Review

Dense ceramic oxygen permeable membranes and catalytic membrane reactors

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HIGHLIGHTS

- Progress of oxygen permeable membrane materials and architecture is presented.
- Membrane reactor design, applications in energy and environmental fields are given.
- Challenges related to industrialization and future research are proposed.

GRAPHICAL ABSTRACT

A dense ceramic oxygen permeable membrane reactor (OPMR) not only combines a membrane separation unit with a chemical reaction, but couples them in such a way that a synergy is created between the two units. This technical concept is expected to be a promising approach to achieve green and sustainable chemistry with less energy consumption and lower pollution.

ABSTRACT

A dense ceramic oxygen permeable membrane reactor (OPMR) not only combines a membrane separation unit with a chemical reaction, but couples them in such a way that a synergy is created between the two units. This technical concept is expected to be a promising approach to achieve green and sustainable chemistry with less energy consumption and lower pollution. This article presents a review of the recent progress of dense ceramic OPMR, including membrane materials, membrane architecture, membrane reactor design, new applications in energy and environmental fields, current challenges related to industrialization and future research.

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Contents

1. Introduction ........................................................................................................... 186
2. Development of OPM materials ........................................................................ 187
3. Development of dense ceramic OPM architecture .......................................... 190

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journal homepage: www.elsevier.com/locate/cej
4. Oxygen separation by OPM ................................................................. 191
4.1. Production of O_2-enriched air .......................................................... 191
4.2. Production of pure oxygen ................................................................. 194
5. Dense oxygen permeable membrane reactor ........................................ 195
5.1. Dense OPM reactor as oxygen distributor ........................................... 195
5.1.1. Partial oxidation of methane to synthesis gas .................................. 195
5.1.2. Oxidative coupling of methane to C_2-hydrocarbons ......................... 196
5.1.3. Oxidative dehydrogenation of light alkanes to olefins ......................... 197
5.1.4. Oxyfuel combustion concept for CO_2 capture .................................. 198
5.2. Dense OPM reactor as oxygen extractor ............................................ 199
5.2.1. Water splitting to hydrogen ......................................................... 199
5.2.2. N_2O decomposition ................................................................. 200
5.2.3. CO_2 decomposition ................................................................. 200
6. Conclusions and outlook .................................................................. 201
Acknowledgements ............................................................................ 202
References .......................................................................................... 202

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>J_{O_2}</td>
<td>oxygen permeation flux (ml/min cm²)</td>
</tr>
<tr>
<td>F</td>
<td>faraday constant (F = 96,485 C/mol)</td>
</tr>
<tr>
<td>R</td>
<td>gas constant (R = 8.3145 J/mol K)</td>
</tr>
<tr>
<td>T</td>
<td>temperature (K)</td>
</tr>
<tr>
<td>P_{O_2}</td>
<td>oxygen partial pressures (bar)</td>
</tr>
<tr>
<td>x</td>
<td>length along the axis of membrane thickness (mm)</td>
</tr>
<tr>
<td>P_{O_2}^e</td>
<td>oxygen partial pressures on the feed side (bar)</td>
</tr>
<tr>
<td>L_{O_2}</td>
<td>membrane thickness (mm)</td>
</tr>
<tr>
<td>L_c</td>
<td>characteristic membrane thickness (mm)</td>
</tr>
<tr>
<td>K_s</td>
<td>coefficient of surface exchange (m/s)</td>
</tr>
<tr>
<td>D'</td>
<td>coefficient of bulk diffusion (m²/s)</td>
</tr>
<tr>
<td>K_p</td>
<td>equilibrium constant</td>
</tr>
<tr>
<td>P_{O_2}</td>
<td>hydrogen partial pressure (bar)</td>
</tr>
<tr>
<td>\sigma_e</td>
<td>conductivity of electrons (S/cm²)</td>
</tr>
<tr>
<td>\sigma_i</td>
<td>conductivity of oxygen ions (S/cm²)</td>
</tr>
<tr>
<td>\mu_{O_2}</td>
<td>chemical potential (J/mol)</td>
</tr>
<tr>
<td>\delta</td>
<td>number of oxygen defects, 0 &lt; \delta &lt; 1</td>
</tr>
</tbody>
</table>

1. Introduction

The global energy requirements are forecasted to be twice of the current demand in the next 20 years. Such a huge demand will be filled by the use of the traditional fossil fuel, including crude oil, natural gas and coal, or the use of some renewable and new energy sources, such as the hydrogen from photocatalytic water splitting. Chemical and petrochemical industries play significant roles in the energy structure, environmental problems and the world economy. There is an urgent need to control the energy consumption and lower the waste streams through some novel technologies of engineering process, especially for the chemical and petrochemical industry. The coupled chemical reaction with separation, chemical reaction process intensification or some novel catalysts development will promote this process. Membrane reactors have the potential to fundamentally change chemical processes when combining under in situ conditions a separation with a chemical reaction because the chemical reaction performance will be improved when it is operated in a membrane reactor, i.e. the chemical reaction process can be intensified by the membrane separation, which will lead to a higher conversion of reactant and higher selectivity of product. For example, the application of membrane in a chemical reaction could break the limitation of thermodynamic equilibrium by selective removal of the product and the reaction rate can be maintained with a high conversion of reactant. Therefore, not only can the natural resources be used efficiently, but also the economics of the chemical reaction process can be improved in such membrane reactors. As a result, the energy consumption will be reduced and it will also lead the increase of the selectivity towards the desired products and to reduce the formation of by-products [1].

Dense ceramic oxygen permeable membranes (OPMs), which shows a mixed conducting of electronic and oxygen ionic, has gained much attention in the oxygen production from air or other oxygen containing atmosphere, pure oxygen production and as membrane reactor for the chemical upgrading cleanly, efficiently and economically [2]. Instead of the form of molecules or atoms, the oxygen transports through the ceramic oxygen permeable membranes as oxygen ions and it is presented in Fig. 1. If the partial pressure of oxygen on the two sides of an OPM is different, an oxygen flux starts to compensate this difference. The molecular oxygen flux through an OPM is related to the gradient of chemical potential (\mu_{O_2})

\[ J_{O_2} = -\frac{1}{4F} \cdot \frac{\sigma_i - \sigma_e}{\sigma_i + \sigma_e} \cdot \nabla \mu_{O_2} \]  

with \( F \) as Faraday constant, \( i \) and \( e \) denote the partial conductivities \( \sigma \) of oxygen ions, and electrons, respectively. The chemical potential gradient can be expressed by the derivative of the chemical activity of molecular oxygen

\[ \nabla \mu_{O_2} = RT \frac{\partial \ln P_{O_2}}{\partial x} \]  

where \( R \) and \( T \) denote the gas constant and temperature, respectively and \( x \) stands for the distance along the axis of membrane thickness, as shown in Fig. 1.

There are two main steps in the process of oxygen transporting through perovskite OPMs: (i) oxygen exchange reaction on the membrane surface, i.e. the adsorption and disorption of O_2; (ii) bulk diffusion of oxygen in forms of ions or vacancies. If the rate control step of the oxygen transporting is only the bulk diffusion, for a membrane of thickness L with the partial pressures of oxygen on the feed side (\( P_{O_2}^e \)) and permeate side (\( P_{O_2}^p \)), the oxygen permeation flux can be calculated according to the Wagner equation [3,4]:
environmental and economic for the chemical reactions operated on membrane surface. It will be more technical, activation of hydrocarbon through the OPM in forms of the in situ ane. Compared to the direct oxygen supply from air or pure oxygen, the process of the oxygen permeation through OPM can be applied in oxygen-enriched air, but also in many other catalytic reactions. OPM not only can be applied in the production of pure oxygen or oxygen permeation selectivity [2]. Furthermore, the ceramic materials and the operation conditions, such as the membrane thickness, stand for the membrane thickness which the rate of the oxygen ion bulk diffusion is comparable to that of the oxygen surface exchange. The oxygen permeation flux becomes 

\[ J_{O_2} = \frac{RT}{4F^2} \frac{1}{L} \frac{\sigma_{O_2}}{\sigma_{O_2} + \sigma_e} \cdot \ln \frac{p_{O_2}^e}{p_{O_2}^i} \]  

In the oxygen transporting process through the OPM, if the surface oxygen exchange becomes rate limiting rather than bulk diffusion, a characteristic membrane thickness, \( L_c \), is used to describe the oxygen permeation flux. \( L_c \) stands for the membrane thickness which the rate of the oxygen ion bulk diffusion is comparable to that of the oxygen surface exchange. 

The oxygen permeation flux becomes 

\[ J_{O_2} = \frac{RT}{4F^2} \frac{1}{L + 2L_c} \frac{\sigma_{O_2}}{\sigma_{O_2} + \sigma_e} \cdot \ln \frac{p_{O_2}^e}{p_{O_2}^i} \]  

\[ L_c = \frac{D^*}{K_s} \]  

\( K_s \) and \( D^* \) denote the coefficient of surface exchange and bulk diffusion, respectively [2]. Because the activation energies of the bulk diffusion and membrane surface exchange are different, the oxygen permeation flux through the OPM is also related to the properties of the ceramic materials and the operation conditions, such as the temperature and the oxygen partial pressure gradients. As a result, the characteristic membrane thickness can be of the order of 0.01–10 mm. In other words, there will be no linear relationship between \( J_{O_2} \) and the reciprocal membrane thickness \( L^{-1} \) if the membrane thickness is lower than \( L_c \) [2]. It can explain why the oxygen permeation flux through some extremely thin membrane, such as a supported ceramic layer, is not as high as expected. Because the oxygen surface exchange cannot be ignored in this situation.

