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Oxygen permeation and stability investigations on MIEC membrane materials under operating conditions for power plant processes

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ABSTRACT

MIEC membranes (mixed ion-electron conducting membranes) are attracting increasing interest for industrial applications in which oxygen-enriched air or pure oxygen is used. One of these applications is the oxyfuel power plant process. High oxygen permeability and adequate chemical stability under operating conditions, especially with respect to CO_2 and SO_2, are therefore essential. In the work described here, permeation and chemical stability tests were performed with tubular membranes made of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), $Sr_{0.5}Ca_{0.5}Mn_{0.8}Fe_{0.2}O_{3-\delta}$ (SCMF) and $La_2NiO_{4+\delta}$. To investigate the effects on the materials, microstructure analysis were performed before and after each experimental run by means of energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results show that the highest permeability can be reached with BSCF membranes, but BSCF displays instability with respect to CO_2. The other materials show higher chemical stability without any significant degradation effects caused by CO_2, but they do display instability if the sweep gas contains 360 ppm SO_2. Furthermore, poisoning of the membrane materials by chromium evaporated from the steel was detected in the case of BSCF and SCMF membranes.

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1. Introduction

In recent years, MIEC membranes have been attracting increasing interest due to their ability to separate oxygen from air with 100% selectivity. Promising applications for MIEC membranes include the partial oxidation of natural to synthetic gas and processes which require oxygen-enriched air or pure oxygen, such as oxyfuel power plants [1–3]. For these applications both a high O_2-permeation rate and an adequate chemical stability under the operating conditions are essential. For instance, in the oxyfuel power plant process the membrane is integrated in a recirculated flue gas stream [4], which consists of 25–30 vol.% water vapor, 70–75 vol.% CO_2, 1–3 vol.% O_2 and a SO_2 content of about 400 ppm [5,6]. So the membrane material has to be stable at least against these major components.

For BSCF, the state of the art material with the highest oxygen flux [7–9], some information has been published so far about the chemical stability concerning a CO_2-containing atmosphere. Arnold shows a negative but reversible effect on oxygen permeability [10], which is caused by the fact that alkaline earth metals tend to form carbonates in the presence of CO_2. Shao and Parka investigate, if the CO_2 content of ambient air has an impact. Their results show a slight decrease of the oxygen permeation rate at 500 ppm CO_2. A formation of carbonates could not been detected [11,12]. Further publications discuss the influence of humidified atmospheres with different material compositions comparable to the BSCF-material [13–16]. In the field of oxygen sensors and cathode materials for fuel cells the impact of CO_2 has been studied as well [17–20].

Concerning the impact of SO_2 there are much less publications available. Studies can be found in related fields, for example catalysts. Here the lanthanum of the perovskite material reacts with SO_2 to sulphates and sulphides [21,22]. Publications about the impact of SO_2 on the O_2-permeation rate of perovskite membranes for air separation are not available from the literature.

There is still a lack of investigations on alternative perovskite materials and alkaline-earth-free compositions such as $La_2NiO_{4+\delta}$ regarding CO_2- and especially SO_2-containing atmospheres. No detailed study of the microstructure after treatment has yet been published either.

In the present paper, oxygen permeation investigations for three selected membrane materials are presented, which were performed under a feed air pressure comparable to the conditions expected in power-plant processes [4,5]. Additional investigations of the microstructure before and after treatment under CO_2- and SO_2-containing atmospheres were carried out by energy-dispersive

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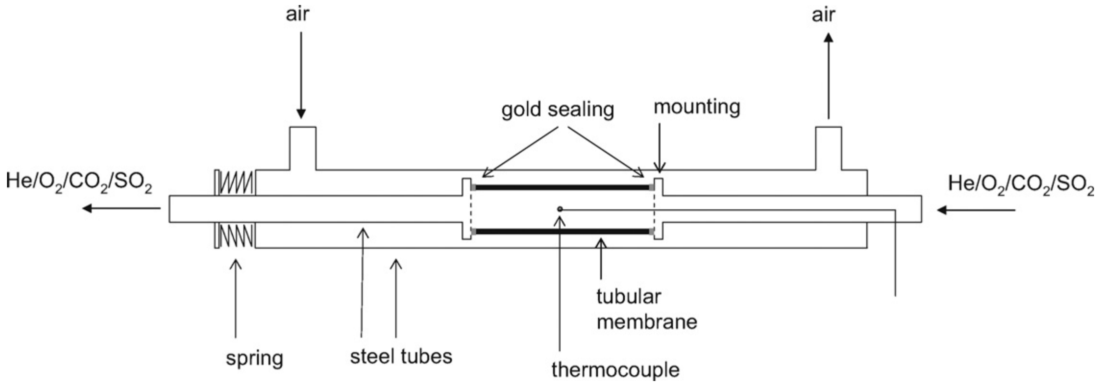

Fig. 1. Permeation cell for tubular membranes.

