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Perovskite Membranes for Oxygen Separation and Oxy-Combustion Processes

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Abstract

Mixed oxides with the perovskite-like structure, possessing mixed electronic and ionic electrical conductivities, are proposed for dense ceramic membranes production for both oxygen separation and oxy-combustion processes. In the study three perovskite-type mixed oxides $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3+\delta}$ (LSCF), $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3+\delta}$ (BSCF) and $La_2Ni_{0.9}Co_{0.1}O_{4-\delta}$ (LNC), considered to be the most promising materials due to high oxygen fluxes, are utilized for both plate and tubular membranes fabrication. For providing the appropriate efficiency of the oxygen production, the main role is played by thickness as well as outer surface development of membranes. On account of this, three configurations of plate membranes were tested, *i.e.* thick dense membranes, thin dense diaphragms on porous support and thick dense membranes coated on both sides with porous thin layers. Tubular membranes, more useful in industrial practice due to their larger effective surface, mechanical stability and easiness of application, were prepared in two configurations, *i.e.* dense thin-walled tubes made by isostatic pressing and extrusion methods, as well as thin dense membrane, coated on the porous tube. The basic physicochemical properties of the obtained diaphragms were determined. Some of them were characterised by the measurement of the oxygen permeation flux.
Keywords: Perovskite like materials, Oxygen membranes, Tubular membranes

MEMBRANY PEROWSKITOWE DO SEPARACJI TLENU I DO PROCESÓW SPALANIA W TLENIE

Tlenki mieszane o budowie typu perowskitu, mające mieszane przewodnictwo elektronowe i jonowe, są materiałami proponowanymi do produkcji gęstych ceramicznych membran wykorzystywanych w procesach separacji tlenu i spalania tlenowego. W prezentowanych badaniach wykorzystano do wytwarzania membran, zarówno w kształcie płytek jak i rurek, wykorzystano trzy tlenki typu perowskitu: $La_{0,6}Sr_{0,4}Fe_{0,8}Co_{0,2}O_{3+\delta}$ (LSCF), $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3+\delta}$ (BSCF) i $La_2Ni_{0,9}Co_{0,1}O_{4-\delta}$ (LNC), rozważane jako najbardziej obiecujące materiały z powodu dużych strumieni tlenu. Przy zapewnieniu odpowiedniej wydajności wytwarzania tlenu główną rolę odgrywa grubość oraz rozwinięcie powierzchni zewnętrznej membrany. Z uwagi na to, badaniom poddano trzy konfiguracje membran płytkowych: gęste grube membrany, gęste cienkie diafragmy na porowatym podkładzie i gęste cienkie membrany pokryte obustronnie grubymi warstwami porowatymi. Membrany rurkowe, bardziej przydatne w praktyce produkcyjnej w związki z ich większą powierzchnią efektywną, mechaniczną stabilnością i łatwością stosowania, przygotowano w dwóch konfiguracjach: gęste grubościenne rurki wykonane metodami prasowania izostatycznego i odlewania termoplastycznego oraz gęste cienkie membrany stanowiące pokrycie porowatych rur. Oznaczono podstawowe właściwości fizykochemiczne otrzymanych diafragm. Niektóre diafragmy scharakteryzowano za pomocą pomiarów strumienia przenikania tlenu.
Słowa kluczowe: materiały perowskitowe, membrany tlenowe, membrany rurowe

1. Introduction

The majority of papers on the oxygen permeation through membranes deal with plate diaphragms in a disk shape, whose the effective surface is very limited. However, this type of diaphragms is extremely useful for their property characteristics. In the industrial application the dense tubular membranes revealing mechanical stability, effectiveness and easiness of application are preferred. In order to elaborate them, two methods mainly are used, namely plastic or thermoplastic extrusion and isostatic pressing [1-3].

