

# 1

## Ceramic Membranes and Membrane Processes

### 1.1 INTRODUCTION

In general, a ceramic membrane can be described as a permselective barrier or a fine sieve. Permeability and separation factor of a ceramic membrane are the two most important performance indicators. For a porous ceramic membrane, they are typically governed by thickness, pore size and surface porosity of the membrane, while for a dense ceramic membrane, the principle for permeation and separation is more complex. In porous ceramic membranes, their applications and separation mechanisms correspond to the pore size of the ceramic membranes as shown in Table 1.1.

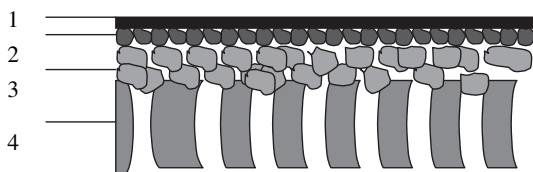
Ceramic membranes are usually composite ones consisting of several layers of one or more different ceramic materials. They generally have a macroporous support, one or two mesoporous intermediate layers and a microporous (or a dense) top layer. As shown in Figure 1.1, the bottom layer provides mechanical support, while the middle layers bridge the pore size differences between the support layer and the top layer where the actual separation takes place. Commonly used materials for ceramic membranes are  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$  etc. or a combination of these materials. An example of the pore characteristics of a four layer alumina membrane is given in Figure 1.2. It can be seen that the pore sizes of the top separation layer, intermediate layers and bottom support layer are in the range of 6 nm (mesoporous), 0.2–0.7  $\mu\text{m}$  and 10  $\mu\text{m}$ , respectively. A more sophisticated multilayer membrane, consisting of a  $\alpha$ -alumina macroporous support, two  $\gamma$ -alumina mesoporous intermediate layers and a microporous silica top layer was reported by Vos and Verweij [1]. As shown in Figure 1.3 (a micrograph taken by transition electron microscopy (TEM)), a very thin silica layer  $\sim 30\text{nm}$  with a pore diameter of 5  $\text{\AA}$  was obtained. The TEM micrograph further indicates that the silica layer is deposited on top of the  $\gamma\text{-Al}_2\text{O}_3$  layer. A clear division between silica and  $\gamma\text{-Al}_2\text{O}_3$  is visible. The boundary between the first and second  $\gamma\text{-Al}_2\text{O}_3$  layers at approximately 250 nm from the surface is clearly visible.

The ceramic membranes mentioned above can only be achieved through multiple steps. As illustrated in Figure 1.1, a support layer is first prepared to provide mechanical strength for the membrane, followed by coating one or more intermediate layers on the support layer before a final dense separation layer can be fabricated. Each step involves a high temperature

**Table 1.1** Category of ceramic membranes

Type <sup>a</sup>	Pore size (nm)	Mechanism	Applications
Macroporous	>50	Sieving	UF, MF
Mesoporous	2–50	Knudsen diffusion	UF, NF, Gas Separation
Microporous	<2	Micropore diffusion	Gas Separation
Dense	—	Diffusion	Gas Separation, Reaction

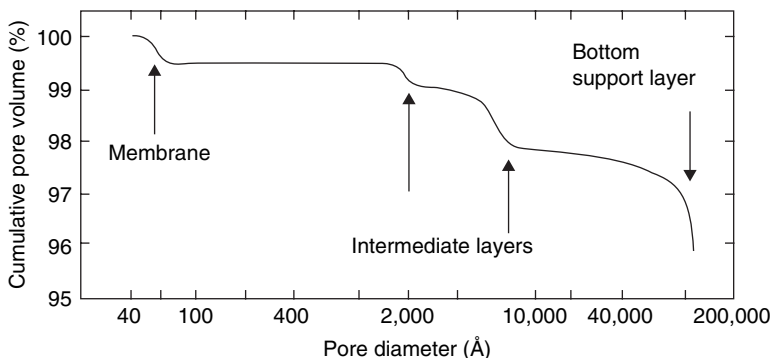
<sup>a</sup> IUPAC classification [53]



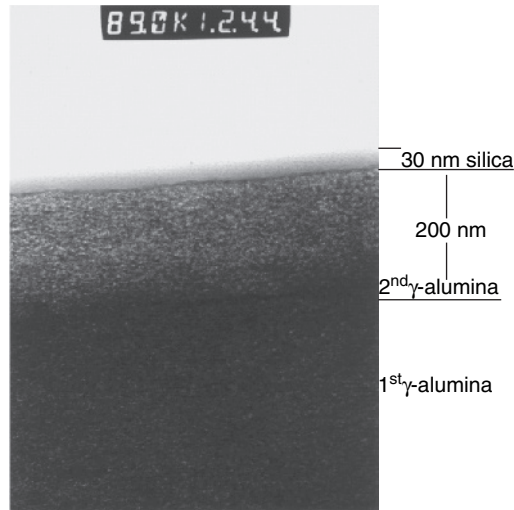
- 1. Modified separation layer (Dense or <2nm)
- 2. Separation layer (3–100nm)
- 3. Intermediate layer(s) (100–1500nm)
- 4. Porous support (1–15µm)

- 1 + 2 + 3 + 4 nanofiltration or gas separation membranes
- 2 + 3 + 4 ultrafiltration membranes
- 3 + 4 microfiltration membranes

**Figure 1.1** Schematic representation of an asymmetric composite membrane



**Figure 1.2** Pore size distribution of a four layered alumina membrane/support composite [3]. Reprinted from Journal of Membrane Science, 39 (3), Hsieh *et al.*, *Microporous alumina membranes*, p. 221–241. Copyright (1988), with permission from Elsevier