The OPM applications in pure oxygen production or oxygen-enriched air production will achieve some potential benefits [5]. In recent years, great progress can be stated in the dense ceramic oxygen permeable membranes have been published [6–12]. In recent years, great progress can be stated in the dense ceramic oxygen permeable membrane reactor (OPMR) area. Therefore, this paper focuses on the recent progress of dense ceramic OPMR, including membrane materials, membrane architecture, membrane reactor design, especially the membrane reactors for the chemical upgrading and pollution controlling, current challenges related to the industrialization and possible future research.

2. Development of OPM materials

There are some requirements for the OPM materials in industrial applications [6]: (i) The materials should exhibit remarkable high oxygen permeation flux. An oxygen permeation rate higher than 1 ml/cm² min (STP) is required for an economical application, which is reported by Steele [13]. (ii) The materials should have a good stability under various atmospheres, especially under some harsh reducing atmosphere, such as CO, H₂, CH₄ and CO₂ etc. The materials should be operated with a steady oxygen permeation flux at elevated temperatures for a fairly long time. (iii) The membranes made from the materials should have enough mechanical strength in order to construct the membrane reactor. (iv) The cost for the materials should be low enough for the economic industrial applications. Whereas most of the OPM materials presently studied are of perovskite type structure (ABO₃), also fluorite (AO₂), Brownmillerite (AₓBₓO₉) and pyrochlore (AₓBₓO₀) structures are evaluated [14]. Herein, only the perovskite type structure oxides are discussed in this study. Since Teraoka et al. [15,16] developed the OPM material made of Laₓₐ₋₁Co₁₋ₓ₋₁FeₓOₙ₋₃₋ₓ and supplied it for oxygen production for the first time, there are much R&D effort in the following 27 years after these pioneering studies. However, none of
the perovskite membranes has been applied in industry. It is mainly because the OPMs cannot be operated steadily for a long time, especially when the oxygen partial pressure is relatively low. Often high oxygen fluxes reduce the stability and vice versa. To summarize most of the current research results of OPMs, one can state that both the oxygen permeation stability and the oxygen permeation flux are important: some of the OPM materials have good oxygen permeation flux but poor stability, such as \( \text{La}_{0.1}\text{Sr}_{0.9}\text{CoO}_3 \) [17]; some OPM materials exhibit excellent stability but low oxygen permeation flux, such as \( \text{Sr}(\text{Ba})\text{Ti}(\text{Zr})_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 \) [18]. The purpose of substituting is developing attractive OPM materials with good oxygen permeation flux and enough phase structure stability, chemical stability and mechanical stability. For example, some cations with lower charge but similar size can substitute in A or B site in the \( \text{ABO}_3 \) perovskite structure.

Yang’s group has used Ba to partially substitute Sr in \( \text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3 \) (SCF), such as \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 \) (BSCF), to enhance the material stability [17]. The results indicated that the material’s perovskite structure maintained stable at relative low partial pressure of oxygen \( (P_{O_2} < 10^{-5} \text{ atm}) \) with high oxygen permeation flux. Compared with SCF, the results of \( O_2 \)-temperature programmed desorption (O\(_2\)-TPD) (in the atmosphere of He, \( P_{O_2} < 10^{-5} \text{ atm} \)) showed that the oxygen desorption peak of BSCF was much small, which implied that the barium doping has effectively suppressed the metal ion oxidation, e.g. \( \text{Co}^{3+} \) and \( \text{Fe}^{3+} \) to the higher valence states \( \text{Co}^{4+} \) and \( \text{Fe}^{4+} \). With 30\% doping content of Ba, the oxygen permeation flux could be increased up to about 1.19 ml/cm\(^2\) min at 850 °C with an 1.5 mm-disk membrane [19]. The life time test of the oxygen permeation through the BSCF membrane was also studied. However, as a result of some decomposition of the bulk phase and a tiny surface segregation at 850 °C, there is a very slow decrease on the oxygen permeation flux in the 1000 h operation [17].

However, in a medium temperature window between 500 and 800 °C, stability problems are reported for BSCF [17,20–27]. At these temperatures, the cubic BSCF phase decomposes partially in a cobalt-rich hexagonal \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.4}\text{Nb}_{0.6}\text{O}_{3-\delta} \) and in a cobalt-rich trigonal phase [23,25,26]. These new phases are known as poor oxygen conductors, further the materials became mechanically decomposed because of a volume expansion [28]. Fig. 2 shows the formation of the \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \) phase at 750 °C in air and the absence of this phase when the operation temperature was 900 °C. By analyzing the membrane after oxygen permeation, Liang et al. [25] showed that the decomposition process is correlated with the local oxygen potential, which is high in the medium temperature window. The low valence stability of cobalt is considered as the reason for the BSCF decomposition [25,29].

The relationship between the stability of perovskite-type mixed conductors based on \( \text{SrCo}_3 \) and the cation substitution have been investigated by Nagai [30] and his co-workers. They reported that it is necessary to substitute the cation for improving the OPM stability. However, in order to avoid any degradation of the oxygen permeation flux, the substitution dose should be controlled. After comparing \( \left( \text{La}_{0.1}\text{Sr}_{0.9}\text{CoO}_3 \right) \) and \( \text{Sr}(\text{Co}_{0.9}\text{X}_{0.1})\text{O}_3 \) where \( \text{X} = \text{Zr},\text{Sn},\text{V},\text{Ni},\text{Cu},\text{Zn},\text{Ga},\text{In},\text{Ce},\text{Ti},\text{Cr},\text{Fe},\text{Al} \) and \( \text{Nb} \), they gave the stability sequence of the perovskite materials according different cation substituting: \( \text{Zn},\text{In},\text{Ce},\text{Ni},\text{Cu} < \text{Cr},\text{Al},\text{Ga},\text{Zr},\text{Sn},\text{V} < \text{La} < \text{Fe} < \text{Ti} < \text{Nb} \) [30]. Many researchers consider the perovskite oxygen permeation flux as a trade-off relation against the stability of the perovskite phase. However, the results of Nagai et al. [30] call this into question. They found the oxygen permeation flux order of these OPM disks at 900 °C can be shown as [30]: \( \text{SCF} < \text{La}_{0.1}\text{Sr}_{0.9}\text{CoO}_3 \) \( < \text{SrCo}_{0.9}\text{Fe}_{0.1}\text{O}_3 \) \( < \text{SrCo}_{0.9}\text{Ti}_{0.1}\text{O}_3 \) \( < \text{SrCoO}_3 \) \( < \text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_3 \). Within these samples, \( \text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_3 \) exhibited the highest stability of the perovskite structures, as well as the highest oxygen permeation flux of 4.24 ml/min/cm\(^2\) at 900 °C. Many other researchers have also investigated the effect of the partial substitution of Co (Fe) by metal cations such as Mn, Ni, Cr, Cu or Ti [17,19,31]. Although the oxygen permeation flux would be decreased due to the introduction of higher valence cations, e.g. Cr or Ti onto the Fe or Co lattice positions with moderate doses, the OPM material structural stability can be improved [31].

