

# Inorganic membranes for harsh conditions - viewpoints on materials issues

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Inorganic membranes have for many years been used in MF and UF applications. Despite large efforts of research and development the introduction of inorganic membranes in other areas as NF, pervaporation and gas separation has been very modest. Evidently, important hurdles exist that must be identified and overcome. In the presentation this feature is discussed looking at limitations of current membrane materials. Relevant membranes for gas and liquid applications are used as examples to elucidate degradation mechanisms originating from insufficient chemical, thermal and mechanical materials properties. These include C, zeolite, SiO<sub>2</sub>, Pd-based and mixed ion and electron conducting membrane materials. Also shortcomings of existing membrane support materials are pointed out. In conclusion it is necessary in further work to: i) Develop new membrane materials that have better stability than current ones. ii) Improve the membrane preparation methods so that the materials properties are optimized. iii) Improve the quality of existing and/or develop new supports designed for specific membranes and applications. iv) Improve the understanding about mechanisms leading to slow membrane degradation under severe conditions.

Key words: Inorganic membranes, harsh conditions, gas separation, liquid applications, materials issues

## 1. INTRODUCTION

It is often argued that inorganic membranes have favourable properties compared to polymeric types under harsh operating conditions (high or low temperature, high pressure, chemically aggressive environment, etc). Generally, this is correct as inorganic materials normally can tolerate higher temperature-pressure combinations and are less susceptible to chemical degradation. It should, however, also be made clear that after many years of research and development, some significant challenges still exist that need to be solved before a broad expansion of inorganic membrane technology can be foreseen in many important areas.

Within each area (commonly divided into MF, UF, NF, RO, Pervaporation, Gas separation, CMR, etc...) many applications exist that force strong demands on the membrane properties. Development of membranes that perform sufficiently well in a large variety of applications has proved difficult and is one of the main hurdles for easy expansion of (inorganic) membrane technology. Such process dependency implies tailor-making of membrane-process combinations, which add to cost, but also requires high competence of personnel both on the producer/supplier side and the user side. Besides costs related to process adaptation, other cost driving factors are related to performance (life time, flux and separation characteristics) and membrane production technology (incl. sealing and modules). These factors strongly depend on the properties of membrane materials, which is the main issue of this presentation.

When considering all the research and development continuously reported in the field of inorganic membranes, materials issues are widely discussed and the subject is too large to be covered by any single person. Instead the author's ambition is to draw some general lines to illustrate why current applications are limited to a fairly narrow window of operating conditions. This will be done by use of examples from the literature and from research where SINTEF is involved.

## 2. GAS SEPARATION

Except a very limited use of metal and carbon membranes, inorganic membranes have not made any important commercial impact in gas separation technology. Development of mesoporous inorganic membranes for gas separation started already in the 1940s as a means to separate UF<sub>6</sub> uranium isotopes based on Knudsen diffusion<sup>1</sup>. From this extensive non-commercial activity, where several millions square meter membrane surface area were produced, production technology came out that later were used for production of MF and UF membranes. Also dense metal membranes, particularly Pd-based, have for several decades been subject to numerous gas separation studies. However, it is only during the last 20-25 years that real progress has been made towards technology that could result in broader commercial use in gas separation. This development, driven by the cost effective potential of membrane technology, is due to the discovery of new materials and more advanced production methods. In Table I the most common membrane types for gas separation and some relevant properties are summarized.

### 2.1 Separation and transport

Before discussing properties of inorganic gas separation membranes it is useful to shortly repeat how mass transport and separation are accomplished. Gas separation can be obtained in porous membranes when Knudsen diffusion transport, size exclusion or specific surface adsorption and diffusion occur. Simple Knudsen diffusion will only give a separation factor for molecules 1 and 2 close to  $(M_1/M_2)^{0.5}$ , where M<sub>1</sub> and M<sub>2</sub> are molecule weights. When the pore size approaches the kinetic diameter of the molecules,

Table I. Most common inorganic membrane types and some selected properties.

