Electrodialysis, a mature technology with a multitude of new applications

H. Strathmann

Institut fuer Chemische Verfahrenstechnik, Universitaet Stuttgart, Boeblinger Str. 72, 70199 Stuttgart, Germany

ABSTRACT

Electrodialysis is a mature process which is applied since more than 50 years on a large industrial scale for the production of potable water from brackish water sources. But more recently electrodialysis in combination with bipolar membranes or with ion-exchange resins has found a large number of new interesting applications in the chemical process industry, in the food and drug industry as well as in waste water treatment and the production of high quality industrial water.

In this paper the principle of electrodialysis is described and its advantages and limitations in various applications are pointed out. More recent developments in electrodialysis as well as in related processes such as electrodialytic water dissociation or continuous electrodeionization are discussed and their present and potential future applications are indicated. Research needs for a sustainable growth of electrodialysis and related processes are pointed out.

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1. Introduction

Electrodialysis has been utilized for over 50 years for the production of potable water from brackish water sources. Since then the basic process has been significantly modified and several electrodialysis related processes such as continuous electrodeionization, diffusion dialysis or capacitive deionization etc. have been developed, and a number of new applications of these processes in water and waste water treatment and in the food and chemical process industry have been identified. In brackish water desalination electrodialysis has been replaced more and more by nanofiltration. However, in other applications such as the production of high quality industrial process water or the treatment of certain industrial effluents electrodialysis, especially in combination with bipolar membranes or with ion-exchange resins, has become of increasing relevance. Electrodialysis and related processes and their applications are summarized in Table 1. Several of these processes are used on a large industrial scale today and can be considered as state-of-the-art technology. Other processes such as continuous electrodeionization or the electrodialytic water dissociation with bipolar membranes and the power generation with reversed electrodialysis are still under development. But the interest in these processes is rapidly growing and a number of new applications have been identified. However, all of today's available electromembrane processes and components used in these processes have still technical and commercial limitations and in spite of a substantial ongoing development there is a need for further research to improve products and processes.

1.1. Fundamental aspects of electrodialysis and related processes

To gain a better understanding for the advantages and limitations of electrodialysis and related processes in certain applications a brief discussion of some fundamental aspects of these processes is quite helpful. Key components in electrodialysis and all related processes are the ion-exchange membranes. Their properties determine to a very large extent the usefulness of a process in a certain application. Other aspects such as the process design or operation mode are also of importance.

1.1.1. Ion-exchange membranes, their structures and properties

Ion-exchange membranes can be considered as ion-exchange resins in film form. There are two different types of ion-exchange membranes: (1) cation-exchange membranes which contain negatively charged groups fixed to the polymer matrix, and (2) anion-exchange membranes which contain positively charged groups fixed to a polymer matrix. In a cation-exchange membrane the fixed anions are in electrical equilibrium with mobile cations in the interstices of the polymer as illustrated in Fig. 1 which shows schematically the matrix of a cation-exchange membrane with fixed anions and mobile cations.

The mobile cations are referred to as counter-ions. The mobile anions are called co-ions and are more or less completely excluded from the membrane matrix because of their electrical charge which is identical to that of the fixed ions. Due to the exclusion of the co-ions, a cation-exchange membrane is preferentially permeable to cations. Anion-exchange membranes carry positive charges fixed on the polymer matrix. They therefore exclude cations and are preferentially permeable to anions. To which extent the co-ions are excluded from an ion-exchange membrane depends on membrane as well as on

E-mail address: heiner.strathmann@t-online.de.

Table 1
Electrodialysis and related processes and their applications.

State-of-the-art processes	Technical relevant applications
Electrodialysis	Water desalination and salt pre-concentration
Diffusion dialysis	Acid and base recovery from industrial waste waters
Donnan dialysis	Water softening, and exchange of ions
Developing processes	Technical relevant present and future applications
Bipolar membrane electrodialysis	Production of acids and bases from corresponding salts
Continuous electrodeionization	Production of ultra pure water
Capacitive deionization	Water desalination and water softening
Reverse electrodialysis	Electrodialytic energy generation

solution properties. Furthermore, cation- and anion-exchange membranes are classified as strong acid and strong base or weak acid and weak base membranes depending on the degree of dissociation of the charged groups. Strong acid membranes contain sulfonic acid as charged groups. In weak acid membranes carboxylic acid is the charge carrying group. Quaternary and tertiary amines are the fixed charges in strong and weak base ion-exchange membranes, respectively. Furthermore, ion-exchange membranes can also be distinguished according to their structure as homogeneous and heterogeneous. Homogeneous membranes are prepared by introducing an ion-exchange moiety directly into the structure of the polymer the membrane is made of. This leads to a relatively even distribution of the charged groups over the entire membrane matrix. Heterogeneous membranes are prepared by mixing a fine ion-exchange resin powder with a binder polymer and pressing and sintering the mixture at an elevated temperature. This results in a structure where the ion-exchange groups are clustered and very unevenly distributed in membrane matrix as indicated in the schematic drawings of Fig. 1a) and b).

The properties of ion-exchange membranes are determined by different parameters, such as the density of the polymer network, the
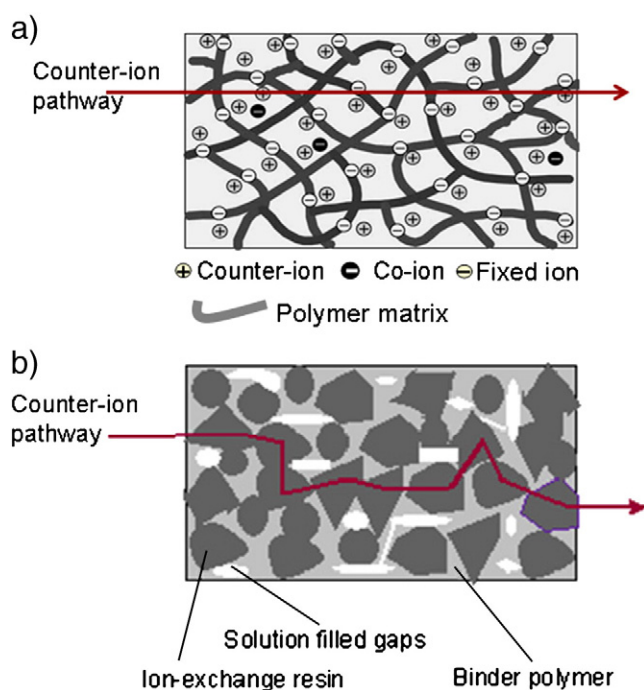
hydrophobic or hydrophilic character of the matrix polymer and the type and concentration of the fixed charges in the polymer, and the morphology of the membrane itself [1]. The most desired properties of ion-exchange membranes are: high permselectivity, low electrical resistance, good mechanical and form stability, high chemical and thermal stability and low production costs. Heterogeneous ion-exchange membranes have generally a higher electrical resistance due to the longer pathway of the mobile ion in the heterogeneous structure and a lower permselectivity because of a leakage of co-ions through water filled gaps in the membrane matrix as indicated in Fig. 1b).

Many of today's available membranes meet most of the required properties [2]. But there are large differences in the properties of ion-exchange membranes. The fluorocarbon polymer based Nafion-type® cation-exchange membrane, for example, has quite satisfactory chemical and thermal stability, but its production costs are presently extremely high. Most heterogeneous membrane structures have relatively low production costs but their permselectivity is generally low and their electrical resistance is high [3].

2. Electrodialysis and electrodialysis related processes

Electrodialysis and processes such as electrodialysis with bipolar membranes, continuous electrodeionization or capacitive deionization and energy generation by reverse electrodialysis are all based on ion-exchange membranes and an electrochemical potential as driving force. But the process design and their applications can be rather different.

2.1. Conventional electrodialysis

The principle of conventional electrodialysis is illustrated in Fig. 2 which shows a series of anion- and cation-exchange membranes arranged in an alternating pattern between two electrodes.

The cation- and anion-exchange membranes are separated by a spacer gasket and form individual cells. If an electrolyte solution is pumped through these cells and an electrical potential between the electrodes is established the cations migrate towards the cathode. They pass through the cation-exchange membrane but they are retained by the anion-exchange membrane. Likewise the anions migrate towards the anode and pass through the anion-exchange membrane but are retained by the cation-exchange membrane. The overall result is that an electrolyte, i.e. a salt or an acid or a base is concentrated in alternate compartments while the other solutions are depleted of ionic components. A cation-exchange membrane, a concentrate containing cell, an anion-exchange membrane and a diluate containing cell is referred to as a cell pair.

In an industrial size electrodialysis stack 100 to 200 cell pairs are arranged between the electrodes. Various spacer and stack constructions such as the so-called sheet flow or tortuous path flow stack design are used in practical applications [4]. The concept of a sheet flow stack is illustrated in Fig. 3.

In a tortuous path stack design the membranes and spacers are arranged horizontally in a stack. The design of a sheet flow and a tortuous path flow spacer design is illustrated in Fig. 4a) and b).

The spacers not only separate the membranes, they also contain the manifold for the distribution of the two different flow streams in the stack and provide the proper mixing of the solutions in the cells. The main difference between the sheet flow and the tortuous path flow spacer is that in the sheet flow spacer the compartments are vertically arranged and the process path is relatively short. The flow velocity of the feed is between 2 and 4 cm/s and the pressure loss in the stack is correspondingly low, i.e. between 0.2 and 0.4 bars. In the tortuous path flow stack, the membrane spacers are horizontally arranged and have a long serpentine cut-out which defines a long narrow channel for the fluid path. The feed flow velocity in the stack is
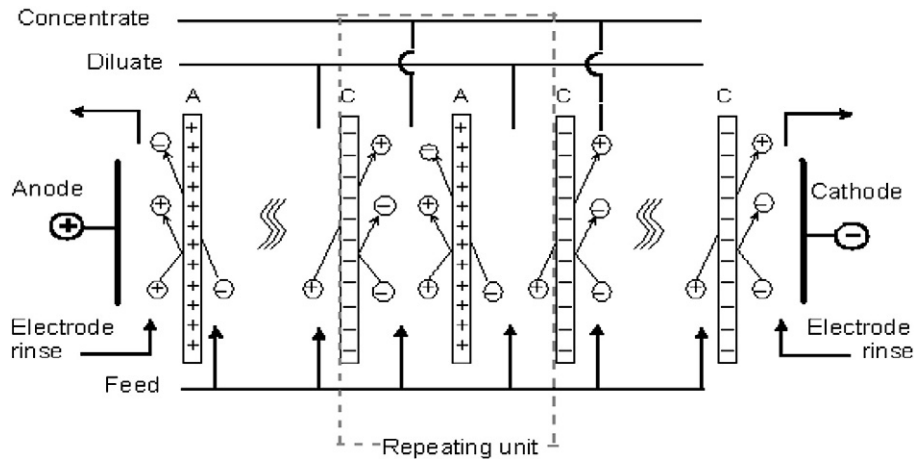

Fig. 1. Schematic drawing illustrating a) a cation-exchange membrane with a homogeneous structure and b) an ion-exchange membrane with a heterogeneous structure prepared from an ion-exchange resin powder and a binder polymer.

Fig. 2. Schematic diagram illustrating the principle of electrodialysis.

relatively high, i.e. between 6 to 12 cm/s which provides a better control of concentration polarization and higher limiting current densities, but the pressure loss in the feed flow channels is quite high, i.e. between 1 and 2 bars.

In most electrodialysis stacks used in practical applications the geometries of the diluate and concentrate cells as well as the linear flow velocities are identical and in the same direction to avoid hydrostatic pressure differences, and thus, a convective flow between the two solutions. This operation mode leads to a recovery rate of 50% of the feed as product water. The degree of desalination that can be achieved in passing the feed solution through a stack is a function of the solution concentration, the applied current density and the residence time of the solution in the stack. If the degree of desalination or concentration that can be achieved in a single path through the stack is insufficient several stacks are operated in series. If a recovery rate different of 50% shall be achieved part of the diluate or concentrate is fed back to the feed solution as shown in Fig. 5.

In the so-called feed and bleed operating mode both the brine and the product concentration can be determined independently and very high recovery rates or brine concentrations can be obtained.

2.1.1. Concentration polarization and limiting current density

Concentration polarization occurs in all membrane separation processes. In electrodialysis it is the result of differences in the transport numbers of ions in the solution and in the membrane. The transport number of a counter-ion in an ion-exchange membrane is generally close to 1 and that of the co-ion close to 0 while in the solution the transport numbers of anions and cations are not very different. At the surface of a cation-exchange membrane facing the diluate solution the concentration of ions in the diluate solution is reduced due to a transport number of the cations that is lower in the solution than in the membrane. Because of the electroneutrality requirements the number of anions is reduced in the boundary layer by migration in the opposite direction. The net result is a reduction of the electrolyte concentration in the solution at the surface of the membrane and a concentration gradient is established in the solution between the membrane surface and the well mixed bulk. This concentration gradient results in a diffusive electrolyte transport. A steady state situation is obtained when the additional ions, that are needed to balance those removed from the interface due to the faster transport rate in the membrane, are supplied by the diffusive transport. The other side of the cation-exchange membrane is facing the concentrate solution the electrolyte concentration at the membrane surface is increased. The effect of concentration polarization is illustrated in Fig. 6 which shows the salt concentration profiles and the fluxes of cat- and anions in the concentrate and diluate solution at the surface of a cation-exchange membrane.

