

CHAPTER 20

APPLICATIONS OF CHARGED MEMBRANES IN SEPARATION, FUEL CELLS, AND EMERGING PROCESSES

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20.1 INTRODUCTION

A great advantage of membrane separation processes is their high selectivity and very low need for chemical additives. It makes them a very effective, environmentally friendly tool for resolving numerous industrial problems related to liquid and gas separation; in particular, the treatment of certain industrial effluents containing toxic components, which should not be released into the environment, or valuable materials, which can be recovered and reused. Membrane processes seem indispensable in realization of zero liquid discharge (ZLD) systems, meaning such industrial engineering where only solid wastes may leave the boundary of the plant.¹

Techniques involving charged membranes occupy an important place among membrane technologies in general. The structure and properties of charged membranes were considered in Chapter 9. Their main structural feature is a network of nanometer aqueous domains serving as conducting channels and embedded into a hydrophobic polymer matrix. The ions fixed on the charged pore walls are the reason for the channel hydrophilicity and permselectivity. The most extensively used charged membranes are ion exchange, reverse osmosis (RO), and nanofiltration (NF) membranes. Historically, ion exchange membranes (IEMs)^{2,3} and their practical applications⁴⁻⁷ have appeared earlier than the pressure-driven ones.^{8,9} The RO process is definitively suitable in water and wastewater desalination where the pressure-driven processes have demonstrated greater growth than that of

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electrodialysis (ED) and electrodeionization (EDI). Desalination systems produce a huge amount of freshwater; *Global Water Intelligence*¹⁰ evaluates worldwide desalination as 40 million m³ day⁻¹ in 2006 with a growth up to 64 million m³ day⁻¹ in 2010 and up to 97.5 million m³ day⁻¹ in 2015. This large market is dominated by RO (about 50%) and thermal (40%) technologies while ED and EDI occupy only about 5%.¹ However, the interest in IEMs and electrotransfer phenomena in membrane systems increases rather rapidly due to novel or renovated applications. The opinion that for water treatment applications hybrid systems (including RO together with ED and/or EDI units) are the most effective solution is becoming generally recognized. Some researchers call the use of ED for concentrating RO brines a “new niche” for ED¹¹ (see also Section 20.2). Second, electromembrane processes are much demanded in other domains that emerged within the last decade: clean energy systems (fuel cells and other devices for the production and accumulation of electric power), micropumps and other micro- and nanofluidic devices (microelectromechanical-systems), analytical sensors, and others. Finally, there are traditional applications, such as chlor-alkali production, electrochemical synthesis, and the wine, food, and whey industries, where the use of IEM is rapidly growing.

Strathmann¹² proposed a quite useful classification of electromembrane processes. He separated them in developed (conventional ED, diffusion, and Donnan dialysis) and developing (bipolar membrane electrodialysis [BMED], continuous electrodeionization [CEDI], capacitive deionization [CDI]) categories, and marked out the processes emerging from the ongoing research (catalytic membrane reactors, reverse electrodialysis (RED), overlimiting current density operation, and others). In this chapter, we give a survey of traditional and emerging applications of charged membranes, including overlimiting and pulse current ED, micro- and nanofluidic desalination devices, and others.

This chapter is conceived to describe the main ideas of how membranes can be used to solve different practical problems.

20.2 DESALINATION AND DEIONIZATION

The predominance of charge membrane processes in desalination and deionization is attributed to their remarkable ion removal efficiency, particularly in natural and wastewater treatment. These technologies include mainly RO and ED, as was mentioned in the introduction. Both of these processes use membranes to separate the feed stream into two streams differing in concentration: a dilute and a concentrated stream.

The main product of a desalination process is freshwater (potable water as well as water for agriculture and industry). This product is critical to human habitation on this planet. Actually, most of the 98% of our waters are either sea or brackish waters. Typical concentration of dissolved salts in seawater and

brackish water is 35,000 and 1000–10,000 mg L⁻¹, respectively. Besides RO and ED with its derivatives (electrodialysis reversal [EDR], EDI), novel techniques involving charged membranes have emerged: CDI¹³ and micro-/nanofluidic desalination.¹⁴ At the same time, there is a stable trend of applying hybrid membrane systems accumulating the advantages of individual membrane processes. In this section we consider all of the abovementioned techniques.

20.2.1 Reverse Osmosis

Consider a system wherein a charged membrane separates an electrolyte solution and water. An osmotic pressure difference causing water to move from the dilute to the concentrated compartments occurs in the system. The phenomenon is known as osmosis. When a pressure higher than the osmotic pressure difference is applied in the concentrated compartment, the direction of water transfer changes and water passes through the membrane into the dilute compartment. This is known as RO. The main difference of RO from other biomembrane processes is that the solvent molecules and dissolved substances, which are separating, are of comparable size.

The scheme of RO desalination mechanism is shown in Figure 20.1. The main role is played by charge sites fixed on the pore walls (see Chapter 9 for the structure of charged membranes). Under the action of pressure gradient, water molecules pass freely through a pore with a charged surface; however, the charged particles are retained. In the case where the fixed ions are charged negatively (Fig. 20.1), the anions from the external solution cannot pass because they are excluded from the pore as co-ions (Donnan exclusion, Chapter 9); the cations are retained by the electric field formed by themselves: a small amount of these ions transferred with the forced convection flow creates an excess of positive charge at the outlet of the pore, while an excess of negative charge appears at the inlet. As a result, an electric potential difference (pd) (named streaming potential)^{15,16} is created. This electric pd produces an electric force opposite to the mechanic force created by the pressure gradient. In steady state, both forces are equal and directed in opposite sides, so that the resultant driving force is zero.

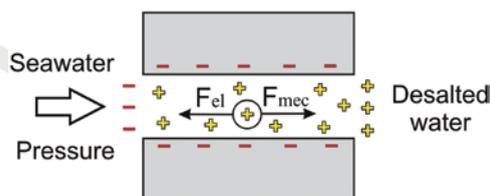


FIGURE 20.1. Scheme of seawater desalination by a RO membrane; a nanopore with negatively charged walls, and the forces applied to a cation within the pore are shown. Adapted from Nikonenko et al.²⁹

Besides RO, another pressure-driven process essentially related to the charge of pore walls of the membrane is widely applied: NF. The main difference between two kinds of membranes is in the pore radius, r . NF membranes contain mesopores with a radius in the range 2–4 nm, while in RO membranes there are micropores whose radius is about two times lower.¹⁷ Larger pores of NF membranes produce a lower Donnan exclusion, so that monovalent ions pass through NF membranes relatively easily, while multivalent ones do not. As a result, RO membranes effectively reject all ions and only water (or another solvent) may pass through. NF is used where mono- and multivalent ions should be separated, for example, in the water softening process.¹⁸

Cationic NF membranes have negative groups attached to the polymer backbone. Their negative charges selectively repel negative, particularly multivalent, anions such as SO_4^{2-} , while attracting positive cations, particularly divalent cations such as Ca^{2+} . The result is an order of salt rejection¹⁹:



In the case of anionic NF membranes, their positive fixed groups repel cations, particularly divalent ones, and attract anions. The order of salt rejection is then¹⁹:



In order to enhance the rejection performance, NF membranes frequently combine both size and Donnan exclusion effects. This kind of pressure-driven membranes, called low pressure RO membranes, have very high salt rejections and low hydraulic resistance at low salt concentrations, but lose their selectivity at salt concentrations above 1000 or 2000 ppm in feedwater since the thickness of the electric double layer (EDL) at the pore wall becomes small compared to the pore diameter. The membranes are therefore used to remove salt from already relatively clean water. The membranes are usually operated at a very low pressures (3–15 bars).⁷

Mathematical description of RO and NF processes is carried out by applying capillary space charge models.^{20–22} These models allow quantitative description for the increase of the capacity and separation ability of charged membranes with the charge of the walls, and why multivalent ions are better rejected.

The well-known applications of RO and NF stem from the seminal discovery by Loeb and Sourirajan.²³ They invented bilayer RO membranes that contained a thin (about 1 μm) selective surface layer and a much thicker (about 100 μm), more permeable macroporous support providing the mechanical strength. The water permeability of the first RO membrane prepared by Loeb and Sourirajan was 10 times larger than that of any membrane then available.

Nowadays, about 20 million $\text{m}^3 \text{ day}^{-1}$ of water are desalted by RO.¹⁰ According to Baker,¹⁹ about half of this capacity is mainly used to produce

ultrapure industrial water in the United States, Europe, and Japan; the other half is used to produce municipal drinking water in the Middle East and other desert regions from seawater or brackish groundwater.

There is a wide variety of designs of RO/NF membrane modules.¹⁷ The most common are spiral-wound modules and those with hollow fiber membranes. The outer diameter of these fibers can be less than 100 μm , wall thickness is about 20 μm , and specific surface area can be larger than 1000 $\text{m}^2 \text{m}^{-3}$.^{17,19} Modern composite membranes provide more than 99% salt rejection at 1.2 $\text{m}^3 \text{m}^{-2}$ day at 55 bars in the seawater version and 15 bars in the brackish water version.¹⁹

In addition to desalination, RO is also increasingly being used in other applications^{24,25} due to the high and stable quality of the water produced and the relatively low cost. Some of these applications are described in Section 20.6. The economically justifiable range of RO application is from 2–5 mg L^{-1} of dissolved salts (the resistivity of 0.2 Mohm cm) in the permeate (desalted product) to 50–70 g L^{-1} in the retentate (brine), which are obtained in processing seawater and other electrolyte solutions. In the production of more dilute solutions, the energy costs are larger, since it is necessary to separate water from the solution. Production of more concentrated brines is limited by the need to overcome the osmotic pressure, the magnitude of which in the case of seawater (salt concentration about 30 g L^{-1}) is close to 25 bars.

The main problems in the operation of RO/NF modules are fouling of the membranes and relatively large liquid waste emission.⁷ Moreover, RO membranes are sensitive to chlorine and other oxidants often present in feedwater, which provokes their degradation. Heavy metal ions such as iron are able to catalyze chlorine degradation.^{26,27} As a result, RO operation needs pretreatment, entailing high investment costs.

20.2.2 Conventional ED

ED is an electromembrane process for the separation of ions across charged membranes from one solution to another under the influence of an electrical potential difference used as the driving force. Nonionic and macromolecular species are retained as they cannot permeate through IEMs. The cation exchange membranes (CEMs) and anion exchange membranes (AEMs) are normally separated by a spacer gasket and form individual cells. As a rule, an electrolyte solution is pumped through these cells. An electrical potential difference applied between the electrodes forces the cations (C^+) to migrate toward the cathode. They pass through the CEMs but are retained by the anion exchange ones. Likewise, the anions (A^-) migrate toward the anode and pass through the AEMs but are retained by the cation exchange ones. The overall result is that the feed electrolyte solution is separated into a concentrated solution, found in concentrate compartments (CC), and a dilute solution, in diluate compartments (DC). CC and DC alternate in an ED stack (Fig. 20.2).

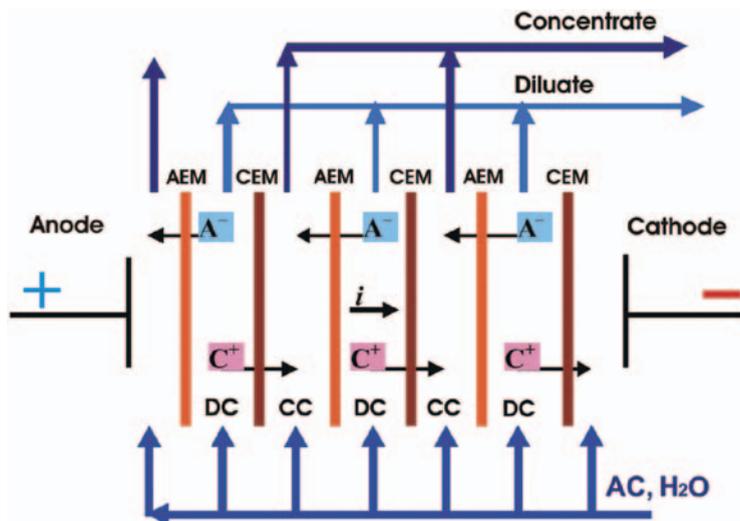


FIGURE 20.2. Scheme of anions (A^-) and cations (C^+) transfer through anion (AEM) and cation exchange (CEM) membranes forming alternate diluate (DC) and concentrate (CC) compartments in a conventional ED stack.

In an industrial-sized ED stack, 100–1000 cell pairs are arranged between the electrodes. Various stack constructions such as the plate-and-frame (another name for sheet flow) or the spiral-wound stack design are used in practical applications.^{12,28}

The flowing of current through an IEM results in concentration polarization, which is the formation of concentration gradients at the membrane/solution interface.^{7,29,30} The cause of this phenomenon is that the membrane has the ability to transport some species (counterions) more readily than the other(s) (co-ions) (see also Chapter 9, Section 9.3). The selective transport of counterions through an IEM leads to a decrease in salt concentration at the depleted interface facing a DC, and to an increase at the other interface facing a CC. Concentration polarization is an inherent but undesirable phenomenon in ED process. The salt concentration at the depleted interface decreases with increasing current density. At a certain value called the limiting current density, i_{lim} , the interfacial concentration becomes much lower than the bulk concentration. The equation relating i_{lim} to the thickness of diffusion boundary layer at an IEM, δ , and phenomena occurring when the current density is close or higher than i_{lim} are considered in Chapter 9. As the interfacial concentration approaches zero, an increase in the cell resistance and potential difference occurs. Depletion of the interface in salt ions also leads to a water splitting process producing H^+ and OH^- ions. These ions carry a part of the current, thus lowering the ED current efficiency. Moreover, this process gives rise to variation in pH of the solutions in the DC and CC. Normally, the rate of H^+ and OH^- ion generation is higher at the AEM in comparison with the CEM

forming a cell pair. In this case, the DC solution becomes acid, and the CC one, alkaline. High pH value at the enriched interface of an IEM provokes here the deposition of salts (scaling), mainly CaCO_3 .^{31,32} When treating solutions containing macromolecules or colloidal substances, their deposition is also possible. Feed solutions often contain negatively charged colloid particles or large organic anions. Under the action of applied electric field these components migrate to the AEM and can be deposited on its surface to form a so-called fouling layer.¹² The formation of a fouling (or biofouling, if biological substances such as bacteria or algae are present) layer is favored by a pH variation, and an increase in temperature (T) at membrane surface provides polymerization of organic matter.

Membrane scaling and fouling lead to a significant increase in the resistance of IEMs, which can eventually reduce limiting current density and raise the operating costs. However, it should be remarked that ED membranes show better resistance to fouling and scaling in comparison with the RO ones.¹² This resistance can be improved by application of ED reversal and pulsed current (see Section 20.2.3). As a consequence, RO modules demand a more careful pretreatment than ED. Other advantages of ED compared to RO are high water recovery rates, long useful life of membranes up to 5 years or higher, and operation at elevated T up to 50°C.^{31,33} Among the disadvantages of ED compared to RO, Strathmann¹² remarks that neutral toxic components such as viruses or bacteria are not removed from a feed stream. Note that overlimiting operation of ED results in killing bacteria and allows production of apyrogenic water.^{34,35}

Conventionally, desalination ED process is carried out in underlimiting current modes in order to prevent scaling and fouling of IEMs as well as elevated energy costs. Since the limiting current density is approximately proportional to the feed solution concentration, the rate of ED decreases with decreasing concentration. As a result, conventional ED becomes inefficient when the salinity of the feed solution becomes lower than about 400 mg L⁻¹. The upper limit for the application of this process is approximately 5000 mg L⁻¹ of total dissolved salts (TDS) in the feed solution, as higher salt concentration causes large energy costs.^{12,36} In the range of salinity of feed solution between 400 and 5000 mg L⁻¹, other membrane processes are more effective: EDI in the low concentration range, and RO in the high one.

