Performance and stability of $(\text{ZrO}_2)_{0.89}(\text{Y}_2\text{O}_3)_{0.01}(\text{Sc}_2\text{O}_3)_{0.10}$ - $\text{LaCr}_{0.85}\text{Cu}_{0.10}\text{Ni}_{0.05}\text{O}_3$ - oxygen transport membranes under conditions relevant for oxy-fuel combustion

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Performance and stability of $(\text{ZrO}_2)_{0.89}(\text{Y}_2\text{O}_3)_{0.01}(\text{Sc}_2\text{O}_3)_{0.10}\text{-LaCr}_{0.85}\text{Cu}_{0.10}\text{Ni}_{0.05}\text{O}_{3-\delta}$ oxygen transport membranes under conditions relevant for oxy-fuel combustion

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Abstract

Self-standing, planar dual-phase oxygen transport membranes consisting of 70 vol.% $(\text{ZrO}_2)_{0.89}(\text{Y}_2\text{O}_3)_{0.01}(\text{Sc}_2\text{O}_3)_{0.10}$ (10Sc1YSZ) and 30 vol.% $\text{LaCr}_{0.85}\text{Cu}_{0.10}\text{Ni}_{0.05}\text{O}_{3-\delta}$ (LCCN) were successfully developed and tested. The stability of the composite membrane was studied in simulated oxy-fuel power plant flue-gas conditions (CO_2 , SO_2 , H_2O). The analyses of the exposed composites by X-ray diffraction (XRD), X-ray fluorescence (XRF), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and Raman spectroscopy revealed an excellent stability. Oxygen permeation fluxes were measured across 1000 μm thick and 110 μm thick self-supported 10Sc1YSZ-LCCN (70-30 vol.%) membranes from 700 $^\circ\text{C}$ to 950 $^\circ\text{C}$ using air as the feed gas and N_2 or CO_2 as the sweep gas. The 110 μm thick membrane, prepared by tape-casting and lamination processes, showed oxygen fluxes up to $1.02 \text{ mL}_\text{N} \text{ cm}^{-2} \text{ min}^{-1}$ (950 $^\circ\text{C}$, air/ N_2). Both membranes demonstrated stable performances over long-term stability tests (250-300 h) performed at 850 $^\circ\text{C}$ using pure CO_2 as the sweep gas.

Keywords

Oxygen transport membrane, Dual-phase membrane, CO_2 stability, SO_2 tolerance, Oxy-fuel combustion

Highlights

- 10Sc1YSZ-LCCN membranes show stability under oxy-fuel relevant conditions.
- Long-term (300 h) stability test under CO_2 showed stable performance.
- Oxygen fluxes-up to $1.02 \text{ mL}_\text{N} \text{ min}^{-1} \text{ cm}^{-2}$ (950 $^\circ\text{C}$, air/ N_2) through 110 μm thick membrane.

Introduction

Now and in the coming decades, one of the most important challenges for our society is to reduce greenhouse gas emissions, responsible for global warming. The dominating sources of anthropogenic CO₂ emission are the use of fossil fuels in the energy and transport sectors and industrial production of cement, iron and steel [1]. To reduce these emissions, Carbon Capture and Utilization (CCU) or Storage (CCS) are important concepts currently under development. There are three fundamentally different approaches to carbon capture from point sources: pre-combustion separation, post-combustion separation and oxy-fuel combustion. In the latter, pure oxygen is used to combust the fossil fuel, resulting in flue-gases consisting mainly of CO₂ (90-95%) and steam. The CO₂ can then be captured much more easily than when air is used in the combustion process resulting in a flue gas lean in CO₂ (10-14% in dried gas) [2]. The oxygen required for the oxy-fuel process can be produced by several methods which all require considerable energy. Producing the oxygen locally via *oxygen transport membranes* (OTMs) that are both thermally and chemically integrated in the oxy-fuel process results in the least overall efficiency losses [3][4].

OTMs are typically made of Mixed Ionic Electronic Conductors (MIEC). Such materials allow simultaneous transport of oxygen (via oxygen vacancies in the crystal lattice) and electrons. The membranes are fully dense, which results in very high selectivity in the separation. An oxygen partial pressure differential between an oxidizing gas (air at 0.21 atm) and a reducing gas (recirculated flue gas at $p_{O_2} \approx 10^{-2}$ atm [5]) exists across the membrane and serves as the driving force for the oxygen transport. To reduce cost and maximize efficiency it is beneficial to directly integrate the OTMs in the oxy-fuel process, which entails that the membranes are exposed directly to recirculated flue-gases at the permeate side of the membrane. This imposes very stringent requirements to the membrane materials, specifically requiring chemical stability in CO₂, SO₂ and H₂O, which are inevitable constituents/impurities arising from the combustion of fossil fuels. In literature, the OTM materials achieving the highest oxygen fluxes are based on single-phase MIEC materials, such as Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-δ} (BSCF) and La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-δ} (LSCF) [6][7][8][9][10][11][12][13][14][15]. However, most of these materials, which show good transport properties, are not chemically stable in atmospheres containing CO₂ and SO₂

[9][16][17][18][19][20][21][22], and therefore are not suitable for direct integration in oxy-fuel combustion power plants. Membranes prepared from two thermodynamically very stable materials, an ionic conductor and an electronic conductor, is an interesting alternative to overcome the stability limitations of single-phase membrane materials in CO₂ and SO₂.

Several studies in the literature showed that the fluorite phase and the perovskite are compatible with each other and can effectively form composite membranes for oxygen permeation [23][24]. In this study, dual-phase membranes consisting of 70 vol.% (Y₂O₃)_{0.01}(Sc₂O₃)_{0.10}(ZrO₂)_{0.89} and 30 vol.% LaCr_{0.85}Cu_{0.10}Ni_{0.05}O_{3-δ} (10Sc1YSZ-LCCN (70-30 vol.%)) were prepared and tested with respect to chemical stability and oxygen transport properties under conditions simulating direct integration in oxy-fuel combustion power plants.

