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Current Developments of Mixed Conducting Membranes on Porous Substrates

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The fabrication of mixed ionic-electronic conducting (MIEC) ceramic-based membranes for oxygen separation has extensively increased in the last three decades as a promising alternative of clean energy delivery. In recent years, the interest on supported MIEC membranes has increased due to their attractive properties such as higher mechanical strength and oxygen flux compared to self-supported membranes. This work presents a literature review on the development of supported MIEC membranes of perovskite structure. The concepts and transport mechanism of those membranes are explained and recent works on supported MIEC membranes are presented. Finally, manufacturing methods of self-supported membranes and their influence on oxygen permeation are discussed.

Keywords: *perovskite, MIEC, porous substrates, self-supported membranes*

1. Introduction

The reduction of CO_2 emissions due to electric power generation is one of the global challenges currently. Carbon capture and storage (CCS) is an approach to relieve global warming by capturing CO_2 and storing it instead of releasing it into the atmosphere[1-4]. Different fossil fuel power plant concepts for CCS are currently being developed, such as oxyfuel power plants. In this process, the fossil fuel is combusted using pure oxygen and the result is a gas stream with almost pure CO_2 (90-95%) in the dried flue gas. The CO_2 can then be captured more easily than when air is used in the combustion process and stored in a safe geological site[5].

Mixed ionic-electronic conducting (MIEC) membranes are promising alternatives for oxyfuel power plants due to their high selectivity for oxygen separation and their significantly lowest efficiency losses compared with currently existing cryogenic distillation technology for oxygen separation[6]. The MIEC family is rich in structures and the perovskite structure is within them. The perovskite structure exhibits good ionic and electronic conductivity leading to attractive oxygen flux[7]. In the last decade, intensive research has been dedicated to the preparation and characterization of MIEC membranes[1-18]. However, a few reports can be found regarding to the preparation of crack-free membranes (with thicknesses less than 25 μm) for planar or tubular geometries.

Based on the Wagner equation[7], the oxygen flux through a mixed-conducting dense membrane can be increased by reducing the thickness of the membrane until its thickness becomes less than a characteristic value at which the oxygen flux is simultaneously determined by the bulk diffusion and surface exchange kinetics. The surface exchange kinetics involves different elementary steps such as: adsorption, dissociation and reduction of O_2[19]. Therefore, the improvement of O_2 permeation flux in the controlled surface system involves increasing the available surface area for the exchange process as well as the increase of catalytic properties of the membrane top layer. In this case, when the membrane thickness becomes very low, a porous support is needed for mechanical stability, particularly in the case of planar membranes. Thin porous catalytic layers can be also deposited on the other side of surface membrane to assist the increase of the available surface area for the exchange process.

Hence, in recent years the interest in the supported MIEC membranes has increased. The membranes that have been investigated vary widely in terms of thickness (10-500 μm) and chemical composition[20]. Catalytic layers are also employed in some cases. A major challenge in processing supported MIEC membranes is the selection of a suitable fabrication method and material for the porous substrate, taking into account requirements as chemical compatibility, similar thermal expansion coefficient (TEC), good mechanical strength and porosity for adequate diffusion of gas.

This review paper aims to assess the concepts of perovskite MIEC membranes and relate them to the manufacturing process of MIEC membranes on porous substrates. Recent works on supported MIEC membranes as well as main fabrication methods are reported and discussed.

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2. MIEC membranes

2.1. *Concept*

The two main types of oxygen separation systems based on ceramic membranes are mixed ionic–electronic conducting membranes (MIEC membranes) and pure oxygen conducting membranes for example, solid electrolytes for solid oxide fuel cells (SOFC electrolytes). An advantage of the MIEC membranes is that those membranes require no electrodes to operate as in SOFC electrolytes[7,21]. The MIEC membranes also stand out due to its potential application of high purity oxygen production.

The oxygen separation is performed at high temperatures, typically 800-900 °C and high O_2 flux are observed in dense membranes and with a perovskite structure[22]. As shown in Figure 1, the electronic conductivity is presented as a small internal circuit involving oxygen partial pressure gradient. The O_2 permeates from the high oxygen partial pressure side to the low oxygen partial pressure side, while the overall charge neutrality is maintained by opposite movement of electron flow[23].

