

Nanostructures in sol–gel derived materials: application to the elaboration of nanofiltration membranes

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Abstract

Development of membranes resistant to heating and chemicals is expected for the separation of small molecules in biotechnologies, pharmaceuticals, chemical industries, water treatment and also in gas separation. When aiming at separation of small molecules (molar mass less than 1000) or multivalent ions, nanoscale pores or almost dense materials will be required. Pure inorganic materials as well as organic/inorganic polymers are very good candidates for preparing this new generation of membranes. The nanostructural organization of sol–gel derived materials means that the sieve concept developed for microfiltration (MF) and ultrafiltration (UF) membranes can be surpassed and an “intelligent membrane” concept can be recognized for nanofiltration membranes. In fact, specific interactions are expected between the nanophased membranes and solubilized species or gas molecules passing through the membrane. Provided that these interactions can be managed, an increase in membrane performances is obtained, with the possibility of developing new application fields. Examples are given showing the important role played by the basic properties of ceramics and organically modified ceramics in the production of tailored nanofiltration membranes.

1. Introduction

Among membrane technologies, considerable attention has been paid to inorganic membranes because of their inherent properties such as an enhanced resistance to high temperature and corrosive environments. A recent business opportunity report predicts a growing market for these membranes within the next ten years [1]. The major part of inorganic membrane development is based on ceramic materials. Microfiltration (MF) membranes are concerned with macropores while in ultrafiltration (UF) and nanofiltration membranes with connected mesopores and nanopores are required. In the last two cases sol–gel processing can advantageously be used to prepare thin porous layers active in ultra- and nanofiltration. The efficiency of an inorganic membrane depends on the basic properties of the final layer which must exhibit uniform pore size, high permeation rate and high mechanical and chemical resistances. Microfilters were the first inorganic membranes available on the market. With pore diameter larger than 200 nm, these MF layers are active in bacteria and particle separation. They can be produced by preparing slurries of inorganic powders, then using a coating process such as slip or tape casting. Because colloidal particles are needed to generate mesopores of less than 100 nm, conventional ceramic processing cannot yield UF layers. The first UF membranes made of alumina,

zirconia and titania were obtained using a sol–gel technique [2, 3]. Commercial ceramic ultrafilters are now available which allow separation of colloids, macromolecules, pyrogen and viruses.

Development of new inorganic membranes is expected for the separation of small molecules in biotechnologies, pharmaceuticals, chemical industries, water treatment and also in gas separation and catalysis. When aiming at separation of small molecules (molar mass less than 1000) or multivalent ions, nanoscale pores or almost dense materials will be required. Preparation of ceramics and organically modified ceramics by the sol–gel process typically results in nanoscale structures which have been recently pointed out as conferring novel material properties, especially when the microstructural scale is comparable to the physical dimensions that characterize the phenomena or when the property is dependent on large surface areas. Pure inorganic materials as well as organic/inorganic polymers are very good candidates for preparing this new generation of membranes.

2. Basic properties of sol–gel derived membrane materials

Different kinds of sol–gel derived materials can be successfully used in designing inorganic membranes for nanofiltration:

(i) Pure inorganic membranes made of oxide nanocrystallites sintered at low temperature.

(ii) Organically modified ceramics in which organic groups are attached to an inorganic backbone.

(iii) Nanocomposite layers made of an organic/inorganic polymer embedded in an inorganic matrix.

Generally speaking, the basic properties of a membrane can be tailored by a proper choice of membrane material and preparation process. The nanoscale approach used in material science can be applied both to sol-gel derived materials and to nanofiltration membranes. Nanofiltration is concerned with the separation of small organics and ionic species [4]. Pore size and surface charge in the membrane are two important parameters affecting flux and selectivity. The evolution of these parameters in different sol-gel derived materials will now be discussed.