Yttria stabilized zirconia ((ZrO₂)_{1-x}(Y₂O₃)_x (YSZ)) has previously been studied as the ionic conductor in composite OTMs due to high ionic conductivity, high stability at high temperature in both oxidizing and reducing atmospheres, and good mechanical properties [25][26][27]. The highest ionic conductivity for (ZrO₂)_{1-x}(Y₂O₃)_x electrolytes is observed for x= 0.08 (8YSZ). At 850 °C the conductivity is 0.03 S.cm⁻¹ [28]. However, higher ionic conductivity can be reached by co-doping of scandium and yttrium in zirconia. Artemov et al. reported an ionic conductivity of 0.12 S.cm⁻¹ for (Y₂O₃)_{0.01}(Sc₂O₃)_{0.10}(ZrO₂)_{0.89} (10Sc1YSZ) at 850 °C [29]. Moreover, a recent study has demonstrated excellent stability of 10Sc1YSZ under CO₂, SO₂ and H₂O containing atmospheres [30].

Lanthanum chromite is a very stable compound, which has been studied as ceramic interconnect material in solid oxide fuel cells [31][32][33][34][35]. It is a fair p-type electronic conductor [35][36][37][38], it is chemically compatible with zirconia, and is therefore a candidate for the electronic conductor in a dual-phase membrane designed for integration in oxy-fuel combustion power plants. The conductivity of pure lanthanum chromite is rather low (0.96 S cm⁻¹ at 800 °C in air, [39]), but it can be increased through doping. The substitution of Cr with lower valence cations like Cu or Ni (+2 valence state) results in a change of the valence state of chromium from Cr³⁺ to Cr⁴⁺ which maintains electroneutrality and contributes to the enhancement of p-type conduction via the

increase of electron holes [40][41][42]. Thus the electrical conductivity of $\text{LaCr}_{0.85}\text{Cu}_{0.10}\text{Ni}_{0.05}\text{O}_{3-\delta}$ (LCCN) reaches 11.4 S cm^{-1} at 800°C in air (electrical conductivity of pure LCCN and 10Sc1YSZ-LCCN composites is detailed in the supplementary material (Figure S 1)).

The stability of the 10Sc1YSZ-LCCN was investigated on loose powder under simulated oxy-fuel combustion conditions (CO_2 , SO_2 , H_2O). Analytical techniques such as X-ray diffraction (XRD), X-ray fluorescence (XRF), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), Raman spectroscopy and scanning electronic microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) were used to characterize the material before and after exposure to the gases. The performance of the composite for transporting oxygen was evaluated by oxygen permeation measurements. The influence of (i) membrane thickness, (ii) catalyst activation layers on the membrane surface, and (iii) operation time on the oxygen permeation flux through the membranes was investigated.

2. Experimental

2.1. Thermochemical stability and characterization of 10Sc1YSZ-LCCN composite powders

2.1.1. Thermochemical stability tests

The thermochemical stability of 10Sc1YSZ-LCCN (70-30 vol.%) powder in the presence of CO_2 , SO_2 and H_2O was tested at 850°C in an up-flow vertical testing unit. Loose powders were used to maximize the contact area between the mixture and the gases. The unit is based on a quartz tube equipped with a liner with a porous sample holder which facilitates an even distribution of the gas. A detailed description can be found elsewhere [30]. For each run, 1 g of fresh 10Sc1YSZ-LCCN (70-30 vol.%) powder was placed on the holder. A thermocouple was located within the bed of material to monitor the temperature. Once the sample was loaded, the testing unit was introduced in an oven and heated up to 850°C under a stationary air atmosphere. At 850°C , the gas composition was switched to the different mixtures of $\text{CO}_2/\text{SO}_2/\text{H}_2\text{O}$, according to the compositions shown in Table 1. This table also shows the total amount of sulfur passed through the samples in each of the experiments where SO_2 was

supplied. A high quantity of SO₂ was intentionally used in contact with the sample in order to be able to detect sulphates, which might be formed by reactions between SO₂ and the 10Sc1YSZ-LCCN composite material. Blank runs in atmospheres of 100 % air and 100 % CO₂ were also performed. Two gas cylinders were used for preparing the gas mixtures, one with CO₂ (purity > 99.8 %) and one with a mixture of 2000 ppm of SO₂ in CO₂. An evaporator, fed by a syringe pump to control the amount of water added, was used to generate the steam in the experiments performed in humid conditions. The experiments were carried out at atmospheric pressure using a gas flow rate of 0.25 L_N min⁻¹ for 8 h. The exhaust gases were cooled down to room temperature to remove steam before passing through two saturated NaOH solutions with the aim of removing SO₂ prior to their disposal. Once the experiment was finished, the testing unit was quenched under the reaction atmosphere to avoid the presence of oxygen, which would lead to the decomposition of species formed during the treatments. Finally, the treated material was recovered for characterization.

Table 1: Composition of simulated flue gases used in the thermochemical stability tests performed on 10Sc1YSZ-LCCN (70-30 vol.%) powder. Tests were carried out for 8 h at 850 °C and atmospheric pressure using a gas flow rate of 0.25 L_N min⁻¹.

Test	CO ₂ (vol.%) ⁽¹⁾	SO ₂ (ppm v/v) ⁽¹⁾	H ₂ O (vol.%) (2)	pO ₂ (atm)	Total sulfur (g) ⁽³⁾
Blank ⁽⁴⁾	0	0	0	0.21	0
CO ₂	100	0	0	< 5·10 ⁻⁶	0
500SO ₂	Balance	500	0	< 5·10 ⁻⁶	0.0
500SO ₂ 10H ₂ O	Balance	500	10	< 5·10 ⁻⁶	0.08
2000SO ₂ 10H ₂ O	Balance	2000	10	< 5·10 ⁻⁶	0.32
500SO ₂ 30H ₂ O	Balance	500	30	< 5·10 ⁻⁶	0.08

⁽¹⁾ Dry basis; ⁽²⁾ Percentage of the total flow, including steam; ⁽³⁾ Total sulfur seen by the sample in the treatment;

⁽⁴⁾ Performed in air

2.1.2. Characterization of 10Sc1YSZ-LCCN composite powders

Before and after the gas exposure treatment the 10Sc1YSZ-LCCN (70-30 vol.%) powders were characterized by a series of analytical techniques to detect and identify changes induced by the experiments.