Type/ material	T range °C	Permeate/ comment	ref.
Mesoporous/	< 1000	Knudsen separation, low	

Many oxides		selectivity	
Microporous/ C, Zeolite	< 500	CO <sub>2</sub> , H <sub>2</sub> , N <sub>2</sub> , NH <sub>3</sub> , hydrocarbons/ Strong adsorption effects at low Temp. Limited selectivity at high Temp. H <sub>2</sub> / based on size excl.	2-4
SiO <sub>2</sub>	200-500	H <sub>2</sub> / based on size excl.	4
Si-O-C, SiC	200-500	H <sub>2</sub> /Surface and bulk	5,6
Noble metals	200-500	transport	7
Dense/ Pd/Pd-alloys, Trans. met. Gr, IV, V	200-500 200-500	H <sub>2</sub> H <sub>2</sub>	8,9 10
Dense/ Perovskite related	700-1000	O <sub>2</sub> /MIEC	11
Fluorite related	700-1000	O <sub>2</sub> /Mainly electrolytes	12
Bismuth based	400-800	O <sub>2</sub> /Electrolyte+electr. conducting phases	13
Dual phase	400-1000		14
Dense Perovskites+ Various oxides	600-1000 600-	H <sub>2</sub> /Mainly proton conductors	15
Dual phase	1000	H <sub>2</sub> /Electrolyte+electr. conducting phases	16

simple Knudsen diffusion will no longer occur due to strong interaction with the pore structure. In this case the importance of the molecule kinetic diameter on diffusion becomes more pronounced, i.e. smaller molecules diffuse faster than larger, and one may also observe that the permeance increases with temperature, contrary to what is expected for Knudsen diffusion. When the pore neck becomes smaller than the kinetic diameter of the larger molecules the flow path through the membrane is closed for these and selectivity is based on size exclusion. Obviously, a gliding transition from Knudsen diffusion dominance to size exclusion exists, depending on, besides the pore size, also on temperature, pressure and gas composition. The importance of the molecule-surface interaction is enhanced when strong surface adsorption occurs. In this case the selectivity is closely linked to the adsorption capability of the different molecules; the membrane normally being selective to the component with highest surface coverage. Separation is in this case supposed to occur by pore blocking and migration of adsorbed molecules. In dense inorganic membranes, transport will only occur for components that can dissolve at the feed side, diffuse in the membrane layer and evolve at the permeate side. The dissolution/evolution processes at the surfaces involve a change between gas molecules and species that are transported in the matrix. The total mass transport is therefore dependent on two different surface processes and bulk diffusion. The bulk diffusion may take place by activated movement along interstitial or empty lattice positions and grain boundaries depending on the material. Typical dense inorganic membranes for gas separation constitute metal membranes for hydrogen separation and mixed conductor membranes for

hydrogen and oxygen separation. Some of the best oxide ion conductors have low electronic conduction. This could limit the flux as this parameter depends on the ambipolar conductivity, which is proportional to the product of the ionic and electronic conductivities. Mixed conduction can also be accomplished by mixing of two phases, an electrolyte and an electron conducting phase, in so-called dual phase materials.

Inorganic membranes for gas separation may be divided in two groups, i) those for low temperature applications where the performance is dominated by selective adsorption effects, ii) those for high temperature applications where separation is determined by other mechanisms. The first type is by large an extension of the polymeric membrane development, and will mainly compete in the same market. The second type represents a field of new possibilities.