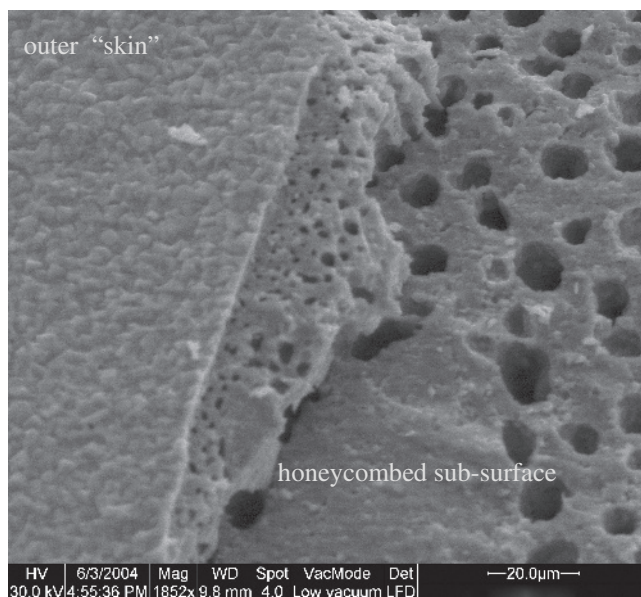
**Figure 1.3** TEM micrograph of Si(400) membrane cross section showing a part of  $\gamma\text{-Al}_2\text{O}_3$  layer and silica layer [1]. Reprinted from *Journal of Membrane Science*, **143** (1–2), Vos *et al.*, *Improved performance of silica membranes for gas separation*, p. 37–51. Copyright (1998), with permission from Elsevier

sintering treatment, making the ceramic membrane fabrication extremely expensive. Clearly, combining the multiple steps into a single one is desirable in cutting production time and costs, and hence membrane price. Li *et al.* [2] demonstrated that the above multiple step fabrication process could be combined into a single step using a phase inversion process. Figure 1.4 shows a scanning electron microscopy (SEM) micrograph of an asymmetric dense ceramic membrane prepared by Li *et al.* using such a technique. As can be seen, a dense and thin skin layer is integrated on the porous support of the same ceramic material, confirming that such a layered ceramic membrane can be prepared in one step.

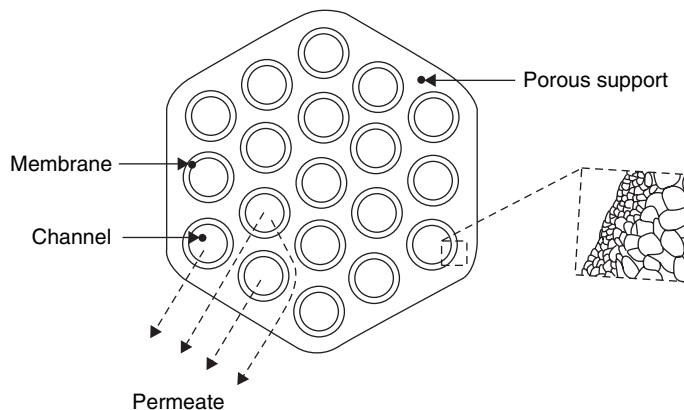
Most commercial ceramic membranes are in disc, plate or tubular configuration. They are usually assembled as a plate and frame module using disc or sheet membranes or as a tubular module using membrane tubes. In order to increase the surface area to volume ratio, which gives more separation area per unit volume of membrane element, alumina multichannel monolithic elements have been developed as shown in Figure 1.5 [3]. These monolithic elements can be combined into modules. Hsieh [4] reported that the surface area to volume ratios are round  $30\text{--}250\text{ m}^2\text{ m}^{-3}$  for tubes,  $130\text{--}400\text{ m}^2\text{ m}^{-3}$  for multichannel monolithics and up to  $800\text{ m}^2\text{ m}^{-3}$  for honeycomb multichannel monolithics. Similar modules have also been developed by CeraMem Corporation as shown in Figure 1.6.

Similarly, a plate and frame ceramic module can be assembled by stacking many membrane cells (made from ceramic sheets) together. In this way, a high packing density can also be obtained for the disc or sheet membranes. The principle is shown in Figure 1.7. It can be seen that the feed flows into a porous spacer sandwiched by two membrane sheets. The fluid permeates through the membranes and the permeate flows out of the system through cell spacers which provide space for permeate flow between the cells. Detailed description of the plate and frame system can be found elsewhere [5].

To further increase the packing density, hollow fibre membrane modules, as shown in Figure 1.8, can be employed, as they offer substantially high packing density, i.e. around

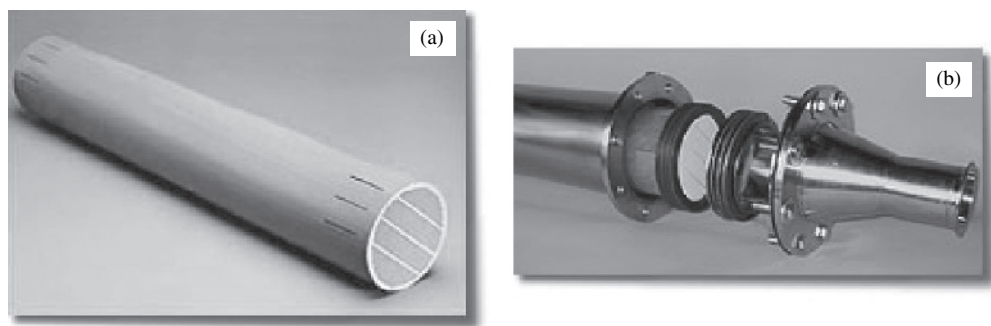


**Figure 1.4** SEM micrograph of a layered ceramic membrane [2]. Copyright (2006) Elsevier. *Journal of Membrane Science*, **272** (1–2), Li, K., Tan, X. and Liu, Y., *Single step fabrication of ceramic hollow fibres for oxygen permeation*, 1–5

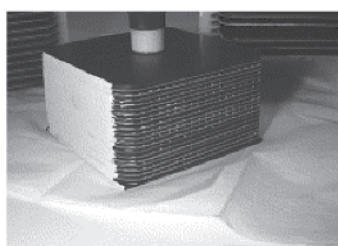


**Figure 1.5** Cross section of a monolithic multichannel membrane element [3]. Reprinted from *Journal of Membrane Science*, **39** (3), Hsieh *et al.*, *Microporous alumina membranes*, p. 221–241. Copyright (1988), with permission from Elsevier

$9000 \text{ m}^2 \text{ m}^{-3}$  as compared to packing density of around  $30\text{--}500 \text{ m}^2 \text{ m}^{-3}$  offered by the plate and frame or tubular membrane format. The greatest challenge in the preparation of a ceramic hollow fibre membrane lies in overcoming the physical brittleness often associated with ceramic materials, especially for high temperature industrial applications. Ceramic hollow fibre membranes have been produced in porous or dense form depending on their application