X-ray diffraction (XRD) patterns were obtained in a PANalytical diffractometer equipped with a Ni-filtered Cu K α radiation (40 mA, 45 kV) over a 2 Θ -range of 5 to 80° and a position-sensitive detector using a step size of 0.05° and a step time of 120 s. The patterns were processed with the aim of identifying the species present in the samples, using the software X'Pert Highscore Plus.

X-ray fluorescence (XRF) and elemental analysis were performed to determine the chemical composition of the samples. XRF spectra were obtained in a PANalytical Epsilon3XLE X-ray fluorescence spectrophotometer with a 50 kV silver anode tube as source of radiation. Elemental analysis was performed in an Elementar Vario Microcube, using a combustion chamber that works up to 1800 °C. The gases leaving the combustion chamber are absorbed in a trapping column and then are desorbed following a temperature program to be detected using a thermal conductivity detector.

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) analyses were performed using a Perkin Elmer FTIR 100 spectrometer. Spectra were collected at room temperature and baseline-corrected using the Spectrum 10™ software.

A Renishaw InVia Raman spectrometer equipped with a charge-coupled device and a Leica microscope was used for collecting Raman spectra. A 785-nm HPNIR diode laser with maximum power of 300 mW was used as an excitation source. A 1200 mm⁻¹ grating was utilized for all measurements, providing a spectral resolution of +/- 1

cm^{-1} . The laser spot was focused on the sample surface using a magnification of 50x. The laser beam spot size was around 1.28 μm .

A JEOL JSM6400 operated at 20 KV equipped with energy dispersive X-ray spectroscopy (EDX) and a wavelength dispersive X-ray spectroscopy (WDS) systems was used for the microstructural/chemical characterization (SEM with EDS and WDS).

2.2. Membrane preparation

1000 μm thick and 110 μm thick self-supported membranes made of 70 vol.% $(\text{Y}_2\text{O}_3)_{0.01}(\text{Sc}_2\text{O}_3)_{0.10}(\text{ZrO}_2)_{0.89}$ - 30 vol.% $\text{LaCr}_{0.85}\text{Cu}_{0.10}\text{Ni}_{0.05}\text{O}_{3-\delta}$ (10Sc1YSZ-LCCN (70-30 vol.%)) (named in this article as “thick membrane” and “thin membrane”, respectively) were prepared using two different procedures as described below.

2.2.1. Thick membrane

The $\text{LaCr}_{0.85}\text{Cu}_{0.10}\text{Ni}_{0.05}\text{O}_{3-\delta}$ (LCCN) powder was prepared in-house via a nitrate-glycine synthesis [43] using stoichiometric amount of nitrates precursors ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and glycine powder. Subsequently, the powder was calcined at 1200 $^\circ\text{C}$ for 3 h in air (heating/cooling ramp = 100 $^\circ\text{C h}^{-1}$). The 10Sc1YSZ powder was purchased from Tosoh Daiichi Kigenso Kagaku Kogyo Co. Ltd (Japan). The ionic and electronic conductors were mixed in a 70/30 volume ratio to form the 10Sc1YSZ-LCCN (70-30 vol.%) composite material. A small amount (3 vol.%) of NiO (Alfa Aesar, United States) was mixed with the composite material to serve as sintering aid during the membrane preparation. The particles size of the powders was adjusted to the submicron range ($d_{v50} < 1 \mu\text{m}$) using ball-milling in ethanol. After drying, a 15 mm diameter membrane was formed using a uniaxial press (1000 kg load). The membrane was sintered at 1400 $^\circ\text{C}$ for 6 h in air. After sintering, the membrane was polished down to 1000 μm thick and an in-house prepared ink of $(\text{Y}_2\text{O}_3)_{0.08}(\text{ZrO}_2)_{0.92}$ - $(\text{La}_{0.80}\text{Sr}_{0.20})\text{MnO}_{3-\delta}$ (8YSZ-LSM (50-50 vol.%)) was screen-printed on both sides of the membrane to serve as oxygen oxidation/reduction catalyst. Finally, the membrane was heated to 980 $^\circ\text{C}$ for 2 h in air in order to dry the printed catalyst and make it adhere to the membrane surface.

2.2.2. Thin membrane

Thin membranes were developed by a tape-casting and lamination process. The $\text{LaCr}_{0.85}\text{Cu}_{0.10}\text{Ni}_{0.05}\text{O}_{3-\delta}$ powder used for the preparation of the thin membranes was purchased from Cerpotech (Norway). The raw powders $10\text{Sc}1\text{YSZ}$, LCCN and NiO were mixed by ball-milling for 48 h with appropriate amounts of solvents (ethanol, acetate) and organic additives (dioctyl phthalate, PVB-76, BYK-103) to form the slurry for tape-casting. The slurry was cast using a doctor blade gap of 300 μm . After drying, the green tape was cut and multiple layers of tape were laminated at 70 $^{\circ}\text{C}$ under a warm isostatic press (WIP) pressure of 40 MPa to obtain the desired thickness of membrane. Subsequently, 25 mm diameter disks were cut out using a laser cutter (model ILS-3NM, LTT, Taiwan), and sintered using a two-step process including a peak temperature of 1500 $^{\circ}\text{C}$ (3 min) and a dwell temperature of 1450 $^{\circ}\text{C}$ (3 h). Heating ramps of 60 $^{\circ}\text{C h}^{-1}$ and 300 $^{\circ}\text{C h}^{-1}$ were used from room temperature to 1200 $^{\circ}\text{C}$ and from 1200 $^{\circ}\text{C}$ to 1500 $^{\circ}\text{C}$, respectively. Cooling ramps of 300 $^{\circ}\text{C h}^{-1}$ and 180 $^{\circ}\text{C h}^{-1}$ were applied from 1500 $^{\circ}\text{C}$ to 1450 $^{\circ}\text{C}$ and from 1450 $^{\circ}\text{C}$ to room temperature. As for the thick membrane, 8YSZ-LSM (50-50 vol.%) was applied on both sides of the membrane and dried at 980 $^{\circ}\text{C}$ for 2 h in air.

