High-Performance Ceramics

Ceramic Membranes for Gas Separation – Recent Developments and State of the Art


1 The need for gas separation in industry

The need for hydrogen will increase dramatically in the coming years due to the increasing demand for it as a raw material for the chemical industry, and for clean fuels in cars and home heating.

In the coming decade hydrogen will be produced mainly as a spin-off from chemical processes and by the reforming of fossil fuels.

The problem of hydrogen production in chemical processes and from fossil fuels is that the hydrogen is mixed with large quantities of non-desired components such as light hydrocarbons, CO and CO₂. These components are currently separated by cooling followed by condensation of the heavier components or selective adsorption and desorption (PSA, pressure swing adsorption). Both processes produce relatively impure hydrogen at very high costs.

Depending on the application, chemical processes need high-purity or at least moderately pure hydrogen.

The purification or separation of hydrogen from industrial gases by means of membrane technology serves several purposes, including the improvement of existing processes and cheaper production of pure hydrogen. One industrial application is the separation of hydrogen out of a gas stream from an ethane and naphtha cracker. In this pre-purified stream, all the saturated and unsaturated hydrocarbons are present from C1 up to approx. C6. Several products are separated by compression followed by stepwise cooling down in order to condensate the separate product groups. The cooling temperature necessary to condense products is reduced by the presence of the non-condensable hydrogen. By removing hydrogen completely or partly, the different condensation levels will increase considerably; hence less compression energy is needed for the cooling machines and/or the production capacity can be significantly increased.

Depending on its purity, the separated hydrogen can then be used for several hydrogenation reactions. The surplus can be sold as clean fuel. Naphtha crackers produce raw materials for commonly used plastics such as ethylene, propylene, butadiene and styrene.

The worldwide hydrogen production from ethane and naphtha crackers is approx. 2,400,000 t/a. If 50% of the hydrogen can be separated using hydrogen separating membranes, 1,200,000 t/a will be retrieved.

2 Ceramic membranes for gas separation

In the past decade, intense research efforts have been made in the development and improvement of inorganic membranes for use in separations that are difficult to achieve by conventional polymer membranes, i.e. high-temperature separations and separations of aggressive media.

Membranes are basically barriers allowing some species to pass while blocking others. They must combine several structural and functional properties. Desirable properties typically include a combination of high permeation rate and species selectivity, sufficiently mechanical, chemical and thermal stability under the applied operating conditions, a low fouling rate, long and reliable service life and cost effective production. In general it is quite difficult for one single material to satisfy all these requirements.

An important consideration in designing gas separation membranes is the thickness of the membrane itself, since the permeation rate is maximised when the thickness is minimised. Additionally during its performance the membrane must withstand the pressure drop in combination with aggressive reagents and/or high temperatures. For (high-temperature) gas separation applications, two types of inorganic membranes are suitable: microporous and dense membranes.

2.1 Microporous inorganic membranes

These membranes, with pore sizes smaller than 2 nm, are composed mainly of either amor-
phous silica, carbon or zeolites. A microporous ceramic membrane system generally consists of a macroporous ceramic support, some ceramic intermediate layers, and eventually a highly selective top layer. The support provides mechanical strength to the system. The intermediate layers bridge the gap between the large pores of the support and the small pores of the top layer. The top layer has separating capacities. Membrane properties such as permeation and selectivity depend on the microstructures of the membrane/support composites such as pore size and distribution, porosity and the affinity between permeating species and the pores walls. Separation of a gas mixture can take place based on differences in molecular mass, size or shape, or on differences in the affinity of the gas molecules to the membrane material. An increase in selectivity is generally at the expense of a decrease in membrane permeation, due to decreasing not only the pore size but also the overall porosity of the membrane. The best answer to permeation/selectivity optimisation would be to synthesize very thin layers of materials with high porosity and with pore sizes in the range of 0.3–0.8 nm so as to achieve molecular sieving effects.

