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# On the use of supported ceria membranes for oxyfuel process/syngas production

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ABSTRACT

Ceramic oxygen transport membranes (OTMs) enable selective oxygen separation from air at high temperatures. Among several potential applications for OTMs, the use in (1) oxygen production for oxyfuel power plants and (2) the integration in high-temperature catalytic membrane reactors for alkane upgrading through selective oxidative reactions are of special interest. Nevertheless, these applications involve the direct contact of the membrane surface with carbon-rich atmospheres. Most state-of-the-art permeable membranes are based on perovskites, which are prone to carbonation under operation in $CO_2$-rich environments and/or decomposition in reducing gas environments. The oxygen flux through supported thin film membranes of $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ (CGO) with 2 mol.% of cobalt was measured for oxygen separation in oxyfuel processes and in syngas production and degradation was compared to perovskite membranes. The CGO membranes consist of a 27 μm-thick gastight CGO layer supported on a porous CGO substrate. The flat surface of the membrane was coated using two different porous catalytic layers aiming to improve the oxygen activation rate on the permeate side while the porous substrate was infiltrated with an oxygen reduction catalyst. Oxygen separation was studied using air as feed and argon/$CO_2$ or argon/$CH_4$ mixtures as sweep gas in the temperature range 750–1000 °C. The supported membrane exhibited a maximum oxygen flux of ca. 5 ml min$^{-1}$ cm$^{-2}$ at 1000 °C when diluted methane was used as sweep gas. The CGO membrane showed high stability in $CO_2$ (in contrast to tests on $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) membranes) and no detrimental effect on the oxygen flux is observed when $CO_2$ is present in the sweep gas even at temperatures below 800 °C. Moreover, the SEM analysis showed that membrane integrity remained stable after the permeation tests using $CO_2$.

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## 1. Introduction

Ceramic mixed ionic-electronic conducting (MIEC) membranes enable the selective oxygen separation from air at high temperatures. Two key industrial applications of oxygen-transport membranes are (1) oxygen production for power generation from fossil fuel in oxyfuel power plants [1,2] and (2) the integration in high-temperature catalytic membrane reactors for methane or alkane upgrading by selective oxidative conversions, for instance, partial oxidation of methane (POM) to produce syngas [3,4]. However, these applications involve the contact with carbon-bearing atmospheres and most of state-of-the-art highly permeable MIEC membranes do not tolerate the operation under $CO_2$-rich environments, due to carbonation processes [5–7]. The most promising materials are perovskites with the formula $ABO_3$ [8], comprising alkali-earth metal cations in the *A*-position. High oxygen permeation fluxes have been reported even in oxidizing conditions, for single phase materials such as $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) [9], $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) [10,11], $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [12]. However, these perovskites are chemically unstable under large oxygen chemical potential gradients (e.g. air/methane) and in presence of $CO_2$, $SO_2$ or $H_2O$, leading to degradation in oxygen flux and possibly mechanical integrity with time [6,7,13].

Lanthanide substituted ceria materials present a combination of high oxygen-ion mobility and chemical compatibility with water and carbon dioxide at high temperatures. *n*-type electronic conductivity can be introduced into the structure by partial reduction of the cerium (IV) ion at high temperatures under reducing conditions. Recent reports show the potential of oxygen separation in monolithic doped/multidoped ceria membranes [14–16]. Moreover, gadolinium doped ceria ($Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$, CGO) was suggested as oxygen separation membrane for syngas application. On planar, thin film CGO membranes on porous NiO-YSZ supports oxygen fluxes as high as 16 ml min$^{-1}$ cm$^2$ could be obtained by placing the membrane between air and humidified hydrogen (or methane) at 900 °C [17,18].

The present work shows the functional characterization of oxygen separation membranes made of a gastight thin film layer of

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$Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ (CGO), supported on a porous CGO substrate. The top flat surface of the membrane was coated using two different porous catalytic layers aiming to improve the oxygen activation rate on the permeate side. Oxygen separation was studied using air as feed and argon/$CO_2$ or argon/$CH_4$ mixtures as sweep gas in the temperature range 750–1000 °C. Special attention is paid to the membrane stability in $CO_2$ under operation.

## 2. Experimental

A thin film CGO membrane supported by a porous CGO substrate was prepared using tape casting, lamination, co-sintering and cutting. The ethanol based slurries for tape casting of the support and membrane layer were prepared by ball milling an ultra low surface area powder of CGO from Rhodia S.A. (France), a PVB based binder system and a polyethylene imine (PEI, branched, M.W. 10,000, 99% Alfa Aesar) as a dispersant. 2 mol.% of cobalt(II) nitrate (cobalt(II) nitrate hexahydrate, 97.7% min, Alfa Aesar) was added as a sintering aid after drying in a desiccator to remove excess water. In the slurry for tape casting of the porous CGO substrate about 5 vol.% graphite (V-UF1, 99.9, Graphit Kropfmühl AG, Germany) was added as a pore former. The tape casted layers of the thin film CGO membrane and the porous CGO support were combined by lamination (i.e., application of heat and pressure on to the tubes between two rolls). Round membranes (Ø = 34 mm) were stamped out from the green membrane tapes before sintering. In a binder removal step the organics were removed by a very slow de-bindering profile to avoid damage of the structure. Subsequently, the structure was sintered in air at 1300 °C for 2 h. The sintered membrane structures were laser-cut to the final dimensions (diameter of 15 mm, total thickness of about 0.3 mm and a CGO membrane thickness of about 25 μm). After sintering, the porous supports of CGO were impregnated with nitrates corresponding to the nominal composition $La_{0.6}Sr_{0.4}Co_{1.05}O_{3-\delta}$ (LSC40). In a previous study it has been shown that LSC40 impregnated in a very porous (>70%) and thin (25 μm) backbone structure provided a highly active oxygen reduction electrode/activation layer [19]. In that case it was found that an optimal performance was found if LSC40 was impregnated in an amount corresponding to 17 vol.% in the CGO backbone. The impregnation for the supports characterized here was carried out in a similar way as by Samson et al. [19], except that the cells between each impregnation were inserted directly into a furnace at 350 °C.