The symbols J and C in Fig. 6 denote the fluxes and the concentrations of ions, the superscripts mig and diff refer to migration and diffusion, the superscripts d and c refer to diluate and concentrate solution, and the superscripts b and m refer to bulk phase and membrane surface, respectively, the subscripts a and c refer to anion and cation.

Concentration polarization in electrodialysis leads to an accumulation of ions on the membrane surface facing the concentrate cell which can result in a precipitation of salt when the concentration exceeds the solubility limit of a salt. In the diluate cell the concentration polarization
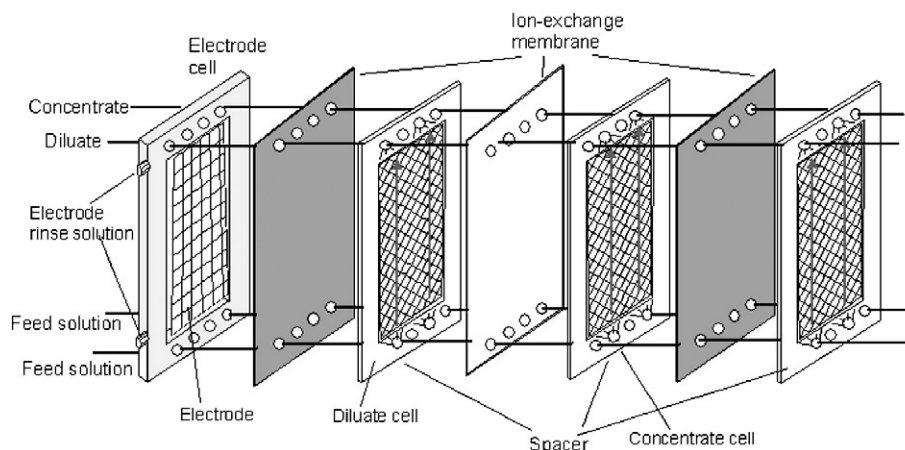

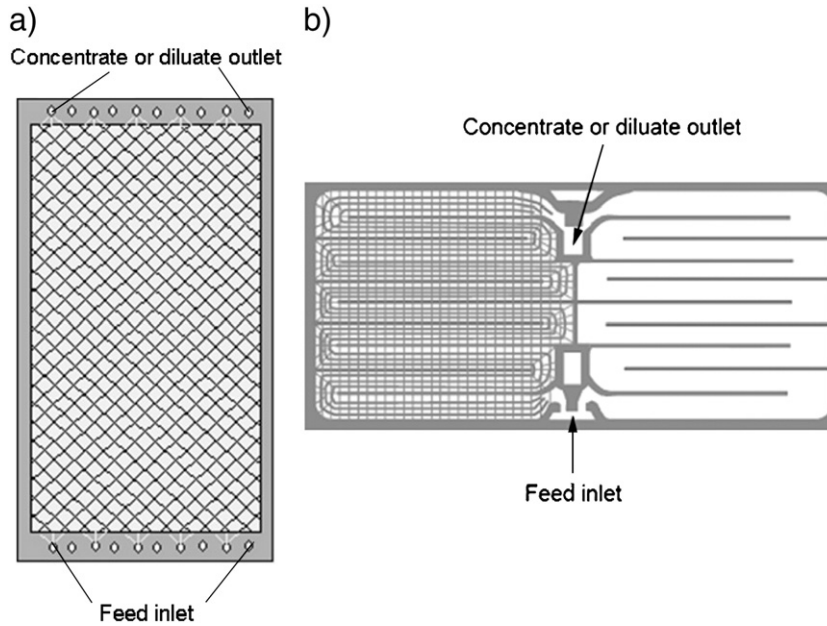Fig. 3. Schematic drawing illustrating the construction of a sheet flow stack design.

Fig. 4. Schematic drawing illustrating a) the design of a sheet flow and b) a tortuous path flow spacer.

leads to a depletion of ions at the membrane surface and determines the so-called limiting current density which is reached when the ion concentration at the membrane surface approaches 0 as indicated in Fig. 6. When the limiting current density is reached a further increase of the applied voltage does not result in an increase of the current as illustrated in the diagram of Fig. 7, which shows the current through an electrodialysis stack as function of the applied electrical potential. The curve indicates that the current density and thus resistances are changing drastically with the applied voltage. First the resistance of the stack is constant, i.e. the current density is increasing linearly with the applied voltage according to Ohm's law. When a certain current density, which is referred to as limiting current density, is reached the cell resistance increases drastically and an increase of the applied voltage does not lead to a significant increase in the current density until at a certain applied voltage the current density increases again with the applied voltage. The current density which occurs when the applied voltage exceeds a certain critical value is referred to as overlimiting current density. The limiting current density is determined by the intersection of the first and the second slope of the current versus voltage curve. The overlimiting current density is caused by electro-convection and is, at least partially, caused by the transport of H^+- and OH^--ions which are generated at the membrane/solution interface by water dissociation. The water dissociation affects the current utilization and can lead to a drastic pH-value decrease in the diluate and increase in the concentrate solution. The reasons for electroconvection are still not yet completely understood [5,6].

The limiting current density can be calculated by a mass balance taking into account all fluxes in the boundary layer and the hydrodynamic conditions in the flow channel between the membranes. To a first approximation the salt concentration at the membrane surface

can be calculated by applying the so-called Nernst film model which assumes that the laminar boundary layers are constant between the cell entrance and exit. In a practical electrodialysis stack, however, there will be entrance and exit effects and the idealized model hardly exist. Therefore, the limiting current density in practical applications is generally experimentally determined and described as a function of the feed flow velocity in the electrodialysis stack by the following relation [7]:

$$i_{lim} = au^b FC_s^d. \tag{1}$$

Here C_s^d is the concentration of the solution in the diluate cell, u is the linear flow velocity of the solution through the cells parallel to the membrane surface, F is the Faraday constant, and a, b and d are characteristic constants for a given stack design and must be determined experimentally. This is done in practice by measuring the limiting current density in a given stack configuration at constant feed solution salt concentration as a function of the feed flow velocity. Eq. (1) also indicates that the limiting current density is proportional to the diluate concentration. Thus, low product water concentrations require large membrane areas for a given capacity plant independent of the feed solution concentration.

A major problem which affects the efficiency of almost all membrane separation processes is membrane fouling. Also in electrodialysis suspended solids which carry positive or negative electrical charges such as polyelectrolytes, humic acids, surfactants, and biological materials, which can increase the resistance of the membrane dramatically, are deposited on the membrane surface. However, in electrodialysis the problem has been eliminated to a large extent by reversing in certain time intervals the polarity of the applied electrical
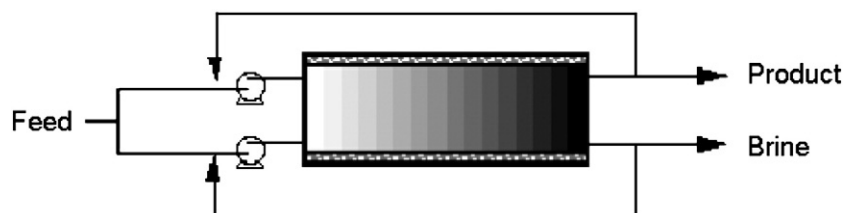

Fig. 5. Flow scheme of an electrodialysis stack operated in a feed and bleed mode, i.e. with partial recycling of the diluate and concentrate solutions.
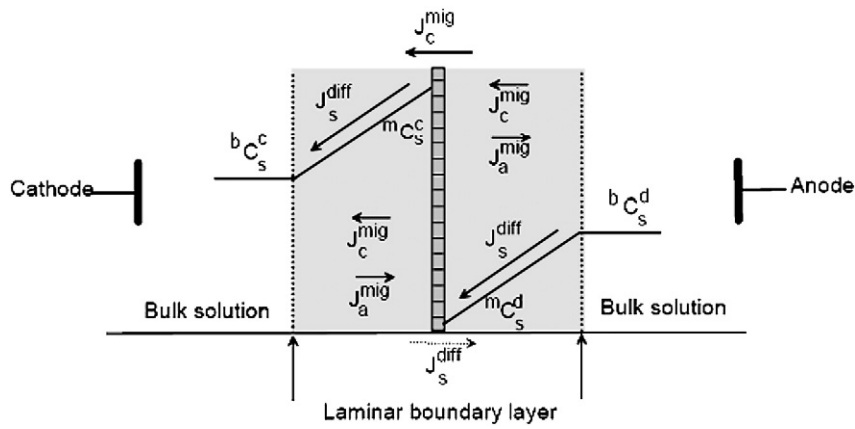
Fig. 6. Schematic drawing illustrating the concentration profiles of a salt in the laminar boundary layers on both sides of a cation-exchange membrane and the flux of ions in the solutions and the membrane.

potential which results in a removal of charged particles that have been precipitated on the membranes. This technique is referred to as "clean in place" or electrodialysis reversal [8].

The principle of the electrodialysis reversal operating mode is illustrated in Fig. 8a) and b) that shows an electrodialysis cell formed by a cation- and anion-exchange membrane between two electrodes. If an electric field is applied to a feed solution containing negatively charged particles or large organic anions these components will migrate to the anion-exchange membrane and will be deposited on its surface to form a so-called "fouling layer". If the polarity is reversed the negatively charged components will now migrate from the anion-exchange membrane back into the feed stream and the membrane properties are restored. This procedure has been very effective not only for the removal of precipitated colloidal materials but also for removing precipitated salts and is used today in almost all electrodialysis water desalination systems.

To be effective the reversing 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. The flow scheme of an electrodialysis plant operated with reversible polarity is shown in Fig. 9. In the reverse polarity operating mode, the hydraulic flow streams are reversed simultaneously with the reversing of the polarity, i.e. the diluate cell will become the brine cell and vice versa. In this operating mode the polarity of the current is changed at specific time intervals ranging from a few minutes to several hours.

During the reversal of the polarity and the flow streams, there is a brief period when the concentration of the desalted product exceeds the product quality specification. Therefore, the product water outlet has a concentration sensor which controls an additional three-way valve. This valve diverts product flow with too high concentration into the brine and then, when the concentration returns to the specified quality, the product flow is directed back to the product outlet. Thus, in electrodialysis reversal there is always a certain amount of the product lost to the waste stream. This is generally no problem in desalination of brackish water. It might, however, be not acceptable in certain applications in the food and drug industry when feed solutions with high value products are processed. In these applications electrodialysis is operated in a unidirectional mode in which the applied electric field and the diluate and concentrate flow streams are permanently fixed.
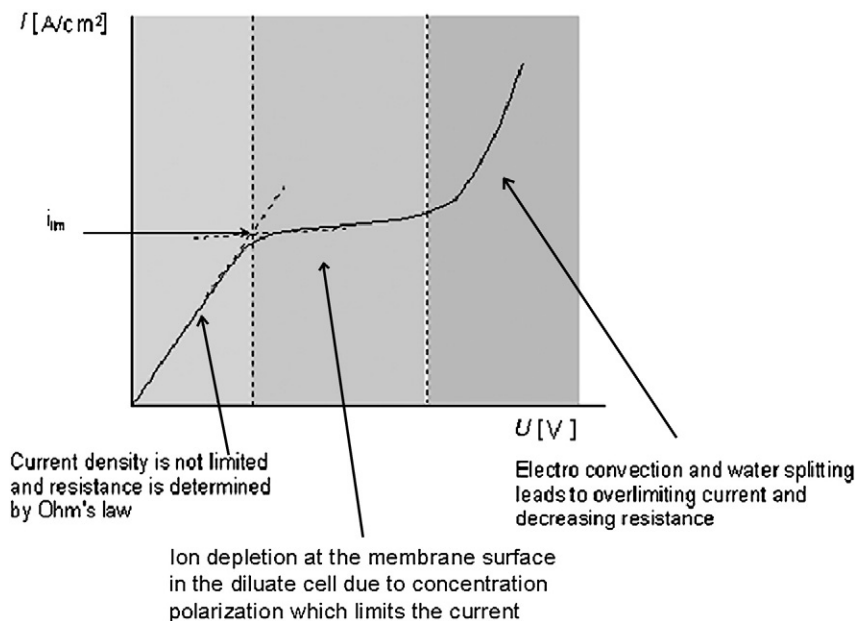

Fig. 7. Schematic drawing of a current versus voltage curve of an electrodialysis stack operated at constant solution flow velocities and feed and diluate concentrations indicating the limiting and the overlimiting current density.
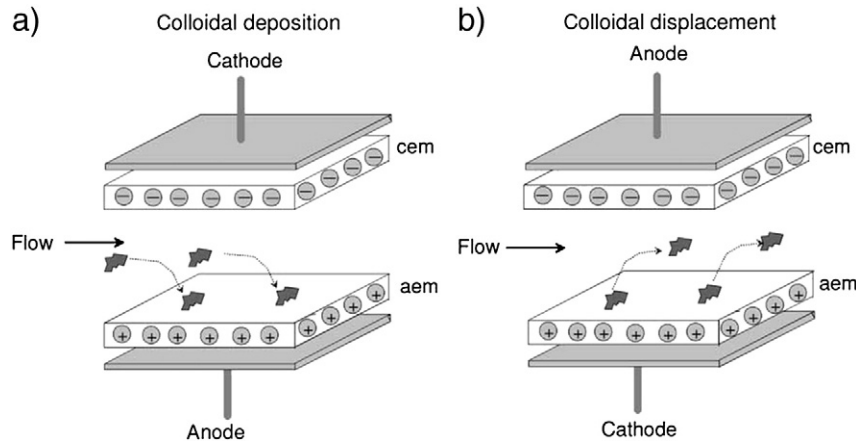
Fig. 8. Schematic drawing illustrating the removal of deposited negatively charged colloidal components from the surface of an anion-exchange membrane by reversing the electric field.