The most widely studied application is the purification of hydrogen, or the selective removal of hydrogen from gas mixtures or from the reaction products of a chemical reaction. Dehydrogenations have been the most widely studied reactions in this field. The small molecule size of hydrogen compared to that of hydrocarbons to be dehydrogenated allows high selectivities for these microporous membranes.

### 2.2 Dense inorganic membranes

These membranes are prepared as unsupported ones as well as thin films on porous supports. They are made of polycrystalline ceramic material, in particular perovskites, or metal (palladium), which allows specific gas species to permeate the dense material. Depending on the nature of the dense membrane material, hydrogen selectively permeates in atomic (Pd alloys), molecular (dense SiO₂) or protonic (proton-conductive solid electrolytes) form.

Both hydrogen and oxygen can permeate selectively through various types of dense membranes. Dense membranes are impermeable to all gases except for a very limited number of gases that can permeate the material (i.e. H₂ through Pd) or can be incorporated into the structure of the membrane and transported through the material (i.e. O₂ through perovskites).

### 3 State of the art and developments worldwide

In this section the state of the art and developments in microporous (silica, carbon, zeolite) and dense inorganic membranes for gas separation are discussed in further detail.

#### 3.1 Amorphous silica membranes

Amorphous silica membranes are produced by sol-gel techniques. The micropore structure of the silica layers is determined by both the reactivity and the size of the precursors. Microporous silica membranes prepared by sol-gel processing and consisting of a three-layer system, i.e. a support prepared from α-alumina powder, γ-alumina intermediate layer, and a molecular sieving silica top layer, have been described by Benes [1]. The surface polarity of the sol-gel materials can be controlled by co-condensation of MeSi(OR)₃ with Si(OR)₄. Microporous silica membranes (Fig. 1) have a high potential for gas separation and pervaporation at high-temperatures in chemically aggressive environments. Such membranes are of particular interest for high-temperature industrial hydrogen separation and purification.

In recent years ultra thin microporous silica membranes have been prepared and they offer significantly improved gas permeation compared with earlier types [1–4]. Such membranes can separate H₂ from N₂ with an H₂/N₂ selectivity of up to ~100 and a permeation of the order of 1 × 10⁻⁶ mol/m²·Pa·s at 400 °C. A major challenge is to increase the stability of the silica layer towards hot steam. In this respect the development of hydrophobic silica membranes is considered to be of interest. Preliminary studies have shown that hydrophobic membranes are much easier to handle and show less deactivation than hydrophilic materials [5]. Alumina (3%), zirconia (10–70 mol %) or titania may be added to silica to increase the stability of the composite in high humidity environments [3].

#### 3.2 Carbon membranes

Carbon membranes are produced by pyrolysis (carbonisation at 500–900 °C) of polymeric precursor films (e.g. polyimide, polyfur-furyl alcohol, polyvinylidene chloride or phenolic resin) on a macroporous carbon substrate [6] or an alumina support tube. Alternatively, carbon membranes are produced by CVD of methane at 1000 °C on multi-layered porous ceramic tubes [3, 7–10]. Carbon membranes prepared by the carbonisation of a phenolic resin film have been transformed into adsorption-selective carbon membranes by an additional short time air oxidation prior to or after carbonisation. In this way the separation properties of carbon membranes towards multi-component mixtures of hydrocarbons with and without N₂ can be tailored [11, 12]. The predominant transport mechanism of most carbon membranes is molecular sieving. Hollow fibre carbon molecular sieve membranes have been made via pyrolytic carbonisation of organic polymers [13]. Mixed carbon-silica membranes with excellent gas separation properties have been prepared by the pyrolys-sis of imide-siloxane co-polymers at 600, 800, and 1000 °C [14]. Microporous carbon membranes are classified into activated carbons with pore size 0.8–2 nm and ultra microporous carbons or carbon molecular sieves with pores 0.3–0.6 nm [15]. The thermal stability of the carbon membrane depends on the nature of the contact gas, as can be seen in Table 1.