## 2.2 Carbon and zeolite membranes – adsorption dominated separation

The most commonly studied membrane materials based on adsorption dominated separation are microporous carbon and zeolite types. Carbon membranes are made by pyrolysis of polymers, thus offering the possibility of flexible shaping and compact module design. By control of the pyrolysis process the pore size can be tailor-made for various applications. A severe limitation to exploitation is the inherent brittleness of carbon material, but also the relatively low permeance (though high surface area can compensate this) and variable selectivity. The advantageous chemical inertness of C-membranes is counteracted by the very strong adsorption dependency of the performance. For instance traces of oxygen may change surface properties from organophilic to hydrophilic<sup>17</sup>. Pore blocking due to water vapor or organics is one particular troublesome example of adverse adsorption effects<sup>18</sup>. Control of surface properties is therefore essential and a key issue in further development. In high temperature gas separation, C-membranes may offer some advantages with respect to stability in non-oxidising gas atmosphere up to temperatures of 500-700 °C, however, selectivity appears determined by Knudsen diffusion limiting practical applications<sup>19</sup>.

As C-membranes, zeolite membranes also show good chemical and thermal resistance. The many different zeolite structures showing a variety of well defined pore sizes imply great possibilities for zeolite membranes. Zeolites have strong adsorption ability and the membrane selectivity is very dependent on ambient gas composition, temperature and pressure. As for C-membranes, tailor-making of membrane-process combinations is very important. Compared to other membrane types, zeolite membranes have some unique possibilities in isomer separation due the uniform pore size. Today, zeolite membranes can be made with a thickness down to about 1 μm<sup>20</sup>. For improving flux and reducing stress in thermal cycling, thinner membranes would be very desirable. Moreover, further development of membrane synthesis is expected to give better and oriented zeolite layers with fewer defects and diffusion barriers between crystals. Compared to silica

membranes (see below) zeolite membranes typically have 5-10 times lower hydrogen permeance despite somewhat larger pore sizes<sup>3,4</sup>. When adsorption effects are low, selectivity is also fairly low, partly due to diffusion paths between grains, and zeolite membranes have less practical interest in such cases.

### 2.3 High temperature gas separation membranes

High temperature membrane separation offers new possibilities for efficient process integration that could give better heat management, lower energy consumption, higher transport, reaction rates and yields. An overwhelming amount of literature describing studies of high temperature membrane processes illustrates clearly the industrial importance and possible impact. Some examples are production of bulk chemical commodities as oxygen and hydrogen, dehydrogenations and hydrocarbon separations, methane partial oxidation, etc.

*SiO<sub>2</sub> membranes:* Amorphous SiO<sub>2</sub> is the only sol-gel type membrane material with a pore structure sufficiently small (3-3.5 Å) for hydrogen separation dominated by size exclusion. The transport of hydrogen and other gas species has been a subject of numerous studies reporting very different permeance (range ~ 0.1-10·10<sup>-7</sup> mol/m<sup>2</sup> s Pa) and selectivity (H<sub>2</sub>/N<sub>2</sub> ~ 10-10000) values. This probably reflects the difficulty in preparing thin (< 100 nm) defect-low membranes, and that several synthesis parameters are important for the final properties. More dense SiO<sub>2</sub> membranes can be prepared by CVD methods. These typically have higher selectivity, but on the expense of a significantly lower permeance.

Several studies have shown that in the presence of water vapour the permeance of SiO<sub>2</sub> membranes decrease with time (see e.g. ref 21) in the temperature range 400-600°. The effect of water vapour has even been reported at room temperature. A SiO<sub>2</sub> membrane in contact with air containing 60% relative humidity showed an order of magnitude reduction in permeance when measured at 300°C over a period of 200 days<sup>22</sup>. It was suggested that SiO<sub>2</sub> dissolves in the silica pore network filled with water at room temperature. When the membrane was heated up periodically for permeance measurements some high rate diffusion paths in the network were densified by the silica rearrangement. For applications in water containing atmospheres, pure SiO<sub>2</sub> membranes are therefore questionable. Also investigations of Si-O-C or SiC membranes have shown similar permeance decrease in contact with water vapour, which could indicate that densification at high temperature is related to similar mechanisms as for pure SiO<sub>2</sub>; i.e. densification by condensation of Si-OH terminal hydroxyl groups. Doping or mixing SiO<sub>2</sub> with more stable oxides to increase stability is a strategy that deserves further attention. It has been shown that improved stability could be obtained in composites of SiO<sub>2</sub>+ZrO<sub>2</sub> (ZrO<sub>2</sub> > 40 mol%), but these membranes had somewhat larger pore size<sup>22</sup>.