Amorphous or crystallized ceramics can be produced by processing and firing oxide precursors according to the sol-gel technique [5]. A coating of this ceramic on a macroporous support will yield an almost dense membrane when an amorphous material is obtained, while a connected porosity is expected in a crystallized material. Provided that crystals generated in the ceramic do not exceed 10 nm, partial sintering will provide a connected nanoporosity. In the separation of small organics and ions in water media, the role of pH will be decisive in adjusting the separation capability of a ceramic membrane. Indeed, electrical charges on the oxide surface depend on pH variation and a certain pH, called the isoelectric point (IEP) or point of zero charge (pzc), results in a zero net charge. The occurrence of neutral and charged surfaces at the oxide-solution interface has been attributed to its amphoteric behaviour. The negative surface charge originates from acidic dissociation of surface hydroxyl groups (at $\text{pH} > \text{pzc}$) and increases with increasing pH. The pH dependence on pzc varies with the nature of the oxide and with heat treatment. Table 1 gives the pzc values for the main oxides used in membrane preparation; these values are important when producing membranes for nanofiltration of aqueous media containing charged and neutral species.

In the first instance the nature of the charged ceramic membrane and its influence on mass transfer in nanofiltration can be predicted according to the pH evolution of the feeding solution during filtration. Figure 1 illustrates these phenomena for a titania nanofiltration membrane working at pH varying under and above pzc. When the size of pores and negative charged species is about the same, the rejection will depend on the pH of the solution.

A more complex situation arises when charged species to be rejected exhibit their own pzc, as with amino acids. Charges can be inverted at the same time both for the molecule and at the membrane surface. Finally,

TABLE 1. Point of zero charge for ceramic oxides used in membrane preparation

Material	pzc	Comment	Ref.
$\gamma\text{-Al}_2\text{O}_3$	8–9	Sol-gel method	6
$\alpha\text{-Al}_2\text{O}_3$	7–9	Treated $>1000^\circ\text{C}$	7
ZrO_2	6–7	Sol-gel method	8
TiO_2	5–6	Hydrolysed TiCl_4	9
SiO_2	2–3	Precipitated	10

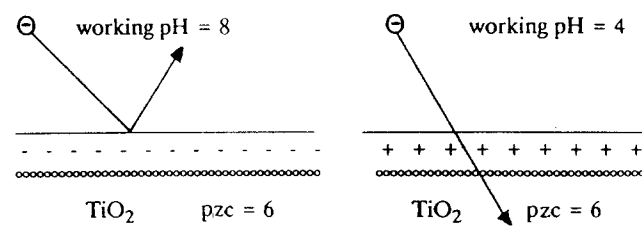


Fig. 1. Schematic illustration of the selectivity characteristics of a TiO_2 nanofilter at different working pH.

pzc can be modified by the ionic strength of the feeding solution. These characteristics mean that tailored ceramic membranes for nanofiltration are not easy to produce.

Organically modified ceramics can be considered as organic/inorganic polymers. Heteropolysiloxanes (HPS) are a good example of such material with Si-C and Si-O bonds providing a composite material at the molecular level. Although polyphosphazenes cannot be included in sol-gel derived materials, they exhibit some similarities with heteropolysiloxanes insofar as an inorganic backbone made of a P-N arrangement is modified by organic groups attached to phosphorus atoms. Used as a membrane material, the basic properties of these organic/inorganic polymers have to be discussed in terms of cross-linking level, network rigidity or elasticity, specific properties related to organic groups such as hydrophilicity or hydrophobicity, charged or non-charged sites. Depending on the organic/inorganic ratio present in the material a more pronounced organic or inorganic behaviour can be expected. The versatility of organically modified ceramics is shown in Fig. 2. Both basic properties of organic and inorganic membranes can be found in this new class of nanophased material.

Ceramic matrices and organic/inorganic polymers can also be combined to produce composite membranes with enhanced selectivity. At this stage the concept of "intelligent membranes" can be developed. If active sites responsible for specific interactions can be distributed inside the membrane at a nanometric scale it is possible to go beyond the sieve concept in which separation is performed related to size criteria. New membranes can emerge from sol-gel derived materials,