2.3. Oxygen flux measurements

Oxygen permeation measurements were carried out in a membrane test rig described elsewhere [30]. Air was used on the feed side with a flow rate of 200 $\text{mL}_\text{N} \text{ min}^{-1}$, while N_2 or CO_2 was fed as a sweep gas on the permeate side using various flow rates in the range from 20 $\text{mL}_\text{N} \text{ min}^{-1}$ to 200 $\text{mL}_\text{N} \text{ min}^{-1}$. Inlet gases were individually controlled and monitored by mass flow controllers (Brooks), while the outlet flow of the permeate side was determined by a mass flow meter (Bronkhorst). Thermocouples were placed in direct contact with the membrane in order to monitor the temperature. The membranes were sealed between two alumina tubes using tape-cast aluminosilicate glass rings (NAS, Na_2O : 17.8 mol%, Al_2O_3 : 9.4 mol% and SiO_2 : 72.8 mol% [44]) with an inner diameter of 9 mm and an outer diameter of 14 mm. The glass transition temperature of the applied glass is 515 $^{\circ}\text{C}$ [45]. The exterior surfaces of the samples were also coated with NAS paste to ensure that there are no gas leaks from the surrounding atmosphere into the sweep chamber. The sealing procedure was completed prior to the measurements by heating

the membranes to 950 °C in air for 1 h before cooling down to 750 °C to conduct the flux measurements. No gas was fed during the sealing procedure and slow heating/cooling ramps were used (30 °C h⁻¹). The leak in the system was assessed by means of a mass flow meter on the permeate stream. When a perfect sealing is achieved, the outlet gas flow rate should be equivalent to the inlet flow. If it is not the case, any oxygen leaks into the permeate stream (oxygen (and nitrogen) that enters the permeate compartment via pinholes or insufficient sealing at the membrane periphery) can be quantified using a gas chromatography station connected to the outlet of the permeate side. In the data reported here the leakage rate of the sealing was estimated to be within 1 %. In-house built zirconia-based P_{O_2} sensors were used to determine the P_{O_2} of the inlet gas on the permeate side (before feeding to the membranes) and of the outlet gas (after passing over the membrane). The oxygen permeation flux was deduced from the P_{O_2} difference between the inlet and the outlet of the gas flowing on the permeate side:

$$J_{O_2} = \frac{P_{O_2,permeate}^{out} \cdot \dot{n}^{out} - P_{O_2,permeate}^{in} \cdot \dot{n}^{in}}{A} \quad (1)$$

where J_{O_2} is the oxygen permeation flux, $P_{O_2,permeate}^{in}$ and $P_{O_2,permeate}^{out}$ are respectively the oxygen partial pressures in the inlet and outlet gases on the permeate side, $\dot{n}^{in}$ and $\dot{n}^{out}$ are molar flow rates of inlet and outlet gases, respectively, and A is the net area of the permeate side of the membrane. The Nernst equation (2) was used to calculate the oxygen partial pressure from the measured sensor voltage (V):

$$P_{O_2} = P_{O_2,ref} \cdot e^{\frac{4FV}{RT}} \quad (2)$$

where V is the open circuit voltage of the oxygen sensor, $P_{O_2,ref}$ is the oxygen partial pressure at the reference electrode (maintained at 0.21 atm during the measurements), and T is the temperature of the oxygen sensor.

3. Results and discussion

3.1. Chemical stability of 10Sc1YSZ-LCCN under conditions relevant to oxy-fuel combustion

Figure 1 shows results of the XRD characterization of the composite material before and after exposure to different concentrations of impurity in the gases. The XRD patterns of the untreated sample showed a combination of Sc and Y doped ZrO_2 and $\text{LaCr}_{0.85}\text{Cu}_{0.1}\text{Ni}_{0.05}\text{O}_{3-\delta}$ peaks. None of the XRD patterns of the samples that were exposed to impurities show any additional peaks or changes in intensity indicating that within the detection limits of the technique ($< 2\%$) no new crystalline phases were formed.

Figure 1: XRD patterns of the 10Sc1YSZ-LCCN (70-30 vol.%) untreated powder (black), treated with pure CO_2 (blue), treated with 500 ppm of SO_2 in CO_2 (green), treated with 500 ppm of SO_2 in CO_2 and 10 % of steam (brown), treated with 2000 ppm of SO_2 in CO_2 and 10 % of steam (dark blue) and treated with 500 ppm of SO_2 in CO_2 and 30 % of steam (cyan).

However, X-ray diffraction is not sensitive to small amounts of second phases and is not able to detect non-crystalline species. For this reason, complementary characterization was needed before concluding that no new phases formed in 10Sc1YSZ-LCCN on exposure to CO_2 , SO_2 and H_2O . Raman and ATR-FTIR spectroscopies were used for this purpose. Figure 2 shows the ATR-FTIR and Raman spectra of treated and untreated samples. In the case of the FTIR, the spectrum of the untreated sample was almost flat. After the treatments, the shape of the spectra did not vary, conserving the flat profile. The presence of new species in form of carbonates was

excluded due to the absence of signals in the range of 850-900 cm^{-1} and/or 1400-1600 cm^{-1} [46][47][48]. Similarly, no newly formed sulfates, which would have led to signals in the range from 900-1300 cm^{-1} , were found [46][49][50][51]. Raman spectra of the treated samples did not show any additional signals when compared to the spectrum of the untreated 10Sc1YSZ-LCCN (70-30 vol.%), further indicating that neither carbonates (recognizable by signals in the range of 100-300 cm^{-1} and 1000-1100 cm^{-1}) nor sulfates (recognizable by signals in the range of 900-1000 cm^{-1}) [52][53][54][55][56][57] were formed.

