Membrane Separation Processes: Current Relevance and Future Opportunities

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During the last 35 years membranes have evolved from a laboratory tool to industrial products with significant technical and commercial impact. Today, membranes are used for desalination of sea and brackish water and for treating industrial effluents. They are efficient tools for the concentration and purification of food and pharmaceutical products and the production of base chemicals. Furthermore, membranes are key components in artificial organs, drug delivery devices, and energy conversion systems. In combination with conventional techniques membranes often provide cleaner and more energy-efficient production routes for high-quality products. Fundamental aspects of membranes and membrane processes are discussed, as well as technically and economically effective applications. The present and future membrane market is assessed and new developments and future research needs are discussed.

Introduction

When about 40 years ago the first synthetic membranes became available, the expectation for their technical and commercial relevance was very high. A multitude of potential applications were identified and a several billion dollar market was predicted for the membrane-based industry by the turn of this century (Lonsdale, 1982). The overall success of the membrane technology, however, is lagging behind these expectations. In some applications, such as in hemodialysis, in reverse-osmosis seawater desalination, in micro- and ultrafiltration of surface water, or in the separation, concentration, and purification of food and pharmaceutical products, in fuel cells, and as battery separators, and so on, membranes indeed play an important role today. In other applications today's available membranes find it difficult to compete with conventional separation processes. With the development of new membranes with improved transport properties and better chemical and thermal stability in recent years, a large number of new potential applications have been identified and the membrane-based industry is responding to the market needs by rapidly exploiting these applications on an industrial scale.

In this article the principles of relevant membrane processes and their applications are briefly reviewed. An assessment of the present and future membrane market is given. The structure of the membrane-based industry and its strategies toward the market are described. Recent developments of new or improved membranes and membrane processes are discussed, and further research needs for a continuous growth of membrane technology are pointed out.

Fundamentals

For a better understanding of the technical and commercial relevance of membranes and membrane processes, some fundamental relations describing the function of a membrane and the basic principles of membrane processes shall briefly be reviewed.

Membranes and membrane processes are used in four main areas, which are, in the separation of molecular and particulate mixtures, in the controlled release of active agents, in membrane reactors and artificial organs, and in energy storage and conversion systems. In these applications a large variety of processes, membrane structures, and membrane materials is used (Ho and Sircar, 1992).

The processes in which membranes are used can be classified according to the driving force used in the process. The technically and commercially most relevant processes are pressure-driven processes, such as reverse osmosis, ultra- and microfiltration, or gas separation, concentration-gradient-driven processes, such as dialysis, partial-pressure-driven processes, such as pervaporation; and electrical-potential-driven processes, such as electrolysis and electrodialysis.

There are other processes, such as pertraction, membrane contactors, and hybrid processes, in which membrane separation is combined with conventional processes. Membranes used today in the various applications consist of solid dense or porous polymer, ceramic or metal films with symmetric or asymmetric structures, liquid films with selective carrier components, and electrically charged barriers.

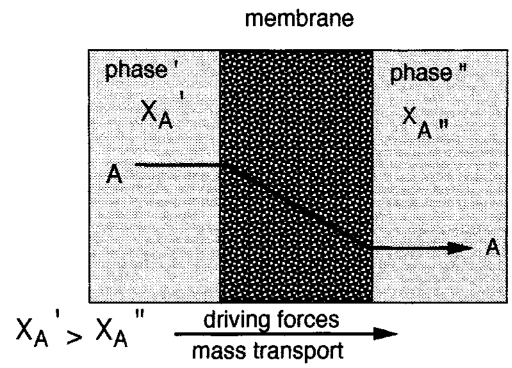
The key properties determining membrane performance are high selectivity and fluxes; good mechanical, chemical, and thermal stability under operating conditions; low fouling tendency and good compatibility with the operation environment; and cost-effective and defect-free production.

Membranes are manufactured as flat sheets, hollow fibers, capillaries, or tubes. For practical applications membranes are installed in a suitable device, which is referred to as *membrane module*. The most commonly used devices are pleated cartridges, tubular and capillary membrane modules, plate-and-frame and spiral-wound modules, and hollow-fiber modules. There are several other module types used in special applications, such as the rotating cylinder and the transversal flow capillary module. The key properties of efficient membrane modules are high packing density, good control of concentration polarization and membrane fouling, low operating and maintenance costs, and cost-efficient production. For the efficiency of a membrane process in a certain application, the choice of the proper membrane module is of great importance.

Function of synthetic membranes

The function of a membrane in a separation process is determined by its transport properties for different components in a mixture. The transport rate of a component through a membrane is determined by its permeability in the membrane and by the driving force. Driving forces in membrane processes are gradients in the chemical potential, in the electrical potential, and in the hydrostatic pressure, resulting in a diffusion of individual molecules, a migration of ions, and a convection of mass, respectively. The function of a membrane is illustrated in Figure 1, which shows the transport of a component A from a phase ($'$) through a membrane into the phase ($''$) due to a driving-force gradient. The main driving forces in the different membrane processes are also indicated in Figure 1. Hydrostatic pressure differences are used in micro- and ultrafiltration, as well as in reverse osmosis and gas separation as driving force for the mass transport through the membrane. The mode of transport in micro- and ultrafiltration is convection. In reverse osmosis and in gas separation, diffusion and the actual driving forces are chemical potential and a fugacity gradients. In dialysis the mode of transport is diffusion with concentration or activity gradients as driving forces, and in electrodialysis an electrical potential gradient is used to achieve a migration of charged components, such as ions across the membrane.

The permeability of a certain component in a membrane is determined by its concentration and its mobility in the membrane structure. In a homogeneous polymer matrix, the concentration of a component in a membrane is determined by its solubility in the polymer. In a porous structure, the concentration of a component in the membrane is determined by its size and by the pore size of the structure. The concentration of a component in the membrane often can be increased by a selective carrier. This carrier can have a certain mobility in the membrane, as in so-called liquid membranes, or it can be fixed to the membrane matrix. The facilitated transport in a liquid membrane is illustrated in Figure 2. If the carrier is a charged component such as an ion, the transport of certain components can be coupled. This is also indicated in Figure 2. There are two forms of coupled transport, one referred to as a cocurrent and the other as a countercurrent coupled transport. The coupling force is the electroneutrality requirement for ions in the mixture.



process	driving force	transport mode
microfiltration	Δp	convection
ultrafiltration	Δp	convection
reverse osmosis	Δp ($\Delta\mu_i$)	diffusion
dialysis	ΔC (Δa)	diffusion
gas separation	Δp (Δf_i)	diffusion
pervaporation	Δp_i (Δf_i)	diffusion
electrodialysis	$\Delta\varphi$	migration

Figure 1. Mass transport through a synthetic membrane.