As in RO, the macrocomponent, water, is moved away from the feed solution, the energy consumption only slightly depends on the feedwater salinity and constitutes about 5 kWh m⁻³.³⁷ In ED, the energy consumption is approximately proportional to the amount of the extracted salt. It is evaluated as approximately 300 kWh per 1 ton of extracted salt in the case of brackish water treatment,³⁸ and 150 kWh t⁻¹ in the case of seawater.³⁹ (Note that the energy consumption depends on the current density applied, type of membranes, and other parameters.^{38,39}) To desalinate seawater, ~7–15 kWh m⁻³ are needed⁴⁰; for brackish water with 10 g L⁻¹ salinity, the energy consumption is close to 3 kWh m⁻³.³⁸

ED has an economic advantage over other desalination processes in cases of particular feedwater salt composition. This chemical-free technology competes directly with RO especially when it is necessary to remove nitrates⁴¹ or fluorides⁴² from brackish waters.

Conventional ED, which is now frequently displaced by EDR, is widely used in desalination of brackish river waters. This application was developed in the United States^{43,44} and recently in Spain where 4.5 million inhabitants of the Barcelona metropolitan area are mainly supplied with surface water treated by EDR.⁴⁵ More often, ED is used in small- to medium-sized plants with capacities of less than a few $100 \text{ m}^3 \text{ d}^{-1}$ to more than $20,000 \text{ m}^3 \text{ d}^{-1}$.^{12,46} Another large application of this process is predemineralization of industrial solutions. For example, this process is applied in boiler feedwater treatment as a step before the use of ion exchange (or EDI).¹² Such systems allow significant savings in recovery chemicals needed for the ion exchange step. The savings increase with increasing feedwater salinity. In ultrapure water production needed for microelectronics and power plants, ED is used for predemineralization in water recycling systems.^{35,47} A typical application of industrial water reuse is the recycling of cooling tower blowdown water. ED is particularly suited for this purpose since high recovery rates up to 95% and high brine concentrations can be achieved, resulting in saving of feedwater costs and in a reduction of wastewater discharge. Furthermore, in a majority of cases, IEMs can be operated at T of up to 50°C , which is in the range of most cooling systems.

The characteristics of IEMs important in ED desalination process are as follows: (1) mechanical strength, thermal stability, and durability in aggressive environments, as well as (2) high permselectivity and ionic conductivity in combination with low diffusion permeability.^{7,48}

Mechanical strength is needed since rather large IEM sheets are used, up to 1 m and even greater. Often the T of solutions under treatment is elevated, and pH changes in a wide range; normally IEMs elaborated for ED are stable between 1 and 11 of the pH range.³³ The properties denoted by (2) should provide a high current efficiency (high permselectivity and low diffusion permeability) as well as a low electricity consumption. The salt counterion transport number characterizing the permselectivity of commercial IEM in NaCl solution (up to 0.1 M) for homogeneous membranes (such as CM2, Neosepta®, Tokuyama Corporation, Shibuya, Japan) is higher than 0.99. For heterogeneous membranes (MK-40, SchekinoAzote, Schekino, Russia), this parameter is higher than 0.97.⁴⁹ The salt diffusion permeability is about 0.1×10^{-11} and $1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for these membranes, respectively.⁴⁹ The surface membrane resistance is about 2 ohm cm^2 for CM2 and 6 ohm cm^{-2} for MK-40 in 1 M NaCl.

20.2.3 EDR and Pulsed Current ED

EDR is a variation of the ED process, wherein electrode polarity reversal is used to automatically clean membrane surfaces.⁵⁰ EDR works in the same way

as the conventional ED, except that the polarity of the DC power is reversed at specific time intervals ranging from a few minutes to several hours. When the polarity is reversed, the DC and CC are also reversed and so are the chemical reactions at the electrodes. If water splitting takes place at IEM surface, these reactions will also be reversed. As was explained in the previous section, water splitting reaction can produce a shift in pH value in the diluate and the CC: an increase in pH together with increasing salt concentration leads to the scale formation, mainly calcium and magnesium carbonates. The electrode polarity reversal also results in reversal of pH shift. The acidification of the earlier alkaline solution tends to dissolve any calcium carbonate present on membrane surface.^{43,51} Similar effects occur with the organic matter fouling the membrane surface. Negatively charged particles or large organic anions present in feed solution may form a deposit on the AEM in DC under the action of a direct current (Fig. 20.3a). When the polarity is reversed, the large organic anions will migrate from the AEM surface back into the core stream and the membrane properties are restored (Fig. 20.3b).

A similar effect takes place when a pulsed current is applied without reversing the solution streams. Imposing of current pulses contributes to the formation of loose, easy-to-wash with the flowing solution, fouling layers.^{52–55} Moreover, the local variation in T and pH near the membrane interface are essentially lower than in conventional ED that mitigates the fouling of IEMs.^{52,54} However, this promising technique needs to be more comprehensively studied.

We have also mentioned the rapidly rising application of EDR in the desalination of brackish waters. The recently started potable water production in the Barcelona area with capacity up to $4 \text{ m}^3 \text{ s}^{-1}$ (about $350,000 \text{ m}^3 \text{ day}^{-1}$)⁴⁵ serves as a telling example.

Another application of EDR is the treatment of water obtained in the oil and gas industries. In recent years, a systematic study of various desalination

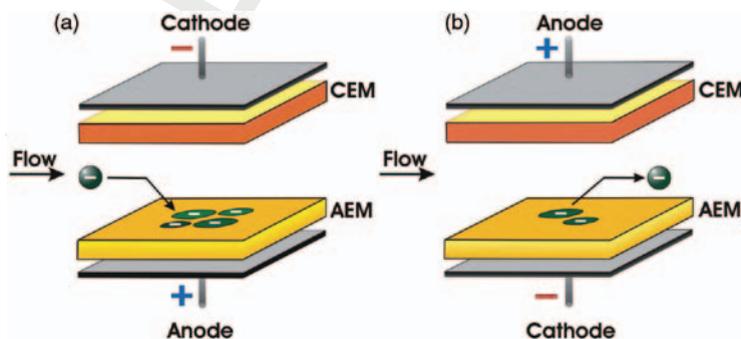


FIGURE 20.3. Schematic drawing illustrating the removal of deposited negatively charged colloidal components from the surface of an AEM by reversing the electric field. (a) Direct current; (b) reverse current. Adapted from Strathmann.¹²

methods for polymer flooding-produced water has been made in Canada, the United States, and China.^{56,57} It was found that RO and EDR are reliable and economically feasible techniques. After membrane treatment, polymer flooding-produced water may have two beneficial uses. First, the diluate obtained from this water can be used for preparing polymer solutions. Second, the concentrate can be used as the injecting water in the water-flooding process for high permeability layers.⁵⁷

The use of EDR allows a significant decrease in the requirements to the quality of the feed solution as for the presence of substances critical for membrane scaling and fouling. Consequently, very little feed pretreatment is required, making EDR attractive in treating natural and wastewaters. As compared to RO, IEMs are more stable in aggressive and oxidizing solutions: they can operate on waters with up to 0.5 mg L⁻¹ chlorine, and can also be shock chlorinated up to 30 mg L⁻¹.⁴⁵

However, to be effective, the reversal of the polarity of a stack has to be accompanied with a reversal of the flow streams. This always leads to some loss of product and requires a more sophisticated flow control. Besides, some pretreatment of the feedwater is required. In particular, the iron and manganese ion concentrations must be kept below 0.3 and 0.05 mg L⁻¹.¹² We have also mentioned the fact that neutral toxic components such as viruses or bacteria are not removed from the feed stream in ED and EDR. The use of pulsed current mode may be quite beneficial as it makes it possible to avoid the loss of the product.

Even if IEMs are less prone to scaling and fouling in EDR stacks, pH variation in the stack compartments should be avoided. Besides, high roughness of membrane surface leads to the consolidation of the deposit on the membrane. Therefore, in order to minimize the surface fouling, it is preferable to use membranes with smooth surface, which does not generate H⁺ and OH⁻ ions and has minimal adhesion to the solid precipitations from the feed solutions. The latter may be obtained, for instance, by hydrophilization of the membrane surface.

20.2.4 Deionization

CEDI To obtain high purity water, electro dialyzers with a special stack design are applied, the process is named CEDI.^{7,58} These apparatuses are able to produce deionized water, the resistivity of which is close to that of pure water (18 Mohm cm at 25°C). The process design and the different hardware components needed in CEDI are very similar to those used in conventional ED. The main difference is that in a CEDI stack the diluate cells and sometimes also the concentrate cells are filled with an ion exchange filler: a bed of ion exchange resin granules,^{6,7,59-61} ion exchange textile,^{35,62,63} conducting spacer,^{59,64-67} or organic porous ion exchange material.⁶⁸ The stacks with profiled (relief/undulated) IEMs^{12,60,69-71} occupy an intermediate position between CEDI with ion exchange bed and conventional ED with smooth membranes and nonconductive spacer. The range of feed solutions with TDS from 5 to

500 mg L⁻¹ (from 10⁻⁴ to 10⁻² M NaCl) is the most effective field of profiled membranes application, as it can be seen in Figure 20.4.

The ion exchange resin increases the conductivity in the diluate cells; as a result, the resistance of CEDI stack is significantly lowered. However, the main difference from conventional ED lies in the mechanism of deionization: the electromigration transfer of salt ions in CEDI is combined with ion exchange: the salt ions are exchanged with the H⁺ and OH⁻ ions present in the ion exchange material.^{59,70,72} The latter enter ion exchange resins or membranes due to the water-splitting reaction⁷³ occurring at $\overline{A/C}$ contacts where *A* is an anion and *C* is a cation exchange material; the arrow shows the direction of the current flow (Fig. 20.5). The active mass exchange surface in a CEDI stack is much higher than that in an ED stack due to the presence of an ion exchange bed. The ion exchange can occur on the all ion exchange particle surface, including the part normal to the current flow direction, thus enhancing the rate and the depth of deionization. Besides, ion exchange particles or profiles on the membrane surface contribute to improving hydrodynamics and reducing the diffusion layer thickness.

The source of H⁺ and OH⁻ ions in CEDI can be not only the $\overline{A/C}$ contacts between ion exchange fillers, but also BPMs^{58,60} or electrochemical reactions occurring at the electrodes.⁷⁴

Two different concepts of CEDI stacks are shown in Figure 20.6.

Most often, in the production of ultrapure water, EDI/CEDI devices are combined with RO, which provides predemineralized water after pretreatment (normally including water softening) and sterilization of feedwater.^{12,75–77} There are different solutions to the layout of such hybrid schemes, differing in pretreatment methods and the direction of diluate and concentrate flows.⁷⁶ CEDI devices replace in these systems the mixed-bed ion exchanger. The integration of CEDI in the ultrapure water production systems results in a simpler process which does not need regeneration chemicals. Besides, the raw water consumption is lower and the costs are essentially reduced; in systems with separated beds of ion exchange resins and BPMs, the removal of weakly dissociated acids is more efficient.¹²

Among the limitations of EDI devices, note the higher requirements on the quality of feedwater in comparison to conventional ED units.³⁵ Normally, these requirements can be met by applying single- or double-pass RO.³⁵ When the quality of produced water approaches high purity one (the resistance higher than 15 Mohm cm or the conductivity less than 0.07 mS cm⁻¹), high permselectivity of AEM becomes crucial.¹²

There are now several thousand continuous EDI systems in commercial operation for the production of high purity water at capacities ranging from less than 0.1 to more than 1500 m³h⁻¹.³⁵ This includes a CEDI system that has been in continuous operation for over 18 years, producing deionized water for a university laboratory.³⁵

CEDI technology of high purity, industrial-process water production is used in microelectronic/semiconductor, chemical, and pharmaceutical manufacturing; steam generation at power plants^{12,35,78,79}; academic and clinical

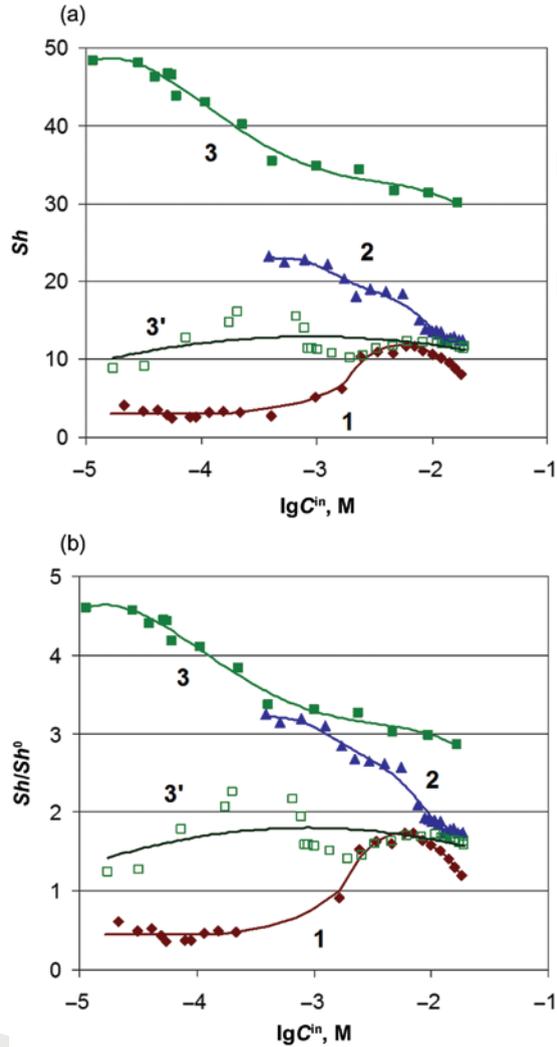


FIGURE 20.4. The Sherwood number, Sh , (a) and the ratio Sh/Sh^0 (b) as functions of the inlet feed NaCl solution concentration for different ED and CEDI stacks (of length 2 dm) formed by MK-40 and MA-40 membranes and containing: a nonconducting network spacer (**1**); an ion exchange monolayer bed KU-2/AV-17 (**2**); or a profiled membrane MA-40P (instead of MA-40) (**3**, **3'**). **1**, **2**, **3**: the solution flow rate through one desalination compartment normalized to a width of 1 dm, w , is close to $3 \text{ dm}^3 \text{ h}^{-1} \text{ dm}^{-1}$; **3'**: $w = 7.5 \text{ dm}^3 \text{ h}^{-1} \text{ dm}^{-1}$. The potential difference per cell pair in all cases was 2.5 V. Sh^0 is calculated for a reference channel formed by flat membranes without spacer and the same intermembrane spacing as the channel under study; Sh/Sh^0 is equal to the ratio of the effective diffusion boundary layer thickness in the reference channel to that in the channel under study. Adapted from Larchet et al.⁷⁰

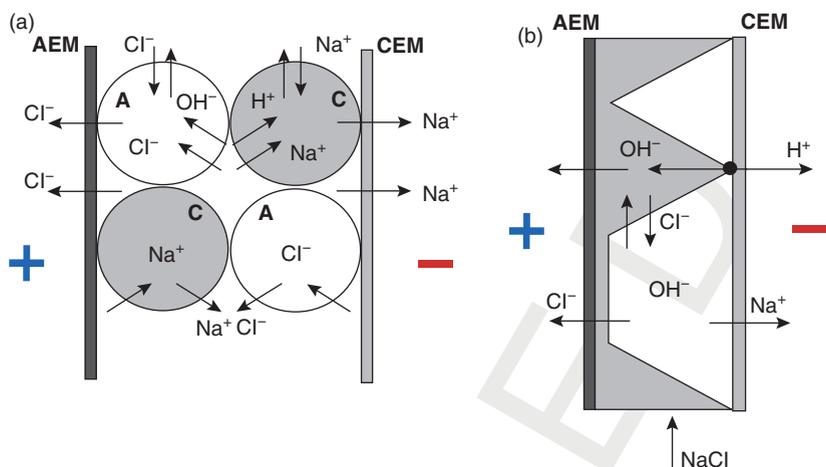


FIGURE 20.5. Scheme of ion fluxes in an EDI diluate compartment with an ion exchange bed (a) and with a profiled membrane (b). **A**, An anion exchange resin bead; **C**, a cation exchange resin bead. Arrows show the ion fluxes flowing through the interfaces of ion exchange materials. Adapted from Larchet et al.⁷⁰

laboratories; the food and beverage industry; and other such processes.⁸⁰ Additionally, this process is used for removal of traces of heavy metal and hardness ions^{74,77} or radioactive salts.^{81–83}

In ED of dilute solutions under intensive currents, at least when using profiled membranes, the electrical conductivity and diffusion permeability of IEMs no longer play a decisive role. The resistivity of the solution in the diluate compartment is much higher than that of the membranes. The membrane permselectivity increases with diluting solution, hence, the electrolyte back diffusion is insignificant (if only it is not the last step of high purity water production).¹² Properties which grow in significance are those which allow enhancing the mass transfer and the control of water splitting. Besides, prevention of the surface degradation in intensive electric fields represents another important problem.