Silica membranes may undergo phase transitions to silicates and grain growth when poisoned by alkali elements. Such elements form volatile oxides and may be a problem in high temperature applications (alkali

elements are used in some catalysts, e.g. for steam reforming).

*Metal membranes for hydrogen separation:* Candidate metal membranes for hydrogen separation are found in the transition metal groups IV and V, in addition to Pd. The capability is due to a high hydrogen solubility and diffusivity. Unfortunately, the low activity for incorporation of hydrogen atoms, the high tendency to corrosion and the possibility of hydrogen embrittlement in relevant atmospheres, are major drawbacks of the cheaper membrane materials. To overcome these basic materials problems the use of a protective and catalytically active Pd-based layer has been a subject of many studies<sup>23</sup>. The resulting composite membrane structure can be compared to systems where various porous substrates are mechanically supporting a thin Pd-based membrane. Despite much effort over many years composite Pd-based membranes (supported either by dense or porous materials) have not reached broad industrial application. The main reason is the need for a fairly thick Pd-alloy layer. The layer is about 20 µm or more for commercially available membranes. A thickness reduction has a double effect on the total cost, i.e. flux enhancement and reduction of materials cost. Reducing thickness is therefore a main issue in the further development of Pd-based membranes.

A number of different materials issues should be addressed in the further membrane development: i) chemical stability towards gaseous reactants and support, ii) mechanical strength and microstructural stability to accommodate differences in thermal/chemical expansion, and pressure gradients, and iii) stability and permeability of the support.

i) Pd-based membranes are vulnerable to deactivation by components adsorbing on the membrane surface. Deactivation is due to blocking of H<sub>2</sub> adsorption sites and occurs readily in H<sub>2</sub>O, H<sub>2</sub>S (< approx. 20 ppm), CO, and other carbonaceous atmospheres at moderate temperatures (9). An active surface can be recovered by high temperature treatment in flowing H<sub>2</sub> or under light oxidizing atmosphere. Irreversible and detrimental poisoning occurs in corrosive environments containing sufficient amounts sulfur; chlorine, bromine, mercury or Zn vapour<sup>24</sup>. The tolerability towards irreversible poisoning depends on the membrane material. An interesting relationship between microstructure and resistance to sulfur poisoning has also been observed<sup>25</sup>. Since sulfur prefers adsorption at Pd-sites with high coordination number, as crystalline faces, nanocrystalline materials with a high number of grain boundary atoms of low coordination number are seemingly less prone to poisoning. Segregation of impurities and alloying elements can be significant in Pd-alloys, e.g. about 3 % in bulk may result in a ten-fold concentration of silver at the surface<sup>26</sup>. This feature can drastically affect the concentration of hydrogen-Pd-adsorption sites and may therefore also control permeability.

High temperature and pressure induce conditions for pronounced interdiffusion between membrane and support. For ceramic supports like alumina this problem is small, but it is relevant for most metal supports. In practice, the problem may be solved by

applying a material that acts as a diffusion barrier in the interface and by lowering the maximum operation temperature<sup>27</sup>.