![Fig. 2. Top view (a) and polished cross-section (b) of a BSCF perovskite membrane after exposure to oxygen for 5 days at 750 °C. White arrows in (a) mark the phase of hexagonal perovskite \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \) [24].](image-url)
In order to improve the stability of the perovskite materials, especially under harsh conditions, including the big gradients of oxygen partial pressure, reducing atmosphere of CO, CH₄ or H₂, and atmosphere with high concentrations of CO₂, researchers have developed several stable materials. Yang's group investigated the incorporation of Zr⁴⁺ ions into a perovskite structure oxide giving BaCO₃₋ₓFeₓZrₓO₃₋ₓ (BCFZ) [32] which shows a high oxygen permeation rate of 0.87 ml/cm² min at 950 °C under a He/Ar gradient. However, because the ionic radius of Zr⁴⁺ is too big to introduce into the structure, it is hard to get the pure phase of BCFZ [33–35]. In order to obtain the perovskite with a pure phase structure, smaller ions should be used. It is found that Zn [36,37] can be easily integrated into the perovskite structure due to its relatively small and high-ionic radius. Therefore, the OPM material based on BaCo₀.₇Fe₀.₂Ta₀.₁O₃ has been developed, which exhibits good phase stability and excellent oxygen permeation flux, especially under low oxygen partial pressure. SrSc₀.₃Co₀.₇Fe₀.₁O₆₋ₓ was also reported to be a good perovskite-type OPM material with high oxygen permeation flux [38,39]. However, the high cost of Sc limits the development of this material. Recently, another novel perovskite material based on BaCo₀.₇Fe₀.₂Ta₀.₁O₃ (BCF) has been developed by Luo et al. [40]. The TEC can be reduced and the material stability can be improved by the introduction of Ta. At 950 °C, an oxygen permeation rate of 2.22 ml/cm² min could be obtained through the 0.60 mm-disk membrane based on BCF. The production of syngas through the partial oxidation of methane (POM) has also been operated in such a BCF membrane reactor. It shows a steady performance without failure for more than 800 h at 900 °C. The oxygen permeation flux obtained was up to 16.8 ml/min cm² at a much lower oxygen partial pressure in the sweep side due to the presence of CH₄ [41]. Investigating the oxygen permeation flux and the material stability of SrCo₀.₆₇Ta₀.₃O₃₋ₓ (0 ≤ x ≤ 0.3) [42], it was found that when doping only 0.1 dose of the B site of SrCoO₂ by tantalum, the perfect cubic perovskite structure of the SrCoO₃ is still stable. A high oxygen permeation rate of 1.83 ml/min cm² can be obtained under a He/air oxygen partial pressure gradient at 900 °C through a 0.65 mm-disk membrane. The electronic conductivity of the perovskite SrCo₀.₉⁵Nb₀.₀⁵O₃₋ₓ membrane was reported very high, as well as the oxygen permeation flux [43]. Furthermore, the SrCo₀.₇Nb₀.₃O₃₋ₓ membrane can be operated steadily with a relatively high oxygen permeation flux under an air/helium oxygen partial pressure gradient for more than 200 days [44]. In other words, to improve the stability of the OPM materials, the reducible B-site ions (Co⁴⁺/Co³⁺, Fe⁴⁺/Fe³⁺) can be partially substituted by cations with constant radii (Na⁺, Ni⁺¹, Zr⁴⁺, Al³⁺). Examples are BaCo₀.₇Fe₀.₃Ta₀.₁O₃ [40,41], BaCo₀.₇Fe₀.₂O₃₋ₓNb₀.₁O₃₋ₓ [45], BaCo₀.₇Fe₀.₃ₓZrₓO₃ [33], BaCo₀.₇Fe₀.₂Zn₀.₃Zr₀.₁O₃₋ₓ [37], La₉₋ₓSrₓFeₓGa₉O₃₋ₓ [46], Sr(Fe, Al)O₃₋ₓ [47].

Co-based perovskite oxides like (La₊Sr₇₋ₓCoₓFe₇₋ₓO₁₉₋ₓ) or (Ba₆Sr₇ₓCoₓFe₇₋ₓO₁₉₋ₓ) are often thought to be the most promising materials because they show very good oxygen permeation flux as stated above. However, there is a problem of the co-based membranes, the cobalt ion in the material is easily evaporated and reduced [48]. Therefore, there are activities in the development of high oxygen permeation flux cobalt-free membranes. The series materials based on La(Sr/Ga)MgO₃ as a popular cobalt-free group whose oxygen ionic conductivity is 0.08 S/cm at 800 °C [49]. The electronic conductivity can be improved by some introduction of the light transition metals, such as Fe and Ni. Doped of them on the B-site position of the La(Sr)Ga⁻¹MgO₃ structure makes it an attractive OPM material [50,51]. The properties of the double-doped material based on LaGaO₃ on both La-site and Ga-site has been studied by Ishihara et al. [50]. On the Ga-site doping, it was reported that Fe-doped La₀.₈Sr₀.₂Ga₁₋ₓFeₓO₃₋ₓ was much stable under the reducing atmosphere, although the oxygen permeation flux was lower than that of the Ni-doped ones. The substitution of Mg on B-site of the framework of La₁₋ₓSrₓGa₁₋ₓFeₓO₃₋ₓ has also been investigated [52]. The oxygen permeation flux was greatly improved. It was assumed that the improved oxygen permeation flux is probably because the weaker bonds of Mg–O compared to Fe–O, and that the lower and permanent oxidation state of Mg²⁺ can create more oxygen vacancies. Although the substitution of Mg is really helpful to increase the oxygen permeation fluxes, however, the oxygen permeation flux through the membrane based on Mg-doped La₁₋ₓSrₓGa₁₋ₓFeₓO₃₋ₓ is still not high enough for industrial application. Furthermore, the usage of the expensive gallium also blocks the application of these materials. Another cobalt-free OPM material with composite of BaCe₀.₈Fe₀.₂O₁.₇ was developed [53] due to the known excellent resistance of the perovskite BaCeO₃ to a reducing atmosphere when it was employed as hydrogen-permeable membrane. It is found that the oxygen permeabilities of the series OPMs have been improved greatly with increasing iron-doping. CaTiₓFe₁₋ₓO₂O₇ was developed as another cobalt-free material by Figueiredo et al. [54]. However, only 0.02 ml/min cm² of the oxygen permeation rate was achieved with a 1.0 mm-disk membrane at 900 °C, which seems far away from the practical application.

Our group recently developed a novel perovskite OPM material free in cobalt with the composite of Ba₀.₅Sr₀.₅Zn₀.₂Fe₀.₈O₃₋ₓ (BSZF) [36]. Because the doped SrFeO₃₋ₓ shows a mixed conducting of oxygen ion and electron [55], Compared to the materials of La₀.₆₅Sr₀.₃₅Fe₀.₈O₃₋ₓ and La₀.₅Sr₀.₅Ga₀.₄Fe₀.₆O₃₋ₓ. BSZF membrane shows higher oxygen permeation flux and more excellent chemical stability. So far, several cobalt-free membrane materials have been developed, such as La₁₋ₓSrₓFeO₃₋ₓ [56], Ba₉₀.₃Sr₀.₇Fe₀.₃O₇₋ₓ [57], Ba₅Sr₀.₅T₁Fe₁₋ₓAlₓO₇₋ₓ [58], Ba₆₀Sr₀.₅Fe₀.₈Cu₀.₂O₃₋ₓ [59], BaFe₁₋ₓZrₓO₃₋ₓ [60] and Ba₀.₉₅La₀.₅Fe₀.₇O₃₋ₓ [61].

An alternative to the single OPM can be dual phase membranes. Here a nanoscale ion conductor is in intimate contact with an electronic conductor forming percolation networks. The noble metals were used as electronic conductor while the oxides were used as oxygen ionic conductor in the design of the first kind of dual phase OPM materials: (Bi₁₋ₓYₓ)₀.₁SrₓFe₀.₈O₃₋ₓ–Ag [62], Bi₁₋ₓYₓSrₓMn₀.₅O₃₋ₓ–Ag [63,64], Bi₁₋ₓYₓSrₓMn₀.₅O₃₋ₓ–Ag [65], Bi₁₋ₓYₓSrₓMn₀.₅O₃₋ₓ–Ag [66]. Unfortunately, there are several disadvantages for this kind dual phase OPM: (i) the oxygen permeation flux should be improved; (ii) the compatibility between the two phases should be improved, such as the coefficient of the thermal expansion; (iii) the expensive noble metals limit the application. After that, the noble metals were replaced by fluoride type or perovskite oxides as the electronic conductors. The oxygen permeation performances of Ce₀.₇Gd₀.₃O₁.₇–La₀.₉Sr₀.₁Fe₀.₈O₃₋ₓ [70], Ce₀.₇Gd₀.₃O₁.₇–La₀.₉Sr₀.₁Fe₀.₈O₃₋ₓ [72], Ce₀.₇Gd₀.₃O₁.₇–La₀.₉Sr₀.₁Fe₀.₈O₃₋ₓ [72], Ce₀.₇Gd₀.₃O₁.₇–La₀.₉Sr₀.₁Fe₀.₈O₃₋ₓ [72] were studied [62,67,68]. Yang et al. developed Ce₀.₇Gd₀.₃O₁.₇–La₀.₉Sr₀.₁Fe₀.₈O₃₋ₓ [69], Ce₀.₇Sc₀.₃O₁.₇–Sm₀.₅Sr₀.₅Fe₀.₈O₃₋ₓ [70]. Ce₀.₇Sc₀.₃O₁.₇–Sm₀.₅Sr₀.₅Fe₀.₈O₃₋ₓ [70], Ce₀.₇Sc₀.₃O₁.₇–Sm₀.₅Sr₀.₅Fe₀.₈O₃₋ₓ [72], Ce₀.₇Sc₀.₃O₁.₇–Sm₀.₅Sr₀.₅Fe₀.₈O₃₋ₓ [72]. Chen et al. reported Ce₀.₇Sc₀.₃O₁.₇–Sm₀.₅Sr₀.₅Fe₀.₈O₃₋ₓ [72], Ce₀.₇Sc₀.₃O₁.₇–Sm₀.₅Sr₀.₅Fe₀.₈O₃₋ₓ [72], Ce₀.₇Sc₀.₃O₁.₇–Sm₀.₅Sr₀.₅Fe₀.₈O₃₋ₓ [72]. These dual phase membranes have two perovskite phases (ABO₃, A = lanthanide element or alkaline earth metals; B = transition metal) as electronic and oxygen ionic mixed conductors.