The aim of this work was to elaborate both plate and tubular membranes in a different configuration *e.g.* thick dense membranes, thick dense diaphragms coated with porous layer and thin membranes on porous support. The plate diaphragms were used to determine the basic properties of perovskite materials. The tubular diaphragms were fabricated as dense thin-walled tubes by isostatic pressing and plastic extrusion as well as the thin perovskite layer was obtained on porous alumina support in tube-shaped.

2. Experimental

As raw materials for the oxygen membranes fabrication three perovskite-type mixed oxides, $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3+\delta}$ (LSCF), $La_2Ni_{0.9}Co_{0.1}O_{4-\delta}$ (LNC) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3+\delta}$

(BSCF), were used. They were synthesized by the solid state reaction method which ensures appropriate properties of the obtained powders and high efficiency of the process. High purity oxides and carbonates of appropriate metals were used. The precursors were milled with ethanol in the attritor for 2 hours at 280 rpm. The slurry, obtained in this manner, was dried at 70ºC. The calcination of the obtained powders was performed in the electric furnace at 850ºC (LSCF), 1150ºC (LNC) and 950ºC (BSCF) for 5 hours. Perovskites materials for oxygen membranes manufacturing have to strongly fulfil two demands: powders have to be monophasic and possess the assumed chemical composition. To gain monophase powders it was necessary to carry out the multiple operations of milling and calcination processes. The XRD analyses of the prepared materials are presented in Fig. 1.

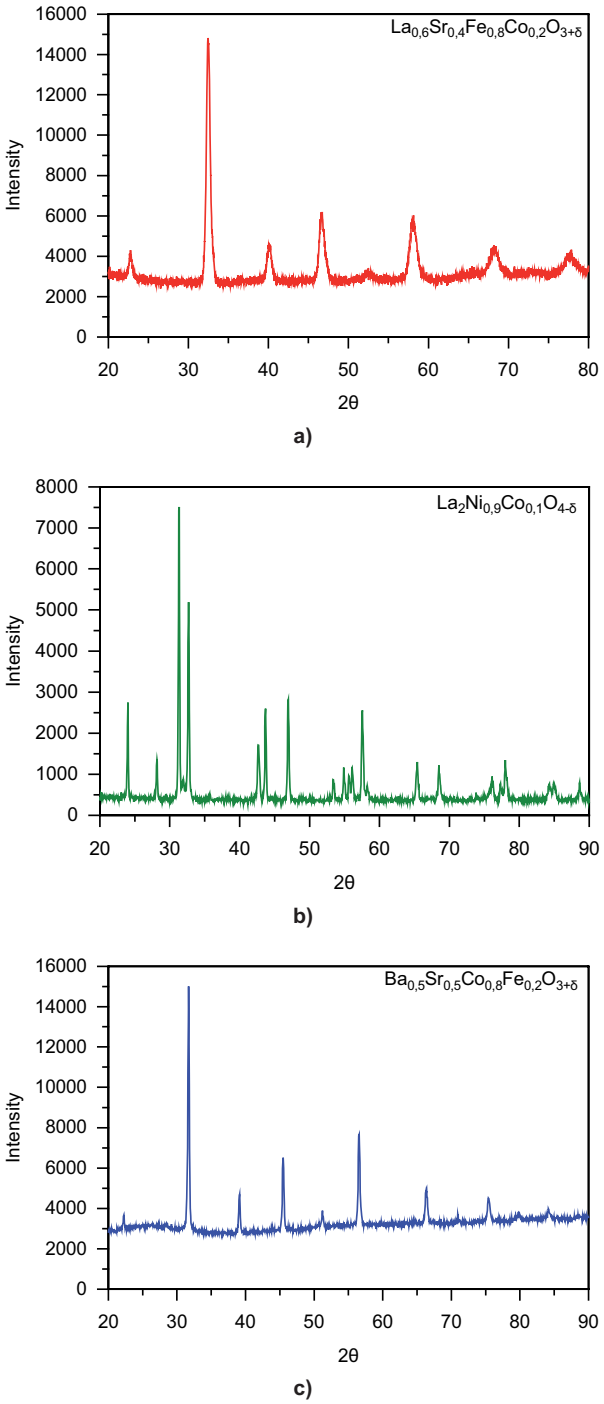

Fig. 1. XRD analysis of LSCF, LNC and BSCF perovskite materials.