2.2. *Structure*

The general crystal structure of an ideal perovskite, ABO_3, is cubic and is shown in Figure 2. The A-site ion may be a rare earth, alkali or alkaline earth ion, such as La, Na, Ca, Sr or Ba. The B-site ion is a transition metal, such as Fe, Co, Ni or Cu[22].

The relative sizes of the A and B ions dictate the shape of the crystal structure. The perovskite structure is maintained if the value of tolerance factor (*t*) is between 0.75 e 1 (Equation 1) as proposed by Goldschmidt in 1927[24]:

$$t = \frac{R_A + R_O}{\sqrt{2}\left(R_B + R_O\right)} \quad (1)$$

where R_A, R_B e R_O are the ratios of A-site, B-site and oxygen ions, respectively.

In crystals several types of defects can be present including zero dimensional or point defects. Those defects are generally separated into vacancies (particles missing in the lattice), interstitial particles (particles on lattice sites which are not normally occupied) and substitutional particles (lattice site that are occupied by foreign particles). The diffusion of oxygen ions is provided by vacancy defects present in the perovskite structure, because the ideal structure is unable of conducting those ions[22,25]. The presence of vacancies is due to the high tolerance of perovskite materials to non-stoichiometric structures, which allows obtaining a high ionic conduction of oxygen[26].

When the A-site of the perovskite is doped with a metal ion with lower valence state, oxygen vacancies are created as well as a change in valence state of ions B occurs, in order to maintain electronic neutrality. The stability of perovskite structure oxides is also improved by doping B-site with a more stable ion to produce $A_xA'_{1-x}B_yB'_{1-y}O_{3-}\delta$. It is important to note that the term δ is regarded as the number of vacancies or defects; therefore, the higher number of vacancies, higher will be oxygen permeation flux[27]. A large number of oxygen vacancies can be formed in perovskite crystals by doping of

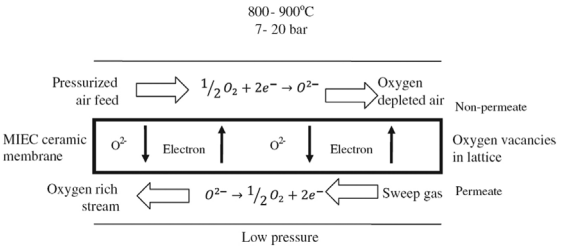

Figure 1. Schematic representation of O_2 transport in dense ceramic MIEC membranes[7].

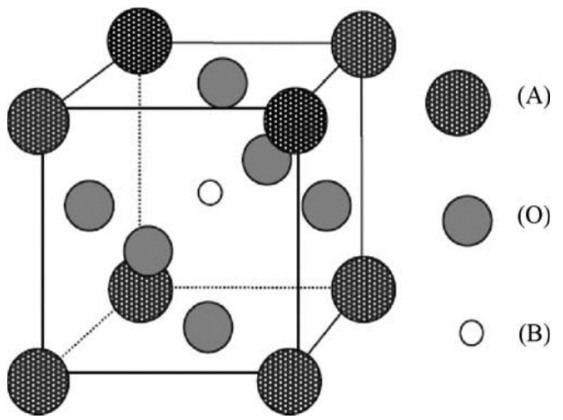

Figure 2. General structure of perovskite[1].

ions with different valences. At high temperatures, oxygen is incorporated into perovskite crystal structure resulting in the annihilation of an oxygen vacancy and the formation of two electron holes, as expressed as in Equation 2.

$$V_o^{\cdot\cdot} + \frac{1}{2}O_2 \leftrightarrow O_O^X + 2h^{\cdot} \quad (2)$$

where $V_o^{\cdot\cdot}$ is the oxygen vacancy, O_O^X is the lattice oxygen and $h^{\cdot}$ is the electron hole[25].