Figure 2: a) ATR-FTIR spectra; and b) Raman spectra of the 10Sc1YSZ-LCCN (70-30 vol.%) untreated powder (black), treated with pure CO_2 (blue), treated with 500 ppm of SO_2 in CO_2 (green), treated with 500 ppm of SO_2 in CO_2 and 10 % of steam (brown), treated with 2000 ppm of SO_2 in CO_2 and 10 % of steam (dark blue) and treated with 500 ppm of SO_2 in CO_2 and 30 % of steam (cyan).

XRF and elemental analysis were performed to confirm the absence of carbon and sulfur in the samples, thus discarding the incorporation of these elements in other species that could not be detected by XRD or vibrational spectroscopy. Neither carbon nor sulfur was detected by any of these techniques. Finally, SEM-WDS analyses were performed on the sample treated with the higher concentration of SO_2 in the gas (Supplementary Material (Figure S 2)). It was observed that the signal of sulfur was even lower than that corresponding to the background of Zr, thus discarding its presence in the treated sample.

The chemical characterization performed for the treated and untreated samples confirmed the absence of secondary phases in the samples post-treatment, proving the excellent stability of this composite in the tested environments. These results suggest that 10Sc1YSZ-LCCN (70-30 vol.%), in terms of thermochemical stability, is a good candidate for use in OTMs to be directly integrated in an oxy-fuel combustion processes.

3.2. Membrane microstructure

Figure 3 shows SEM images of cross-sections of the thick membrane (Figures 3.a, 3.c and 3.e) and the thin membrane (Figures 3.b, 3.d and 3.f) before and after the permeation tests. Figures 3.a and 3.b present the microstructures of the membranes before that the 8YSZ-LSM (50-50 vol.%) was coated on both sides of the membranes to serve as oxygen oxidation/reduction catalyst, while Figures 3.c, 3.d, 3.e and 3.f display the microstructures of the membranes after the tests. No change of the microstructures was observed which indicates no degradation of the materials. The brightest phase in the SEM images corresponds to LCCN, while 10Sc1YSZ appears slightly darker and NiO can be assigned to the darkest one. The porosity of the membranes was determined by image analysis and corresponds to 2 vol.% and 6.5 vol. % for the thick and the thin membranes, respectively. The closed pores of the thin membrane had an average diameter of approximately 3 μm . The difference in porosity between the thick membrane and the thin membrane could results from the different shaping techniques used. A higher densification was obtained for the thick membranes (conventional sintering at 1400 °C for 6 h), this could be because the membranes were prepared by powder pressing, a method that results in a very high green density. On the other hand, tape-cast thin membranes have a lower green density due to organic additives, and require higher temperatures to be sintered. In addition, LaCrO_3 -based materials have poor sinterability due to volatilization of chromium vapor species above 1000 °C creating pores on the sides of the membranes [42][58][59][60]. As a result, conventional sintering could not be used to obtain gastight thin membranes while at the same time avoiding the chromium volatilization. The two-step sintering process used (peak temperature 1500 °C (3 min), dwell temperature 1450 °C (3 h)), helped to maximize the densification of the 10Sc1YSZ-LCCN membranes while keeping the chromium content in the LCCN phase.

Figure 3: SEM pictures of the polished cross-sections of thick (a, c, e) and thin (b, d, f) 10Sc1YSZ-LCCN membranes. Figures a and b show the microstructures of the membranes before oxygen permeation tests while Figures c, d, e and f are post-mortem SEM pictures.

3.3. Oxygen permeation measurements on 10Sc1YSZ-LCCN membranes

This section shows the influence of the membrane thickness (Section 3.3.1.), the catalytic activation layers (Section 3.3.2.) and the exposure time in CO_2 (Section 3.3.3.) on the oxygen permeation flux of the 10Sc1YSZ-LCCN membranes.

3.3.1 Influence of the membrane thickness on the oxygen permeation flux

Figure 4 presents the oxygen permeation fluxes through the thick (black symbols) and the thin (red symbols) membranes in the temperature range of 700-950 °C. The membranes were coated on both sides with 8YSZ-LSM (50-50 vol.%) porous activation layers to enhance the rate of the oxygen exchange reactions (oxidation/reduction) taking place at the surfaces. Figure 4 reports the oxygen permeation fluxes obtained using 200 mL_N min⁻¹ of air as the feed gas, and the same flow of N₂ (filled symbols) or CO₂ (open symbols) as sweep gas. The better performances were obtained in air/N₂ at 950 °C, with fluxes of 0.27 mL_N cm⁻² min⁻¹ and 1.02 mL_N cm⁻² min⁻¹ recorded for the thick and the thin membranes, respectively. Slightly lower oxygen fluxes were measured in CO₂ compared to N₂ as sweep gas. Comparable results were reported in other studies [17][61][62][63][64][65][66], where it was suggested that this phenomenon is a consequence of suppressed oxygen surface exchange rate due to the chemisorption of CO₂ on the surface possibly blocking some oxygen vacancies [17][65]. Figure 4 also presents the calculated oxygen permeation flux (red line) considering (i) the contribution of the 8YSZ-LSM catalytic layers to the overall resistance of the membrane and (ii) a tortuosity factor. For these calculations the 8YSZ-LSM resistances were taken from a study published by Kim *et al.* [67], and the tortuosity factor was estimated at 2 from the literature [45]. The ambipolar conductivity of the membrane was approximated as $\sigma_{amb} \approx \sigma_i \approx x * \sigma_{ion,10Sc1YSZ}$, where x is the volume percentage of 10Sc1YSZ in the composite membrane. The ionic conductivities of 10Sc1YSZ from 750 °C to 950 °C were selected in a study of Irvine *et al.* [68]. It is important to mention that these calculations give only an approximate value of the theoretical oxygen permeation flux since values of several parameters required for the calculations (the polarization resistance of LSM/YSZ, the ionic conductivity of 10Sc1YSZ and the tortuosity) were taken from published studies where the experimental situation was different. Moreover, to simplify the calculations it was assumed that the resistances of the oxygen incorporation and ex-corporation reactions are equal. More details concerning the calculated oxygen permeation fluxes can be found in the supplementary material (Figure S 3 and Section S 1). As predicted by the Wagner equation (supplementary material: Figure S 3 and Section S 1), the thinner membrane (110 µm thick) showed a better performance in the complete temperature range studied. However, it performed only 2 to 4 times better than

the thick membrane, while the ratio of their thicknesses is about 9. These results indicate in fact that the oxygen permeation through the thin membrane is not exclusively limited by the diffusion of the oxide ions in the bulk.

