



Towards the fabrication of $\text{La}_{0.98-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ perovskite-type oxygen transport membranes

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Received 5 March 2014; received in revised form 5 June 2014; accepted 11 June 2014

Available online 30 June 2014

Abstract

$\text{La}_{0.98-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) is a candidate material for use as an oxygen transport membrane (OTM). In this work, fabrication-relevant properties (sintering behaviour, thermal and chemical expansion) of LSCF ($x = 0.2, 0.4, 0.6, 0.8$) were investigated in order to select the preferred composition for fabricating a thin-film supported membrane able to withstand the thermochemical stresses encountered during manufacturing and operation with simultaneously high oxygen permeation flux.

Partial substitution of La by Sr ions in LSCF is beneficial for increasing the oxygen permeation rate, but it causes drawbacks regarding manufacturing and operation. A Sr content of $x \geq 0.6$ results in a swelling of the material during sintering, which complicates the manufacturing of thin, leak-free membranes. This swelling is related to oxygen release during heating, combined with the formation of a liquid phase above 1200 °C. Furthermore, an increase in total strain with Sr content is observed. This is caused by the chemical expansion, while there is no significant change in thermal expansion with increasing Sr content.

The compositions $x = 0.4$ and $x = 0.6$ showed tolerable expansion coefficients as well as adequate sintering behaviour and were therefore selected for the fabrication of thin supported membranes. These supported membranes with a thickness of 30 μm were manufactured by sequential tape casting and characterised regarding microstructure and oxygen flux.

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Keywords: Oxygen transport membrane; LSCF; Expansion behaviour; Sintering; Tape casting

1. Introduction

$\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) perovskite-type oxides are candidate materials for application as oxygen transport membranes (OTMs). As found by Teraoka et al.,¹ oxygen flux increases with increasing Sr and Co contents, due to the concomitant increase in oxygen vacancy concentration and hence in ionic conductivity.^{2,3} Increasing Sr-content is beneficial for the functional properties of the OTM, but on the other hand it also has a strong influence on manufacturing properties.

In the present work, LSCF with a small A-site deficiency ($\text{La}_{0.98-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$) was used, which increases the oxygen vacancy concentration, but at the same time enhances

sintering activity and reduces surface segregation of Sr.^{4,5} The composition $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ has attracted major interest for use as a cathode in solid oxide fuel cells.^{1,2,6} Good stability of LSCF compositions in reducing atmospheres⁷ and with respect to the flue gas components CO_2 , H_2O and SO_x ^{8–14} has also been reported, which makes this composition with 20% Co and 80% Fe on the B site suitable for application as OTMs.

The oxygen flux j_{O_2} through a dense MIEC membrane is given by

$$j_{\text{O}_2} \approx -\frac{D_V}{4V_M L} \int_{\ln p'_{\text{O}_2}}^{\ln p''_{\text{O}_2}} \delta \, d \ln p_{\text{O}_2} \quad (1)$$

where L is the membrane thickness, D_V the oxygen vacancy diffusion coefficient, V_M the molar volume of the oxide, δ the molar fraction of oxygen vacancies, and p'_{O_2} and p''_{O_2} the oxygen partial pressures maintained on opposite sides of the membrane. Eq. (1)

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may be derived using the Wagner and Nernst-Einstein relationships, assuming the MIEC to display predominantly electronic conductivity. A detailed derivation of Eq. (1) has been provided elsewhere.¹⁵

In accord with Eq. (1), the oxygen flux increases by decreasing the membrane thickness L . If the thickness of the membrane becomes less than about 150 μm , a porous support is needed to provide sufficient mechanical integrity.^{15–20} Mismatch in the thermal expansion between the thin MIEC membrane and the porous support may cause tensile stresses, and thus may induce membrane failure. This is the major reason why the porous support is usually made from the same material as the membrane layer.

Since oxygen permeation improves with increasing Sr content and decreasing membrane thickness, the manufacturing properties of sintering and expansion behaviour are extremely important. In the present study, the influence of the partial substitution of La by Sr on sintering properties, and the thermal and chemical expansion of $\text{La}_{0.98-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) was investigated. Oxygen permeation measurements were performed on LSCF bulk membranes. Data were collected to select the preferred composition for fabrication of a thin-film supported membrane able to withstand thermochemical stresses exposed during manufacturing and operation. Supported thin membranes with a thickness of 30 μm were manufactured by tape casting and were characterised by oxygen flux measurements.

