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Ceramic membranes with mixed conductivity and their application

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Abstract. Data on the catalytic reactors with ceramic membranes possessing mixed oxygen ion and electronic conductivity that make it possible to integrate the processes of oxygen separation and oxidation are analyzed and generalized. The development of this approach is of interest for the design of energy efficient and environmentally friendly processes for processing natural gas and other raw materials. The general issues concerning the primary processing of light alkanes in reactors with oxygen separating membranes are expounded and general demands to the membrane materials are discussed. Particular attention is paid to the process of oxidative conversion of methane to synthesis gas. The bibliography includes 110 references.

I. Introduction

At the current level of energy consumption, the coal and hydrocarbon reserves would be able to meet the requirement in energy for a foreseeable period of about a hundred years or little more.[1,2] Therefore, along with the development of power engineering based on renewable resources and thermonuclear power, the efficient use of fossil energy resources and creating new resource-saving clean technologies, such as processes for conversion of hydrocarbons to more convenient energy carriers and chemical products, are becoming increasingly important. Due to high oil prices, the value of natural gas increases. In addition, natural gas (methane) is a renewable raw material as it is formed in the course of anaerobic destruction of biomass of plant and animal origin. Currently, the major part of the natural gas is burned to produce heat and electricity, some of it is consumed as automotive fuel. Only relatively small part of natural gas is chemically processed into products of organic and inorganic synthesis. For example, only 2% – 3% of the natural gas produced all over the world is used for hydrogen production. Such inefficient use of the valuable raw material is largely due to imperfection of available methods of its processing.

The early attempts at the synthesis of more complex organic products from methane were based on its direct oxidation to methanol or formaldehyde. However, decades of research have not yet led to the development of a catalyst that would make this approach promising. Oxidative dehydrogenation and dimerization of methane to give ethylene seems to be more attractive. At present, there are catalysts which ensure 60% – 80% selectivity at 20% – 30% methane conversion in this reaction.[3 – 8]

Despite certain progress along this line, currently the only method of methane processing that has practical significance is its conversion into synthesis gas, which represents a mixture of carbon monoxide and hydrogen and finds its use in some synthetic processes. The most common method for production of synthesis gas is steam reforming of methane

$$CH_4 + H_2O = CO + 3\ H_2,\ \Delta H^\circ_{298\,K} = 206.1\ kJ\ mol^{-1} \qquad (1)$$

Synthesis gas is produced in tube furnaces in the presence of a nickel catalyst at 870 – 880 °C and 20 – 30 atm. Since a large amount of heat is required to maintain reaction (1), air is fed into the furnace together with steam, which results in burning of more than 40% of the natural gas supplied. This results in so-called ballasted synthesis gas, which contains large amounts of nitrogen, and in addition, the ratio of hydrogen and carbon monoxide

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is not suited for further use in methanol synthesis and in the Fischer–Tropsch process. Therefore, additional treatment is required to remove nitrogen and improve the ratio of hydrogen to carbon monoxide. The structural materials of the reformer are extremely expensive as they should withstand exposure to steam and the reductive gas phase atmosphere. Additional increase in the production cost is due to the large consumption of water. Thus, steam reforming of methane to synthesis gas is complicated in design and energy-intensive; the production cost equals 50% to 75% of the cost of the target products such as hydrogen, ammonia, methanol, liquid hydrocarbons, *etc*.[9] Moreover, its economic efficiency, like that of any process proceeding with heat consumption, increases with increasing production scale.

Carbon dioxide reforming of methane is an alternative to steam reforming

$$CH_4 + CO_2 = 2\,CO + 2\,H_2,\ \Delta H^\circ_{298\,K} = 247.3\ \text{kJ mol}^{-1} \quad (2)$$

This process is additionally attractive as it utilizes anthropogenic carbon dioxide. However, this 'dry' carbon dioxide reforming is not used in practice as there is no catalyst sufficiently stable for application in industrial production. Pure oxygen can also be used for production of synthesis gas

$$CH_4 + 0.5\,O_2 = CO + 2\,H_2,\ \Delta H^\circ_{298\,K} = -35.7\ \text{kJ mol}^{-1} \quad (3)$$

The ratio of hydrogen to carbon monoxide in the resulting product is suitable for further processing. Quite a lot of heat is released in reaction (3), which is favourable for a compact implementation of the process.

Combinations of reactions (1)–(3) are usually utilized in the industrial production to improve the composition of synthesis gas and to enhance the economic efficiency. The product composition at the reactor outlet is usually close to the equilibrium and is determined by temperature, pressure and the ratio between components in the starting reaction mixture. An important process aspect is associated with the occurrence of side reactions

$$CH_4 + 2\ O_2 = CO_2 + 2\,H_2O,\ \Delta H^\circ_{298\,K} = -802\ \text{kJ mol}^{-1} \quad (4)$$

$$CH_4 = C + 2\,H_2,\ \Delta H^\circ_{298\,K} = 75\ \text{kJ mol}^{-1} \quad (5)$$

$$2\,CO = C + CO_2,\ \Delta H^\circ_{298\,K} = -172\ \text{kJ mol}^{-1} \quad (6)$$

$$CO + H_2 = C + H_2O,\ \Delta H^\circ_{298\,K} = -131\ \text{kJ mol}^{-1} \quad (7)$$

which result in the formation of elemental carbon, catalyst passivation and destruction, increase in the flow resistance of the catalyst bed, local overheating and even complete termination of the process.

Thus, the improvement of the process of natural gas reforming is related to the advances in oxygen production and delivery to the reaction zone, enhancement of stability of catalysts and other materials contacting with the gas flow and also to the whole process arrangement. Here we discuss a promising method for separation of oxygen from air with the use of high-temperature ceramic membranes with mixed electronic and ionic conductivity.† It can be combined with important catalytic processes like methane reforming to synthesis gas. The catalytic membrane reactors attract much attention because they can significantly reduce the cost of synthesis gas production and, hence, the cost of products formed from it.

† The relevance of investigation of the membranes with mixed conductivity and reactors based thereon is evidenced by the fact that two reviews [10, 11] devoted to these studies have already been published this year. However, there are very few scientific publications on this topic in Russian literature.