As it can be seen in Fig. 1, all manufactured materials are monophasic. Also the chemical composition of each material was in good agreement with the one assumed for fabrication. The specific surface area of prepared perovskite powders was slightly lower in comparison to the powders manufactured by other methods described in the literature. This feature strongly influences shaping properties, which, for such a low specific surface area, were not sufficient. In order to improve shaping properties of powders, granulation of these materials was performed; the powder was milled with deionised water in an attritor for 30 minutes, then dispergants, a binder and lubricants were added and the a mixture was dried in a spray drier.

3. Results and discussion

3.1. Plate membranes

LSCF oxygen membranes were made by filling the die for uniaxial pressing (inner diameter of 41 mm and height of 70 mm) with 4.24 g of LSCF granulate. Firstly, the plates were pressed uniaxially under pressure of 10 MPa and then pressed isostatically under pressure of 190 MPa. The obtained green bodies were sintered at 1350ºC with the dwell time of 2 hours as well as the heating and cooling rate of 100ºC per hour. Obtaining the dense sinter was confirmed by the determination of water absorbability, density and open porosity: respectively A = 0.00 %, ρ = 6.18 g/cm^3, P = 0.00 % were found. The membranes were polished by coarse-grained emery paper to develop the external surface area and improve membrane efficiency in this way. The dimensions of the polished membranes were ϕ = 32.81 mm and h = 0.85 mm (Fig. 2).

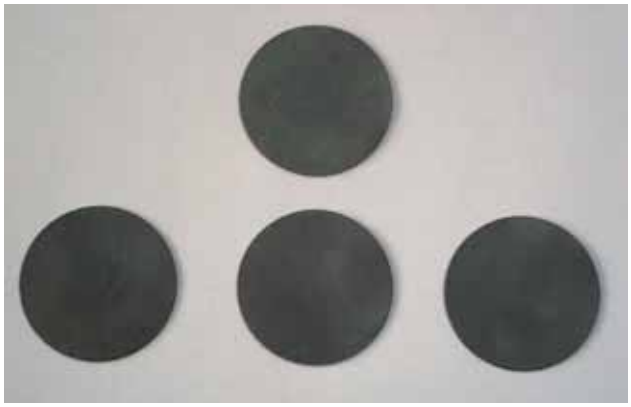

Fig. 2. LSCF thick dense oxygen membranes.

The parameters affecting the value of oxygen permeation flux through the membrane are: density of membrane (> 90 % of theoretical value) and appropriate microstructure. It is advisable to receive close packing of huge particles because short and wide grain boundaries are barriers for oxygen transport. Therefore the microstructure of the prepared membrane was determined using the scanning electron microscope (Fig. 3).

The obtained sinters (Fig. 3) consist mainly of particles of quite large dimensions and of smaller ones which fill empty spaces between large particles. The grain boundaries are

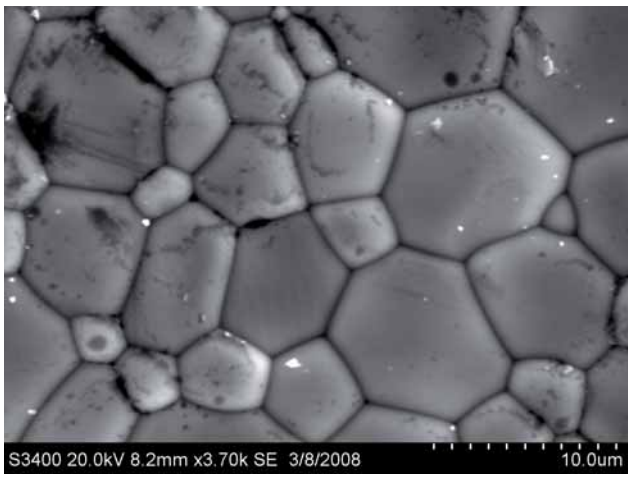

Fig. 3. SEM micrograph of LSCF dense membrane surface.

narrow and long what suggests receiving the appropriate microstructure.