Coating the surface of a heterogeneous membrane with a conducting homogeneous film seems to be a promising way to improve the membrane properties pertinent to ED of diluted solutions. The use in the coating film of functional groups not catalytically active toward the water splitting allows decreasing generation of H^+ and OH^- ions. Even if the chemical nature of the functional groups in the film is the same as in the original membrane, this aim is achieved because the distribution of current lines becomes more homogeneous. Intensification of electroconvective mixing is obtained due to two effects. First, the use of a film with a high surface hydrophobicity leads to enhancement of fluid slipping at the surface and facilitates the generation of electroconvective vortices. Second, the use of coating allows optimization of the current line distribution. More details are given in Chapter 9 and in Nikonenko et al.²⁹

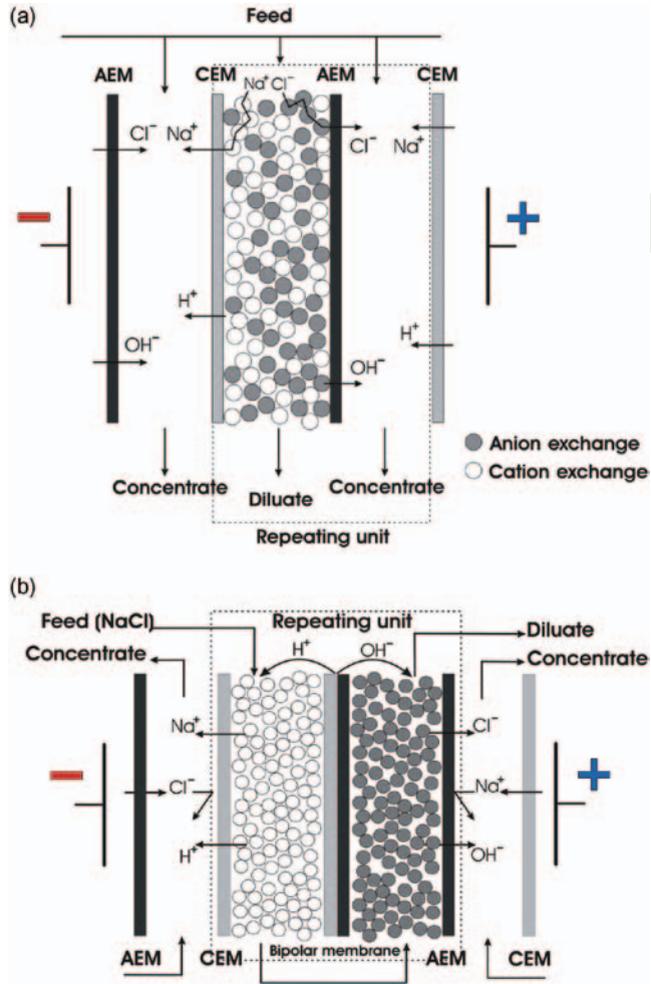


FIGURE 20.6. Schemes illustrating different CEDI stack concepts. (a) Conventional stack with diluate cells filled with a mixed-bed ion exchange resin; (b) stack with cation exchange and anion exchange resins in different diluate cells and regeneration of the ion exchange resins by H^+ and OH^- ions produced in a bipolar membrane. Adapted from Strathmann.¹²

CDI with IEMs CDI is an electrosorption process that can be used to remove ions from an aqueous solution by charge separation.^{12,13,84,85} CDI operates by adsorbing ions in the double layer formed at the electrodes by the application of an electric potential difference. The principles of the process are traced to the studies of Helmholtz and to the modeling of the electrical double layer by Guoy and Chapman.¹³

A CDI cell unit consists of two electrodes made out of activated carbon and separated by a spacer. A solution to be treated flows in the channel between the electrodes. When one electrode is charged positively, and the other negatively, anions from the solution are adsorbed on the first, and cations on the second. The solution outgoing from the channel is found partially desalted. At the next (ion release) step, the polarization of the electrodes is reduced to zero or inverted, and the retained ions are desorbed. A small product stream concentrated in salt is obtained. The potential difference applied in CDI is not high, in the range of 0.8–1.5 V, in order to avoid electrochemical reactions (usually water splitting) at the electrodes.

Conventional CDI is known to be energy inefficient because ion adsorption and desorption steps are not completely separated. When an electric potential is applied, counterions in the pore are adsorbed onto the electrode, but simultaneously co-ions are expelled from the pore volume of this electrode, seriously reducing the degree of desalination.⁸⁶ To solve this problem, Andelman⁸⁷ suggested a charge barrier (IEMs) placed adjacent to an electrode of a flow-through capacitor.

The membrane capacitive deionization (MCDI) is a two-step process. In the first step, application of an electrical potential between two electrodes results in the migration of cations through a CEM, and anions through an AEM, separating the cathode and the anode, respectively, from the feed solution (Fig. 20.7a). The amount of the ions passed through the membranes will be determined by the electric capacity of the anode and cathode. During this step, a partially deionized water is obtained. In the second step, the polarity of the electrodes is reversed and the ions are desorbed at the electrodes and

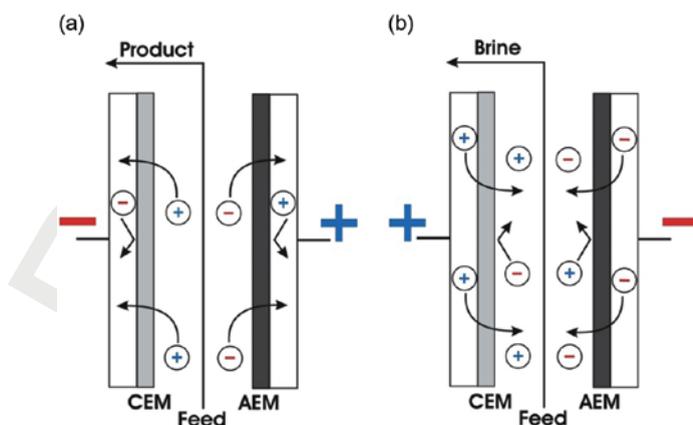


FIGURE 20.7. Schematic description of the MCDI process: an IEM is placed between the feed solution and the porous carbon electrodes. In the deionization step, the ions from the feed solution are adsorbed onto the electrodes (a); in the ion release step, desorption of ions takes place due to a reverse of electrode polarity. Adapted from Strathmann.¹²

then released into the feed solution, thus producing the brine. The advantage of the use of IEMs is that the efficiency of both steps becomes much higher in comparison to that of the conventional CDI.^{85,88,89} During the deionization step, the CEM prevents the transfer of anions from the cathode pore volume, and the AEM the transfer of cations from the anode pore volume, into the feed solution, as shown in Figure 20.7b. Hence, the process of ion adsorption is not deteriorated by the ion desorption. Similarly, the use of IEM avoids ion adsorption at the electrodes during the regeneration step.

Besides IEMs, the key component in this process is the carbon electrode.¹³ The amount of ions adsorbed at the electrodes is directly proportional to the available surface area. The role of the electrode nature and properties in MCDI processes has been intensively investigated. Many studies utilize carbon aerogels,⁹⁰ while others use carbon cloths,⁹¹ carbon sheets,⁹² carbon nanotubes,⁹³ or carbon nanofibers⁹⁴ coated with a thin-film nanoporous inorganic⁹⁵ or organic membranes.^{84,86} The electrode internal area for ion adsorption is in the order of $1000 \text{ m}^2 \text{ g}^{-1}$.

Note that MCDI technology is young and needs testing. The benefits of MCDI systems over those of RO and CEDI desalination are in the low pressure applied in the process and, therefore, as expected at least for brackish waters, lower energy consumption (1/3 less energy).¹³

The disadvantage of CDI is the large surface area of the electrode which is necessary when feed solutions with high salt concentration are deionized. MCDI systems may also suffer from fouling similar to that observed in ED operation. However, it is found that the fouling may be drastically reduced by switching potentials of electrodes.⁹⁶ Lastly, it is conceivable to apply a pulsed field to the electrodes to reduce both inorganic and organic fouling.⁹⁷

Micro- and Nanofluidics Desalination Device There are nontraditional, exciting applications resulting from research in the very novel and pioneering field of micro- and nanofluidics.^{14,29,85,98,99} A promising micro-/nanofluidic desalination device was proposed by J. Han's group¹⁴ (Fig. 20.8).

Seawater is pumped through a microchannel (with a width of $500 \mu\text{m}$ and depth of $100 \mu\text{m}$) and bifurcated into two other microchannels (each with a width of $250 \mu\text{m}$ and depth of $100 \mu\text{m}$), one of which is used for collecting desalted and the other for concentrated streams. The desalination is due to an ion-selective (cation-selective in Fig. 20.8) membrane, which serves as a nano-junction between the region of bifurcation and an additional microchannel. An electric current through the membrane is generated with help of three anodes and one (or two) grounded (GND) electrode(s). A high voltage (of the order of 70 V cm^{-1}) applied across the membrane gives rise to a space charge region (SCR) repulsion zone just before the bifurcation of the seawater microchannel. This zone plays the same role as the charged solution inside an RO membrane with fixed negatively charged sites (Fig. 20.1). Water molecules pass through this zone under the action of pressure gradient, while the charged particles are retained. The anions do not enter this zone because these ions

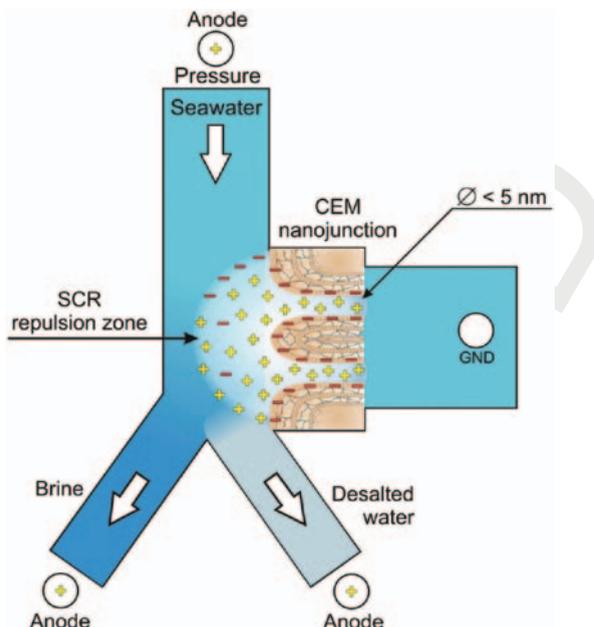


FIGURE 20.8. A micro-/nanofluidic desalination device (description in the text). Adapted from Kim et al.¹⁴

are expelled by the fixed ions and the applied electric force. The cations are retained by the electric field induced by the separation of charges. A small amount of cations transferred with the convection flow creates an excess of positive charge at the outlet of the SCR, while an excess of negative charge appears at the inlet. In steady state, the mechanical force (due to the pressure gradient) and the convection-induced electric force applied to a cation are equal and directed to opposite sides, so that the resultant driving force is zero.

Preliminary tests have shown¹⁴ that both salts and larger particles (cells, viruses, and microorganisms) are expelled from the SCR near the membrane, which significantly reduces the risk of membrane fouling. The tested device has shown ~99% salt rejection in the case of seawater desalination at 50% recovery rate and at a power consumption of less than 3.5 W h L^{-1} , which is comparable to current state-of-the-art systems. The authors¹⁴ believe that this method could be used to produce small- or medium-scale systems (for families or small villages), with the possibility of battery-powered operation, instead of competing with larger desalination plants.

Overlimiting Current ED As was shown in Chapter 9, the limiting current density, which is characterized by a sharp increase in the electric resistance of ED cells due to depletion of electrolyte concentration at the membrane surface, is attained at about 1 V per cell pair. In most cases of practical

use of ED, this or a slightly lower voltage is steadily applied. The increase in voltage leads to some undesirable effects: growing electric consumption, lowering current efficiency, and increasing scaling and fouling. However, the use of overlimiting current modes attracts a number of researchers and engineers.^{12,29,30,71,78,79,100,101} The interest is in the fact that the overlimiting mass transfer rate at reasonable voltages close to 2 V may be up to three times higher than i_{lim} (see, e.g., Fig. 9.24 in Chapter 9). This means that even if the costs related to electric consumption increase, the total costs per 1 m³ of treated water may be lower owing to decreasing capital costs since a lesser amount of membranes and membrane devices is needed. Besides, smaller sizes of the membrane installation may give other advantages, especially in production facilities of limited dimensions.

The mass transfer rate in the overlimiting current range strongly depends on the morphology and chemical composition of the surface membrane layer that promotes the need for the optimizing surface (see Chapter 9 and Nikonenko et al.,²⁹ Balster et al.^{71,100}). The main mechanism of mass transfer enhancement at overlimiting currents is electroconvection, which arises due to the action of the electric field on the electric space charge in the depleted solution near the membrane surface produced by the same electric field (current-induced electroosmosis or electroosmosis of the second kind).^{29,30,101,102} The electroconvection provides additional mixing of depleted solution, in addition to the forced convection. By applying a more hydrophobic surface with tailored heterogeneity, it is possible to essentially enhance the overlimiting mass transfer (Chapter 9, Section 9.5.1).

To reduce the risk of scaling and fouling, several methods may be used. The first one is in pretreatment of water prior to ED. The elimination of salts causing hardness from water eliminates the cause of salt deposition on the membrane surface. Another method is the application of membrane pairs where the water-splitting rate is higher at the CEM surface than at the AEM one. In this case, the desalinating stream becomes alkalized while the concentrating stream becomes acid.⁷⁹ The latter prevents the deposition of carbonates and oxides on the concentrating membrane surface. The alkalization of the desalinating stream increases the degree of weak acid anion ionization that improves the removal of weak acids (such as silicic and boric) from feedwater. The third way is the use of pulsed current mode. This mode not only allows mitigation of scaling and fouling, but also results in an increasing rate of ED desalination. Mishchuk³⁰ supposes that the gain in applying pulsed currents may be due to electroconvection mixing, which continues during the pause owing to inertial properties of liquid movement. This residual convection could partially restore the electrolyte concentration near the membrane.