It shows the driving forces applied in the various membrane separation processes (p, μ_i, C_i, a_i, p_i, f_i, and φ are the hydrostatic pressure, the chemical potential, the concentration, the activity, the partial pressure, and the fugacity of a component i, respectively, and φ is the electrical potential).

The mass transport through membranes can be described by various mathematical relations. Most of these are semiempirical, postulating membrane models, such as Fick's law, Hagen-Poisseuille's law, and Ohm's law. A more comprehensive description which is independent of the membrane structure and thus applicable to any membrane, is based on a phenomenological equation that connects the fluxes of the electrical charges, volume, that is, viscous flow, and individual components with the corresponding driving forces by a linear relation:

$$J_i = \sum_k L_{ik} X_k. \quad (1)$$

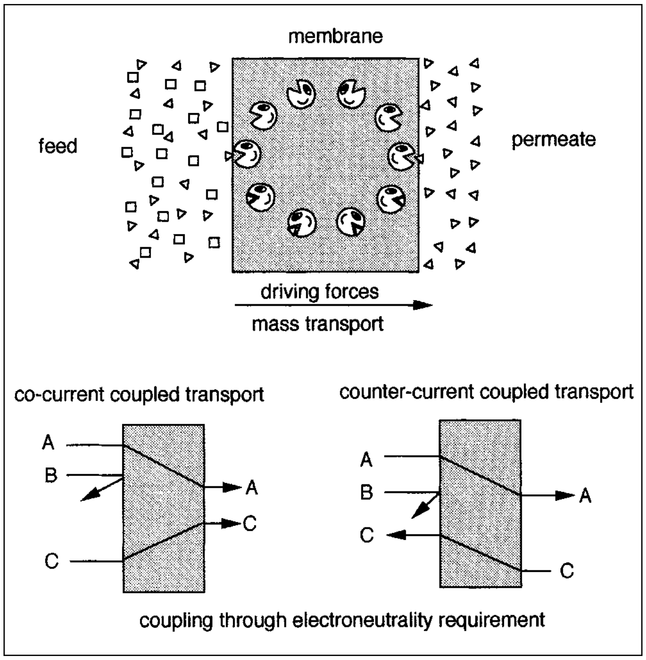


Figure 2. Facilitated and co- and countercurrent couple transport in membranes.

Here J is a flux per unit area and X is a generalized driving force; the subscripts i and k refer to individual components, volume, and electrical charges; and L is a phenomenological coefficient relating the fluxes to the driving forces.

For multicomponent systems with fluxes of individual components, volume, and electrical charges, Eq. 1 can be written as a matrix in which the diagonal coefficients relate the fluxes to the directly corresponding driving forces, and the cross-coefficients express the coupling of fluxes with nonconjugated driving forces. Thus, Eq. 1 describes the mass transport through a membrane not only as a linear function of the corresponding driving forces as, for example, Fick's or Ohm's law, but it also considers a possible kinetic coupling between different fluxes.

Another approach to describe the mass transport in membrane processes is based on a relation developed by Maxwell and Stefan. In this relation the forces are expressed as a linear function of the fluxes:

$$X_i = \sum_k C_i f_{ik}(\upsilon_i - \upsilon_k) = \sum_k C_i \frac{RT}{Đ_{ik}}(\upsilon_i - \upsilon_k). \qquad (2)$$

Here X is the driving force, C is the concentration, υ is the linear velocity, f is the friction coefficient, and $Đ$ is the Maxwell-Stefan diffusion coefficient. The subscripts i and k refer to individual components.

Equations 1 and 2 provide a complete description of transport processes through a membrane separating two homogeneous mixtures. All phenomena observed in membrane systems, such as osmosis, electroosmosis, diffusion, viscous flow of a bulk solution, electric current, or the buildup of an osmotic pressure, a streaming, and a diffusion potential, can be described. The practical value of the equations, however, is limited when multicomponent systems in a heterogeneous medium with viscous flow have to be treated. Therefore, usually certain assumptions are made, and by postulating certain membrane models, relatively simple relations are obtained that describe the mass transport adequate in porous media, homogeneous films, or electrically charged barriers.

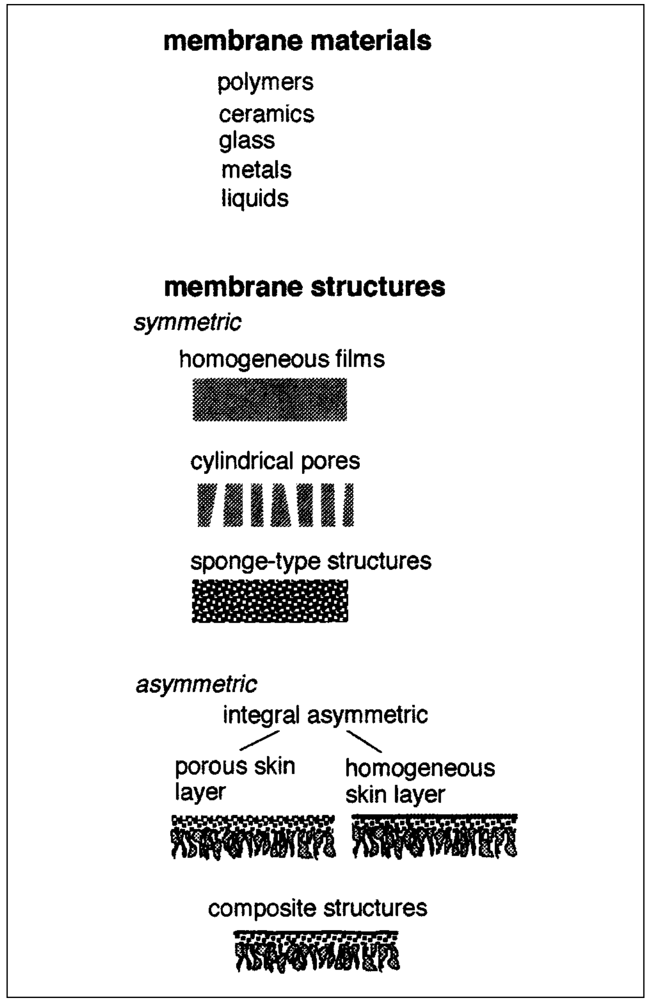


Figure 3. Materials and structures of various synthetic membranes.

Structures of synthetic membranes

Typical structures and materials used today in membrane processes are illustrated in Figure 3.

Membranes are made of various materials, including metals, ceramics, polymers, and even liquids. Their structures include dense films and porous media that can have cylindrical pores or just a sponge-type structure. The membranes can be symmetric, that is, their structure is identical over the entire cross section of the membrane, or they can be asymmetric, that is, their structure is different on the top side and on the bottom side. Very often these membranes have a thin layer at the surface, a so-called ''skin'' supported on a highly porous substructure. The skin can be homogeneous or porous. Asymmetric membranes can be prepared in one step by a so-called phase inversion process or as composite films where a thin barrier layer is placed in an additional preparation step on a porous support structure.