<table>
<thead>
<tr>
<th>Gas</th>
<th>He</th>
<th>H₂</th>
<th>CH₄</th>
<th>CO₂</th>
<th>O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum operating temperature / °C</td>
<td>700</td>
<td>&gt;500</td>
<td>500</td>
<td>400</td>
<td>&lt;200</td>
</tr>
</tbody>
</table>

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**Table 1 • Thermal stability of carbon membranes in different media**

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**Fig. 1 • Microporous silica top layer applied to a hollow fibre ceramic substrate with intermediate ceramic layers. This silica hollow fibre membrane is manufactured at CEPA**
At present the most important large scale application of carbon membranes is in the production of low cost and high purity N₂ from air, although they are also used for the separation of other mixtures, i.e. H₂ from gasification gas, purification of CH₄, etc. [6] (Fig. 2).

3.3 Zeolite membranes

Zeolite membranes are generally formed on porous supports by hydrothermal synthesis. The pores in zeolite membranes are part of the crystal structure and, hence, have uniform dimensions. The size of the micropores, with molecular dimensions generally less than 1 nm, can be varied by the crystal structure. Zeolites can separate molecules based on size, shape, polarity and degree of unsaturation, amongst other things. Many zeolites are thermally stable above 500 °C. Some are stable in alkaline environments and some are stable in acidic media. Numerous available materials have been reported as support material, such as steel-wool sintered steel composites and porous alumina supports. In the production of zeolite membranes, the ability to prepare reproducibly very thin (<1.5 µm) and oriented zeolite layers with an almost complete absence of defects, as well as sufficient mechanical strength, has still to be reached. Elimination of small defects can be achieved by CVD. Major steps forward still have to be taken to render these highly selective porous membranes reliable and cheap enough to be produced on an industrial scale.

Zeolite membranes offer good separation properties for gas molecules. At low temperatures the permeation rate increases with molecular weight, being essentially zero for H₂. At high temperatures (about 500 °C), however, the trend is reversed, and permeation decreases with increasing molecular weight. At high temperatures the permeation rate for H₂ is higher than for hydrocarbons, making the membrane particularly useful for H₂ separation, e.g. in dehydrogenation reactions.

The majority of zeolite membranes are of an MFI zeolite-type and show a CO₂/N₂ selectivity of the order of 10, CO₂ permeations being around 10⁻⁷ mol/m²·Pa·s in the temperature range of 30–150 °C. With a potassium-ion exchanged Y-type zeolite, a CO₂/N₂ selectivity of the order of 30, with CO₂ permeations being around 10⁻⁶ mol/m²·Pa·s, has been achieved [16].

3.4 Dense membranes for hydrogen separation

- Palladium thin films are known to selectively transmit hydrogen via an adsorption–desorption mechanism. A variety of methods, such as electroleo plating, chemical vapour deposition (CVD), sputtering and spray pyrolysis, have been applied to prepare palladium membranes for hydrogen separation by depositing a palladium film with a thickness of several microns on a porous ceramic support. Dense palladium membranes are obtained as a result of pore plugging by pyrolysis of a palladium precursor in the macropores of a ceramic support. Permeabilities to hydrogen as high as 10⁻⁶ mol/m²·Pa·s at a H₂/N₂ permselectivity higher than 10,000 have been achieved [16]. Palladium membrane reactors that are resistant to high temperatures (300–600 °C) are used for the production of hydrogen from methanol and methane reforming reactions. γ-Al₂O₃ membranes modified by the deposition of metals such as Ru, Pd, Rh, and Pt possess hydrogen separation values that exceed the limitations of Knudsen diffusion.

- Mixed proton- and electron-conducting materials consisting of barium cerate doped with rare-earth ions, that is BaCeₓ₁₋ₓδMₓO₃₊δ, where M = Nd³⁺, La³⁺, Y³⁺ or Gd³⁺, have been intensively studied and have been found to be of potential interest for hydrogen separation [17]. When exposed to water vapour, the oxygen vacancies in BaCeₓ₁₋ₓδMₓO₃₊δ are occupied by water to create mobile protons and thereby proton conductivity in these materials. Research into H₂ separation membranes is being conducted within the framework of the DOE Vision 21 Program [18] aiming at a hydrogen separation rate > 10 ml/min · cm² (74 × 10⁻⁸ mol/m² · Pa · s at 1 bar pressure difference) in thin films (100–300 µm) of perovskites. Proton-conducting materials are expected to be of great interest for the realization of a hydrogen-driven economy in the not too distant future.