X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and X-ray diffraction (XRD)

2. Experimental

Fig. 1 shows the configuration of the high-temperature permeation cell used in this work for permeation measurements of tubular membranes. The membrane tube was connected to two chromium nickel steel (1.4841) tubes (OD = 10 mm, ID 8 mm) by means of adapted mountings. At the mountings, the membrane tube was sealed with gold and loaded with a spring force at both ends.

Another steel tube (ID = 18 mm) surrounded the membrane and served as the shell of the permeation cell. The membrane was kept in the isothermal zone of a three-zone tubular furnace (GERO, Germany). The temperature was measured by a type K thermocouple, positioned on the sweep/permeate gas side in the middle of the membrane tube.

The complete experimental setup is shown in Fig. 2. The permeation cell, Fig. 1, and all inlet gas fluxes were heated up to temperatures in the range of 650–900 °C.

Hydrocarbon-free synthetic air from bottles was used as feed gas. A mass flow controller (EL-Flow F201AC, Bronkhorst Mättig, Germany) was used to regulate the flux up to 20 l/min. On the retentate side, a pressure controller (El-Press P 702C, Bronkhorst) maintained the absolute pressure of the air side in the range of 1–20 bar. Additional pressure sensors (WIKA GmbH, Germany) located near the permeation cell measured the absolute pressure of the feed and retentate side.

The sweep gas was mixed from the helium, oxygen and CO_2 bottles by means of mass flow controllers (EL-Flow F-201C, Bronkhorst Mättig) with a maximum total flux of 1 l/min helium/CO_2 and 0.1 l/min oxygen. Additionally, a cylinder with a mixture of CO_2 and 360 ppm SO_2 was used for chemical stability tests. On the permeate side, the pressure was controlled by a pressure controller (type EL-Press P-702C, Bronkhorst Mättig). In analogy to the feed/retentate side, pressure sensors measured the absolute pressure near the membrane sample.

A gas chromatograph (Agilant, Germany, type 6890 equipped with J&W GS-GASPRO, GS-Q and HP MoleSieve columns) was used to analyze the composition of the gas fluxes. A multiposition valve (VICI Valco Instruments, USA) allows the composition of the sweep, permeate and retentate fluxes to be analyzed. In combination with a loop-filling manager (LFM205, Teuner-Analysetechnik, Germany), the automatic sampling system provides gas analysis independent of the system pressure.

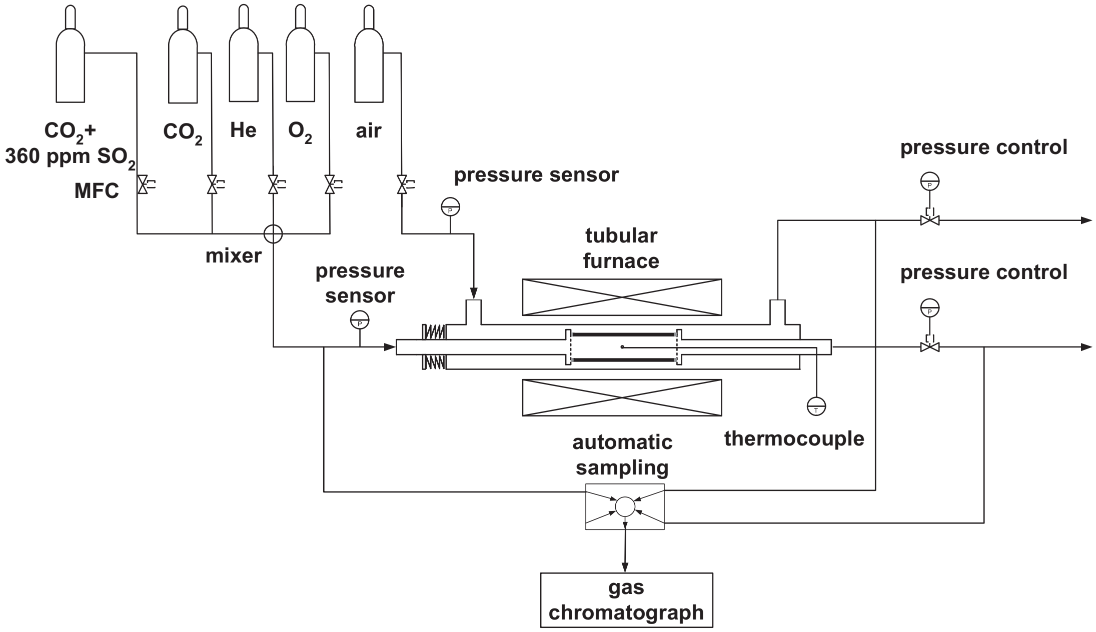

Fig. 2. Experimental setup for permeation measurement.

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