S.E.M. STUDY OF SOME SUBSTITUTED BARIUM COBALTATE DENSE CERAMIC MEMBRANES

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abstract: $Ba(Bi_{0,1}\ Co_{0,2}Fe_{0,7})\ O_{3-\delta}$ and $Ba_{0,5}\ Sr_{0,5}\ (Co_{0,8}\ Fe_{0,2})\ O_{3-\delta}$ mixed conduction ceramic membranes for oxygen separation were investigated by optical and scanning electron microscopy (SEM Quanta 400) in order to investigate the influence of temperature on the sintering quality and to study pore appearance and texture of the obtained sample pellets. Optical microscopy was done on the as sintered pellet surface and S.E.M. determinations on both prepared pellet surface and rupture zone.

keywords: oxygen separation, ceramic membrane, S.E.M., fracture image.

Introduction

Economical issues brought about by the advantage of conducting pure oxygen directly to the reaction zone in membrane reactors induced new orientations in oxygen selective dense ceramic membrane research [1-4]. Ceramic membranes show chemical, thermal and structural stability and high oxygen selectivity. By oxygen electroreduction on the feed side:

$$2O^{2-} = O_2 + 2e^- \quad (1)$$

followed by ambipolar diffusion of the O^{2-} ions down the p_{O_2} gradient and electrons in the opposite direction, across the membrane, and by reoxidation on the delivering side, oxygen may accurately be separated from mixtures, for organic syntheses or syngas production [5,6].

The oxygen flux through the mixed conduction membrane mainly depends on:
- The diffusion coefficient of the oxygen ion through the ceramic material;
- The kinetics of the redox exchange on the two sides of the membrane and
- The membrane conductivity by electrons and holes.

The control of these parameters on the process global rate may be used to classify oxygen ion conducting ceramic materials:

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- diffusional control characterizes ceramic materials with negligible ionic conduction. Some are used as cathodic connector materials in hot fuel cells (SOFC).
- Electronic conduction limitations are typical for solid electrolytes, like ytria, stabilized zirconia or gadolinium oxide stabilized ceria used as electrolyte in hot fuel cells [7,8], but also in electrochemical oxygen pumps and in hot oxygen sensors.[9]
- Mixed control of the process characterizes mixed conduction ceramic materials used in hot fuel cell cathodes or in passive oxygen separation membranes.
- Control by slow kinetics of the electrode reaction (1) at the membrane surface is a disadvantage in most applications. Depending on application functionality, this kind of limitation may appear even for materials having good electrocatalytic properties, if:
- The membrane is very thin and the diffusion process has to deliver large oxygen fluxes, which oxygen reduction and subsequent reduction can not keep up with.
- The material has good diffusivity and allows reduction of working temperature, which in turn reduces reaction rate more than diffusion rate. This can be overcome by specific area enlargement or by applying an electrocatalyst on both membrane sides.

Scanning electron microscopy determinations presented here aimed at surface characterization, pore structure and crystallite dimension assessment. Texture was investigated both in prepared pellet surfaces, as well as in rupture zones.

Experimental

$Ba(Bi_{0,1}\ Co_{0,2}Fe_{0,7})\ O_{3-\delta}$, referred to as **BBC2F7** and $Ba_{0,5}\ Sr_{0,5}\ (Co_{0,8}\ Fe_{0,2})\ O_{3-\delta}$, referred to as **CF2SB** were obtained by chemical synthesis from salts containing the appropriate metals. The obtained ceramic powders were ground and pressed to 1 mm thick pellets 20 mm in diameter and then sintered at a series of temperatures close to 1000 and respectively 1100 ^{o}C.

Scanning electron microscopy on pores and prepared surface was performed on a Quanta-400 scanning electron microscope [10]. Probes were examined under vacuum (0.45 Torr) and electron acceleration voltage was 15 kV. The gaseous detector was used. The working distance was 10 cm. Fig. 1 presents the overall scheme of the SEM.

Results and discussion

For both $Ba(Bi_{0,1}\ Co_{0,2}Fe_{0,7})\ O_{3-\delta}$, (BBC2F7) and $Ba_{0,5}\ Sr_{0,5}\ (Co_{0,8}\ Fe_{0,2})\ O_{3-\delta}$, (CF2SB), the density and porosity results obtained during structural characterization are presented in Table 1 for the optimum and for one of the lower sintering temperatures used.

