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Oxygen permeation and creep behavior of $\text{Ca}_{1-x}\text{Sr}_x\text{Ti}_{0.6}\text{Fe}_{0.15}\text{Mn}_{0.25}\text{O}_{3-\delta}$ ($x=0, 0.5$) membrane materials

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ABSTRACT

Oxygen permeation measurements were performed on dense symmetric samples of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Ti}_{0.6}\text{Fe}_{0.15}\text{Mn}_{0.25}\text{O}_{3-\delta}$ and compared to $\text{CaTi}_{0.6}\text{Fe}_{0.15}\text{Mn}_{0.25}\text{O}_{3-\delta}$ in order to assess the influence of the perovskite lattice volume on oxygen permeation. Oxygen flux measurements were performed in the temperature range 700–1000 °C and as function of feed side p_{O_2} from 10^{-2} to 1 bar, and at high pressures up to 4 bar with a p_{O_2} of 3.36 bar. The O_2 permeability of the Sr-doped sample was significantly lower than that of the Sr-free sample, amounting to $3.9 \times 10^{-3} \text{ mL min}^{-1} \text{ cm}^{-1}$ at 900 °C for a feed side p_{O_2} of 0.21 bar. The O_2 permeability of $\text{CaTi}_{0.6}\text{Fe}_{0.15}\text{Mn}_{0.25}\text{O}_{3-\delta}$ shows little variation with increased feed side pressures and reaches $1.5 \times 10^{-2} \text{ mL min}^{-1} \text{ cm}^{-1}$ at 900 °C for a feed side p_{O_2} of 3.36 bar. This is approximately 1.5 times higher than the O_2 permeability with a feed side p_{O_2} of 0.21 bar. Furthermore, in order to assess the applicability of $\text{CaTi}_{0.6}\text{Fe}_{0.15}\text{Mn}_{0.25}\text{O}_{3-\delta}$ as an oxygen membrane material, creep tests were performed under compressive loads of 30 and 63 MPa, respectively, in air in the temperature range 700–1000 °C; the results indicate a high creep resistance for this class of materials. The measured O_2 permeabilities and creep rates are compared with other state-of-the-art membrane materials and their performance for relevant applications is discussed in terms of chemical and mechanical stability.

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1. Introduction

Ceramic membranes based on mixed ionic and electronic conductors may be utilized for high temperature oxygen separation from air – enabling, for instance, oxy-fuel combustion or gasification of coal and biomass at higher efficiency compared to cryogenic distillation of oxygen [1,2]. Catalytic membrane reactors may also utilize such membranes for partial oxidation of methane to synthesis gas, oxidative coupling of methane and oxidative dehydrogenation processes [3–9].

The key properties of the membrane material are oxygen flux and stability at operating conditions comprising (1) chemical stability under oxidizing and reducing conditions, CO_2 and sulfur containing atmospheres and temperatures above 700 °C (depending on the process conditions); (2) kinetic stability (resistance to kinetic demixing) in oxygen chemical potential gradients; (3) mechanical stability in terms of creep and thermal/chemical expansion [3,4,9–14]. Integration of the membrane in a module also requires chemical compatibility and adequate matching of

thermal expansion coefficient with appropriate high temperature alloys. Additionally, cost and toxicity of the materials are important issues for up-scaled production. It has proven challenging to develop membranes that can meet all of these criteria. The Sr/Ba and Co-containing perovskites exhibit high O_2 fluxes [15–18], but suffer from kinetic demixing and poor thermodynamic and mechanical stability [13,16,19–24]. We have recently pursued a stable base material – $\text{CaTi}_{0.85}\text{Fe}_{0.15}\text{O}_{3-\delta}$ (CTF15) – towards improved O_2 flux [25–31].