II. Production of oxygen from air

At present, the most efficient and widely used method for oxygen production is cryogenic distillation of air. The capacity of a typical cryogenic plant is 30 000 m^3 of oxygen per hour. Nevertheless, even at such a large production scale, the oxygen cost is too high for the subsequent production of chemicals. For instance, in the Fischer–Tropsch process, the cost of a ton of the final product increases by 80–100 US dollars. The high oxygen cost is due to high operational cost of cryogenic production.

Separation of oxygen from air by means of polymeric membranes is also widely used. The separation process is based on the difference between the diffusion coefficients of oxygen and nitrogen. Thin tubular membranes several tens of micrometres thick supported on a porous substrate (to increase the mechanical strength of the material) are used to intensify the separation. The temperature of the process is restricted by the thermal stability of the polymer used. Poly-(2,6-dimethylphenylene oxide) is stable up to ~100–150 °C; polyamide membranes are somewhat more stable. The process is modular, so it can be easily adapted for both large and small production volumes. The product oxygen contains a large quantity of nitrogen; several consecutive separation stages should be used to increase its purity, and this leads to the increase in the final product cost.

Another known method is based on the ability of some materials to reversibly sorb nitrogen and oxygen. For example, molecular sieves selectively adsorb nitrogen under increased pressure, and this gives a possibility of air separation by short-cycle adsorption with production of a gas mixture with increased oxygen content.[12] Similarly, materials (metals or metal oxides) easily oxidized by atmospheric oxygen can be used, their subsequent heating results in formation of gaseous oxygen. Such materials can also be used directly for methane oxidation without getting gaseous oxygen.

The complex oxide $YBaCo_4O_{7+\delta}$ attracts researchers' attention as a material for separation of oxygen from air since it is capable to adsorb and desorb large amounts of oxygen ($\delta \approx 1.56$) at 200–400 °C;[13, 14] its capacity with respect to oxygen is ~ 2700 μmol of O_2 g^{-1} (Ref. 15). This amount of oxygen can be evolved reversibly to the surrounding gas phase and if the gas phase contains methane, the evolved oxygen can react with it immediately. The composition of the formed synthesis gas will depend on the catalyst and the process conditions.

This active oxide may be applied to a highly porous support like Al_2O_3 to enlarge the reaction area and prevent local overheating. Encouraging results, 95% methane conversion and ~60% selectivity to carbon monoxide, were obtained in a study devoted to the partial methane oxidation [16] in experiments lasting up to 1500 h. The advantage of this method consists in its simplicity. The disadvantages include high consumption of materials, cumbersome equipment and the necessity for cyclic regeneration of the active substance.

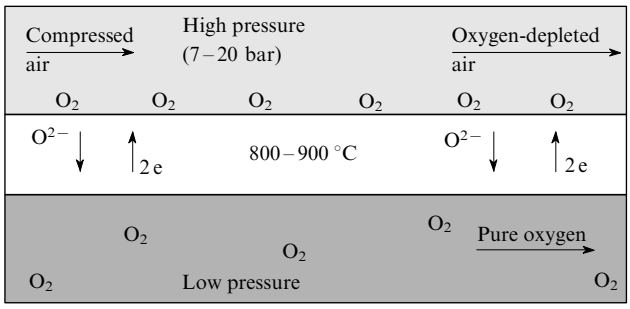


Figure 1. Principle of operation of a membrane with mixed conductivity for isolation of oxygen from air.

The use of ceramic membranes with mixed ionic and electronic conductivity (MIEC) opens up new opportunities for separation of atmospheric oxygen.[17] As in the case of polymeric membranes, the driving force of the oxygen separation is the difference between the partial pressures of oxygen in the gas half-spaces separated by the membrane. However, oxygen is transported through the membrane in the ionic rather than in the molecular form, the electric neutrality of the membrane being provided by a counterflow of electrons (Fig. 1). The ionic mechanism of oxygen diffusion determines 100% selectivity of the membrane with respect to oxygen. The membrane temperature should be within 800–1000 °C to ensure its sufficiently high ionic conductivity. It is expected that this method could reduce the cost of oxygen by approximately one third.[18]

Note that it is not necessary to use pure gaseous oxygen in the reforming process; however, it should not contain nitrogen, the presence of which sharply deteriorates the composition of synthesis gas and the economic efficiency of the process decreases. To implement this process, one may use membranes of a material with mixed conductivity. If one side of the membrane is in contact with methane and partial pressure (p'_{O_2}) or activity of oxygen on it is low, whereas the other side of the membrane is in contact with air or other gas with high oxygen partial pressure (p''_{O_2}), then the driving force of the separation process will be the gradient of oxygen chemical potential.

III. General principles of operation of membranes with mixed conductivity

The efficiency of MIEC membranes is determined by two major factors. The first one is related to bulk transport of oxygen ions and oppositely directed movement of electrons, the second is characterized by processes on the membrane surface, *viz.*, adsorption and desorption processes, dissociation of molecules and recharge of oxygen ion. The density of oxygen flux (j_{O_2}) through a MIEC membrane of thickness d can be expressed through oxygen partial pressures at the opposite sides of the membrane and oxygen-ionic (σ_i) and electronic (σ_e) components of conductivity [19]

$$j_{O_2} = -\frac{RT}{16F^2 d}\int_{p'_{O_2}}^{p''_{O_2}} \frac{\sigma_i\sigma_e}{\sigma_i+\sigma_e}\,d\ln p_{O_2} \qquad (8)$$

where R and F are the universal gas constant and the Faraday constant, respectively. The surface processes change the flux density; this can be taken into account by the following modification of Eqn (8)

$$j_{O_2} = -\frac{RT}{16F^2(d+2d_c)}\int_{p'_{O_2}}^{p''_{O_2}} \frac{\sigma_i\sigma_e}{\sigma_i+\sigma_e}\,d\ln p_{O_2} \qquad (9)$$

$$d_c = \frac{D^*}{K}$$

where D^* is the oxygen diffusion coefficient in the MIEC membrane, K is the rate constant for surface exchange.[20] As can be seen from Eqn (9), slow surface kinetics results in growth of the parameter d_c and decreases the permeability to oxygen. A simple technique for determining the rate-limiting process is measurement of the permeability of the membrane depending on its thickness.