Membrane Market and the Membrane Industry

The worldwide membrane market in 1998 can be summarized as follows:

- Sales of membranes and modules > 4 billion U.S. $
- Sales of membrane systems > 15 billion U.S. $
- Market growth is 8−10% per year
- Largest market segment is the biomedical sector

The sales of membranes and membrane systems is rather moderate; however, it has to be realized that membranes are often key components in many applications resulting in superior high-value products or substantial savings in energy and raw materials (Baker et al., 1991).

Assessment of the present and future membrane market

The membrane market is extremely heterogeneous and requires a large number of different membrane structures and processes as well as peripheral components and specific application know-how. Some market segments, such as that for the hemodialysis and reverse-osmosis seawater desalination membranes, are quite large and require low-cost membranes. In other applications, such as in diagnostic devices or sensors, the value of the membranes is very small compared to the costs of the device, and membrane function is more important as membrane costs.

Table 1 lists membrane sales in different processes, and Table 2 shows membrane sales in major applications.

To utilize a membrane process in a certain application, a suitable membrane is needed as the key component. However, a substantial amount of additional equipment such as pumps and electronic process control devices, and such skills as basic engineering and especially a specific application know-how, are required for a membrane process to be successfully utilized. In many applications the membrane costs are irrelevant compared to the costs of the peripheral components. In these cases the added value of using a membrane process lies in the system or in the product that is obtained by the membrane processes. In Table 3 added values of various membrane applications are summarized.

The development of the membrane market is determined by energy costs, required product quality, environmental protection needs, new medical therapies, and of course by the availability of new and better membranes and membrane processes. Some of the factors affecting the future membrane market, such as the industrial relevance of an application or the competitive situation of the membrane process compared to conventional techniques, are summarized in Table 4. Some applications of membrane processes, such as water desalination or wastewater treatment, have high industrial relevance. However, in these applications the membrane processes compete with conventional water desalination or water treatment techniques, such as multistage flash evaporation or biological sewage treatment plants. In other applications of high commercial relevance, such as in hemodialysis or in fuel cells, membranes are key components, and no economic alternative technique that could compete with membranes is currently available. There are other applications, such as the production of ultrapure water, where membrane processes compete with conventional techniques, but have a clear advantage. There are also a large number of membrane applications of lower industrial relevance, such as the dehydration of organic solvents by pervaporation or the recovery of organic vapors from waste air streams by gas and vapor permeation membranes. In certain biosensors and diagnostic devices, membranes are key components, but in terms of the total costs of the final device, the cost of the membranes in these devices is negligibly low. Therefore, this application is often of lesser interest to the membrane producing industry.

Table 1. Sales of Membranes and Modules in Membrane Processes

Membrane Process	Sales 1998 M U.S. $	Growth %/yr
Dialysis	1,900	10
Microfiltration	900	8
Ultrafiltration	500	10
Reverse osmosis	400	10
Gas exchange	250	2
Gas separation	230	15
Electrodialysis	110	5
Electrolysis	70	5
Pervaporation	> 10	?
Miscellaneous	30	10
Total	Σ 4,400	> 8

Table 2. Sales of Membranes and Modules in Various Applications

Market Segment	Sales 2000 M U.S. $	Growth %/yr
Hemodialysis/filtration	2,200	8
Blood oxygenator	350	2
Water desalination	350	10
(waste) Water purification	400	10
Oxygen/nitrogen separation	100	8
Food processing	200	10
(bio)Chemical industry	150	15
Electrochemical industry	150	8
Analytical/diagnostic	150	10
Miscellaneous	350	10
Total	Σ 4,400	> 8

Structure of the membrane-based industry

The development of a certain membrane process or application passes through different stages, starting with research and development of a certain membrane or process. The next step is the production of the membrane and the membrane

Table 3. Added Value of Membrane Applications

Application	Added Value or Costs			
	Membrane	Module	System	Product
Hemodialysis	Very low	Very low	High	Very high
Water desalination	Low	Medium	Medium	High
Ultrapure water	Low	Low	High	High
Bioseparation	Medium	High	Medium	Very high
O_2-enriched air	Medium	Medium	Medium	Low
Natural gas treatment	Medium	Medium	High	Low

Table 4. Present and Future Membrane Market

Industrial Relev.	Membranes Competing with Conv. Processes	Membrane Processes with Clear Adv.	No Alternative to Memb. Processes
State-of-the-art processes			
High	Water desalination (waste)Water treatment	Production of ultrapure water	Artificial kidney, fuel cell separators
Medium	Natural gas treatment Air separation	Down-stream processing of bioproducts	Therapeutic devices for controlled drug release
Low	Dehydration of solvents	Biosensors	Diagnostic devices
Emerging processes			
High	Membrane reactors	Membrane bioreactors	Artificial liver
Medium	Organic/organic separation	Recycling of effluents	Immune isolation of cells
Low	Organic vapor recovery	Affinity membranes	

modules, followed by the system design. The final step is marketing and sales of the membrane or membrane process. The membrane-based industry includes a variety of enterprises with very different production and marketing strategies. Some companies concentrate on the production of membranes and modules only and cooperate with equipment manufacturers that are often highly specialized on certain applications, while other companies focus their effort on applications only and use various membranes and hardware components supplied by different manufacturers. Still other companies concentrated on a single application, but they produce all components needed in this application, including the membranes and the peripheral equipment themselves. A typical example of this strategy can be seen in the hemodialysis industry, where companies focus on one product, and have technology from research and development and membrane and equipment production to marketing and sales in one place. Others have adopted the so-called ‘‘boot strategy,’’ which means build, own, operate, and transport the product to the customer. This strategy is often used by the water-supply companies.

An important parameter in the market strategy of the membrane-based industry is the market size of the various products or processes and their position on a life-cycle curve. A typical life-cycle curve of different membrane processes is shown in Figure 4, in which the sales of different membrane processes are shown as a function of its state of development.

The life-cycle curve of membrane processes indicates four phases in the life of a membrane process: the development phase, the growth phase, the mature phase, and the declining phase. None of the membrane processes is in the declining state yet. The mature processes such as hemodialysis, microfiltration, and reverse osmosis, have the highest sales but moderate profits. For these processes production efficiency is very important because sales are determined mainly by product costs. Therefore, the market is dominated by a relatively small number of companies with a highly automated and efficient production. Processes in the rapidly growing phase, such as gas separation, pervaporation, membrane reactors, and bipolar membranes, show higher profits but lower sales in smaller market segments that are generally served by smaller companies. For these processes the availability of components with the required properties and application know-how are key criteria for the sales. Finally, there are a number of emerging processes that are still in development on a laboratory scale or are only conceptually available. The processes and products are available only on a very limited scale and we can only speculate about their potential future markets.

