Membrane Materials for Addressing Energy and Environmental Challenges

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Abstract

Our modern society must solve various severe problems to maintain and increase our quality of life: from water stress to global warming, to fossil fuel depletion, to environmental pollution. The process intensification (PI) strategy is expected to contribute to overcoming many of these issues by facilitating the transition from a resource-intensive to a knowledge-intensive industrial system that will guarantee sustainable growth. Membrane operations, which respond efficiently to the requirements of the PI strategy, have the potential to replace conventional energy-intensive separation techniques, which will boost the efficiency and reduce the environmental impact of separations as well as conversion processes. This work critically reviews the current status and emerging applications of (integrated) membrane operations with a special focus on energy and environmental applications.

INTRODUCTION

The past century has been characterized by resource-intensive industrial development, particularly in some Asian countries because of population growth; a significant prolongation of life expectancy; and an overall increase in living standards and quality of life. These positive aspects of our recent history are combined, however, with the appearance of related problems such as water stress, global warming, fossil fuel depletion, and environmental pollution. These negative aspects are related to the speed at which the social transformations have occurred and to the inadequate introduction of new strategies to control and to minimize the negative aspects of industrial development worldwide.

To minimize and overcome these problems, the need to achieve knowledge-intensive industrial development is well recognized. This will permit the transition from an industrial system based on quantity to one based on quality. Human capital is increasingly becoming the driving force of this socioeconomic transformation, and meeting the challenge of sustainable growth relies on the use of advanced technologies.

Process intensification (PI) has been suggested as the best answer to the problems characterizing the world today and in the near future. The PI strategy consists of innovative equipment design and process development methods that are expected to produce substantial improvements in manufacturing and processing that will decrease production costs, equipment size, energy consumption, and waste generation as well as improve process efficiency, remote control, information fluxes, and process flexibility (1, 2). Van Gerven & Stankiewicz (3) have developed a fundamental vision of PI that encompasses approaches in the spatial, thermodynamic, functional, and temporal domains, which are used to realize four basic principles of PI from molecular to meso- and macroscale (**Figure 1**).

Separation processes are used intensively in nearly all industrial processes. Approximately 40–50% of the energy use in the major commodity-producing industries is utilized in separations, but most of these are still carried out by traditional thermally driven processes characterized by elevated energy consumptions (4). The necessity to realize sustainable growth through more rational and efficient energy use calls for additional and substantial developments in separation systems.

Membrane operations respond efficiently to the requirements of PI strategy because they use intrinsically cleaner and more energy-efficient separation routes when compared with conventional separation technologies. Membrane operations have well-established applications in many industrial processes ranging from water desalination to wastewater treatments, from agro-food product formulation to chemical production. Various membrane operations are available for a wide spectrum of industrial applications. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), gas separation (GS), pervaporation (PV), dialysis (D), and electrodialysis (ED) are only some of the best-known membrane unit operations. Integration of various membrane operations in the same process or in combination with conventional separation units in many cases yields better performance in terms of product quality, plant compactness, environmental impact, and energy use (5). Moreover, the availability of new membrane operations, such as membrane crystallization (MCr), is widening the skyline of membrane technology.

In many fields membrane operations are already recognized as among the best available technologies able to contribute to sustainable development. A typical example is membrane bioreactors (MBRs) for wastewater treatments. The capacity of installed MBR plants is increasing continuously, even though fouling problems still limit their performance and their costs need to be further reduced (6). Moreover, many large-scale applications of membrane operations are limited by the lack of membrane materials with appropriate properties. This is evident, for example, in some GS

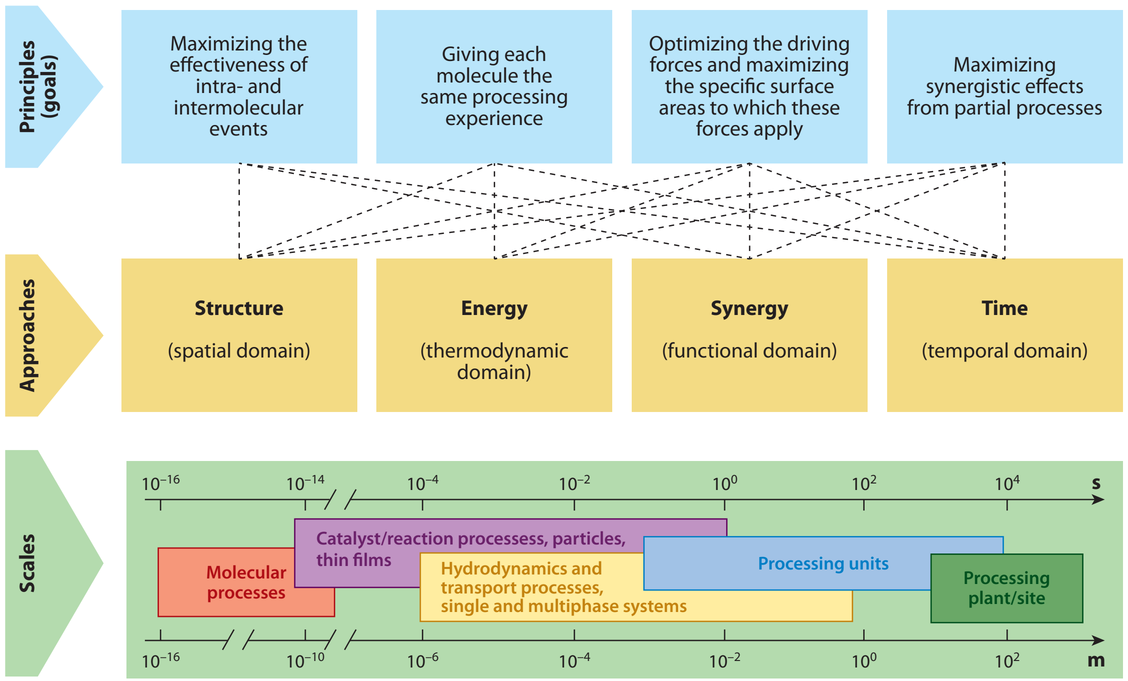

Figure 1

A fundamental view of process intensification for reaction and separation systems. Reproduced from Reference 3.

applications (7, 8) in which the challenge is to obtain membranes able to combine high selectivity with high permeability as well as appropriate long-term durability and acceptable costs. These materials need to be tailored to obtain nanostructured membranes with improved performance. Use of computational methods to obtain a better understanding of the molecular-level transport mechanism is key for the development of new materials and advanced membrane structures (9, 10).

Interestingly, many of the membrane operations realized today at an industrial level already exist in biological systems, in which biological membranes play a central role in a large variety of very efficient separation processes and chemical transformations as well as in energy, mass, and information transfer. Numerous parallels between biological and artificial membrane systems are possible, including: (*a*) cellular osmosis and pressure- and osmotically driven membrane processes [RO, forward osmosis (FO), pressure-retarded osmosis (PRO)]; (*b*) blood filtration in the kidney and artificial blood filtration; (*c*) heat and mass transport through the skin and membrane contactor (MC) technology; and (*d*) bioelectricity of biological membranes and energy conversion in polymer electrolyte membrane fuel cells (PEMFCs).

However, artificial membranes are far from being able to reproduce many features of biological membranes, including their complexity and efficiency, their integration of various functionalities, their capability to repair damage, and their ability to maintain their specific activities for long times, avoiding fouling problems and degradation of the various functions, and keeping the system alive. This work gives a critical appraisal of the current status and emerging applications of (integrated) membrane operations, with a special focus on energy and environmental applications. It highlights some of the latest advances in membrane material research and provides a look at the major challenges for further development of membrane technology.

MEMBRANES FOR ENERGY APPLICATIONS

The growing energy demand, combined with the need for fundamental changes in energy production to enable sustainable development and reduction of dependence on fossil fuels, is the driving force of the impressive research efforts in membrane operations in energy applications. The most prominent and popular example is fuel cells (FCs). FCs, in particular PEMFCs, are considered to be among the most promising clean energy conversion systems for automotive as well as domestic applications and portable devices, and they are currently reaching the threshold of commercialization. However, interest is increasing in new membrane operations able to use green energy sources, such as energy conversion from salinity gradients by FO, PRO, and reverse electrodialysis (RED). The following sections provide a short overview of the main achievements and limitations of PEMFC, FO, PRO, and RED technologies.

Polymer Electrolyte Membranes for Energy Conversion in Fuel Cells

FCs are electrochemical devices for chemical energy conversion into electricity. They are characterized by high efficiency and low environmental impact, and they have a lot of potential to reduce the use of fossil fuels. Unlike the classical battery, FCs do not store energy within chemicals internally; rather, they use a continuous supply of the fuel from an external storage tank. In addition, although the electrodes within a battery react and change as the battery is charged or discharged, in an FC the electrodes are catalytic. FCs have many advantages in comparison with traditional energy conversion systems: zero or near-zero emissions, low noise emissions, reliability and simplicity, modularity, and easy up- and downscaling. Moreover, because they do not convert thermal to mechanical energy, they are not subject to the Carnot efficiency limit typical of an heat engine (e.g., steam or gas turbine) and are characterized by high energy efficiency (11) (**Table 1**).