ii) Development of thin membranes implies a nanocrystalline microstructure. Grain growth is commonly observed in such microstructures and should be reduced to a minimum to avoid detrimental effects on mechanical properties and membrane integrity. Another feature that needs further investigation is the optimization of the physical and chemical integration of membrane and support. It is sometimes claimed that that it is advantageous with good physical integration, e.g. with the membrane partly deposited into the pores of the support. This can be achieved by preparation methods such as electroless plating, electrodeposition and CVD. On the other hand, such strong integration will create high shear stress in the membrane-support interface as a result of hydrogen dissolution and differences in thermal expansion<sup>28</sup>. An analysis of the shear stress for a Pd-Ag/ceramic interface showed that failure occurs in membranes with thickness of 15  $\mu\text{m}$  and 9  $\mu\text{m}$  at 500 and 600 K, respectively<sup>29</sup>. This corresponded to a shear stress of 10 MPa, which was found to be the interface metal-ceramic strength in membranes prepared by electroless plating and sputtering. The generated interfacial stress is proportional to the membrane thickness, which further underlines the importance of being able to produce thin membranes without defects.

iii) In processes like steam reforming and water gas shift (WGS) a high membrane feed pressure is desirable (20-40 bars) in order to reduce reactor size. In these processes it may be desirable that the composite membrane can withstand a significant total pressure difference as well. Such requirement on the membrane-support system has implications also for the properties of the support. It is desirable to have a small flux resistance in the support, which in the case of porous substrates imply a compromise between high porosity and large pores, and at the same time sufficient mechanical strength. With current flow rates in thin Pd-based membranes ( $> 100 \text{ cm}^3/\text{cm}^2 \text{ min}^{10}$ ), it is clear that the permeance of the support is critical for the total permeance. In the further development towards commercialization of thin composite Pd-based membranes the support properties will need more attention than previously received.

*Dense membranes for oxygen and hydrogen separation:* Dense mixed ion and electron conducting (MIEC) membranes have been given much attention during the last 10 years. The MIEC technology has similarities with the Solid Oxide Fuel Cell (SOFC) technology, but represents a simpler case with respect to materials since electrodes and interconnects are not required. The perovskite related structures ( $\text{ABO}_3$ ,  $\text{A}_2\text{B}_2\text{O}_5$ ,  $\text{A}_4\text{B}_6\text{O}_{13}$ ,...) show a remarkable ability for hosting a large amount of mobile oxygen vacancies in the lattice. Typical elements on the A-site are Sr, Ba and La while Co, Fe, Ni, Mn, Cr, Cu, are typical B-site elements. Also some other classes of structures such as fluorite-related ( $\text{AO}_2$ ,  $\text{A}_2\text{O}_3$ ,  $\text{A}_2\text{B}_2\text{O}_7$ ), and Aurivillius-type ( $\text{Bi}_2\text{O}_2$ )<sup>2+</sup>( $\text{A}_{n-1}\text{MnO}_{3n+1}$ )<sup>2-</sup> have high oxygen conductivity. However, these generally show fairly low electronic conduction and behave more as electrolytes.

By appropriate doping the electronic conduction can be enhanced, but this will not be considered further in this presentation. A mixed conducting material can also be obtained by mixing an electrolyte and an electron conducting phase (dual phase membranes).

Perovskite based MIEC membranes for oxygen separation operate at temperatures above 800°C. The main applications studied have been air separation, partial oxidation of natural gas to synthesis gas and methane coupling. Air separation where both sides of the membrane are kept at non-reducing conditions imposes fewer requirements on membrane material stability compared to applications where one side is operating under very reducing conditions.

Several groups with significant industrial involvement are developing MIEC membranes and recently a group lead by Air Products and Chemicals announced a plan for commercialization around 2007<sup>30</sup>. Oxygen production, representing the milder operation condition, will probably be the first large scale gas separation process developed based on inorganic membrane. The impact on membrane research and development in general, and for the acceptance of inorganic membranes in gas separation in particular, should not be underestimated by successful introduction of this technology. Many technical and scientific issues that are relevant for other applications are dealt with in this development. These are, e.g. operation at high temperature under chemical gradients, sealing technology, module design, scale-up of membrane production and technology validation on pilot scale. In particular, the similar MIEC technology based on proton conductors for hydrogen production (see below) can be given a flying start as soon as a membrane material with appropriate properties has been established.

