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*Publication date:*  
2015

*Document Version*  
Peer reviewed version

[Link back to DTU Orbit](#)

*Citation (APA):*

Ovtar, S., Gorauskis, J., Bjørnetun Haugen, A., Hendriksen, P. V., & Kaiser, A. (2015). Oxygen permeation of dense dual phase tubular membranes supported on porous magnesium oxide. Abstract from Summer school on Ionic and protonic conducting ceramic membranes for green energy applications, Valencia, Spain.

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# OXYGEN PERMEATION OF DENSE DUAL PHASE TUBULAR MEMBRANES SUPPORTED ON POROUSE MAGNESIUM OXIDE

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**Keywords:** Oxygen permeating membrane, dual phase composite, dense thin membrane, supported membrane

Acceptor doped ceria is an alternative to the perovskite based mixed ionic and electronic conductive oxygen separation membranes, because of the high ionic conductivity at low temperature and wide oxygen partial pressure ( $pO_2$ ) stability range. For gadolinium doped ceria (CGO) the ionic conductivity at 900 °C is 0.155 S/cm, but the electronic conductivity is only  $6.8 \times 10^{-4}$  S/cm [1]. The oxygen permeation flux in CGO membranes is therefore limited by the electronic conductivity, thus it is expected that better performance can be achieved if the electronic conductivity can be enhanced. Two different routes to increase the electronic conductivity have been extensively studied [1, 2]. The first is aliovalent substitution, for example with Pr, where the p-type electronic conductivity is significantly increased [1]. The second is adding a second phase with high electronic conductivity to the CGO [2]. An advantage of forming such a composite is greater flexibility in combining high ionic and high electronic conductivity.

In this study, a dual phase membranes consisting of  $Ce_{0.9}Gd_{0.1}O_{2-\delta}$  as a high ionic conductor and  $(La_{0.6}Sr_{0.4})_{0.98}FeO_{3-\delta}$  (LSF) as a high electronic conductor were investigated. The LSF was chosen due to a high stability in low  $pO_2$ . Samson et al. [2] showed that for 1 mm thick pellets oxygen permeation flux of composite CGO-LSF is larger than for pure CGO. The oxygen permeation flux can be increased by reducing a membrane thickness. Furthermore, parallel studies of the oxygen transport properties in the CGO-LSF composites have shown that the limiting thickness below which the process is limited by surface exchange rather than bulk diffusion is 70  $\mu m$ . Therefore, in this study, the main focus was on the preparation of thin dense CGO-LSF composite membranes with thickness between 10 and 30  $\mu m$  on a tubular porous support.

The first step in the production of membranes was manufacture of a tubular porous support of MgO by thermoplastic extrusion. Different poreformers (like graphite and polymethyl methacrylate) were used as sacrificial particles to form connected macro-pores. The tubular porous supports with open porosity around 40 % and with interconnected channels of 0.3 – 0.5  $\mu m$  have been produced [3]. The second step was application of active layers on the porous support. Three different layers with a thickness between 5 and 30  $\mu m$  were applied on one side of the porous support by dip coating. The layers prepared from ethanol based slurries with or without poreformers were porous CGO, dense CGO-LSF composite and porous CGO layer [4]. After final calcination and sintering of the membranes an additional infiltration was carried out. The inner porous CGO layer was infiltrated by a precursor solution of nano-CGO to increase the active surface area, and the outer porous CGO layer was infiltrated with an electronic conductor like  $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ ,  $LaNi_{0.6}Co_{0.4}O_{3-\delta}$  or  $LaCoO_{3-\delta}$ . The oxygen permeation flux of the tubular membranes was measured using a constant air flow on the outside of the membranes, and vacuum or a flow of different gasses ( $N_2$ ,  $CO_2$ ,  $H_2$ , and  $CH_4$ ) on the inside. The membranes were tested in the temperature range between 700 °C and 850 °C. Long term tests on the stability of the membranes in  $CO_2$  and high reducing conductions were also carried out.

The oxygen permeation flux for a 10  $\mu m$  thick dense CGO-LSF composite membrane layer on the MgO porous support in  $N_2$  at 850 °C was  $2.1 \text{ mlcm}^{-2}\text{min}^{-1}$ , with the activation energy of 24 – 37 kJ/mol. The oxygen permeation flux strongly depends on the  $pO_2$  difference between the inside and outside of the membrane, and for humidified  $H_2$  ( $pO_2 = 1.5 \times 10^{-14}$  atm.) at 850 °C for the same membrane the flux of  $15 \text{ mlcm}^{-2}\text{min}^{-1}$  was measured. The long term stability tests in  $CO_2$  and  $H_2$  showed that an initial degradation took place, followed by stable flux after 80 h or 200 h, respectively. The high oxygen permeation flux and fair stability show that the MgO supported thin dense CGO-LSF tubular membrane is a promising candidate for an oxygen separation process, combustion reactions or partial oxidation reactions.

## References

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