2.1.2. Electrodialysis process costs

The total costs in electrodialysis are the sum of fixed charges associated with the amortization of the plant capital costs and the plant operating costs. Both the capital costs as well as the plant operating costs are proportional to the number of ions removed from a feed solution, i.e. the concentration difference between the feed and the product solution. But they are also strongly affected by the plant capacity and location and the composition of the feed water and the overall process design.

2.1.2.1. Capital related costs.
The capital costs in electrodialysis are mainly determined by the required membrane area for a given feed and product concentration. Other items such as pumps and process control equipment are considered as a fraction of the required membrane area. This fraction depends on the plant capacity.

The required membrane area for a given capacity plant can be calculated from the current density and the feed and product solution concentrations. It can be calculated by:

$$A = \frac{Q_{st}^d \; F \; \left(C^f - C^d \right)}{i \xi} \tag{2}$$

Here i is the electric current density passing through a cell pair, A is the cell area, Q is the volume flow, C is the concentration expressed in equivalent per volume, F is the Faraday constant, and ξ the current

utilization. The subscript st refers to the stack, and the superscripts d and f refer to diluate and feed solution.

For a given plant capacity and feed and product water composition the required membrane area is inverse proportional to the limiting current density.

The total investment related costs for a given plant capacity depend not only on the required membrane area and the price of the membranes but also on their useful life under operating conditions which is in practical application 5 to 8 years.

2.1.2.2. Operating costs.
The operating costs are composed of labour, maintenance and energy costs. The labour and maintenance costs are directly proportional to the size of the plant and usually calculated as a certain percentage of the investment related costs. The energy required in an electrodialysis process is an additive of two terms: The electrical energy to transfer the ionic components from one solution through the membranes into another solution and the energy required to pump the solutions through the electrodialysis unit. Depending on various process parameters, particularly on the feed solution concentration, either one of the two terms may be dominating and thus determining the overall energy costs. The energy consumption due to electrode reactions can generally be neglected since more than 200 cell pairs are placed between the two electrodes in a modern electrodialysis stack. The energy required for operating the process control devices can be neglected in large industrial size plants also.
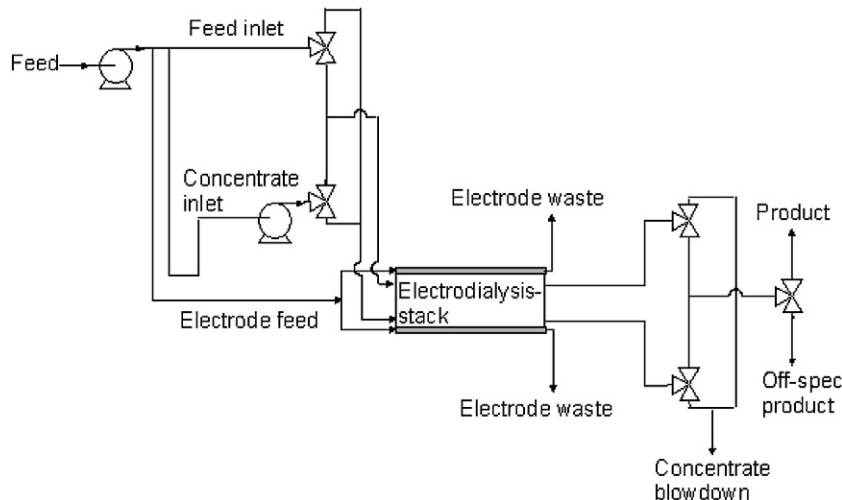

Fig. 9. Flow scheme of electrodialysis reversal in a continuous operating mode.

The total energy required in electrodialysis for the actual desalination process is given by the current passing through the electrodialysis stack multiplied with the total voltage drop encountered between the electrodes:

$$E_{des} = I_{st} U_{st} \, t. \tag{3}$$

Here E_{des} is the energy consumed in a stack for the transfer of ions from a feed to the concentrate solution, I_{st} is the current passing through the stack, U_{st} is the voltage applied across the stack, i.e. between the electrodes.

The current passing through the stack is proportional to the number of electrical charges removed from a feed solution and is given by:

$$I_{st} = \frac{Q_{st}^d F \left(C^f - C^d\right)}{\xi}. \tag{4}$$

Furthermore is:

$$U_{st} = I_{st}^2 \overline{R}_{st} \tag{5}$$

Introducing Eq. (5) into Eq. (4) gives the required desalination energy as function of the stack resistance, the amount of the produced product, the feed and diluate concentration and the current utilization:

$$E_{des} = \overline{R}_{st} I^2 t = \overline{R}_{st} t \left[\frac{Q_{st}^d F \left(C^f - C^d\right)}{\xi} \right]^2 \tag{6}$$

Here E_{des} is the desalination energy, I is the total current, t is the time of operation; C^f and C^d are the equivalent concentrations of the feed and the diluate, F is the Faraday constant, ξ is the current utilization, and Q^d is the diluate flow through the stack, and $\overline{R}_{st}$ is the average resistance of the stack.

Eq. (6) shows that the desalination energy is proportional to the difference between the feed and the diluate concentration and the resistance of the solutions and membranes in the stack. Thus, for a given feed solution and required diluate concentration the desalination energy is directly proportional to the current density, while according to Eq. (2) the required membrane area for a given plant is decreasing with the current density.

The total desalination costs are the sum of energy costs and investment costs. Therefore the total desalination costs will reach a minimum for a certain applied current density. The relation between energy costs, membrane costs, total costs and the current density is illustrated in Fig. 10 which shows the various cost items as a function of the applied current density for a given plant capacity and feed and product water composition. The current density which leads to a minimum in overall desalination costs depends to a large extent on the membrane costs and their life time under operating conditions. It must be experimentally determined for a given stack design and feed, diluate, and concentrate.

However, due to concentration polarization effects the current density should not be exceeded by the so-called limiting current density which is a function of the diluate concentration, the stack design and operation parameters as indicated in Eq. (1). For very low required diluate concentrations the limiting current density is very low and generally much lower than the current density required for a plant operation at minimum total costs.

The operation of an electrodialysis unit requires one or more pumps to circulate the diluate, the concentrate, and the electrode rinse solution through the stack. The energy required for pumping these solutions is determined by the volumes of the solutions to be pumped and the pressure drop. It can be expressed by:

$$E_p = k_{eff}\left(Q^d \Delta p^d + Q^c \Delta p^c + Q^e \Delta p^e\right). \tag{7}$$
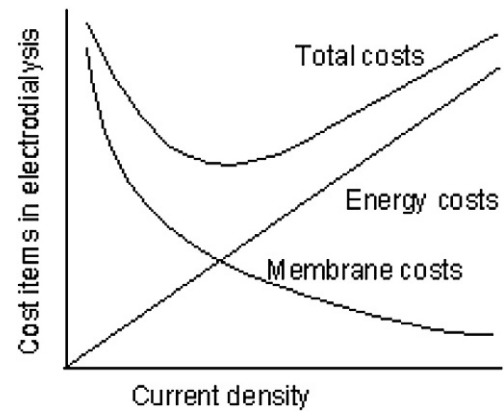

Fig. 10. Schematic diagram illustrating the various cost items in electrodialysis as function of the applied current density.

Here E_p is the total energy for pumping the diluate, the concentrate, and the electrode rinse solution through the stack per unit diluate water, k_{eff} is an efficiency term for the pumps, Q^d, Q^c, and Q^e are the volume flow rates of the diluate, the concentrate, and the electrode rinse solution through the stack.

The energy consumption due to the pressure loss in the electrode rinse solution can be neglected in most practical applications because the volume of the electrode rinse solution is very small compared to the volumes of the diluate and concentrate.

The pressure losses in the various cells are determined by the solution flow velocities and the cell design. The energy requirements for circulating the solution through the system may become a significant or even dominant portion of the total energy consumption for solutions with rather low salt concentrations.

2.1.3. Applications of electrodialysis

Some of the more important large scale industrial applications of conventional electrodialysis and the stack and process design used in these applications as well as the major limitations are listed in Table 2.

2.1.3.1. Brackish water desalination by electrodialysis. The production of potable water from brackish water sources is presently the largest single application of electrodialysis. In brackish water desalination electrodialysis is competing directly with reverse osmosis. However, in a certain range of feed water salt composition electrodialysis has an economic advantage over other desalination processes. Electrodialysis is mainly used in small to medium size plants with capacities of less than a few $100 \, m^3 \, d^{-1}$ to more than $20{,}000 \, m^3 \, d^{-1}$ with a brackish water salinity of 1000 to 5000 $mg \, L^{-1}$ total dissolved solids. Reverse osmosis is

Table 2
Industrial applications of conventional electrodialysis.

Industrial applications	Stack and process design	Status of application	Limitations	Key problems
Brackish water desalination	Sheet and tortuous path, reverse polarity	Commercial	Process costs	Costs
Boiler feed and process water	Sheet and tortuous path, reverse polarity	Commercial	Product water quality and costs	Costs
Waste treatment	Sheet or tortuous path, unidirectional	Commercial	Membrane properties	Membrane fouling
Demineralization of food products	Sheet flow or tortuous path, unidirectional	Commercial pilot plants	Membrane selectivity	Membrane fouling
Table salt production	Sheet flow unidirectional	Commercial	Process costs	Membrane fouling

considered to have an economic advantage for the desalination of water with total dissolved salts in excess of 10,000 mg L^{-1}. The advantages of electrodialysis compared to reverse osmosis are: high water recovery rates, long useful life of membranes, operation at elevated temperatures up to 50 °C, and less membrane fouling or scaling due to process reversal. The disadvantage of electrodialysis compared to reverse osmosis is that neutral toxic components such as viruses or bacteria are not removed from a feed stream. In spite of the fact that electrodialysis reversal is significantly less sensitive to membrane fouling than reverse osmosis some pretreatment of the feed water is required. Especially, the iron and manganese ion concentrations must be kept below 0.3 and 0.05 mgL^{-1}.

A typical industrial scale electrodialysis plant for the production of potable water is shown in the photograph of Fig. 11.

Next to brackish water desalination the industrial process water demineralization and waste water treatment are the most important applications of electrodialysis. Industrial water processing includes demineralization of boiler feed water and desalination of contaminated industrial water for reuse. Because of a substantial increase in fresh water costs and problems related to the discharge of certain industrial waste waters which often contain high salt concentrations or toxic water constituents waste water recycling can result in substantial cost savings. A typical application of industrial water reuse is the recycling of cooling tower blow-down water. Electrodialysis is particularly suited for this purpose since high recovery rates up to 95% and high brine concentrations can be achieved, which results in savings of feed water costs and in a reduction of waste water discharge. Furthermore, ion-exchange membranes can be operated at temperatures up to 50 °C which is in the range of most cooling systems. Very often toxic or valuable components such as heavy metal ions can be removed to avoid pollution of the environment and save disposal costs by recycling valuable materials. A large number of interesting applications for electrodialysis are in the galvanic industry and in metal surface treatment processes. A typical example is the recovery and concentration of nickel from the still rinse water and the recovery of acids such as HCl, HNO$_3$, HF, etc. from spent pickling solutions. There are many more interesting applications of electrodialysis in waste water treatment. Most of these applications require only relatively small electrodialysis units [9].

Electrodialysis has also found several applications in the food industry and in biotechnology. Some of these applications can be considered as state-of-the-art processes such as the deionization of whey. Other applications such as the removal of salts from protein and sugar solutions or organic acids such as lactic acid and certain amino acids from fermentation have been studied on a pilot plant scale. However, only a few applications have been commercialized so far.

Of very special interest is the concentration of NaCl from sea water prior to evaporation for the production of table salt in Japan which has no native salt deposit. The use of electrodialysis as a pre-concentration step prior to evaporation leads to substantial savings in energy costs [10]. Large plants with a capacity of 20,000 to more than 200,000 tons of salt per year are in operation in Japan. A typical plant for sea water concentration is shown in the photograph of Fig. 12.