The LNC and BSCF plate membranes were prepared in the same manner. However, in the case of LNC diaphragms the weight of granulate was increased to 5.12 g and the pressure of uniaxial pressing to 13 MPa. In order to receive dense membranes the sintering temperature was increased to 1400ºC and the dwell time amounted one hour. The water absorbability, density and open porosity of LNC membrane were found as follows: A = 0.00 %, ρ = 7.06 g/cm^3, P = 0.03 %, respectively.

In the case of BSCF membranes, the die having a diameter of 34.5 mm was used as a result of a lower value of shrinkage of BSCF material. Also smaller amount of material (3.3 g) was pressed uniaxially under 9 MPa. In order to receive dense membranes the sintering temperature was decreased to 1000ºC and the dwell time amounted one hour. The water absorbability, density and open porosity for BSCF membrane A = 0.19 %, ρ = 5.08 g/cm^3, P = 0.94 % indicate that 88 % of theoretical density was achieved. It suggests the necessity of working out technology of manufacturing of the higher sintered BSCF membrane.

One of the manners of oxygen permeation flux improving through the dense membrane is obtained by coating the thin porous layer on the one or on both sides of membrane. It causes the development of the active surface which in turn brings about predominance of surface processes revealed by higher permeation outcomes. Also in this approach the thin porous layer on the LSCF dense membrane was fabricated by the screen printing method (Fig. 4).

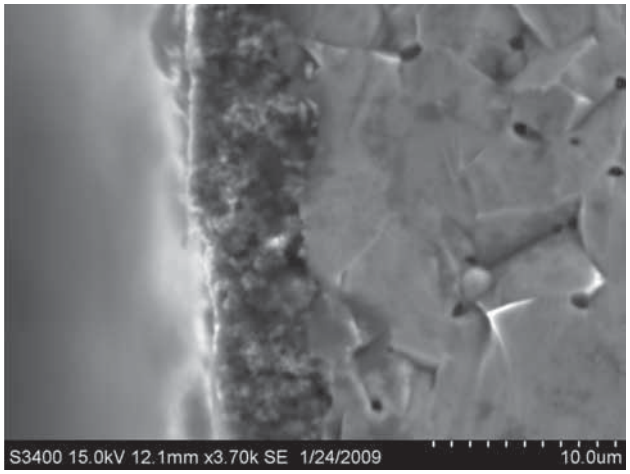

Fig. 4. SEM micrograph of cross-section of porous layer deposited on dense LSCF membrane.

As it can be seen in Fig. 4, by means of the screen printing method it was possible to obtain a porous layer of the thickness of 6 μm which well adheres to the dense membrane.

The second manner of gaining the higher oxygen permeation flux through the membrane consists in decreasing of its thickness to the optimal value, assuring of the appropriate mechanical strength. Such a solution results in controlling the oxygen permeation only by surface processes which are more effective than the diffusion ones. To satisfy such requirements the designed membranes consist of thick porous support ensuring mechanical strength and the thin dense layer, fulfilling the membrane function. In our approach we also prepared membranes in such a configuration. In order to fabricate porous support, LSCF granulate was mixed with 25 wt% of SAPEX carbon black (pores generating agent) and then ethylene glycol was poured. The body prepared in this way was pressed uniaxially in the die of diameter of 41 mm under pressure of 8 MPa. The sintering process of that body was slower in comparison to the dense membrane and the maximal temperature was slightly lower as well, which ensured a good adhesion between porous support and the dense membrane. After sintering, both external surfaces of carrier disk were polished with coarse-grained emery paper. Then the perovskite paste was prepared and deposited on support by Surface Impregnation Method [4] and sintered slightly faster than porous support. To receive the appropriate thickness of the dense layer, the next layer was deposited and again this membrane was sintered. The last, third layer was sintered at 1350ºC according to the curve for which dense membranes were gained. Fig. 5 presents SEM micrograph of such a membrane cross-section.