The primary components of a FC are the anode, the cathode, and the ion-conducting electrolyte. In an FC the selective transport of ions through an electrolyte occurs in combination with a redox reaction. In a PEMFC the electrolyte is a polymer electrolyte membrane (PEM) that allows the transport of protons (but not electrons) from the anode, where they are produced during the oxidation of the fuel, which is typically H_2 (H_2-PEMFC) or methanol (DM-PEMFC), to the cathode, where the protons react with O_2 to produce water. The properties required for PEMs are high proton conductivity, no electron conductivity, low permeability to the reagent species (H_2 and O_2 in H_2-PEMFC; methanol and O_2 in DM-PEMFC), and appropriate chemical, thermal, and mechanical stability.

The flow of ionic charges through the PEM is balanced by the flow of electrons through the outside circuit, which produces electrical power. The only secondary products in the overall

Table 1 Typical ranges of energy efficiencies obtained using fuel cells and heat engine systems in electric power plant and transportation applications (data from Reference 11)

	Energy efficiency	
Application	Heat engine	Fuel cell
Electric power plant	30–37%[a]	70–80%[b]
Transportation	20–35%[c]	40–50%[d]

[a] Combustion engine.

[b] Solid oxide fuel cell (SOFC) including heat recovery.

[c] Internal combustion engine.

[d] Polymer electrolyte membrane fuel cell or SOFC.

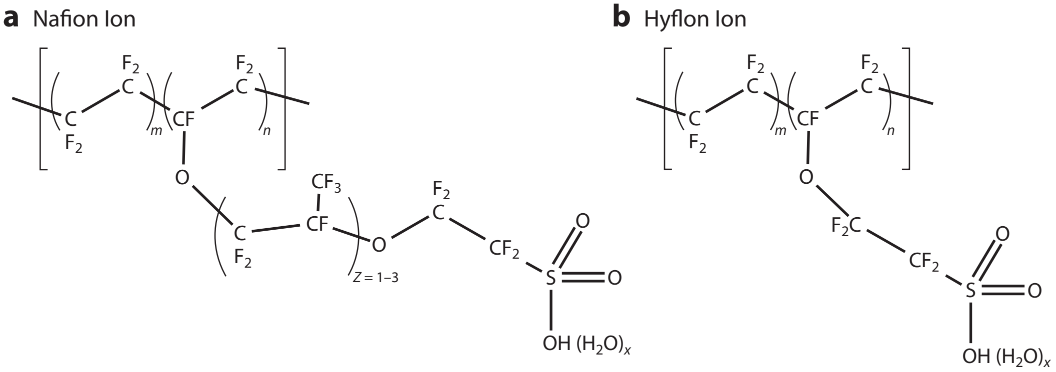

Figure 2

Chemical formulas of the (*a*) Nafion and (*b*) Hyflon Ions.

reaction are water, heat (eventually recoverable), and CO_2, if the fuel contains carbon (methanol, ethanol, etc.). The low operating temperatures (50–130°C) and the high power densities (400–1,000 W kg^{-1}) of PEMFCs make them ideal for automotive applications, distributed power generation, and portable electronic devices (12).

Although PEMFCs recently passed the demonstration phases and have reached a partial commercialization stage (13), many issues remain to be solved, including the high investment cost and problems related to fuel production and storage. The large-scale application of this technology requires additional efforts to develop new materials with improved properties and reduced cost for the FC components, starting with the PEM. The membranes in a PEMFC stack may account for as much as 30% of the total material cost (14). PEM durability also hinders the full commercialization of PEMFCs. Despite the promising results obtained on the laboratory scale, most of the PEMs available today for FCs are far from meeting the commercial durability targets for stationary and transportation applications (lifetimes greater than 40,000 and 5,000 hours, respectively) (15).

Mechanical and chemical failures often reduce the long-term performance and durability of the membrane electrode assemblies (MEAs, which are composed of the PEM sandwiched between porous electrode layers and a catalyst layer present at the interfaces between membrane and electrode). While operating in a FC, membrane swelling or shrinking owing to changing relative humidity can induce fractures in the MEA; moreover, radical species produced at the electrodes in the presence of crossover phenomena can attack the polymer.

Currently, the PEMs most commonly used in PEMFCs are made of perfluorosulfonic acid (PFSA) polymers such as Nafion (Du Pont; **Figure 2*a***), Aciplex (Asahi Chemical), Flemion (Asahi Glass), and Gore-Select (Gore and Associates) (16). These polymers are known as long-side-chain (LSC) perfluoro-ionomers to distinguish them from the so-called short-side-chain (SSC) perfluoro-ionomers initially proposed in the 1980s by Dow (under the trade name Dow Ionomer) and more recently by Solvay Solexis (under the trade name Hyflon Ion; **Figure 2*b***) (17). SSC ionomers are characterized by a shorter pendant group carrying the ionic functionality, higher crystallinity, and a higher glass transition temperature (T_g) than LSC ionomers at a given equivalent weight (18).

Among the various PFSA polymers developed, Nafion membranes still dominate the PEMFC market because of their high proton conductivity and elevated chemical, thermal, and mechanical stability. However, Nafion has high costs (US\$600–1,200/m^2) (19) that limit its practical applications. Nevertheless, importantly, the cost depends on the market volume, and future widening of the PEMFC market will probably lower the prices of PEMs, including Nafion.

Furthermore, Nafion membranes have elevated methanol and water permeabilities that reduce their performance. The methanol crossover during operations in a DM-PEMFC can lead to significant decreases in the overall performance in three main ways: poisoning of the cathode catalyst, reduction of the fuel utilization efficiency, and decrease of the electrode potential owing to methanol oxidation at the cathode (20). The excessive hydraulic permeability of the membrane also can have severe consequences for membrane dehydration, with successive loss of conductivity, and cathode flooding, with consequent restriction of oxygen transport through the porous gas diffusion electrode (21).

A further disadvantage of Nafion membranes is the decay in proton conductivity when operated for a long period of time above a critical temperature, which depends on the operating conditions (20, 22). For example, when operating, at 85% relative humidity, a Nafion 117 membrane clamped between the electrodes at a pressure of 130 N cm^{-2}, the critical temperature is approximately 95°C (23). Below this value, the proton conductivity increases with temperature; above this temperature, a strong decrease in the proton conductivity is observed. This decay is associated with the membrane dehydration processes favored at temperatures greater than the T_g of the polymer. For dry Nafion, the T_g is reported to be between 100 and 110°C, but it decreases in the presence of water, which has a plasticizing effect.

Moreover, the formation of a sulfonic anhydride by the condensation of two SO_3H groups of the polymer, accompanied by the loss of a water molecule, was also observed (23, 24). The increase in polymer chain mobility above T_g favors the cross-linking process because it increases the potential to have two sulfonic groups at appropriate distance to react. The loss of performance of Nafion membranes at high temperature and pressure is also related to irreversible morphology changes in the polymer that depend not only on the operating conditions (temperature, humidity, pressure) but also on the thermal history of the sample (25, 26). Despite this, the use of relatively high temperature (>80°C) is fundamental to improve the reaction kinetics and reduce the poisoning by CO of the Pt-based catalysts used in PEMFCs (CO covers the catalyst to prevent the H_2 reaction; as a consequence, the CO content in the fuel should be <10 ppm). The effect is temperature dependent and can be partially suppressed at elevated temperature (27).

In the past decades, the development of PEMs with improved properties for long-term FC operation has received much attention. In addition to perfluoropolymers, partially fluorinated, nonfluorinated hydrocarbon, nonfluorinated aromatic, and acid-base blend membranes have been proposed. Various other reviews give an overview of the progress made in the development of proton-conducting polymer materials for PEMFCs (28–32).