Usually, the perovskite material is one kind popular mixed conductor, in which the alkaline earth metals are normally used in A-site, which unfortunately easily generate impermeable carbonates under CO₂-containing atmosphere. Several groups [33,77–81] reported that the oxygen permeation flux through the alkaline earth metals-containing perovskite membranes had a serious damage under the CO₂-containing atmosphere resulted from the carbonate formation. It was even found that the oxygen permeation flux through the BSCF membrane decreased to nearly zero when the sweep gas was changed from He to CO₂ [77]. For the membrane...
of La0.85Sr0.1Ga0.3Fe0.65Al0.05O3 after a desorption process by using CO2 as desorption sweeping gas treatment at a temperature of 800 °C [78], it has been demonstrated decomposed to carbonate and metallic oxide. The effect of CO2 in the oxygen-feed side (air side) on the oxygen permeation flux through the alkaline earth-containing OPM cannot be ignored either [33,82,83]. Jin et al. [84,85] also found that the operation time of a perovskite membrane reactor which coupled the partial oxidation of methane with the thermal decomposition of CO2 was less than 40 h. Many intense efforts have been focused on the CO2-stable ceramic oxygen separation membranes. Firstly, the chemical stability of the OPM materials can be improved by proper doping. It was found that Zr-doped BaCe0.8Y0.2O2-δ (BCY) [86] shows an enhanced stability under CO2. Ti-doping can improve the stability of SCF under CO2-containing atmosphere [87]. Secondly, the chemical stability of the OPM materials can also be improved by avoiding the usage of alkaline earth metals. It was reported that La0.8Sr0.2Ga0.3Fe0.7Al0.05O3 (LGGFA) [88] kept its original structure even after CO2 treatment at 900 °C. Luo et al. [89] reported an alkaline earth metal-free dual phase OPM material, which shows an excellent stability against CO2. Very recently, our group [90,91] developed a new CO2-tolerant membrane material of the composition Pr0.9La0.1(Ni0.74C0.5Fe0.5O3)/La2NiO4+δ (PLNCG). The PLNCG powder maintains the K2NiF4-structure with increasing CO2 concentration even under pure CO2 between 100 °C to 950 °C without formation of carbonate [90]. The comparison of the oxygen permeation flux through the PLNCG (alkaline earth metal-free) and BSCF (alkaline earth metal-containing) hollow fiber membranes under different CO2-containing atmosphere is presented in Fig. 3. The oxygen permeation rate through the BSCF membrane was above 4.0 ml/min cm2 when He=180 ml/min, Fsweep=60 ml/min [91]. Pure He, 20% CO, 40% CO, 50% CO, and 100% CO were used as the sweep gas, which can be operated steadily over 310 h, as shown in Fig. 4 [91]. No decrease of the oxygen permeation fluxes of up to 12.2 ml/min cm2 at 1000 °C was observed and the spent membrane kept the original K2NiF4-type crystallographic structure and the dense microstructure without carbonate formation, which recommends this material for the potential for the practical application for CO2 capture and storage according to the oxyfuel concept and light hydrocarbon oxidation such as the POM to synthesis gas or the oxidative coupling of methane.

On the other hand, SO2 tolerance of the membrane material is also important when it is applied in the oxy-fuel combustion process due to the presence of SO2 in the flue gas of the power plant. The erosion effect of SO2 on the oxygen permeation flux has been investigated in correlation with the microstructure of BSCF, Sr0.5Ca0.5Mn0.5Fe0.5O3-δ and La2NiO4+δ [92]. The oxygen permeation flux drops immediately once SO2 was added in the sweep gas. Some sulfur-containing layers were observed on the membrane surface, which were identified as sulfate. A similar phenomenon was observed by Xu et al. [93]. So, the development of SO2-stable materials turns out as another bottleneck for the industrial use of oxygen permeable membranes.

3. Development of dense ceramic OPM architecture

The oxygen permeation of the different geometry OPMs is usually tested in devices as shown in Fig. 5. Currently, the disk membranes are often used in most investigations, since they can be prepared easily by pressing, especially in the stage of material development. The oxygen permeation flux can be increased by fabricating supported thin dense layers on porous supporting layers. It was shown by Baumann et al. [94] that a sophisticated material processing using tape casting and co-firing results in high oxygen fluxes of up to 12.2 ml/min cm2 at 1000 °C for an oxygen partial pressure gradient of air/Ar. The disc-shaped membrane consists of only the material BSCF as shown in Fig. 6: a gas-tight layer (70 μm) is deposited by tape casting on a porous substrate (830 μm) with 34% open porosity. An open-porous surface activation layer on the air side was prepared via screen printing and increases the oxygen exchange reaction on the membrane surface substantially and the oxygen permeation flux greatly.

In order to solve some engineering difficulties, especially the sealing problem at high temperatures, the tubular membranes appear. A tubular system is considered as an optimal choice to separate oxygen from air after the calculations of a full-scale module [95]. In recent decades, the thin wall-hollow fiber membranes become more and more popular, even though there are new engineering problems related to the large pressure drops associated with hollow fiber geometry. By keeping the two sealed ends of a single hollow fiber outside the high temperature zone, on a laboratory scale polymer O-rings can be used. In industry, the hollow fiber membranes bundled together should be sealed well to make sure the membrane system is gas-tight. Epoxy resins can be used as the sealant at room temperature outside the oven, while some mixtures of inorganic polymers, glasses or/and nanoparticles can be used to seal the membranes at high temperatures within the oven. The big membrane area per permeator volume is an essential advantage of the hollow fiber membranes, which is more attractive than that of the disk or tubular membranes. Furthermore, due to the thin wall, the materials costs of the hollow fiber membranes are reduced. During the last 10 years, significant development has been made in the spinning techniques for hollow fiber production. Many OPM hollow fiber membranes based on diverse OPM

![Fig. 3. Oxygen permeation fluxes through the U-shaped BSCF and PLNCG hollow fiber membranes with different CO2 concentrations in the sweep gas. Conditions: CO2 concentration in the sweep gas varied from 0% to 100%; BSCF: T = 950 °C, Fsweep = 150 ml/min, Fsweep = 100 ml/min; PLNCG: T = 975 °C, Faair = 180 ml/min, Fsweep = 60 ml/min [91].]
materials were investigated in the groups of Li [96–101], Liu [102–104], Schiestel and Caro [105–107], Trunec [108] and Diniz da Costa [109]. The hollow fiber membranes are prepared through a phase inversion method followed by a sintering process. The asymmetric structure of the membrane wall can be obtained due to the process of phase inversion. Recently, a novel technique combining the co-extrusion and co-sintering in one step has been developed due to the shrinkage and expansion can be also avoided. The BSCF membranes were found to be at 800°C with an amount of 9.3 and 17.8 times of the original oxygen permeation flux, respectively [116]. However, the surface loading of the Ag catalyst was not homogenous and Ag species were concentrated on the grain boundaries of the perovskite [117]. Also Pd coating on the LSCF hollow fibers was used to reduce the resistant of the surface exchange. The maximum loadings of the Ag catalyst were concentrated on the grain [116].

Due to the high packing density, many researchers have focused on the hollow fiber membranes with linear shape till now. However, one undesired thing tends to take place for the linear hollow fiber membrane during the heating and cooling process. For the linear hollow fiber membrane, two ends are fixed tightly in a rigid reactor at the beginning. And then the heating of the membrane system to a high temperature will cause the breakage of the hollow fiber due to their thermal expansion. In order to solve this problem, the U-shaped hollow fiber membrane is developed [119]. In this permeation module, a ceramic sealant will be used to fix the both ends of the hollow fiber membrane on one side. During the cooling or heating process, the membrane can freely shrink or expand. As a result, the sealing problem can be solved by the U-shaped hollow fiber membrane and the breakage of the membrane due to the shrinkage and expansion can be also avoided. The BSCF U-shaped hollow fiber membranes prepared by phase inversion technic are shown in Fig. 8.

4. Oxygen separation by OPM

Oxygen can be separated from air as the cheapest source of oxygen, if the oxygen partial pressure gradient exists between the two sides of the OPM. The oxygen-enriched air can be produced with OPMs by using pressurized feed air and air at atmospheric pressure on the sweep side, or to produce pure oxygen (i) by using sweep gases like steam, which can be easily separated from the permeated oxygen by condensation, (ii) by applying vacuum pumps to drain off the permeated oxygen, (iii) by using pressurized feed air of the OPM having pure oxygen on the permeate side at atmospheric pressure.

4.1. Production of O2-enriched air

Many industrial applications demand the oxygen-enriched air, such as the synthesis of ammonia, combustion of methane, the Claus process, in steel plants and for waste burning. Therefore, oxygen-enriched air production has been investigated. Recently, it was shown that the oxygen-enriched air can be produced by pressurizing the feed air through the OPMs to another air side with lower pressure (Fig. 9) [120]. For example, an oxygen-enriched air with the oxygen content of 40–50% can be produced to satisfy the demand of ammonia production. The oxygen content on the sweep side increases with the increasing air pressure difference between the two sides, while the oxygen permeation flux can also be increased. Because the two sides of the OPM are exposed to an oxidizing atmosphere in the production of oxygen-enriched air, no stability problem of the OPM occurs, which has been proved by a stable operation of the OPM for at least 800 h with the production of 42% oxygen-enriched air, as shown in Fig. 10. It is noteworthy that BCFZ shows orders of magnitude higher selectivities and permeabilities than the polymer membranes. However, the perovskite membranes need 800–900°C operation temperature, which is energy-intensive.

