



Fabrication and performance of a tubular ceria based oxygen transport membrane on a low cost MgO support



D.K. Ramachandran^{a,*}, M. Søgaaard^a, F. Clemens^b, J. Gorauskis^a, A. Kaiser^a

^a Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, Building 779, DK-4000 Roskilde, Denmark

^b EMPA, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for High Performance Ceramics, Ueberlandstrasse 129, CH-8600 Dübendorf, Switzerland

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ABSTRACT

A 30 μm thin-film tubular CGO ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95-\delta}$) membrane with catalytic layers on both sides has been prepared by dip-coating on a low cost, porous magnesium oxide (MgO) support. The MgO support was fabricated through a thermoplastic extrusion process. Support, thin membrane and catalytic layers were sintered in individual steps at temperatures between 1250 and 1300 $^{\circ}\text{C}$ to achieve a controlled removal of binder and organic additives and to obtain the desired, defect free microstructure. The prepared asymmetric tubular CGO membrane has been tested at elevated temperatures (up to 900 $^{\circ}\text{C}$) using atmospheric air and N_2 , H_2 for the feed and sweep side respectively. The oxygen permeation was 4 $\text{N ml min}^{-1} \text{cm}^{-2}$ at 850 $^{\circ}\text{C}$ using H_2 on one side and air on the other side.

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1. Introduction

Gadolinium doped ceria, CGO, is widely used in high temperature electrochemical devices such as solid oxide fuel/electrolysis cells (SOFC/SOEC), membranes and flue gas purification devices. The high phase stability of CGO under both oxidizing and reduction atmospheres and the high ionic conductivity, makes CGO an interesting material for an Oxygen Transport Membrane (OTM). Furthermore, it has been shown CGO becomes a mixed ionic and electronic conductor (MIEC) at high temperatures and low oxygen partial pressure, with sufficiently high electronic conductivity above 800 $^{\circ}\text{C}$ and under strongly reducing atmosphere [1]. An OTM is a gas-tight component permeable only to oxygen, giving 100% theoretical selectivity. The use of such membranes to provide oxygen for different industries i.e. steel, cement and syngas production, can improve the energy efficiency in the production cycle and further in some cases facilitate an easier CO_2 capture and sequestration. Developing a high performance OTM-system is a challenging task as material development, ceramic processing and system integration must be considered.

The oxygen permeation flux of various fluorite structured membrane materials for wide range of membrane thickness (50–2000 μm) have been reported [2]. In order to achieve fluxes that are of commercial interest for most of the large scale applications

it is clear that thin film membranes with thicknesses below <100 μm must be prepared. Such thin membrane are typically not mechanically stable. In order to reduce the membrane thickness without sacrificing mechanical properties of the overall component, an asymmetric membrane configuration can overcome the problems associated with mechanical stability. Previously, Kaiser et al. [3], have reported oxygen fluxes of more than 10 $\text{N ml min}^{-1} \text{cm}^{-2}$ at 850 $^{\circ}\text{C}$ on a 30 μm thick planar CGO membrane supported by a Ni-YSZ cermet support in which the different layers were prepared by tape casting and subsequent lamination. The CGO membrane showed good thermal and chemical stability at syngas operation conditions.

When the membrane layer gets below a certain characteristic thickness, the catalytic processes on the surface of the membrane might become a limiting factor of the membrane performance. In order to improve the oxygen flux further the surface exchange kinetics have to be enhanced on both sides of the membrane, which is typically done using electro-catalytic materials. Ni- $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (Ni-CGO), ceramic-metal composites (cermet) have been widely used as electro catalytic material in SOFCs [4,5] in which the metallic form of Ni acts as catalyst for fuel oxidation and provides electronic conductivity, whereas CGO not only acts as a matrix to support the catalyst but it also transports oxygen ions out from the structure [6–8]. Moreover, a Ni-CGO cermet can easily be combined with a CGO membrane instead of using the traditional yttria stabilized zirconia (YSZ) due to the thermal expansion coefficients (TEC) of YSZ (i.e. $\sim 10.5 \times 10^{-6} \text{K}^{-1}$) which

* Corresponding author. Tel.: +45 4677 4800; fax: +45 4677 5858.

E-mail address: dhavaa@gmail.com (D.K. Ramachandran).

is significantly lower than that of CGO and MgO which was $\sim 12.7 \times 10^{-6} \text{ K}^{-1}$ and $\sim 13.9 \times 10^{-6} \text{ K}^{-1}$ respectively [9,10].

Perovskites structured materials such as $(\text{La, Sr})(\text{Co, Fe})\text{O}_3$ have been vastly used as oxygen reduction catalysts in SOFC and for OTMs [11]. It has also been demonstrated that electrodes with very high catalytic activity can be prepared by infiltration of these materials into porous ionic conducting backbone structures [12]. Additionally, Zhao et al. [13], have reported that LSC catalytic layers prepared by this route show remarkable performance in terms of high resistance to thermal cycling and thermal shock due to using of impregnated nano catalytic particles rather than bulk particles.