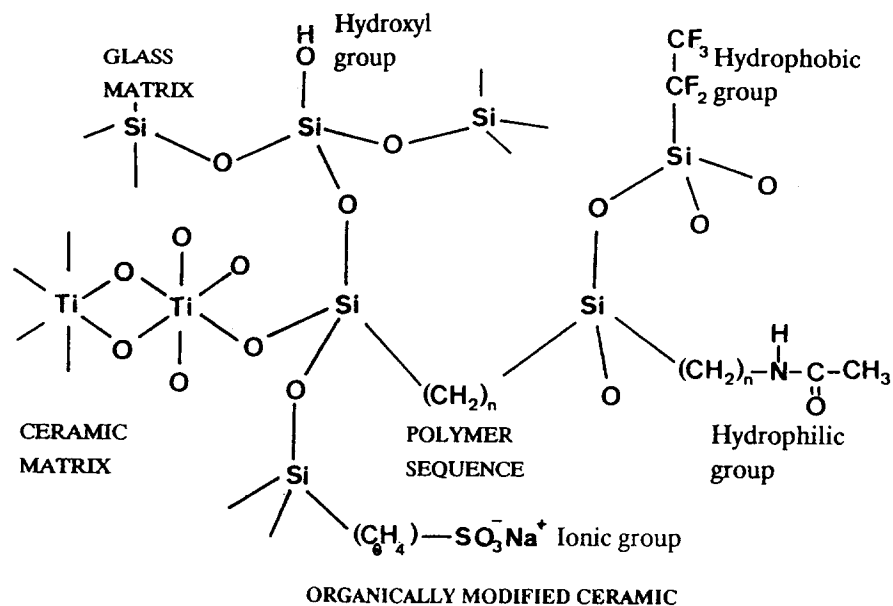


Fig. 2. Schematic illustration of an organic/inorganic material exhibiting nanoscale domains with tailored properties.

which are able to discriminate between chemical species not only on size criteria but also on the basis of physicochemical differences such as chirality, electric charge, functionality, hydrophilicity or hydrophobicity. Another aspect which can be developed is the preparation of membranes used as catalysts or catalyst carriers. The following examples of sol-gel derived membranes prepared in our laboratory try to point out some key steps in the structural evolution of membrane materials together with the appropriate methods for characterizing them at a nanometric scale. An exhaustive survey of attainable tailored properties cannot be given in this paper but gas separation, facilitated transport, biocatalytic membranes, water softening and antibiotic separation are some of the application fields which can be investigated with these membranes.

3. Application to nanofiltration membranes

3.1. Zirconia nanofiltration membrane

In sol-gel processing, particulate sols of hydrous oxides can be formed with identifiable primary particles larger than 1 nm. In the course of film deposition the colloidal particles can evolve in a variety of ways, producing after sintering a nanocrystalline ceramic material obtained with the unique advantage of not having to isolate fine particles from the sol during the process. This is the case with zirconia sols obtained from zirconium oxychloride, which have been used for the preparation of inorganic membranes active in nanofiltration. Previously described conditions for achieving high selectivity and flux during nanofiltration can be

expressed in terms of structure requirements for membrane material. Here the two main parameters to be considered are the stability of the different zirconia phases and the crystallite size. If the zirconia is a well-adapted membrane material, different polymorphs (tetragonal, monoclinic, cubic) can be found in the amorphous state obtained at room temperature. A neutron diffraction study has been performed on this material to analyse its crystallization kinetics and crystallite growth during the transformation sequence under different firing atmospheres (air, nitrogen, hydrogen/nitrogen mixture). Several phenomena have been evidenced which can affect the basic properties of the membrane. The size of the tetragonal crystallites of less than 6 nm obtained from the amorphous state makes them very suitable for generating nanopores of less than 2 nm after sintering. As the temperature increases up to 500 °C, the tetragonal/monoclinic phase transition occurs, with a dramatic effect on crystallite size which moves abruptly from 6 nm to more than 12 nm depending on the firing atmosphere: see Fig. 3. Crystallite size can be maintained under 6 nm up to 600 °C when a non-oxidizing atmosphere is used. This clearly shows that an upper limit exists for membrane sintering which keeps nanoporosity inside the membrane. Using these results, a zirconia nanofilter has been obtained by coating a 1 μm thick layer on an MF zirconia layer. This membrane has been characterized with model solutes in aqueous media and its separation performance is in the nanofiltration range [11].