4.2. Production of pure oxygen

Pure oxygen can be used in the catalytic oxidations, especially of hydrocarbons, and the power plants with CO2 sequestration.
Usually, under laboratory conditions various inert gases are used as sweep gases, such as He, Ar etc. However, there are only a few percent of oxygen in the sweep inert gas in the outlet gas. Thus, the pure oxygen production needs a second oxygen separation from the inert gas. Therefore, we proposed a novel method to produce the pure oxygen by using steam to sweep the permeated oxygen which can be easily separated from the permeated oxygen by condensation. Surprisingly, the BCFZ membrane showed a very good long-time stability at 850 °C in the pure oxygen production as shown in Fig. 11 [121,122]. Therefore, it is a good choice to produce pure oxygen in steam sweeping mode if only the high temperature sealing problem can be solved since the membrane material is sufficiently stable to endure the steam atmosphere. Leo et al. [123] also produced high purity oxygen using steam to sweep the permeated oxygen through BSCF membrane. Unfortunately, their steady operation was not longer than 20 h due to the unstable material.

Instead of the sweeping mode, decreasing the oxygen partial pressure in the permeated side by applying vacuum can be also used to produce pure oxygen, as shown in Fig. 12. In this case, dead end perovskite hollow fibers or capillaries/tubes can be used, which has been studied by Tan [124,125], Yang [126], Caro [127] and Wang et al. [128] in recent years. From the point of operation cost, it was found that the vacuum mode is the optimal choice to produce pure oxygen. Tan et al. [124] obtained 97.15% purity of oxygen using the vacuum mode. The energy consumption and the scaling-up effect of the membrane system with hundreds of La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃ₖ₃/₀₂ hollow fibers for oxygen separation using vacuum mode has been studied [125]. Zhu and his co-workers [126] also investigated the oxygen separation through the perovskite BSCF tubular membranes under vacuum. The steady high oxygen purity of 99.4% was obtained in the 100 h long-term operation. Pure oxygen production through the BaCoₓFe₁₋ₓZr₁₋ₓ₋₉O₃₋₉ hollow fiber membrane with a dead end sealed by an Au plug was investigated [127]. The large partial pressure gradient of oxygen between the membrane two sides and a high space–time yield
is important for oxygen production with a high oxygen permeation flux. Using the O$_2$-enriched air as feed air is benefit for increasing the oxygen partial pressure gradient. A two-step operation mode for oxygen separation has been proposed to increase the permeated oxygen space–time yields. In the first step, the oxygen-enriched air with oxygen content above 50% is produced from air through the OPM by reducing the oxygen partial pressure on the permeate side. In the second step, the oxygen with high purity is

![Diagram](image)

**Fig. 7.** Perovskite hollow fiber membranes based on Ba(Co$_{x}$Fe$_{y}$Zr$_{1-x-y}$O$_{3-d}$ (BCFZ) which were developed by a spinning process [115].

![Images](image)

**Fig. 8.** Photos and microstructure of U-shaped perovskite BSCF hollow fiber membranes. (A) hollow fiber membrane precursor; (B) sintered hollow fiber membranes; (C) cross-section of sintered fiber; (D) sintered membrane wall; (E) cross-section in the bent region of sintered fiber and (F) sintered membrane wall in the bent region [119].
produced through vacuum mode in which the pressurized oxygen-enriched air produced in the first step and a low pressure air are used in the feed and permeate sides [127]. A high oxygen permeation flux of 10.2 ml/min cm\(^2\) is obtained at 900 °C in this two-step operation, which is enhanced by the increasing temperature, the oxygen content and the pressure of the feed air in the second step. All the results when varying the permeation parameters are in accord with the Wagner equation [11].

In summary, oxygen can be separated from air, the cheapest source of oxygen, if the oxygen partial pressure gradient exists between the two sides of the OPM. This difference of the oxygen partial pressures can be achieved (i) by using sweep gases like steam, which can be easily separated from the permeated oxygen by condensation, (ii) by using vacuum pumps to drain off the permeated oxygen, (iii) by pressurizing the feed air of the OPM and having pure oxygen on the permeated side at atmospheric pressure, or (iv) by combining of pressurizing the feed air and pumping the permeated gas.

5. Dense oxygen permeable membrane reactor

OPMs can be used as a distributor for oxygen supplying for the activation of hydrocarbon and partial oxidation. Compared to the direct oxygen supplying of air or pure oxygen, it is more economic, environmental friendly and technical. This type of membrane reactor was called oxygen distributor (Fig. 13a). Because the oxygen is separated from the hydrocarbon, it is much safe in the OPM reactors. No formation of NO\(_x\) can be found due to the impermeability of OPMs to nitrogen. In the OPM reactor, (i) the desorbed molecular oxygen from the OPM will be the reactant in the reaction zone; (ii) the lattice oxygen on the membrane surface following a Mars-van Krevelen mechanism will be the reactant if a catalyst layer is coated on the OPM surface, or if the OPM has catalytic properties. The OPMs can distribute the oxygen uniformly with controllable low partial pressure in the OPM reactors. As a result, the different reaction rates along the axial dimension of the OPM reactor can be avoided, which is an undesired weakness in the conventional co-feeding reactors. The typical applications are the oxidative dehydrogenation of light alkanes to olefins, syngas production of POM, ethylene production of oxidative coupling of methane (OCM) etc.

Furthermore, the OPMs can also be considered as an extractor to selectively remove the oxygen from a reaction mixture (named oxygen extractor, shown in Fig. 13b) e.g. to overcome the thermodynamic limitation or/and kinetic limitation. In order to raise the product yield, the OPMs can be used to avoid the restriction of the reaction equilibrium by in situ removal of oxygen. Thermal water splitting to hydrogen and oxygen, N\(_x\)O (x = 1, 2)
decomposition into nitrogen and oxygen, and CO₂ decomposition belong to these reactions. Both of the function in oxygen insertion and extraction into reactors will be discussed in the following chapter.

5.1. Dense OPM reactor as oxygen distributor

5.1.1. Partial oxidation of methane to synthesis gas

Production of syngas consisted of H₂ and CO is an interesting way for usage of the natural gas. Compared to the strongly endothermic steam reforming (STR), which produce the syngas with a ratio of H₂/CO is not proper for Fischer–Tropsch synthesis or methanol production. Therefore, most researchers have focused on the slightly exothermic POM for syngas production. Furthermore, the ratio of H₂/CO is not proper for Fischer–Tropsch synthesis or methanol production. Therefore, most researchers have focused on the slightly exothermic POM for syngas production. The operation downstream cannot tolerate N₂, pure oxygen is required for POM, which will cost a large part of the investment. The OPM reactor provides a promising way for syngas production which couples POM with the oxygen separation simultaneously.

Because only oxygen can permeates through the dense OPMs to the other side of the membrane as oxygen ions at high temperatures, where the permeated oxygen can be consumed by POM, while electrons transport through OPM spontaneously to keep the charge neutrality. In POM, cheap air is the oxygen source and no external circuit is required. Due to the coupling of POM and oxygen separation, the oxygen can be supplied gradually along the OPM reactor, which is benefit for avoiding the explosion limits, as well as the hot spots, which is common in conventional reactor with co-feeding mode. Many R&D programs have been proposed by the worldwide alliances consisted of companies of Praxair and Air Products etc. due to the operational and potential economic advantages of OPM reactors applied in syngas production of POM. One key issue for the industrial application is the stability of the long-term operation for the OPM reactors, which has been indicated in many previous investigations related on POM operated in OPM reactors.

Tubular OPM reactors based on SCF and La₀.₂Sr₀.₈Co₀.₃Fe₀.₇O₃₋₄ has been applied in syngas production of POM by Balachandran et al. [129–131], in which the OPM reactors failed once CH₄ was added into the membrane system. For the OPM reactor based on SCF, it has been found two different fractures in the operation [132]. One type fracture is because of the mismatch of the lattice plane distances of the membrane resulted from the big oxygen partial pressure gradient between two sides of the membrane, which happens shortly after POM starts. The other type of membrane failure is due to the chemical decomposition of OPM material under the reductive atmosphere, which normally occurs several days after POM starts.

It is reported that membranes made of La₀.₂Sr₀.₈Co₀.₃Fe₀.₇O₃₋₄ cracked in the 350 h-operation of POM at 900 °C [48]. There was also found a serious damage of BCFZ hollow fibers in the POM over 200 h [133]. The formerly dense hollow fiber membrane showed a porous and amorphous structure, especially the cross-section of the membrane wall near the outer side which has been exposed to CH₄ atmosphere contacting with the catalyst. The spent hollow fiber OPM was characterized by EDS showing a complex damage mechanism. Surprisingly, in the cross section of the outer part and even some middle part of the damaged membrane wall, Al damage mechanism. The diffusion of Al into the OPM may cause its damage in combination with a reduction of the oxide perovskite to oxides with a low oxidation state and even to the metals. There was no aluminum in the inner intact part of the spent hollow fiber OPM from the result of EDS.