For the preparation of asymmetric membranes, a planar structure configuration is usually chosen because of the simple fabrication [14]. Changing to a tubular design has some advantages compared to a planar design especially in terms of mechanical strength when the component is in a temperature gradient. Additionally, the sealing of tubular components, especially if high pressure is considered is much less difficult [15]. Some studies on the preparation and testing of an asymmetric tubular perovskite membrane structure have been reported earlier [16]. In these studies identical materials for dense layers and porous supports were mainly used. Recently, Liu et al. [17] demonstrated that a crack-free asymmetric tubular perovskite membrane with a thickness of $20 \mu\text{m}$ could be prepared using extrusion and a spray drying processing step. With the asymmetric design the oxygen flux performance was almost 1.35 times higher than with the symmetric configuration and the membrane was stable under low $p\text{O}_2$ conditions over 200 h. It is evident to see that the membrane performance and stability could be improved by an asymmetric configuration. Moreover, to the author's knowledge studies are not available that deal with the preparation and testing of

asymmetric tubular CGO membranes for use in syngas reactors or in similar applications. Hence this work contribute to closing the research gap in this area.

This present work addresses the preparation and characterization of a gastight membrane layer of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95-\delta}$ (CGO10), supported on a low cost porous MgO tubular substrate [18]. On each side of the CGO membrane a catalytic layer is present in order to improve the electro-catalytic reaction. The optimization of the de-binder and sintering cycle is optimized as to allow for an effective removal of binder organics and co-sintering of a defect free asymmetric membrane multi-layer structure. The oxygen permeation flux for the tubular, MgO supported CGO membrane is measured in the temperature range of $750\text{--}900^\circ\text{C}$ under conditions relevant for syngas operation.

2. Material and methods

Fig. 1(a) shows a schematic of the prepared asymmetric tubular membrane architecture in which the porous MgO support was fabricated using thermoplastic extrusion and the membrane and catalytic layers were prepared through a dip-coating process from stabilized ceramic suspensions. This was followed by impregnation of catalytic material into the porous backbone on the outside of the membrane. Please notice that the colors in the schematic in Fig 1(a) do not correspond to the colors of the layers shown in different processing steps in Fig. 1(b)–(e). This is due to the fact that most of the layers do change color during firing. Fig. 1(b)–(e) shows photographs of tubular membranes after each progressing step, before and after firing (left and right part of the pictures). The process starts from the extrusion of the MgO tubes, followed by dip-coating and sintering of the catalytic NiO–CGO layer (brown after dip-coating, green in color after firing at 1250°C , Fig. 1(c)),

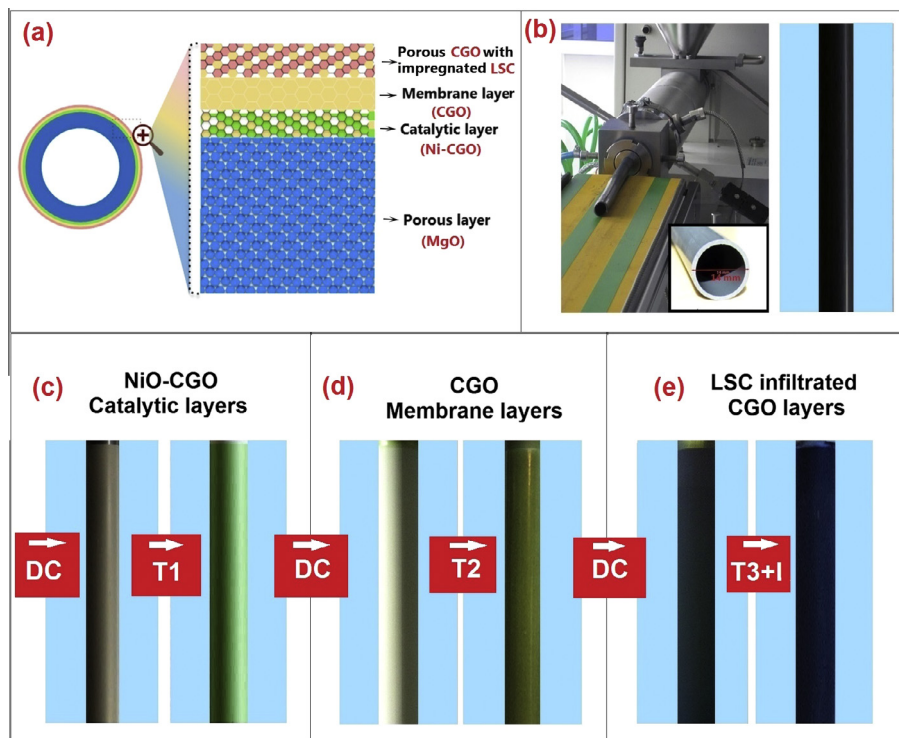


Fig. 1. (a) Schematic of the structure of the asymmetric tubular membrane including the used materials, (b) the thermoplastic extrusion of MgO tubes (black in green state due to graphite pore former) and the subsequent dip coating and firing steps with (c) MgO tube with dip coated Ni–CGO layer (brown, on left) and after pre-sintering at $T_1 = 1250^\circ\text{C}$ (green, on right), (d) dense CGO membrane layer after dip coating (DC) (white, on left) and sintering at $T_2 = 1300^\circ\text{C}$ (transparent on green NiO–CGO layer), (e) “porous” CGO layer after dip coating (black, on left) and after sintering at $T_3 = 1250^\circ\text{C}$ and infiltration (I) with LSC nano particles (blue, on right). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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