Table 1. Properties of the sintered membranes

No	Material designation	BBC2F7		CF2SB	
1	Sintering temperature (^{0}C)	1030	1040	1135	1145
2	Apparent density (g/cm^{3})	5.30	5.44	3.86	3.65
3	Porosity (%)	4.89	0.84	5.88	1.01

With apparent density values of 0.84% for BBC2F7 and 1.01% for CF2SB for the higher sintering temperatures, both membranes satisfy the porosity limit given for dense ceramic membranes ($P_a \cong 1\%$). Only pellets sintered at the higher temperature were subjected to further characterization tests.

Optical microscopy was performed at 600x magnification. Figs. 2 and 3 show the corresponding micrographs.

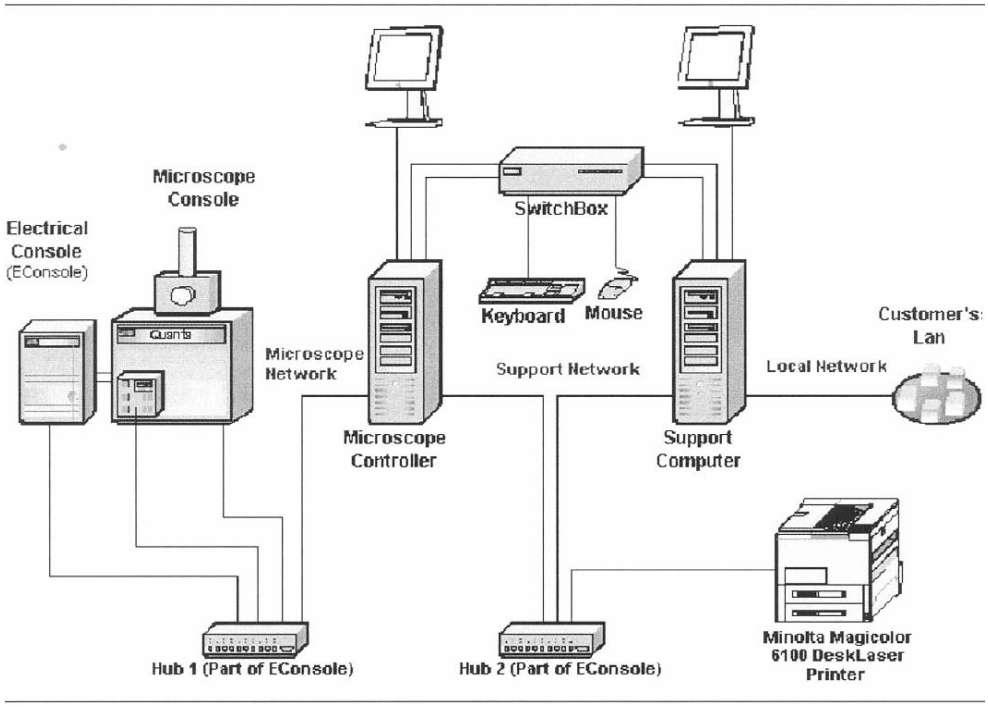

Fig. 1: *Overall scheme of Quanta-400 SEM used for pore imaging.*

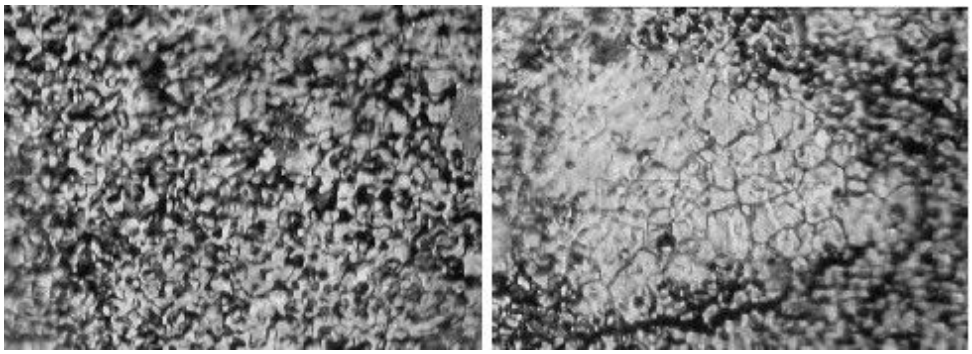

Fig. 2: *Micrographs of sample BBC2F7 sintered at 1030°C (left) and at 1040°C (right).*