The integration of processes of oxygen separation and partial oxidation of light hydrocarbons (such as methane) resolves several problems, particularly, it eliminates the need for large energy consumption to isolate oxygen, and oxygen having entered the reaction zone immediately reacts and forms oxidation products, thus reducing the risk of local overheating and ensuring safety of the process. If suitable catalyst and conditions of the methane partial oxidation are chosen, the overall process resulting from simultaneously proceeding reactions (1), (2) and (4) is expressed by reaction (3), with the composition of thus produced synthesis gas being suitable for its further processing to methanol and liquid hydrocarbons. Since reaction (3) proceeds with release of heat, the process can be carried out in the autothermal (or nearly autothermal) regime, which is favourable for implementation of the process in a compact installation. Simultaneously, there is no need for excessive combustion of the starting raw material, and this remarkably reduces the cost of the produced synthetic gas and lowers carbon dioxide emission.

However, these advantages are achievable provided that a series of requirements to the membrane material are fulfilled, *viz.*:

— the membrane has to be sufficiently permeable to oxygen;

— the membrane material has to possess long-term stability in strongly reductive conditions in the presence of oxygen partial pressure gradient;

— the membrane material should not have phase transition with volume change, which can have negative effect on its mechanical strength;

— the membrane has to be stable against high-temperature creep;

— the material cost should not be high.

Furthermore, the problem of sealing the nozzles between the membrane and the load-bearing reinforcement of the reactor has to be solved.

Since the MIEC membranes perform simultaneously two different functions such as separation of oxygen from air and partial oxidation of methane, the reactors with these membranes may be assigned to one of the types of membrane reactors that are widely used in the gas phase chemistry, and particularly, for dehydrogenation of organic compounds and production of extra-pure hydrogen.[8,21] Highly selective membranes based on metallic palladium

or its alloys able to absorb and release hydrogen are used most often in conventional membrane reactors.‡

IV. Materials for membranes with mixed conductivity

Development of materials possessing the combination of characteristics necessary for membrane methane conversion is a complicated task. One way is to construct a composite membrane comprising a phase with predominantly ionic conductivity and a phase with mainly electronic conductivity.[22,23] The ratio and degree of disperion of the phases should ensure continuous routes for charge carriers. A composite metal ceramic membrane has been patented,[24] in which the metallic phase possesses high electronic conductivity, while the oxide component with predominantly ionic conductivity ensures oxygen ion transport. A multiphase oxide membrane $Ce_{0.8}Gd_{0.2}O_2 - La_{0.7}Sr_{0.3}MnO_3$ was proposed[25] where one of the components was a perovskite phase. Presumably, the extended area of grain boundary contacts can provide high oxygen fluxes. A composite containing perovskite-like phases $La_{0.15}Sr_{0.85}Ga_{0.3}Fe_{0.7}O_{3-\delta}$ (LSGF) and $Ba_{0.5}Sr_{0.5}Fe_{0.2}Co_{0.8}O_{3-\delta}$ (BSFC) was studied.[26] The prepared membrane consisted of LSGF grains coated by the BSFC film. The density of oxygen flux through this membrane was 0.45 ml cm^{-2} min^{-1} at 915 °C, *i.e.*, an order of magnitude higher than that observed for LSGF membrane. The $Ce_{0.85}Sm_{0.15}O_{1.925}$ electrolyte was used as an ionic conductor in another study[27] where the electronic conductivity was provided by the perovskite-like $Sm_{0.6}Sr_{0.4}FeO_{3-\delta}$ phase.

It is worth noting that the known oxygen ion conductors based on ZrO_2 and CeO_2 do not provide the necessary densities of oxygen ion fluxes, while electrolytes based on Bi_2O_3 having higher conductivity are unstable under the strongly reductive conditions of the partial oxidation process.[28,29] Therefore, the development of new solid electrolytes represents an important task; however, its solution seems unlikely in the short run. Moreover, if this problem were solved, it would be difficult to find a metal or metal-like phase possessing low activity in contact with the ceramic phase at high temperatures and simultaneously compatible with it by the thermal expansion coefficient. The above restricts the long-term structural and thermal stability of composite membrane materials in the methane conversion process. The indicated problems are eliminated if the membrane consists of only one MIEC phase where both oxide ions and electrons can move simultaneously.

In the search of materials for MIEC membranes, compounds of different structural types (fluorite, pyrochlore, brownmillerite, Raddlesden–Popper phases) were studied.[30–36] The highest permeability to oxygen was shown by perovskite-like oxides $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (Refs 37 and 38). The highest permeability of 3.1 ml cm^{-2} min^{-1} was achieved for 0.1 cm-thick $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ membranes with large cobalt content at 850 °C and p_{O_2} gradient in air–helium. Since these pioneering publications, much effort has been made to optimize the functional properties of perovskite-like MIEC membranes.

‡ This review is devoted to membranes with mixed oxygen ion and electronic conductivity; therefore, the membranes permeable to hydrogen are not considered here.

Particularly, a reactor with a tubular membrane composed of $La_{0.2}Sr_{0.8}Co_{0.4}Fe_{0.6}O_{3-\delta}$ was reported.[39–42] The membrane collapsed immediately after introduction of methane into the system. In the authors' opinion,[42] this was due to large mechanical stresses arising owing to pronounced change in the oxygen content across the membrane section and to reduction of the membrane material. Properties of the $La_{0.2}Sr_{0.8}Co_{0.1}Cr_{0.1}Fe_{0.8}O_{3-\delta}$ composition were discussed in a review,[43] and it was noted that cracks appeared in the membrane after 350 h of operation at 900 °C. To extend the lifetime of the $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes in the reductive atmosphere, a protective layer of cerium oxide with samarium additives was suggested.[44] Similarly, the $Ce_{0.8}Gd_{0.2}O_2$ layer was used to protect the $La_{1-x}Sr_xCoO_{3-\delta}$ membranes.[45]

High oxygen permeability was exhibited by the $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ oxides of perovskite type.[46,47] To improve the properties, cations that are difficult to reduce were introduced in the membrane compositions in several studies. Stable operation of the $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ membrane for 300 h was observed.[48] The use of tantalum[49] made it possible to increase the operating time of the $BaCo_{0.7}Fe_{0.2}Ta_{0.1}O_{3-\delta}$ membrane up to 400 h. In these and many other studies (for instance, Refs 50–52), cobalt-containing compounds were used to ensure high oxygen permeability. Since the thermodynamic stability of the cobalt–oxygen bonds is low under reductive conditions, the operating time of these membranes rarely exceeded a few hundreds of hours.