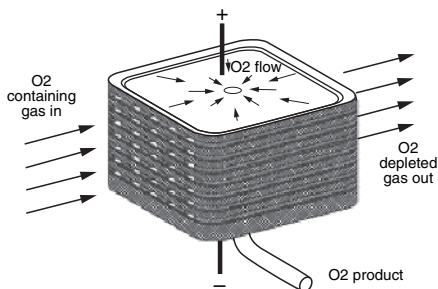


**Figure 1.6** Multi-channel ceramic module: (a) membrane element 142 mm diameter × 864 mm length 10.7 m<sup>2</sup> membrane area; (b) membrane element in stainless steel housing with simple compressive seal design. Reprinted with permission from CeraMem Corporation



- Ceramic stack
  - ◆ front - inlet air
  - ◆ left - insulated air baffle
  - ◆ top - O<sub>2</sub> gas port
- Cells electrically in series

- Layered components
  - ◆ interconnect
  - ◆ cell
  - ◆ insulator
- Gas flow
  - ◆ air - cross flow
  - ◆ O<sub>2</sub> - radial flow
    - central port out

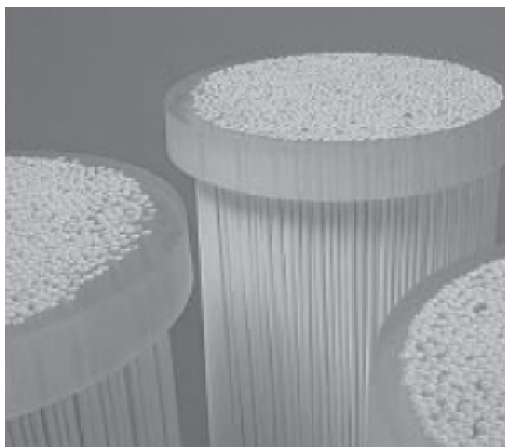


**Figure 1.7** SEOS™ Oxygen Generator multiple planar cell stack [5]. Reprinted from Solid State Ionics, 134, Dyer *et al.*, *Ion transport membrane . . .*, p. 21–23. Copyright (2000), with permission from Elsevier

requirements. They have been investigated in areas such as gas separation, membrane reactor, solvent recovery, etc. [6–9].

## 1.2 MEMBRANE PROCESSES

Membrane processes have become an accepted unit operation for a variety of separations in industries. The processes are driven by pressure, concentration or electric field across the



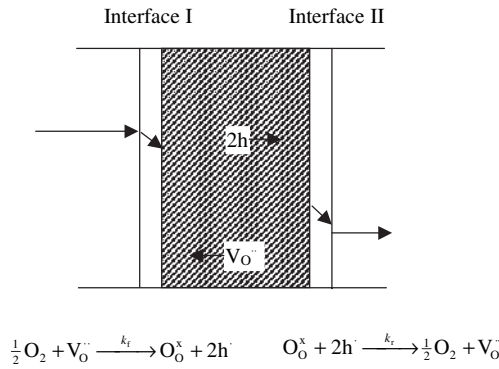
**Figure 1.8** Ceramic hollow fibre modules. Reprinted with permission from Hyflux CEPA ration BV

membrane and can be differentiated according to type of driving force, molecular size or type of operations. Some common membrane processes are briefly introduced below.

### 1.2.1 Gas Separation

Gas mixtures can be separated by either dense or porous ceramic membranes. The dense ceramic membranes are made from crystalline ceramic materials such as perovskites or fluorites, which allow permeation of only oxygen or hydrogen through its crystal lattice. Therefore, they are mostly impermeable to all other gases, giving extremely high selectivity towards oxygen or hydrogen.

Oxygen permeation through a dense ceramic membrane is due to a large number of oxygen vacancies that are generated by doping and the electron holes produced by the defect reaction exist in the solid electrolyte. Under a gradient of oxygen partial pressure imposed on the membrane at a high temperature, the oxide ions are transported along with holes from the high partial pressure side to the low partial pressure side as illustrated in Figure 1.9. In addition to the bulk diffusion, oxygen permeation through a mixed ionic–electronic conducting membrane also undergoes the surface exchange reactions at both the oxygen rich and oxygen lean sides of the membrane, which involves many sub-steps such as oxygen adsorption, dissociation, recombination and charge transfer [10, 11]. Therefore, the permeation process from the high oxygen partial pressure side to the low oxygen partial pressure side includes the following steps in series: (1) mass transfer of gaseous oxygen from the gas stream to the membrane surface (high pressure side); (2) reaction between the molecular oxygen and oxygen vacancies at the membrane surface (high pressure side); (3) oxygen vacancy bulk diffusion across the membrane; (4) reaction between lattice oxygen and electron holes at the membrane surface (low pressure side) and (5) mass transfer of oxygen from the membrane surface to the gas stream (low pressure side). However, the resistances between the gas phase and membrane (steps 1 and 5) are usually small and negligible [12] and as a result, only the membrane bulk diffusion, the surface reactions need to be taken into consideration for the oxygen permeation. Similarly, when hydrogen is exposed to a mixed proton conducting



**Figure 1.9** Schematic diagram of oxygen permeation in a mixed ionic–electronic conducting membrane

membrane, it may be transferred through the membrane under a hydrogen partial pressure gradient. Again, apart from the membrane bulk diffusion, the surface reactions are also important and need to be taken into consideration for the hydrogen permeation. Dense ceramic membranes for oxygen or hydrogen separations will be discussed in detail in Chapters 6 and 7, respectively.

In microporous ceramic membranes, the gas permeation behaviour may be dominated by Knudsen diffusion, surface diffusion, multilayer diffusion, capillary condensation or molecular sieving (i.e. configurational diffusion) and is strongly dependent on the pore size and pore size distribution of the membrane, operating temperature and pressure, and the nature of the membrane and the permeating molecules [13]. The progression from Knudsen diffusion to molecular sieving is in parallel with increasing permselectivities. For pores that are large relative to the molecular size of the permeating gases, Knudsen diffusion is the likely mechanism controlling the rate of transport. In this case, the gases permeate in proportion to their molecular velocity and hence, in inverse proportion to the square root of their molecular weight. If the gas is strongly adsorbed in the membrane pores, surface diffusion will enhance the permeation rate relative to Knudsen diffusion. When the pores of the membrane are roughly the same size as the gas molecule’s diameter, molecular sieving may take place. This mechanism is characterized by a strong temperature dependence and more importantly, sharp decline in permeabilities for larger gas molecules [14]. Gas separation using porous ceramic membranes is one of the important research topics and a comprehensive discussion on this will be given in Chapter 4.