3.2. Heteropolysiloxane membrane

As mentioned above, heteropolysiloxanes are another example of a membrane material which can be pro-

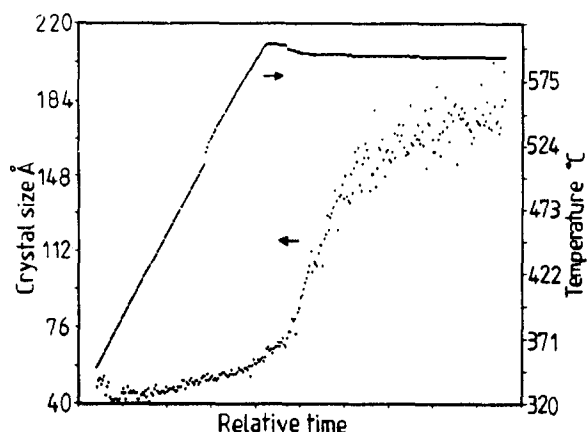


Fig. 3. Neutron diffraction analysis of the influence of tetragonal/monoclinic phase transition on zirconia crystallite size, with example of a nitrogen firing atmosphere.

cessed by sol-gel technique. Their preparation consists first of the synthesis of a gel precursor with both condensable alkoxo groups and appropriate organic groups. The first are necessary for sol-gel processing and produce, depending on condensation rate, either a porous or an almost dense membrane structure. The organic groups permit an adjustment to the physico-chemical properties of membrane materials. By this method a basic heteropolysiloxane membrane with amide groups has been prepared and its potentiality for liquid and gas separation evaluated [12]. Variation in the chemical composition was achieved by replacing the alkoxo groups in the precursor with methyl groups. The membrane hydrophilicity then changes to hydrophobicity. In order to control cross-linking of the organic/inorganic network, membrane materials have been investigated by ^{29}Si MAS NMR [13]. The respective spectra in Fig. 4 show the influence of catalysis on silicon atom substituents. Different correlations have been established between physicochemical characteristics and separation capability in liquid and gas media.

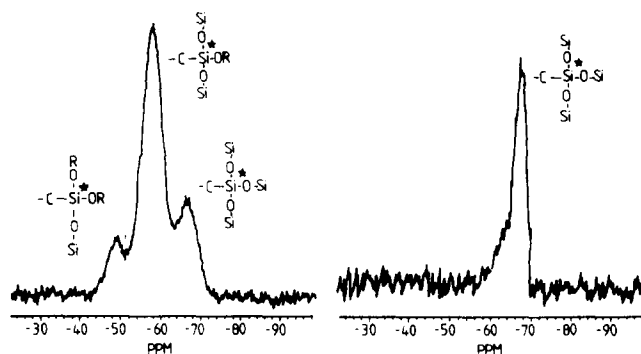


Fig. 4. ^{29}Si nuclear magnetic resonance analysis of the influence of an acid catalyst on silicon atom substituents in a heteropolysiloxane-derived membrane material: left, uncatalysed reaction; right, acid catalysed reaction.

Membranes with identical condensation level have been investigated, one with hydrophilic groups, the other with hydrophobic groups. Hydrophilic membranes performed well in nanofiltration of a model solute (molar mass = 759) with a 100% rejection rate, while high flux and bad selectivity were evidenced in gas separation. On the other hand the hydrophobic membrane, which was not suitable for aqueous nanofiltration, was active in gas mixture separation [12].

3.3. Polyphosphazene nanofilter

The special features of this study are, first, the concept of composite membranes, and then the adaptability of such membranes to nanofiltration. We have synthesized a cycloliner polyphosphazene according to Allcock's method [14], which is intrinsically composite, combining at the molecular level a large number of hydrophilic organic groups with an inorganic cycloliner backbone. This last feature confers better thermal stability than that found in the currently used linear polyphosphazenes. The composite concept also exists at the microscopic level as the polymer is embedded in an inorganic mesoporous support. This combination results in a new type of composite material, with a ceramic matrix support which reinforces the pressure and abrasion resistances of the embedded polymer, yielding a very selective and versatile composite membrane. The great innovation is the application of such membrane to nanofiltration. Membrane characterization was performed with model solutes which revealed the efficiency of this membrane in removing organic dyes from water, in simultaneously concentrating and separating saccharose from saline solutions, and in rejecting anions according to their charge density [15].