A TSX-200 electrodialyser unit used for the concentration of sea water contains 3500 cell pairs in a stack. The cell pair area is 2 m^2 and the cell thickness is 0.4 mm. The production capacity is ca. 30,000 tons NaCl per year. The power consumption of the electrodialyser is 155 kWh/ton NaCl.

Another application which is presently studied on a laboratory scale is the integration of ion-exchange membranes in the so-called membrane reactors. In many chemical and biochemical reactions the reaction products or the reaction by-products inhibit the reaction when a certain concentration is exceeded. This often limits the achievable product concentration and requires additional separation and concentration steps. A continuous electrodeionization removal of the reaction inhibiting components often makes a continuous and more economic production possible.

2.1.3.2. Advantages and limitations of electrodialysis in water desalination. Electrodialysis is well established in water desalination as a reliable process since more than half a century. Compared to competing processes such as reverse osmosis or distillation and conventional ion-exchange it has advantages but also significant limitations for certain feed water compositions and required product water qualities. The main advantages of electrodialysis compared to reverse osmosis are that very little feed pretreatment is required since membrane fouling and scaling is reduced to a minimum due to

Fig. 11. Industrial size electrodialysis reversal (EDR) drinking water plant (photograph courtesy of Ionics Incorporated).
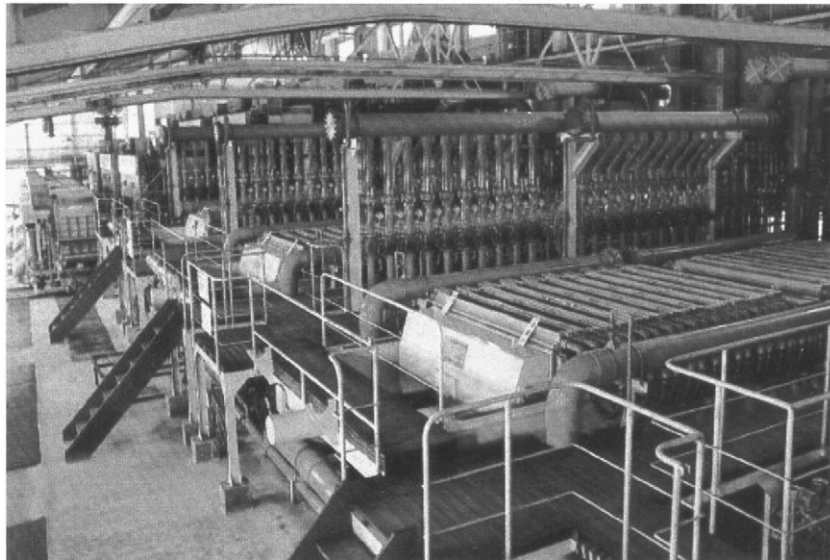
Fig. 12. Table salt production plant using 6 electrodialysis TSX 200 units to concentrate sea water from ca. 3.5 wt.% salt to ca. 20 wt.% NaCl (photograph courtesy of Tokuyama Corporation).

reverse polarity operation. Also much higher brine concentration can be achieved in electrodialysis than in reverse osmosis since there are no osmotic pressure limitations. The chemical and mechanical stability of ion-exchange membranes guaranties a long useful life even in feed waters with aggressive and oxidizing components. Compared to distillation processes electrodialysis has the advantages of lower energy as well as investment costs for certain feed and product water compositions. Compared to conventional ion-exchange processes electrodialysis has the advantage that no regeneration chemicals are required which makes the conventional ion-exchange process rather costly for deionization of feed solutions with high salt concentration.

But electrodialysis has several severe technical and economic limitations. A major disadvantage especially for the production of potable water is the fact that only ions are removed while uncharged components such as microorganisms or organic contaminants will not be eliminated. Another disadvantage of electrodialysis is the relatively high energy consumption when solutions with high salt concentrations have to be processed. Likewise, the investment costs are prohibitively high when very low salt concentrations must be achieved in the diluate because of the low limiting current density which requires a large membrane area. Thus, electrodialysis can only cost effectively be applied in water desalination in a certain range of feed water salt concentration and required product water quality. Outside this range of feed water

composition and required product water quality electrodialysis is not competitive to other desalination processes.

2.2. Electrodialysis with bipolar membranes, process design and key components

The conventional electrodialysis can be combined with bipolar membranes and utilized to produce acids and bases from the corresponding salts [11]. In this process mono-polar cation- and anion-exchange membranes are installed together with bipolar membranes in alternating series in an electrodialysis stack as illustrated in Fig. 13. A typical repeating unit of an electrodialysis stack with bipolar membranes is composed of three cells, two mono-polar membranes and a bipolar membrane. The cell between the mono-polar membranes contains a salt solution and the two cells between the mono-polar and the bipolar membranes contain a base and an acid solution. When an electrical potential gradient is applied across a repeating unit, protons and hydroxide ions generated in the bipolar membrane produce with the cations and anions removed from the salts solution an acid and a base, respectively. The process design is closely related to that of the conventional electrodialysis using the sheet flow stack concept. However, because of the significantly higher voltage drop across a cell unit only 50 to 100 repeating cell units are placed between two electrodes in a stack.
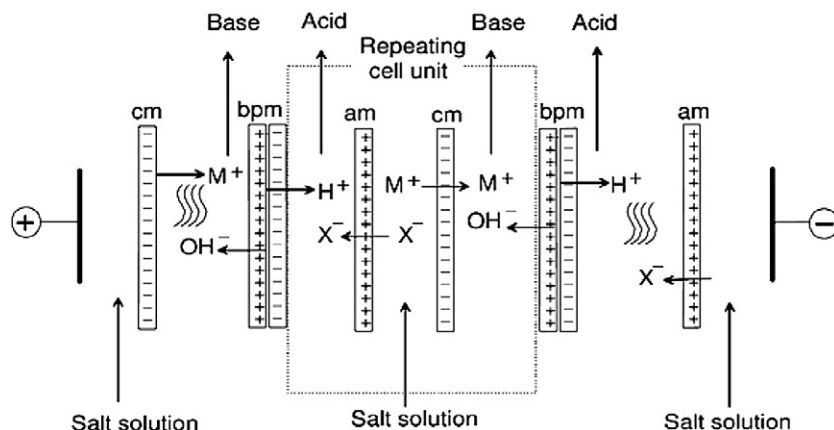

Fig. 13. Schematic drawing illustrating the principle of electrodialytic production of acids and bases from the corresponding salts with bipolar membranes.

Generally the acid, the base and sometimes also the salt solution is recycled in the stack to obtain a certain acid or base concentration as indicated in Fig. 14 which shows a simplified flow diagram of an acid and a base production by electrodialysis with bipolar membranes.

The utilization of electrodialysis with bipolar membranes to produce acids and bases from the corresponding salts is economically very attractive and has a multitude of interesting potential applications in the chemical industry as well as in biotechnology and water treatment processes.

The key component in electrodialysis is the bipolar membrane. The function and structure of a bipolar membrane is illustrated in Fig. 15 which shows an anion- and a cation-exchange membrane with a 4 to 5 nm thick transition layer arranged between two electrodes.

The energy required for the water dissociation can be calculated from the Nernst equation for a concentration chain between solutions of different pH-values [12]. It is given by:

$$\Delta G = F\Delta\varphi = 2.3RT\Delta pH. \tag{8}$$

Here ΔG is the Gibbs free energy, F is the Faraday constant, R is the gas constant, T is the absolute temperature and ΔpH and $\Delta\varphi$ are the pH-value and the voltage difference between the two solutions separated by the bipolar membrane.

For 1 mol L^{-1} acid and base in the two phases separated by the bipolar membrane ΔG is 0.022 [kWh mol^{-1}] and $\Delta\varphi$ is 0.828 [V] at 25 °C.

2.2.1. Electrodialysis with bipolar membrane process costs

The determination of the costs for the production of acids and bases from the corresponding salts follows the same general procedure as applied for the cost calculation in electrodialysis desalination. The contributions to the overall costs are the investment related costs, i.e. membrane costs and the operating costs, i.e. energy costs. The required membrane area for a given capacity plant can be calculated from the current density in a stack which is in electrodialysis with bipolar membrane generally not limited by concentration polarization effects. A unit cell contains a bipolar membrane, a cation- and an anion-exchange membrane. The bipolar membrane is rather expensive and its useful life as well as that of the anion-exchange membrane is rather limited in strong bases. Therefore, the stack related investment costs are dominating the total investment costs.

The operating costs in electrodialysis with bipolar membranes are strongly determined by the energy requirements which are composed of the energy required for the water dissociation in the bipolar membrane and the energy necessary to transfer the salt ions from the feed solution, and protons and hydroxide ions from the transition region of the bipolar membrane into the acid and base solutions. The energy consumption due to the pumping of the solutions through the stack can generally be neglected.
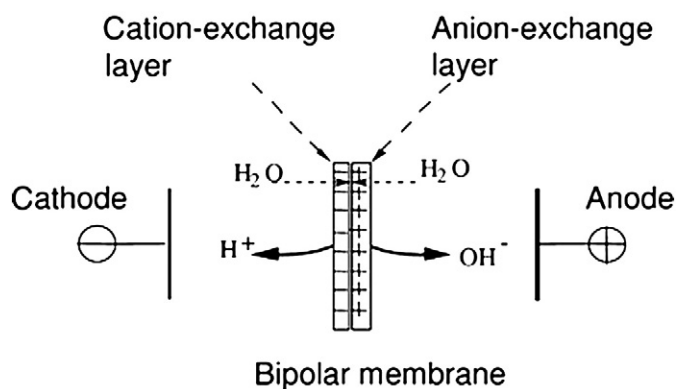

Fig. 15. Schematic diagram illustrating the structure and the function of a bipolar membrane which is composed of a cation- and an anion-exchange layer with a 4 to 5 nm thick transition layer arranged between two electrodes.

2.2.2. Applications of bipolar membrane electrodialysis

Since bipolar membranes became available as commercial products a large number of applications has been identified and studied extensively on a laboratory or pilot plant scale. However, in spite of the obvious technical and economical advantages of the technology large scale industrial plants are still quite rare. The main reasons for the reluctant use of bipolar membrane electrodialysis are shortcomings of the available bipolar and mono-polar membranes which result in a short useful membrane life, poor current utilization, and high product contamination. Nevertheless, there are a number of smaller scale applications in the chemical process industry, in biotechnology, in food processing and in waste water treatment. Some of the potential applications are listed in Table 3 which also indicates the present state of the application, its potential advantages and its problems.

The largest potential application of bipolar membrane electrodialysis is the production of acids and bases from the corresponding salts. Utilizing bipolar membrane electrodialysis for the caustic soda and an acid production is an interesting alternative to the conventional chlorine/alkaline electrolysis because of lower energy consumption. However, the process is impaired by poor membrane stability and insufficient permselectivity at high ion concentrations which results in substantial product salt contamination, low current utilization and short membrane life. Extensive laboratory tests have shown that presently the production of mineral acids and bases by bipolar membrane electrodialysis does not meet the product quality requirements under economic conditions. However, the situation is quite different when acids or bases must be recovered from salts obtained in chemical reactions or neutralization processes. In these cases the requirements for the concentration and the purity of the recovered acids or bases are not as stringent as in the production of high quality commercial products and electrodialysis with bipolar
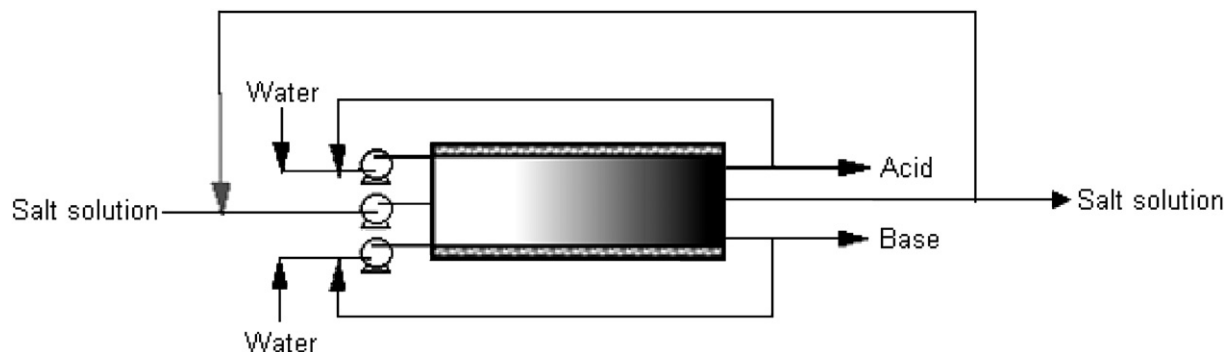

Fig. 14. Simplified flow diagram illustrating the production of acids and bases from the corresponding salts by electrodialysis with bipolar membranes.

