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Structural and functional properties of $SrTi_{1-x}Fe_xO_{3-\delta}$ $(0 \leqslant x \leqslant 1)$ for the use as oxygen transport membrane

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ABSTRACT

Perovskitic oxides are widely investigated as oxygen transport membrane materials for the efficient generation of pure oxygen or the use in membrane reactors. However, most of high performance perovskites suffer from low stability in operation conditions. Therefore, solid solutions of $SrTi_{1-x}Fe_xO_{3-\delta}$ (STF) are investigated due to the initial high stability of the strontium titanate host lattice. Self-synthesized powders with substitution of Ti by 0%, 25%, 35%, 50%, 75%, and 100% Fe were studied. Crystal structure, functional properties i.e., diffusion coefficient, surface exchange rates, and oxygen permeation rates as well as membrane fabrication and operation related material properties i.e. sintering behaviour and thermal/chemical expansion were investigated. Substitution of Ti by Fe increases oxygen mobility and, hence, oxygen permeation rates, but reduces stability in operation relevant atmospheres such as $Ar/4\%H_2$ or CO_2. At the same time thermal/chemical expansion increases. This makes the fabrication of supported thin membranes and their integration into membrane modules more challenging. It turned out that 25–35% Fe substituting Ti seems to be a good compromise between structural and functional properties. Oxygen permeation rates achieved are comparable to that of standard materials such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF). At the same time stability is higher and thermal expansion coefficients lower compared to LSCF, which makes STF with limited Fe-content (max. 35%) a promising oxygen transport membrane material.

1. Introduction

H_2 and CO containing syngas generated from oil, natural gas, coal, or biogas is the main feedstock for many chemical processes e.g. gas-to liquid technology, methanol or hydrogen production [1,2]. By the integration of oxygen transport membranes (OTM) into an autothermal reforming process, capital and energy savings for syngas production are possible by the use of a membrane reactor [2,3]. OTMs consist of gastight, mixed ionic–electronic conductors (MIEC) and allow oxygen diffusion via oxygen vacancies in the crystal lattice [4] (see Fig. 1). These membranes can be used to provide the oxygen for the syngas production process. One promising class of materials are ceramics with a perovskite crystal structure. For application in a membrane reactor these materials must possess a high oxygen flux as well as a high chemical stability in reducing or corrosive atmospheres. The highest oxygen flux was achieved using high performance materials such as $La_{1-x}Sr_xCo_{1-x}Fe_xO_{3-\delta}$ (LSCF) [5,6] or $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) [7,8]. However, the performance is maximized by increasing the defect concentration, which naturally leads to limited stability. In practice, Fe and particularly Co are chosen because those B-cations can easily be reduced in order to form mobile oxygen vacancies. But, in case of applications with very low p_{O_2}, e.g. for BSCF below 10^{-14} bar [9], the reduction of the B-cations leads to chemical decomposition of the perovskite lattice. In case of membrane reactors in addition to the low p_{O_2} aggressive gases such as CO, CH_4, and CO_2. attack the membrane material. In addition, the alkaline earth A-site cations are relatively weakly bonded, so that these materials in the presence of acid gases such as CO_2 and SO_x are easily forming carbonates, and sulphates. [10–12] Even in clean conditions the cubic perovskite phase of BSCF is stable only above 840 °C. At lower temperatures hexagonal polymorphs are formed drastically decreasing the permeability. Thus, different stabilization approaches were started mainly based on additional doping on the B-site by e.g. Zr, Nb, or Y [13–18]. However, although these

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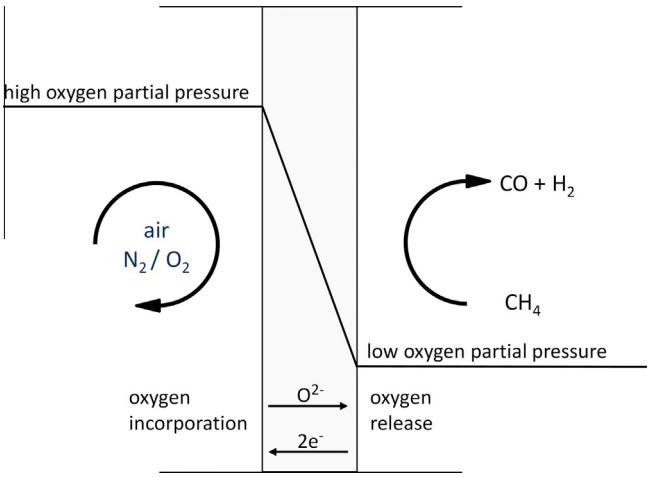

Fig. 1. Scheme of oxygen transport through a membrane for production of synthesis gas.

approaches are successful to some extent, these materials are still not sufficiently stable against the reducing and corrosive atmospheres under membrane reactor conditions [7].

Another interesting approach, which recently attracted great interest, is the development of dual phase membranes, which consist of a composite of a mainly ionic conducting phase and a mainly electronic conducting phase. The main advantage is that one can choose two stable materials, which are compatible to each other with regard to thermal expansion as well as chemical reactions at the grain boundaries [19–21].

