membrane can even be limited by gas

diffusion in a fine porous support structure with a thickness below 0.5 mm if the pores are narrow and if the pores are then partly infiltrated with catalyst material [16].

It was reported that an open percolating porous network can be formed in a ceramic body if inclusions (e.g. pore former with similar sized particles as the ceramic) exceed a volume fraction of 16% [17]. Alternatively, porosity may be introduced in the support structure by inhibiting the sintering activity of the ceramic by using a relatively coarse-grained powder (with particle size in the micron range). However, this can introduce a differential sintering shrinkage between the (coarse-grained) porous support and the fine-grained membrane layer which will result in stresses that cause defects in the bi-layer structure during the subsequent co-firing [18]. It is also a requirement that the support structure has sufficient porosity to ensure the infiltration of catalyst material into the region close to the support/membrane interface.

For requirement (b), a good thermal and chemical expansion match and full material compatibility (avoiding reactions between support and membrane layer) can be ensured by using a membrane architecture based on the same material (CGO) in both layers. Such an asymmetric membrane of a CGO membrane on a porous CGO support was therefore chosen as a starting point for a proof of concept demonstration, as visualized schematically in Fig. 1b.

Furthermore, CGO is known to be a good ionic conducting (or under reducing conditions a mixed ionic-electronic conducting) electro catalyst that can extend the reaction zone (3 phase boundary) for oxygen removal into the catalytic layer [19] by increasing the “active” interface between the membrane layer and the active catalytic layer (here porous CGO support with respective catalysts). Finally, for the implementation of a porous CGO support in such an asymmetric CGO bi-layer, one of the most critical steps is the identification of a suitable co-firing procedure (requirement (c)). In this step the membrane layer should be completely densified, simultaneously the porous support layer should sinter to a degree that sufficient mechanical strength is achieved (with open porosity between 30% and 45%), whereas at the same time thermally induced stresses between the two layers due to mismatch in differential shrinkage should be minimized. Based on previous studies on asymmetric porous/dense CGO bilayer structures, it is known that such structures can be produced by a co-firing process at relatively low temperatures (~ 1050 °C) if sintering additives, such as Co_3O_4 are used [20,21]. Furthermore, theoretical sintering models have been developed that describe and confirm the distortion (camber) and shrinkage kinetics for such porous/dense CGO bi-layers [18,22].

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