### 1.2.2 Pervaporation

Pervaporation, as shown in Figure 1.10, is a separation process where a liquid mixture is in direct contact with one side of the membrane and where the permeate stream is removed in the vapour state from the other side of the membrane. Because of the presence of the membrane, the liquid–vapour equilibrium is perturbed as shown in Figure 1.11. Application of pervaporation includes separation of azeotropic mixtures, mixture of closed boiling point components, heat-sensitive products, etc.

Ceramic membranes for pervaporation offer some significant advantages over polymeric ones, such as much higher chemical and thermal stability than most polymeric materials.

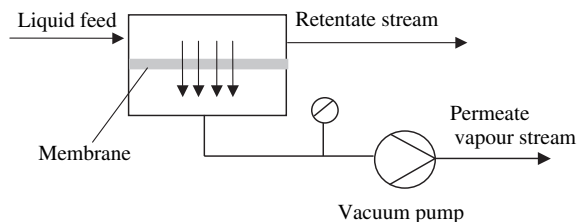


Figure 1.10 A pervaporation process

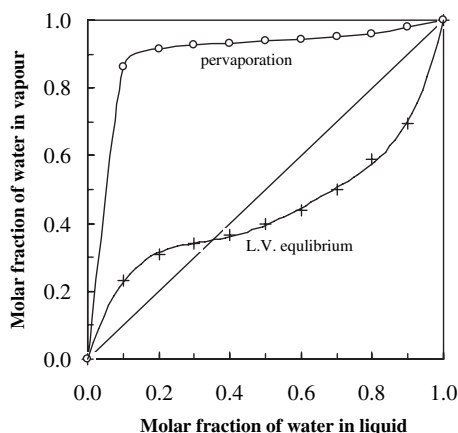


Figure 1.11 Perturbation of liquid–vapour equilibrium by membranes

Thus membranes made from ceramic materials can be operated at higher temperatures and in the presence of solvents that would cause polymeric membranes to fail. They offer much better mechanical stability and do not swell and thus achieve a more constant performance with varying feed concentration. Their ability to operate at higher temperatures with higher fluxes also reduces the required membrane area for operation much below that required for a polymeric membrane. Ceramic supported membranes are much harder than the thin polymer structure of the polymeric membranes. Ceramics offer advantages such as being chemically inert and therefore better at operating with highly reactive compounds present and in acidic or alkaline conditions.

Gallego-Lizon *et al.* [15, 16] conducted pervaporation experiments for *t*-butanol and isopropanol dehydration using a range of commercially available ceramic membranes. They found that when dehydrating a 90 wt% *t*-butanol solution, microporous silica membranes offered the highest flux, followed by zeolites, both being better than that of polymeric membranes. The separation factors are the greatest for the zeolite membrane. Van Veen *et al.* [17] also tested ceramic membranes for pervaporation and found that the ceramic membranes show many advantages over polymeric membranes: (1) giving an extremely constant operation over several weeks, (2) allowing operation at much higher temperatures than polymeric membranes (up to 300 °C) and (3) giving much higher fluxes whilst retaining high selectivity. This, in turn, suggests that the required membrane area can be vastly reduced.

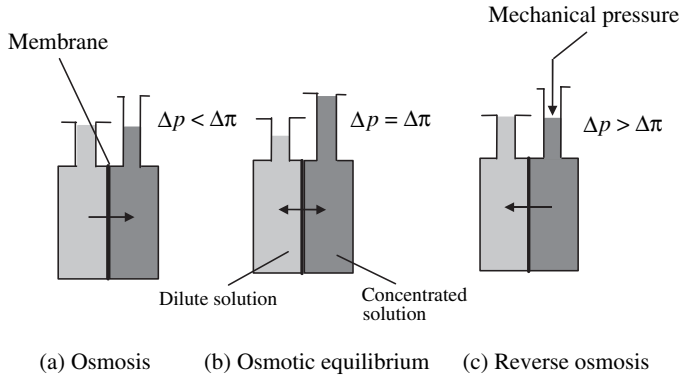


Figure 1.12 Phenomenon of osmosis

### 1.2.3 Reverse Osmosis and Nanofiltration

Reverse osmosis (RO) and nanofiltration (NF or loose RO) processes allow selective passage of a particular species (solvent), while other species, i.e. solutes, are retained partially or completely. Solute separation and solvent permeability are the membrane characteristics and are dependent on the membrane material and the structure of the membrane layer. The main difference between RO and nanofiltration membranes is that RO rejects all the solutes, including monovalent ions, while the nanofiltration membrane can only reject multivalent ions with no selectivity towards monovalent ions.

As illustrated in Figure 1.12, osmosis is a natural phenomenon where water passes (Figure 1.12a) through a membrane from one side with lower solute concentration to a higher solute concentration until the osmotic equilibrium is reached (Figure 1.12b). To reverse the water flow, mechanical pressure (Figure 1.12c) is applied, providing a pressure difference greater than the osmotic pressure difference; as a result, separation of water from a solution becomes possible. This phenomenon is referred to as reverse osmosis. Applications of reverse osmosis processes include: seawater desalination, waste water treatment and ultrapure water production.

Reverse osmosis (RO) is a well established membrane technology for the treatment of water in a variety of applications. Today, only polymeric RO/NF membranes are commercially available. Major problems associated with polymeric RO/NF membranes are: (1) excessive fouling due to poor feed flow hydrodynamics; (2) low resistance to chlorine and other oxidants; (3) extensive pretreatment/chemical usage and associated waste generation and (4) lack of desirable surface charge to reduce fouling potential. Ceramic membranes, in this context, display a number of performance advantages over commercially available polymeric membranes. Of particular importance in RO and NF applications are the excellent resistance to chlorine, oxidants, radiation and solvents; the high thermal and chemical stability and the long reliable life of ceramic membranes. RO/NF membranes have been available from the outset with ceramic materials. However, the high cost, low packing density and/or poor selectivity renders commercially available ceramic membrane technology economically untenable for RO/NF applications.