- Dense silica membranes are produced by CVI/CVD (chemical vapour infiltration/deposition) techniques. CVI/CVD silica membranes are produced by reaction of a gaseous silica precursor such as tetraethoxysilane, Si(OEt)₄ with an oxidising agent in the pores and/or on the surface of a macroporous alumina layer such as an α-alumina layer or a γ-alumina layer deposited on an α-alumina support by a sol-gel process. CVI silica membranes have very high permselectivities towards hydrogen, however combined with a relatively low permeation rate. Higher hydrogen permeation can be achieved, though at the expense of selectivity [19]. Silica membranes formed by CVD were both H₂ and H₂O selective depending on preparation procedure and post-treatments conditions [16].

3.5 Dense membranes for oxygen separation

Dense membranes that conduct only oxygen ions by the motion of oxygen vacancies through the oxygen lattice offer very promising technological and commercial opportunities for oxygen separation applications [17, 20–22]. Membrane materials are based on fluorite (AO₂) and perovskite (ABO₃) related structures, which are able to transport oxygen ions and/or on the surface of a macroporous material or a coating of a different material. In general high operating temperatures (>800–1000 °C) are required to obtain an adequate oxygen flux. At present, there is a great deal of interest in developing new materials that have higher oxygen permeability at lower temperatures (600–800 °C).

Ceramic ion conducting membranes (CICM) with high ionic oxygen conduction at intermediate temperatures, and exhibiting high chemical and thermal stability, are under investigation. New membrane materials with markedly high-
er permeation rates, amongst other things, are based on LaCaCoFe₂₋ₓZrxO₃-δ and SrCaCo₀.4Fe₀.6₋ₓZrxO₃-δ. Zr doping in perovskites as in BaCo₀.4Fe₀.6₋ₓZrxO₃ had a great effect on oxygen permeation flow, with reports of e.g. a flow of 0.90 ml/cm² · min (7 × 10⁻⁸ mol/m² · Pa · s at 1 bar pressure) at 950 °C and long-term operational stability at 800 °C [23]. Worldwide there are high expectations for large-scale commercial applications of dense ceramic oxygen transport membranes for oxygen separation in a variety of industrial processes. Large development projects involving a variety of industrial companies, universities and research institutes are in progress. The potential for applications of dense ceramic oxygen transport membranes is enormous, e.g. in oxygen pumps, oxygen generators, solid oxide fuel cells, and catalytic membrane reactors. Demonstrators and prototype plants are being developed [20–21, 24]. In the USA, Air Products and Chemicals together with the DOE (US Department of Energy), Ceramatec and other partners are actively engaged in developing, upscaling and commercialising ion-conducting membrane technology for oxygen separation and syngas production [24]. An overview of several gas transport results obtained with microporous inorganic membranes is shown in Table 2.

### 4 Patent status on gas separation by ceramic membranes

A patent search was conducted to determine the most important (review) papers and to determine the key players in the field of gas separation by ceramic membranes. The CAPLUS and MEDLINE databases were consulted, resulting in a total of 5964 references (both patents and open literature publications) on the concepts 'ceramic membranes' or 'inorganic membranes'. A total of 1480 references remained after selecting only the patents and rejecting the open literature publications. Of these 1480 patents, a total of 595 were published in 1999 or later; i.e. 40 % of the patents on ceramic membranes have been published in the last five years. Of these 1480 references, 238 patents remained when including the term ‘gas separation’. Of these 238 patents, 114 patents (48 %) were published between 1999 and now.

According to this patent search, Creavis, Praxair Technology, Kyocera, and Sumitomo Electrical Industries are the main players in the field. Other gas producing companies are also key players in the field. The exact status of their interest and efforts being undertaken to develop pilot plant systems is not known.