Table 3
Potential applications of electrodialysis with bipolar membranes, their state of development and possible advantages and experienced problems.

Application	State of process development	Potential advantages	Problems related to application
Production of acids and bases from salts	Pilot plant operation	Low energy consumption	Contamination of products
Recovering of acids from fermentation	Commercial plants	Integrated process, lower costs	Unsatisfactory membrane stability
pH-control in chemical processes	Laboratory studies	Less chemical costs and salt deposits	Application experience, process costs
Removal of SO₂ from flue gas	Pilot plant tests	Decreased salt production	Long term membrane stability
Regeneration of ion-exchange resins	Pilot plant tests	Less ion-exchanger regeneration costs	High investment costs

waste disposal is one of the more promising applications of bipolar membrane electrodialysis.

Recovering hydrofluoric and nitric acid from an effluent stream containing potassium fluoride and nitrite generated by neutralization of a steel pickling bath has been one of the first large scale commercial applications of electrodialysis with bipolar membranes. The process which also contains a conventional electrodialysis unit is illustrated in the simplified flow diagram of Fig. 16.

In a first step of the process the spent pickling acid bath is neutralized with potassium hydroxide. The solution is then filtered and the precipitated heavy metal hydroxides are removed in a settling tank. In the second step the neutral potassium fluoride and nitrite containing solution is fed to the bipolar membrane electrodialysis unit in which the salts are converted to the corresponding acids and potassium hydroxide. The potassium hydroxide is recycled to the neutralization tank and the acids to the pickling bath. In the last step the depleted salt solution from the bipolar membrane electrodialysis unit is concentrated in a conventional electrodialysis system and recycled directly to the bipolar membrane unit. The diluate is discharged.

The treatment of the effluent of alkaline or acid scrubbers that are used to remove components, which are harmful to the environment such as NO$_x$, SO₂ or NH₃ from waste air streams, is another interesting application for bipolar membrane electrodialysis. In alkaline and acid scrubbers large amounts of acids or bases are consumed and salts are produced which are often contaminated with toxic materials such as heavy metal ions. Recycling of the acids or bases saves substantial chemical and sludge disposal costs.

Another promising application of electrodialysis with bipolar membranes is the recovery of organic acids from fermentation processes. The process is illustrated in Fig. 17 which shows the production of lactic acid by continuous electrodeionization fermentation with an integrated product recovery process based on bipolar membrane electrodialysis [13].

Conventionally lactic acid is produced in a batch process and the separation and purification of the lactic acid is achieved mainly by ion-exchange resulting in a large volume of waste water with regeneration salts. In the production process with integrated electrodialysis which is shown in Fig. 17, a minimum of ion-exchange resin is needed in a final purification step. The concentration of the lactate salt is achieved by conventional electrodialysis and the conversion of the lactate into lactic acid by bipolar membrane electrodialysis. The simultaneously produced base is recycled to the fermenter to control the pH-value.

Other possible applications of bipolar membrane electrodialysis in biotechnology are the recovery of gluconic acid from sodium gluconate and the production of ascorbic acid from sodium ascorbate.

2.2.3. Problems related to the use of electrtrodialysis with bipolar membranes

The limited stability of ion-exchange membranes in strong acids and bases and the high costs of the bipolar membranes affect the economy of the process. The precipitation of multi-valent ions in the base containing flow stream of a bipolar membrane stack is a technical problem which requires an extensive pretreatment of a feed solution. But in many applications the contamination of the products by salt ions which permeate the bipolar membrane is the most serious problem. Especially, when high concentrations of acids and bases are required the salt contamination is high [14] as illustrated in Fig. 18a) and b) which shows the conversion of Na₂SO₄ into H₂SO₄ and NaOH by electrodialytic water dissociation. Panel a) shows the ion transport in the bipolar membranes indicating the desired and undesired ion transport. But recently membranes with lower H⁺- permeability are developed [15,16].

Desired is a flux of H⁺- and OH⁻-ions from the transition region due to the applied voltage into the outer phases. However, there is also an undesired transport of Na⁺- and SO₄²⁻-ions through the bipolar membrane due to the incomplete permselectivities of the ion-exchange layers of the bipolar membrane. Since the permselectivity of the ion-exchange layers of the bipolar membrane decreases with increasing acid and base concentration due to the Donnan exclusion effect the contamination of the products is increasing with the acid and base concentrations as demonstrated in Fig. 18b) which shows experimentally determined salt concentrations in the acid and base as a function of their concentration.

The salt leakage through the bipolar membrane also effects the current utilization to some extent. However, the current utilization is mainly determined by the properties of the anion-exchange membrane which has very poor retention for protons due to the tunneling mechanism of the proton transport as illustrated in the schematic drawing of Fig. 19 which shows a) the undesirable transport of protons through the anion-exchange membrane. The same is true for the hydroxide ions which can permeate the cation-exchange membrane. The net result is that H⁺- and OH⁻ -ions generated in the bipolar membrane neutralize each other and thus reduce the current utilization. The fluxes of the protons and hydroxide ions depend on their concentration. At high acid and base concentrations the current utilization can reach uneconomically low values of less than 30% as indicated in Fig. 19b) which shows the experimentally
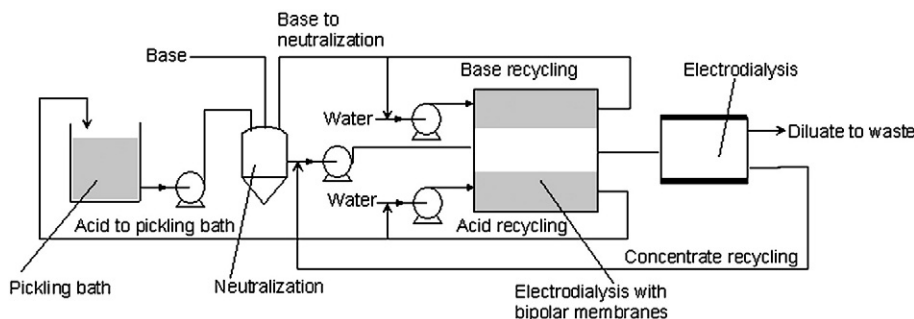

Fig. 16. Simplified flow diagram of acid recovery and recycling from steel pickling neutralization bath.
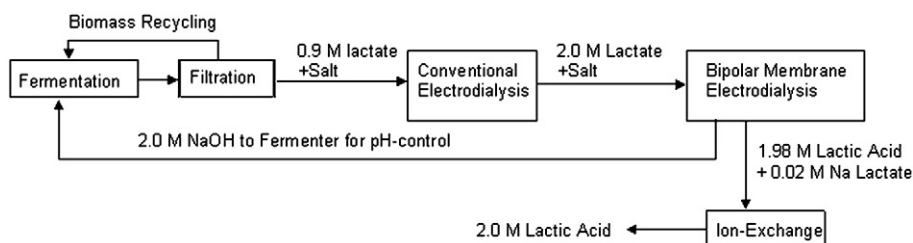
Fig. 17. Simplified flow diagram illustrating the lactic acid production process with integrated electrodialysis with bipolar membranes.

determined current utilization as a function of the acid and base concentration.

2.3. Continuous electrodeionization

Continuous electrodeionization is very similar to conventional electrodialysis. However, the cells which contain the diluate stream are filled with ion-exchange resins. The conductivity in these cells is substantially increased and highly deionized water can be obtained as a product [17].

There are some variations in the basic design of a continuous electrodeionization unit as far as the distribution of the ion-exchange resin is concerned. In some cases the diluate cell is filled with a mixed bed ion-exchange resin, in other cases the cation- and anion-exchange resins are placed in series in the cells. More recently also bipolar membranes are used in the process.

The process design and the different hardware components needed in continuous electrodeionization are very similar to those used in conventional electrodialysis. The main difference is the stack construction. In a continuous electrodeionization stack the diluate cells and sometimes also the concentrate cells are filled with an ion-exchange resin. The different concepts used for the distribution of the cat- and anion-exchange resins in the cells are illustrated in Fig. 20a)

and b). In the conventional process the diluate cell is filled with a mixed bed ion-exchange resin with a ratio of cation- to anion-exchange resin being close to 1 as shown in Fig. 20a). The mixed bed ion-exchange resin in the diluate cells removes both the cat- and anions of a feed solution. Due to an applied electrical field the ions migrate through the ion-exchange bed towards the adjacent concentrate cells, and highly deionized water is obtained as a product. The ion-exchange resin increases the conductivity in the diluate cells and the stack resistance is significantly lowered. But continuous electrodeionization using a stack with mixed bed ion-exchange resins in the diluate cell has also disadvantages. The most important one is the poor removal of weak acids and bases such as boric or silicic acid [18]. Much better removal of weakly dissociated electrolytes can be obtained in a system in which the cation- and anion-exchange resins are placed in separate beds with a bipolar membrane placed in between as illustrated in Fig. 20b) which shows a diluate cell filled with a cation-exchange resin facing towards the cathode separated by a bipolar membrane from a diluate cell facing the anode. A cation-exchange membrane, a cation-exchange resin, a bipolar membrane, an anion-exchange resin, and a concentrate cell form a repeating unit between two electrodes.

The main difference between the system with the mixed bed ion-exchange resins and the system with separate beds is that in the mixed bed systems anions and cations are simultaneously removed
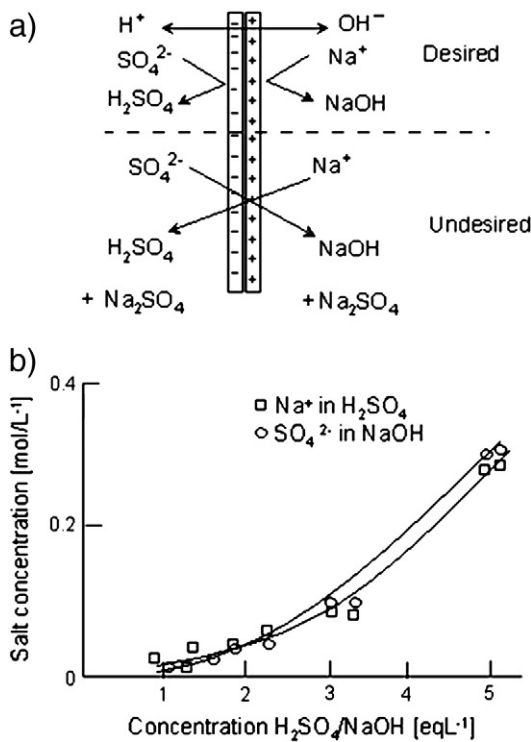

Fig. 18. Schematic diagram illustrating a) the contamination of acids and bases by salt due to the incomplete permselectivity of the bipolar membrane for salt ions and b) the experimentally determined salt concentration as a function of the acid and base concentration.
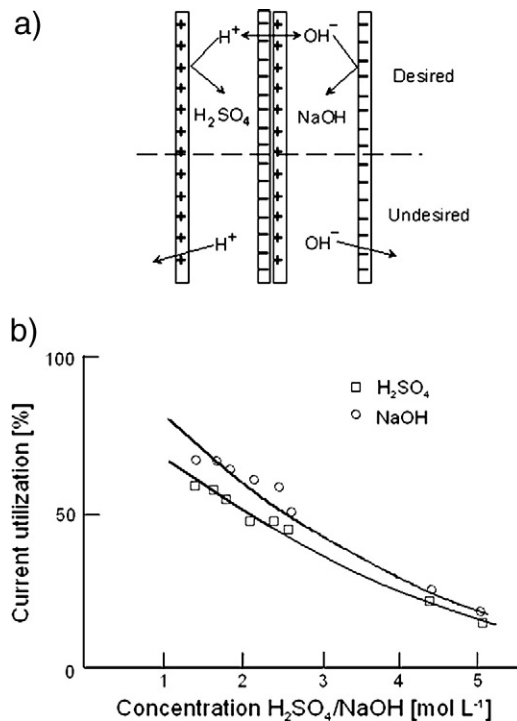