In order to improve the lifetime of the OPM reactor at relatively low oxygen partial pressure, many methods have been tried. A protective layer made of Sm-doped CeO₂ was coated on a tubular OPM based on La₀.₂Sr₀.₈Co₀.₈Fe₀.₂O₃₋₄ to enhance the membrane stability to the reductive atmosphere [134]. Bilayer membranes with Ce₀.₈Sr₀.₂O₃₋₂ as a protective layer on La₀.₂Sr₀.₈Fe₀.₂ and La₀.₂Sr₀.₈Co₀.₈Fe₀.₂O₃₋₄ were also proposed [135]. It is found that if some nitrogen was added in the feed methane, the lifetime of the OPM reactor based on YSZ-promoted SrCo₀.₄Fe₀.₆O₃₋₄ was improved up to more than 70 h [136].

The stability of the OPM can also be improved by co-doping the OPM materials with less-reducible metals, e.g. Zr⁴⁺, Ga³⁺, Nb⁵⁺ and Ta⁵⁺ as well as different dopings on the A-site of the perovskites oxides, or reducing Co amount in the OPM materials. Lots of OPM materials with good stability to POM conditions have been developed in recent several years. A steady oxygen permeation rate of 4.4 ml/min cm²² was achieved in the OPM reactor based on La₀.₂₂Ba₀.₈Fe₀.₈Co₀.₂O₃₋₄ in the 850 h operation of POM [137]. The membrane made of BSCF produced syngas with 95% CO selectivity, 94% CH₄ conversion and an O₂ flux of 8.0 ml/cm² min steadily for 500 h [138]. Yang et al. developed the novel membrane BCFZ, which was doped with the non-reducible ion Zr⁴⁺ to prolong the membrane lifetime under the POM conditions [33]. The OPM reactor made of BCFZ showed a stable performance for syngas production during 2200 h operation at 850 °C [18]. The lifetime of an OPM material with brownmillerite structure was more than 1 year in the reductive atmosphere of POM at 900 °C with an O₂ flux of 10–12 ml/min cm² and the syngas yield of 60 ml/min cm² [139]. Makoto et al. developed a POM reactor based on BaCo₀.₇Fe₀.₃Nb₀.₁O₃₋₄.
which presented a huge high O₂ rate of 20 ml/min cm² in the 300 h stable operation, which is the highest value till now [45]. Our group developed a novel Ta stabilized BaCo₁₋ₓFeₓO₃₋ₓTa₀.₁O₁.₇ (BCFT) because Ta locates in the catercorner of Zr and same group as Nb, which was expect an excellent stability and good oxygen permeation flux for syngas production [40,41]. Fortunately, the BCFT reactor shows a good stability in 420 h long-term POM operation. Recently, a disk-membrane made of La₀.₈Sr₀.₂Co₀.₁Fe₀.₆Cr₀.₁O₃₋ₓ (LBFZ-0.2) was used in a membrane reactor for the POM [140]. An oxygen permeation flux of 12 ml/cm² min was obtained in the LBFZ-0.2 disk membrane reactor applied in POM with the thickness of 0.5 mm, which can be operated steadily for more than 500 h at 900 °C. The excellent chemical stability under the reductive atmosphere is the most attractive property of the OPM material of LBFZ-0.2, which was also proved by the intact structure of the spent membrane. Markov et al. [141] also found the long-term stability of a tubular membrane with lanthanum-stromitite ferrite, which can be operated in POM steadied for more than 7000 h with the CO selectivity and CH₄ conversion above 90% and 98.8%, respectively. These results have been summarized in Table 2 [137–143].

<table>
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<tr>
<th>Material</th>
<th>T (°C)</th>
<th>jₒ₂ (ml/min cm²)</th>
<th>Stability in POM (h)</th>
<th>Refs.</th>
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<td>–</td>
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<td>130</td>
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<tr>
<td>Improved La₀.₈Sr₀.₂Co₀.₁Fe₀.₆Cr₀.₁O₃₋ₓ</td>
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<td>3–4</td>
<td>500</td>
<td>129</td>
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<td>2–4</td>
<td>1000</td>
<td>48</td>
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<td>–</td>
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<td>17</td>
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<td>AₓLa₁₋ₓBaₓFe₁₋ₓO₃</td>
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</table>

5.1.2. Oxidative coupling of methane to C₂-hydrocarbons

As an important intermediate of the industries, ethylene and its production methods have gained much attention. Ethylene production from CH₄ through OCM gives an attractive way. Following with the forerunners of Keller and Bhasin [148], catalysts for OCM with good performance have been explored [149–152]. However, the C₂ yields obtained with all the developed catalysts cannot arrive above 30% when the selectivity of C₂ is above 50%. High C₂ yields are resulted from the high selectivity of C₂ or/and high conversion of CH₄. Unfortunately, the selectivity of C₂ is always reduced by the increasing conversion of CH₄. Most yields of C₂ are below 25% in the traditional static-bed reactor due to the undesired combustion in the gas phase [6]. Usually, the O₂/air and CH₄ were fed into the traditional packed-bed reactor together in the mode of co-feeding, which caused the deep oxidation of methane and led to a low selectivity of C₂ because of the existence form of O₂ in the gas phase is molecule. Since the 1990s, lots of OCM related investigations have been devoted to the development of new reactor configurations, which can match the interplay of the OCM reaction with new catalysts better.

The good news is that the ceramic OPM reactors can provide higher selectivity and yield of C₂ due to several features of the membrane reactor [2]. Both porous [153,154] and dense [155,156] ceramic membranes have been applied in OCM. The CH₄ and O₂ can be separated by the dense OPM and the oxygen permeates through the OPM selectively and the CH₄ can be reformed on the membrane surface with the surface oxygen species. As a result, a higher selectivity of C₂ can be obtained due to the avoiding of the oxygen molecule in gas phase [155,156]. The dense OPM reactor applying in OCM eliminates the defects of the cyclic packed-bed reactors and the co-feed mode, the advantages can also be taken [157,158]. Several requirements for the proper OPM material applied in OCM are shown below: (i) enough oxygen permeation flux under the OPM conditions; (ii) excellent phase structural stability, chemical stability and mechanical stability; (iii) attractive catalytic performance for OCM [159].

In the fluorite-structured 25 mol% Y₂O₃ doped Bi₂O₃ (BY25) membrane reactor, the yield and selectivity of C₂ varied in 16–4% and 20–90%, respectively [160,161]. In La₀.₈Sr₀.₂Co₀.₁Fe₀.₅O₃₋ₓ membrane reactor [162], 10–18% yield and 70–90% selectivity of C₂ were obtained with a feed ratio (He/CH₄) of 40–90 when the temperature was higher than 850 °C. The highest C₂ yield of 17% and the C₂ selectivity of 80% were achieved in the Bi₁.₅Y₀.₅SnO₃₋ₓ.
When OCM was performed in a dead end tubular OPM reactor made of BYS at 900 °C, the highest one-pass C2 yield was 35% with a C2 selectivity of 54%, although the feed methane was diluted to 2%[164]. The yield of C2 can be decreased to 1% if the undiluted methane was used as the feed gas. Some other OPM reactors made of LaSrCoFeO[165] and BaCeGdO3[166] were also applied in OCM with the performance of <10% conversions of CH4 and 70–90% selectivities of C2 with diluted feed.

At the high operation temperature of OCM, some undesired side reactions may take place, like the radical reactions and thermal cracking. Catalyst for OCM is necessary to promote the process: (i) syngas production through POM on the membrane surface; (ii) formation of radicals on the membrane and/or catalysts surface; (iii) radical reactions both in the gas phase and on the catalyst surface take place simultaneously. We have investigated the BSCF tube membrane reactor for OCM with and without catalyst[167]. We found that the OPM tube reactor with La–Sr/CaO as OCM catalyst presented better performance compared with that without catalysts. The highest C2 yield of 15% was obtained with the catalyst of La–Sr/CaO in OPM reactor made of BSCF, which is comparable to that in a packed-bed reactor. However, the C2H2/C2H4 ratio in the membrane reactor was found to be around 12.0, which was much higher than the ratio of 1.0 achieved in the packed-bed reactor.

Recently, Bhatia et al.[168] investigated the OCM in three different reactor configurations: catalyst packed bed Ba0.5Ce0.4Gd0.1-Co0.8Fe0.2O3 (BCGCF) tubular OPM reactor, BCGCF tubular reactor and catalyst packed bed membrane reactor. The best performance of 67.4% C2 selectivity and 34.7% C2 yield with 51.6% CH4 conversion were achieved in the catalytic OPM reactor. This C2 yield is higher than the 28% in the traditional packed-bed reactor. However, the C2H4/C2H6 ratio in the membrane reactor was found to be around 12.0, which was much higher than the ratio of 1.0 achieved in the packed-bed reactor.

5.1.3. Oxidative dehydrogenation of light alkanes to olefins

Steam cracking of naphtha is the main production way of Ethylene and propane, which is an energy-consuming process due to its strongly endothermic reaction. The coke formation can be limited by introduction of steam to dilute the hydrocarbons. Because no equilibrium restricts the oxidative dehydrogenation of ethane (ODE) and propane (ODP) in the production of olefins, they give a promising pathway compared to the thermal dehydrogenation. Unfortunately, the yields of the desired product in the traditional reactors with co-feeding mode are too low to apply in industry till now. The activity of olefine is always better than that of the feed alkanes, which causes a deep oxidation of olefine and a low yield of objective product. In order to eliminate the problem, the lattice oxygen (O2−) is proposed as oxidant in a Mars-van Krevelen type mechanism, such as in a periodic fixed bed shift reactor. Although
the objective product with a high selectivity can be obtained because of the lattice oxygen (O$_2$) in this way, it cannot be operated continuously but periodically.