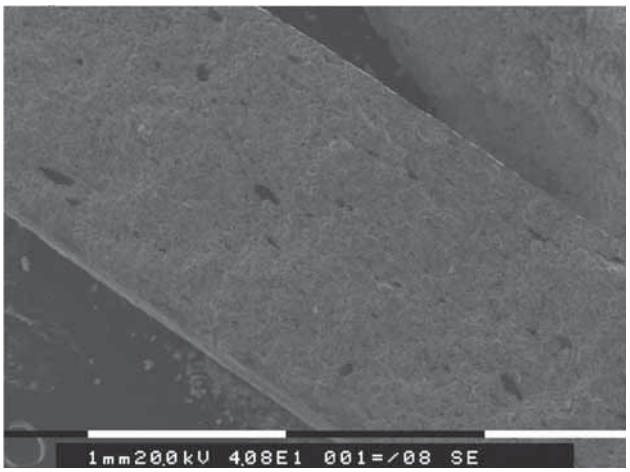

Fig. 5. SEM micrograph of cross-section of dense layer deposited on porous LSCF membrane.

3.2. Measurement of the oxygen permeation flux

The most important parameter for membranes which characterizes its possibility to be effectively used for oxygen production is the oxygen permeation flux. Therefore, the

special apparatus for measurement of the oxygen permeation flux was designed and built. In general, it consists of a pipe furnace and a flow chamber. The internal furnace chamber is made of the alumina tube and the flow chamber consists of the silica tube and teflon pugs used for this tube sealing and gases inserting inside the flow chamber by means of alumina tubes. Inside the chamber there is an alumina tube on which the tested membrane is fixed. In order to stabilize the gases flow, two automatic flow regulators were applied. The first one with maximal flow of 1dm^3/min for regulation of helium flow in the main chamber and the second one with the maximal flow of 50 cm^3/min for regulation of gasses flow inside the ceramic tube on which the tested membrane was assembled. This stand also consists of a gas analyser for measurement of the content of oxygen in helium on the exit from the flow chamber in the range of 0–25 %. Before the measurement, the furnace is heated to 900ºC and then sealed by means of pugs and teflon tape and rinsed by helium until the whole oxygen is removed. Simultaneously the ceramic tube interior is rinsed by nitrogen. Then helium flow intensity is decreased to the assumed value and nitrogen is changed into air. After the conditions stabilization, the measurement of the content of oxygen in gas is carried out. After the measurement end the leak tightness test is carried out. This can be seen in Fig. 6.

The results of measurements are presented in Figs. 7 and 8. Fig. 7 shows the results of oxygen permeation flux

Fig. 6. The apparatus for oxygen membranes testing.

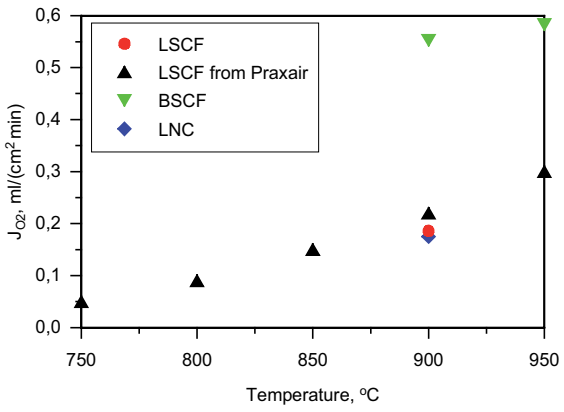

Fig. 7. Oxygen permeation flux through dense membranes.