2.3. *Transport mechanism*

According to the literature[28-31], the oxygen transport through a MIEC membrane can occur by five stages, as follows (Figure 3):

- Mass transfer of gaseous O_2 from the gas stream to the membrane surface (high-pressure side. $\uparrow p'_{O_2}$);
- Adsorption of O_2 molecules followed by dissociation into ions (surface reaction of interface I);
- Transport of oxygen ions trough the membrane (bulk diffusion in MIEC);
- Association of oxygen ions followed by desorption of oxygen molecules (surface reaction of interface II);
- Mass transfer of O_2 from the membrane surface to the gas stream (low-pressure side. $\downarrow p'_{O_2}$).

The stages *b*, *c*, and *d* are the most important in this process. Stages *b* and *d* are governed by the kinetics surface exchange reactions (interfaces I and II) and stage *c* by the properties of bulk transport (bulk diffusion). For a MIEC membrane, the factor that limits the rate of O_2 permeation

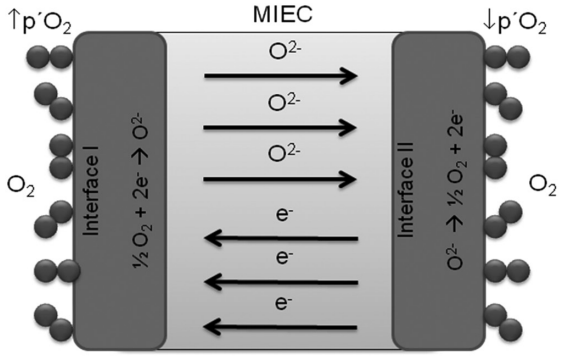

Figure 3. Oxygen transport through a MIEC membrane.

is the region at which the highest resistance occurs. The level of resistance in the interfaces I and II is affected by the nature of the material, such as the composition of perovskite or the exposed surface area. The resistance across the bulk diffusion is proportional to the thickness. For a relative thick membrane, the region of highest resistance is the region of the bulk diffusion. The oxygen permeation flux based on bulk diffusion can be expressed by Wagner equation[7]:

$$J_{O_2} = \frac{RT}{16F^2L}\int_{p''_{O_2}}^{p'_{O_2}} \sigma_{amb}\left(pO_2\right) d\ln pO_2 \qquad (3)$$

where J_{O_2} is the oxygen permeation flux in mol m^{-2} s^{-1}; R is the gas constant; F is the Faraday constant; L is the membrane thickness; σ_{amb} is the ambipolar conductivity; and p'_{O_2} and p''_{O_2} are the oxygen partial pressures at the high pressure side and low pressure side, respectively.

Consequently, reducing membrane thickness will lead an increasing of O_2 permeation rate. However, for thinner membranes, the resistance to oxygen ion conduction will be decreased until a certain limit, known as the characteristic thickness of the membrane (L_c), which also depends on the operating conditions such as temperature and O_2 partial pressure. The L_c of most MIEC membranes typically range from 20 to 3000 μm[32]. For a thickness under L_c, the region of higher resistance becomes the interfaces I and II that are the surfaces with exchange reactions. The Wagner equation is not applicable when the oxygen flux becomes determined by the surface reaction.

Other mechanisms and relations have been proposed to explain the oxygen flux within this regime[33,34]. Surface exchange reactions are expected to be composed of sequential steps which might limit the overall rate. They may consist of adsorption from the gas phase, charge transfer reaction between the adsorbed species and bulk, including the reversed reactions[19]. For this point, a big challenge is finding a mathematical model to explain explicitly both the limiting cases such as bulk diffusion and surface exchange reactions, especially in the case of dense and thin planar MIEC membranes deposited on porous supports and/or modified surfaces.

3. Supported MIEC Membranes

To increase the mechanical strength of thinner ceramic membranes in operational conditions as elevated temperatures and high O_2 partial pressure gradients, an alternative proposed by Bouwmeester et al.[35] is the membrane deposition via different techniques on porous substrates specially prepared. As previously mentioned, the porous substrate strongly influences the properties of the thin MIEC membrane layer, regardless of which deposition technique is used and must satisfy the following requisites:

- Chemical stability at fabrication temperature and in the fabrication atmosphere;
- Similar TEC to membrane layer materials;
- Chemical stability at membrane application temperature (800-900 °C) under operation atmosphere;
- Permeability that does not dominate the rate of permeation for gas diffusion;
- High mechanical strength at membrane application temperature.