OPM reactor was investigated in the alkenes production through the alkanes oxidative dehydrogenation with a continuous supply of lattice oxygen (O$_2$) [171,172]. Molecular oxygen from air becomes adsorbed, dissociates into two oxygen atoms, by taking electrons they become ionized and form O$_2^-$, then O$_2^-$ is transported to the other membrane surface where ethane can react with the O$_2^-$ before the O$_2^-$ can recombine and form O$_2$ molecular. No O$_2$ molecular is found on the ethane side, which indicates that the reaction of the ethane and O$_2^-$ is prior to the formation of O$_2$ molecular from O$_2^-$. The reaction is C$_2$H$_{2n+2}$ + O$_2^-$ → C$_n$H$_2n$ + H$_2$O + 2e on the ethane side. Therefore, the lattice oxygen formed from O$_2$ of the air by OPM can be supplied to the membrane system continuously, which is beneficial for controlling the selectivity. The ODE was selected as model process to probe this concept. A disk OPM reactor made of BSCF was applied in ODE [172] with an ethylene selectivity of 80% and a per pass ethylene yield of 65% stably for 100 h, which also indicated the feasibility for the practical application. However, in the traditional fixed-bed reactor with the co-feeding mode, an ethylene selectivity of 53.7% was achieved under the same conditions. The introduction of Pd-clusters increased the ethylene yield from 66% at 807 °C to 76% at even a lower temperature (777 °C) [173,174], An tubular OPM reactor made of Bi$_{0.5}$Y$_{0.3}$-SmO$_3$ was applied with 80% ethylene selectivity and 56% per pass ethylene yield were obtained at 875 °C [175].

Different from ODE, only a few literatures are about the investigations of ODP in OPM reactors. We have studied the propylene production through ODP to an OPM reactor based on BSCF [176]. With a similar conversion of propane in range of 23–27%, the selectivity of propylene in the fixed bed reactor was about 15% while it was 44.2% in the OPM reactor due to the O$_2^-$ in the OPM reactor. We have studied the propylene conversion through the thermal dehydrogenation of ethane (TDE) was found to be kinetically slow. However, the ethane conversion is not only determined by the reaction kinetics, but also the reaction conditions. The performance of an OPM reactor is also affected by the membrane geometry: in the disk OPM reactor made of Ba$_2$Co$_3$Fe$_2$Zr$_2$O$_9$ for ODE, an ethylene selectivity of 80% was obtained while only 40% was achieved in hollow fiber OPM reactor [177], which was attributed to the different contact times between ethane and the disk/hollow fiber membranes. In the hollow fiber OPM reactor, a deep oxidation of ethane in a parallel and of ethylene in a consecutive reaction to H$_2$O and CO$_2$ could not be avoided. Especially, if once the reactive ethylene is produced, it can react with O$_2^-$ or O$_2$ again to form CO$_2$ and H$_2$O.

A new concept in olefin production is the multistep thermal-catalytic dehydrogenation of short chain alkanes with selective hydrogen combustion using oxygen which is in situ separated from air to minimize the thermodynamic restriction of alkane conversion [178]. Repeatedly the alkane reaction system is brought to the thermodynamic equilibrium by catalytic dehydrogenation due to C$_3$H$_8$ + C$_2$H$_4$ + H$_2$ by using the dehydrogenation catalyst Pt/Sn on Al$_2$O$_3$. Periodically, the separated oxygen through the hollow fiber BCFZ membrane is sent to the equilibrated dehydrogenation system where the oxygen selectively combusts the hydrogen to water as schematically shown in Fig. 15. These steps of catalytic dehydrogenation until equilibrium followed by selective hydrogen combustion can be repeated again and again. Tubular membrane geometry allows the controlled oxygen supply into the OPM reactor along the axial direction, which can avoid the thermodynamic limitation in the oxidative dehydrogenation (DH). Production of propene as well as oxygen permeation could be carried steadily even at a low temperature of 625 °C for a long time in a hollow fiber OPM reactor with a Pt/Sn/K DH catalyst. The highest propene yield of 36% with propene selectivity of 48% could be achieved at 675 °C while the best propene selectivity of 75% with 26% propene conversion was obtained at 625 °C. In the regime of kinetic compatibility between H$_2$ formed in the catalytic dehydrogenation and O$_2$ transported through the perovskite membrane, hydrogen reacts exclusively with O$_2^-$ of the perovskite [179]. If H$_2$, alkane and olefin grab for O$_2^-$ of the BCFZ membrane, hydrogen is the only source of water formation because of the high reaction rate of hydrogen with O$_2^-$ on the membrane surface since the alkane and olefin are less reactive than hydrogen. The principle of catalytic dehydrogenation coupled with the selective hydrogen combustion has been also demonstrated for ethylene production [180].

5.1.4. Oxyfuel combustion concept for CO$_2$ capture

Global CO$_2$ emissions have increased steadily in tandem with the fossil fuels usage. Therefore, CO$_2$ capture and storage (CCS) has to be deployed on a massive scale. In recent years, many researchers focused on different ways for CO$_2$ capture, including solid amine sorbents, organic polymers and metal – organic frameworks etc. [181–190]. It is known that the CO$_2$ emissions for power generation can be reduced by three technologies: pre-combustion, post-combustion and oxy-fuel combustion. In the pre-combustion, the fuel (coal, natural gas) is transformed into a H$_2$/CO$_2$ mixture, the technique is complex and the generating facility is expensive, the separation efficiency of H$_2$ and CO$_2$ also needs to be improved [191]. The CO$_2$ concentration in the flue gas of the post-combustion is about 4–14%, which indicates the high cost of investment resulted from the large amount of flue gas had to be handled. The

![Fig. 15. Stepwise oxidative dehydrogenation of propane with a sequence of dehydrogenation and hydrogen combustion in the OPM reactor [178].](image-url)
oxy-fuel power plant is based on the concept that the fossil fuel is combusted in the oxygen-enriched atmosphere, which produces a gas mixture consisted of CO₂ and water vapor with little trace elements and ash. After condensation, H₂O can be separated quickly and CO₂ can be sequestered easily. The recycled CO₂ from the flue gas acts not only as sweep gas for oxygen transport, it also dilutes the oxygen before combustion, thus controlling the flame temperature and keeping up the gas volume in the boiler [192]. However, the key problem for the oxyfuel concept is to get cheap oxygen on a large scale for the oxyfuel combustion.

In recent years, the R&D on OPMs has attracted increasing attentions in oxygen separation because of their infinite selectivity of oxygen as shown above. Therefore, the OPMs have also gained increasing attention for oxygen supply [192] to power plants with oxygen permeation flux and enough stability in the harsh temperature range from 1400 to 1800 °C. The simulation and the thermodynamic analysis on the OPM reactor as oxygen extractor is likely to become the only economically justified technology for power generation is the aim of this project. Within this project, the so called oxy-fuel technique is developed by the engineers of RWTH Aachen University and a 120 kW pilot-plant has been constructed [10].

5.2. Dense OPM reactor as oxygen extractor

5.2.1. Water splitting to hydrogen

Hydrogen has been considered to be a kind of clean fuel in the further, which has attracted increasing attentions [197,198]. For hydrogen production, water is chosen as the best source. At high temperatures, water undergoes a thermal self-dissociation due to 2H₂O→2H₂ + O₂. According to the low equilibrium constant of Kp = 2 × 10⁻⁸ at 900 °C, only low equilibrium concentrations of P₀₂ = 4.6 × 10⁻⁶ bar and P₁₂ = 9.2 × 10⁻⁶ bar are present. As a result of the small equilibrium constant of water dissociation, only a little hydrogen can be found even at high temperature, e.g. the generated hydrogen concentration is only 0.1% at 1600 °C. However, if the produced oxygen can be in situ-removed through an OPM reactor in time, the water splitting equilibrium will also be moved in the direction beneficial for hydrogen production. Provided that the thermal water splitting is fast enough, the oxygen permeation through the OPM to an oxygen consuming side will be the controlling step of the hydrogen production. Therefore, the oxygen partial pressure on this oxygen consuming side should be lower than that on the side of water splitting. Then hydrogen can be continuously obtained on the retentate side after water condensation.

It has been proved to be possible to produce hydrogen from the decomposition of water through the OPMs at terrific high temperature range from 1400 to 1800 °C. Naito and Arashi [199] have...
produced hydrogen by water splitting through a ZrO$_2$–TiO$_2$–Y$_2$O$_3$ membrane with the hydrogen rate of 0.6 ml/min cm$^2$ at 1683 °C. Obviously, the rate of the oxygen permeation through the OPMs controls the rate for hydrogen production. Based on the Wagner’s theory, higher gradient of oxygen partial pressure between the two sides of membrane will lead to a higher oxygen permeation flux through the OPM [3,4]. Hydrogen was used to consume the permeated oxygen in order to increase the oxygen partial pressure gradient and a high hydrogen rate of 6 ml/min cm$^2$ was achieved at 900 °C [200]. Gd-doped CeO$_2$ membrane with a modified microstructure was used to produce hydrogen and an even higher rate of 10 ml/min cm$^2$ was obtained [201]. But it is impractical to produce hydrogen by consuming the permeated oxygen using the produced hydrogen.