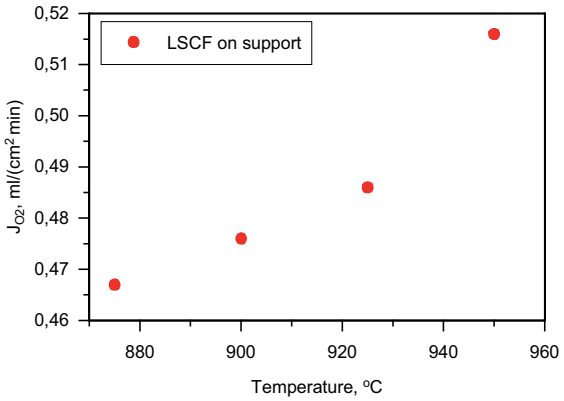

Fig. 8. Oxygen permeation flux through LSCF membrane deposited on porous support.

for LSCF, LNC and BSCF thick dense membranes and, for comparison, the membrane made from commercial LSCF powder bought from Praxair Company.

The highest value of oxygen permeation flux reaching 0.583 ml/(min·cm^2) was obtained for BSCF membrane at 950ºC. It is comparable to the values reported in many papers [4]. The oxygen permeation flux for LSCF membrane prepared from the powder synthesised by solid state method is ca. 15 % lower than flux found for the membrane made from the commercial LSCF powder. However, a considerable increase of oxygen permeation flux is visible in the case of LSCF thin layer deposited on the porous support (Fig. 8). This membrane at 900ºC reveals over 2.5 times higher flux in comparison with the thick dense one (cf. Figs. 7 and 8).

3.3. Tubular membranes

The tubular diaphragms were fabricated as dense thin-walled tubes by isostatic pressing and plastic extrusion as well as the thin perovskite layer on porous alumina support in tube-shaped.

During shaping of LNC tubular membrane by the isostatic pressing method, the elastic mould made from the silicone material was used. LNC granulate was pressed under pressure of 190 MPa. The obtained green body was ϕ16/ϕ11.9×200 mm, and then it was turned on the lathe. As a result the obtained tube was ϕ15.5/ϕ11.9×195 mm. In order to gain a dense tube it was sintered at 1400ºC for one hour of dwell time as well as with the heating and cooling rate equal to 100ºC/h. As a result of the shrinkage effect of the perovskite material after sintering the tube had the following dimensions: ϕ12.5/ϕ9.8×158.4 mm (Fig. 9).

Fig. 9 LNC tubular membrane made by isostatic pressing.

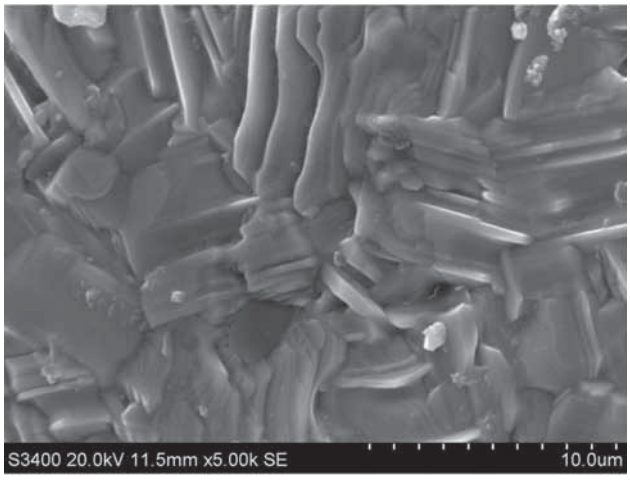

Fig. 10. SEM micrograph of internal surface of LNC dense tubular membrane.