The application of overlimiting currents in ED is in accordance with the rather general trend of process intensification in chemical engineering. However, as was rightly noted by Strathmann,¹² this emerging mode of ED process is under development and needs further study.

20.3 ED CONCENTRATION

In conventional ED (Fig. 20.2), the final product can be both a demineralized solution and a concentrate. The degree of concentration that can be achieved in passing the feed solution through an ED stack is a function of the feed solution concentration, the applied current density, and the residence time of the solution in the stack concentrate. The latter can be increased by reducing the flow rate of the concentrate stream or by using concentrate stream recirculation. In ED, a much higher brine concentration can be achieved, in comparison with RO, since there are no osmotic pressure limitations. To obtain extremely concentrated solutions (close to the saturated ones), CC without entrance for feed solution are used^{4,39,103–105} (Fig. 9.15 in Chapter 9). Ionic species are transferred from the feed solution circulating through the diluate compartments into the CC under the action of the applied electric potential difference. A small amount of water is transported there by electroosmosis, mainly in the hydration shell of ions. The produced concentrate is removed from the compartment through a capillary.

The fundamental basis (briefly presented in Chapter 9) and the main concepts of ED concentration were developed in the 1970s and 1980s.^{33,104–106} Large plants with a capacity of 20,000 to more than 200,000 tons of salt per year are in operation in Japan. Of very special interest is the concentration of NaCl from seawater prior to evaporation for the production of table salt in Japan, which has no native salt deposit. The use of ED as a preconcentration step prior to evaporation leads to substantial savings in energy costs. Similar applications of ED and EDR are described by Turek.^{40,107} A coal-mine brine containing $32.8 \text{ g L}^{-1} \text{ Cl}^{-}$ was desalinated and concentrated by an ED–EDR system¹⁰⁷; the obtained concentrate was then treated by evaporation and crystallization in order to produce a solid salt and lye. The comparison of two systems of solid state production, without and with ED–EDR units, has shown that the overall energy consumption decreased from 970 kWh per 1 ton of salt to 500 kWh t^{-1} in the case where ED–EDR were used to the brine preconcentration.¹⁰⁷

The main advantage of the use of ED–EDR in electrolyte solution concentration is the possibility of obtaining highly concentrated brines (up to saturated solutions) at relatively low energy consumption. The degree of water recovery when treating brackish waters with TDS $1\text{--}2 \text{ g L}^{-1}$ may be higher than 99%.

Furthermore, ED is used for concentration of organic acids (citric, formic, and others) in the food industry,^{108,109} for concentration of liquid radioactive waste,^{81,110,111} and other applications.¹¹¹ It is possible also to recover valuable components of processing solutions and close the loop on the solvent.¹¹¹ As an example, consider the recycling of dimethylacetamide used as a solvent and extraction and concentration (up to 3.5–4 M) of lithium chloride from wastewater in chemical industry.¹¹² Quite successful is the use of ED for the recovery

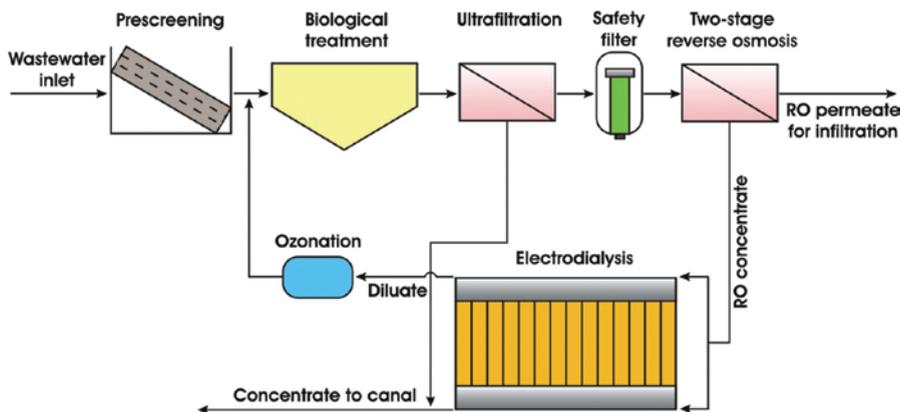


FIGURE 20.9. Schematic diagram of a hybrid system for wastewater treatment. Adapted from Zhang et al.¹¹⁶

of the condensate of juice vapor in the manufacture of ammonium nitrate fertilizer.¹⁰⁴ The condensate of juice vapor contains NH_4NO_3 with a concentration from 0.3 to 3 g L^{-1} . ED allows production of pure water (containing less than 3 mg L^{-1} of NH_4NO_3), which is then used to generate steam and a concentrate of NH_4NO_3 (up to 200 g L^{-1}).

The use of ED–EDR for concentrating RO brine is of a great interest. Traditionally, the RO concentrate is discharged into the natural water body (with or without dilution, depending on the local discharge regulations) or treated by evaporation. The former method is not environmentally friendly and the latter process is very costly.¹¹³ A number of studies^{114,115} have been carried out in order to reduce the liquid discharge and to increase the water recovery in RO–ED–EDR systems. The use of bipolar ED for producing acids and alkalis from the concentrate allows for the generation of agents which can be used for restoring pressure-driven units from fouling.^{114,115}

Figure 20.9 shows a schematic diagram of a hybrid system developed by Zhang et al.¹¹⁶ to treat (mainly domestic) wastewater to produce infiltration water for groundwater recharge. This recharge is needed in coastal areas where overconsumption of groundwater takes place, and, as a consequence, seawater intrusion and soil salinization occur. The wastewater first passes a mechanical screen, biological, and then ultrafiltration (UF) treatment prior to being treated by a two-stage RO. The RO permeate is used as the infiltration water; the concentrate is treated by ED. The ED diluate is reinserted into the biological treatment process, and the concentrate is mixed with the UF concentrate to meet regulations and then discharged to the canal.

Korngold et al.¹¹⁷ have realized a similar process in which RO concentrates were treated by the EDR and the produced diluate was mixed together with the RO permeate. Thus, the overall water recovery of the RO unit was improved (to 97–98%) and the volume of brine was essentially reduced.

As the main mechanism of water permeation through IEMs contacting concentrated solutions is electroosmosis,¹¹⁸ the water transport number in the membranes used for ED concentration should be minimized. Besides, the electrolyte diffusion permeability should be decreased as well. For these aims, modifications of perfluorosulfonated membranes MF-4SK were carried out with tetraethoxysilane¹¹⁸ and polyaniline.^{119,120} It was shown that these modifications result in high reduction of free water electroosmotic transfer, therefore, water molecules are transported only within hydrated shells.¹¹⁸ After modifications, diffusion permeability drops by an order of magnitude, and water transport numbers are reduced by 50–70%. In the process of sodium chloride concentration by ED, the salt content of the concentrate increased by 50–70%.¹²⁰

20.4 BMED

A BPM is a bilayer film containing a cation and an anion exchange layer (Fig. 20.10).

If an electric field is applied in a way that mobile salt cations and anions (Na^+ and Cl^- in Fig. 20.10) move away from the bipolar junction, the junction becomes depleted of salt ions. The charge transfer is then provided by new carriers, the ions H^+ and OH^- , which are generated by water dissociation reaction. The reaction occurs in a thin boundary layer of a thickness of 1–10 nm, where it is catalyzed by functional fixed groups (or a specially introduced catalyst) and strong electric field in the EDL.^{73,121–124} The water splitting rate also depends on the topology/roughness of the bipolar junction.^{122,124–126}

Electromembrane methods for producing acids, alkalis, and bases with the use of BPMs from the respective salts and water are reduced to the realization of the reaction:

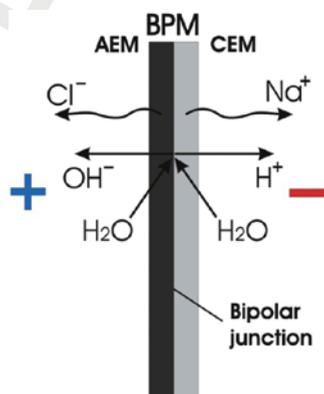


FIGURE 20.10. Schematic drawing of the water splitting function of a BPM.

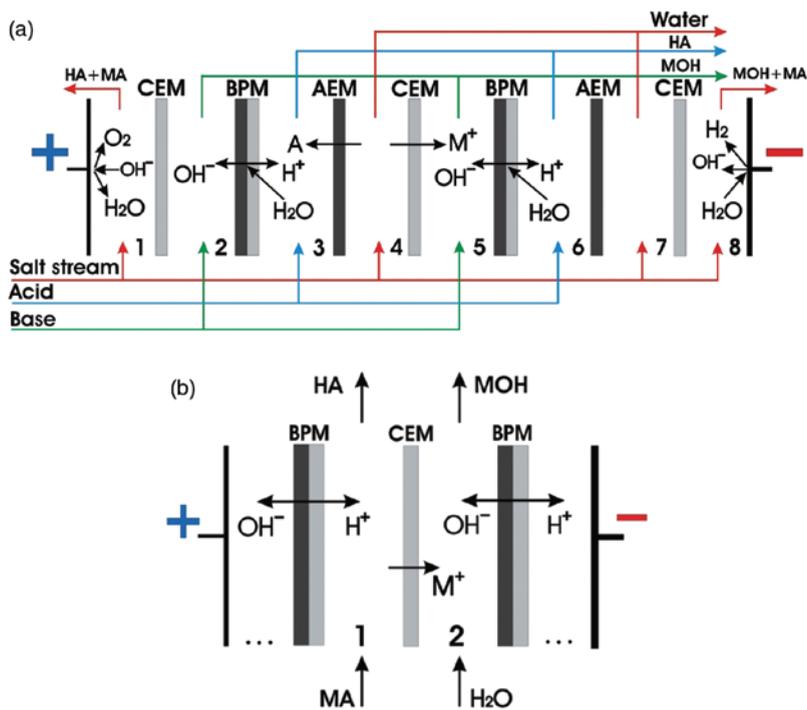


FIGURE 20.11. Schematic diagram of BMED stack for producing strong acids and alkalis (a) and weak bases (b) from their salts.



where M^+ is a (metal) cation, and A^- is an anion.

In the case where strong acids and alkalis are to be obtained from their salts, generally a BMED stack configuration is used with two monopolar membranes (shown in Fig. 20.11a).^{7,12,127,128} The salt anions migrating under the action of applied electric field from compartment 4 through an AEM, and hydrogen ions generated in a BPM, produce an acid in compartment 3. A similar process, but with the participation of hydroxyl ions and salt cations, leads to the formation of an alkali in compartments 2 and 5. A salt solution feeds compartments 1, 4, 7, and 8. Compartments 2, 3, 5, and 6 are fed with distillate or a diluted solution of acid/alkali (Fig. 20.11a). Generation of H^+ and OH^- ions in BMED allows obtaining solutions with controlled pH value up to concentrated (2–3 M) solutions of acids and alkalis.

To obtain weak acids or bases, simpler configurations with a two-compartment repeating cell are mainly used. In the case where a base is produced, the cell with alternate BPM and CEMs is applied (Fig. 20.11b); in the case where the product is an acid, AEMs are used instead of the CEMs. When operating such a cell, hydrogen ions generated into compartment 1 are linked

in weak acid molecules with anion A^- and do not penetrate into compartment 2. The current efficiency and the concentration of the weak acid in this case are higher than these parameters in the case of strong acid, obtained in the cell shown in Figure 20.11a.

An alternative method of producing acids and alkalis is electrolysis. The main advantage of BMED in comparison with electrolysis is that in the ED stack there are no metal electrodes, hence, the solutions are not contaminated by the products of their destruction. Emission of gas, which is especially dangerous in the case of generation of oxidants such as chlorine and oxygen at the anode, is also absent. The elementary cell, including compartments 3–5 (Fig. 20.11a), can be repeated in an ED stack an unlimited number of times. As the stack contains only one cathode and one anode, the requirements for the cost of the anode, often manufactured from platinum or platinized titanium, are essentially reduced. Moreover, the use of buffer compartments 1 and 8 allows one to abandon platinum and to use anodes of base metals.¹²⁹

Typical examples of the use of BMED are the production of acids and bases from corresponding salts,^{12,128,130} the acidification/deacidification of product streams,^{12,128,131,132} and the production of organic acids.^{133–135} The case where BPMs are successfully used in an EDI stack was considered in the section “CEDI” (Fig. 20.6b). Very intensive is the use of BMED in the food, dairy, and pharmaceutical industries.^{132,134,136} This method is effective in the treatment of amino acid-containing solutions, in particular, in the separation of amino acids and proteins on the basis of their isoelectric points.^{128,137,138}

Particularly promising is the production with BMED of malic, succinic, and other organic acids used as precursors for the synthesis of biodegradable polymers and plastic materials.^{139,140} In up-to-date membrane technologies, the process of organic acid recovery from fermentation broth is preceded by the step of concentration of these components (e.g., glyceric acid salts) using conventional ED.^{134,141}

Further examples can be found in books and reviews concerning BMED applications.^{128–130,133,136}

BMED allows for the conversion of salts into acids without yielding byproducts. This advantageously distinguishes it from traditional chemical processes, which require significant amounts of sulfuric acid and are accompanied by the formation of large quantities of gypsum (2 kg of gypsum are needed for production of 1 kg of citric acid).

The main problems in the case of production of strong acids and alkalis by BMED are the pollution of the products with the feed salt ions, and the relatively high specific energy consumption of the electromembrane process. The performance is improved by increasing the hydrogen transport number in the cationic layer and the hydroxide transport number in the anionic layer (and, respectively, decreasing co-ion transport number in both layers), and by enhancing the kinetic energy of the water splitting reaction in the bipolar junction. The latter is generally achieved by introducing between the cationic and anionic layers a thin interface layer, containing a water dissociation

catalyst, and by increasing interface layer area, for example by increasing the surface roughness.¹²⁵ Good catalytic activities have been found for weak acids such as amino groups, pyridines, carboxylic acids, and phosphoric acid groups.^{121,124,125,130} Besides, good catalysts are metal oxides and hydroxides¹⁴² or heavy metal ion complexes.^{124,143}

The introduction of a catalytic interface layer gives more freedom in choice of cationic and anionic layers. Use of an anion exchange layer with quaternary ammonium groups results in BPMs with low electrical resistance.¹²⁴

Note also that the water permeability of both layers should be sufficiently high in order to avoid water lack in the bipolar junction for generation of H^+ and OH^- ions. High concentrations of ionic groups in the bipolar junction not only increase the rate of the water dissociation reaction, but give rise to the hydrophilicity of the interface layer. As a result, water activity in the bipolar junction increases, as well as the water flux from the ion-exchange layers to the interface region.¹²⁴

Another drawback of BPMs is their high value that limits the range of applications, making BMED economically feasible only in the case of expensive products. Some authors^{121,130} investigate the method of preparing low cost BPMs by using heterogeneous cation and/or anion exchange layers and a catalytic interface layer. An effective way to minimize the costs and the impact on the environment is the use of hybrid systems. Wang et al.¹³⁴ report that the integration of conventional ED in the production of gluconic acid by BMED results in the decrease of the process costs from $\$0.39\text{ kg}^{-1}$ to $\$0.31\text{ kg}^{-1}$. Mondor et al.¹³⁸ describe the advantages of combining BMED with UF/diafiltration to produce a soy protein isolate.