Figure 5 shows the oxygen permeation fluxes through the two membranes in the temperature range of 700-950 °C for different N₂ flow rates (sweep gas). The results indicate Arrhenius behavior. The increase of the sweep gas flow (from 20 mL_N min⁻¹ to 200 mL_N min⁻¹) diminishes the local pO₂ at the permeation side, promoting in this way an increase of the oxygen partial pressure gradient across the membrane and avoiding any accumulation of O₂ molecules desorbed on the surface. As a result, the oxygen permeation flux increases with rising sweep gas flow rates. Interestingly, the activation energy (E_a) for the oxygen transport changed as a function of the temperature in the case of the thin membrane (Figure 5.a), which suggests that the rate-limiting step changes with temperature.

The surface exchange kinetics possess a higher activation energy than solid-state diffusion, resulting in a higher apparent activation energy in the low-temperature region. For temperatures below 900 °C, the estimated activation energy of the oxygen transport was 89.8 – 94.7 kJ mol⁻¹. These values suggest that surface exchange kinetics are the main limiting factor of the oxygen permeation. Another hypothesis could be that the oxygen flux is limited by the (bulk) diffusion in the 8YSZ-LSM catalytic layers. This is supported by the E_a values obtained, which are in close agreement with the activation energy associated with the oxygen vacancy diffusion in 8YSZ-LSM (50-50 vol.%) porous active layers, which was reported as 92 kJ mol⁻¹ when the composite was sintered at 980 °C [69]. These values are also consistent with the activation energy of oxide ion conduction in 8YSZ stated in the literature (from 85 kJ mol⁻¹ to 99 kJ mol⁻¹ [70][71][72]). These two hypothesis (oxygen permeation mainly limited by (i) the surface exchange kinetics or (ii) the bulk diffusion in the 8YSZ-LSM-YSZ catalytic layers) could be linked since Kilner et al. demonstrated that the surface exchange kinetics of the oxygen reactions strongly depend to the ionic conductivity of the active material [73]. On the other hand, for temperatures above 900 °C, the activation energy of the oxygen transport was evaluated between 51.1 and 60.5 kJ mol⁻¹. These values, although being slightly lower, are in good accordance with the activation energy of the ionic conductivity of 10Sc1YSZ published by Irvine (62.7 kJ mol⁻¹ in the temperature range 700-950 °C [68]). The slight difference between the activation energy values

could be due to a small degree of replacement of zirconia by Ni, Cr or Cu, which are elements contained in the two other phases (LCCN and NiO) of the dual-phase membrane. Indeed, previous studies showed that the activation energy of the conductivity of zirconia doped materials (e.g. YSZ) can vary according to the dopant content [68][74]. For example, Irvine et al. showed that a small degree of replacement of zirconia by ceria decrease the activation energy associated to the ionic conductivity [68]. Figure 5.b shows the Arrhenius plot of the thick membrane presenting a single range of activation energy ($51.1 - 53.5 \text{ kJ mol}^{-1}$) from 700°C to 950°C . As expected, the diffusion of the oxide ions through the bulk of the membrane is the rate limiting-step in the entire temperature range investigated. The nature of the processes limiting the oxygen permeation flux at these temperatures ($700\text{-}950^\circ\text{C}$) does not seems to be significantly influenced by the sweep gas flow rate, since no important variation in E_a is observed. To summarize: in the complete temperature range studied the oxygen permeation of the thickest membrane ($1000 \mu\text{m}$) is limited by the bulk diffusion in the 10Sc1YSZ-LCCN membrane while for the thinner membrane ($110 \mu\text{m}$) the oxygen permeation is mainly limited by the surface exchange kinetics or bulk diffusion into the catalytic activation layers at low temperatures ($T < 900^\circ\text{C}$) and by the bulk diffusion in the membrane at high temperatures ($T > 900^\circ\text{C}$).

Accordingly, to further improve the oxygen permeation through 10Sc1YSZ-LCCN membranes, it is necessary to both decrease the bulk limitation and improve the surface exchange kinetics. The development of thin asymmetric membranes which combine a relatively thick porous support ($300\text{-}1000 \mu\text{m}$ for mechanical stability) and a thin dense membrane layer ($10\text{-}30 \mu\text{m}$) may be an ideal solution to circumvent bulk diffusion limitations [8]. To overcome surface exchange kinetics limitations further infiltrations of suitable nano-particulate catalysts in the support layers of the asymmetric membranes could be performed. This technique has been successfully applied in previous studies [75][76][77].

Figure 4: Oxygen permeation fluxes through the thick (black symbols) and the thin (red symbols) 10Sc1YSZ-LCCN (70-30 vol.%) membranes ($T = 700\text{--}950\text{ }^{\circ}\text{C}$, feed/sweep gases: air/ N_2 (filled symbols) and air/ CO_2 (open symbols)). The red line represents the calculated oxygen permeation flux of the membrane in air/ N_2 , considering the contribution of the 8YSZ-LSM catalytic layers to the overall resistance of the membrane and a tortuosity factor.

Figure 5: Arrhenius plots of the oxygen permeation flux through the thin (a) and the thick (b) 10Sc1YSZ-LCCN (70-30 vol.%) membranes coated with 8YSZ-LSM porous activation layers on both sides (feed gas: $200\text{ mL}_\text{N}\text{ min}^{-1}$ of air, sweep gas: $20\text{--}200\text{ mL}_\text{N}\text{ min}^{-1}$ of N_2).