Fig. 19. Schematic diagram illustrating a) the decrease of the current utilization during the acid and base production due to the poor acid blocking capability of the anion-exchange membrane and b) experimentally determined current utilization as function of the acid and base concentration.
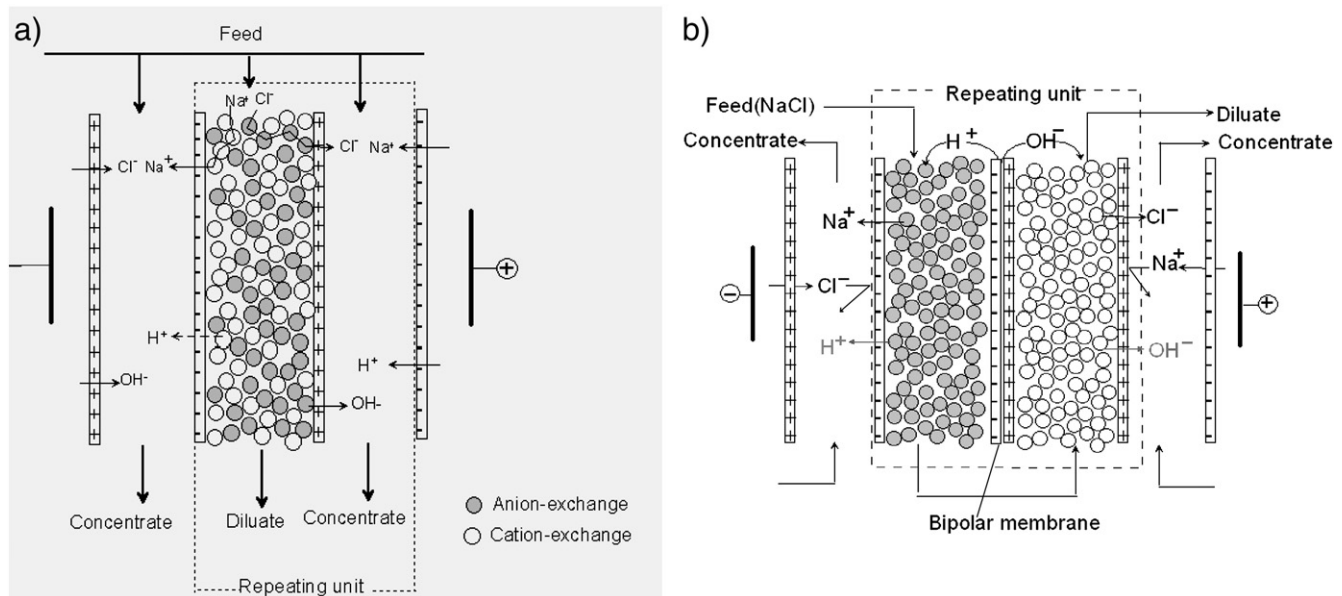
Fig. 20. Schematic drawing illustrating different stack concepts used in continuous electrodeionization, a) conventional stack with diluate cells filled with a mixed bed ion-exchange resin, b) stack with cation-exchange and anion-exchange resins in different diluate cells and regeneration of the ion-exchange resins by H^+- and OH^- -ions produced in a bipolar membrane.

from the feed and the solution leaving the diluate cell is neutral. In the system with separate ion-exchange beds and bipolar membranes the cations of the feed will first be exchanged in the cell filled with a cation-exchange resin by the protons generated in the bipolar membrane with the result that the solution leaving the cation-exchange bed is acidic. This solution is then passed through the cell with the anion-exchange resin where the anions are exchanged by the OH^--ions generated in the bipolar membrane and at the exit of the anion-exchange filled cell the solution is again neutral. Both the mixed and the separate bed ion-exchange continuous electrodeionization systems are widely used today on a large industrial scale.

2.3.1. Practical application of continuous electrodeionization and operational problems

The main application of continuous electrodeionization is the production of so-called ultrapure water, which is used in many industrial processes and in chemical and analytical laboratories. Generally, well or surface water is purified in a series of processes that include water softening, microfiltration, reverse osmosis, ultrafiltration, UV-sterilization, and mixed bed ion-exchange which is used as a final polishing process producing water with a conductivity of less than $0.06 \mu S \, cm^{-1}$. While processes such as reverse osmosis, micro- and ultrafiltration or UV-sterilization can be operated in a continuous electrodeionization mode, the mixed bed ion-exchanger, which is necessary to reach the required low conductivity, must be regenerated in certain time intervals. This regeneration is not only labour intensive and costly but it requires extremely long rinse down times to remove traces of regeneration chemicals. By replacing the mixed

bed ion-exchanger by a continuous electrodeionization, using separate ion-exchange beds and bipolar membranes the ultra pure water production can be substantially simplified yielding consistently high quality water in a completely continuous electrodeionization process as illustrated in Fig. 21.

The advantages of the ultra pure water production with an integrated continuous electrodeionization unit compared to the use of a mixed bed ion-exchanger are a simpler process, no need of regeneration chemicals, less raw water consumption, and a substantial reduction in costs.

But both the systems, i.e. the mixed bed ion-exchange resin as well as that with bipolar membranes and separated beds have certain limitations.

In the system with the mixed bed ion-exchange resin the removal of weakly dissociated acid is very poor. In the system with separated beds of ion-exchange resins and bipolar membranes the removal of weak acids is very efficient. However, there is some contamination of the diluate by cations permeating the anion-exchange membrane from the concentrate into the diluate if the membrane is not completely semipermeable. Since this is generally not the case a complete removal of ions cannot be achieved in practical applications.

2.4. Capacitive deionization

Capacitive deionization is an electrosorption process that can be used to remove ions from an aqueous solution by charge separation [19]. A capacitive deionization cell unit consists of two electrodes made out of activated carbon separated by a spacer that acts as a flow channel for an ion containing solution. In capacitive deionization
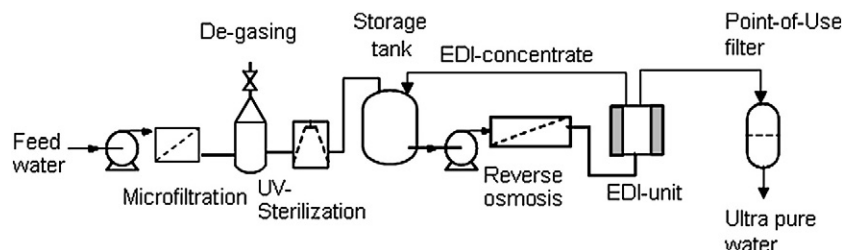

Fig. 21. Simplified flow diagram of an ultra pure water production line.

electrons are not transmuted by oxidation and reduction reactions but by electrostatic adsorption. The system resembles a "flow-through capacitor". If an electrical potential is applied between the electrodes ions are removed from the solution and adsorbed at the surface of the charged electrodes. When the carbon electrodes are saturated with the charges the ions are released from the electrodes by reversing the potential, i.e. the cathode becomes the anode and vice versa the anode becomes the cathode. Thus, capacitive deionization is a two step process. In a first step ions are removed from a feed solution by migration from the feed solution towards the electrodes under an electrical potential driving force and electro-sorption at the electrodes. The result is deionised product water. In a second step the adsorbed ions are released from the carbon electrodes and transported back into the feed solution by reversing the electrical potential, and concentrated brine is obtained. The process is illustrated in Fig. 22a) and b) which shows schematically a capacitive deionization unit and the ion transport during the sorption and desorption step of the deionization process. During the deionization step anions are prevented to diffuse into the product water by a cation-exchange membrane on the cathode and an anion-exchange membrane on the anode as shown in Fig. 22a). During the regeneration step under reverse polarity conditions the cation-exchange membrane prevents the transport of anions towards the anode and the anion-exchange membrane the transport of cations towards the cathode as shown in Fig. 22b) and thus, avoids an ion adsorption at the electrodes during the regeneration step.

A key component in this process is the carbon electrode. The number of ions adsorbed at the electrodes is directly proportional to the available surface area. Therefore, the specific surface area, i.e. the surface area per unit weight of the electrodes should be as high as possible. Activated carbon and carbon nano-tubes are the most promising materials for the preparation of electrodes. Their specific surface area is up to $1100 \, m^2 \, g^{-1}$. Another parameter is the applied potential which should not exceed a certain maximum value to avoid water dissociation caused by electrode reactions. In practical applications capacitive deionization cells are operated at a voltage drop of between 0.8 and 1.2 V.

The advantage of the process is the relatively low energy requirement. The disadvantage is the large surface area of the electrode which is necessary when feed solutions with high salt concentration are deionized.

2.5. Other electrodialysis related processes

In addition to the processes discussed so far there are two more electrodialysis related processes in which the driving force is not an externally applied electrical potential but a concentration gradient. The processes are referred to as diffusion dialysis and Donnan dialysis. Both processes are based on the electroneutrality requirement which postulates that on a macroscopic scale there are no positive or negative excess charges.

Diffusion dialysis is utilizing anion- or cation-exchange membranes only to separate acids and bases from mixtures with salts. The principle of the process is illustrated in Fig. 23 which shows a dialysis cell system that contains anion-exchange membranes only. A feed solution containing a mixture of NaCl and HCl is pumped through alternating cells while water is fed in counter current flow through the other cells of a membrane stack. Protons and anions will penetrate the anion-exchange membranes while the salt cations are rejected [20,21]. The net result is the removal of acids from a mixture with salts. Likewise bases can be removed from salt solutions using a stack with cation-exchange membranes only.

Donnan dialysis can be used to exchange ions between two solutions separated by an ion-exchange membrane. The process has so far gained only limited practical relevance.

2.6. Energy production by reverse electrodialysis

The production of energy by mixing sea water with river water through ion-exchange membranes is a process referred to as reverse electrodialysis. The process which is illustrated in Fig. 24 provides a clean and sustainable energy source and is certainly very interesting.

The design of a stack to be used in reverse electrodialysis is very similar to the stack used in electrodialysis. The main difference is that the cells arranged in parallel between the electrodes are rinsed in alternating series by sea and by river water. The ions in the sea water indicated as Na^+- and Cl^--ions permeate from the sea water into the
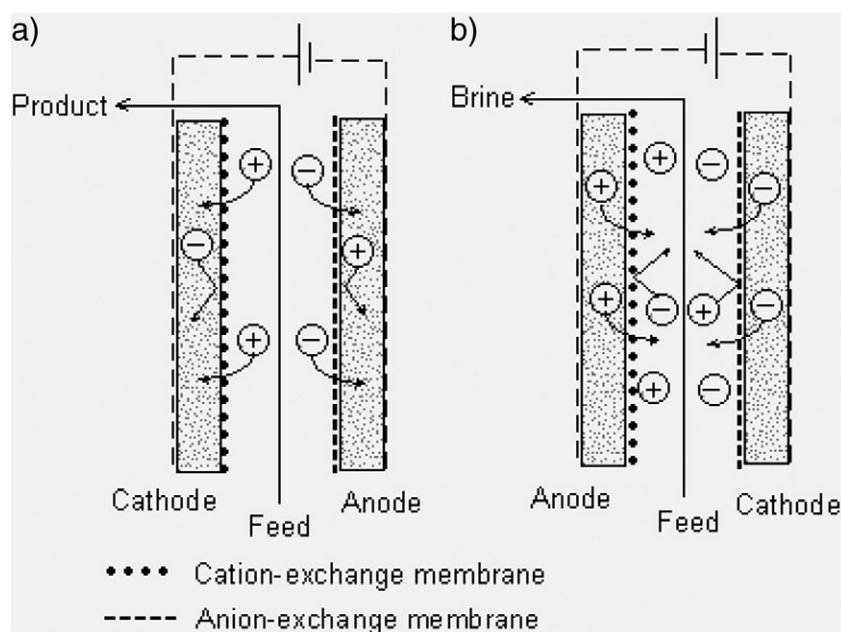

Fig. 22. Schematic diagrams illustrating the capacitive deionization process with ion-exchange membranes between the feed solution and the porous carbon electrodes, a) shows sorption of ions, i.e. the deionization step and b) shows the desorption of ions due to a change of polarity producing concentrated brine.
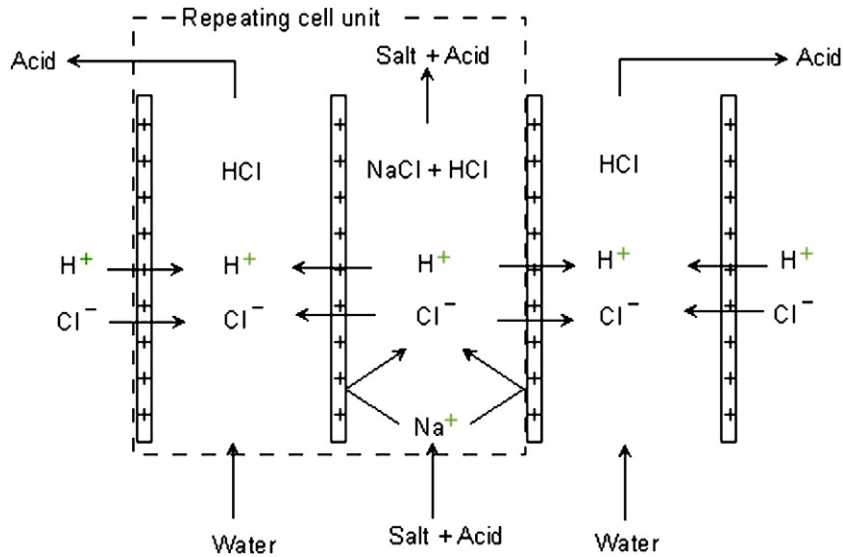
Fig. 23. Schematic drawing illustrating the principle of diffusion dialysis used to recover an acid from a mixture with salt in a stack of anion-exchange membranes only.

river water through the corresponding ion-exchange membrane and produce brackish water due to their electrochemical potential gradient. This leads to an electrical current between the cathode and anode.