Thin perovskites MIEC membrane have been deposited on porous substrates using different techniques, e.g. dry pressing[36-44], dip coating[45-48], screen printing[49,50], spray pyrolisis[51], slip casting[52], tape casting[20,53-56] and others[57-63]. Table 1 lists some of these studies including membrane and support fabrication method, material used for both components, as well as their thickness, pore-forming agent and pore size of the support and oxygen permeation fluxes in different operating conditions.

Chang et al.[37] produced crack-free dense MIEC membranes on porous supports via dry pressing by embedding 40% SCFZ ($SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-}\delta$) onto MgO-based support and 40% MgO onto SCFZ membrane to avoid TEC problems between both materials. It was observed that the O_2 flux is ten times higher in the supported MIEC membrane than in the self-supported membrane due to reducing of thickness. In another work[36] this group verified that O_2 flux is also dependent on the direction of the permeation, i.e., the oxygen flux is higher when permeates in the support-membrane direction, due to increasing surface exchange rate on the dense layer in the high partial pressure side. In other groups an improvement of the oxygen permeation flux in supported MIEC membranes produced by dry pressing was also observed by modifying the microstructure of porous support to straight pores in order to favor gas diffusion[41], by adding a thin porous activity layer in the permeate membrane side to increase surface area for accelerating surface exchange reaction in the low pressure side[39]. Kawahara et al.[48] employed dip coating to produce thin and dense perovskite membranes on porous substrates produced by dry pressing. It was noticed that higher O_2 fluxes were achieved by reducing membrane thickness and controlling porosity in the porous substrate.

Baumann et al.[20] produced thin (70 μm) perovskite membranes on porous supports via tape casting and co-firing. In this case, the porous substrate offered a certain resistance to O_2 flux and the deposition of a thin porous activity layer improved drastically the O_2 permeation flux by varying operational conditions as temperature, O_2 partial pressure and gas flow rates. Figure 4a-d shows SEM images of the cross-sections of those membranes after oxygen permeation

Table 1. MIEC membranes on porous substrates: materials and properties.

Membrane/ Support Material*	Membrane/ Support Process	Pore former	Pore size (μm)	Membrane/Support thickness (μm)	J_{O2} (mol·s^{-1}·cm^{-2})	Ref.
SCFZ-0.4MgO/ MgO-0.4SCFZ	Dry pressing	Active carbon	0.8	200/1000	2.02×10^{-7} (900 °C)	[37]
BSCF	Dry pressing	Inorganic	1.18	200/1300	6.17×10^{-7} (850 °C)	[39]
SCFZ	Dry pressing	Graphite, starch	5-30	500/1400	1.78×10^{-7} (930 °C)	[43]
BSCF	Dry pressing	Graphite	3-20	170/1050	1.2×10^{-6} (900 °C)	[44]
LSTF	Dry pressing	Organic	10	50-70/400	8.41×10^{-6} (1000 °C)	[48]
LSCF	Screen printing/ Warm pressing	Organic	1.4	10-20/1200	0.5×10^{-7} (900 °C)	[49]
LSCF	Slip casting/ Dry pressing	Methyl cellulose	0.5	200/1500	1.41×10^{-7} (800 °C)	[51]
BSCF	Tape casting	Starch	2-25	70/830	5.04×10^{-5} (900 °C)	[20]
LSFG/ LSF	Tape casting	Starch	8-20	80/1000	1.19×10^{-8} (900 °C)	[55]
LSFG	Tape casting	Starch	8-20	120/820	1.12×10^{-7} (920 °C)	[56]
CSTF	Spin coating/ Dry pressing	Carbon black	10-50	35/500	1.56×10^{-6} (950 °C)	[57]
LCC	Slurry dropping/ Dry pressing	Oxalate	1-3	10/1200	3.54×10^{-6} (930 °C)	[59]
LCC-BFZ/ LCC	Slurry dropping/ Dry pressing	Oxalate	1-3	30/1200	1.19×10^{-6} (780 °C)	[60]
BLF	Slurry dropping/ Dry pressing	Oxalate	1-2	46/500-1000	1.78×10^{-5} (930 °C)	[61]