The optical microscopy analysis of sample BBC2F7 sintered at 1040°C shows good densification with crystallite dimensions within the range from 10 to 20 μm (Fig. 2, right

side), whereas the micrograph of an identically prepared pellet of BBC2F7, sintered at only 1030°C, shows poor densification (Fig. 2, left side).

Optical microscopy put to evidence the influence of sintering temperature on densification for the CF2SB ceramic material as well. Best sintering occurs at 1145°C and leads to very good densification with crystallites as small as 5 μm (Fig. 3, right side) as compared to the CF2SB pellet sintered at 1135 °C, which shows poor densification and the appearance of some holes in the structure (Fig. 3, left side).

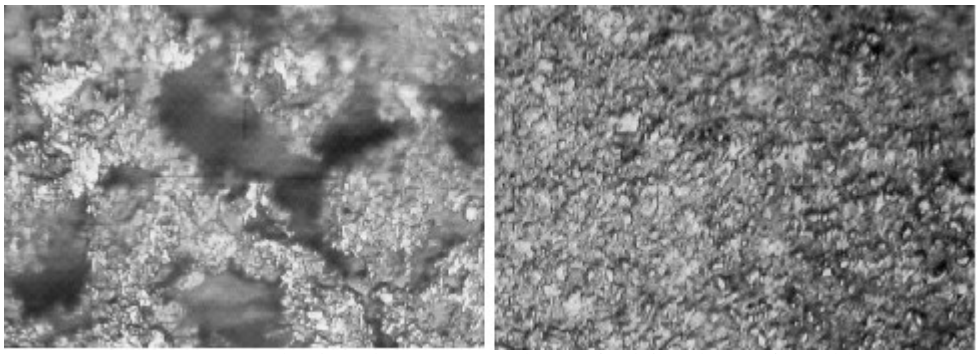

Fig. 3: *Micrographs of sample CF2SB sintered at 1135°C (left) and at 1145°C (right).*

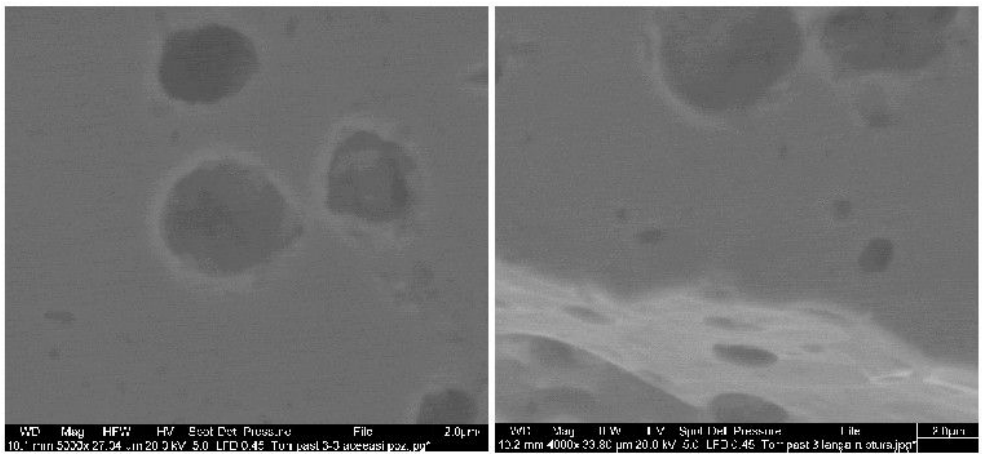

Fig. 4: *Surface detail (left, 5000x) and rupture detail (right, 4000x) of the CF2SB membrane*