Compounds based on iron oxide are much more attractive from the standpoint of stability against reduction (Fig. 2).[35,53,54] In the series of compounds with the perovskite structure, solid solutions $La_{1-x}Sr_xFeO_{3-\delta}$ seem most promising for ceramic membranes. These compounds have high electronic[55–57] and ionic[58,59] transport characteristics. It was found for the first time[60] that the maximum oxygen ion and electronic conductivity is observed for compounds with $x = 0.5$ (Fig. 3). This is due to formation of large number of vacancies, while maintaining their maximum disorder. In the range of p_{O_2} corresponding to the conditions of reaction (3), the oxygen flux through a 1 mm thick membrane was 5–8 ml cm^{-2} min^{-1} at 900 °C

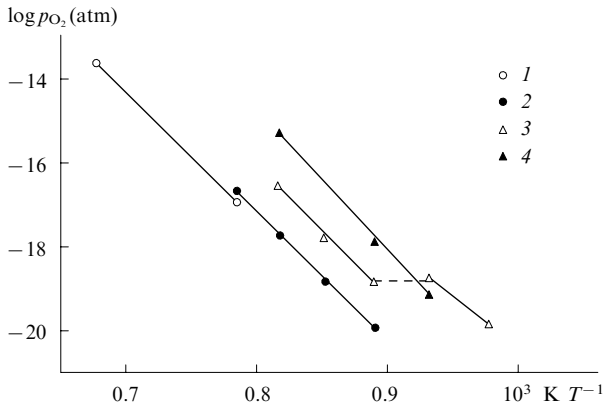


Figure 2. Ferrite stability boundaries under reducing conditions. A sharp change in the stability of $SrFeO_3$ at ~1100 K is owing to the perovskite → brownmillerite structural phase transition.[35] (*1*) $LaFeO_3$, (*2*) $Sr_3Fe_2O_{7-\delta}$, (*3*) $SrFeO_{3-\delta}$, (*4*) $Sr_4Fe_6O_{13-\delta}$.

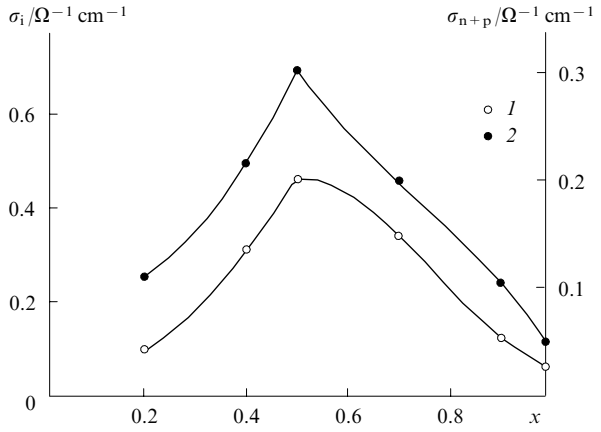


Figure 3. Concentration dependencies of ionic conductivity (*1*) and total electronic conductivity (*2*) for $La_{1-x}Sr_xFeO_{3-\delta}$ under the conditions of the electron–hole equilibrium at 900 °C.[60]

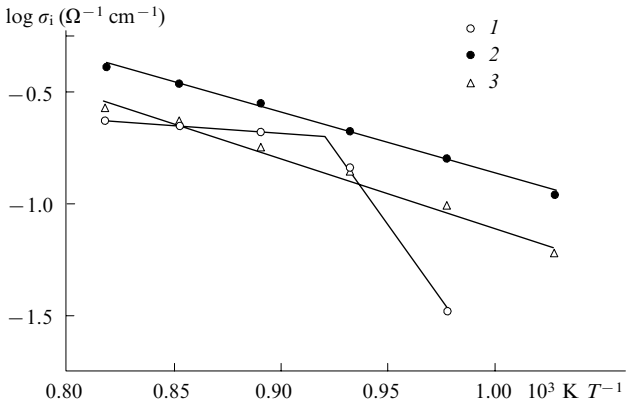


Figure 5. Temperature dependences of oxygen ion conductivity for $SrFe_{1-x}Mo_xO_{3-\delta}$. The knee in the curve for $x = 0$ is due to the perovskite → brownmillerite structural phase transition.[70] $x = 0$ (*1*), 0.05 (*2*), 0.10 (*3*).

(Fig. 4).[60] According to the thermogravimetry data, reduction of the composition with $x = 0.5$ by a 5% H_2 + 95% He mixture starts at >850 °C at $p_{O_2} \approx 10^{-16}$ atm. Moderate doping of strontium ferrite with aluminium, gallium, titanium or chromium increases its stability under reductive conditions.[61–64]

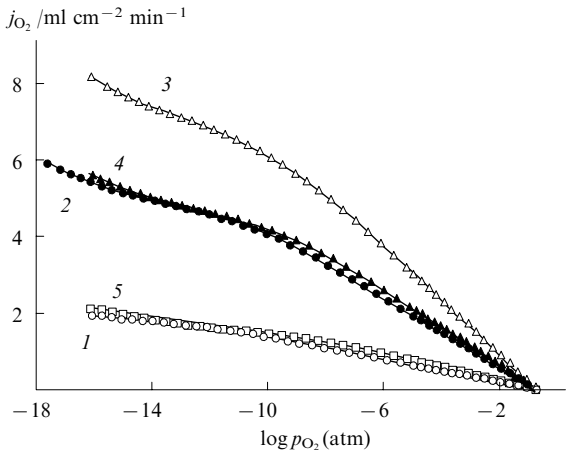


Figure 4. Calculated oxygen flux densities through a 1 mm-thick $La_{1-x}Sr_xFeO_{3-\delta}$ membrane at 900 °C *vs.* oxygen partial pressure on the low-pressure side ($p_{O_2} = 0.21$ atm on the opposite side).[60] $x = 0.2$ (*1*), 0.4 (*2*), 0.5 (*3*), 0.7 (*4*), 0.9 (*5*).