20.5 FRACTIONATION AND SEPARATION PROCESSES WITH CHARGED MEMBRANES

Membrane fractionation and separation processes are perhaps the most developed and commonly used. They are extensively applied in the electrochemical industry, water treatment, wastewater treatment, and the food industry. A very large area of their application is medicine. Following Baker,¹⁹ the total membrane area produced for medical applications almost matches all industrial membrane applications together. In the United States, the medical membrane market approaches $\$1.5$ billion per year and grows steadily.¹⁴⁴ The biggest part of this market involves membranes in drug delivery, hemodialysis (kidney–blood purification), other artificial organs (oxygenators, pancreas, liver, etc.), and tissue engineering. Historically, in medical applications, porous membranes separating the components via a sieve mechanism were used. However, in recent years the share of charged membranes in this area is continuously increasing, especially in combination with porous membranes. Some of these applications are considered in this section.

20.5.1 Electro-Electrodialysis

Electro-electrodialysis (EED) or membrane electrolysis¹³³ combines electrolysis and ED. The term “membrane electrolysis” is sometimes reserved for two-compartment cells with one IEM. In this kind of ED technique, electrode reactions play a critical role in feed treatment. A large number of different EED processes using CEMs and/or AEMs have been proposed so far.^{48,133} The most important example of this technique is chlor-alkali production. The chlor-alkali industry is currently one of the largest industries producing annually more than 48 million tons of sodium hydroxide (NaOH) and more than 42 million tons of chlorine (Cl₂).¹⁴⁵ The raw material is sodium chloride (NaCl) and the reaction proceeds according to:



To obtain the products of this reaction with a sufficiently high yield, it is necessary to separate chlorine from hydrogen (because they react explosively) and from NaOH (because chlorine dissolves in contact with NaOH to form a hypochlorite solution). As can be seen in Figure 20.12, a two-compartment EED cell with a CEM simultaneously allows the realization of reaction (20.2) and the separation of the reaction products.

A saturated NaCl brine is fed to the anolyte compartment where Cl₂ gas is produced at the anode. Under the action of applied electric field, Na⁺ ions migrate through the CEM into the catholyte compartment where they form

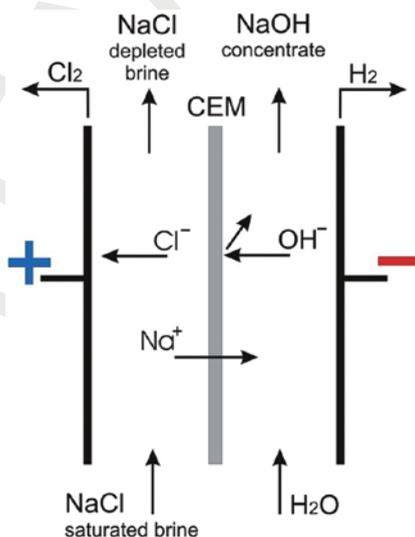


FIGURE 20.12. Schematic diagram illustrating the chlorine-alkaline production process by EED. Adapted from Nagarale et al.⁴⁸

sodium hydroxide with OH^- generated at the cathode.⁴⁸ The process utilizes perfluorinated CEMs such as Nafion® (DuPont, Wilmington, DE), and is operated at an elevated T (80–90°C). The produced caustic soda is concentrated up to 35%. In this medium, even extremely corrosion-resistant Nafion® membranes suffer from degradation. Moreover, back migration of OH^- at high NaOH concentration results in significant loss in current efficiency. The situation can be improved by using composite CEM containing carboxylic groups.⁴⁸ These membranes are more stable; they have a lower water content and are less permeable to OH^- ions. Their lifetime in a chlor-alkali plant is evaluated as more than 5 years.⁴⁸

Another example of application EED, where the role of the electrode reactions is essential, is the chromic acid recovery from plating bath. A schematic diagram illustrating the process in the cases of two-compartment and three-compartment cells is shown in Figure 20.13.

In the case of two-compartment EED, exhausted plating solution containing chromic acid and metallic impurities, such as copper, iron, zinc, aluminum, nickel, and trivalent chromium flows through the anolyte compartment where trivalent chromium is oxidized (Fig. 20.13a). The other cations (impurities) migrate through a CEM (normally, a Nafion® membrane) into the cathode compartment where they are collected. Some amount of Cr(III) and Cr(VI) may be lost due to the migration into the cathode compartment.¹⁴⁶

In the case of three-compartment EED, the rinse water from the plating process containing chromic acid and metallic impurities passes through the central compartment (Fig. 20.13b). Cationic impurities migrate toward the cathode through the CEM. The cathode compartment is fed with diluted sulfuric acid to form dissolved metal sulfates. The acidic conditions prevent precipitation of metal hydroxides. Hexavalent chromium anions (chromates) migrate toward the anode through the AEM. There, the chromate and dichromate anions form chromic acid together with the protons generated at the anode. The treated rinse water is reused in the rinsing process and the pure chromic acid is returned to the plating bath. This process provides purification of chromium plating solutions and the treatment of the rinse water in a single step without need of either water or chemicals. The main process limitations are the poor stability of the AEM against the oxidative chromic acid solution and the increase in the AEM resistance due to the formation of polychromates in the membrane.¹⁴⁷

When ED is applied to organic acid production, the role of electrode reactions is similar to that of BPMs (see Section 20.4). Both electrodes and BPMs provide H^+ and/or OH^- for the acidification or ionization of organic anions. Generally, a monomembrane EED process (sometimes coupled with extraction)¹³³ is used to recover organic acids (butyric, valeric, adipic, caproic, and oxalic acids).¹⁴⁸

In hydrogen energy, one of the most suitable process of H_2 production is the iodine–sulfur (IS) cycle.^{149,150} Iodhydric acid (IH) is an intermediate product which generates H_2 during its decomposition. It is difficult to concentrate HI

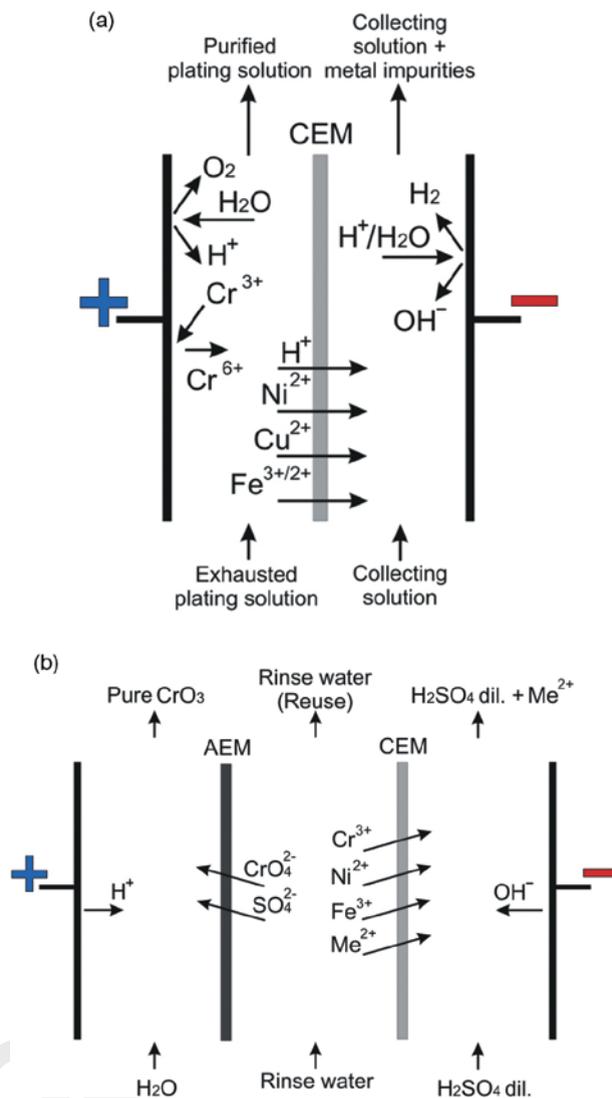


FIGURE 20.13. Principles of electro-electrodialysis (EED) for chromic acid recovery by applying two-compartment (a) and three-compartment (b) cells. Adapted from Huang et al.¹⁴⁶

solution by conventional distillation, since HI forms with water an azeotropic solution $\text{HI}/\text{H}_2\text{O} = 1:5$ (molar ratio). However, HI acid can be effectively concentrated through EED with CEM, and its concentration could exceed the azeotropic composition.¹⁵¹

EED can be used in other separation process, such as phosphoric and sulfuric acid separation¹⁵² and concentration of inorganic acids over its azeotropic

composition.¹⁵¹ There are designs with more than three compartments in an EED cell. Cheng et al.¹⁵³ have proposed a system for bovine serum albumin and hemoglobin separation with six compartments. The electrode compartments served as sources of H^+ (the anolyte one) and OH^- (the catholyte one) ions. The H^+ ions migrated from the anolyte compartment through a CEM into the neighboring compartment in order to maintain there a stable pH close to 4. In turn, the OH^- ions migrated through an AEM into the neighboring compartment in order to establish there a pH equal to 9.8. There are also two central compartments wherein pH is equal to 7 and 8.5, the first one being closer to the anode, and the second one to the cathode. Quasi-stable pH values in the four central compartments allow separation of proteins due to the fact that they can be ionized under various pH. A protein can spontaneously move toward the location where the medium pH is equal to its pI (isoelectric point) value and be stationary at that location. Thus the protein molecules can migrate across membranes and be relocated into different compartments according to their pI values.

20.5.2 Dialysis (Diffusion Dialysis, Donnan Dialysis)

When charged membranes are used in diffusion separation processes, referred to as diffusion dialysis (DD) and Donnan dialysis, the contribution of electric force is essentially due to the electroneutrality requirement, which must be held on a macroscopic scale.

The principle of DD is presented in Figure 20.14, which describes the process in the case where a mixture of a salt and an acid is separated. The dialysis cell contains AEMs only. A feed solution containing a mixture of NaCl and HCl flows through alternating cells while water is fed in countercurrent flow through the other cells of the stack. Cl^- (or SO_4^{2-} , NO_3^- , PO_4^{3-}) anions pass through the AEMs into neighboring compartments, while the salt cations are rejected from AEMs due to the Donnan exclusion effect. The transfer of anions leads to the formation of an excessive positive charge in the feed compartments and a negative charge in the neighboring ones. The separation of charges results in the creation of an electric force (due to diffusion potential difference). Under the influence of the electric and diffusion forces acting in the same direction, the H^+ ions pass through AEMs. Although positively charged, the H^+ ions are very mobile, and hence have higher competition in diffusion than metal ions.¹⁵⁴ Therefore they can diffuse through AEMs along with salt anions to meet the requirement of electrical neutrality.¹⁵⁵ The net result is the removal of acids from a mixture with salts. Similarly, bases can be removed from salt solutions using a stack with CEMs only.^{12,48}

In the case of Donnan dialysis, there is ion exchange across an IEM. For example, in softening of hard water, divalent ions, such as Ca^{2+} and Mg^{2+} or SO_4^{2-} are exchanged for monovalent ions such as Na^+ or Cl^- .^{48,156,157} The principle of this process is as follows. Feedwater containing NaCl and ions of hardness (Ca^{2+}) is separated by a CEM from an auxiliary NaCl solution of a

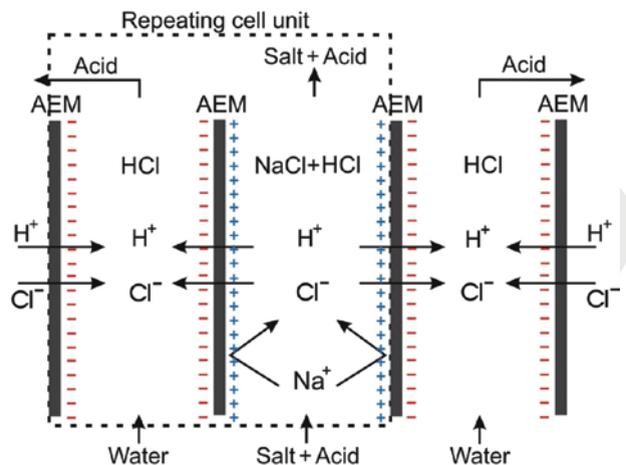


FIGURE 20.14. Schematic drawing illustrating the principle of DD used to recover an acid from a mixture with salt in a stack containing AEMs only. Adapted from Strathmann.¹²

sufficiently high concentration. Since the Na^+ concentration in the auxiliary solution is significantly higher than the concentration in the feed solution, there will be diffusion of this ion into the feed solution. The transfer of Na^+ ions gives rise to an excessive positive electric charge in the feed solution. These electric forces produced by the separation of the charges will assist the transport of Ca^{2+} ions from the feedwater into the auxiliary solution.

The advantages of both methods of dialysis are in low energy consumption and low installation and operating costs. The methods are stable, reliable, and easy for operation, as well as being less susceptible to membrane fouling.^{155,158} They are effective in the recovery of acids and alkalis from mixtures with salts in wastewaters from steel production, metal refining, electroplating, cation exchange resin regeneration, nonferrous metal smelting, aluminum etching, and tungsten ore smelting.^{155,159}

Besides its uses for water softening mentioned above, Donnan dialysis is successfully applied for boron,¹⁶⁰ nitrate,¹⁵⁸ and bromate¹⁶¹ removal from aqueous solutions and the recovery and concentration of transition and rare metals.^{162,163} An example of the anion Donnan dialysis is the sweetening of citrus juice. In this process, hydroxide ions furnished by a caustic solution replace the citrate ions in the juice.¹⁵⁵

The dialysis methods are well developed and find many applications in the United States and Japan as well as in China and North African countries.¹⁵⁵

In comparison with pressure-driven and electro-driven processes, dialysis has a relatively low processing capability and efficiency: a relatively high amount of membranes is needed to provide a given quantity of product. Another weakness is the low stability of AEMs in acidic solution and their high H^+ permeability. The dialysis membranes should have a high selectivity

and a high diffusion permeability that is difficult to achieve simultaneously. As a result, the variety of membranes suitable for dialysis is limited, and only few of them satisfactorily meet the requirements.^{155,161}

20.5.3 Electrofiltration (ED with UF Membranes)

The electrofiltration process occurs under the action of pressure and electrical potential gradients as driving forces. This process is used for the separation of polyamino acids, proteins or bioactive peptides, and other organic compounds.^{144,164,165} An important example is the treatment of β -lactoglobulin, which is one of the major whey components.¹⁶⁶ β -Lactoglobulin can release, by enzymatic hydrolysis, different bioactive peptides according to the enzyme used. Figure 20.15 shows an ED cell in which UF and IEMs are used for fractionation of β -lactoglobulin hydrolysate, to obtain peptides in a more purified form. Under the action of applied electric field, negatively charged peptides (P^-) migrate through a UF membrane from the central feed compartment to the neighboring compartment fed with a KCl solution. Cl^- ions leave this compartment through an AEM toward the anolyte one. As a result, they are substituted by P^- . Similar processes occur in the right-hand side of the cell: in the compartment between a UF membrane and a CEM, K^+ ions are substituted by positively charged peptides, P^+ . The neutral fraction of peptides remains in the central compartment.