The maximum amount of energy that can be recovered is the Gibbs free energy of mixing fresh water and sea water which is given by:

$$\Delta G_m = G_b - (G_c - G_d). \tag{9}$$

Here ΔG_m is the Gibbs free energy of mixing, G_b is the Gibbs free energy of the mixture, i.e. the brackish water, G_c is the Gibbs free energy of the concentrate, i.e. the sea water and G_d is the Gibbs free energy of the diluate, i.e. the river water.

If 1 m^3 of fresh water is mixed with 1 m^3 of sea water having a total salt content of ca. 35 kg m^{-3} the maximum obtained energy is ca. 0.4 kWh. If 1 m^3 of river water is mixed with a larger amount of sea water the recovered energy is increasing accordingly.

The power that could be obtained by mixing the water of a river such as the Rhine which discharges ca. 2,000 m^3/s into the North Sea with sea water is correspondent to a power plant of ca. 4.700 MW.

Unfortunately, the maximum energy that can be recovered is significantly lower. It can be calculated from the "open voltage"

multiplied with the current carried by the ions diffusing from the seawater into the river water and the electrical resistance of the stack [22].

The open voltage with completely semipermeable ion-exchange membranes is given by:

$$U_{st}^o = \frac{RT}{F} \ln \left(\frac{a_c}{a_d} \right). \tag{10}$$

Here U_{st}^o is the so-called "open voltage" of a stack, R is the gas constant, T the absolute temperature, F the Faraday constant, a_c and a_d are the equivalent activities of the components in the concentrate and diluate cells.

The maximum power that can be generated is given by:

$$W_{max} = IU_{st}^o = I^2 R_{st} = \frac{(U^o)^2}{R_{st}}. \tag{11}$$

Here W_{max} is the maximum power output, I is the current of the stack and R_{st} is the stack resistance.

For the maximum power output the stack resistance is a critical parameter. It is determined by the resistances of the membranes and the solution. The resistances should be minimized by making the
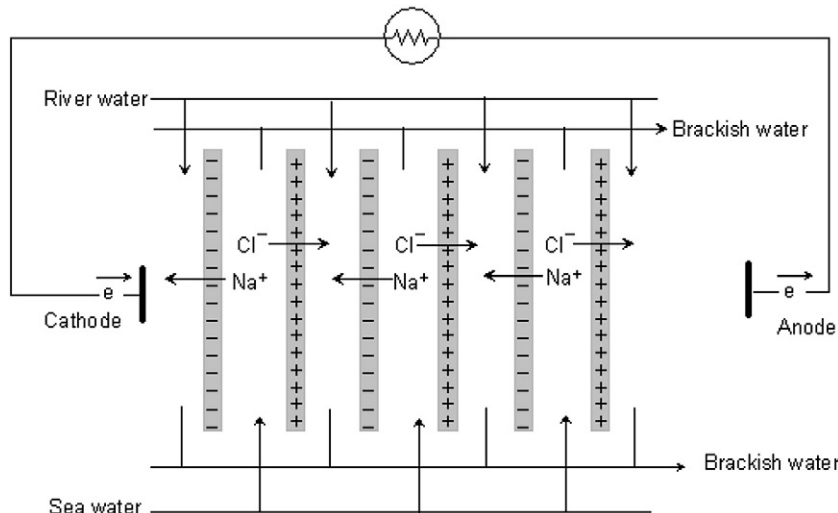

Fig. 24. Schematic drawing illustrating the concept of reverse electrodialysis used to generate electrical energy by mixing river and sea water.

membranes as well as the individual cells in the stack as thin as possible and reducing concentration polarization effects.

A critical cost factor is also the required membrane area for a given capacity reverse electrodialysis power plant which is determined by the power density w_{max} and given by:

$$w_{max} = \frac{W_{max}}{A} \qquad (12)$$

The maximum power density that can be achieved today in practical applications is in the order of 0.5 to 1 W/m^2 [23]. Therefore, it seems that membrane costs must also be drastically decreased to make reverse electrodialysis a competitive energy production process. But better thinner membranes and cells as well as low cost membranes, which most likely will be developed, will increase the competitiveness of reverse electrodialysis in the future.

3. Recent developments in electrodialysis and related processes

Recent developments in electrodialysis and related processes include new membranes with improved properties, new processes and new applications. New ion-exchange membranes with very special properties such as anion-exchange membranes with acid blocking capability or high stability in strong bases or strong acids have been developed. New electrodialysis stacks with conductive spacers or membranes with a special surface geometry, which can be operated without spacers, have also been prepared and tested on a laboratory scale.

3.1. Ion-exchange membrane developments

Due to the growing interest in low temperature fuel cells which require a solid polymer electrolyte for the transport of protons a large number of new cation-exchange membranes has been developed. An example of a cation-exchange membrane that is suited also for electrodialysis and has become recently available is prepared by introducing sulfuric acid groups as fixed charges into polyetherketone [24,25] as illustrated in the following reaction scheme.
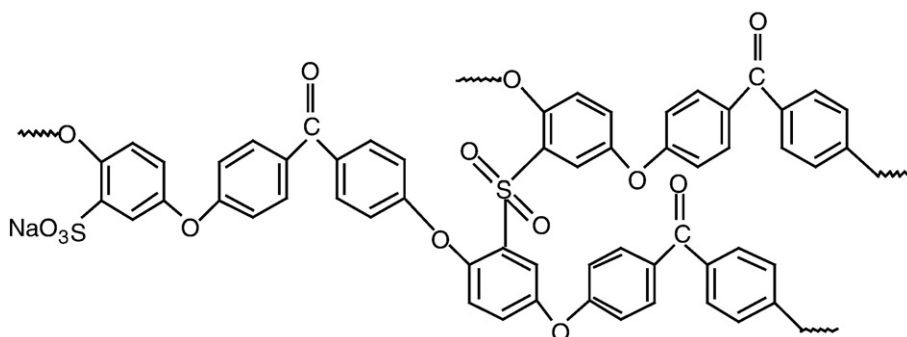
The membrane is chemically very stable and has high permselectivity and low swelling due to the partial cross-linking during the membrane formation step.

Anion-exchange membranes with excellent alkaline stability are obtained by incorporating a quaternary ammonium ion consisting of the mono-quaternary salt of 4,4′-diazabicyclo-[2.2.2]-octane into a polysulfone matrix as indicated in the following reaction scheme:
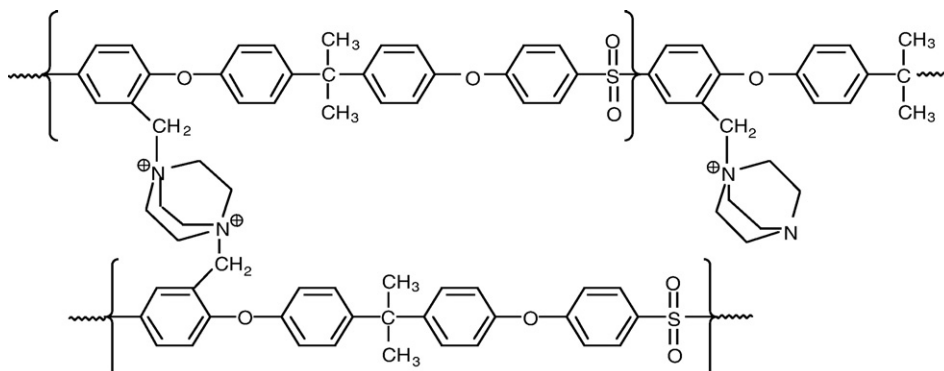

The anion-exchange membranes are prepared from a solution of chloromethylated polysufone by adition of the 4,4′-diazabicyclo-[2.2.2]-octane. The partially cross-linking membrane has good chemical stability and electrochemical properties [26].

The preparation of anion-exchange membranes with special properties are reported in the literature [27].
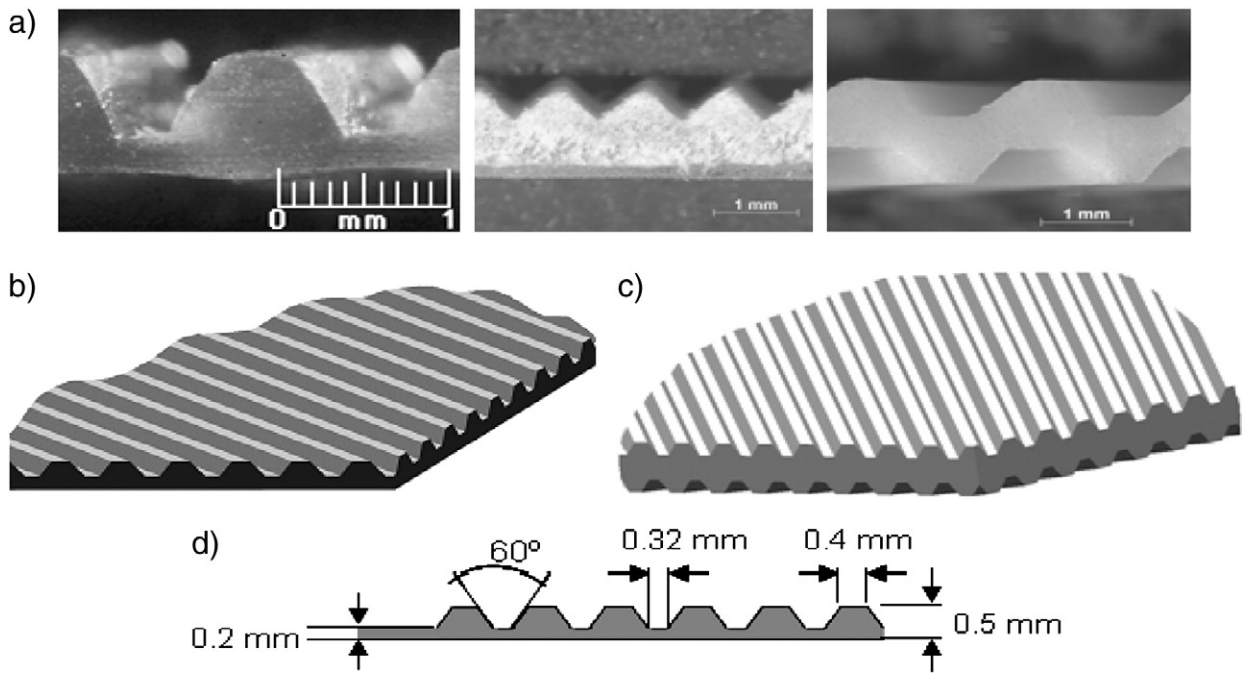
Fig. 25. a) Shows photographs of membranes with different surface profiles on one or both sides of the membrane, b) and c) show schematic drawings of membranes with profiles on one or both sides and d) shows the dimensions of membrane profiles.
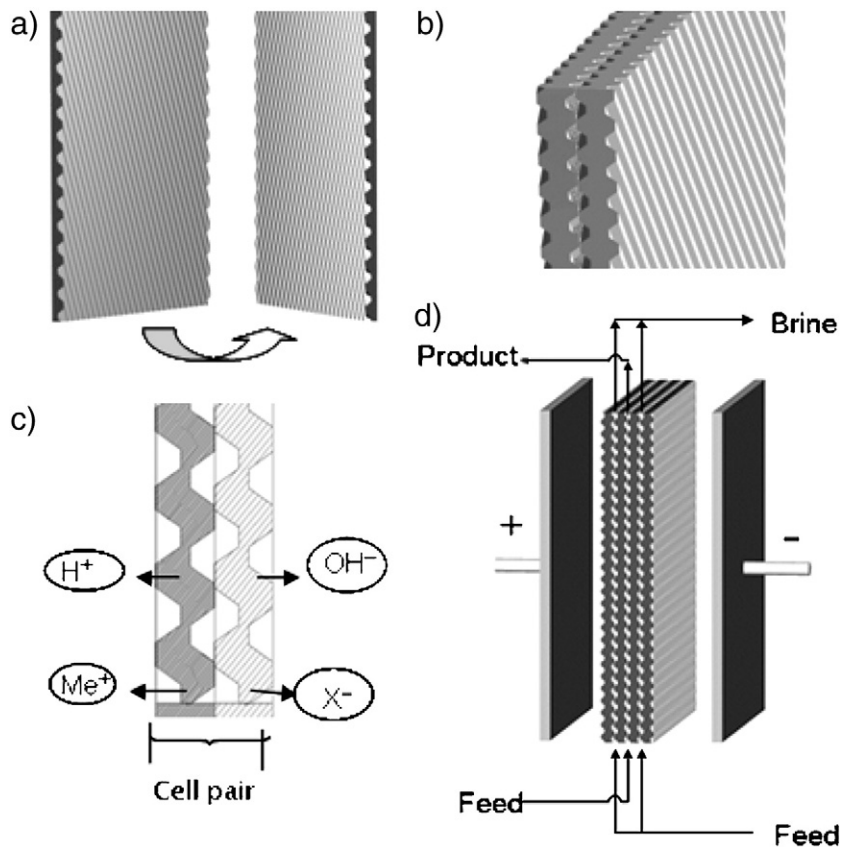
Fig. 26. Schematic drawing showing the arrangement of profiled membranes in a stack, a) illustrates the orientation of the profiled surfaces to each other, b) shows the cross-section of two membranes forming the flow channels, and c) indicates the transport of salt, H^+- and OH^--ions through profiled membranes from the concentrate to the diluate and d) shows part of a stack between electrodes.