It is worth noting that a large number of oxygen vacancies necessary for ionic transport may have a negative effect on the stability of the crystal lattice. An alternative approach to increase the ionic conductivity can be formation, in the oxide, of microheterogeneous structure in which a relatively small number of oxygen vacancies would form the paths for rapid ion transport.[65–67] Indeed, it was demonstrated[68–70] that the replacement of some iron atoms in $SrFeO_{3-\delta}$ by niobium, molybdenum or tungsten atoms favours the formation of nanosized heterogeneities owing to the formation of local structural domains in the perovskite matrix. The presence of numerous coherent intergrowth domains results in the development of disordered phase boundaries, the suppression of phase transition to the brownmillerite structure, a significant reduction in the activation energy for ion hopping and increase in the ionic conductivity (Fig. 5).[70, 71]

V. The geometry of membranes with mixed conductivity

Small flat disk-shaped membranes are most often used in the laboratory tests because they can easily be fabricated by usual pressing of MIEC material powder followed by high-temperature treatment. The membrane is fixed between alundum tubes (Fig. 6),[72] the nozzles are sealed by gold gaskets or using a glass sealant. One side of the membrane is washed with air, the other conacts a gas with low oxygen partial pressure (in the studies of oxygen permeability, it is

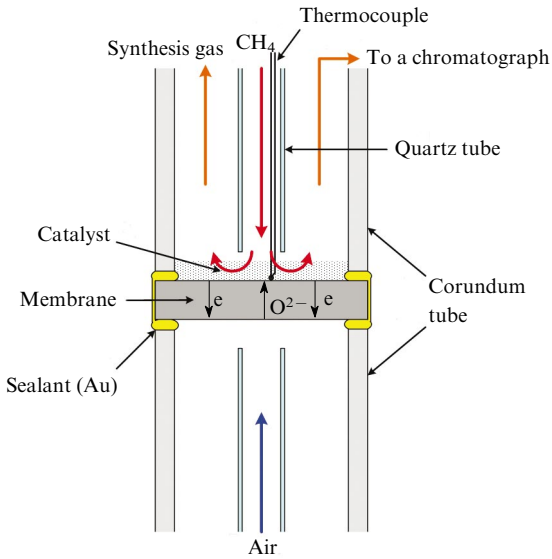


Figure 6. Schematic of a planar reactor for partial oxidation of methane.[72]

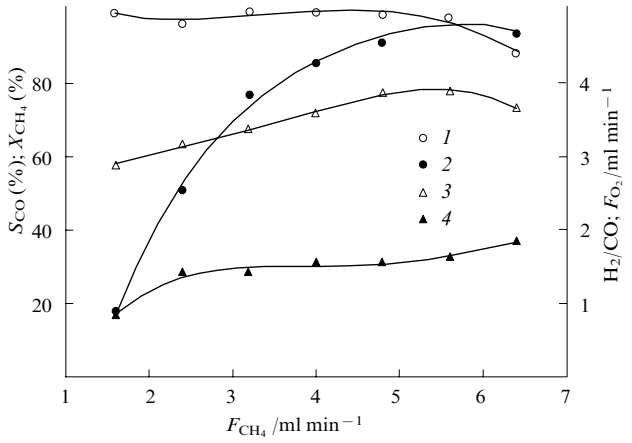


Figure 7. Process parameters of the partial oxidation of methane in the planar membrane reactor at 900 °C.[76]
(*1*) Degree of conversion, X_{CH_4}; (*2*) selectivity to carbon monoxide

$$S_{CO} = \frac{p_{CO}}{p_{CO} + p_{CO_2} + p_{CH_4}};$$

(*3*) oxygen flux, F_{O_2}; (*4*) H_2 : CO ratio; F_{CH_4} is methane flux.

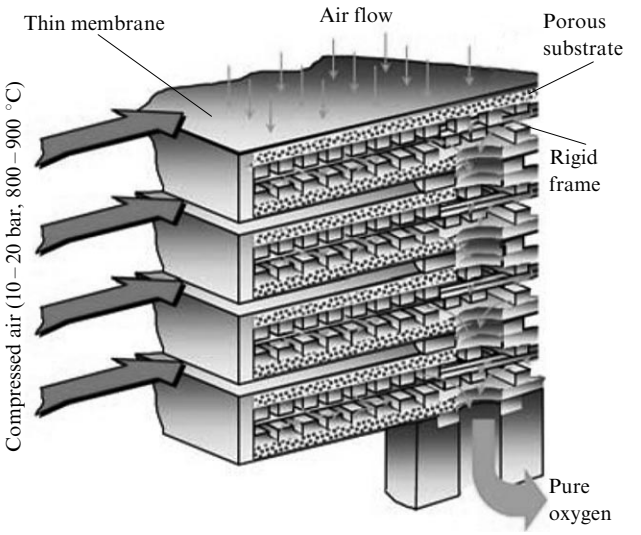


Figure 9. Modular assembly of asymmetric membranes developed by Air Products.[85]

usually helium or argon, in which oxygen pressure is fixed at the level of 10^{-4}–10^{-3} atm by means of gas mixers; to get lower oxygen pressure, oxygen electrochemical pumps can be used).[73] When hydrocarbon reforming is investigated, the corresponding side of the membrane is coated by a catalyst.[74,75] In addition, free space near the membrane should also be filled with the catalyst to increase the methane conversion (X_{CH_4}) because the supplied methane should have time to react with H_2O and CO_2 molecules, which are formed intensively on the membrane surface according to reaction (4). Also noteworthy is that in reactors with planar membranes, large gradients of the oxygen partial pressure can hardly be reached even if X_{CH_4} values are high (Fig. 7) because the H_2O and CO_2 concentrations near the membrane surface are high. As a result, the oxygen flux is restricted.[76] The construction of the reactor for partial oxidation of methane with a tubular membrane (Fig. 8) is favourable for achievement of larger gradients of oxygen partial pressure and densities of oxygen flux.