Recently, we applied POM to consume the oxygen on the permeate side through the reaction CH$_4$ + 1/2O$_2$ → CO + 2H$_2$. The advantages of this concept are: (i) the oxygen permeation flux can be increased by the decreased oxygen partial pressure on the permeate side; (ii) syngas can be produced in the same operation, which can be applied in the production of oxygenates (methanol) and hydrocarbons (diesel), as well as the hydrogen production through CO + H$_2$O → H$_2$ + CO$_2$, the water gas shift reaction operated at relatively low temperatures [202–204]. Fig. 17 shows the BCFZ hollow fiber OPM reactor used for the syngas and hydrogen production simultaneously. At the beginning, water decomposition takes place in the core side of the hollow fiber at temperature range of 800–900 °C. When the gradient of the oxygen partial pressure between the membrane two sides appears, the oxygen starts to permeate through the OPM to the oxygen quick consuming side by POM. That’s why the water splitting continues. The advantage of this process is the continuous production of pure hydrogen as well as syngas. Furthermore, by heat transfer the highly endothermic water splitting can be partially compensated by the exothermic POM reaction. At 950 °C, 70% CH$_4$ conversion and 60% CO selectivity with the hydrogen rate of 3.5 ml/min cm$^2$ was obtained. In our recent work [203], a porous catalyst layer of BaCo$_{0.9}$Zr$_{0.1}$FeO$_{3-δ}$ (BCFZ-Pd) was coated on the surface of BCFZ hollow fiber membrane. The production rate of hydrogen raised to 2.1 ml/min cm$^2$ at 950 °C, which was about three times of that with blank BCFZ membranes. Following this idea, ethane was used for water splitting by consuming the permeated oxygen according to C$_2$H$_6$ + O$_2$ → C$_2$H$_4$ + H$_2$O + 2e$^-$ [205]. 90% ethylene selectivity and 55% ethylene yield with 1.0 ml/min cm$^2$ hydrogen production rate was obtained at 800 °C.

5.2.2. N$_2$O decomposition

Nitrogen oxide (N$_2$O, x = 1, 2) is one kind of important pollutant to the atmosphere, especially the destructive effect of the nitrous oxide (N$_2$O) on the ozone layer [206]. NO and N$_2$O can be decomposed by the non-selective catalytic reduction (NSCR) with hydrocarbons or NH$_3$, or the selective catalytic reduction (SCR) [207–209]. Considering the efforts, it seems to be more promising to control the emissions of NO and N$_2$O through the direct catalytic decomposition. Some perovskite oxides [210,211], Cu–ZSM-5 zeolites [212], metal-doped Co$_3$O$_4$ [213] and Pd/Al$_2$O$_3$ [214] have been applied in the direct decomposition of N$_2$O as the catalysts. In all the catalysts mentioned above, the perovskite oxides exhibit their superiorities in the excellent long-term stability, as well as the good activities at high temperatures. Unfortunately, the produced oxygen tends to restrain the decomposition of N$_2$O using the perovskites as the catalysts [215], resulting in a low N$_2$O conversion. In order to avoid the negative effect, we conducted the N$_2$O decomposition in the OPM reactor based on BCFZ (Fig. 18) for the first time [216,217].

N$_2$O can be decomposed on the OPM with the catalysts firstly according to N$_2$O → N$_2$ + O$^*$ (surface oxygen) [216]. If the surface oxygen can be removed through the OPM, the decomposition of N$_2$O will continue. Therefore, the conversion of N$_2$O can be increased at a higher temperature or under a bigger gradient of the oxygen partial pressure, which can be realized by using methane to consume the permeated oxygen. As a result, the negative inhibition of oxygen on the N$_2$O decomposition can be avoided due to removal of the surface oxygen. Therefore, the complete N$_2$O decomposition with a starting content of 20% on one side of the OPM, while 90% CH$_4$ conversion and 90% CO selectivity on the other side were achieved simultaneously at 875 °C.

In this membrane reactor, we also investigated the NO decomposition in a similar process [217]. An almost 100% NO conversion and 95% N$_2$ yield was achieved at 875 °C. Furthermore, the undesired formation of NO$_2$ resulted from the deeper oxidation of NO can be inhibited due to the in situ removal of oxygen.

5.2.3. CO$_2$ decomposition

Thermal decomposition of CO$_2$ (TDCD) into CO and O$_2$ is an alternative process for the consumption and utilization of CO$_2$. However, the thermodynamic equilibrium controls this reaction and the conventional fixed-bed reactors are not suitable for it. Jin and Xu group [84] proposed the coupling of syngas production of POM with the TDCD in the SrCo$_{0.4}$Fe$_{0.5}$Zr$_{0.1}$O$_{3-δ}$ (SCFZ) OPM reactor (Fig. 19). On one side of the OPM, thermal decomposition of CO$_2$ takes place and the oxygen produced permeates through the OPM to the other side, where is consumed by methane with the production of syngas simultaneously. Here shows several advantages of these coupled reactions: (i) CO$_2$ can supply the oxygen for POM; (ii) the syngas as the significant chemicals can be produced.

![Fig. 17. Concept of simultaneous production of hydrogen and synthesis gas by combining water splitting with POM in a perovskite oxygen permeable hollow fiber membrane [202].](image1)

![Fig. 18. Mechanism of the direct decomposition of N$_2$O to N$_2$ with in situ removal of the rate inhibiting surface oxygen by perovskite hollow fiber membrane [216].](image2)
The TDCD reaction was found to occur heterogeneously mainly on the OPM surface and not as a homogeneous gas phase reaction. In this case, cobalt-rich perovskite membranes are unstable. Therefore, cobalt-less or cobalt-free perovskite membranes or dual phase membranes can be a good choice. Furthermore, the oxygen permeation flux through the membrane should be further increased, especially at low temperatures. However, many important catalytic reactions, such as the selective oxidations of alkanes, are operated at relatively low temperatures (<500 °C) while the operation temperatures for the OPMs are usually high (>600 °C). Therefore, there is an urgent need to develop the OPM materials with enough oxygen permeation flux at low temperatures to satisfy these reactions. Recently, the OPMs have attracted great interest for CO₂ utilization and CO₂ capture based on the oxy-fuel combustion. In this case, the membrane is exposed to a high CO₂ concentration; therefore, the stability of the membrane material under CO₂ is a very important issue. According to the oxyfuel combustion concept with CO₂ sequestration, some of the flue gas is recycled as sweep gas, which contains 80 vol.% CO₂ and 20 vol.% water vapor. The alkaline earth-metal containing perovskites are not stable at high CO₂ concentrations due to carbonate formation. For CO₂-rich sweep gases CO₂-resistant alkaline earth-metal-free membranes double-perovskites like doped La₂NiO₄ oxides or dual phase membranes are recommended.

(ii) Engineering of the membrane: In order to screen the OPM materials’ properties and optimize some reaction parameters, the disk, tube, capillaries and hollow fiber membranes are good choices. The advantage of the disk membranes is that they can be prepared easily by conventional pressing way. On the other hand, the sealing problem of the disk membranes is a fatal disadvantage for the applications, especially under harsh conditions, such as high temperatures and/or high pressure. Tubular membranes can avoid this high-temperature sealing problem which can be sealed at room temperature outside of the oven. Therefore, hollow fiber membranes appear to overcome these limitations of the disk and tubular membranes, including the low oxygen permeation flux due to the relatively thick membrane walls, small membrane areas per unit volume and so on. For partial application, the hollow fibers will be bunched together and the membrane system should be gas-tight. A novel approach is needed as e.g. full-ceramic modules with bunches of hollow fibers potted using a ceramic binder. The coefficient of the thermal expansion of the fibers and the housing should be matched. Full ceramic membrane system at operation temperatures from 700 to 900 °C still represents a challenge.

(iii) Reactions in membrane reactors: Although the catalytic OPMs materials’ properties have been investigated widely and the kinetic performance of OPM has helped us to find the bottlenecks in applications, whether such studies are conducted under the similar conditions as that of the expect applications or not is important. It is obvious that new smart materials (membrane, catalyst, etc.) are necessary for the application of OPM reactor, as well as the design of the reactions coupling, especially for the large-scale reactor for practical industry. The analysis of the optimal operation parameters is also affect by the design of the whole process, great improvement of the oxygen permeation flux through these submicron membranes by surface chemistry and/or microstructures modification due to the change of surface exchange kinetics. For the application in reducing atmospheres such as syngas production by POM, membranes have to be stable under reducing atmospheres, such as in the presence of CH₄, CO and H₂. In this case, cobalt-rich perovskite membranes are unstable.
where the OPM reactor plays an important role. Here the experimental procedures in combination with mathematical modeling will provide a better understanding.

Overall, on a long-term scale, the field of dense ceramic oxygen permeable membrane and membrane reactors for clean energy production to deliver environmentally benign processes is considered to be promising.

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References