The high operation temperature of MIEC requires careful matching of thermal expansion coefficients and elimination of interdiffusion between support and membrane. This suggests the use of similar materials for support and membrane in an asymmetric membrane structure. Stress generation may also originate from chemical expansion/contraction of the lattice across the membrane due to a gradient in oxygen content. This problem is obviously more severe for large gradients. Another potential instability problem when operating under chemical gradients is related to the finite cation diffusion rates. Cations will move to the side of high oxygen partial pressure, which can if the rate is high enough, create a displacement of the membrane. An additional possibility in multicomponent materials is kinetic demixing due to differences in mobility of different cations. This phenomena has so far been given modest attention, but could be important for long term stability. It is important to notice that kinetic demixing is a kinetic effect only, and may lead to breakdown of thermodynamically stable phases. Other bulk related phenomena important in high temperature applications like grain growth, impurity segregation, defect and structural ordering, etc. should be controlled in order to maintain sufficient membrane lifetime.

The driving force for oxygen transport is used to transfer the oxygen via two surface reactions and bulk diffusion. For sufficiently thin membranes, the surface

kinetics may be rate limiting. The use of a catalyst may reduce this limitation, but may also introduce other material problems. Surface limitations will give a smaller oxygen gradient in the bulk, which is beneficial if stability problems as described above exist.

Current MIEC membrane materials are potentially prone to chemical attack by common pollutants. The stability of site A elements in the oxide phase towards impurities like SO<sub>x</sub>, H<sub>2</sub>S and SiO<sub>2</sub> (dust) is very limited. Surface reactions and formation of new stable phases (e.g. sulfates, sulfides or silicates) could have great impact on the oxygen transport. This feature, which has similarities to the discussion on Pd-based membranes, may also enhance segregation phenomena and be particularly harmful to surface reactions rates. CO<sub>2</sub> and H<sub>2</sub>O may potentially have the same effect at lower temperatures, e.g. during unexpected shut downs.

It should be mentioned that MIEC membranes are currently also developed for hydrogen separation. The most studied are also in this case perovskites, with larger transition or rare earth elements on the B-site (e.g. SrCeO<sub>3</sub>, BaZrO<sub>3</sub>). As for the oxygen membranes, doping with aliovalent elements is used to increase the ion conductivity. At present the most promising proton conductors have fairly low electronic conductivity. This limits the hydrogen flux since the transport rate is dependent on the ambipolar conductivity. Investigations have, however, shown that by addition of an electron conducting phase the hydrogen flux can reach values above 1 cm<sup>3</sup>/cm<sup>2</sup>min<sup>16</sup>. Mixing two phases may impose new materials stability problems, and this should be studied further.

### 3. LIQUID APPLICATIONS

Inorganic membranes are used in many liquid applications, particularly in MF and UF. At ambient temperatures many existing membranes have good chemical resistance. In the further presentation two applications close to 100°C will be discussed to illustrate some current limitations.

#### 3.1 Pervaporation

Inorganic membranes are commercially available for use in pervaporation<sup>31</sup>. The ability of inorganic membranes to dewater organic solutions is closely linked to the hydrophilic nature of the surface. Zeolite A-type membranes have been commercially available for some years, while silica membranes are currently entering the pervaporation market. Zeolite membranes appear to have lower flux, but also higher selectivity than silica membranes. Zeolite A-type has a high aluminium content and has limited stability in acidic solutions. Other zeolite membranes are therefore under development, which combines better stability with high flux and selectivity<sup>3</sup>.

Returning to the discussion about the silica membrane stability, a high temperature stability of silica pervaporation membranes has been claimed<sup>32</sup>. Evidence of limited stability has, however, been observed at temperatures of 120-140 °C<sup>33</sup>. Available SiO<sub>2</sub> membranes are, furthermore, supported on a mesoporous  $\gamma$ -alumina intermediate layer (pore radius 2.5-5 nm) that has very limited pH stability. During the last decade other mesoporous membranes, as TiO<sub>2</sub> and

ZrO<sub>2</sub> have been developed, which may work better as support for pervaporation membranes under harsh conditions. Microporous membranes of these materials have also been prepared, but the author is not aware of studies in the open literature employing such membranes in pervaporation.