Recent Developments in Membrane Science and Technology

Significant progress has been made during recent years in the development of new membranes and their applications. New inorganic and organic materials, super molecular structures with specific binding properties, are used as membrane materials. For the separation of gases, especially oxygen/nitrogen and methane/carbon dioxide, new glassy polymers and inorganic materials such as zeolites are used to produce membranes with better selectivity and higher fluxes. For the separation of enantiomers, carrier-facilitated transport membranes are produced using molecular imprint techniques. In reverse osmosis, membranes with better chemical stability and higher fluxes are now available. Surface-modified membranes with better biocompatibility and affinity membranes for the removal of endotoxins or other toxic components from blood may soon be available. The recent developments in membrane technology have been assisted by new research tools, such as atomic force microscopy, acoustic time-domain reflectometry, molecular dynamic simulations, or computer-aided process design, are applied widely today in membrane science. Some of the recent developments are discussed in more detail below.

Development of improved membranes and membrane materials

Substantial progress has been made in improving the performance of state-of-the-art membranes and in developing novel membrane materials and membrane structures. Some of these developments have had a significant effect on the economics of certain membrane processes, others have led to new applications and markets.

High-Performance Reverse-Osmosis Membranes. The progress that has been made in improving reverse-osmosis seawater desalination membranes during the last years is indicated in Figure 5, which shows the salt rejection and the water flux of various membranes developed by the Nitto Denko Corporation during the last 20 years.

The data of this graph are extracted from a Nitto Denko (1997) annual report. The graph in Figure 5 shows that the fluxes of reverse-osmosis seawater desalination membranes were increased by a factor of 3 in the last 20 years. Today,

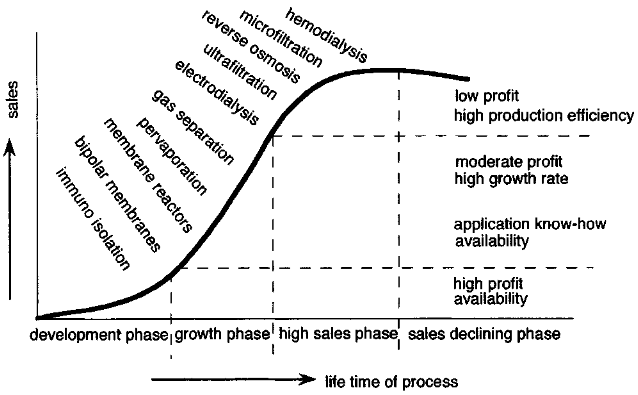


Figure 4. Life-cycle curve of various membrane processes.

It shows the sale as function of the state of development of the processes.

high-performance membranes used in single-stage seawater desalination reject total salts in excess of 99.5 wt. % and have transmembrane fluxes of 1.5 to 2.0 $m^3 \cdot m^{-2} \cdot d^{-1}$ at an effective hydrostatic pressure (that is, $\Delta p_{\text{eff}} = \Delta p_{\text{appl}} - \Delta\pi$) of 15 bar. The reason for this significant increase in flux is based on the preparation technique of the barrier layer of the composite membrane which has many folds, with the result that the surface of the actual barrier layer is about three times larger than the area of the support structure. Figure 6 shows a scanning electron micrograph of the barrier layer of a reverse-osmosis composite membrane, indicating that its surface is significantly enlarged by folding. The reverse-osmosis membranes based on cellulose acetate used earlier have a smooth surface with a barrier layer that has the same area as the membrane.

Today's reverse-osmosis membranes have not only become quite efficient, there has also been a significant reduction in price over the last couple of years. Production capacities of the industry have drastically been increased and the market is dominated by a small number of companies that generally compete on price.

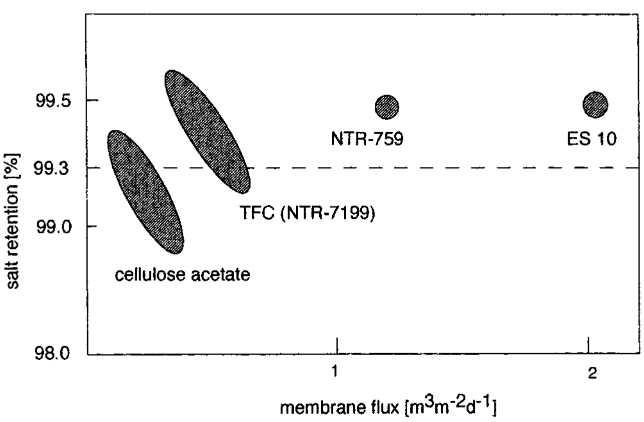


Figure 5. Salt rejection and fluxes of different reverse-osmosis membranes: progress of the recent 20 years.

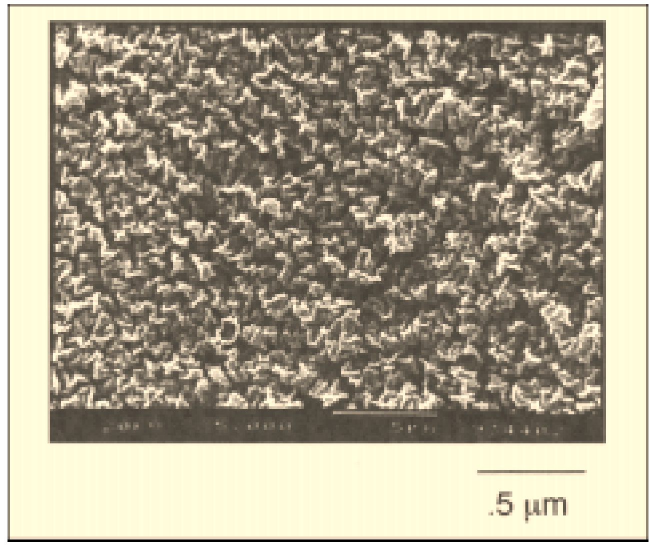


Figure 6. Scanning electron micrograph of the surface of a high-flux reverse-osmosis membrane.

Stabilization of Supported Liquid Membranes. Supported liquid membranes are very interesting in combination with selective carriers for the selective transport of certain components of a mixture. They have been studied extensively on a laboratory and pilot-plant scale, and a large number of important industrial applications have been indicated. However, until today there has been hardly any large-scale industrial utilization of liquid membranes because of certain problems related to the performance of the membranes. One of the shortcomings of today's supported liquid membranes is their short useful life. As indicated in Figure 7, carrier and solvent are lost to the feed or strip solution by dissolution and micelle formation. The rate with which the solvent and the carrier are lost depends on the process conditions. In thin membranes the solvent or carrier can be lost within several hours, which makes the membrane useless.