Research into formation of ceramic nanofiltration membranes has been carried out recently and membranes prepared from titania [18–21], zirconia [22–24], silica–zirconia [25, 26], hafnia [27, 28] and  $\gamma$ -alumina [19, 29] have been reported. Most of these nanofiltration

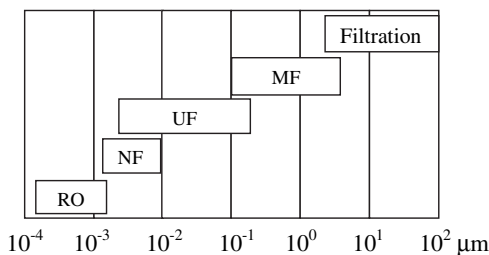
membranes have been prepared for separation of nonaqueous solvent using sol-gel processes, where a mesoporous ceramic support is coated with a layer of a metal oxide which determines the final pore size. This provides a great advantage in controlling the pore diameter through the proper choice of colloidal solutions at the final coating stage. Reported MWCO of these membranes lies between 200 and 1000 g mol<sup>-1</sup>.

## 1.2.4 Ultrafiltration and Microfiltration

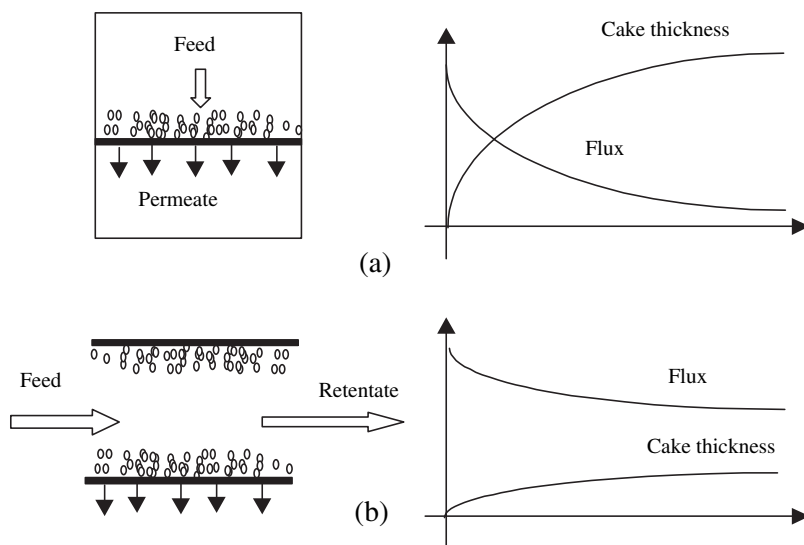
Ultrafiltration is a membrane process where porous membranes are used to separate colloidal particles or large molecular weight solutes from solvent. In ultrafiltration, the mechanism for separation of the solvent from the solute/colloidal particle is similar to that of reverse osmosis/nanofiltration. Therefore, the rejection of solutes is determined based on the pore size and pore size distribution of the membranes, and surface interactions between the membrane surface and solvent/solutes. The overall solvent transfer is often dominated by mass transfer resistances in the membrane as well as at the solution boundaries. Thus, the presence of even a low concentration of retained species can have a profound effect on the solvent permeation.

Although there is no precise definition of the boundary between ultrafiltration and microfiltration as shown in Figure 1.13, microfiltration, as a membrane process, closely resembles conventional filtration processes and separates discrete particles from solution. As can be seen in Figure 1.13, there is also no clear dividing line between coarse filtration and microfiltration, but the accepted upper pore size limit is around several  $\mu\text{m}$ . The lower size limit is set at 0.1  $\mu\text{m}$ . Microfiltration is used to separate small insoluble particles, bacteria and yeast cells from broths and aqueous streams. Conventional depth filters typically consisting of a matrix of fibres are used to perform similar tasks, but the separation is achieved by a mechanism of entrapment within the fibres and adsorption to the surface. There is no defined ‘pore’ size for depth filters but the voids between the fibres are greater than the size of the smallest retained particle. Thus the retention in depth filtration is a statistical function. Microfiltration membranes, on the other hand, have a well defined pore size and separation is achieved on the basis of sieving effects. Because the pore sizes in membranes are large enough, the solvent is usually transported through the pores of the membrane by convection. The rate of transport of solvent through the membrane is thus proportional to the pressure difference across the membrane and can be described by the Hagen–Poiseuille equation, if the pores of the membranes are assumed to be cylindrical.

Ultrafiltration and microfiltration membranes have been prepared from a wide range of polymers such as cellulose acetate, cellulose nitrate, polyacrylonitrile, polyamide,



**Figure 1.13** Relation between the membrane process and the membrane pore size



**Figure 1.14** Schematic diagram of filtration processes: (a) dead-end filtration and (b) cross-flow filtration

polyethersulfone, polyimide, polysulfone, polyvinyl alcohol, polyvinylidene fluoride, etc. Ceramic membranes have also been developed for ultrafiltration and microfiltration applications. The development of ceramic membranes is mainly driven by the need to produce membranes with greater chemical and thermal tolerance, because the upper temperature limit of polymeric membranes is mostly below 200°C. In addition, most polymers mentioned above cannot survive in solvents such as benzene and toluene. Ceramic ultrafiltration and microfiltration membranes are prepared from materials such as aluminium oxide, titanium oxide and zirconium oxide, as they can withstand high temperatures and harsh chemical environments. Typical applications of ultrafiltration and microfiltration processes using ceramic membranes can be found in the dairy, food, pharmaceutical, biological, paint, paper and water industries. A detailed review on use of ceramic membranes in these applications can be found elsewhere [4].

There are two types of operations in ultrafiltration and microfiltration: (1) dead-end filtration and (2) cross-flow filtration. As illustrated in Figure 1.14, dead-end filtration is only suitable for dealing with suspensions with a very low solid content, while cross-flow filtration can be used for much higher concentrations as the deposits on the membrane are swept away by membrane-parallel flow.