#### 3.2 Ceramic membranes operating in acidic solutions

Using the sol-gel technique it has been possible to obtain small pore sizes in TiO<sub>2</sub> and ZrO<sub>2</sub> ranging from less than 1 nm to several nm. The larger pore size is formed at higher firing temperatures giving more crystalline and stable materials<sup>34</sup>. In studies of a wet air oxidation of formic acid at 80°C employing a catalytic contactor with TiO<sub>2</sub> mesoporous membranes containing Pt catalyst particles, it was observed that the catalyst was poisoned by alumina coming from the support containing  $\alpha$ -alumina (pore size 5  $\mu$ m)<sup>35</sup>. There was no evidence of dissolution of TiO<sub>2</sub> in the mesoporous layer (pore size 10 nm). This illustrates that despite a much lower surface area, dissolution of  $\alpha$ -alumina is more severe compared to TiO<sub>2</sub>. Also in other applications similar tendency has been observed. The membrane producer Pall has developed a product with a protective TiO<sub>2</sub> surface layer on  $\alpha$ -alumina supports to reduce the leaching problem.

### 4. REQUIRMENTS TO SUPPORT MATERIALS

In this presentation the stability of the support has not been discussed separately. All support materials such as stainless steel, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> are prone to degradation given certain conditions. When the support is built up by different layers, this is likely to lower the stability. As an example, it was found that the interface between  $\alpha$  and  $\gamma$ -alumina delaminated after 1 week exposure to a H<sub>2</sub>O/CH<sub>4</sub> = 3/1 mixture at 600°C and 30 bar pressure<sup>36</sup>. The reason was probably stress generation in the interface due to microstructural changes in the  $\gamma$ -alumina layer observed as a pore growth from 4.2 to 6.2 nm.

Many techniques have been described in the literature for preparation of inorganic membranes on supports. For ceramic membranes the sol-gel and slip casting methods have been very successful in production of membranes on extruded supports for liquid filtration. On the other hand, for gas separation sufficient membrane quality is very difficult to obtain by the same production techniques. A reason for this difficulty is the insufficient surface quality of supports produced by extrusion. Support development is therefore crucial for improving membrane quality further. This situation is not unique to thin sol-gel silica membranes, but also to other types. In general pinhole free, chemically well defined support surfaces are required. A sharp pore size distribution is also desirable for many membrane synthesis techniques (sol-gel, CVD, electroless plating, etc.). However, these requirements should not result in a high support resistance or impose limitations to efficient use of sweep gas.

### 5. CONCLUDING REMARKS

The rather limited commercial use of inorganic membranes under harsh conditions has been discussed

in terms of limiting factors by use of some relevant membrane examples. The huge variation in application specific demands requires robust membrane material solutions that to a large extent are missing today. Therefore, further research should most of all concentrate on fairly basic membrane materials development, as sufficient evidence of the great potentials of inorganic membrane technology has been established. However, it is evident that the cost and capacity requirement, which demands for thin supported membranes is one main reason for the current shortcomings. Further development of cost effective manufacturing methods that can provide reliable membranes with advanced structures is therefore of vital importance. Some other important issues that have not been treated are, furthermore, sealing technology and module design. Clearly, these subjects also require satisfactory solutions before membrane technology for harsh conditions can enter the market.

In conclusion it is necessary to:

1. Develop new membrane materials that have better stability than current ones
2. Improve the membrane preparation methods so that inherent materials properties are optimised
3. Improve the quality of existing and/or develop new supports designed for specific membranes and applications
4. Improve the understanding about mechanisms leading to slow membrane degradation under severe conditions.

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