3.4. Sol-gel derived catalytic membrane

The sol-gel process has also been investigated in the production of lanthanum oxychloride catalytic supported membranes able to be used in high temperature catalytic reactions such as oxidative methane coupling (800°C) or oxy-dehydrogenation of alkanes (500°C). The advantage of catalytic membrane reactors is linked to their double function: reaction and separation, which are performed in a same operation [16]. This kind of reactor is particularly convenient for equilibrium limited reactions or when contact between product and reactants has to be avoided. For these applications, involving gas-phase reactions, very fine ceramic structures are needed. The colloidal method of preparation from an LaCl_3 aqueous solution has been shown to lead to very different membrane morphologies as a function of the preparation conditions [17]. A judicious choice of the process parameters (salt concentration, choice of the electrolyte, pH and so on) allows a very precise control of the particle size in the sol and thus in the

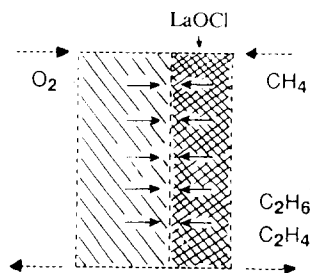


Fig. 5. Schematic illustration showing both sides of a nanoscale active layer working in a catalytic reaction: left, catalyst regeneration; right, catalytic conversion.

corresponding LaOCl final membranes obtained at 800 °C. The LaOCl particle size can be varied from 1 μm to a few nanometers. As shown in Fig. 5, the interesting feature of a catalytic membrane configuration is the partition of oxygen catalyst activation from alkane conversion.

4. Mass transfer aspect

In solute and water transport through a nanofiltration membrane, different forces (osmotic, hydrostatic) may act simultaneously to generate mass transport. The equation for water flux in combined convective and diffusive transport across a porous membrane is

$$J_v = L_p(\Delta P - \sigma \Delta \pi) \quad (1)$$

where $\Delta \pi$ is the osmotic pressure due to the solute concentration gradient between upstream and downstream and σ is a reflective coefficient related to the fraction of molecules reflected back and responsible for the development of this osmotic force. σ can vary from 0 to 1 and is representative of membrane behaviour. $\sigma = 0$ corresponds to a pure ultrafiltration mechanism in which flux decline is related to an additional resistance R_g due to the effect of concentration polarization. In this case the equation for J_v will be

$$J_v = \Delta P / (R_m + R_g) \quad (2)$$

$\sigma = 1$ is for an osmotic membrane and the equation giving J_v then becomes

$$J_v = A_v(\Delta P - \Delta \pi) \quad (3)$$

where A_v is the solvent permeation coefficient. $0 < \sigma < 1$ typically describes a nanofiltration membrane in which both UF and osmosis mechanisms depend on the heteroporosity of the membrane.

Membranes investigated in this work are expected to present a pore diameter of 1–2 nm. In order to establish the separation characteristics of these membranes, a dye molecule (yellow acid 42, molar mass = 759) has been chosen as model solute. Concentration of this

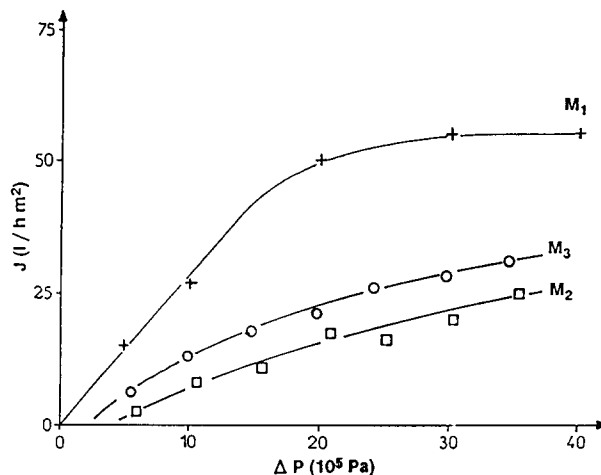


Fig. 6. Flux as a function of transmembrane pressure in yellow acid nanofiltration.

molecule in water media can be easily determined using a UV–visible spectrophotometer. The relationship between molar mass and molecule size can be used to determine an average pore size for the membrane via the rejection rate. The hydrodynamic radius for yellow acid in aqueous media can be considered to be within the range of 0.7–0.8 nm. A 100% rejection for this solute means that the pores should be less than 1.5 nm in diameter. Sieving experiments achieved with yellow acid showed a 100% rejection rate with the M2 and M3 HPS membranes, while an 85% rejection rate was measured with the M1 zirconia membrane in the steady state.