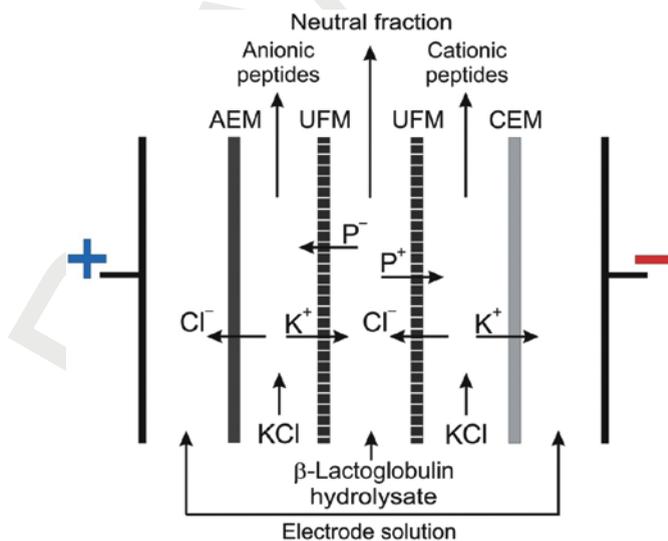


FIGURE 20.15. Configuration of the ED module using two UF membranes for the simultaneous electroseparation of cationic (P^+) and anionic (P^-) peptides from β -lactoglobulin hydrolysate. Adapted from Poulin et al.¹⁶⁶

ED with UF membranes appeared to be a very selective method for separating peptides from protein hydrolysates. The system presented in Figure 20.15, or similar configurations, were used by Vanhoute et al.¹⁶⁴ for the fractionation of a bovine hemoglobin peptic hydrolysate mixture in order to increase the value of slaughterhouse by-products such as blood protein. Firdaous et al.¹⁶⁵ also examined a similar process for alfalfa white protein hydrolysate.

20.6 MEMBRANE-BASED HYBRID ZLD TECHNOLOGIES

Nowadays, ZLD or near-ZLD systems have become more and more often a goal of water and waste treatment industrial engineering for recovery of clean water and minimization of brine streams. Mandatory elements of such systems are thermal methods such as brine concentrators, crystallizers, thermal evaporators, and spray driers, which reduce concentrate to a slurry or solid product that can be disposed of in landfills. These processes are capable of recovering high purity water (95–99% recovery from waste streams) and revenue-generating mineral salts.¹⁶⁷ Although these processes have been proven effective for volume minimization, the capital and operating costs often exceed the cost of the desalting facility.¹⁶⁸

For economic reasons, ZLD has been regarded for many years as an overly expensive solution and therefore was employed in limited cases. However, the increasing rate of population growth, scarcity of water in many places around the globe, and the growing awareness about the need for environment protection has brought this issue back to focus. Accordingly, new ZLD technologies are today developed and new, more cost-effective options are now available. The ZLD approach is becoming an important strategy in managing water resources toward maximizing water savings, reducing desalination and water treatment costs, and protecting water resources and the environment.¹⁶⁹

Nowadays, the situation of water regulation and new technical solutions has prompted those in the field to reconsider the economics of ZLD. First, the requirements to the quality of potable water become stricter and its price rises. And, perhaps more importantly, regulations on the discharge of waste fluids into open waterways are more stringent. When making assessments for water treatment systems, the cost of ZLD should be compared to the cost of fresh-water and the savings on sludge disposal. Hence, regulation represents the biggest incentive to ZLD implementation so far.¹

Another element improving the economics of ZLD is novel separation techniques. More effective evaporation processes, such as mechanical vapor recompression (MVR), are available. Use of membrane distillation (MD) and membrane crystallization (MC) systems could essentially decrease the power consumption in ZLD systems. These are thermally driven processes, in which a relatively low feed T ($<90^{\circ}\text{C}$) is used. This allows the utilization of waste heat, for example, the condensate from turbines or heat exchangers.¹⁷⁰

ED concentration may be a key technique to essentially reduce energy consumption in ZLD systems. By applying ED concentration, it is possible to diminish the volume of liquid, which should be evaporated.

Turek¹⁷¹ has realized several ZLD systems for treatment of coal mine brackish waters. According to Turek,¹⁷¹ water of approximately 10 g L⁻¹ salinity was desalted/concentrated by four ED units arranged in cascade. In another case, a part of coal mine water containing about 35.45 g L⁻¹ Cl⁻ was softened by NF, and the other part of water from another underground level of about 2.25 g L⁻¹ Cl⁻ content was desalinated and simultaneously concentrated by ED with univalent permselective membranes.¹⁷² Partially evaporated, pretreated by NF water was mixed with ED brine containing about 55 g L⁻¹ of Cl⁻ and underwent further evaporation and then crystallization. The value of produced salt was found to be close to the total cost of the system utilization. The benefit was due to the decrease of cost for chloride and sulfate discharge.

Another system using RO and EDR was applied to treat brackish water with high scaling potential from the Sahel region in Tunisia.¹⁷³

The combination of RO and ED concentration seems a very effective way to obtain concentrated brine from feedwater. A schematic diagram of wastewater treatment including an ED unit concentrating RO retentate developed by Zhang et al.¹¹⁶ is shown in Figure 20.9.

Mavrov et al.¹⁷⁴ have applied BMED to produce an acid and an alkaline stream used for regeneration of cation and anion exchange resins, respectively, in a hybrid system including RO and conventional ED. The ion exchange units were installed to produce deionized water from RO permeate.

More recently, Oren et al.^{169,175} proposed an RO-EDR process with a side loop crystallizer to improve water recovery and produce mineral byproducts from brackish groundwater in the Negev Highland, Israel. Inland brackish water desalination is becoming a significant source for water particularly in areas that are remote from the sea. An important element of the process is a wind-aided intensified evaporation (WAIV) unit, which benefits the climate peculiarities of dry desert to produce a dry or semidry solid salt from a slurry obtained in a crystallizer treating the brine produced in an EDR unit (Fig. 20.16). The RO retentate is concentrated in EDR to over 10% TDS concentrate while producing the diluate that was recycled to the RO permeate. The risk of scaling in the CC of the EDR unit was prevented, besides of operation in a reversal mode, by acidification, and the use of a side loop crystallizer. Settlers, inline microfiltration, and side loop UF kept suspended solids from returning to the EDR unit.

In the above cited publications^{169,173,174} the authors have applied underlimiting current modes when using conventional or reversal ED. This allowed them to minimize the risk of scaling as well as the energy consumption. However, the use of low current density results in high membrane surface area needed to provide necessary production capacity. Moreover, the alternation of diluate and concentrate streams leads to losses of product. To avoid the precipitation of poorly soluble salts when applying intensive current densities, some special measures can be undertaken: pH correction (by using special AEMs with

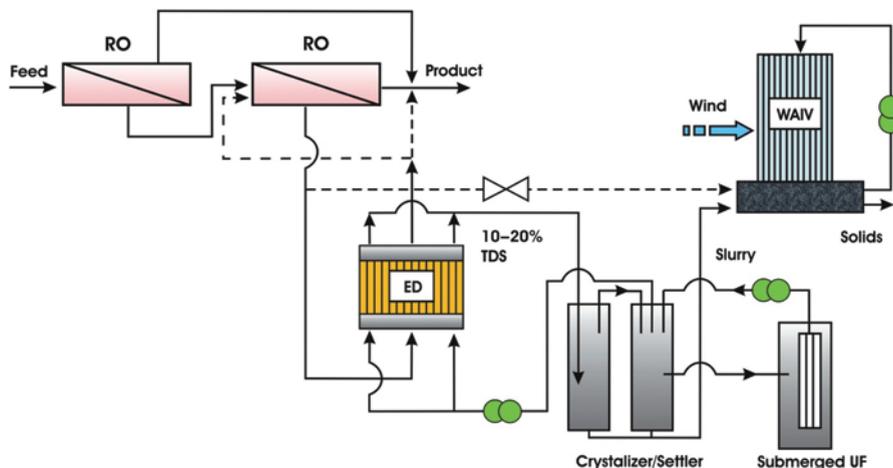


FIGURE 20.16. Schematic presentation of a ZLD system for treatment of brackish water in desert areas using wind-aided intensified evaporation (WAIV). Adapted from Oren et al.¹⁶⁹

lower H^+/OH^- ion generation functions^{29,79} or by adding acid in the concentrate compartment),¹⁶⁹ the use of pulsed currents,^{53,54} and/or reversal ED mode. Some authors^{78,116,117} propose an even more radical solution: removing the scaling components from the feedwater prior to its treatment in membrane modules. The ions causing hardness can be removed by ion exchange techniques. For example, Ca^{2+} and Mg^{2+} can be removed by exchange with Na^+ initially associated to a cation exchange resin. The regeneration of the resin may be carried out by using a part of the ED brine.¹⁷⁶ Another possibility is given by the application of BMED,^{78,174} which produces an acid and an alkaline solution for regeneration of, respectively, cation and anion exchange resins. Tskhay¹⁷⁷ considers different schemes providing sedimentation of salts causing hardness by changing pH of the feedwater and application of BMED for producing acid and alkaline streams. Zhang et al.¹¹⁶ studied an RO–ED system where RO retentate, prior to being treated by ED, was decarbonated via an acidification and an aeration. They found that after this decarbonation, it was possible to operate the ED unit under a steady state for a long-term experiment with a high overall water recovery (95%).

A very important advantage of removing the scaling components from the feedwater is that all membrane units, the NF and/or RO, as well as ED, may be operated at high fluxes; in particular, ED may be operated at overlimiting current density. Moreover, the maintenance of the membrane stacks might be realized much more easily, and the lifetime of membranes significantly increases.

In brief, the idea of realization of ZLD systems with removing scaling components from the feedwater is in the precipitation of hardness salts before the membrane modules and that of well-dissolved salts after.²⁹

Among the areas where ZLD systems seem to be the most suitable are:

- *Power Plants*: steam production, regeneration of liquid wastes from flue gas scrubbers;
- *Oil/Gas Industry (Refineries, Petrochemical)*: steam production for heavy oil and bitumen recovery;
- *Mining*: treatment of drainage wastewater to reuse the water and create saleable salt product (e.g., for deicing of roads);
- *Coal Production, Shale Gas*: reuse of water for fracturing the rocks;
- *Chemical Industry*: ethanol production (production of 1 m³ of ethanol needs 3.5 m³ of water), fertilizer production, and other industries (electronics, food and beverages, pulp and paper, etc) which use industrially desalinated water as process water, boiler feed water, make-up water, and ultra-pure water.

20.7 MEMBRANE-BASED ENERGY CONVERSION TECHNIQUES

20.7.1 Fuel Cells

Fuel cells are electrochemical devices with high energy conversion efficiency, minimized pollutant emission, and other advanced features. Proton exchange membrane fuel cells (PEMFC; see Fig. 20.17 for general knowledge) are considered a key issue against oil rarefaction and greenhouse gas emissions.¹⁷⁸ Although some companies have produced vehicles fuelled by PEMFCs, they have to face problems of water management, carbon monoxide poisoning of

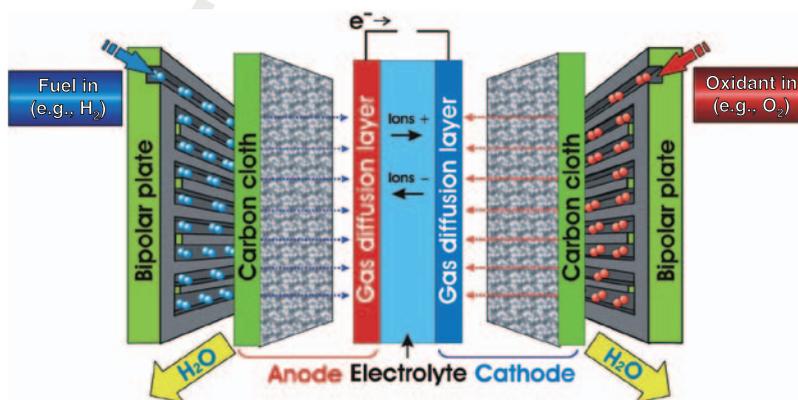


FIGURE 20.17. Scheme diagram illustrating the structure of PEMFC and the principle of operation. In the case of H₂ and O₂, the key reactions are: H₂ - 2e⁻ → 2H⁺; 0.5O₂ + 2H⁺ + 2e⁻ → H₂O. The electrons ceded by the hydrogen at the anode pass via the external load circuit to be accepted by the oxygen at the cathode side; the arriving protons form water molecules.

fuel cell catalysts, membrane behavior, and costs. High T PEMFCs have been proposed to solve problems of catalyst poisoning by CO and fuel cell electrode flooding, as well as to improve fuel cell efficiency, reduce the amount of noble metal catalyst, and avoid reactant humidification.¹⁷⁹

Most PEMFC research efforts are aimed at increasing performances (yield efficiency, power density, reduction of catalyst content, durability); improving mechanical, thermal, and electrochemical stabilities; and decreasing mass, volume, and costs. Operating at an increased T (120–150°C) causes greater challenges for PEMFC.¹⁸⁰ Novel materials that can give high performance and high durability under such conditions are prerequisites for high T PEMFC, among which alternative electrolyte membranes that can work at high T (120–150°C) and low relative humidity (RH = 25–50%) are of the greatest relevance. Many current research efforts are therefore devoted to the development of alternative electrolyte membranes,¹⁸⁰ including nonfluorinated hydrocarbon polymers,¹⁸¹ inorganic polymer composites,¹⁸² and anhydrous proton-conducting polymers¹⁸³ such as PBI/H₃PO₄^{184,185} (phosphoric acid doped polybenzimidazole polymer) or Nafion®/H₃PO₄¹⁸⁶ (phosphoric acid doped perfluorosulfonic acid-*tetrafluoroethylene* copolymer).

In this section we discuss the remaining bottlenecks for low T PEMFC and focus on the material challenges for high T PEMFC membranes. A great number of publications are devoted to fuel cells.

We will consider new and powerful methods allowing the study of the dynamics of solvent and molecules concentration profiles, which are developed during diffusion and current flow through the membrane.

Voltage–Current Response of a Membrane Electrode Assembly (MEA)

Voltage–current response (VCR, Fig. 20.18) is perhaps the most important dynamic characteristics of an MEA.

The VCR curve reveals three regions. The first one is governed by the electrode catalysis (reduction of the charge transfer overvoltage); the second one reflects the membrane behavior (reduction of the ohmic losses); and the third one reflects the cell design (improvement of fluid management). The development of an optimized MEA entails work in all these aspects.