With the decrease in the MIEC membrane thickness, the intensity of oxygen separation increases, therefore asymmetric membranes, in which a thin gas-tight functional layer is combined with a porous substrate providing the mechanical strength of the membrane, were studied in a series of works.[18,77–83] Particularly, a thin workpiece of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was obtained by rolling,[84] then it was pressed to a porous substrate made of the same material and sintered. The functional layer in the membrane thus prepared was 0.07 mm thick, the supporting layer of 0.83 mm thickness had porosity of ~ 34%. The permeability of this membrane at p_{O_2} gradient in the air–argon medium was 12.2 ml cm^{-2} min^{-1} at 1000 °C. Air Products Inc. (USA) developed a technology of assembly of large modules of flat asymmetric membranes for production of pure oxygen (Fig. 9).[85]

In recent years, much attention has been paid to the development of capillary tubular membranes.[86–89] The outer diameter of this membrane is ~1 mm, its thickness is ~ 0.1–0.5 mm (Fig. 10). Such a thin membrane can easily be bent into U-like shape; therefore, its ends can be located in the cold part of the reactor where sealing is much easier than in the hot zone. The advantage of capillary membranes consists in their large specific surface area, which determines high performance in the oxygen separation from air.

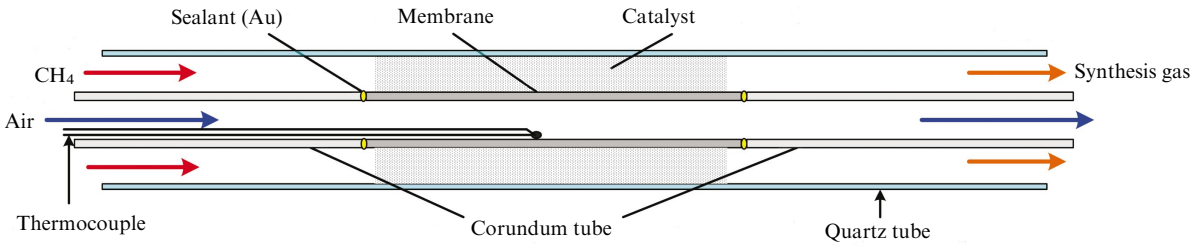


Figure 8. Schematic of a tubular reactor for partial oxidation of methane.

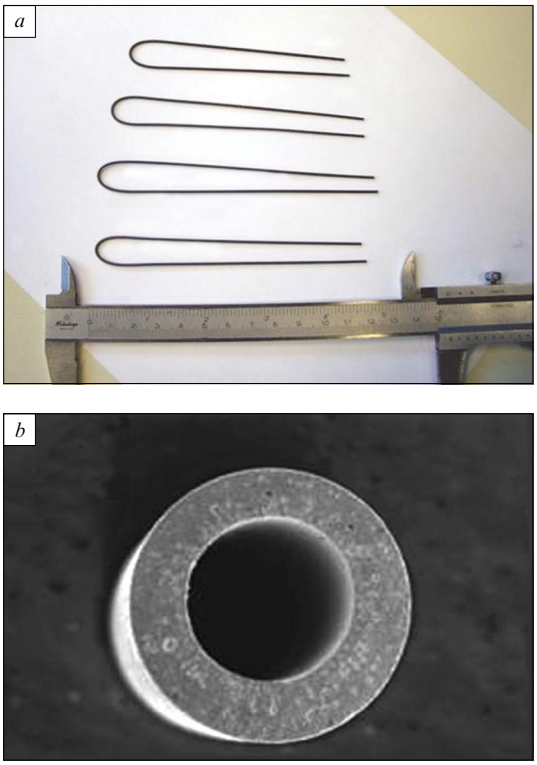


Figure 10. Appearance of the capillary U-shaped tubular membrane (*a*) and its cross-section (*b*).[90]
The outer tube diameter is 1.2 mm, the inner diameter is 0.7 mm.

VI. Partial oxidation of methane

The experiments on methane oxidation using MIEC membranes without a catalyst showed that all oxygen having entered the methane-containing half-space transforms into the products of complete oxidation, H_2O and CO_2. This means that conventional nickel catalyst for steam and carbon dioxide reforming can be used for production of synthesis gas. The temperature of the process should be above 830 °C to enable reaction (3).

The conversion of methane increases with increasing temperature; however, simultaneously, the requirements to materials become much tougher. Therefore, the upper temperature limit for the operation of catalytic membrane reactor is ~ 900 °C. For instance, stable methane conversion to synthesis gas at 875 °C with the >95% selectivity to CO and the ratio $H_2:CO \approx 2$ was observed[91] during 50 h when microcapillary membrane of perovskite-like oxide $Ba(Co,Fe,Zr)O_{3-\delta}$ and a standard commercially available catalyst for methane steam reforming were used. Degradation of the catalyst due to soot formation occurred at longer operation times. Addition of steam to the supplied methane suppressed the formation of soot. More serious problem was related to degradation of the membrane due to interaction with carbon dioxide, which was contained in the oxidation products, and the formation of barium carbonate. Methane conversion in the reactor with a flat $La_{0.4}Ba_{0.6}Fe_{0.8}Zn_{0.2}O_{3-\delta}$ membrane and nickel catalyst was also studied.[92] With 1 mm thick membrane at 900 °C, the specific oxygen flux through the membrane was 3.8 ml cm^{-2} min^{-1} at almost complete conversion of methane and 95%–99% selectivity with respect to CO; the time of continuous operation of the reactor reached 500 h. It was noted that the presence of zinc may favour reduction of the membrane material, hamper the recharge of oxygen and retard oxygen transport.

A composite asymmetric capillary membrane with the 0.075 mm thick outer separating layer made of a mixture of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ and $ZrO_2(Y_2O_3)$ and the inner supporting layer composed of the $NiO/ZrO_2(Y_2O_3)$ cermet was reported.[93] Nickel contained in cermet served as the catalyst of methane conversion. The 20% conversion of methane at ~ 90% selectivity to CO was reached at 900 °C; the testing time did not exceed 1 h.