In addition to the synthesis of new high-performance electrolyte polymers, a promising strategy for the development of PEM materials is the realization of hybrid functional materials in which more than one phase coexist to have a synergistic effect on ionic transport and stability as well as to reduce crossover problems. Other possible solutions include morphology control for better water channel formation and proton transport without excessive water swelling as well as surface modification of membranes for better adhesion with the electrodes and for control of interfacial phenomena. A deeper knowledge of existing materials might also contribute to overcoming the existing limits of PEMs. Interesting examples are the investigation of the evolution of permanent deformations (or memory) in Nafion membranes with changes in temperature, relative humidity, and time as well as research on the role of polymer memory in improving the stability of Nafion conductivity at temperatures greater than 90°C by a suitable combination of hydrothermal/thermal treatments that can modify the polymer conformation (26). On the basis of an osmotic model, an index (n_c, Equation 1) proportional to the counter-elastic force of the polymeric matrix (the force

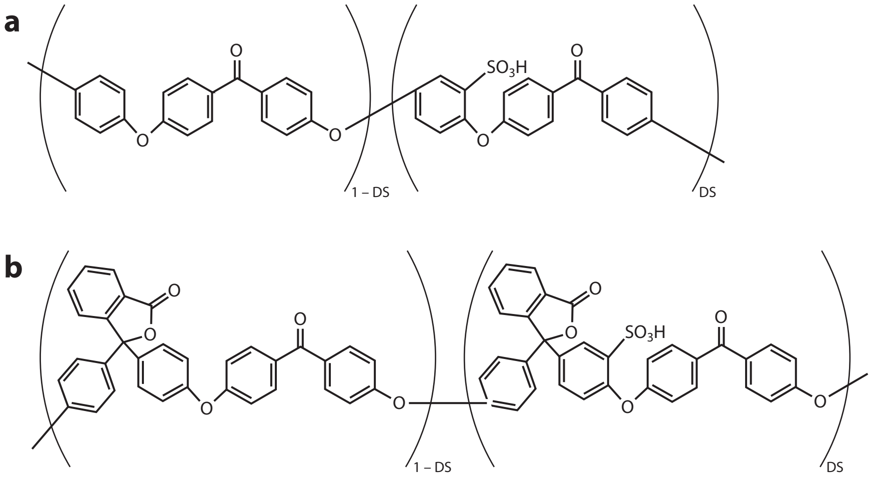

Figure 3

Repeating unit of the (*a*) sulfonated polyetheretherketone (SPEEK) and (*b*) SPEEK with Cardo (SPEEK-WC) polymers [degree of sulfonation (DS) was assumed to be ≤1].

generated by the polymer that opposes the enlargements provoked by water uptake) has been derived, and the overall effect of a given hydrothermal/thermal treatment has been evaluated by the variation of n_c (33),

$$n_c = \frac{100}{\lambda - 6}, \qquad 1.$$

where λ is the number of water molecules absorbed per sulfonic group.

Among the different nonfluorinated polymers investigated as possible alternatives to expensive PFSA membranes, sulfonated aromatic polymer (SAP) membranes, such as those made of sulfonated polyetheretherketones (SPEEKs, **Figure 3*a***), present particularly interesting properties for PEMFC applications (22, 34, 35). Although the presence of the fluorinated backbone induces a higher acidity of the sulfonic group in PFSA membranes and, in general, a higher proton conductivity in comparison with the sulfonic group in SAP membranes (16), SAP membranes have lower costs (30). Another interesting aspect of the SAP membranes is their lower water and methanol permeability compared with PFSA membranes. The different behaviors can be explained by differences in the microstructures of these systems (16).

In PFSA membranes the extremely high hydrophobicity of the perfluorinated backbone is combined with the high hydrophilicity of the sulfonic acid side groups. In the presence of water, the sulfonic groups aggregate to form hydrophilic domains connected by larger and less branched channels compared with those present in SAPs (16). As observed by small angle X-ray scattering experiments, in SAP membranes the separation into a hydrophilic and a hydrophobic domain is less pronounced because of the minor hydrophobicity of the backbone and the less acidic and polar sulfonic group (16). In SAP membranes these groups are attached directly to the stiff aromatic polymer backbone, and this does not allow a clear microphase separation as in PFSA, in which the sulfonic acid groups are attached to flexible side chains. As a consequence, the polymer microstructure is less flexible and offers more resistance to water and methanol transport (16). For these reasons the water and methanol diffusion coefficients of the SAP membranes are usually lower compared with those of PFSA (16, 36).

The SPEEK polymer is usually prepared by sulfonation of polyetheretherketone (PEEK), a semicrystalline thermoplastic polymer. PEEK is used in a wide range of industrial applications, but it is insoluble in common organic solvents under mild conditions and therefore not suitable for the preparation of membranes by the casting technique (37). Unlike native PEEK, SPEEK is amorphous and soluble in many organic solvents. However, the low solubility of the starting material generally complicates the sulfonation process, which usually is carried out using concentrated sulfuric acid at room temperature for long reaction times. The sulfonation reaction is initially a heterogeneous process and, as a consequence, it produces different fractions of polymer with a variable degree of sulfonation (DS) (34).

Unlike classical PEEK, a modified PEEK known as PEEK-WC or poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxa-*p*-phenylene-oxy-*p*-phenylene) (**Figure 3*b***), is amorphous and soluble in numerous organic solvents with medium polarity (e.g., chloroform, dichloromethane, dimethylsulfoxide, dimethylacetamide, dimethylformamide, 1-methyl-2-pyrrolidinone), whereas it is not soluble in water and alcohols. PEEK-WC has a lactonic group called the Cardo group (WC in the polymer name means with Cardo), which prevents the crystalline organization of the polymer chain; as a consequence, PEEK-WC is amorphous and suitable for the preparation of membranes by the casting technique (38). Moreover, PEEK-WC has a high T_g (222°C) and good chemical, thermal, and mechanical stability (39). Membranes with excellent transport properties for gases and liquids (40, 41) can be obtained with this polymer.

Moreover, PEEK-WC properties can be modified by introducing specific chemical groups on the polymer chain. For example, reaction with chlorosulfonic acid at room temperature introduces a sulfonic group on the aromatic ring, which provides the polymer SPEEK-WC with ion exchange capacity (42). The polymer DS can be modulated by changing the reaction time (42). SPEEK-WC is a promising nonfluorinated material for application in PEMFCs that is suitable for the preparation of membranes by casting and solvent evaporation techniques (43). The DS of the polymer influences the membrane properties, in particular the ion exchange capacity and the proton conductivity, both of which improve with increasing DS.

SPEEK-WC membranes offer a higher resistance to water vapor and methanol vapor transport than commercial Nafion 117 membranes. Also, the H_2 and O_2 pure gas permeabilities of SPEEK-WC membranes are lower in comparison with Nafion (23). These results justify the conclusion that fewer crossover problems may occur in PEMFCs operating with SPEEK-WC membranes compared with PEMFCs operating with Nafion. The lower permeability of the SPEEK-WC-based membranes is due to their lower diffusion coefficients, which are caused by the higher stiffness of the aromatic polymer chains of SPEEK-WC with respect to those of Nafion (23). Functional additives also have been heterogenized in SPEEK-WC membranes to improve their properties for applications in PEMFCs.

Hybrid membranes have been prepared by dispersing amorphous zirconium phosphate sulfophenylenphosphonate [$Zr(HPO_4)(O_3PC_6H_4SO_3H)$, hereafter Zr(SPP)], in the SPEEK-WC matrix (44). The membranes obtained are characterized by a homogeneous distribution of the inorganic filler. Zr(SPP)-loaded SPEEK-WC membranes exhibit a significantly lower degree of swelling degree in water and methanol compared with the polymeric membranes without the filler.

Inorganic proton conductors (heteropolyacids, hereafter HPAs) have been also dispersed into the membrane casting solution to prepare nano-hybrid membranes (23). The embedding of the inorganic HPAs, in particular silicotungstic acid ($H_4SiW_{12}O_{40}\cdot nH_2O$), in SPEEK-WC membranes enhances the proton conductivity because the HPAs, which are uniformly distributed on the nanometer scale, interconnect better with the ionic cluster of the polymeric matrix to provide a favored pathway for proton hopping (23). Although all of the composite membranes exhibited lower resistance to proton transport over the entire range of temperatures investigated, proton conductivity does not increase linearly with additive loading (23). These results provide evidence for the critical role of the microstructural organization of the hybrid membranes (polymer and inorganic additive) in the proton transport mechanism.

The water and methanol vapor permeabilities of the composite membranes are similar to those of neat polymeric membranes with similar DS. In fact, the good adhesion between the inorganic particles and the polymer phase allows the formation of hybrid systems without pinholes or defects. The gas permeability of the composite membrane is slightly lower than that of the pure polymeric membranes because the fillers act as an impermeable barrier to uncharged species.

Membrane Operations for Energy Conversion from Salinity Gradients

The importance of clean and sustainable energy sources is evident considering the well-known drawbacks of fossil fuels such as emissions of greenhouse gases and depletion of finite resources. An alternative source of energy is salinity gradient power (SGP). SGP is based on the chemical potential difference between concentrated and dilute salt solutions. The conversion of the osmotic energy of salt solutions into mechanical or electrical energy can be realized by osmotically driven membrane operations such as FO, PRO, and RED (**Figure 4**).