3.3.2. Influence of catalyst activation layers on the oxygen permeation flux

As mentioned in Section 2., a $15\text{ }\mu\text{m}$ thick catalytic layer made of 8YSZ-LSM (50-50 vol.%) was deposited on both sides of the thin 10Sc1YSZ-LCCN dual-phase membrane in order to enhance oxygen permeation. Figure 6

illustrates the effect of the activation layers comparing the measured fluxes with and without these layers. Applying these layers resulted in a significant improvement in the oxygen flux. The improvement was notably higher at low temperatures (J_{O_2} multiplied by 6 at 750-800 °C, Figure 6.a). The inferior performance of the bare membranes confirms that in these the surface exchange kinetics are limiting performance below 900 °C. At 950 °C the oxygen flux was increased by a factor of 3 with respect to the bare membrane. The smaller improvement observed at higher temperatures reflects the relatively low influence of the surface exchange at high temperature. Figure 6.b compares the E_a values for the oxygen transport through the bare membrane (black) and the “activated” membrane (red). In the complete temperature range, the bare membrane presents higher activation energy than the activated membrane. This observation gives some support to the hypothesis that the activated membrane could be limited by bulk diffusion in the 8YSZ-LSM layers at low temperatures ($T < 900$ °C), while oxygen permeation of the bare membrane is unsurprisingly limited by surface exchange kinetics. However, the difference in activation energy could also reflect that for the bare membrane (chromite/YSZ) the incorporation reaction occurs via different mechanisms than in the case for the activated membrane where oxygen exchange takes place at the LSM/YSZ triple phases.

The improvement in flux falls below the expectation given by the thickness ratio between the thick and the thin sample (which would be expected if both membranes were bulk limited). Moreover, the flux of the thin coated membrane falls somewhat below the maximum achievable as calculated from the conductivity of zirconia, which is around $4 \text{ mL}_N \text{ cm}^{-2} \text{ min}^{-1}$ at 950 °C under the p_{O_2} pressures here applied (see supplementary material). These two considerations indicate that despite coating the membrane surfaces with a porous LSM/YSZ layer the rate limitations of the oxygen permeation at the surfaces are not negligible and that it can be possible to increase the flux further by developing a better coating.

Figure 6: Effect of the catalytic activation layers: oxygen permeation flux through the thin 10Sc1YSZ-LCCN membranes with (red) and without (black) 8YSZ-LSM (50-50 vol.%) activation layers (feed gas: 200 mL_N min⁻¹ of air, sweep gas: 200 mL_N min⁻¹ of N₂). Oxygen permeation as a function of the temperature (a) and Arrhenius plots of the oxygen permeation (b).

3.3.3. Long-term stability in CO₂

To investigate the chemical and thermal long-term stability of the 10Sc1YSZ-LCCN membranes, the oxygen permeation through the thick and the thin membranes was measured at 850 °C using 200 mL_N min⁻¹ of pure CO₂ as the sweep gas for 300 and 250 hours, respectively. Figure 7 presents the evolution of the oxygen permeation flux for the thick (black) and the thin membranes (red) as a function of time. The dotted lines represent the first derivative of the oxygen flux as a function of the time. During the experiment, the oxygen permeation fluxes through the thick and the thin membranes decreased by 7.6 % and 6.4 %, respectively. The major part of the degradation takes place over the first 100 h of the tests (6.3 % and 6.0 % for the thick and the thin membrane, respectively). This degradation could be due to the initial surface oxygen desorption and the readjustment of the lattice structure of the membrane under the oxygen gradient [78]. In the remaining time the performance of the membranes was stable (0.4 to 1.3 % of degradation), thus confirming the results of the stability tests performed on 10Sc1YSZ-LCCN powder (Section 3.1).

Figure 7: Oxygen permeation flux through the thick (black) and the thin (red) 10Sc1YSZ-LCCN (70-30 vol.%) membranes as a function of the time at 850 °C, with constant flows of air (feed gas, 200 $\text{mL}_N \text{ min}^{-1}$) and CO₂ (sweep gas, 200 $\text{mL}_N \text{ min}^{-1}$).

4. Conclusions

The stability of the dual-phase membranes made of 70 vol.% of $(\text{ZrO}_2)_{0.89}(\text{Y}_2\text{O}_3)_{0.01}(\text{Sc}_2\text{O}_3)_{0.10}$ (10Sc1YSZ) and 30 vol.% of $\text{LaCr}_{0.85}\text{Cu}_{0.10}\text{Ni}_{0.05}\text{O}_{3-\delta}$ (10Sc1YSZ-LCCN) was studied in conditions relevant to oxy-fuel combustion (CO₂, SO₂, H₂O) using several characterization techniques (XRD, XRF, ATR-FTIR and Raman spectroscopy). The tests underlined the excellent stability of the composite material under application relevant atmospheres making 10Sc1YSZ-LCCN a promising material for directly integrated OTMs applications. Long-term stability tests (250 – 300 h) were performed under CO₂ (as sweep gas) and confirmed that 10Sc1YSZ-LCCN membranes produce a stable oxygen flux in CO₂ atmosphere. Oxygen permeation fluxes up to 0.27 $\text{mL}_N \text{ cm}^{-2} \text{ min}^{-1}$ and 1.02 $\text{mL}_N \text{ cm}^{-2} \text{ min}^{-1}$ (950 °C, air/N₂) were obtained for thick (1000 μm) and thin (110 μm) self-standing 10Sc1YSZ-LCCN membranes, respectively. These encouraging results may be further improved by the development of thin catalyst-impregnated asymmetric membranes, which could be an ideal solution to overcome the main rate limiting factors of the oxygen permeation through developed membranes (bulk diffusion limitations and surface exchange

kinetics limitations). In future, oxygen permeation tests of such thin asymmetric membranes should be performed under simulated oxy-fuel combustion conditions.

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SUPPLEMENTARY MATERIAL

Figure S 1: Electrical conductivity of LCCN, 10Sc1YSZ-LCCN (40-60 vol.%) and 10Sc1YSZ-LCCN (50-50 vol.%) as a function of the temperature. Experiment performed in air.