An asymmetric flat $Ca_{0.8}Sr_{0.2}Ti_{0.7}Fe_{0.3}O_{3-\delta}$ membrane with ~0.02 mm thick separating layer was also reported.[94] The load-carrying part of the membrane with porosity of ~ 30% was made of the same material and served as a support for nickel catalyst. The 80% conversion of methane was achieved at 900 °C, the selectivity to CO being 100%. The measurements carried out with membranes of different thickness indicated that the oxygen flow through the membrane is limited by bulk diffusion.

Taking into account the restrictions on velocities and pressures of supplied gases, sealing characteristics, the packing density of the membrane elements, compatibility of materials of membranes and load-carrying parts of reactors, it was shown[95] that the preferable design of the membrane module is that based on the use of conventional tubular membranes with outer diameters of 10–20 mm and wall thickness of 1–3 mm.

Studies of durability of reactors for methane partial oxidation with the use of $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ tubular membranes demonstrated their stable operation for more than 7000 h at the methane conversion of no less than 98.8% and selectivity to CO of no less than 90% (Fig. 11).[96] Subsequent electron dispersion analysis revealed no changes in the chemical composition across the cross-section of the membrane, and X-ray diffraction data confirmed that the used materials preserved their crystal structure.

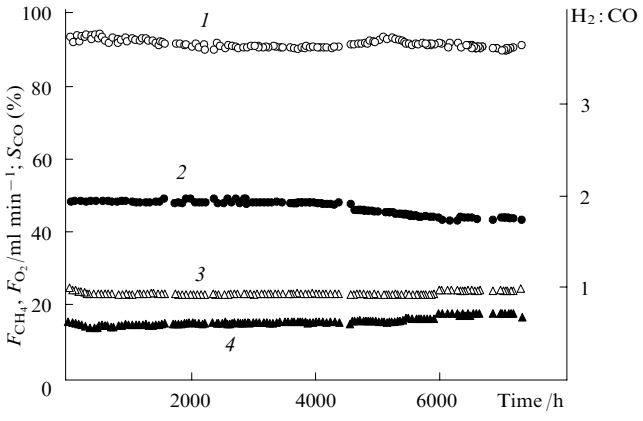


Figure 11. Process characteristics of the partial oxidation of methane on a tubular membrane made of $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ at 850 °C.[96] S_{CO} (*1*), $H_2:CO$ (*2*), F_{CH_4} (*3*), F_{O_2} (*4*). The membrane surface area is 5 cm^2; air flux is 300 ml min^{-1}.

VII. Oxidative coupling of methane and other processes

Ethylene is a large-scale chemical product. Methane can be used as the starting material for its synthesis [97]

$$2\,CH_4 + O_2 = C_2H_4 + 2\,H_2O, \qquad (10)$$
$$\Delta H^{\circ}_{298\,K} = -281.8\ \text{kJ mol}^{-1}$$

Application of MIEC membranes in this process has some advantages because in the presence of an appropriate catalyst, methane can react according to reaction (10) on the membrane surface with participation of charged oxygen species, thus ensuring high selectivity to ethylene.[98] In a $La_{0.8}Sr_{0.2}Co_{0.6}Fe_{0.4}O_{3-\delta}$ membrane reactor at 850 °C, a 70%–90% selectivity with respect to C_2-hydrocarbons was reached.[99] The 90% selectivity to C_2-hydrocarbons was achieved with the use of the $Ba(Ce,Gd)O_{3-\delta}$ membrane.[100] High values of selectivity (~80%) and methane conversion (~50%) were also observed in another study.[101] The essential problem of the membrane oxidative coupling of methane is related to high rate of oxidation of C_2 products that lowers the efficiency of the process. Therefore, additional efforts aimed at the development of more effective catalysts and methods for catalytic activation of the membrane surface are required. The right combination of the membrane and the catalyst also plays a role since the velocity of oxygen penetration through the membrane should correspond to the productivity of the catalyst.

Application of MIEC membranes to oxidative dehydrogenation of alkanes also opens up interesting opportunities. For example, in a tubular reactor with the $Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$ membrane, the 80% selectivity was attained for dehydrogenation of ethane to ethylene at 875 °C.[102] Dehydrogenation of propane to propylene was carried out with the 44% selectivity in a reactor with the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane.[103]

Membranes with mixed conductivity can be used to obtain oxygen from oxygen-containing compounds

$$(CH_4)_a + (H_2O)_c = (CO + 2\,H_2)_a + (H_2)_c \qquad (11)$$
$$(CH_4)_a + (CO_2)_c = (CO + 2\,H_2)_a + (CO)_c \qquad (12)$$

where the subscripts denote the anodic (a) and cathodic (c) sides of the membrane. Reduction of water to hydrogen proceeds on the cathodic side

$$H_2O + 2\,e = H_2 + O^{2-} \qquad (13)$$

Under the action of the chemical potential gradient, the oxide ions are transported through the membrane to the anodic region, where they participate in partial oxidation of methane

$$CH_4 + O^{2-} = CO + 2\,H_2 + 2\,e \qquad (14)$$

while the released electrons move to the cathodic surface of the membrane. Since hydrogen is present in both compartments separated by the membrane, the driving force of the process would be determined by the hydrogen concentration at the cathodic side of the membrane. Low partial pressure of oxygen at the cathodic side prevents the presence of a high gradient and, hence, oxygen flux in contrast to the case where air passes along the membrane (curve *1* in Fig. 12).