The stability of liquid membranes can be increased drastically by placing a thin polymer layer on top of the liquid membrane. Figure 8 shows test results obtained with a supported liquid membrane carrying a thin layer prepared by interfacial polymerization on the feed side. The membrane was used to remove nitrate from water using countercurrent transport. The tests were carried out with a feed solution of 0.004 molar $NaNO_3$, a stripping solution of four molar NaCl,

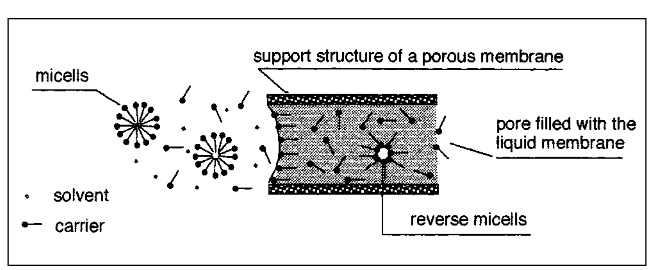


Figure 7. Carrier and solvent loss of liquid membrane in facilitated transport.

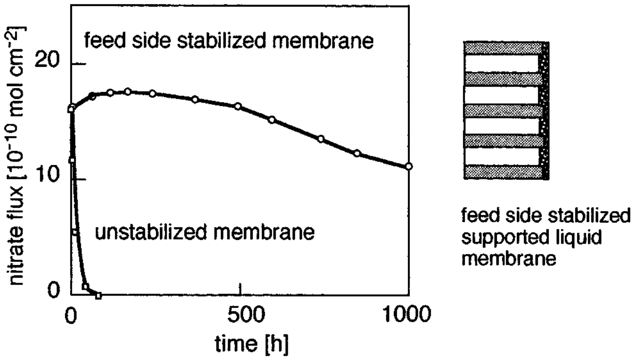


Figure 8. Nitrate flux of a conventional liquid membrane and a membrane supported by thin layer on the feed-facing side of the membrane.

It uses countercurrent transport with NaCl in the stripping solution.

and the carrier was trioctyl methyl ammonium chloride in a 0.2 molar solution of *o*-nitrophenyl ether.

The graph in Figure 8 shows that the useful life of a membrane without a barrier layer is only a few hours, while that of the membrane with a barrier layer at the strip side surface is more than 1,000 hours.

Preparation of Composite Hollow Fiber by the Triple-Nozzle Spinneret. Asymmetric hollow fiber or capillary membranes with a denser skin on the in- or outside of the fibers are generally made by a phase-inversion process. To produce composite hollow fibers by dipcoating, which requires an additional production step, is used most. For the preparation of composite hollow-fiber membranes in a single production step, a triple-nozzle spinneret was developed. The concept of a triple-nozzle spinneret is shown in Figure 9, which shows the cross sections of a conventional tube-in-orifice spinneret and a triple-nozzle spinneret. In a conventional tube-in-orifice construction the outer bore is used as a feed channel for the polymer solution, while the inner bore generally contains a precipitation fluid or an inert gas and symmetric or integral asymmetric membranes with a selective layer made from the same polymer as the support structure. The triple-nozzle spinneret contains two outer bores around an inner tube. Two different polymer solutions can be fed through the two outer bores. The outer layer is precipitated by an outside precipitation bath, while the inner layer is precipitated by a bore fluid. Thus, two different structures made from two different polymers can be obtained on the inner and outer fiber surface. The technique can be used to produce gas-separation membranes with an outside selective barrier layer or to put a hydrophilic coating on a hydrophobic substructure. With the triple-nozzle spinneret, for example, composite membranes have been produced that have a porous substructure based on polysulfone and a thin, dense, negatively charged hydrophilic top layer of sulfonated polyetherketon.

The main advantage of composite hollow fibers made in one step with the triple-nozzle spinneret compared to those made by dip-coating is a simplified production process. Generally, higher fluxes also are obtained in the single-step production, since pore penetration, which is often a problem with dip-coating, is avoided.

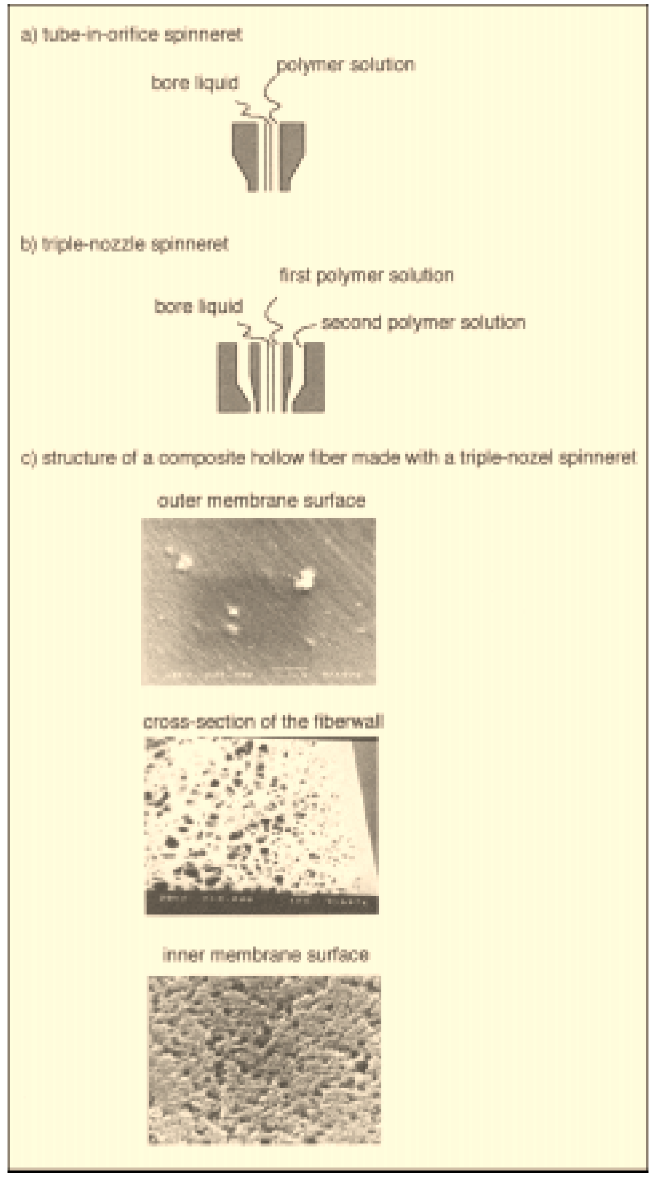


Figure 9. Concept of (a) conventional tube-in-orifice, b) triple-nozzle spinneret, and (c) scanning electron micrographs of outer and inner surfaces and cross section of a composite membrane made with the triple-nozzle spinneret.