In these materials, oxygen permeation proceeds according to ambipolar transport of oxide ions – by means of oxygen vacancies, v_{O}^{\bullet} , in Kröger–Vink [32] notation – and electronic charge carriers. Ambipolar conductivity is therefore facilitated by the addition of lower-valent dopants such as Fe^{3+} on the Ti-site, which, according to electroneutrality, will promote the concentrations of oxygen vacancies and electron holes [33]. Increasing the Fe-dopant concentration beyond $x=0.15$ –0.2 in $\text{CaTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, however, lowers the O_2 flux due to lower oxide ion conductivity associated with trapping of oxygen vacancies and partial transition to an ordered brownmillerite $\text{Ca}_2\text{Fe}_2\text{O}_5$ [26,34–38].

Recently, we have shown that addition of Mn on the Ti-site enhances the O_2 permeability with a maximum flux obtained for $\text{CaTi}_{0.6}\text{Fe}_{0.15}\text{Mn}_{0.25}\text{O}_{3-\delta}$; the improvement was associated mainly

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with increased electronic conductivity [27,28]. The activation energy of the O₂ permeability was found to increase close to linearly with Mn-content. This was ascribed to an increased activation energy of oxide ion transport due to a linear lowering of the lattice volume with Mn-content. In light of these findings, we have investigated the effect of substituting Sr on the Ca-site of CaTi_{0.6}Fe_{0.15}Mn_{0.25}O_{3-δ} as a means to increase the lattice volume and potentially lower the activation energy of oxide ion transport, while presumably attaining a cubic symmetry compared to introducing a larger cation on the Ti-site.

In this work, we present structure data and O₂ permeation measurements of densely sintered disc samples of Ca_{0.5}Sr_{0.5}Ti_{0.6}Fe_{0.15}Mn_{0.25}O_{3-δ} (CSTFMn25) in comparison with the respective Sr-free composition. The effect of pressures of up to 4 bar and p_{O_2} of 3.36 bar is evaluated with respect to the O₂ permeability of CaTi_{0.6}Fe_{0.15}Mn_{0.25}O_{3-δ} (CTFMn25). While Sr-containing compounds tend to exhibit limited stability towards CO₂, this may not be the case for the addition of Sr to the CaTiO₃ based material; the higher stability of the cubic SrTiO₃ structure compared to CaTiO₃ more than compensates for the higher stability of SrCO₃ relative to CaCO₃ [39]. Furthermore, creep measurements were performed on compressively loaded CTFMn25 specimens in order to determine mechanical stability under operating conditions. The creep behavior of an Mn-free composition, CaTi_{0.6}Fe_{0.1}O_{3-δ} (CTF10), was also measured for comparison. Finally, the results from O₂ flux and creep rate measurements are reviewed in relation to state-of-the-art membrane materials.

2. Experimental

2.1. Sample preparation and characterization

Ca_{0.5}Sr_{0.5}Ti_{0.6}Fe_{0.15}Mn_{0.25}O_{3-δ} (CSTFMn25) was synthesized according to a Pechini-type route using nitrate salts as starting agents, citric acid as a complexing agent and ethylene glycol for polymerization. Sols were pre-calcined at 400 °C, and the resulting powders were manually crushed in an agate mortar, and further annealed at 900 °C for 6 h in ambient air. Details of the synthesis procedure, which was also used for preparation of the CTFMn25, are described in Ref. [27]. Uniaxially pressed disc samples (Ø=20 mm) were sintered at 1300 °C for 6 h in ambient air. The sintered disc samples were gradually polished to a roughness of 6 µm and 1 µm with SiC grinding paper and diamond paste, respectively. The final thicknesses of the membranes for flux measurements were 1.23 and 1.50 mm for CSTFMn25 and CTFMn25, respectively.

For creep measurements, uniaxial pressed cylindrical specimens of CTFMn25 (Ø=7 mm) were sintered according to the same procedure. The final dimensions were 12 mm length and 5.4 mm diameter. Additionally, porous tubular CTF10 specimens were prepared by plastic extrusion including pyrolyzable pore formers as described in Ref. [40]. The tubular specimens were sintered at 1380 °C for 5 h in air, and the final dimensions were 30 mm length, 9.3 mm outer diameter and 1.1 mm wall thickness.