The principles of FO have been known for many decades (it is the classical osmosis); however, no large-scale applications have yet been realized (45). In FO two solutions of different concentrations are kept in contact by a semipermeable membrane that allows the solvent (water) to permeate and retains the solute (dissolved salts). The difference in chemical potential between the two solutions is the driving force of water transport from the dilute solution to the more concentrated solution (or draw solution) (**Figure 4**). Unlike RO and other pressure-driven membrane operations, FO does not require high pressure for separation; as a consequence, it is characterized by lower energy consumption. The FO process also offers better performance with respect to fouling and scaling on the membrane surface (46). However, before FO can reach a commercialization stage, it is

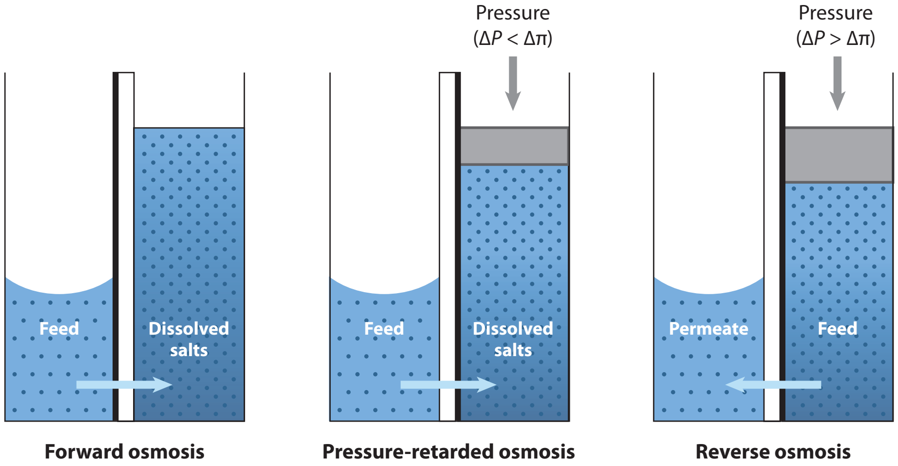

Figure 4

Water flow in forward osmosis (FO), pressure-retarded osmosis (PRO), and reverse osmosis (RO). $\Delta\pi$ is the osmotic pressure difference between the two solutions; ΔP is the hydraulic pressure applied in PRO and RO. Membrane orientation is indicated in each system by the thick black line, which represents the membrane-dense layer. Figure reproduced from Reference 48.

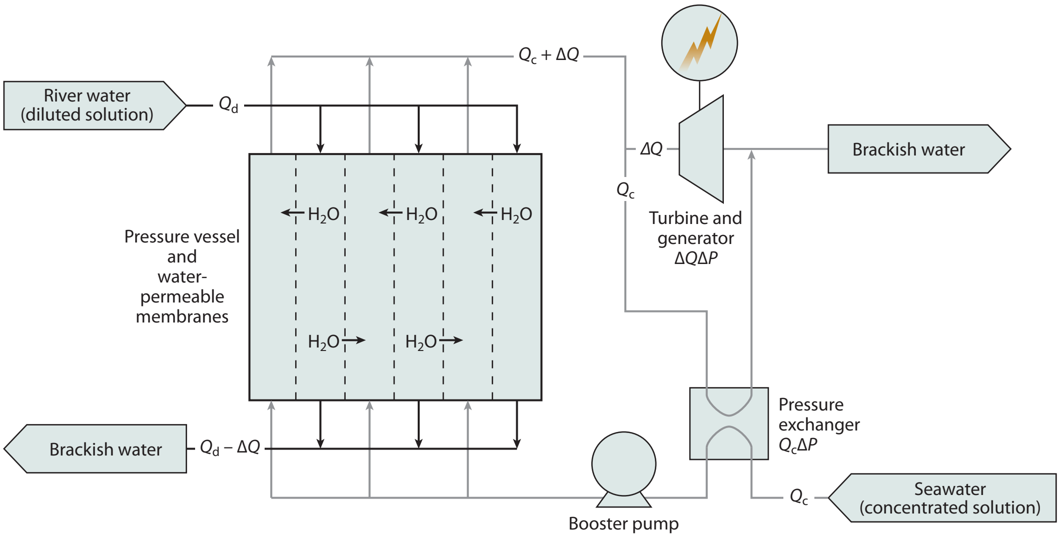

Figure 5

Conceptual representation of an energy conversion scheme using pressure-retarded osmosis; Q is the volumetric solution flow (m^3 s^{-1}), ΔQ the transported amount of water per time through the membranes (m^3 s^{-1}), and ΔP the applied hydrostatic pressure difference between both solutions (Pa). The power generated by means of a turbine and generator is $\Delta Q - \Delta P$ (W). Figure reproduced from Reference 52.

necessary to develop new membranes and supports specifically designed for FO that are able to reduce internal concentration polarization. In addition, more efficient recovery of the draw solutions employed is a necessity (47).

PRO is another osmotically driven membrane process that uses a membrane to separate two solutions with different concentrations. If hydrostatic pressure is applied to the concentrated solution, the water transport will be partly retarded, which results in a pressurization of the volume of transported water. This pressurized volume can be used to generate electrical power in a turbine (**Figure 5**).

A predictive model that includes the influence of draw solution, feed solution, concentration polarization, and hydraulic pressure on water flux and subsequent power output in PRO was used to determine the optimal membrane characteristics and module configuration (48). The model was tested using results from a bench-scale PRO system employing a flat-sheet cellulose triacetate asymmetric membrane, and experimental data closely matched model predictions. With the membrane employed, the power density was substantially reduced with respect to the theoretical value owing to severe internal concentration polarization and, to a lesser degree, to reverse salt diffusion. External concentration polarization (accumulation or depletion of solutes near an interface) exhibited a relatively small effect on reducing the osmotic driving force (48).

The model highlights the importance of optimizing the membrane support layer to reduce the internal concentration polarization, which reduces the effective osmotic pressure difference across the membrane. The use of a very thin membrane support layer with low tortuosity and high porosity can allow a substantial improvement (up to 70%) in the power density output (48). Moreover, the hydrophilic properties of the membrane support layers are critical for the flux performance in osmotically driven membrane processes (PRO and FO) (49). Insufficient support layer wetting of asymmetric membranes, which were designed for pressure-driven membrane processes but are also employed in osmotically driven membrane processes, not only favors internal

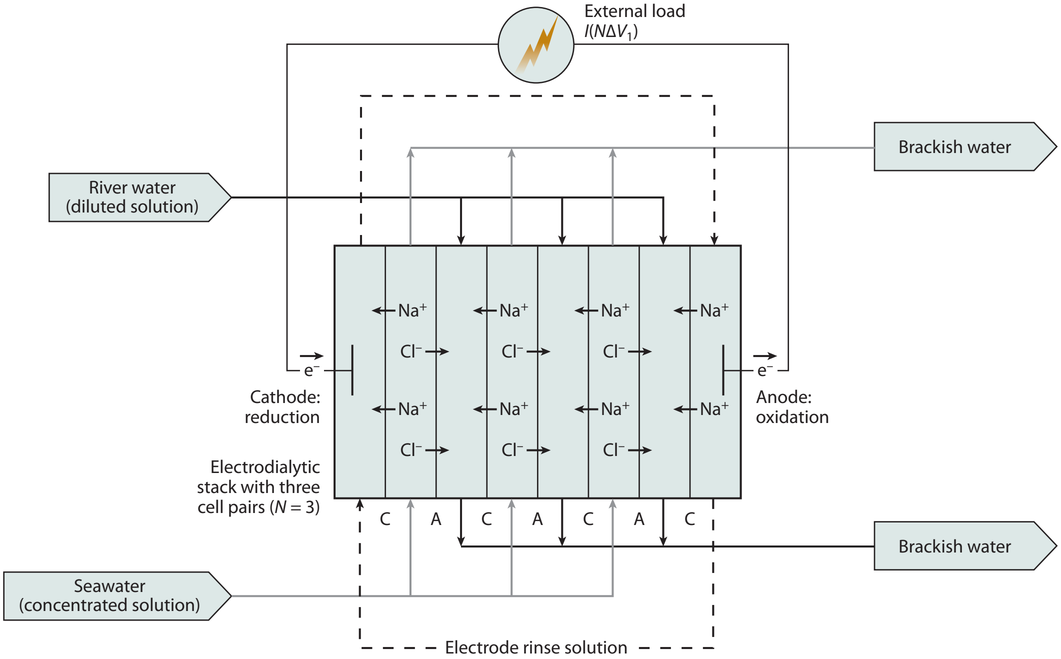

Figure 6

Conceptual representation of an energy conversion scheme using reverse electrodialysis. Abbreviations: A, anion exchange membrane; C, cation exchange membrane; I, the electrical current or transported charge (A); N, the number of cell pairs (in this case $N = 3$); $N\Delta V_1$, the potential difference over the applied external load (V). The power generated is $I - (N\Delta V)$ (W). Reproduced from Reference 52.

concentration polarization phenomena but also disrupts water continuity within the membrane because of the presence of vapor or air trapped in the pores, resulting in a marked decrease in water flux (49). For these reasons the development of membranes and supports specifically designed for FO and PRO is essential before these operations can offer a real challenge to conventional systems.