Inorganic Membranes for Gas and Vapor Separation with High Selectivity. Historically, the use of inorganic membranes started with the separation of $U^{235}F_6/U^{238}F_6$ isotopes for the preparation of nuclear fuels. The process is based on Knudsen diffusion of gases through porous membranes. Porous membranes with pore diameters of 0.01 to 10 μm are prepared by a slip-coating and sintering procedure based on metal oxides such as α-Al_2O_3 powders as the support structure and a selective barrier prepared by the sol-gel process. These membranes can be considered as state-of-the-art structures and are used today in micro- and ultrafiltration.

An interesting recent development is the preparation of zeolite membranes. Because of the unique properties of zeolite crystals such as molecular sieving, ion-exchange, selective adsorption, and catalysis, these membranes have a large number of potential applications in gas and vapor separation and in membrane reactors and chemical sensors. NaA-Zeolite membranes composed of continuous intergrowth of NaA-zeolite crystals have been synthesized hydrothermally on the surface of porous ceramic support structures. The membranes that are highly selective for water are used in pervaporation and vapor permeation.

Dense inorganic membranes based on palladium and palladium alloys have been used for many years for the selective transport of hydrogen. These membranes have practically infinite selectivity for hydrogen. However, their large-scale industrial applications are limited due to the high price of the metal.

Dense ceramic membranes based on perovskites exhibit high mixed electronic and oxygen ion conductivitiy, and for this reason they are widely studied for applications in solid oxide fuel cells, oxygen sensors, and membrane reactors. A substantial disadvantage for the large-scale production of oxygen with perovskite membranes is their low oxygen permeability at room temperature. To obtain reasonable oxygen fluxes, these membranes must be used at temperatures in excess of 600°C.

An increasingly important research area is related to nanoporous ceramic membranes with well-defined pore structures prepared by template-assisted, self-assembling methods. Furthermore, an increasing amount of research effort is concentrated on the development of proton-conducting membranes for high-temperature applications in fuel cells and membrane reactors.

Development of improved membrane modules

In large-scale applications of membranes in separation processes, the membranes are installed in modules that must provide high packing density, good control of concentration polarization, low pressure losses of the feed and permeate solution, and low production costs. The overall performance of the state-of-the-art membrane modules, such as the plate-and-frame, the spiral-wound, and the hollow-fiber and capillary membrane modules, has been improved gradually over recent years, and production costs have been reduced significantly. But only very few completely new module concepts have been developed. Two exceptions are the so-called transversal flow capillary membrane module and the spiral-type tubular module.

The transversal flow module is used mainly in dialysis where boundary-layer effects must be controlled on the feed and permeate side of the membrane. In most commonly used capillary modules, axial flow is applied. These modules are characterized by straight membrane capillaries and axial flow through the fiber lumen and the shell. In spite of the poor flow distribution, and thus mass transfer, at the shell-side membrane surface, this type of module is preferred because of its high packing density and low production costs. In a transversal flow capillary module the capillary membranes are installed in a tubular housing in such a way that the shell-side solution is flowing through the module perpendicular to the capillaries. This perpendicular flow provides a certain turbulence at the membrane surface, and thus a significantly better control of concentration polarization effects than a flow parallel to the capillary membrane axis.

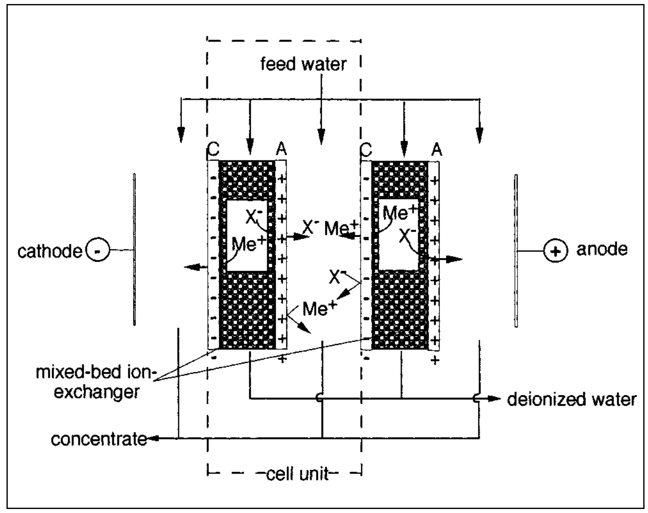


Figure 10. Electrodeionization process.

Spiral-type tubular membrane modules involve flow around a curved tube at a sufficiently high velocity so as to produce centrifugal instabilities and secondary flow from the membrane surface to the center of the tube. This phenomenon is referred to as Dean flow or Dean vortices, and results in a substantial increase in flux in micro- and ultrafiltration of colloidal suspensions and macromolecular solutions compared to feed flow in straight tubular membranes at identical feed flow velocities. However, higher production costs of the spiral-type membrane modules have so far limited any large-scale industrial application.

Development of novel membrane processes and applications

A number of novel membrane processes have been studied, both on a laboratory and on a pilot-plant scale, and new applications in the biomedical and food industry have been identified. Membrane reactors, hybrid, and integrated membrane processes have gained increasing attention as efficient techniques in the chemical and petrochemical industry, in biotechnology, and in water and wastewater treatment.

Electrodeionization and the Use of Bipolar Membranes. Electrodeionization is used for the production of deionized water of high quality by combining conventional ion-exchange techniques with electrodialysis. The principle of the process is illustrated in Figure 10. A mixed-bed ion-exchange resin is placed into the diluate cell of a conventional electrodialysis cell unit. The resin increases the conductivity in the cell substantially and, at very low salt concentrations in the feed solution water, is dissociated at the contact point of the cation- and anion-exchange resin beads, generating protons and hydroxide ions that further replace the salt ions in the resins. The result is completely deionized water as the product. The process can be operated continuously without chemical regeneration of the ion-exchange resin. The only disadvantage of the process is the relatively poor current utilization, which can, however, be tolerated in most applications.

