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Oxygen transport and stability of asymmetric $SrFe(Al)O_{3-\delta}$-$SrAl_2O_4$ composite membranes

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Abstract

In order to appraise a two-stage compaction procedure using pore-forming additives for the fabrication of asymmetric mixed-conducting membranes where the porous and dense layers are made of the same composition, the oxygen permeability of a series of $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ composite samples with varying architecture was studied at 1073–1223 K. The preparation route for the crack-free supported membranes included pressing of the starch-containing and pure dual-phase composite powders, sintering at 1623 K, and subsequent surface modification of the dense layers having the thickness of 0.12–0.15 mm. Analysis of the oxygen permeation fluxes show a significant limiting effect of oxygen diffusion through the support, where the porosity and average pore size are 20% and 2–4 μm, respectively. The overall level of oxygen transport, higher than that in the symmetric surface-activated membranes, was only achieved at 1173–1223 K for the porous layer thickness of 0.4 mm. Slow microstructural degradation due to the support sintering, evidenced by dilatometry, leads to a moderate decrease in the oxygen fluxes with time. At 1973 K, the corresponding changes were approximately 16% during 220 h. The results suggest that increased total porosity, preferential pore orientation perpendicular to the dense layer and incorporation of nano-sized catalyst particles into the pores are needed to increase the performance of asymmetric ferrite-based membranes.

Keywords: Oxygen permeability; Mixed ionic-electronic conductor; Asymmetric ceramic membrane; Ferrite-based composite; Microstructural stability

1. Introduction

Technologies for high-purity oxygen separation from air and partial oxidation of light hydrocarbons using dense ceramic membranes with mixed oxygen-ionic and electronic conductivity have high potential for the gas and energy industries [1–3]. However, commercialization of such devices requires meeting of often incompatible goals, namely high oxygen permeability, chemical stability and moderate thermal expansion for both oxidizing and reducing conditions, respectively encountered at the membrane feed and permeate sides. While the search for novel materials with improved transport and mechanical properties is still a major challenge, research effort was also directed towards optimization of the membrane architecture. In particular, one promising concept to improve both oxygen permeation flux and thermodynamic stability of the ceramic membrane relates to asymmetric configuration comprising a thin dense high-permeable layer applied on a porous support [2–10]. Depending upon the thickness of the gas-tight layer, the rate-determining step of the overall oxygen transport may be associated with bulk diffusion and/or surface exchange; as a rule, the latter contribution increases with decreasing thickness of the dense layer. When the permeation is controlled by kinetics of surface processes, such as recombination of lattice oxygen into gaseous O_2 or oxidation reactions on the membrane surface, the oxygen chemical potential on the membrane permeate side is higher than that in the gas environment. This effect may result in kinetic stabilization of the mixed-conducting materials, which are often thermodynamically unstable in reducing atmospheres under equilibrium conditions [1,2,11]. The porous support should also satisfy a number of requirements, including sufficient mechanical strength, low resistance to the gas flow,

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and a stable microstructure with narrow pore-size distribution [9,10]. Using the support and dense layer made of the same composition, one can ensure the chemical and mechanical integrity of the asymmetric membrane structure. A variety of methods have been proposed for the fabrication of dense thin layers on porous supports, including sputtering, spray or dip coating, slip or solution casting, pulsed laser deposition, and chemical or electrochemical vapor deposition (e.g., [2,8,12–15] and references therein).

The present work was focused on the evaluation of ferrite-based asymmetric membranes, where the porous and dense layers are both made of $SrFe(Al)O_3$–$SrAl_2O_4$ composite comprising strontium-deficient perovskite and monoclinic $SrAl_2O_4$ phases. Previous works [16,17] showed that combination of these phases makes it possible to decrease thermal expansion and to improve mechanical strength of the ceramics, whereas the oxygen permeation is governed predominantly by the perovskite component. A promising combination of ionic transport and thermomechanical properties was revealed for $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ composition. For the fabrication of asymmetric membranes, a simple two-stage compaction procedure using pore-forming additions was applied.