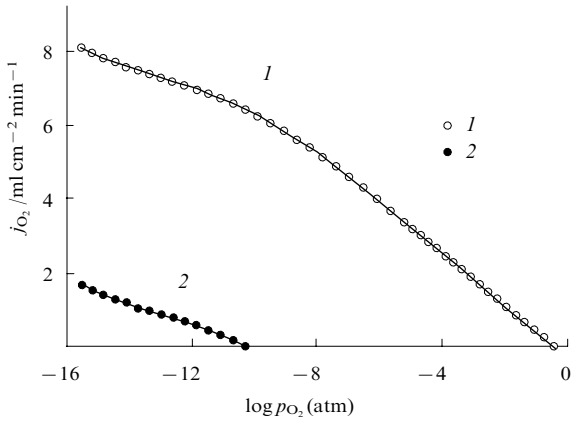


Figure 12. Calculated oxygen flux densities through the $La_{1-x}Sr_xFeO_{3-\delta}$ membrane of 1 mm thickness at 900 °C *vs.* oxygen partial pressure at the cathodic side.
(*1*) The high-pressure membrane side contacts with air ($p_{O_2} = 0.21$ atm), (*2*) high-pressure membrane side contacts with steam containing 0.1% hydrogen ($p_{O_2} = 2 \times 10^{-10}$ atm).

Estimates made from expression (8) for the 1 mm-thick $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ membrane at 900 °C with a H_2O + 0.1% H_2 mixture at the cathodic side demonstrated (curve *2* in Fig. 13) that the density of the oxygen flux through the membrane can be up to ~1.5 ml cm^{-2} min^{-1}, this corresponds to production of ~3 ml cm^{-2} min^{-1} of hydrogen.

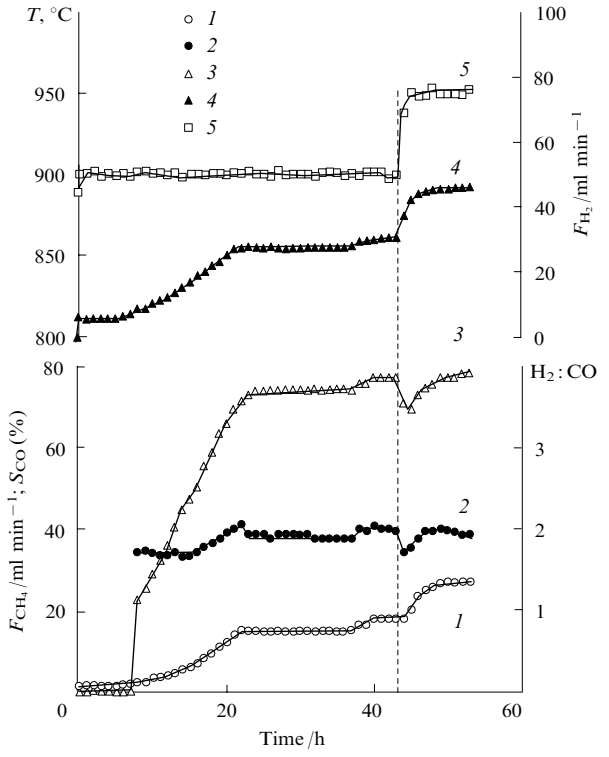


Figure 13. Experimental process parameters of hydrogen production by reduction of steam with methane with the use of a $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ ceramic membrane of 1 mm thickness.
(*1*) F_{CH_4}; (*2*) H_2 : CO; (*3*) S_{CO}; (*4*) F_{H_2}; (*5*) T, °C. The effective membrane area is 12.5 cm^2; F_{H_2} is hydrogen flux.

The results obtained with the use of a tubular membrane (Fig. 13) are in good agreement with the estimates, *viz.*, hydrogen flux per cm^2 of the membrane surface at 900 °C is 2.2 ml min^{-1}. With increasing temperature of the membrane to 950 °C, this value increases up to 3.6 ml min^{-1}. This result corresponds to the data obtained earlier [104] when hydrogen flux of $\sim$3.5 ml cm^{-2} min^{-1} was obtained with the use of a capillary membrane and nickel catalyst at 950 °C. These experiments indicated that the oxygen membranes of oxides with mixed conductivity can be successfully applied not only to production of synthesis gas, but also to preparation of hydrogen.

A $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ membrane with the CO_2 side coated with platinum was used.[105] The CO_2 conversion at 900 °C was $\sim$16%. No soot formation was observed.

The $BaZr_{0.9-x-y}Pt_{0.1}Co_xFe_yO_{3-\delta}$ membranes ($x = 0.5$ and 1) were used for reduction of nitrogen oxides [106, 107]

$$2\,x\,CH_4 + 2\,NO_x = 2\,x\,(CO + 2\,H_2) + N_2 \qquad (15)$$

The 90% conversion of methane with the 90% selectivity to CO was observed at 875 °C, while almost complete reduction of nitrogen occurred on the opposite side of the membrane.

VIII. Conclusion

Membranes with mixed oxygen ion and electronic conductivity can be used for oxygen enrichment of air, production of pure oxygen and hydrogen, partial oxidation of methane, oxidative dehydrogenation and coupling of hydrocarbons, conversion and recovery of nitrogen and carbon oxides. However, to use the MIEC membranes in practice, further studies are required aimed at the development of new materials most suitable for particular applications. For instance, materials for membranes which are used for oxygen production should ensure high oxygen fluxes, but it is not necessary that they be chemically stable under reductive conditions. The materials based on perovskite-like cobaltites are most interesting for these applications because they exhibit the highest permeability to oxygen among all known oxides. The progress in this field is related to the development of ceramic technologies for production of ultrathin asymmetric membranes, including those based on nanostructured materials.[108, 109]

Upon oxidative conversion of light hydrocarbons, for instance, of methane to synthesis gas, the membrane material should be chemically stable against action of methane and products of its oxidation. The materials composed of perovskite-like ferrites are most suitable for these purposes. The geometry of membranes plays an important role in the design of the corresponding membrane device. For example, capillary membranes can be sealed in the cold zone of the reactor, whereas the nozzles of tubular membranes and supporting fittings are at high temperature. This requires matching of the thermal expansion coefficients of the membrane, fittings and sealant materials. In addition, the sealant must be inert to the membrane material.

Development of more practically feasible catalysts has essential significance. Particularly, the problem of suppression of soot formation in the partial oxidation of methane has to be solved [110] along with the problem of designing reactors that would ensure equal oxygen fluxes from all membranes in the reactor assembly and steady yield of synthesis gas from each unit volume of the catalyst.

The available results on ceramic membranes with mixed conductivity indicate that they have good potential for industrial applications as a basis for development of compact, cost effective and environmentally safe processes for processing of natural gas.

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