## 1.2.5 Dialysis

Dialysis is basically a diffusion process and it describes the separation of substances in solution by means of their unequal diffusion rate through porous membranes; therefore, dialysis is achieved by imposing a concentration gradient across the membrane. Typical application for this process is the artificial kidney as shown in Figure 1.15. The dialysis unit consists of a membrane module comprising a bundle of hollow fibres. Blood flows through the hollow fibre where the dialysis fluid flows through the shell side of the module. The dialysis fluid is

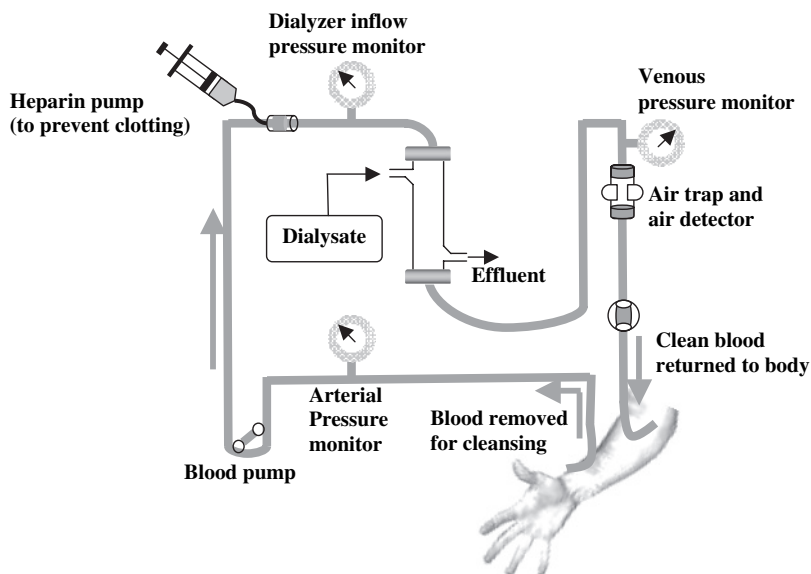


Figure 1.15 Typical dialysis

pumped at a sufficiently high rate to prevent concentration build up in the shell. The toxic species in the blood diffuse through the porous wall (i.e., membrane) and are carried away by the dialysis fluid. The membrane permeability is determined by the characteristics of the membrane and the specific solutes. However, the length, inside diameter and thickness of the membrane itself are all important design variables. Also, operating conditions such as transmembrane pressure and flow velocity in hollow fibre lumen must be optimized.

Most of the membranes used in artificial kidneys are made of polymers, mainly from cellulose based materials. More recently, synthetic membranes including polysulfone, polymethylmethacrylate and polyacrylonitrile have been developed for use in dialysis as they are more biocompatible. These new membranes are all synthetic and show high fluxes.

There are so far no ceramic membranes used in dialysis. However, Bender *et al.* [30] and Czermak *et al.* [31] suggested the use of ceramic membranes for removal of endotoxins from dialysis water and dialysate for the reason that ceramic membranes are more resistant to harsh operating conditions.

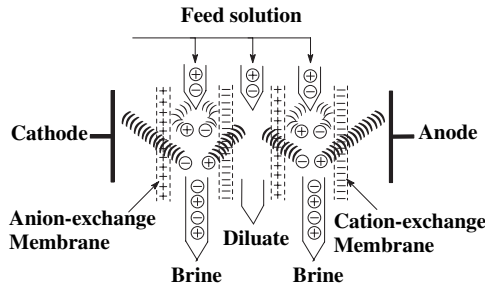
### 1.2.6 Electrodialysis

Electrodialysis is a process where solute ions move across ion exchange membranes by application of an electrical field. Although electrodialysis was started as a modification of ordinary dialysis by adding a couple of electrodes, the two processes are distinctly different in many ways as shown in Table 1.2.

The principle of the electrodialysis has been described by Strathmann [32] with an example of desalination of brackish water. As can be seen in Figure 1.16, a typical electrodialysis process, where a series of anionic and cationic membranes are placed alternately and an electrical potential is applied from a cathode and an anode stationed at either end, is used for desalination of brackish water. When the brackish water, containing sodium chloride, is fed into the individual cells, the positively charged cations such as sodium ions are driven by the

**Table 1.2** Difference between ordinary dialysis and electro dialysis

Ordinary dialysis	Electrodialysis
Based on concentration gradient	Based on external electrical field
Use of normal membranes	Use of ion exchange membranes
Flow direction: high concentration → low concentration	Flow direction: high concentration ↔ low concentration
Concentration gradient diminish as results of mass transfer	Desired degree of separation is achievable



**Figure 1.16** Principle of electro dialysis [32]. Reprinted from H. Strathman *Electrodialysis*, in *Synthetic Membranes: Science, Engineering and Applications*, P. M. Bungay, H. K. Lonsdale and M. N. de Pinho, Editors. (1983), D. Reidel Publishing Company: Dordrecht. p. 199. With kind permission of Springer Science and Business Media

electrical potential to the cathode. The sodium ions can permeate through the negatively charged cationic membrane, but are rejected by the positively charged anionic membrane. Similarly, the negatively charged anions such as chloride ions migrate toward the anode through the anionic membrane, but are rejected by the cationic membrane. As a result, both sodium and chloride ions are depleted in chambers referred as ‘dilute’ and are concentrated in the neighbouring chambers called ‘brine’. Electro dialysis can thus be used either to concentrate the salt or to produce potable water from brackish water.

Ion exchange membranes have also been used in caustic soda industries for the electrolysis of sodium chloride solution to produce sodium hydroxide and chlorine. The process is schematically illustrated in Figure 1.17. As can be seen, a cationic membrane made from a perfluorocarbon polymer is placed at the centre of an electrolysis chamber. When a sodium chloride solution is introduced to the left side of the cationic membrane, the sodium ions are attracted toward the cathode and move to the right side of the membrane. On the surface of the cathode, water is decomposed into proton and hydroxyl ions. The protons are immediately reduced into hydrogen atoms by receiving one electron from the surface of the cathode. Two hydrogen atoms are combined to form a hydrogen molecule, and leave the cathode compartment. Sodium hydroxide solution is thus produced in the cathode compartment. On the other hand, chlorine ions move toward the anode. Upon reaching to the anode, the chlorine ions donate an electron to the anode and become chlorine atoms. Two chlorine atoms are then combined to form a chlorine molecule, before leaving the anode compartment.