In RED a concentrated solution (e.g., seawater) and a dilute solution (e.g., river water) flow through a stack of alternating cation and anion exchange membranes (CEMs and AEMs) between a cathode and an anode (**Figure 6**). The chemical potential difference between the two solutions (e.g., 80 mV for seawater and river water) induces a voltage over each membrane (membrane potential), and the total potential of the system is the sum of the potential differences over all membranes. The chemical potential difference activates ion transport through the membranes from the concentrated solution to the dilute solution. Cations permeate through the CEM membrane toward the cathode, and anions permeate through the AEM toward the anode. A redox couple is used at the electrodes to maintain the electroneutrality of the solutions, and electrons are transferred from the anode (where oxidation occurs) to the cathode (where reduction occurs) via an external electric circuit supplying electrical power.

A hybrid RED system using highly concentrated solutions recovered from a seawater desalination plant (based on RO or evaporation) and further concentrated by solar evaporation, and seawater (or brackish water) as the dilute solution, has been proposed (50). Model simulations of this system demonstrate the relevance of parameters such as membrane thickness, feed solution temperature, and dilute solution compartment thickness. These simulations indicate that the development of thin CEMs and AEMs with specific characteristics (resistivity, permselectivity) in an adequate RED stack design is necessary for producing a high RED output, and corrugated membranes or spacers offer viable options in this respect (50).

Various commercially available CEMs and AEMs have been compared in RED applications (51) using a theoretical model (52) that allows the calculation of the maximum power density output using experimental data on membrane permselectivity and resistance. Application of the model to a theoretical system composed of only one membrane showed that the best AEM reached a maximum power density of more than 5 W m^{-2}, whereas the best CEM exhibited a theoretical power density of more than 4 W m^{-2}. According to the model calculations, power densities higher than 6 W m^{-2} could be obtained by using thin spacers and tailor-made membranes with low membrane resistance and high permselectivity that were especially designed for RED (51).

The use of ion-conductive spacers (made using AEM and CEM material) can also increase power generation in RED by eliminating the spacer shadow effect; this occurs when nonconductive spacers are employed, blocking the ionic transport in the stack and thus reducing the effective area available for ionic transport (53). The use of ion-conductive spacers decreases the stack resistance by a factor of two and increases the power density by a factor of three to four compared with the use of nonconductive spacers with the same open area and shape (53). Although the SGP concept was recognized more than 50 years ago (54), many research and development issues, especially those related to membrane properties and costs, still need to be resolved before FO, PRO, and RED are available for large-scale commercial application.

MEMBRANE REACTORS FOR CHEMICAL PRODUCTION AND ENVIRONMENTAL APPLICATIONS

Membrane reactors (MRs) are multifunctional reactors combining a chemical reaction (usually catalytically promoted) with a membrane-based separation. MRs, primarily those employing polymeric membranes for enzymatic reactions or metal membranes for high-temperature reactions, have been investigated since the 1970s. The necessity to realize sustainable growth is driving the increasing worldwide interest in MRs in different fields not only biochemistry and petrochemistry, but also chemical production, environmental remediation, and energy.

Reactive separations respond well to the requirements of the PI strategy, as they combine a reaction with a separation process, not only at the equipment level (multifunctional reactors) but also by introducing functional interrelations between the operations involved to result in improved processes (55). In comparison with other reactive separations (e.g., reactive distillation, reactive adsorption, reactive crystallization/precipitation), MRs use intrinsically cleaner and more energy-efficient separation routes for high-quality products. In numerous cases, membrane separation processes operate at much lower temperature, especially when compared with thermal processes such as distillation. As a consequence, they might provide a solution in the case of limited thermal stability of either catalyst or products. Furthermore, membrane separation processes also can separate nonvolatile components.

The combination of advanced separation and chemical conversion realized in an MR has many advantages in comparison with traditional reactors depending on the specific functions performed by the membrane (56). The selective membrane-based separation and transport of the products and/or the reagents from or toward the reactor can increase the yield and/or the selectivity of some processes. The downstream processing of the products can be substantially facilitated by an appropriate process design in which they are removed from the reaction mixture by means of a membrane (57). Moreover, when a membrane is used to immobilize a homogeneous catalyst, the catalyst recovery, regeneration, and reuse in successive catalytic runs is generally easier than in other heterogeneous catalytic systems.

The membrane can also define the reaction volume (for example, by providing a contact zone for two immiscible phases, as in phase transfer catalysis), thus excluding polluting solvents and reducing the environmental impact of the process membrane (57). However, to have a synergistic combination of the separation and reaction process that yields optimal performance, a multidisciplinary approach to MR design is necessary. In this approach different disciplines, such as chemistry, chemical engineering, membrane engineering, and process engineering, each contribute to the general objective of improved performance in terms of productivity and sustainability. MRs are today accepted as proven technology for many biotechnological applications; however, there is huge potential for these integrated systems in various industrial sectors.

High-temperature inorganic membranes have found many applications in MRs for power generation with CO_2 capture (58). However, significant plant design optimization and membrane performance improvement is still required to reach a mature technological stage and offer a real challenge to conventional systems. Advanced biomimetic MRs are also used in new fields such as artificial organs and tissue engineering, imposing new development requirements for biocompatible materials that traditional materials do not completely satisfy (59, 60).

In the past years significant progress has also been made in modeling and simulation for investigating the overall performance of MRs. The ultimate goals are to improve reactor performance by optimization of the reactor design and operating conditions as well as to give important input for membrane and catalysts realization through understanding and optimization of structural/functional relationships at the molecular level in the systems investigated. New metrics such as the volume index and conversion index also have been proposed recently as simple and valuable tools to evaluate quantitatively the contribution of an MR to volume reduction or improved conversion in the PI strategy (61). Although the scientific literature on MRs is significant today, only a few large-scale industrial applications have been reported, principally in the biotechnology field. MRs are today successfully applied in small-scale operations, but for their use on the industrial scale, additional efforts, mainly related to the optimization of membrane manufacturing and reactor design, are required.

Because catalysts and membranes can be combined in different ways in an MR, numerous categorizations of these systems are possible (62–65). Probably the most useful is based on the transport function of the membrane, and extractor, distributor, and contactor MRs exist (**Figure 7**) (63).

In a membrane extractor, the removal of one or more products allows enhanced conversion in thermodynamically controlled reactions, such as esterification and dehydrogenation reactions, in which the removal of water or hydrogen, respectively, increases the reaction yield. In a membrane extractor the selectivity toward an unstable intermediate product also may be improved by its selective extraction from the reaction zone. Such extraction generally facilitates downstream processing as well. Numerous examples of extractor-type MRs have been applied in H_2-producing reactions such as methane steam reforming (MSR; Equation 2) and water-gas shift (WGS; Equation 3) (66):

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad (\Delta H_{298\,K} = 206\,\text{kJ mol}^{-1}), \qquad 2.$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (\Delta H_{298\,K} = -41\,\text{kJ mol}^{-1}), \qquad 3.$$

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \quad (\Delta H_{298\,K} = 165\,\text{kJ mol}^{-1}). \qquad 4.$$

According to Le Chatelier's principle, H_2 removal by a Pd-based membrane (which has a theoretically infinite selectivity for H_2) allows a shift in these equilibrium-limited reactions and a consequent yield increase. The reforming operating temperatures can be reduced from the conventional 700–800°C to 500–550°C thanks to this equilibrium shift.

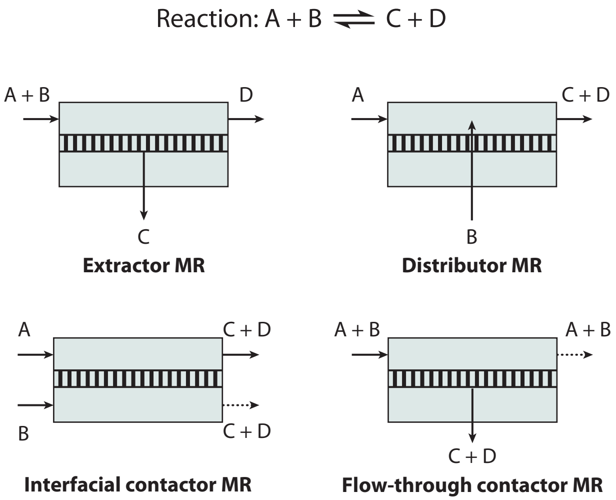

Figure 7

Schematic representation of extractor, distributor, and contactor types of membrane reactors (MRs). Dotted arrows indicate that products (C + D) or reagents (A + B) may or may not be present.