*BFZ = $BaFe_{0.975}Zr_{0.025}O_{3-\delta}$; BLF = $Ba_{0.95}La_{0.05}FeO_{3-\delta}$; BSCF = $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$; CSTF = $Ca_{0.8}Sr_{0.2}Ti_{0.7}Fe_{0.3}O_{3-\delta}$; LCC = $La_{0.6}Ca_{0.4}CoO_{3-\delta}$; LSCF = $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$; LSF = $La_{0.8}Sr_{0.2}FeO_{3-\delta}$; LSFG = $La_{0.6}Sr_{0.4}Fe_{0.9}Ga_{0.1}O_{3-\delta}$; LSTF = $La_{0.6}Sr_{0.4}Ti_{0.3}Fe_{0.7}O_{3-\delta}$; SCFZ = $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$.

measurements. A suitable adhesion of the dense membrane on porous support may be observed, Figure 4a, b, as well as the thin (17 μm) porous active layer deposited by screen printing, Figure 4c, d. The highest O_2 fluxes values achieved in the case of porous activity layer deposition are due to increased available surface area in the membrane, since the limiting factor becomes the surface exchange reaction when the membrane thickness is too thin, depending on the characteristic value (L_c) of each material. Watanabe et al.[59] have used slurry dropping deposition technique to produce thinner (10-30 μm) perovskite membranes on porous support. Higher O_2 fluxes were measured in supported MIEC membranes with porous active layer deposited on the low partial pressure side when compared with supported membranes without active layer and even lower values for self-supported membranes.

In almost all revised works, such as in those with highest oxygen permeation fluxes showed in Table 1, the authors used the same material for membrane and substrate. The same approach was applied to active layers to avoid differences of thermal expansion coefficient (TEC), thereby preventing delamination and cracks during sintering and operating conditions. Table 1 also shows that the average pore size in the support materials varies from < 1 μm to around 50 μm. Within this range it can be observed that the average pore size had no significant influence on the O_2 flux results. High oxygen flux results were found either for smaller (1-2 μm)[61] or larger pores (5-25 μm)[20].

An important aspect is to ensure an open and interconnected porosity, providing the adequate permeability for gas diffusion. The most of studies employed the sacrificial template technique to create porosity in support material. This concept is based on incorporating an organic agent in the material composition to be removed in a slow thermal treatment after shaping and before sintering. In this context, it is interesting to select available routes for processing macroporous ceramics in order to find an inexpensive, environmentally friendly and suitable method for the manufacture of porous supports. An extensive review on processing techniques of macroporous ceramics and its relationship to control the porosity was made by Studart et al.[64] Further information can be found elsewhere[65-70].

A more recent and innovative method to fabricate ultra thin MIEC membranes, different of those proposed for planar configurations, is the formation of asymmetric hollow fibers via an immersion induced phase inversion and sintering techniques. These hollow fibers might be processed with very thin and dense skin layer integrated on the porous support of the same perovskite material. In addition to its ability to support very thin walled membranes, the hollow fiber geometry also maximizes the surface area per unit volume. Recent developments show large improvements in oxygen permeation rates in hollow fibers[1,12,13,15,17,18] compared with flat, self-supported membranes. Similar results might be compared with some of the best results in the literature on flat supported membranes. Hollow fiber membranes can be fabricated using simple processing steps, without the use of porous substrate. Perovskite capillaries with an outer diameter from 0.5 to 3 mm and wall thicknesses from 50 to 500 μm have been manufactured[12,13]. However, material