So far, electro dialysis processes primarily employ polymeric ion selective membranes because they show desirable features, such as low electrical resistance and mechanical flexi-

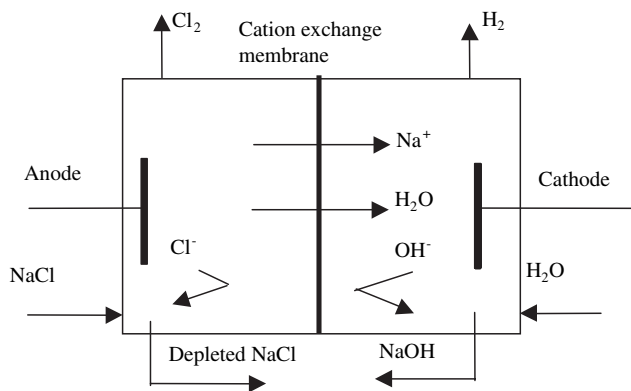


Figure 1.17 Electrodesialysis for caustic soda industry

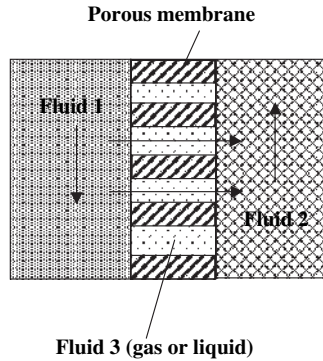
bility. The drawbacks of the polymeric ion selective membranes are their relatively low selectivity and thermal stability [33]. Sodium selective ceramic membranes, in this context, provide enhanced current efficiencies and can operate at high temperatures without being damaged [34]. However, the thickness required for self supporting ceramic membranes leads to high resistance and increases the energy consumption to unacceptable levels. Cormier *et al.* [35] proposed a composite membrane consisting of a thin film of a ceramic of NASICON composition ( $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ,  $0 \leq x \leq 3$ ) deposited on a cation selective polymeric membrane. They demonstrated that the presence of this ceramic thin film on a polymer membrane increases current efficiency and prevents fouling [36], as the membrane combines the advantages of both polymer (mechanical flexibility and low electrical resistance) and ceramic membranes ( $\text{Na}^+/\text{H}^+$  selectivity and low multivalent ion fouling rates).

### 1.2.7 Membrane Contactors

Unlike conventional membrane processes, where the membrane is a selective layer towards the fluids to be separated, the membranes used in membrane contactors are nonselective. Therefore, separation achieved in membrane contactors is primarily based on the same principle as in conventional contact processes, i.e. based on phase equilibria. Figure 1.18 illustrates the principles of the process. As can be seen, the applied porous membrane separates two fluids (gas or liquid) from each other and a diffusive mass transfer takes place through the porous membrane. Depending on the membrane material, the physicochemical properties of the liquid and the operating pressures employed, the pores of the membrane can be filled with either gas or liquid, which would result in great differences in the mass transfer resistance of the membrane employed [37].

Membrane contactors represent a technology where porous membranes are used as ‘packing materials’ for interphase mass transfer. Therefore, all traditional gas stripping and absorption [38, 39], distillation [40, 41], liquid–liquid extraction [42, 43], as well as emulsification [44], crystallization [45, 46] and phase transfer catalysis [47] can be carried out in membrane contactors.

The performances of membrane contactors are strongly dependent on the properties of the membranes, physicochemical properties of the fluids and the operating pressures employed.

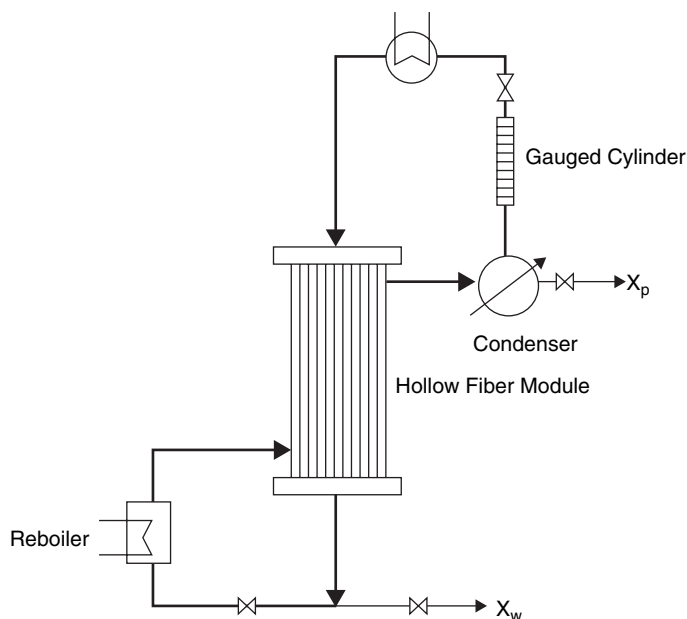


**Figure 1.18** Operation principle of a membrane contactor

In general, a membrane with relatively uniform pore size and hydrophobic surface is required so that wetting and mixing between contacting phases can be prevented. Membranes with big pore size, high porosities and asymmetric structures can provide high permeation fluxes, but may cause bubble formations in gas–liquid operations. Thus, operating pressures in the liquid phase need to be properly controlled. In spite of the difficulties in membrane selection and some operational complexity, membrane contactors have been applied to almost all the unit operations due to its considerable advantages, such as larger interfacial area per unit volume, independent control of gas and liquid flow rates without any flooding, unloading, foaming, etc., known gas–liquid interfacial area and high modularity and compatibility for an easy scale up. Disadvantages are mainly related to the presence of an additional mass transport resistance and to the quite limited range of the operating pressures below the wetting pressure threshold. In addition, currently, the membrane contactors are mainly made of polymeric membrane and replacement cost is considered to be another disadvantage. However, new ceramic hollow fibre membranes [48] have been recently developed for membrane contactors. This would certainly prolong the lifetime of the membrane contactor, overcoming this disadvantage.

Zhang and Cussler [40] explored the use of hollow fibre membrane contactors as a potential route to faster distillation. Because of the foreseeable advantages in hollow fibre distillation, a system as shown in Figure 1.19, was set up. As can be seen, the system consists of a column, a reboiler and a total condenser. The only difference is that the column is not staged or filled with packing, but is built with hollow fibres. It is quite clear that such a hollow fibre column has a several advantages over a conventional distillation tower. Firstly, it offers a large interfacial area per volume. All of this area is actively involved in the mass transfer between vapour and liquid. Secondly, because the liquid always fills the hollow fibres, this contact area is maintained, even at very low flows. There is thus no constraint of column ‘loading’, and the turndown ratio of the column is infinite. Thirdly, no flooding is caused by any two phase flow, as the liquid and vapour flows are not in direct contact, thus, it can be routinely operated in regions which are not accessible to normal packed columns. Also, because the flows of liquid and vapour are now not around submerged objects, pressure drops in the column are more modest than in conventional equipment.