Tokyo Gas Co., Ltd. and Mitsubishi Heavy Industries have recently developed a membrane reformer system with nominal high-purity hydrogen (99.999% level) production capacity of 40 N m^3 h^{-1} from natural gas (typical composition used: 88.5% CH_4, 4.6% C_2H_6, 5.4% C_3H_8, and 1.5% C_4H_{10}) (67). The reformer has 112 reactor tubes, each of which has two planar membrane modules composed of stainless steel supports and palladium-rare earth metal–based alloy films that are less than 20-μm thick. A Ni-based catalyst supported on alumina (Ni/Al_2O_3) is used in two forms: a pellet form of 2–3 mm diameter in the primary catalyst bed and a specially designed monolithic corrugated form placed close to the membrane modules to prevent mechanical damage to the membrane surface as a result of friction between the catalyst and membrane.

The CO produced in a MSR reaction and separated from H_2 can be burned to yield CO_2 through the WGS reaction (Equation 3). The WGS increases H_2 yield (Equation 4) and decreases the concentration of CO, which is a poison for some catalysts used in downstream processing, such as in ammonia synthesis or oil dehydrogenation. Moreover, the heat released in the exothermic WGS reaction can be used in the endothermic MSR.

Many interesting advantages have been demonstrated in PV-assisted catalysis in which the membrane functions as an extractor. PV is an advantageous alternative for the separation of liquid mixtures that are difficult or impossible to separate by conventional distillation methods. In PV-assisted catalysis, in contrast to reactive distillation, the separation efficiency is not limited by the relative volatility of the species to be separated; moreover, in PV only a fraction of the feed is forced to permeate through the membrane and to undergo a liquid-to-vapor phase change. As a consequence, energy consumption is generally lower compared with distillation. In PV-assisted catalysis, the continuous extraction of one of the formed products is used to improve conversion of the reactants or to increase reaction selectivity.

By far the most-studied reaction combined with PV is esterification, an equilibrium-limited reaction with significant industrial relevance. The conversion can exceed the equilibrium limit owing to selective removal of water through the membrane. The esterification of acetic acid with ethanol (Equation 5) has been investigated using zeolite membranes grown hydrothermally on the surface of a porous cylindrical alumina support (the membrane was catalytically inert; the catalyst used was the Amberlyst 15 cation exchange resin kept in the reactor under stirring at 343 K) (68):

$$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O. \qquad 5.$$

The conversion exceeded the equilibrium limit owing to the selective removal through the membrane of water and reached almost 100% within 8 h.

The membrane can also function as a distributor in the MR by dosing the reactants and increasing the selectivity of kinetically controlled reactions, such as hydrogenation and selective oxidation, to prevent hot spots and side reactions. The controlled addition of the reactants by the membrane can reduce potentially dangerous interactions (e.g., with flammable or explosive mixtures) through control of local reactant composition. The membrane also can be used as an upstream separation unit, selectively dosing (and distributing) one component from a mixture.

In numerous examples of distributor MRs, inorganic membranes are employed for reagent dosing/separation; these include perovskite membranes for O_2 (69) and Pd/α-Al_2O_3 (70) as well as zeolite membranes (71, 72) for H_2. These systems are used in high-temperature hydrogenation or oxidation reactions. However, selective hydrogenation or oxidation reactions at mild conditions also can be carried out by means of solid electrolyte MRs working as distributors and by employing low-temperature proton conductors with catalytic layers coated on their surfaces or hot pressed between two catalytic gas diffusion layers (73).

The membrane can also define the reaction volume to facilitate the contact between the reactants. An interfacial MC can provide a contact zone for two immiscible phases that excludes polluting solvents and thus reduces the environmental impact of the process. An efficient process using a catalytic MC for oxidation of dissolved compounds in water has been developed to reduce the chemical oxygen demand and the total organic carbon in industrial wastewaters (74).

Oxygen has been employed as a green oxidant in catalytic MRs (CMRs) using porous ceramic membranes containing Pt nanoparticles in the top layer in an interfacial gas–liquid contactor configuration (75). Wastewater is pumped along the catalytic layer side, whereas air or oxygen flows along the other side. The gas–liquid interface is located within the membrane wall by means of a transmembrane differential pressure used to compensate for the gas/liquid capillary pressure. In this configuration the reactants have better access to the catalyst, which improves conversion rates (75). The catalytic activity of the catalyst was up to four times higher in this configuration than in a conventional perfectly mixed stirred tank reactor (76, 77). This process can operate at much lower temperatures and pressures than conventional wet air oxidation or incineration, and it has much smaller volume requirements than biological treatment plants. This catalytic MC has been successfully upscaled from lab scale to pilot unit (74).

When the membrane is catalytically active, because it is made of a catalytic material (many metal membranes have catalytic activity) or the catalyst is immobilized in the membrane, the contact time between reactants and catalyst is under the control of the convective flux in the flow-through CMR, which can improve the reaction selectivity (78). This is a fundamental advantage of MRs in comparison with traditional heterogeneous reactors. In classical heterogeneous catalysis (catalyst absorbed or linked in porous polymeric or inorganic solids) the conversion and selectivity of the catalytic process is often limited by the diffusion of the reagents to the catalytic sites and of the product from them. In contrast, the convective flux in a CMR is easier to control and to adjust to the reaction kinetics through control of the driving force and/or the membrane structure and properties. Moreover, in a catalytic membrane, especially if polymeric, catalyst entrapment in the functional microstructured environment created by the membrane can have a positive influence on the transition states and reaction kinetics.

The embedding of a catalyst in membranes is today recognized as a promising strategy to develop highly efficient and eco-friendly heterogeneous catalytic processes. When a catalyst is

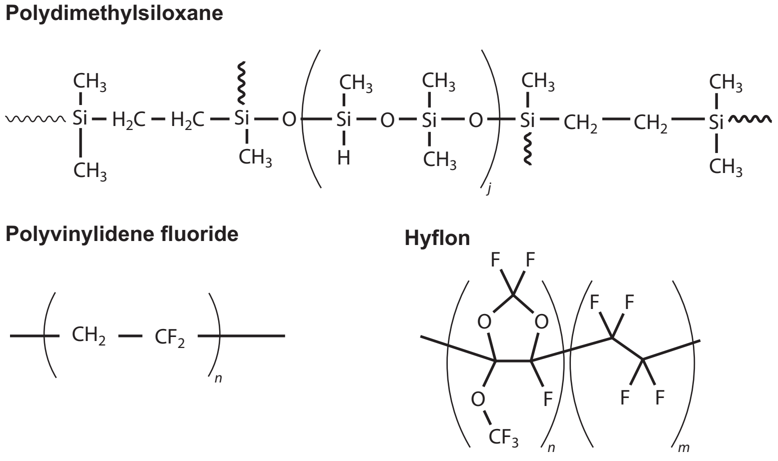

Figure 8

Some polymers used as membrane materials for decatungstate catalyst immobilization.

heterogenized in a membrane, the membrane composition (hydrophobic or hydrophilic material, presence of chemical groups with specific functionality) and membrane structure (dense or porous, symmetric or asymmetric) can positively affect the catalyst performance, not only by the selective sorption and diffusion of reagents and/or products, but also by influencing catalyst activity through electronic and conformational effects (79). These effects are similar to those in biological membranes.

The design of an efficient polymeric catalytic membrane must be derived from an application-based multidisciplinary approach. Tailored functionalizations of the catalysts and/or the polymeric membranes are useful tools for the realization of smart membranes that are more than just a selective barrier. Novel polymer catalytic membranes have been developed through the heterogenization of photocatalytic polyoxometallates (such as decatungstate, $W_{10}O_{32}^{4-}$) in polymeric membranes made of polydimethylsiloxane (PDMS), polyvinylidene fluoride (PVDF), and Hyflon (**Figure 8**) (79–83). The catalytic composite membranes prepared were characterized by various tunable properties that depended on the nature of the polymeric microenvironment in which the catalyst was confined.

Appropriate catalyst/polymer design, and eventually functionalization, allows the creation of new heterogeneous photocatalysts for the oxidation of organic substrates under an oxygen atmosphere that have tailored properties and improved performance (higher stability and selectivity than the analogous homogeneous reactions). Through comparison with the homogeneous reactions, membrane-induced discrimination of the substrate was evident in the oxidations of a series of alcohols by PDMS- and PVDF-based catalytic membranes containing the tetrabutylammonium salt of decatungstate dispersed on the nanometer scale in the polymeric matrix (80). PVDF membranes containing decatungstate also have been employed successfully in stable and recyclable photocatalytic systems, such as in the aerobic mineralization of phenol in water, which was used as a model of an organic pollutant. The polymeric environment in which the catalyst is confined positively influenced catalyst stability. Moreover, the selective separation function of the membrane enhances phenol mineralization in comparison with the homogeneous reaction (81).

