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Publication date:
2015

Document Version
Peer reviewed version

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Citation (APA):

Ovtar, S., Søgaard, M., Gorauskis, J., Hendriksen, P. V., & Kaiser, A. (2015). *Magnesium oxide supported thin dual phase composite oxygen permeation reactors*. Abstract from 12th International Conference on Catalysis in Membrane Reactors, Szczecin, Poland.

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MAGNESIUM OXIDE SUPPORTED THIN DUAL PHASE COMPOSITE OXYGEN PERMEATION REACTORS

Introduction

Mixed ionic electronic conducting (MIEC) perovskites with the composition $A_x\text{Sr}_{1-x}\text{Fe}_y\text{B}_{1-y}\text{O}_{3-\delta}$ have been intensively investigated for the application as high temperature oxygen permeation membranes in last decades. These membranes can be applied to reactors for oxygen separation, oxidation of hydrocarbons, waste reduction, etc. and for those the tubular membranes are preferable. The driving force for oxygen permeation through the material is the gradient in the chemical potential of oxygen on the different sides of the membrane. On the feed side oxygen is reduced on the surface of the membrane and diffuses through the membrane to the permeate side. A major problem with MIEC perovskites is the thermodynamic and dimensional instability at low oxygen partial pressures and a low thermodynamic stability in CO_2 . As an alternative, doped ceria shows high oxide ion conductivity and high thermodynamic stability in various gasses (e.g. SO_2 , CO_2), but the material lacks electronic conductivity especially under oxidizing conditions. Composites materials of doped ceria and MIEC can meet simultaneously the requirements of chemical stability and good transport properties. Additionally high enhancement of surface exchange coefficient (k_{ex}) of composite compares to the MIEC was observed, which contributes to faster oxygen ion transport properties [1].

The present work describes the oxygen transport properties of a composite material of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95-\delta}$ (CGO) and $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.98}\text{FeO}_{3-\delta}$ (LSF), when characterized by electrical conductivity relaxation and through flux measurements on a thin film tubular membrane. Further, results of “long term” (300-500 hours) tests of a thin film composite membrane (20 μm thickness) of CGO and LSF supported on porous MgO tube are presented for test under syngas relevant conditions.

Experimental

Bars of dense dual phase composite material with 70 vol% of CGO and 30 vol% of LSF were prepared and the electrical conductivity was measured using a 4-point measurements in the temperature range 650-850 °C and the $p\text{O}_2$ range 10^{-14} - 10^{-18} atm. The experimental setup allows for a fast change in the $p\text{O}_2$ (switching time is 10s) and based on the change of electrical conductivity versus time, the k_{ex} and chemical diffusion coefficient (D_{chem}) of oxygen can be derived by fitting the conductivity response to Fick's law of diffusion with a first order surface exchange reaction [2].

The same composite was used as a thin dense ceramic membrane supported on a porous MgO. The membrane layer was prepared by dip coating of MgO supports were prepared by thermoplastic extrusion [3] using a procedure described by Gurauskis [4]. Three

different layers were applied on the MgO support: porous CGO catalytic layer, dense dual phase membrane layer and a porous CGO layer on the surface of membrane. Membranes with length up to 1 m were prepared. The outer porous CGO layer was infiltrated with LaCoO_3 which improves the catalytic activity of the oxygen surface reaction. $J(\text{O}_2)$ was measured on a tubular membrane using a constant air flow on the outside of the membrane and a flow of different gasses (N_2 , H_2 , CO_2 , CH_4) on the inside, in the temperature range between 700 °C and 850 °C. Durability tests were done at different temperatures in pure CO_2 and humidified hydrogen.

Results and discussion

Using electrical conductivity relaxation a k_{ex} of 5.4×10^{-5} cm/s and D_{chem} of 3.8×10^{-6} cm²/s was measured at 800°C and $p\text{O}_2$ of $6 \cdot 10^{-17}$ atm. A characteristic thickness defined as $D_{\text{chem}}/k_{\text{ex}}$ is therefore of the order 70 μm and for membranes below this thickness must be applied to the membrane layer.

In Fig. 1 the microstructure of MgO supported membrane is shown. The thicknesses of the inner porous CGO layer, dense composite layer and porous outer layer are around 10, 20 and 20 μm, respectively. The surface exchange on the feed side was further enhanced by infiltration of LaCoO_3 nanoparticles into the porous CGO layer (insertion in Fig 1).

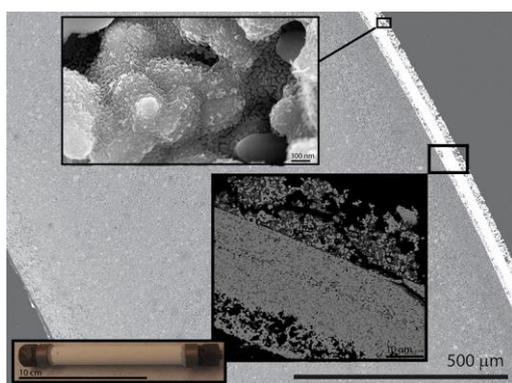


Fig. 1. SEM image of cross-section of MgO supported dual phase composite membrane

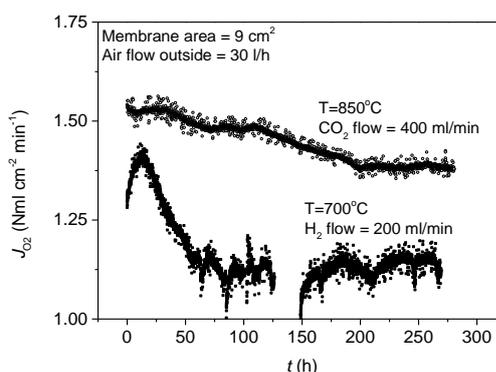


Fig. 2. Durability test: J_{O_2} of membrane in pure H_2 and CO_2

It has been found that $J(\text{O}_2)$ increases with temperature and with increasing $p\text{O}_2$ gradient. The highest $J(\text{O}_2)$ of these membranes measured for pure H_2 at 850°C was 15 Nml cm⁻² min⁻¹. Durability tests (250 h) show that when using both CO_2 and humidified H_2 , respectively an initial degradation takes place, followed by stable flux values (Fig. 2). The high $J(\text{O}_2)$ and fair stability in pure CO_2 shows that the developed MgO supported tubular membranes are a promising candidate for oxygen separation and combustion or partial oxidation membrane reactors.

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