In this paper we follow a different approach, based on the chemically very stable but nearly oxygen impermeable perovskite material $SrTiO_{3-\delta}$. Functionality i.e. mixed ionic and electronic conductivity is introduced by substitution of Ti by Fe. Such $SrTi_{1-x}Fe_xO_{3-\delta}$ (STF-($x*100$)) perovskite materials are widely investigated as oxygen sensor material [22–24]. Recently, it was also considered as cathode for solid oxide fuel cells [25], but it is hardly considered as membrane material yet [26–29].

In this work compositions of $SrTi_{1-x}Fe_xO_{3-\delta}$ with iron contents of x = 0, 0.25, 0.35, 0.5, 0.75, and 1 were synthesized and characterised regarding their functionality and manufacturing related properties. The influence of the partial substitution of Ti by Fe on sintering properties, thermal and chemical expansion of STF-x and stability is investigated. Oxygen permeation measurements were performed on STF-x bulk membranes. Based on these data a composition was chosen which possesses sufficient functional properties and is able to withstand thermochemical stresses exposed during manufacturing and operation.

2. Experimental

2.1. Sample preparation

STF-x (with x = 0, 0.25, 0.35, 0.5, 0.75, 1) ceramic powders with a perovskite structure were prepared by a modified Pechini synthesis. Titanium(IV)isopropoxide ($Ti[OCH(CH_3)_2]_4$) (Sigma Aldrich) was hydrolysed in deionised water. After removal of the organic part, the formed $TiO_2{\cdot}xH_2O$ was dissolved in nitric acid and stabilized in citric acid. The Ti concentration of the formed titanium complex solution was determined by thermogravimetry. Sr- and Fe-nitrates were dissolved in water and the titanium/citric acid complex solution was added. Additionally, Citric acid (Merck KGaA) and ethylene glycol (Merck KGaA) were added and are used for complexation and polymerisation respectively. After polymerisation and evaporation of the water a gel was formed, followed by pyrolysis of the organic parts at 600 °C in air. The powders were subsequently calcined at different temperatures between 800 °C and 1100 °C in steps of 100 °C with a heating and cooling rate of 5 K/min in air, to determine the optimal calcination temperature to achieve the single phase cubic perovskite for each composition.

All raw powders were ball milled in ethanol for 24 h, using 3 mm ZrO_2 balls. A monomodal, narrow particle size distribution with an average particle size (d_{50}) of 1–6 μm was achieved.

Samples for the determination of the expansion coefficient, oxygen permeation, and for annealing under Ar/4%H_2 and under CO_2 atmosphere were uniaxially pressed at 50–200 MPa and subsequently sintered using the parameters shown in Table 1.

2.2. Characterisation

Phase purity of the powders and CO_2 annealed samples were examined by X-ray diffraction (XRD) at room temperature, using a D4 Endeavor (Bruker AXS). Quantitative phase analysis and lattice parameter determination was done by TOPAS V4.2 (Bruker AXS) [30]. Chemical composition of synthesized powders was verified by inductively coupled plasma optical emission spectroscopy (ICP–OES). Specific surface area of the calcined and ball milled powders was determined in an AreaMeter (Ströhlein, Germany) by nitrogen adsorption and particle size distribution by laser granulometrie using a Horiba LA-950V2. Additionally the grain morphology was analysed by SEM (Zeiss Ultra 55).

Dilatometric measurements were performed using a Netzsch 402E for sintering behaviour of green, dry pressed pellets and a Netzsch 402C to characterise the expansion behaviour of sintered samples. The overall expansion was determined in synthetic air F_{air} = 100 ml/min at a heating and cooling rate of 3 K/min up to 1000 °C. The thermal expansion was determined in a flowing argon atmosphere F_{Ar} = 100 ml/min using the cooling branch. The difference between thermal and overall expansion is regarded as the chemical expansion [31–33].

Microstructures (porosity and average grain size) of the sintered bodies were analysed on polished cross sections by SEM (Zeiss Ultra 55 and FEI Phenom) and quantitative image analysis using the commercial software analySIS. Elemental analysis was carried out by energy-dispersive X-ray spectroscopy (EDS; Inca, Oxford).

Electrical conductivity relaxation (ECR) measurements were used to analyse the oxygen transport kinetics of STF. During ECR measurements, the normalized conductivity was monitored as a function of time after a step-wise change in the ambient p_{O_2} from 0.21 to 0.105 atm in the range 700–900 °C. The transient conductivity was fitted to the appropriate solution of Fick's second law of diffusion [34].

Oxygen permeation measurements of 1.5 mm thick disk shaped 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. Samples were ground with P1200 emery paper, prior to oxygen permeation measurements, to remove possible contaminations from sintering and to provide a comparable surface roughness. Gold rings with a diameter of 15 mm and a thickness of 1 mm were used to seal the samples to the gasket of the quartz glass reactor at 1000 °C

Table 1
Sintering temperature and dwell time for STF-x.

Composition	STF-0	STF-25	STF-35	STF-50	STF-75	STF-100
T_{sinter}	1400 °C	1400 °C	1400 °C	1350 °C	1250 °C	1200 °C
t_{dwell}	10 h	10 h	10 h	15 h	20 h	20 h