Decatungstate also has been heterogenized in membranes made of Hyflon, an amorphous perfluoropolymer. The formation of irregular catalyst aggregates has been observed when using the tetrabutylammonium salt of decatungstate because of its low affinity for the polymeric matrix. However, affinity between the polymer and the catalyst can be improved by appropriate functionalizations of the latter. In particular, a fluorine-tagged decatungstate, $([CF_3(CF_2)_7(CH_2)_3]_3CH_3N)_4W_{10}O_{32}$, which is indicated as $(R_fN)_4W_{10}O_{32}$, has been well dispersed in the Hyflon membranes as spherical clusters with uniform size. The cationic amphiphilic R_fN^+ groups induce the self-assembly of surfactant-encapsulated clusters (R_fN^+ groups capped on $W_{10}O_{32}{}^{4-}$) that, during the membrane formation process, give supramolecular assemblies of the catalyst stabilized by the polymeric matrix. This self-assembly process can be tuned by a proper choice of the membrane preparation conditions (79). Hyflon-based catalytic membranes have been used in the solvent-free photooxygenation of benzylic C–H bonds with a turnover number of up to 6,100 (calculated as the ratio of moles of product to moles of catalyst) in 4 h and remarkable alcohol selectivity; thus they provide a convenient alternative to other radical-centered oxygenation systems (84).

From a general analysis of the MR technology, it is evident that the limitations of this technology are principally related to the manufacturing costs of the membranes and membrane modules as well as their limited durability over long periods. A key issue to be addressed in the near future is the development of advanced (catalytic) membranes and modules that have acceptable costs, are stable in a wide range of solvents and conditions, and exhibit high and reproducible performance over the long term. Of course, strategies to obtain advanced membrane materials must be combined with novel polymer processing technologies to obtain tailored structures in which the density, size, size distribution, shape, and alignment of membrane pores are controlled on a nanometric scale. The driving idea is to obtain ordered structures, similar to those of track-etched polymers and anodically oxidized alumina membranes, as well as tailored surface properties, such as those in biological membranes, that are prepared by simple, reliable, reproducible, and economical methods. Microfabrication, self-assembly, and phase separation micromolding are tentative steps in this direction, but more work is necessary to obtain systems that are commercially competitive and available on a large scale (85–88).

MEMBRANE OPERATIONS FOR EFFICIENT AND ENVIRONMENTALLY FRIENDLY DESALINATION

Membrane technology is today recognized as the better choice for water desalination because thermal options for desalting are approximately 10 times less energy efficient (4, 89), and it is expected to further consolidate its leadership in the future through the availability of new technologies such as MCs operating in integrated systems. Membrane desalination installations account for approximately 80% of the total number of desalination plants and for approximately 50% of the total capacity (89). The RO membrane market is dominated by thin film composite polyamide membranes (90) (**Table 2**). The spiral-wound membrane module configuration is the most extensively used, and research on the design of RO modular elements currently focuses on the optimization of hydrodynamics to minimize the concentration polarization effect (90).

Increasing RO element size is also attracting industrial attention to reduce the number of pressure vessels and connections as well as the system footprint and capital costs. The world's largest RO spiral-wound module (18-inch diameter and 61-inch length) is today produced by Koch Membrane Systems, Inc. under the MegaMagnum® trade name. Minimization of the energy requirements for RO desalination can be realized not only through efficient system design (e.g., integrated membrane systems), high-efficiency pumping, and energy recovery devices, but also through the development of advanced membrane materials that are able to improve membrane performance (increased flux and rejection, reduced feed pressure and fouling) (91). From this

Table 2 Some of the state-of-the-art saltwater reverse osmosis (SWRO) membrane modules in application (reproduced from Reference 90)

Membrane module brand name	Material and module	Permeate flux (m^3 day^{-1})	Salt rejection (%)	Energy consumption (kWh m^{-3})[d]
DOW FILMTECTM 8-inch SW30HRLE	Thin film composite (TFC) cross-linked fully aromatic polyamide spiral wound	28.0[a]	99.60–99.75[a]	3.40 at Perth SWRO Plant, Australia
Hydranautics 8-inch SWC4+	TFC cross-linked fully aromatic polyamide spiral wound	24.6[b]	99.70–99.80[b]	4.17 at Llobregat SWRO Plant, Spain
Toray 8-inch TM820C	TFC cross-linked fully aromatic polyamide spiral wound	19.7–24.6[a]	99.50–99.75[a]	4.35 at Tuas SWRO Plant, Singapore
Toyobo 16-inch HB10255	Asymmetric cellulose triacetate hollow fiber	60.0–67.0[c]	99.40–99.60[c]	5.00 at Fukuoka SWRO Plant, Japan

[a] Test conditions of 32 g $liter^{-1}$ NaCl solution, 55 bar, 25°C, pH 8, and 8% recovery.

[b] Test conditions of 32 g $liter^{-1}$ NaCl solution, 55 bar, 25°C, pH 7, and 10% recovery.

[c] Test conditions of 35 g $liter^{-1}$ NaCl solution, 54 bar, 25°C, and 30% recovery.

[d] These numbers should not be compared directly because of the different operating parameters at the different desalination plants.

perspective, nanotechnology and biomimetic approaches will play a more fundamental role in the future. The use of renewable energy resources (solar, wind, and geothermal) in place of fossil fuels as the energy supply for membrane-based desalination is also recognized as a tool to further minimize energy consumption and greenhouse gas emissions (91).

Although RO water desalination is today considered the most cost-effective solution, key improvements needed in membrane-based desalination systems are cost reduction, enhancement of the water recovery factor, improvement of water quality, and new brine disposal strategies. All of these issues can be addressed in an integrated approach in which various membrane operations are used in RO pretreatment and/or posttreatment.

Traditional RO pretreatments make extensive use of chemicals (NaClO as disinfectant, $FeCl_3$ as flocculant, H_2SO_4 as antiscaling agent) and mechanical filtration units (sand filtration, media filtration, cartridge filtration). An interesting alternative to these systems is the use of pressure-driven membrane processes. In particular, MF and UF are becoming standard and efficient pretreatment options for sea- and brackish-water desalination. For wastewater treatment, MF/UF pretreatment technology also can efficiently reduce the highly fouling nature of the feed. UF is typically used to retain macromolecules, colloids, and solutes with molecular weights greater than a few thousand. MF is a low-pressure membrane process for separating colloidal and suspended micrometer-size particles (92). Although the capital cost of membrane pretreatment usually is higher than that of conventional pretreatment, the additional cost of MF/UF is more than paid for by the reduction in RO replacement and in the chemical costs for both dosing and RO cleaning (93). Other potential benefits arise from the smaller footprint of MF/UF and the opportunity to increase RO flux and water recovery.

Further improvements to RO pretreatment also can be obtained through the utilization of an NF unit for the removal of turbidity, microorganisms, hardness, and most multivalent ions. As a consequence of the reduced osmotic pressure of the RO feed, higher recovery factors can be achieved (94). As a further pretreatment operation to reduce natural organic matter from seawater, a submerged hollow fiber UF unit has been used as a pretreatment in SWRO because of its low energy consumption and great potential to reduce particle deposition on the RO membrane (95). Use of an MBR as RO pretreatment is also being investigated in the MEDINA (membrane-based desalination: an integrated approach; **http://medina.unical.it**) FP6 research project.

A fundamental problem in desalination is the environmental effects of brine discharge from RO desalination plants. The most frequent disposal practice is direct discharge into the sea. However, increasingly stringent environmental regulations in many cases preclude this low-cost option to protect the aquatic environment. Various process engineering strategies have been investigated for environmentally friendly brine disposal in RO desalination. A suitable solution is complete redesign of a desalination system to introduce MC operations (96).

MCs are systems in which the membrane facilitates diffusive mass transfer between two contacting phases (e.g., liquid-liquid, liquid-gas) without dispersion of one phase within another (97). The membrane does not act as a selective barrier but rather creates and sustains the interfaces immobilized at the pore mouths; the separation process is based on the principles of phase equilibrium. With respect to conventional systems, MCs have some important advantages: nondispersed phases in contact, independently variable flow rates, no limitations owing to phase-density difference, extremely high surface area/volume ratio, modular design, and easy scale-up. Drawbacks are related to the presence of an additional mass transport resistance (the membrane itself) and to the rather limited range of the operating pressures below the breakthrough threshold. The performance of MCs strongly depends on the properties of the membranes used. In general, a high hydrophobicity (for aqueous applications) is required to prevent wetting and mixing between phases in contact; elevated porosity leads to high fluxes but may cause bubble coalescence in gas–liquid operations. Polymers frequently used as membrane materials for MCs are polypropylene (PP), PVDF, and polytetrafluoroethylene (PTFE) (97). In addition, membranes based on amorphous fluoropolymer materials (such as Hyflon and Cytop) are of increasing interest for MC applications.