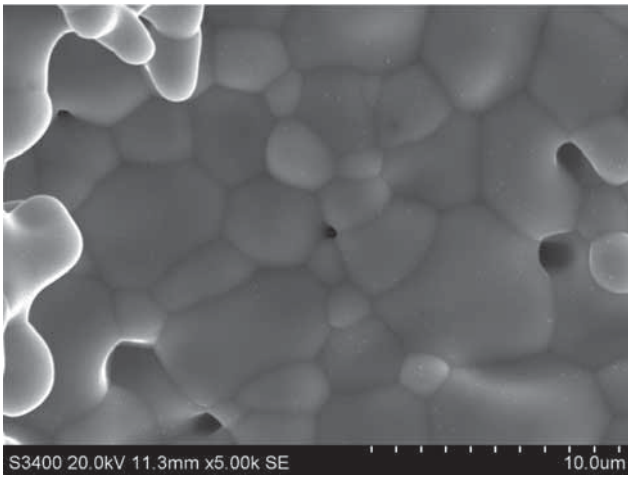

Fig. 12. SEM micrograph of external surface of LSCF dense tubular membrane.

The water absorbability, density and open porosity were determined to be as follows: A = 0.02 %, ρ = 6.88 g/cm^3, P = 0.14 %. Additionally, the microstructure of both sides of the tubular membrane was examined by the scanning electron microscope. Fig. 10 presents the SEM micrograph of internal surface of the membrane.

As it can be seen in Fig. 10, the microstructure of the obtained tube looks like a mosaic consisting of plate-shaped crystals. This microstructure is quite compact without any visible pores.

In order to form a thin-walled tube by the extrusion method, pug mill Dorst V 10/5 was utilized. The LSCF perovskite powder was mixed in a stirrer with plasticizer. In the forming process the shaping set was used consisting of a die of diameter of 17.2 mm and mandrel of diameter of 11.2 mm. Extruded tubes were dried on a wood tray for one hour at 60ºC in a drier and then in ambient air. After drying LSCF tube was ϕ16.3/ϕ10.3x225 mm and was sintered at 1350ºC with the dwell time of 2 hours as well as the heating and cooling rate of 100ºC per hour. As a result of shrinkage, the tube dimension after sintering reached ϕ11/ϕ7.5×130 mm (Fig. 11).

Unfortunately, in the consequence of unappropriate homogeneity of the plastic body during tube forming, after sintering on its external surface, numerous spots and craters appeared (Fig. 11). Additionally, water absorbability, density and open porosity were determined: A = 1.13 %, ρ = 5.74 g/cm^3, P = 5.74 %. These results indicate that the obtained tube density is 91 % of the theoretical one. Additionally, the surface microstructure of each side of the tubular membrane was examined by the scanning electron microscope. Fig. 12 presents SEM micrograph of external surface of membrane.

Fig. 11. LSCF dense tubular membrane manufactured by extrusion method.

From Fig. 12 one can conclude that the external membrane surface consists of fine particles of a comparable size and spherical shape. In comparison with dense membrane (Fig. 3) this microstructure reveals the presence of small single pores.

On the basis of the obtained results, one can draw a conclusion that in the process of tube forming by the extrusion method, the continuity of the green body structure is of crucial significance. Such a property can be controlled by appropriate plastic body homogenizing.