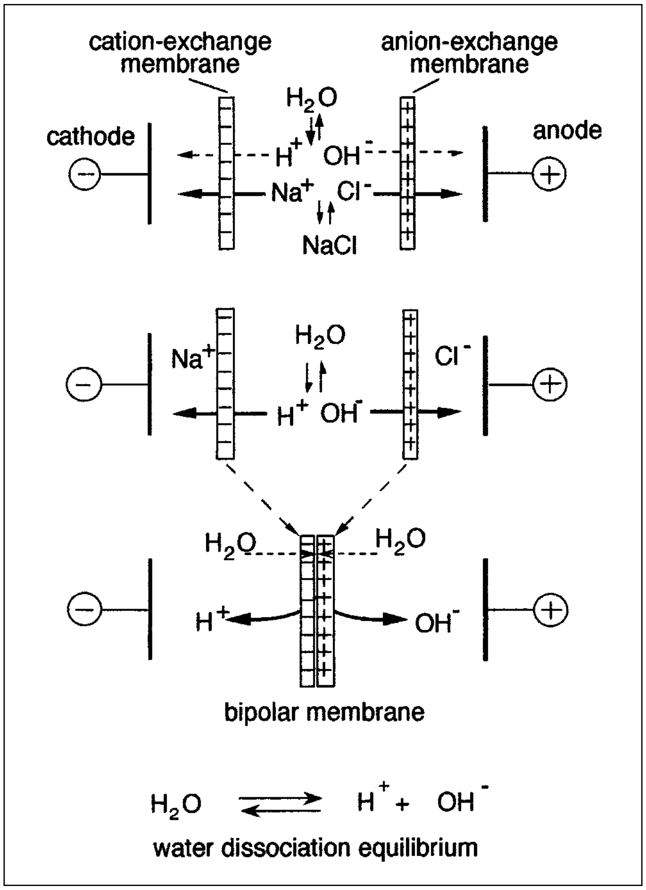


Figure 11. Principle of electrodialytic water dissociation in bipolar membranes.

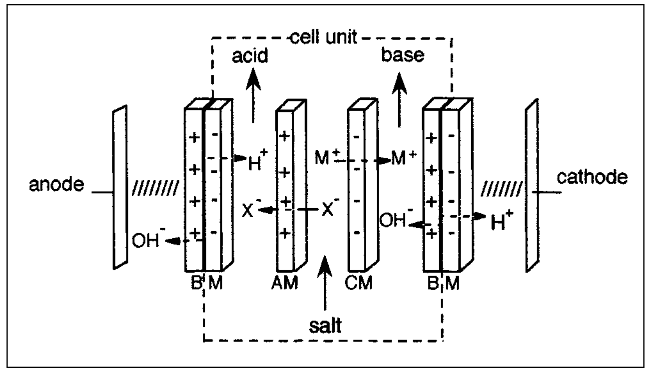


Figure 12. Principle of electrodialytic production of acids and bases from the corresponding salts with bipolar membranes.

Bipolar membranes are used today in combination with regular ion-exchange membranes for the production of acid and bases from the corresponding salts in a process referred to as electrodialytic water dissociation. The process and the structure of a bipolar membrane is illustrated in Figure 11, which shows a bipolar membrane consisting of a cation- and an anion-exchange layer arranged in parallel between two electrodes.

If an electrical potential difference is established between the electrodes, charged species are removed from the interphase between the two ion-exchange layers. When all salt ions are removed from the solution between the two ion-exchange membranes further transport of electrical charges can be accomplished only by protons and hydroxide ions, which are available in a concentration of about 1×10^{-7} mol/L. Protons and hydroxide ions removed from the interphase between the cation- and anion-exchange membranes are replenished due to the water dissociation equilibrium. In a practically used bipolar membrane, the cation- and anion-exchange layers are laminated together, keeping the distance between the two layers as small as possible, and the water consumed in the interphase is supplied by diffusion from the outside solutions.

When bipolar membranes are combined with cation- and anion-exchange membranes, as illustrated in Figure 12, acids and bases can be produced from the corresponding salts. In this process three separate flow streams are necessary: the salt solution, and the produced acid and base. Thus, a cell unit consists of three individual cells. As in electrodialysis, up to 100 cell units can be stacked between two electrodes. Electrodialytic water dissociation is a very energy efficient way to produce acids and bases from the corresponding salts. However, there are still severe problems, such as salt leakage into the products and low current utilization at high concentrations of the acids and bases.

Membrane contactors. In most membrane processes the membrane acts as a selective transport barrier. In membrane contactors the membrane functions as a barrier between two phases that avoids mixing but does not control the transport rate of different components between the phases. Membrane contactors typically utilize porous capillary membranes in a shell-and-tube device. The membrane pores are sufficiently small so that capillary forces prevent direct mixing of the two phases. Membrane contactors can be used for separation of two liquids or a liquid and a gas mixture. A key advantage of membrane contactors is a large mass-transfer area in a relatively small device. A typical large-scale application of a liquid/gas contactor is the removal or delivery of dissolved gases from or to a liquid. One example is the blood oxygenation during open-heart surgery. Another example is the removal of oxygen during the production of ultrapure water. Another type of gas/liquid contactor that applies in the liquid-phase silver nitrate as a selective carrier component is used for the separation of olefin/paraffin gas mixtures. The principle is depicted in Figure 13, which shows the process for the separation of ethylene and ethane. Two contactors are used in the process. One functions as an absorber to remove ethylene from pressurized gas mixture into a silver nitrate solution, and the other as a stripper to remove the ethylene from the silver nitrate solution into a low-pressure ethylene gas stream.

Membrane reactors. A membrane reactor is a device that utilizes the properties of a membrane to improve the efficiency of chemical or biochemical reactions. Various forms of membrane reactors are applied mainly in catalytic and enzymatic reactions. In the most simple form of a membrane reactor the membrane is used as a contactor that separates the catalyst from the reaction medium. The reactants diffuse from the reaction medium through the membrane to the catalyst, and the reaction products diffuse back into the reaction

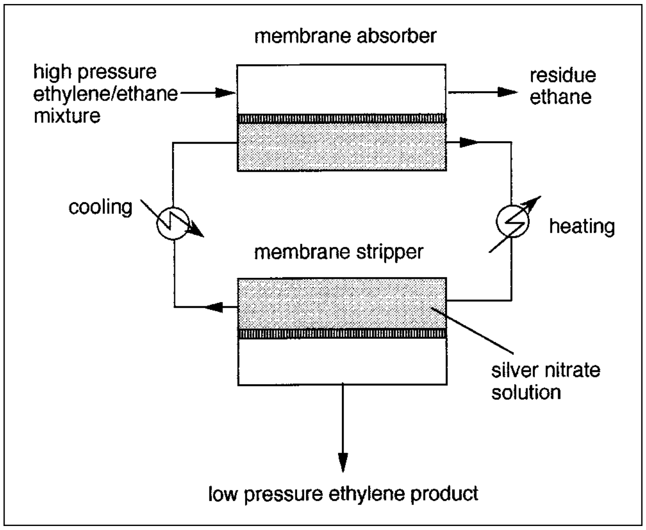


Figure 13. Ethylene/ethane separation process using two membrane contactors.

medium. The membrane merely provides a large exchange area between the catalyst and the reaction medium, but performs no separation function. This type of membrane reactor is illustrated in Figure 14a. It is often used in cell culture and fermentation processes such as the enzymatic degradation of pectin in fruit juice.