### 5 Concluding remarks on the worldwide state of the art and developments

The world market for membranes in 2003 was estimated to be 8 billion US $, of which inorganic membranes make up approx. 7 % (0.6 billion US $). The expected annual growth rate for inorganic membranes is high (14 %), while the expected annual growth rate for organic membranes is just below 8 % [25]. A huge number of patents for inorganic membrane modules and reactor manufacturing have been filed all over the world, which suggests that commercialisation of new types of inorganic membranes with improved performances may only be a few years away.

### Table 2: Gas transport results obtained with different types of microporous and dense inorganic membranes

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Perselectivity</th>
<th>H₂ permeation / mol/m² · Pa · s</th>
<th>T / °C</th>
<th>α (mixture)</th>
<th>Area / cm²</th>
<th>Key players</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microporous silica</td>
<td>561 (H₂/CH₄) 844 (H₂/CH₄) 10-400 (H₂/D₂) 188 (He/CH₄) 125 (He/N₂)</td>
<td>185 × 10⁻⁸ 73 × 10⁻⁸ 10⁻⁷-10⁻⁸ (H₂/O) 75 × 10⁻⁸ (He)</td>
<td>200 25 &lt;150 145 145</td>
<td>321 (H₂/CH₄) 7 14 14</td>
<td>2 [16] CEPA-ration</td>
<td></td>
</tr>
<tr>
<td>Zeolite</td>
<td>330 × 10⁻⁸ 27</td>
<td>10-4</td>
<td>10 (He/N₂) 27 (He/N₂) 4.4</td>
<td>6 [16]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microporous carbon</td>
<td>31 (He/N₂) 127 (He/N₂)</td>
<td>0.31 × 10⁻⁸ 0.27 × 10⁻⁸</td>
<td>150 25</td>
<td>10 (He/N₂) 27 (He/N₂)</td>
<td>16 [16]</td>
<td></td>
</tr>
<tr>
<td>Perovskite (H⁺)</td>
<td>16 × 10⁻⁸</td>
<td>950</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd (supported)</td>
<td>1 × 10⁻⁸ 100 × 10⁻⁸</td>
<td>300 10000 (H₂/N₂) 10000 (H₂/N₂)</td>
<td></td>
<td></td>
<td>[16]</td>
<td></td>
</tr>
</tbody>
</table>

The fundamental problem to be solved is how to develop technologies capable of producing, at relatively low costs, very thin membranes with large surface-volume ratios. Results should be achieved not only on a lab scale but should also be reproducible on an industrial scale. Such membranes should not be unacceptably expensive in either their initial or replacement costs. The following main aspects and limitations were found for the different types of membranes investigated:

- Microporous silica membranes: high hydrogen permeation (increasing with temperature) and moderate to high selectivities. Stability at high temperatures in steam-containing atmosphere may be an issue.
- Zeolite membranes: low hydrogen permeation, especially at room temperature. Zeolite membranes may deteriorate in steam-containing atmospheres at temperatures higher than originally used in the synthesis of these membranes.
- Carbon membranes: low hydrogen permeation, not stable in oxygen-containing atmospheres above 200 °C. Furthermore they are prone to becoming progressively plugged by the adsorption of organic contaminants [15].
- Dense palladium membranes: low hydrogen permeation combined with very high selectivities, lack of stability. Palladium membranes may suffer from hydrogen embrittlement at temperatures below 295 °C and membrane failure from exposure to reactive gases such as chlorine, sulphur and olefins. Alloying and multi-layer structures have been reported to be effective in overcoming these disadvantages, albeit with the drawback of high production costs.
- Dense perovskite membranes: not commercially available yet, possibly due to stability problems.

