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Evaluation of thin film ceria membranes for syngas membrane reactors—Preparation, characterization and testing

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ABSTRACT

Gadolinium doped ceria ($Ce_{0.1}Gd_{0.9}O_{1.95-\delta}$, CGO10) was investigated as oxygen separation membrane material for application in syngas production. Planar, thin film CGO10 membranes were fabricated by tape casting and lamination on porous NiO-YSZ supports and subsequent co-sintering. High oxygen fluxes, up to 16 N ml cm^{-2} min^{-1} at 900 °C, were obtained when placing the membrane between air and humidified hydrogen ($H_2/H_2O = 20$). Initial experiments for syngas production were performed by testing the CGO10 membrane with methane and steam feed.

The mechanical integrity of CGO10 membranes during operation (heat up, cooling, reduction and re-oxidation) was also investigated. Chemically induced stress in the CGO10 membrane due to harsh reduction of the CGO10 material at high temperatures and very low pO_2 values can lead to mechanical failure by lattice expansion. Calculations of the oxygen non-stoichiometry profile in the 30 μm thin CGO membrane under operation reveal that due to oxygen permeation in the membrane the largest non-stoichiometry at the permeate (fuel) side is more than a factor of 6 times smaller at 850 °C than that expected for CGO10 at equilibrium. The related relative expansion of the thin film CGO membrane should therefore lie below the expansion limit of 0.1% expected to be critical for mechanical stability and thereby allows for operation at high temperatures and low oxygen partial pressures.

1. Introduction

Methane (CH_4) is one of the main components of natural gas and biogas and a very important energy carrier. Considerable effort has been invested recently in upgrading of methane into higher hydrocarbons by Fischer Tropsch synthesis or into methanol [1,2]. Both routes require the conversion of methane into syngas. Oxygen membrane reactors have been investigated as potentially cleaner and more energy efficient technology for producing syngas than conventional technologies (e.g., conventional steam reforming). Oxygen membrane reactors can be seen as the integration of an oxygen separation unit that feeds pure oxygen into a chemical reaction, and a catalytic process in a single reactor. For the case of syngas production, dense mixed oxygen ion and electron conductors (MIECs) can be used to feed pure oxygen into a catalytic partial oxidation (CPO) reaction to convert methane into syngas. Partial oxidation with direct feed of pure oxygen is an efficient and clean process and results in the desired product ratio of H_2/CO of 2 suitable for Fischer Tropsch synthesis [2].

Research and development is therefore focused on the investigation of MIEC membrane materials, which are suitable for the use in syngas or oxygen membrane reactors regarding high oxygen flux and stability in syngas atmosphere [3–6]. Furthermore, for the application of the membrane in syngas specific catalyst coatings on both sides of the membrane are required to promote the desired chemical reactions at the electrode surfaces. At the feed side of the membrane a catalyst promoting the splitting of gaseous oxygen should be used, typically air electrodes (cathodes) similar to those developed for solid oxide fuel cells. At the permeate side, a catalyst that promotes the formation of the desired product should be used; for syngas production this would typically be a catalyst based on noble metals or nickel. In the past, various perovskite based membrane materials have been proposed for application as oxygen membranes due to the relatively high mixed conductivity of this class of materials [7]. In most studies the perovskites were applied as self-supported membranes with a considerable thickness in the range of millimeters, which makes processing easier, but requires well conducting materials due to a thickness limited (bulk-diffusion limited) oxygen flux. Less data are reported on thin film perovskite membranes for syngas application,

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but the target value of oxygen flux for commercial application of 10 N ml min^{-1} cm^2 can be reached [6–10] at temperatures between 850 and 950 °C or possibly exceeded, with measured oxygen fluxes as high as 31 N ml min^{-1} cm^2 for a $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ component at 1000 °C [11]. Materials with the perovskite structure that have a high ionic conductivity are generally unstable at high temperatures and low pO_2, and therefore unsuitable for the application of syngas production. Furthermore many of those perovskites are intolerant towards CO_2 [12].

A class of materials that offers high stability, tolerance against CO_2 and high ionic conductivity at high temperatures is doped ceria. Gadolinium doped ceria (CGO), has attracted much interest as electrolyte material for intermediate temperature solid oxide fuel cells (IT-SOFC) operating at temperatures below 550 °C [13–16]. At such low temperatures ultra-thin CGO electrolytes (<10 μm) have sufficiently high ionic conduction and negligible electronic conductivity. Furthermore, doped ceria materials are attractive as the ceramic component in Ni ionic conductor-composite anodes in SOFC, because of the high electronic conductivity of doped cerias in a fuel atmosphere [17,18]. Another potential advantage of doped ceria materials is their (potential) use as catalysts for chemical reactions, such as oxidation or partial oxidation of hydrocarbons. Therefore, doped ceria seems suitable as a catalyst for methane reforming or partial oxidation at the anode of a SOFC or in a syngas reactor, because of its ability to inhibit carbon deposition [19].