2. Experimental

All membranes studied in this work were fabricated from a commercial $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ powder (Praxair Specialty Ceramics, Seattle), produced by the combustion spray pyrolysis technique. Prior to compaction, the powder was milled for 0.5 h in acetone in order to break-up any agglomerates, compacted at 180–300 MPa and sintered under similar conditions, namely at 1623 K during 5 h in atmospheric air. Dense ceramic disks were uniaxially pressed at 180–250 MPa and sintered at 1623 K during 5 h in atmospheric air. X-ray diffraction (XRD) analysis confirmed the formation of dual-phase composite comprising a cubic perovskite-type $SrFe(Al)O_{3-\delta}$ and monoclinic $SrAl_2O_4$ phases (Fig. 1); the structural, microstructural and physicochemical characterization of this material was performed in previous work [17]. The planar asymmetric membranes with a diameter 20 mm and total thickness 0.8–2.5 mm were fabricated by uniaxial compaction in two steps. A part of $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ powder was mixed with maize starch (Meritana 100, Amylum, The Netherlands) used as a pore-forming agent. The additions of starch varied in the range 40–50 wt.%; one SEM micrograph of the typical starch particles is shown in Fig. 2A. After homogenization by submerging in acetone, mixing in a mortar and subsequent drying, a calculated amount of the resultant powder was introduced to a mold and uniaxially compacted at 50 MPa. Then a known amount of milled $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ powder without starch was added on the top of the first compact, and the whole structure was pressed at 150 MPa. The sintering conditions of the green compacts were similar to those of thick ceramics. The corresponding temperature profile included heating up to 1273 K with a constant rate of 0.5 K/min followed by dwell at 1273 K for 1 h, further heating up to 1623 K at 2 K/min, annealing at 1623 K for 5 h, and slow cooling down to room temperature with a rate of 1 K/min. The microstructure of the asymmetric membranes was examined using a Hitachi S-4100 scanning electron microscope (SEM) with a Rontec UHV detection system for the energy dispersive spectroscopy (EDS). SEM/EDS inspection showed that the processing conditions enable fabrication of thin dense crack-free composite layers, simultaneously preserving porous structure of the support (Fig. 2B and C). The thicknesses of both dense (DL) and porous (PL) layers were controlled adjusting the amounts of green components introduced during the two-step compaction procedure; the corresponding values and abbreviations are listed in Table 1.

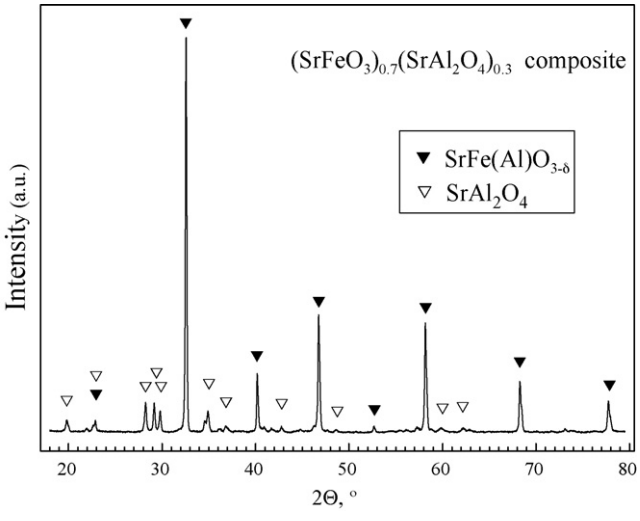

Fig. 1. XRD pattern of $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ composite sintered in air at 1623 K for 5 h.

For the analysis of pore size distribution and dilatometric studies, a series of porous ceramics were produced from the starch-$(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ powder mixtures using the same processing conditions. The results of mercury intrusion porosimetry (Autoscan-33, Quantachrome Instruments) were analyzed by the Washburn equation assuming cylindrical pores [18]. Characterization of the ceramic membrane materials included also dilatometry, gas-tightness control and determination of the steady-state oxygen permeation fluxes; description of the experimental procedures and equipment is found elsewhere (Refs. [6,11,17,19–22] and references cited). As shown in these works, the impurity concentration in oxygen, obtained using a gas-tight mixed-conducting membrane, is lower 0.01%. For all membranes studied in this work, zero level of physical leakages was confirmed under the total pressure gradient of 2–4 atm. The data on the oxygen permeation presented below correspond to the membrane feed-side oxygen partial pressure (p_2) equal to 0.21 atm (atmospheric air). In order to distinguish and/or to decrease the limiting effects of surface exchange processes, several membranes were surface-modified as indicated in Table 1. The surface activation procedures included deposition of porous layer consisting of $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ or $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$–Pt mixture (50:50, w/w), sintering at 1373 K for 2 h, impregnation with $Pr(NO_3)_3{\cdot}5H_2O$ solution in ethanol, drying and final annealing at 1393 K. For