Although, as acknowledged by Zhang and Cussler [40], any improvements they obtained would not be of direct commercial value because hollow fibres used by them were made of polymers, the recent development in ceramic hollow fibre membranes may very soon put this process into commercial practice, as ceramic hollow fibre will remain intact in solvents and temperatures routinely used in distillation.



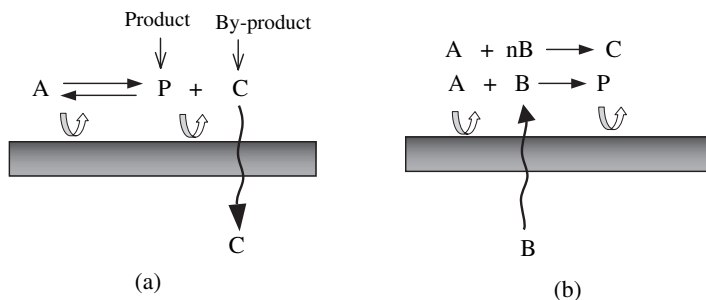
**Figure 1.19** Process for hollow fibre distillation (The hollow fibre module replaces the conventional packed tower used for differential distillation) [40]. Reprinted from Zhang, G. L. and Cussler, E. L., *Distillation in hollow fibres*. American Institute of Chemical Engineers Journal, **49** (9) p. 2344–2351. Copyright (2003), with permission from John Wiley & Sons, Inc.

Detailed discussion on membrane contactors will be given in Chapter 5 with emphasis on one of the unit operations, i.e. gas absorption. Obviously, using the same approach, the results from gas absorption analysis can be easily applied to other unit operation processes such as liquid–liquid extraction and distillation.

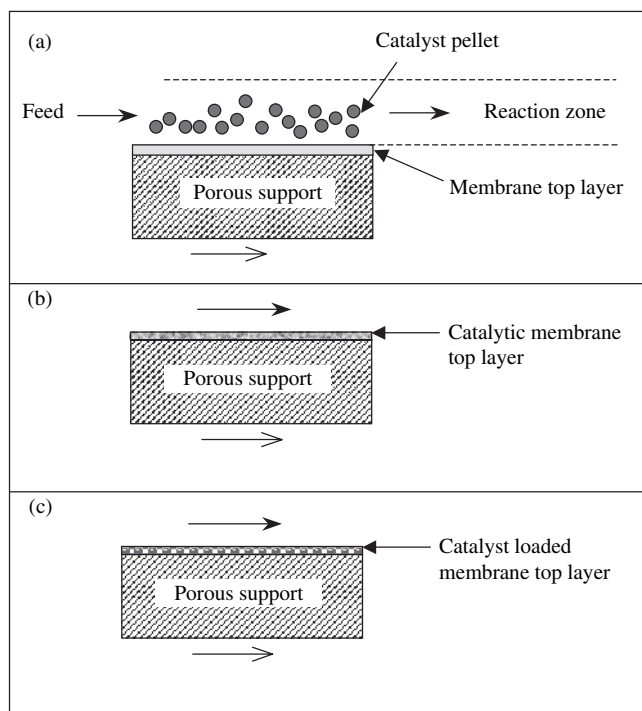
## 1.2.8 Membrane Reactors

A membrane reactor is a device that combines a membrane separation or distribution process with a chemical reactor in one unit. Due to the integration of reaction and separation/distribution, chemical processes become simpler leading to a much lower processing cost. In addition, membrane reactors are capable of promoting a reaction process by: (1) selectively removing at least one of the products from the reaction zone through the membrane, making the equilibrium reaction shifting to the product side; (2) supplying only a particular reactant to the reaction zone giving an optimum concentration ratio of the two reactant streams. As a result, the yield can be increased (even beyond the equilibrium value for equilibrium reactions) and/or the selectivity can be improved by suppressing other undesired side reactions or the secondary reaction of products. Figure 1.20 illustrates the two main functions of the membrane reactors.

Use of membrane reactors to shift the equilibrium in a reversible reaction has been mainly studied for dehydrogenation reactions. For example, as the hydrogen produced in the dehydrogenation reaction is removed continuously through a permselective membrane, the reaction equilibrium shifts to the product side, resulting in a high yield even at lower temperatures, and then the deactivation of catalyst and undesirable side reactions may be avoided.



**Figure 1.20** Principle of membrane reactors to promote reactions: (a) selective permeation of by-product of an equilibrium limited reaction; (b) dosing a reactant through the membrane



**Figure 1.21** Coupling of the membrane with catalysts: (a) membrane coupled with conventional pellet catalysts; (b) membrane itself is catalytically active; (c) catalyst impregnated into the pores of microporous membranes

Use of membranes to control the addition and distribution of a reactant has been mainly studied for partial oxidative reactions of hydrocarbons [49]. The membrane controls the oxygen reactant supply to the hydrocarbon compartment and avoids the direct presence of gas-phase oxygen, which is often deleterious to hydrocarbon selectivity, thus, to some degree, suppressing the deep oxidation of the hydrocarbons. The use of membrane reactors also has advantages in controlling the hot spots in exothermic reactions [50, 51].

In catalytic membrane reactors, coupling of the membrane with catalysts is achieved basically in three ways [52]. As illustrated in Figure 1.21(a), the membrane is coupled with conventional pellet catalysts, the membrane forming the inner wall of the tubular reactor.

It should be noted that the membrane top layer, which facilitates the separation forms only a small part of the overall membrane thickness, with the support layer forming the major part. This configuration has been mostly applied in dehydrogenation reactions. Sometimes, the catalyst in the form of paste is coated on the membrane top layer, but it functions in a similar way to the pellet catalyst. In the second arrangement, the membrane itself is catalytically active as shown in Figure 1.21(b). The active catalyst is a thin dense membrane layer deposited on a surface of a porous support. A potential problem with this configuration is that the membrane may not have sufficient catalytic area to be totally effective. The final configuration shown in Figure 1.21(c) is for a catalyst impregnated into the pores of a microporous material either as individual particles or as a layer. This is a convenient way of introducing catalyst into the membrane and has also been used in dehydrogenation reactions.

Detailed analysis of membrane reactors as product separators and as reactant distributors will be covered in Chapter 8.

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