Figure S 2: EDS/WDS spectra of the: a) fresh 10Sc1YSZ-LCCN (70-30 vol.%); b) 10Sc1YSZ-LCCN (70-30 vol.%) treated with 2000 ppm of SO_2 in CO_2 and 10 % of steam. The results of the WDS are overlaying the EDS spectra (with a different scale). The green lines represent the signal (central line) and backgrounds (lateral lines) corresponding to Zr while the red signals of represent signal and backgrounds of s.

Figure S 3: Experimental (symbols) and theoretical (lines) oxygen permeation fluxes through 10Sc1YSZ-LCCN (70-30 vol.%) membranes coated with a 8YSZ-LSM (50-50 vol.%) catalyst layer on both sides as a function of the temperature. The experiment was performed in air/N₂ atmosphere.

Section S 1: Calculation of theoretical oxygen permeation fluxes

▪ Calculation of theoretical oxygen permeation fluxes from Wagner equation

When the permeation flux is mainly limited by the transport of oxide ions and electrons in the bulk of the material (bulk diffusion limitation), the oxygen permeation flux can be characterized by the Wagner equation (3):

$$J_{O_2} = \frac{RT}{16F^2L} \int_{P''_{O_2}}^{P'_{O_2}} \frac{\sigma_e \sigma_i}{\sigma_e + \sigma_i} (p_{O_2}) d \ln p_{O_2} \quad (3)$$

where J_{O_2} is the oxygen permeation flux (mol m⁻² s⁻¹), R is the gas constant (J mol⁻¹ K⁻¹), T is the absolute temperature (K), F is the Faraday constant (A mol⁻¹), L is the membrane thickness (m), σ_e and σ_i are the electronic and the ionic conductivities (S m⁻¹), and P'_{O_2} and P''_{O_2} are the oxygen partial pressures at the high pressure and low pressure sides (Pa), respectively.

For the calculations of the theoretical oxygen permeation flux through the 1000 μm thick and the 110 μm thick membranes, it was considered that: $\sigma_e \gg \sigma_i$, consequently the integrand in Eq. (3) becomes:

$$J_{O_2} = \frac{RT}{16F^2L} \int_{P''_{O_2}}^{P'_{O_2}} \sigma_i (pO_2) d \ln pO_2 \quad (4)$$

The ionic conductivity value σ_i was approximated as: $\sigma_{i,10Sc1YSZ} \gg \sigma_{i,LCCN}$ and $\sigma_i = x * \sigma_{ion,10Sc1YSZ}$, where x is the volume percentage of 10Sc1YSZ in the composite membrane. The ionic conductivities of 10Sc1YSZ from 750 to 950 $^{\circ}\text{C}$ were selected in a study of Irvine *et al.* [68]. The values of the temperatures (T), the membrane thicknesses (L) and the oxygen partial pressures P'_{O_2} and P''_{O_2} were determined experimentally for the calculations.

- **Calculation of theoretical oxygen permeation flux considering the resistance from the 8YSZ-LSM (50-50 vol.%) catalyst layers**

Oxygen permeation flux through the activated membranes (i.e. membranes coated with 8YSZ-LSM (50-50 vol.%) as catalyst layer on both sides) can be divided into three different steps and represented as three resistances in series: two resistances corresponding to the oxygen transport through the catalytic 8YSZ-LSM layers and one resistance corresponding to the oxygen transport through the 10Sc1YSZ-LCCN (70-30 vol.%) membrane layer.

The resistance corresponding to the oxygen transport through the 10Sc1YSZ-LCCN layer ($R_{10ScYSZ-LCCN}$) was calculated from:

$$R_{10ScYSZ-LCCN} = \frac{L}{\sigma_{amb}} \quad (5)$$

As for the calculation from the Wagner equation, σ_{amb} was approximated as $\sigma_{amb} \approx \sigma_i \approx x * \sigma_{ion,10Sc1YSZ}$, where x is the volume percentage of 10Sc1YSZ in the composite membrane and the ionic conductivities of 10Sc1YSZ from 750 to 950 $^{\circ}\text{C}$ were selected in a study of Irvine *et al.* [68].

The total resistance (R_{tot}) was calculated by summing $R_{10ScYSZ-LCCN}$ with two times the resistance corresponding

to the oxygen transport through the catalytic 8YSZ-LSM layer ($2 \times R_{8YSZ-LSM}$). $R_{8YSZ-LSM}$ values were taken from two studies reported in the literature. Barfod *et al.* [79] stated $R_{8YSZ-LSM}$ values from 700 to 850 °C and Kim *et al.* [67] reported them from 800 to 950 °C. In the Figures 4 and S 2, theoretical oxygen permeation fluxes calculated using data from [79] were quote as “Electrode model from [79]” while the ones calculated using data from [67] were noted “Electrode model from [67]”. The oxygen permeation flux J_{O_2} was calculated from:

$$J_{O_2} = \frac{V}{4FR_{tot}} \quad (6)$$

where

$$V = \frac{RT}{4F} \ln \left(\frac{P'_{O_2}}{P''_{O_2}} \right) \quad (7)$$

- **Calculation of theoretical oxygen permeation flux considering the resistance from the 8YSZ-LSM (50-50 vol.%) catalyst layers and a tortuosity factor**

It is most likely in the 10Sc1YSZ-LCCN composite membranes that the perovskite is in fact blocking the ionic path leading to a larger effective thickness than for the cases with single MIEC membranes. Consequently, the same theoretical calculations were made by adding a tortuosity factor. An accurate assessment of the tortuosity from the microstructure of the membranes was not performed in the study, but an approximated value of 2 was deduced from the literature [45]. The tortuosity factor (τ) was incorporated in Eq. (5) as shown in Eq. (8) and J_{O_2} was calculated using the Eq. (6).

$$R_{10Sc1YSZ-LCCN} = \frac{L}{\frac{\sigma_{amb}}{\tau}} \quad (8)$$