2. Experimental

2.1. Preparation

$\text{La}_{0.98-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ ($x=0.2, 0.4, 0.6, 0.8$) perovskite powders were prepared by spray pyrolysis of the aqueous nitrate solutions containing the corresponding metal nitrates, resulting in a spattered, porous powder with a high specific surface area, which is not appropriate for the tape-casting process. Subsequent calcination at 1200 °C for 5 h resulted in more suitable powders with dense, compact particles. Phase purity and stoichiometry were examined by X-ray diffraction (XRD) using a Bruker, D4 Endeavor and by inductively coupled plasma optical emission spectroscopy (ICP-OES), respectively. All powders were treated by ball milling in ethanol, using 3 mm ZrO_2 balls, to achieve a monomodal, narrow particle size distribution with an average particle size (d_{50}) of 2–7 μm . To eliminate the influence of different powder morphologies, samples for dilatometric and oxygen permeation measurements were uniaxially dry pressed from these powders and sintered at 1200 °C for 5 h.

The supported thin membranes were fabricated by sequential tape casting. A solvent-based slurry without pore former was cast on a polymeric carrier foil by the doctor-blade procedure with a casting gap of 50 μm . After drying, a solvent-based slurry containing rice starch (particle size 2–8 μm ²¹) as the pore forming agent was cast on top of the membrane layer with a casting gap of 1.9 mm. Support and membrane layer were made from identical material. For slurry preparation, ethanol (Merck KGaA) and methyl ethyl ketone (Merck KGaA) were used as solvents, Nuosperse FX9086 (Elementis Specialities Inc.) as the

dispersant, PVB-98 (Solutia Inc.) as the binder, and Solusolv S-2075 (Solutia Inc.) and PEG400 (Merck KGaA) as plasticisers. The slurry preparation procedure is described in detail in [22,23](#). In order to vary the support porosity, slurries with 20 and 30 wt% of starch in relation to the ceramic powder mass were prepared. After the tape had dried, samples 24 mm in diameter were cut out and debindered with a subsequent sintering step. To avoid delamination and/or deflection of the asymmetric membrane during co-firing, a sintering study according to [22](#) was performed. Co-firing was performed at 1200 °C with a dwell time of 5 h. The resulting membrane thickness after sintering was 30 μm with a support thickness of 650 μm . To enhance the surface area for oxygen exchange,^{24,25} an activation layer of LSCF was applied on top of a sintered membrane by screen printing. The screen printing paste contained terpineol (Sigma–Aldrich), ethyl cellulose (Sigma Aldrich) and ceramic powder. The wet layer thickness of the sieve was 100 μm , resulting in a layer thickness of 30 μm after sintering at 1000 °C for 5 h.

2.2. Characterisation

Sintering experiments were carried out using dry-pressed pellets. Dilatometric measurements were performed using a Netzsch 402E for sintering behaviour and a Netzsch 402C to characterise the expansion behaviour. The expansion behaviour was investigated using dry-pressed and sintered (1200 °C for 5 h) samples. The overall expansion was determined in air at a heating and cooling rate of 3 K/min up to 1000 °C. The thermal expansion was determined in a flowing argon atmosphere using the cooling branch. The difference between thermal and overall expansion is regarded as the chemical expansion.^{26,27}

Microstructures obtained after sintering at 1200, 1300 and 1400 °C were analysed on polished cross sections of the sintered bodies by scanning electron microscopy (SEM; Zeiss Ultra 55 and FEI Phenom) and by quantitative image analysis using the commercial software analysis. Elemental analysis was carried out by energy-dispersive X-ray spectroscopy (EDS; Inca, Oxford).

Oxygen permeation measurements of the membranes were conducted in air/Ar gradients at a constant flow rate of 250 ml/min of air as feed gas and 50 ml/min of Ar as sweep gas. The temperature was varied between 750 and 950 °C. Gold rings were used to seal the disc-shaped samples to the gasket of the quartz glass reactor at 1000 °C. The permeated gas was analysed by a mass spectrometer (Omnistar, Pfeiffer Vacuum). Oxygen fluxes were corrected for air ingress into the effluent due to leakage of the sealant. Corrections did not exceed 10% of the total measured oxygen flux. Oxygen permeation measurements on supported membranes were carried out with the support on the feed/air side.

3. Results and discussion

3.1. Powder characterisation

Phase purity of the synthesised and calcined powders was analysed at room temperature by X-ray diffraction. For

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