In most PEMFCs, the proton exchange membranes are currently based on perfluorosulfonic acid (PFSA) polymers, such as Nafion®. This membrane material exhibits high conductivity and excellent chemical stability, mechanical strength, and flexibility. However, its operation requires a highly hydrated state, and therefore is limited to T of up to around 90°C under ambient pressure. Moreover, several challenges for the PEMFC power technology are associated with low operating T.¹⁸⁷ Fuel processors such as hydrogen storage tanks and hydrocarbon or alcohol reformers with subsequent carbon monoxide (CO) removers are voluminous, heavy, and costly. Water management involves appropriate humidification of fuel and oxidant, airflow rate, and power load regulation. Temperature cooling is more critical for larger stacks, and the heat produced is of low value. PEMFC operating at higher T

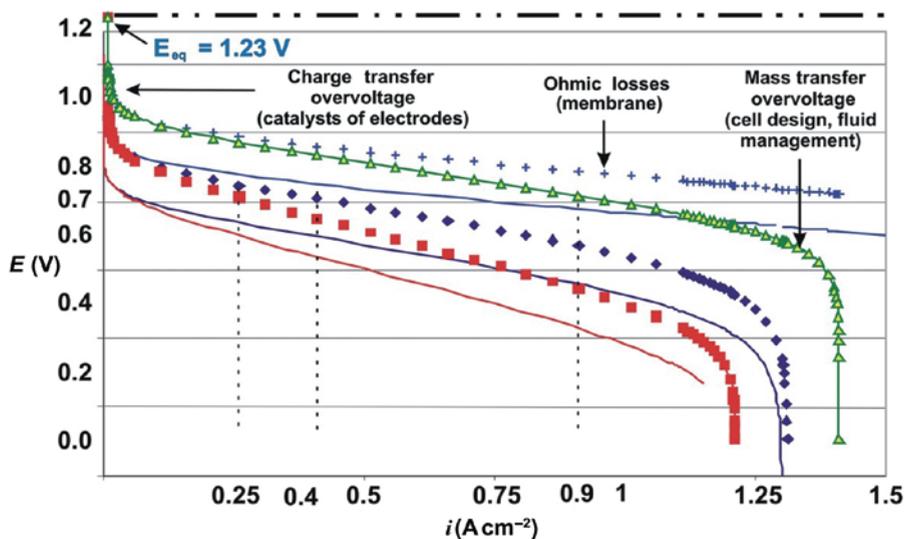


FIGURE 20.18. Voltage–current response of an MEA.

(120–150°C) has been recognized as a promising solution to meet these challenges. Hence, starting in 2001, researchers have aimed to increase operating T (120–150°C) with a 25–50% RH.

Increase of the Operating Temperature of PEMFC: The New Challenges

The theoretical analysis and experimental investigations have shown that working at high T (120–150°C) can provide the following advantages for PEMFC^{188–190}:

- *Electrode Reaction Kinetics*: the overall electrochemical kinetics of PEMFC are mainly determined by the slow oxygen reduction reaction (ORR)¹⁸⁰ accounting for the major overvoltage loss of PEMFC.¹⁸⁰ The reaction kinetics of hydrogen oxidation and ORR are enhanced at high T.¹⁹¹
- *CO Tolerance*: trace CO in hydrogen feed gas drastically depresses the performance of PEMFC due to the strong irreversible adsorption of CO on Pt electrocatalysts.¹⁹² The adsorption of CO on Pt is weakened at high T and CO tolerance is enhanced.
- *Heat Management*: a PEMFC operating at 80°C with an efficiency of 40–50% produces a large amount of heat that has to be removed in order to maintain the working T. The rate of heat transport is proportional to the T difference between PEMFC and environment. For a PEMFC working at low T ($\leq 80^\circ\text{C}$), the heat rejection rate of the conventional automotive radiators is not sufficient to reject continuous full power waste heat. Increase of PEMFC working T to $>120^\circ\text{C}$ will allow the use of the cooling system of present internal combustion engines.

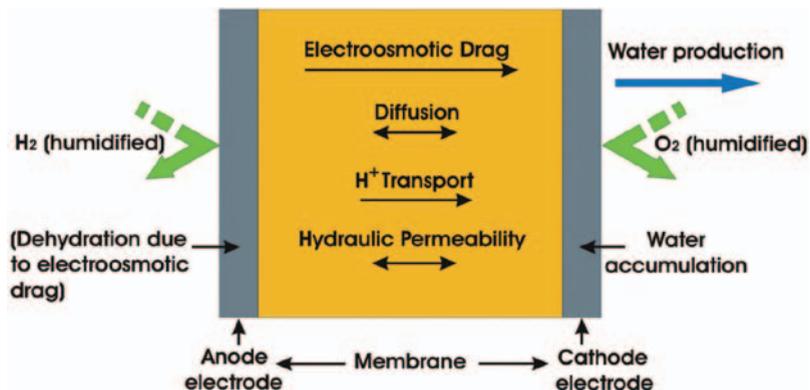


FIGURE 20.19. Modes of water transport in an operating H_2/O_2 PEMFC; adapted from Zhang et al.¹⁸⁰

- **Water Management:** PEMFC working at $T \leq 80^\circ\text{C}$ under atmospheric pressure involves a dual-phase system (liquid and vapor water). When the humidification is too high, water condenses and the electrodes are flooded (mainly the cathode), which makes water management difficult.¹⁹³ If a PEMFC is running at atmospheric pressure and $T > 100^\circ\text{C}$, only a single phase exists,¹⁹⁴ and therefore, the transport of water in the membrane, catalyst layers, and diffusion layers is easier to balance. The water balance in a PEMFC involves the following mechanisms: (1) water supply from the fuel and oxidant (humidification), (2) water production at the cathode (current density), (3) water drag from the anode to the cathode (current density, humidity, T), and (4) back-diffusion of water from the cathode to the anode (gradient concentration, capillary forces, etc.) (Fig. 20.19).
- **Nonplatinum Catalysts:** at higher T , the electrode reaction kinetics are strongly enhanced, making possible the use of nonplatinum catalysts, reducing PEMFC cost.

The advantages of high T PEMFC are therefore very attractive and many researchers are presently devoted to this challenge.

High Temperature Proton Exchange Membranes Great efforts are being devoted to synthesize proton-conducting membranes and other materials operating at T above 100°C .^{180,181,183,188,194,195} Membranes under development can be classified as follows: (1) modified PFSA membranes,^{38,189,190,194,196,197} (2) alternative membranes based on partially fluorinated and aromatic hydrocarbon polymers,^{198,199} (3) inorganic–organic composites,^{182,200,201} and (4) acid–base polymer membranes,²⁰² typically a basic polymer doped with a nonvolatile inorganic acid or blended with a polymeric acid.

Note only that the major drawback of PFSA membranes is their low conductivity and their poor performance under low humidification at elevated T ($>90^\circ\text{C}$) due to the water loss. Here we will consider some new results

in the development of alternative sulfonated polymer membranes and their composites. Among others, sulfonated polymer membranes have the advantage of being low cost compared to PFSA.

Alternative Sulfonated Polymer Membranes and Their Composites

Two main groups of polymers having high chemical and thermal stability have been investigated, the first containing inorganic elements such as fluorine in fluoropolymers and silicon in polysiloxanes, the second is aromatic polymers with phenylene backbones.

Sulfonated polystyrenes were investigated in the 1960s and were the first generation of polymer electrolytes for fuel cells.²⁰³ However, in this type of polymer membrane, the tertiary C-H bonds in the styrene chains are sensitive to oxidation by oxygen and hydrogen peroxide. The bond strength for C-F is about 485 kJ mol⁻¹ and that of C-H bonds in the range of 350–435 kJ mol⁻¹. Polymers containing C-F bonds therefore have high chemical and thermal stability. Partially fluorinated membranes have also been investigated, on a base of poly(tetrafluoroethylene-hexafluoropropylene) (FEP) films, by Scherer's group,²⁰⁴ and polyvinylidene fluoride (PVDF), by Sundholm's group.²⁰⁵ The combination of the PVDF properties with the conductive properties of sulfonated polystyrene gives both high water uptake and conductivity, but low thermal stability.²⁰⁵

Another type of temperature-resistant polymers of interest includes the Si-O chemical bond (445 kJ mol⁻¹). Si-O networks are formed at high T (ceramics) but can also be developed at low T in organic or aqueous solutions. Organic groups can be attached to the silica matrix to give organic-modified silicates (ORMOSIL), organic-modified ceramics (ORMOCER), or organic-modified silicate electrolyte (ORMOLYTE). Attempts have also been made to develop proton-conducting membranes for PEMFC by using arylsulfonic anions or alkylsulfonic anions grafted to the benzyl groups.²⁰⁶ These structures exhibit a proton conductivity of 0.01 S cm⁻¹ at room temperature and thermal stability up to 120°C.

A large group of low cost and commercially available polymers is based on aromatic hydrocarbons. Polymers consisting entirely of linked benzene rings such as poly-p-phenylene are resistant to oxidation. Polyphenylene sulfide and polyphenylene oxide have high melting points with good thermal and oxidative stability above 200°C. Aromatic polymers containing ether links have also been widely investigated, such as polyether(ether)ketones (PEEK).

To create proton conductivity, charged groups must be attached to the polymer chains. This can be done by chemical modification of the polymers (postfunctionalization) through the introduction of an anion, typically sulfonate ($-\text{SO}_3^-$). This sulfonation can be performed (1) by direct sulfonation in concentrated sulfuric acid or chlorosulfonic acid, sulfur trioxide, or its complex with tri-ethyl-phosphate²⁰⁷; (2) by lithiation-sulfonation-oxidation²⁰⁸; (3) by chemically grafting a group containing a sulfonic acid onto a polymer²⁰⁸; (4) by graft copolymerization using high radiation followed by sulfonation of the

aromatic components²⁰⁴, or (5) by synthesis from monomers bearing sulfonic groups.²⁰⁹

Generally, PFSA membranes and sulfonated aromatic polymers have different microstructures. The water-filled channels in sulfonated polyaryls (sulfonated PEEK) are narrow compared to those in hydrated perfluorosulfonic polymers (Nafion®). They are less separated and more branched with more dead-end spaces.²¹⁰ For PFSA membranes, the water content within the membrane is balanced by the extreme hydrophilicity of the sulfonic ion exchange groups. In the presence of water, the hydrophilic domains of the nanostructure are hydrated to maintain the proton conductivity, while the hydrophobic domains provide the mechanical strength. The water uptake of PFSA membranes is high but their conductivity is very sensitive to RH. In the case of sulfonated hydrocarbon polymers, the hydrocarbon backbones are less hydrophobic and the sulfonic acid exchange groups are less acidic and polar. Water molecules are therefore distributed within the nanostructure.²¹¹ Sulfonation of polyphenylene sulfide results in the increase of proton conductivity up to 0.01 S cm^{-1} in the range 30–180°C.

Similar to PFSA, sulfonated hydrocarbon polymers can be modified. In particular, they can be used as a host matrix for preparing inorganic/organic composites for high operating T.

Another effective approach to the development of proton-conducting membranes is acid–base complexation. Three ways may be used there: (1) basic polymers can be doped with an amphoteric acid acting as a donor and with an acceptor in proton transfer, allowing proton migration; (2) H_3PO_4 -doped PBI polymer in which proton hopping from one N-H site to phosphoric acid anions contributes significantly to the conductivity; and (3) organic acid–base blends developed by Kerres.^{202,212}

New Routes in PEMFC Membrane Development

Cross-Linked Terpolymers via a Sol-Gel Strategy To overcome the issues of polymer mechanical stability and swelling, a new class of polymer electrolyte membrane based on a continuous thermostable, nonconductive, organic polymer matrix mixed with a proton-conductive, sulfonated mesostructured silica network has been recently investigated.^{213,214} This approach aims to reproduce the behavior of PFSA membranes where hydrophobic and hydrophilic regions coexist. The hydrophilic regions contain the ionic groups and are supported by the functionalized mesostructured silica network while the hydrophobic regions contain the fluorobackbone of the polymer. The volume fraction of the membrane supporting the proton conductivity represents only 40% of the total volume of the hybrid organic/inorganic membrane. Thus *in situ* sol-gel growth of an acid-functionalized inorganic network in a nonporogenic organic matrix has recently been presented (Fig. 20.20).²⁰¹

The improvement in the water uptake is related to the surface hydroxyl groups and/or the $-\text{SO}_3\text{H}$ groups in the hybrid interfacial region, which can

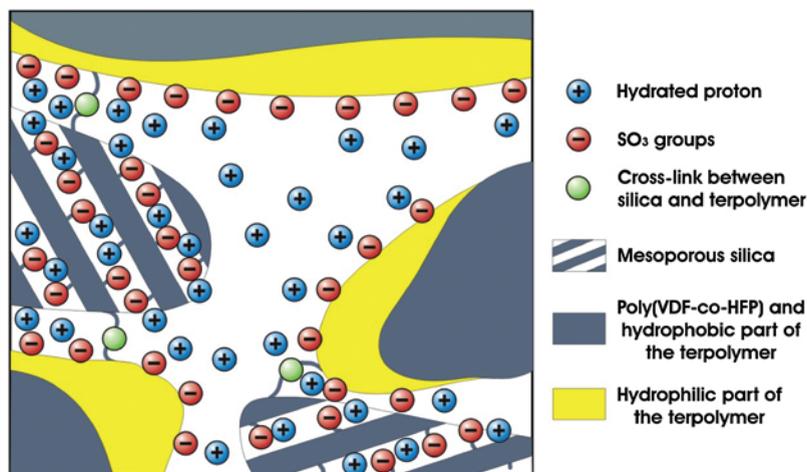


FIGURE 20.20. Schematic illustration of the hybrid SiO₂-SO₃H/terpolymer/poly(VDF-co-HFP) copolymer membrane. The silica domains exhibit a lamellar mesostructure with characteristic size 10 nm, based on SAXS studies. Adapted from Sel et al.²⁰¹

strongly attract water molecules through hydrogen bonding. These organic/inorganic membranes show proton-conductivity values of 0.043 S cm⁻¹ at 65°C under 100% RH and a conductivity value of 0.012 S cm⁻¹ at 120°C.

Inert Polymer Matrix: Proton-Conducting Hybrid Inorganic Particles New composite membranes have been prepared by inserting polystyrene sulfonic acid-grafted silica particles into an inert polymer matrix of poly(vinylidene fluoride-co-hexafluoropropylene), PVDF-HFP.²¹⁵ Power density of 1 W cm⁻² was recorded at 70°C using nonhydrated gas feeds, suggesting that this composite membrane is capable of self-humidification. Figure 20.21 shows single-cell performances of the hybrid membranes, exhibiting higher values than for Nafion® 112 membranes.

New Characterization In Situ Methods As indicated above, a shortcoming of water-mediated ion conductors is that their ion conduction varies widely with water content, the conductivity becoming too low at low water content. The most powerful method to quantify the membrane water content in a running fuel cell is small-angle neutron scattering (SANS). SANS spectra are usually recorded without any driving force applied to the membrane. Since several dynamic operations influence the water management in a PEMFC, a special cell has been designed to record SANS spectra during PEMFC functioning.²¹⁶ The data analysis leads to the determination of water concentration profiles across the membrane that could be used to validate mass transfer models and predict the best operating conditions of the PEMFC (Fig. 20.22).