For X-ray diffraction (XRD), sintered samples were crushed and analyzed using a Bruker D8 Focus diffractometer with Cu Kα radiation and LynxEye detector. The diffraction data were analyzed using the Rietveld method as implemented in the TOPAS software by Bruker. Porosity and grain size were graphically analyzed from optical micrographs using the AnalySIS software, where the grain size was taken as the equivalent circular diameter (ECD) value.

2.2. O₂ flux measurements

The sintered disc samples were sealed to alumina support

tubes (Ø=12 mm) in a ProboStat measurement cell (NorECs, Norway) with gold O-ring gaskets. Each sample was pressed against the gold gasket and alumina support tube with a force of approx. 45 N with an alumina spring load assembly during sealing and measurements. Mass flow controllers were utilized to supply O₂/He feed gas mixtures and Ar sweep gas at 50 and 25 mL min⁻¹, respectively, and back-pressure controllers on the feed and sweep side outlets enabled pressures above ambient. The concentrations of O₂ permeate and He leakage were measured with a Varian CP-4900 gas chromatograph (GC). The measurements cell was mounted in a vertical tube furnace and temperature was monitored with an S-type thermocouple placed in the vicinity of the sample and gold O-ring inside the measurement cell. Gas tight seals were obtained by heating to 1000 °C in air, and the He leakage rate for all measurements was well below 1% of the O₂ permeation. Ambient pressure O₂ fluxes were measured at temperatures between 700–1000 °C and as function of feed side oxygen partial pressure, p_{O_2} , in the range from 10⁻² to 1 bar. O₂ fluxes under high-pressure were measured in ambient feed side mixtures of 0.21, 0.42 and 0.84 bar O₂ pressurized between 2 and 4 bars, corresponding to p_{O_2} of 0.42–3.36 bar. For these measurements, the sweep side Ar was pressurized to 100 mbar below the feed side pressure in order to avoid mechanical failure of the membrane or gold O-ring gasket. The O₂ flux through a dense ceramic membrane, j_{O_2} , can be expressed from ambipolar conductivity, σ_{amb} , according to

$$j_{O_2} = \frac{RT}{16F^2L} \int_{p_{O_2}^s}^{p_{O_2}^f} \sigma_{amb} d \ln p_{O_2} \quad (1)$$

where $p_{O_2}^f$ and $p_{O_2}^s$ refer to the feed and sweep side, respectively, L is the thickness of the membrane and F is the Faraday constant. The O₂ permeability, J_{O_2} , is taken as the thickness normalized O₂ flux with units mL(STP) min⁻¹ cm⁻¹ at specified feed and sweep side conditions.

2.3. Creep measurements

The creep behavior of CTFMn25 and CTF10 was assessed with compression tests carried out on an Instron 1362 machine in the temperature range from 850 °C to 1000 °C in an ambient air. Dense cylindrical CTFMn25 specimens as well as porous tubular CTF10 specimens were uniaxially loaded between the two base plates. In order to minimize surface effects and superimposed bending induced by misalignments, the flatness and the parallelism of these previously ground and polished base surfaces was ensured to be 0.04 mm and 0.1 mm, respectively. The deformation of the specimens was indirectly measured by three equidistant sensors at a radial angle of 60°, which measured the relative movement of the loading and supporting base plate. The sensors were attached to a ceramic extension rod connected to a linear variable differential transformer (Sangamo, LVDT, range ± 1 mm, precision 1.25 µm). The load was measured by a load cell of 10 kN range (1210 ACK, Interface Company). The temperature was controlled by a K-type thermocouple placed in close vicinity of the specimen. The specimens were heated at 8 °C min⁻¹ with a pre-load of 2 N. The applied stresses were 30 MPa and 63 MPa, which is a realistic stress range in a membrane application according to Schulz et al. [41]. The loads were applied stepwise at constant temperature. Heating sequences were applied in the considered temperature range with steps of 50 °C. At each temperature, the sample was allowed to equilibrate for a minimum of 1 h before the actual compressive creep load was applied. In all cases the creep load was applied for at least 24 h to assure that a secondary creep stage is reached.

The compressive strain rate was calculated as the ratio of the

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