In the second type of membrane reactor the membrane shows the selective mass-transport properties, and is used to shift the equilibrium of a chemical reaction by selectively removing the reaction products. This type of membrane reactor is illustrated in Figure 14b. It is used, for example, in dehydrogenation or oxygenation reactions such as the dehydrogenation of *n*-butane.

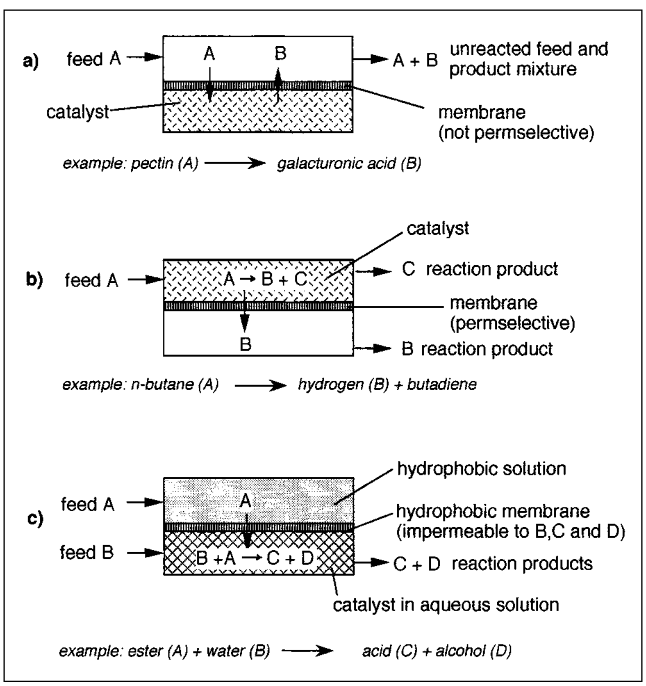


Figure 14. Three types of membrane reactors.

(a) Membrane applied as contactor, (b) membrane applied as selective barrier, and (c) membrane used as contactor between a hydrophobic and hydrophilic phase and as selective barrier permeable to the reactant only.

The third type of membrane reactor combines the membrane contactor and separation function. This type of membrane reactor is illustrated in Figure 14c. It can be used, for example, in enzyme catalyzed deesterification reactions.

Membrane reactors can be and are already used in many processes, such as the continuous fermentation of ethanol or aceton/butanol from food-processing waste. Another application is the dehydrogenation of hydrocarbons for the production of hydrogen. By removing hydrogen selectively from the reactor, the reaction equilibrium is shifted and a higher degree of conversion is achieved. Since these reactions are carried out at 300 to 500°C, the membranes used in this reaction should not only have a high permeation selectivity for hydrogen but must also be stable at elevated temperature. In the petrochemical industry this is true also for most catalytic membrane reactors with potential applications in hydrogenation and oxidation reactions.

Since biological and enzymatic reactions are generally carried out at ambient temperature, polymer membranes with the appropriate permselectivity are used in membrane bioreactors. Most reactions in petrochemical processing are carried out at an elevated temperature, and the membranes used in these reactions must have high thermal stability in addition to the required permselectivity and are prepared from inorganic materials that are generally not as readily available and are more costly than polymer membranes.

Integrated Membrane Processes. The term *integrated membrane process* refers to the integration of one or more membrane processes in a multistep production process. The coupling of a fermentation process with downstream processing by integrating various membrane processes in the overall multistep production procedure is a typical example of integrated processing. The main goal of integrated membrane processes is to increase the productivity and the yield of the product from the substrate. In addition the process design can often be simplified, the cell density increased, and the overall production cost reduced. Today integrated membrane processes are mainly used in the food and drug industry. There are, however, a large number of potential applications in the chemical industry and in water and wastewater treatment.

Synthetic Membranes in Medical Applications. Biomedical applications are by far the most relevant use of synthetic membranes. Membranes are used in medical devices such as hemodialysers, blood oxygenators, and controlled drug-delivery systems. These membrane-based medical devices have experienced few fundamental changes over the past decade, with most technical effort focused upon cost reduction. There is, however, a substantial effort focused on the development of the membrane for the next generation of artificial organs, such as the artificial liver or artificial pancreas. In these devices, as in other novel vehicles for the delivery of cell and gene therapy, synthetic membranes are combined with living cells to form so-called biohybrid organs. In this application the membrane acts mainly as a barrier that isolates living cells from the host defense mechanisms of the human body. Such immunoisolated cells are free to synthesize and secrete low-molecular-weight therapeutic substances. Immunoisolatory devices involving relatively small amounts of xenogeneic cells in selected implant sites are applied in the therapy of Parkinson's disease and are currently tested in clinical trials.

Further recent development

Significant progress has also been made in recent years in the development of inorganic membranes, which until recently were used mainly in micro- and ultrafiltration applications where polymeric membranes failed because of unsatisfactory chemical and thermal stability. Today, the selectivity of inorganic membranes has been significantly improved, for example, by incorporating zeolites. These membranes have a large potential for the separation of isomers such as iso- and *n*-pentane.

Polymeric membranes with specific transport properties to be used in the separation of enantiomers have been developed recently. Affinity membranes that can be applied to remove certain toxic components from blood streams or biological fluids or that can be used in diagnostic devices are currently under development.

Another potential large-scale application of ion conductive membranes is their use as separators in fuel cells and batteries. In particular, a proton-conductive polymer electrolyte with negligibly low methanol permeation, to be used in the methanol direct-conversion fuel cell, is of great interest to the automotive industry.

Research Needs in Membrane Science and Technology

For membrane science and technology also to be attractive in the future there is a need for both fundamental as well as applied research to improve today's available membranes and membrane processes. Considering the versatility of the biological membranes, a multitude of new applications, especially in the biomedical area and in energy conversion, seem possible. But in addition to new and improved membranes and membrane processes there is an urgent need for application know-how, which often requires the cooperation of various scientific disciplines such as chemistry, life science, and process engineering. There is also a need for education in membrane science and technology. While other unit operations are taught at almost all technical schools, no courses in membrane science and technology are offered at most universities.

Future of Membrane Science and Technology

The market for the state-of-the-art membrane products will most likely continue to grow with an annual rate of about 8% per year for the next couple of years and in the year 2000 should reach about 5 billion US$. The market of the membrane-based industry, which includes modules, peripheral equipment, and systems, is an order of magnitude higher. However, the commercial success is only one indicator for the importance of membrane science and technology. In many applications membranes are key components without which certain products or processes could not be achieved, although the commercial value of the membranes in the application may be rather low.

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