Experimental documentation of the suitability of CGO as an oxygen membrane for application in chemical reactors has according to the authors' knowledge so far not been reported. This is most likely because the oxygen fluxes are expected to be very low at temperatures below 800 °C for membrane thickness much above 100 μm, and if the driving force is small. A low driving force at the membrane is expected, if the pO_2 on the permeate side is not very low (not strongly reducing) and if the oxygen partial pressure differences between the feed and permeate side Δp is much smaller than 10^{-12} atm. Nevertheless, under reducing atmospheres ($pO_2 < 10^{-12}$ atm at the permeate side and air at the feed side) and temperatures above 550 °C, the oxygen nonstoichiometry of CGO10 increases accompanied by partial reduction of Ce^{4+}-ions to Ce^{3+} and introduction of electronic conductivity. The mixed conductivity increases with temperature and decreasing oxygen partial pressures. CGO10 has therefore been considered and modeled as membrane material for a membrane reactor for syngas synthesis [20] due to the significant mixed conductivity of CGO10 at temperatures above 750 °C and very reducing atmosphere. According to this study, thin film CGO10 membranes with a thickness below 100 μm should be able to yield oxygen permeation fluxes larger than 10 N ml cm^{-2} min^{-1} above 800 °C in a syngas atmosphere.

For the practical application of CGO10 in membrane reactors a potential drawback of the material is its high linear chemical expansion that can reach values of about 1.5% by switching from air to reducing atmosphere at high temperatures (1000 °C) [21,22]. Sarantaridis and Atkinson [23] calculated that a thin film YSZ membrane would mechanically fail on a Ni-YSZ support, if the linear expansion of the latter would exceed 0.1% creating tensile stresses in the membrane. Hendriksen et al. discussed failure modes for mixed conducting perovskite membranes for syngas production related to chemical expansion and thermodynamic instabilities [24,25] and also reports on expansion in the range of 0.1–0.3% may well be critical for integrity. On the other hand unusual stress relaxation mechanism were recently reported in thin film CGO layers with high concentrations of point defects, which could toughen ceria membranes (described as "chemical stress effect") [26,27].

In this paper we present the preparation and thorough characterization of thin film CGO10 ($Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$) membrane demonstration pieces for potential use in syngas reactors or similar chemical reactors, including oxygen flux measurements, the modelling of non-stoichiometry gradients along the membrane and considerations on resulting mechanical behavior (chemical and thermal expansion).

2. Experimental

2.1. Raw materials

Four different powders of CGO10 from Rhodia S.A. (France) with different surface areas were used for the development of the thin film membrane layers. The specific surface areas were 7 m^2/g for the powder with ultra low surface area (ULSA), 13 m^2/g for the low surface area powder (LSA), 21 m^2/g for the high surface area type (HSA) and 35 m^2/g for the ultra high surface area powder (UHSA). The powders are described in more detail elsewhere [28]. For the preparation of the porous Ni/YSZ membrane support a NiO powder and an YSZ (yttria stabilized zirconia) powder was used.

2.2. Membrane preparation

For the preparation of the membrane layers the CGO10 powders were dispersed in a tape casting slurry by ball milling. The resulting CGO10 slurry was cast to a thickness of approximately 50 μm (after drying), which corresponded to a final tape thickness of about 30 μm after sintering. Additionally, a 300 μm thick NiO/YSZ tape for the porous support structure was prepared in a similar way using NiO and YSZ powders. The details on the preparation of the NiO/YSZ support structure have previously been reported [29]. A catalytic active layer of fine NiO and YSZ powder was applied on top of the tape casted structure by wet powder spraying. The CGO10 thin film membrane layer was then applied on the porous tape casted Ni-YSZ support by lamination (application of pressure and heat between two rollers). Before sintering a very slow de-bindering cycle was applied to avoid damage of the laminated structure. The laminated sandwich structure of the NiO-YSZ support and the CGO10 membrane layer were co-sintered in air at a temperature above 1300 °C for more than 10 h. Fig. 1 shows a picture of a Ni-YSZ supported CGO10 membrane with the dimensions of 13 cm × 13 cm after co-sintering. The CGO10-membrane is transparent, indicating that the layer is dense and free of cracks and pinholes.

For oxygen flux measurements the larger CGO10 membrane pieces (13 cm × 13 cm) were laser-cut into 4 smaller pieces of 5.3 cm × 5.3 cm. In a second step, a porous, 30 μm thick composite air electrode comprising a mixture of an oxygen reduction catalyst of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF, HC Starck GmbH, Germany), and CGO10 (Rhodia S.A., France) was applied on the thin CGO10 membrane layer by screen printing. For the preparation of the screen printing ink the LSCF and the CGO10 powders were dispersed in a screen printing vehicle by ball milling and 3-roll milling. After screen printing the air electrode was dried at approximately 120 °C in a drying furnace and sintered at 1080 °C for 2 h.

For reduction of CGO10 membranes and determination of the potential mechanical failure the larger pieces were cut into strips of 12.5 cm × 1.5 cm (see Section 3.2.2).

2.3. Membrane and membrane layer characterization

The microstructure of the membrane, and in particular the integrity of the thin film CGO10 layer, was investigated by scanning electron microscopy (SEM) using a Hitachi TM1000 and a FE-SEM Zeiss Supra 35 electron microscope. Furthermore, the membrane surface was checked for defects and pinholes by light microscopy and an ethanol test, in which the possible leakage of ethanol through the thin membrane layer was inspected visually.

The gas-tightness of the 30 μm thick CGO10 membranes on the NiO-YSZ supports was additionally tested with a nitrogen based