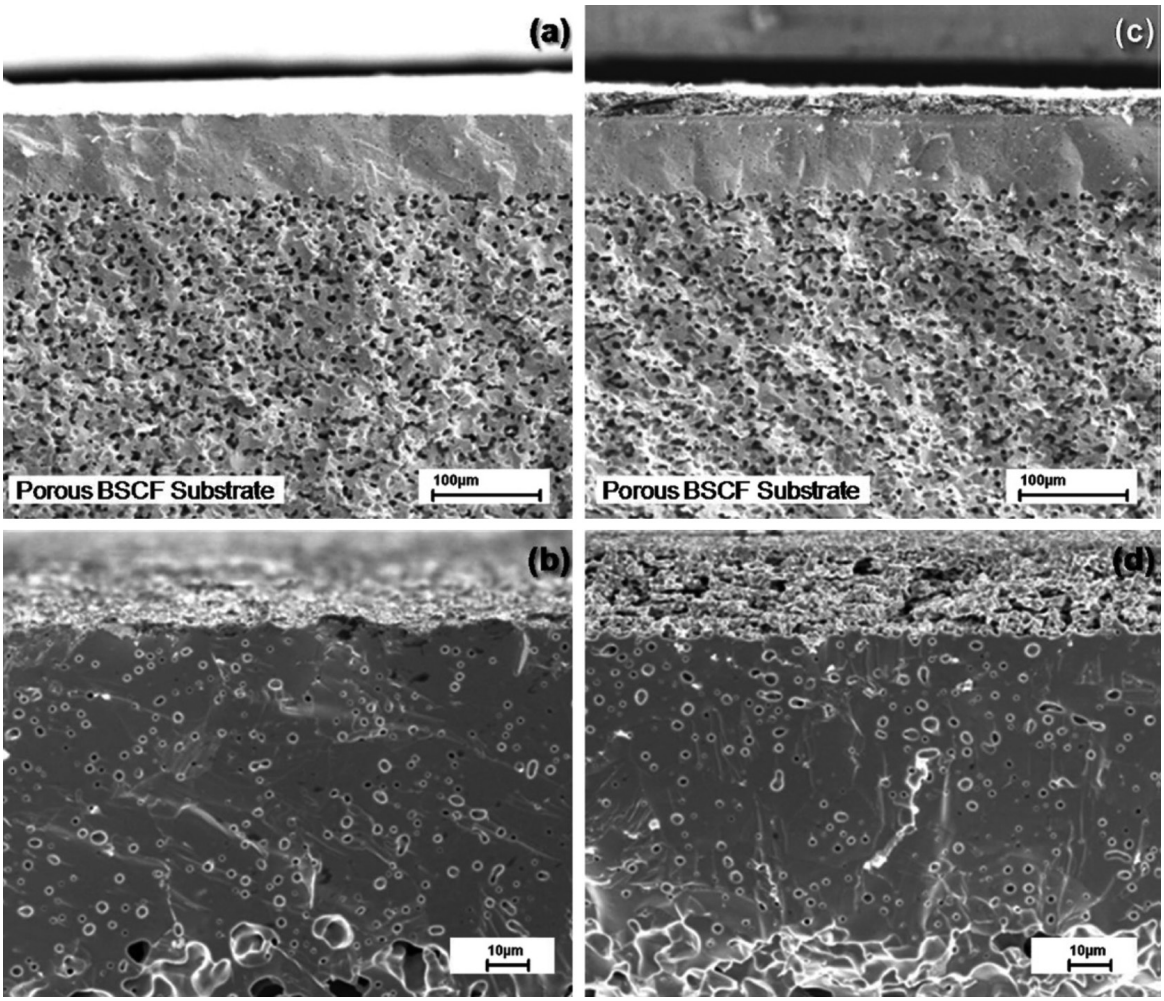

Figure 4. Fracture cross-sections (SEM images) of two membranes after oxygen permeation measurements: (a and b) without oxygen activity layer and (c and d) with an oxygen activation layer[20].

strength limitation prevents wall thickness of hollow fiber membranes to be reduced further below 200 µm.

4. Conclusions

Dense perovskite membranes are promising alternatives to O_2 separation and CO_2 capture in oxy-combustion plants. Improvements in the design of these membranes are being intensively studied and flat configurations of supported MIEC membranes produced with the same material adding a thin porous activity layer has achieved good improvements regarding oxygen flux. The deposition of the membrane may be accomplished by simple methods as dip coating, tape casting and slurry dropping. Besides the need for chemical compatibility and mechanical strength at operating conditions, the porous substrate must be engineered in order not to limit diffusion of gas by controlling its porosity and microstructure. The key point for further improvements in the planar supported MIEC membranes is the definition of an explicit model for explaining the surface exchange reactions of these supported membranes and controlling the porosity and microstructure of the porous substrate.

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