Figure 6 shows solvent flux data as a function of transmembrane pressure drop when yellow acid is used as solute in hyperfiltration experiments. According to eqn. (2) the flux profile for M1 clearly shows a UF mechanism for this membrane. A homoporosity can be assumed to exist in this zirconia membrane with pore diameter larger than 1.5 nm. The increase in rejection rate with increasing time is typically due to the concentration polarization gel layer acting as a second membrane in this process. Results are very different with M2 and M3 membranes. In Fig. 6 water flux for the heteropolysiloxane membranes shows that an osmotic pressure has to be taken into account, according to eqn. (1), in order to explain curve profile. Here the reflective coefficient σ is characteristic of a nanofiltration membrane in which convective and diffusive mass transport are concerned. Finally, rejection measurements for the composite membrane based on a zirconia–polyphosphazene composite material were performed by varying the pH of the feeding solution. Results illustrate the pH dependence on membrane selectivity. The yellow acid is a negatively charged solute which was 100% rejected by the membrane at neutral and basic pH while no rejection was observed

for an acidic pH. This lack of selectivity has been attributed to the net positive charge of the membrane obtained with an acidic pH, according to Fig. 1.

5. Conclusion

Nanofiltration membranes seem to be by the far most innovative and the most promising aspect of membrane development in the near future. By virtue of the nano-structural organization of the solid in nanofiltration membranes, the concept of “intelligent membranes” can be developed, with active sites which are of the same order of magnitude as individual molecules. Specific interaction at the molecular level can then be expected, yielding different effects such as enhanced selectivity in separation or in catalytic reactions. Sol-gel processing can play a prominent role in the development of these new membranes materials.

References

- 1 A. Crull, *Inorganic Membranes*, Business Opportunity Report, BCC Inc., Norwalk, CT, 1989.
- 2 L. Cot, C. Guizard and A. Larbot, *Ind. Ceram.*, 8 (3) (1988) 143.
- 3 A. Larbot, J. P. Fabre, C. Guizard and L. Cot, *J. Am. Ceram. Soc.*, 72 (2) (1989) 257.
- 4 P. Eriksson, *Environ. Prog.*, 7 (1) (1988) 58.
- 5 C. J. Brinker and W. C. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego, 1990.
- 6 R. Fricke and H. Keefer, *Z. Naturforsch. Teil A*, 4 (1949) 76.
- 7 Z. P. Koz'mina, M. P. Belova and V. A. Sannikov, *Kolloidn. Zh.*, 25 (1963) 169.
- 8 J. Randon, A. Larbot, C. Guizard, L. Cot, M. Lindheimer and S. Partyka, *Coll. Surf.*, 52 (1991) 241.
- 9 P. G. Johansen and A. S. Buchanan, *Aust. J. Chem.*, 10 (1957) 398.
- 10 Th. F. Tadros and J. Lyklema, *J. Electroanal. Chem.*, 17 (1968) 267.
- 11 C. Guizard, N. Ajaka, F. Garcia, A. Larbot and L. Cot, *Proc. Vth World Filtration Congress, Nice, France, 1* (1990) 143.
- 12 C. Guizard, N. Ajaka, M. P. Besland, A. Larbot and L. Cot, in M. J. M. Abadie and B. Sillion (eds.), *Polyimides and High Temp. Polymers*, Elsevier, Amsterdam 1991, pp. 537-544.
- 13 M. P. Besland, C. Guizard, N. Hovnanian, A. Larbot, L. Cot, J. Sanz, I. Sobrados and M. Gregorkiewitz, *J. Am. Chem. Soc.*, 113 (6) (1991) 1983.
- 14 H. R. Allcock, *Phosphorus Nitrogen Compounds*, Academic Press, New York, 1972.
- 15 A. Boyé, C. Guizard, A. Larbot, L. Cot and A. Grangeon, in A. J. Burggraaf, J. Charpin and L. Cot (eds.), *Inorganic Membranes*, Vols. 61 & 62, Trans Tech Publications, Zürich, 1991, p. 403.
- 16 H. P. Hsieh, *AIChE Symp. Ser.*, 268 (85) (1989) 53.
- 17 A. Julbe, P. Chanaud, A. Larbot, C. Guizard, L. Cot, C. Milodatos and H. Borges, in A. J. Burggraaf, J. Charpin and L. Cot (eds.), *Inorganic Membranes*, Trans Tech Publications, Vols. 61 & 62, Zürich, 1991, p. 65.