SEM using a Quanta 400 scanning electron microscope was performed to analyze the prepared sample surface as well as the inner surface of pores. We were able to analyze the inner closed pore surface exposed during the probe preparation by grinding. In this regard the aspect of the plane pellet surface which resulted after grinding and lapping was compared to the images of the surface on the bottom of pores. Fig. 4 (left) shows an area on the CF2SB pellet surface. It can be clearly seen that the pore inner surface is continuous, without any holes, which might have given birth to a web of interconnected pores. All analyzed pores showed to have a similar appearance. This lead us to the conclusion that the existing pores, which had been previously evidenced by porosity measurements to be 1 % of the pellet volume, are closed pores and may not sustain free gas diffusion through the

pellet. Fig. 4 (left) shows the pore image with focus on the pore bottom. In spite of the fact that, unlike the pellet surface, the pore bottom was unprepared, its aspect differs from that of the prepared pellet surface only by a higher degree of roughness.

The angular sample rotation facility of the microscope permitted us to scrutinize the rupture zone in its depth. The image showing the rupture zone of the CF2SB pellet in Fig. 4 (right) confirms that pore occurrence does not vary much with advancing to the inner layers of the pellet.

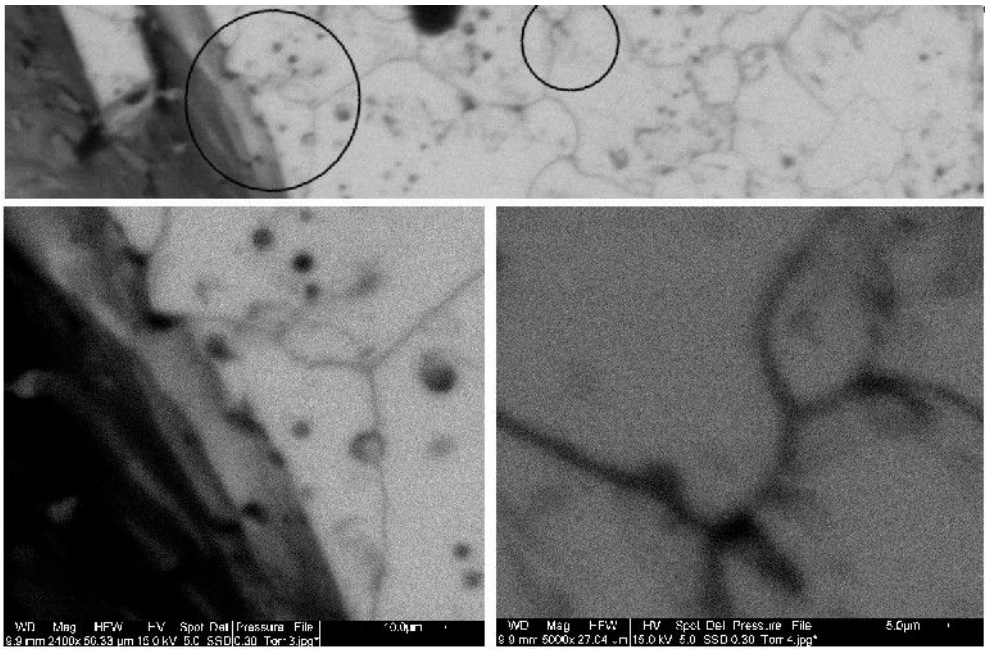

Fig. 5: *Rupture detail (left, 2400x) and surface detail (right, 5000x) of BBC2F7 as targeted in the upper image by circles on the corresponding side.*

Fig. 5 shows in the upper image a large area of the BBC2F7 pellet including the rupture zone. The 300x magnification image was used to target the beam on two areas, one on the rupture zone, marked with the left circle, and the other on the prepared surface, marked with the circle on the right. The magnified images are shown underneath on the corresponding sides in Fig. 5.

Conclusion

Optical microscopy confirms good sintering results for the sintering temperature of 1040 ^{o}C for membranes consisting of BBC2F7 and 1145 ^{o}C for membranes consisting of CF2SB. SEM analysis performed on prepared surfaces at magnifications from 300x to 5000x confirms the dense structure evidenced by porosity measurements. SEM analysis performed on rupture zones shows that porosity is formed mainly by closed pores.

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