The last method of tubular membrane fabrication used in this work, consisted in the deposition of the thin perovskite layer on porous tube-shaped alumina support. This procedure consists of manufacturing of the alumina tubes by the extrusion method, their preliminary sintering at the temperature lower than the one used for perovskite materials and alumina sintering, multiple depositions of perovskite paste and final tubes sintering at the temperature for which the dense perovskite sinters are obtained. The porous alumina tube (support) was made from 99.7 % Al_2O_3 (C799). It was formed from the plastic body of ϕ 20/ϕ14.4x190 mm. After drying, tubes were sintered at 1000ºC for one hour of dwell time. At this stage, it was necessary to control the obtained density, porosity and absorbability of the biscuit tubes. The determined porosity was on the appropriate level larger than 40 %. In order to prepare the perovskite paste, LSCF powder was mixed with terpineal, ethylohexyl (DOP) and ethylocellulose and passed through the rolling mill. The obtained paste was deposited on prepared alumina tubes by Surface Impregnation Method [4]. The tubes with the deposited paste layer were sintered again in the same conditions. Then the next perovskite layer was deposited in the described above manner. The tubes with deposited layers were sintered at 1350ºC for the dwell time of 2 hours as well as the heating and cooling rate of 100ºC per hour was performed. Fig. 13 presents the view of the obtained tubes of ϕ18.6/ϕ13.5×113 mm. Unfortunately, we were not successful in obtaining the perovskite layer of the same thickness on the whole tube length.

Fig. 13. LSCF thin dense membrane deposited on porous alumina tube.

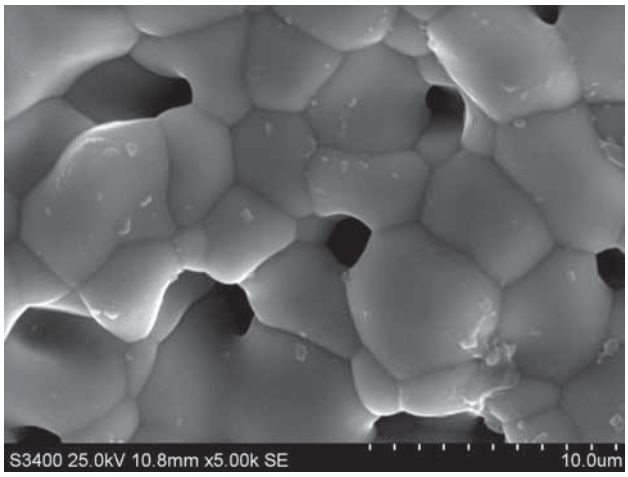

Fig. 14. SEM micrograph of LSCF thin perovskite layer.

It is commonly known that if the porous support could fulfil its function its porosity should be higher than 20 %. Our tubes exhibit the following values of water absorbability, density and open porosity; A = 7.47%, ρ = 3.06 g/cm^3, P = 22.86 %, and these are the appropriate data. The only method to confirm the existence of a thin dense layer on the porous support is to examine the microstructure. Fig. 14 presents SEM micrograph of the prepared perovskite layer.

As it can be seen in Fig. 14, the prepared layer exhibits the microstructure rich in pores which can negatively influence oxygen transport. Indeed, this configuration of oxygen membranes requires further improvements regarding optimization of both paste properties and sintering conditions.

4. Conclusions

The method of perovskite-like powders synthesis has been elaborated and verified on a semi-technical scale. Based on elaborated perovskite-like powders, oxygen permeating membranes were manufactured in various geometrical shapes. The highest oxygen permeation flux (0.58 ml/(cm^2·min) at 950ºC) was obtained for thick dense BSCF membrane and this result is comparable to the ones reported in the literature [5]. Deposition of LSCF thin layer on the porous support caused increasing of oxygen flux in comparison with the thick dense membrane due to predominance of surface processes over diffusion ones. The thin-walled perovskite tube manufactured by isostatic pressing shows high density (more than 98 % of theoretical value [6]) and homogenous microstructure of each tube side. For providing the appropriate efficiency of the oxygen production from membranes, the main role is played by thickness as well as outer surface development of membranes.

In the future a new configuration of a thin dense perovskite layer deposited on the tube-shaped porous perovskite support as well as the dense perovskite honeycomb monolith are planned to be manufactured. Studies on elaboration of new compositions of perovskite-like materials exhibiting higher oxygen flux will also be continued.

Acknowledgments

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