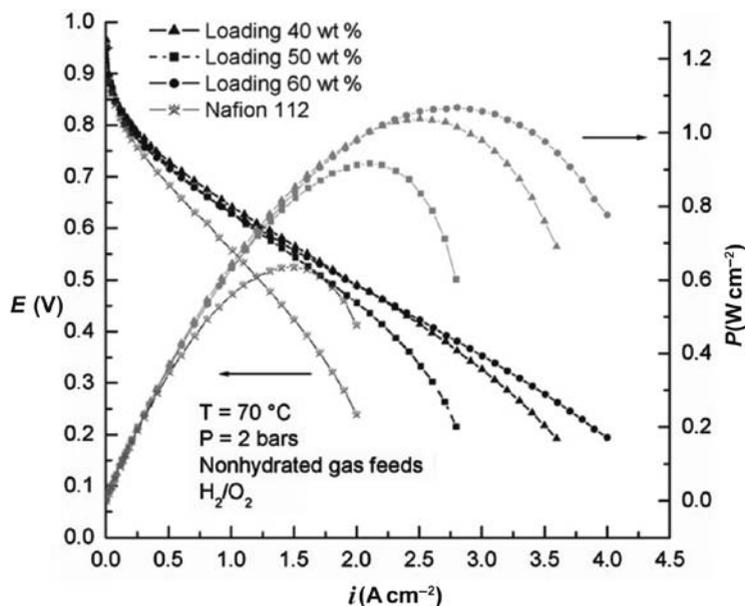


FIGURE 20.21. Single-cell PEMFC performances of hybrid membranes as function of filler loading and a Nafion® 112 membrane at 70°C with nonhydrated gas feeds (H_2/O_2 ; 2 bars). Adapted from Niepceon et al.²¹⁵

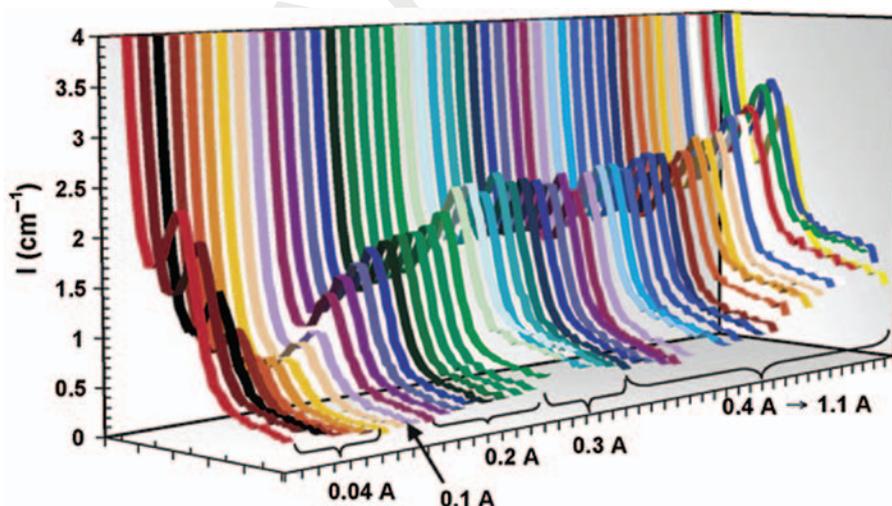


FIGURE 20.22. Series of SANS spectra obtained from a Nafion® 117 membrane using highly porous gas distribution. The membrane is first dried and then the current density is increased step by step from 0 to 1.1 A. Adapted from Gebel et al.²¹⁶

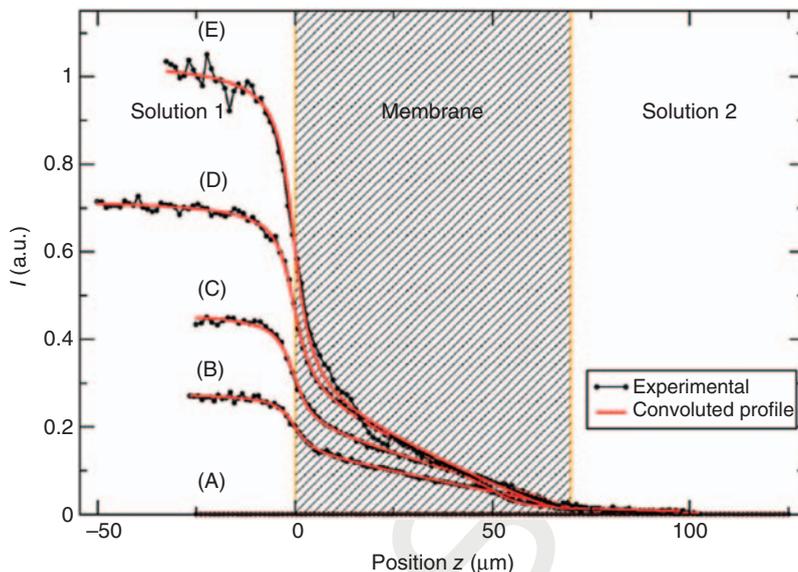


FIGURE 20.23. Experimental and convoluted Raman spectra intensity (in arbitrary units, a.u.) profiles of methanol diffusion through a Nafion® 112, obtained at different methanol (mol percent) content in the water–methanol feed compartment (pure water is in the other compartment). (A) 0%; (B) 25%; (C) 50%; (D) 75%; (E) 100%. Adapted from Deabate et al.²¹⁷

Another tool for measuring the local water (or/and methanol) concentration/ gradients within a proton conducting membrane are the *in situ* confocal Raman measurements.²¹⁷ A specially developed microfluidic cell allows the study of concentration profiles (within and near the surface of IEMs) through the acquisition of Raman spectra during dynamic transport. The results of such measurements are presented in Figure 20.23.

20.7.2 Salinity Gradient Power Generation

Pressure-Retarded Osmosis (PRO) A huge potential for clean energy is based on the mixing of water streams with different salt concentrations: sea water and river water. Salinity gradient power (SGP) is a relatively recent kind of renewable form of energy production, such as wind power, hydropower, or solar power. The global energy output produced by SGP is estimated to be between 2.6²¹⁸ and 2.8 TW,²¹⁹ while the average world energy consumption in 2008 was about 15 TW.²²² Two membrane-based energy conversion techniques were proposed several years ago: pressure-retarded osmosis²²⁰ and RED.²²¹ A considerable number of papers have since been published.^{12,219,222–226} A brief review is presented below.

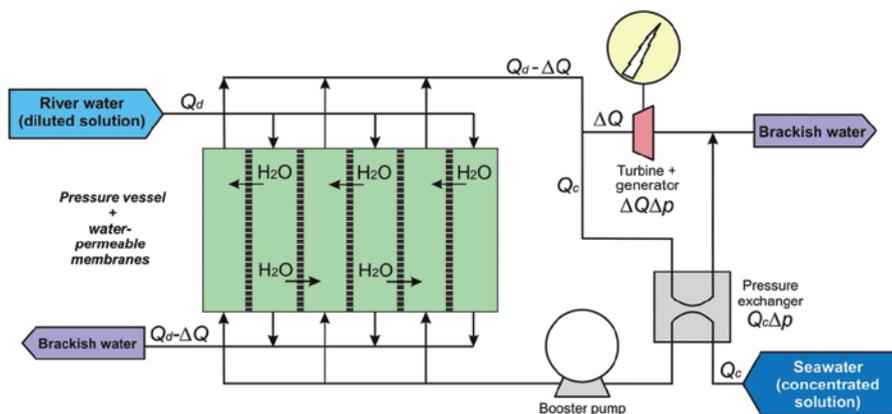


FIGURE 20.24. Schematic representation of an energy conversion scheme using pressure-retarded osmosis; Q is the volumetric solution flow rate (cubic meters per second); ΔQ the volume flux of water through the membranes (cubic meters per second) from the dilute to concentrated solution; and Δp the hydrostatic pressure difference between both solutions (pascals), whereas the power generated by means of a turbine and generator is $\Delta Q \Delta p$ (watts). Adapted from Post et al.²²²

In a pressure-retarded osmosis system, two solutions of different salinity are brought into contact by a semipermeable membrane (Fig. 20.24). The membrane allows the solvent (i.e., water) to permeate and retains the solute (i.e., dissolved salts). Under the action of the chemical potential difference between the solutions, water passes through the membrane from the diluted salt solution to the more concentrated one. This transport of water results in an increasing volumetric flow rate (from Q to $Q + \Delta Q$) and hydrostatic pressure (from p to $p + \Delta p$) of the concentrated solution. This pressurized, transported water can be used to generate electrical power in a turbine equal to $\Delta Q \Delta p$.²²²

Theoretical evaluations made by Post et al.²²² showed that in the case of sea and river waters, the maximum generated power density is 1.2 W m^{-2} . In real systems, the amount of generated power is between 0.11 and 1.22 W m^{-2} .²²² The higher value was obtained using a brine with osmotic pressure 39 bars (larger than the osmotic pressure of seawater, which is in the range 20–25 bars). The loss in power is mainly due to the fact that the driving force, which is determined by the osmotic pressure difference over the semipermeable active skin, is essentially lower than the osmotic pressure difference between the bulk solutions because of concentration polarization in the porous support.

Reverse ED with Monopolar Membranes In a RED system, CEMs and AEMs are stacked in an alternating pattern between a cathode and an anode, similarly to conventional ED (Fig. 20.25). The compartments between the membranes are alternately fed with a concentrated salt solution (e.g.,

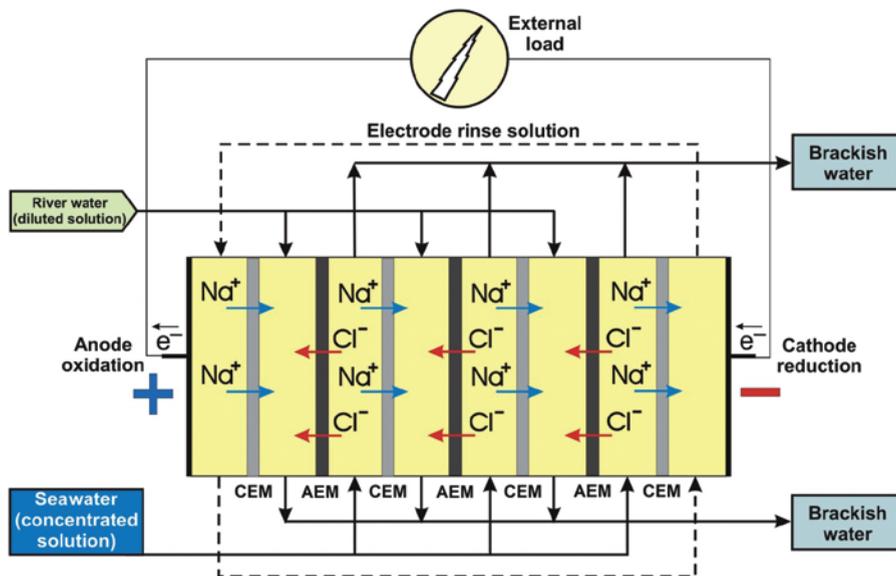


FIGURE 20.25. Schematic representation of an energy conversion system using RED. Adapted from Post et al.²²²

seawater) and a diluted salt solution (e.g., river water). The salinity gradient results in the formation of a potential difference (the so-called membrane potential) equal to about 80 mV for seawater and river water for each membrane. The potential difference between the outer compartments of the membrane stack is the sum of the potential differences for each membrane.

The salinity gradient produces ion transport through the membranes from the concentrated to the diluted solution. The cations pass through the CEMs toward the cathode, and the anions pass through the AEMs toward the anode. The electroneutrality condition causes equal fluxes of charges transported by cations and anions. In the electrode compartments, this condition is maintained via electrochemical reactions at the electrode surface with generation of electrons. The latter, transferred from the anode to the cathode in the external circuit, provide the electric current.

The power generated in the system is equal to the product of the current, I , and the electric potential difference between the electrodes. The latter is approximately proportional to the number of cell pairs and the pd over one cell pair: $P = I(N\Delta\phi)$. The value of $\Delta\phi$ is lower than the membrane potential for a pair of a CEM and an AEM due to ohmic losses and concentration polarization, reducing the concentration drop over the membrane.

Theoretical evaluations made for the case of seawater and river water show that RED has larger potential maximum power density than pressure-retarded osmosis. For RED this value is $2\text{--}4\text{ W m}^{-2}$ according to Post et al.²²² or higher than 6 W m^{-2} according to Długolecki et al.²²³ The losses in power density are mainly determined by the resistance of the diluate compartment; they depend

weakly on membrane properties.²²³ Thinner conductive spacers could essentially improve the characteristics of a RED system. Currently available ED membranes in a RED application on concentrated brines and freshwater yield a maximum power density of 1.2 W m^{-2} ²²⁴ or 1.6 W m^{-2} .²¹⁹ It is important that the obtained power density decreases with increasing size of membranes: the values found for a small stack of $10 \times 10 \text{ cm}^2$ are essentially higher than those found for a stack of $24 \times 75 \text{ cm}^2$.²¹⁹

Analysis made by Długolecki et al.^{225,226} shows that in order to improve SGP processes, the development of pressure-retarded osmosis must focus on membrane characteristics, that is, increasing water permeability of the membrane and optimization of the porous support. On the other hand, the development of RED must focus on system characteristics, that is, optimization of the internal resistance, which is mainly determined by the thickness and conductivity of the spacers. Moreover, the sensitivity for fouling is an important characteristic highly influencing the performance of SGP devices.

The main drawback of membrane-based conversion techniques are the high price of membranes.²²⁷ However, the decreasing prices of membranes for desalination and water reuse applications, as well as the increasing prices of fossil fuels, should make salinity gradient power attractive in near future.

RED with BPMs A minimum potential of 0.828 V could start water dissociation by a BPM unit at 25°C of 1 mol acid and 1 mol base.^{125,228} A similar potential drop will be produced by reacting 1 mol acid and 1 mol base. Thus, electrical energy can be produced in a system involving BPMs and two feed (acid and alkaline) solutions. Figure 20.26 shows the electricity generation process of a BPM battery, which is constructed with a BPM and a couple of electrodes. When acid and alkaline solutions are fed, respectively, from the cationic and the anionic sides of the BPM, H^+ ions diffuse from the acid solution, and OH^- ions diffuse from the alkaline side toward the middle of the BPM and react at the junction. As a result, a current density passes through the BPM, which can be used in the external circuit through the electrodes.

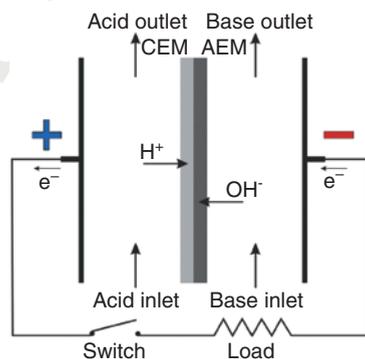


FIGURE 20.26. Schematic representation of an energy conversion system using a bipolar membrane cell.

A BPM with 100 cell units (consisting of a BPM, a CEM, and an AEM) may produce 40–80 V with output power 30–60 kW m⁻².²²⁹ One of the advantages of such devices is that they can provide energy from acid and base wastes.

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LIST OF SYMBOLS

Abbreviations

AEM	anion exchange membrane
BMED	bipolar membrane electro dialysis
BPM	bipolar membrane
CC	concentrate compartments
CDI	capacitive deionization
CEDI	continuous electrodeionization
CEM	cation exchange membrane
DBL	diffusion boundary layer
DC	diluate compartment
DD	diffusion dialysis
ED	electrodialysis
EDI	electrodeionization
EDL	electrical double layer
EDR	electrodialysis reversal
EED	electro-electrodialysis
IEM	ion exchange membrane
MCDI	membrane capacitive deionization
MC	membrane crystallization
MD	membrane distillation
MEA	membrane electrode assembly
MVR	mechanical vapor recompression
NF	nanofiltration
PBI	polybenzimidazole
pd	potential difference
PEEK	polyether(ether)ketones

PEMFC	proton exchange membrane fuel cells
PFSA	perfluorosulfonic acid polymers
PRO	pressure-retarded osmosis
PVDF	polyvinylidene fluoride
PVDF-HFP	poly(vinylidene fluoride-co-hexafluoropropylene)
RED	reverse electrodialysis
RH	relative humidity
RO	reverse osmosis
SANS	small-angle neutron scattering
SCR	space charge region
SGP	salinity gradient power
T	temperature
TDS	total dissolved salts
UF	ultrafiltration
VCR	voltage–current response
WAIV	wind-aided intensified evaporation
ZLD	zero liquid discharge (system)

Symbols

C^{in}	electrolyte concentration at inlet of DC
i	current density
i_{lim}	limiting current density
p	hydrostatic pressure
P	power
Sh	Sherwood number
w	solution flow rate

Greek Symbols

δ	Nernst's diffusion layer thickness
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