In this respect, microporous silica membranes with their high hydrogen permeation values combined with moderate to high selectivities seem the best choice as membranes for gas separation, especially hydrogen from a mixture of hydrocarbons. They can operate both at room temperature and high temperatures and are commercially available (mainly for pervaporation applications). One aspect to be improved with these membranes is the high temperature vulnerability to steam-containing atmospheres. Several scenarios exist to overcome this stability problem.
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6 State of the art and developments at CEPAration

CEPAration is a company that commercialises proprietary (4 patents, 6 patents pending) ceramic hollow fibre membrane and module technology, and develops and produces membranes for hydrogen separation. Keywords for the products of CEPAration are compactness, low cost and durability. Figures 3–4 show the present products of CEPAration. The epoxy potted (blue coloured) products are used for microfiltration to nanofiltration applications, e.g. beverage clarification, cold sterilisation of dairy products, life science applications and waste water treatments, whereas the ceramic potted modules can be used among other things for high-temperature gas separations such as the gaining of hydrogen from process streams. The largest epoxy potted modules comprise a surface area of 5 m². Current ceramic potted modules have a surface area of 0.05 m². Scaling up of this technology for much larger surface areas is in progress. CEPAration operates worldwide. Natural partners for CEPAration are systems engineering companies for specific applications and markets. An example of such a company is Alstom, which designs, builds, sells and services systems for end-user companies such as chemical and petrochemical companies, steelworks, municipalities, breweries, wineries and dairy companies. All the membrane systems manufactured by CEPAration consist of a ceramic hollow fibre support coated with several different intermediate layers and a separating top layer. The support is an alumina hollow fibre with large pores produced by spinning/extrusion. The intermediate layers are sequentially applied onto this support by dip coating into an alumina suspension or sol followed by heat treatment. A silica top layer is applied onto the final intermediate layer by dip coating into a silica precursor followed by heat treatment. Previously manufactured silica hollow fibre membranes with the selective top layer at the outside of the hollow fibre were characterized by single gas permeation. Temperature was found to have a positive influence on helium permeation, indicating microporous transport behaviour in the membrane. For other gases (N₂, CO₂, CH₄) hardly any temperature influence on the permeation was observed. The permeation values for nitrogen and methane were low compared with helium, with values of 6 × 10⁻⁹ mol/m²·Pa·s (N₂) and 4 × 10⁻⁹ mol/m²·Pa·s (CH₄). He/N₂ and He/CH₄ permselectivities were far beyond the Knudsen value, with values at 145 °C of 125 and 188 respectively. At CEPAration, silica coatings are currently being applied to the inside of the hollow fibres which are made into full ceramic membrane modules suitable for applications at high temperatures and pressures. This technology can be scaled up to large membrane area modules needed for gaining of hydrogen from process streams on an industrial scale.

7 Evaluation and further prospects

The most important inorganic membranes for hydrogen separation are based on three types, either microporous silica, zeolite or microporous carbon type. Of these three, silica-based membranes seem to be the most promising for hydrogen separation at elevated temperatures, although the steam/water stability of these membranes may be an issue. Zeolite-type membranes have low hydrogen permeability which increases with temperature, while microporous carbon is not stable in oxygen-containing atmosphere above 200 °C, and at present it still has relatively low permeability for hydrogen due to the thickness of the membrane layers. Pd membranes have long been well known for their high hydrogen selectivity but they have low fluxes and seem to lack stability and hence durability. No breakthrough for large-scale industrial applications has been achieved and it may possibly no longer be expected. Recently dense proton conducting membranes based on perovskite materials have been developed and studied in a large DOE programme for hydrogen technology; This may be an important new type of membrane, although as yet it seems far from the commercialisation stage. An important issue in large scale industrial applications of any type of gas separation membrane is the support onto which the membrane is to be applied. Basically this will be of a ceramic nature and it can be either flat, tubular, multi-hole or the capillary/hollow fibre type. As far as cost and compactness are concerned, the hollow fibre geometry as developed and patented by CEPAration scores high, especially when cheap all-ceramic modules consisting of a large number of ceramic hollow fibre membranes can be produced. The additional expertise of systems engineering companies with a long tradition in designing and building high-temperature and high-pressure equipment for (petro)chemical companies is called for before these all-ceramic modules can be assembled and applied on a large scale in stainless steel systems for high-temperature and high-pressure applications.

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References


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