On top of the CGO membrane layer, a porous catalytic layer was applied by screen-printing. The catalyst layers were composed of either $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) or cobalt-doped $Ce_{0.8}Tb_{0.2}O_{2-\delta}$ (CeTbO + Co). BSCF powder was provided by Fraunhofer IKTS (Hermsdorf, Germany) and cobalt-doped $Ce_{0.8}Tb_{0.2}O_{2-\delta}$ (CeTbO + Co) was prepared by a co-precipitation route following the procedure described in Ref. [14]. Formation of the corresponding crystalline structure (perovskite or fluorite) was checked by X-ray diffraction, using a Philips X'pert Pro equipped with X'celerator detector using monochromatic Cu Kα radiation. XRD patterns were recorded in the $2\theta$ range from 10 to 90° and analyzed using X'pert Highscore Plus software (PANalytical). The screen-printing inks were prepared by mixing the ball-milled powders with a solution of 94 wt.% terpineol and 6 wt.% ethylene cellulose. Graphite (Aldrich) was added as a pore former in the screen-printing ink. Then, graphite is removed in the ulterior sintering step. This process generates a macroporous system that aims to promote the gas transport through the catalytic layer. The ink homogenization was conducted using a three-roll mill. The coated membranes were sintered in air for 2 h. The sintering temperature of the screen printed layers results from the diverse sintering activities of each material, thereby the membrane with a BSCF coating was sintered at 1010 °C and the membrane with a CeTbO + Co coating, at 1050 °C. The material CeTbO + Co has been chosen for the following reasons [14]: (1) stability in $CO_2$-bearing atmospheres; (2) mixed ionic-electronic conductivity at high $pO_2$ and high temperatures; and (3) high surface exchange activity as determined by conductivity relaxation. Fig. 1 shows a schematic cross section of the membrane assembly and details of the testing setup. The microstructure of the membranes was analyzed by SEM and EDS in a JEOL JSM6300 electron microscope.

$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LSCF) monolithic membranes were prepared as reference by uniaxial pressing followed by sintering at 1250 °C. The final membrane dimensions were 15 mm in diameter and ~0.8 mm thickness. After sintering the membrane surface was polished prior to testing.

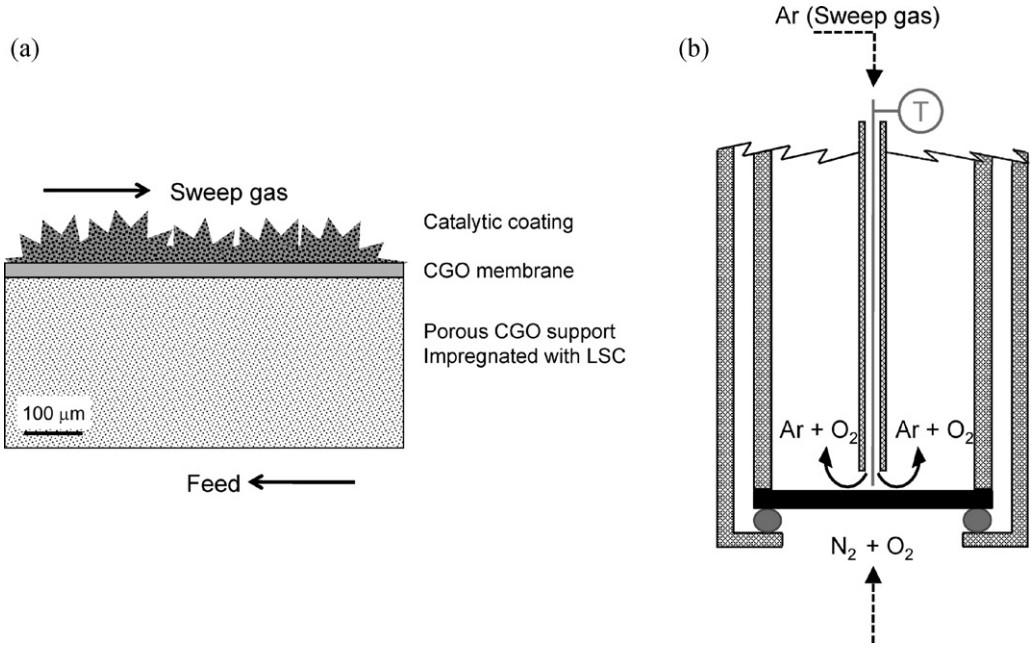


**Fig. 1.** (a) Scheme of a cross section of the assembly thin film CGO membrane. (b) Schematic of the quartz membrane reactor design.

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