Membrane distillation (MD) is an example of an MC applied to the concentration of aqueous solutions of nonvolatile solutes. In an MD process, a macroporous hydrophobic membrane is in contact with an aqueous heated solution on the feed or retentate side. The hydrophobic nature of the membrane prevents mass transfer in the liquid phase and creates a vapor-liquid interface at the entrance of each pore. Here, volatile compounds (typically water) evaporate, diffuse, and/or convect across the membrane, and are condensed and/or removed on the permeate or distillate side. With respect to RO process, MD does not suffer significant osmotic pressure limitations and therefore can be employed when high permeate recovery factors or retentate concentrations are needed. Experimental studies on full-scale spiral-wound MD modules (membrane material PTFE; nominal pore size 0.2 μm; porosity $\approx 80\%$; thickness 70 μm; membrane surface area 5–14 m^2) showed the feasibility of using solar-driven MD technology for desalination (98).

MCr is one of the most interesting and promising proposed extensions of the MD concept. Evaporative mass transfer of volatile solvents through macroporous hydrophobic membranes is employed to concentrate feed solutions above their saturation limit and thus to obtain a supersaturated environment in which crystals may nucleate and grow. In addition, the presence of a polymeric membrane increases the probability of nucleation with respect to other locations in the system (heterogeneous nucleation). MCr is an efficient tool to improve seawater desalination processes such that they approach zero liquid and solid discharges (96). Integration of an MCr unit to process the NF and/or RO retentate (**Figure 9**) could (*a*) reduce the huge amount of brine, (*b*) increase the overall water recovery factor, and (*c*) produce valuable crystalline products (e.g., NaCl, $MgSO_4 \cdot 7H_2O$)

With the integrated membrane system shown in **Figure 9**, the NF retentate and/or the RO brine is further concentrated, up to salt crystal formation, in a controlled way in an MCr unit. NaCl, calcium carbonate ($CaCO_3$), and Epsom salts ($MgSO_4 \cdot 7H_2O$) are obtained as solid products from the NF retentate stream, whereas NaCl is the product from the RO brine, and the pure crystals produced could be a valuable product. Therefore, the adoption of MCr is an interesting

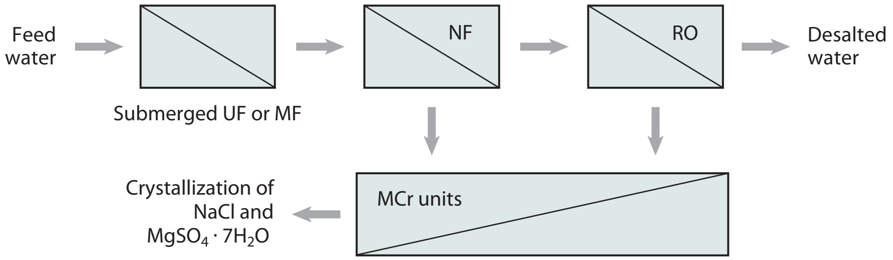

Figure 9

Integrated membrane system for seawater desalination. Abbreviations: MCr, membrane crystallization; MF, microfiltration; NF, nanofiltration; RO, reverse osmosis; UF, ultrafiltration.

possibility for improving desalination operations and meeting the increasing pure water demand at lower cost and with lower environmental impact in the logic of the PI strategy. For example, an MD-MCr bench-scale plant operating on brines discharged from a seawater RO unit achieved a water recovery greater than 90%, with a concomitant reduction in the volume of waste discharged to the environment (99).

MCr operations offer valuable opportunities not only for the crystallization of inorganic salts but also for the crystallization of organic molecules of interest (100). In an MCr unit the supersaturation generation rate is modulated by controlling the transmembrane flux. This kind of control affects the kinetic/thermodynamic balance in the polymorphic crystallization of organic molecules (101). For example, control of the supersaturation rate allowed glycine nucleation to switch between kinetic and thermodynamic control, which triggered the production of either a stable or a metastable form (102, 103) (**Figure 10**).

Clearly, control of supersaturation and the rate of its variation represents a tool to vary the thermodynamic/kinetic balance during the crystallization of a polymorphic system, with the consequent potential to address the growth of a specific phase. As this control can be produced quite precisely by fine-tuning the operating conditions and/or by choosing opportune membrane properties, selective polymorph crystallization is available to operators using MCr. Moreover, the porous structure of the membrane offers cavities that might entrap protein molecules, thus leading to localized supersaturation maxima that promote the nucleation and the formation of crystals at supersaturation conditions that would be inadequate or insufficient for homogeneous nucleation (**Figure 11**) (103–106).

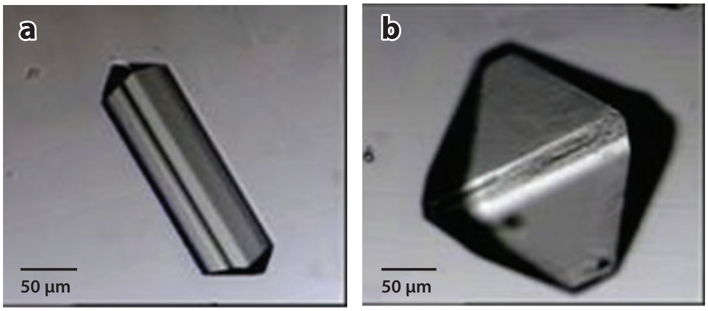

Figure 10

Optical images of the two crystal morphologies obtained during membrane crystallization tests of glycine: (*a*) Form I; (*b*) Form II. Figure reproduced from Reference 102.

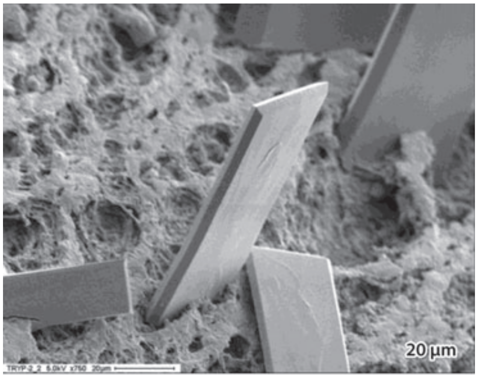

Figure 11

Porcine pancreatic trypsin crystals grown on the surface of a polymeric membrane in static crystallization. Figure reproduced from Reference 103.

In an MCr unit, the crystallizing solution is in direct contact with the membrane surface; therefore, a solute-membrane interaction is likely to occur, depending on the fluid dynamic regime. This effect can result from both the structural and chemical properties of the membrane surface: (*a*) the porous nature of the surface might supply cavities where solute molecules are physically entrapped, leading to locally high levels of supersaturation; (*b*) the nonspecific and reversible chemical interaction between the membrane and the solute can concentrate and orient molecules on the surface without loss of mobility, thus facilitating interaction effective for crystallization.

CONCLUSIONS

Process engineering is one of the disciplines more involved in the technological innovations necessary to face the new problems characterizing modern society. Recently, process engineering has suggested the logic of PI to resolve these problems. How to implement this strategy is, however, not obvious. An interesting and important case is the continuous growth of modern membrane engineering, whose basic aspects satisfy the requirements of the PI strategy.

Membrane operations represent an interesting tool for the realization of more efficient industrial production and energy conversion. The traditional membrane separation operations (e.g., MF, UF, NF, RO, GS, PV, D, ED), which are already widely used in many different applications, are today combined with new membrane systems such as MRs, MCs, and FCs. At present, redesign of important industrial production cycles by combining various membrane operations suitable for separation and conversion units, and thus realizing highly integrated membrane processes, is an attractive opportunity because of the synergistic effects that can be attained.

Membrane technologies are already dominant in water desalination and wastewater treatment. However, a better understanding of material properties and transport mechanisms as well as the development of innovative nanostructured membrane materials (including support-layer materials for osmotically driven membrane processes) with improved properties, advances in membrane permselectivity, appropriate module and process design, and, in general, a deeper engineering analysis, are fundamental for boosting efficiency in membrane technology applications.

Moreover, progress in our understanding of biological processes is offering other interesting opportunities because the best examples of PI strategy applications are present in nature. The possibility for membranologists to make artificial versions of biological membranes and to utilize some of these systems in our life and in our industrial world is becoming an interesting reality. However, we are far from being able to reproduce the complexity and efficiency of biological membranes. Therefore, future generations of membrane scientists and engineers will need to continue to work to understand and reproduce natural systems.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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