3.2. Electrodialysis process developments

Several attempts have been made to reduce the energy consumption and to increase the limiting current density by optimizing the electrodialysis stack using conductive spacers in the diluate cell [28]. Although, the effectiveness of the conductive spacers as far as the energy efficiency in electrodialysis has been demonstrated in extensive laboratory tests they are not yet used commercially. The development of a stack in which membranes with a specific surface geometry are without spacer gaskets are installed has also led to a significant improvement of the overall efficiency of electrodialysis [29]. The membranes used in this stack have a corrugated or profiled instead of a flat surface as shown in the photographs and the schematic drawings of Fig. 25a) to c). The dimensions of the membrane surface structure are given in Fig. 25d). Various geometries of the membrane surfaces have been prepared by various preparation procedures. The selection of a suited profile is based on hydrodynamic considerations to minimize concentration polarization.

Membranes with a trapeze-shaped surface profile were installed in a stack with notches oriented 90° to each other and 45° to the main feed flow direction as shown in Fig. 26b), c) and d).

The increase of the membrane surface due to the profiled surface is between 40 and 45%. The direct contact area between a cation- and an anion-exchange membrane is between 1 and 8% of the total stack membrane area. The cross-section area of the flow channels between the membranes is 0.20 to 0.25 cm^2.

Electrodialysis with profiled membranes has extensively been studied with feed solutions of very different concentrations. Typical results are depicted in Fig. 27a) to c) which show the diluate conductivity as function of the applied voltage obtained with three different feed solutions: a) tap water with a conductivity of 350 µS/cm, b) a NaCl solution with a conductivity of 65 µS/cm, and c) reverse osmosis permeate with a conductivity of 6 µS/cm. All tests were carried out in a test cell with one cell pair between the electrode compartments. Fig. 27a) shows that under the given test condition the minimum diluate conductivity which could be achieved with tap water as feed was ca. 20% lower in the tests with profiled membranes than that obtained with flat membranes. The difference in the diluate conductivity obtained in the tests with flat and with profiled membranes increases with decreasing feed solution concentration as shown in Fig. 27b) and c).

In another set of experiments the current density was measured as a function of the applied voltage in stacks with flat and profiled membranes and two different feed solutions of 350 µS/cm and 6 µS/cm. The results are shown in the current voltage curves of Fig. 28a) and b). The current voltage curves, which were obtained with tap water having a conductivity of 350 µS/cm show that the resistance of the stack with flat membranes is ca. 1.6 times higher than the resistance of the stack with profiled membranes. For the feed solution with a conductivity of 6 µS/cm the resistance of the stack with flat membranes is increasing strongly with the applied voltage to a very high value, while the resistance of the stack with the profiled membrane is much lower and nearly constant over a wide range of the applied voltage as shown in Fig. 28b).

The reason for the drastic increase of the resistance in the stack with flat membranes for the feed solution with low conductivity is the low limiting current density which is exceeded when the applied voltage is higher than ca. 2 V. In the stack with profiled membranes there seems to be no visible limiting current density, and no significant pH-value changes were detected in the diluate or concentrate solutions when a voltage of more than 10 V was applied.

3.2.1. Advantages of an electrodialysis stack with profiled membranes

The advantages of an electrodialysis stack with profiled membranes compared to a stack with conventional flat membranes and spacers are:

1. The effective surface area of profiled membranes is increased by 40 and 45% compared to flat membranes.
2. The profiled membrane surface provides excellent mixing of the solutions without spacers which are no longer required.
3. A stack with profiled membranes has a lower stack resistance and thus lower energy consumption than a stack with flat membranes and spacers.
4. Profiled membranes have higher limiting current densities and thus the membrane area required for a given plant is lower than in a plant with flat membranes.
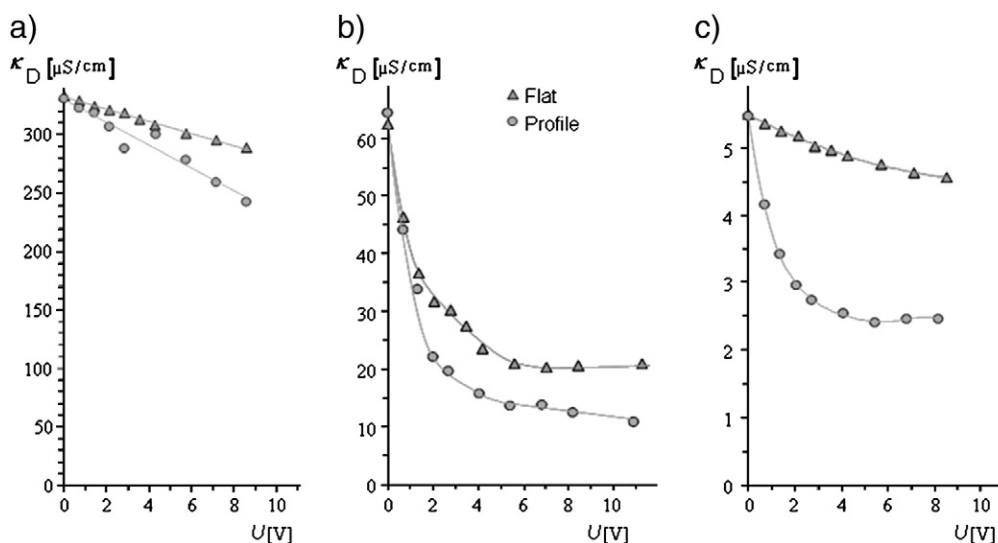

Fig. 27. Experimental results obtained with profiled and flat sheet membranes showing the diluate concentration as a function of the voltage applied in a test cell with one cell pair and feed solutions of a) 350 µS/cm tap water, b) 65 µS/cm NaCl solution and c) 6 µS/cm reverse osmosis permeate.
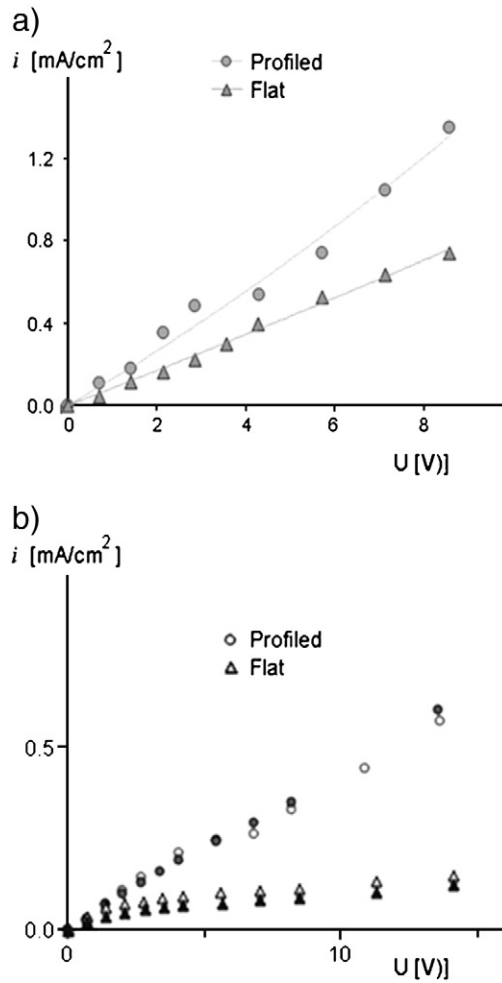
Fig. 28. Experimental results obtained with profiled and flat sheet membranes showing the current density as a function of the voltage applied in a test cell with one cell pair and feed solutions of a) 350 μS/cm tap water and b) 6 μS/cm reverse osmosis permeate.
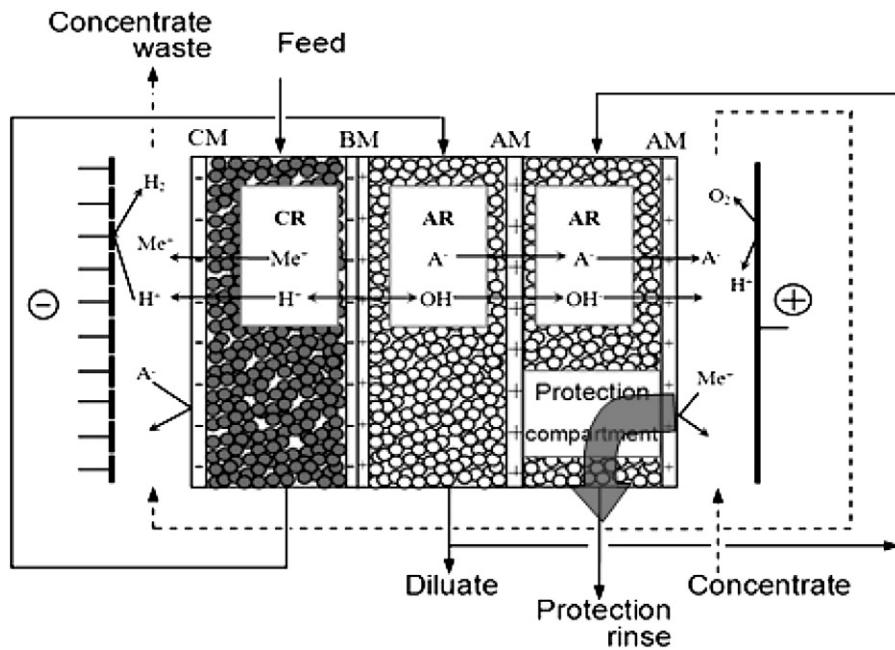

Fig. 29. Schematic drawing showing the feed, the product and the concentrate flow in a repeating unit of a continuous electrodeionization stack with cat- and anion-exchange resin beds separated by a bipolar membrane and an additional protection compartment filled with an anion-exchange resin.

Depending on the concentration of the feed and diluate solutions the electrodialysis stack costs are reduced by more than 50% and energy costs are reduced by more than 40% when profiled instead of flat membranes are used.

3.3. Continuous electrodeionization stack development

While continuous electrodeionization with separate ion-exchange resin beds and bipolar membranes as described earlier leads to an effective removal of weakly dissociated acids, there is still a problem with contamination of the product water by diffusion of the cations from the concentrate through the anion-exchange membrane into the diluate when the anion-exchange membranes are not completely permselective. Therefore, it is difficult to reach in practical applications a complete removal of ions from a feed solution. However, a contamination of the diluate can be avoided when a so-called protection compartment filled with an anion-exchange resin is introduced between the diluate and the concentrate cell as illustrated in Fig. 29 [30] which shows a simplified flow scheme of a continuous electrodeionization stack with separate ion-exchange resin beds and an additional protection compartment which is rinsed by a small portion of the diluate.

An experimental study of a continuous electrodeionization stack with and without a protection compartment has shown that only in a stack with a protection compartment a complete removal of ions including weak acids is achieved and product water having a resistance of 18 MΩ cm is obtained.

There is more research and development work in electrodialysis and related processes currently in progress. Especially the use of ion-exchange membranes in energy conversion and energy storage system has led to several interesting new membrane developments [31,32]. Many of these research activities are not only concentrated on membranes or stack constructions. Much of the work is directed towards specific applications in the chemical process industry, the biomedical area and in membrane reactors [33,34]. New applications of electrodialysis and related processes are rapidly growing.

4. Research needs in electrodialysis and related processes

In spite of the ongoing research in electrodialysis and related processes there is a need for further work addressing both fundamental problems as well as application oriented issues. One of the most urgent problems is the development of ion-exchange membranes with higher permselectivity, lower electrical resistance and better chemical and thermal stability at lower costs. Additionally, there is a substantial amount of research and development needed for the evaluation and optimization of electrodialysis and related processes in new applications in the chemical process industry, in biotechnology and energy conversion. Other problems will require some more fundamental research activities, such as a better understanding of electroconvection or the water dissociation in bipolar membranes and the effect of ion-exchange membrane structures on membrane transport properties [35,36].

5. List of symbols

A	area [m^2]
a	activity [-]
a	constant [-]
C	concentration [mol L^{-1} or eq L^{-1}]
E	energy [W s]
F	Faraday constant [A s eq^{-1}]
G	Gibbs free energy [W s eq^{-1}]
I	current [A]
i	current density [A m^2]
k	constant [-]
p	pressure [Pa]
Q	volume flow [m^3 s^{-1}]
R	resistance [Ω]
R	Gas constant [W s mol^{-1} °K^{-1}]
T	temperature [°K]
t	time [s]
U	voltage [V]
U^o	open voltage [V]
u	linear velocity [m s-1]
W	power [U A]
w	power density [U A m^{-2}]

Subscripts

s	referring to solution
b	referring to mixture
c	referring to concentrate
d	referring to diluate
lim	referring to limited value
m	referring to mixing
max	referring to maximum
p	referring product
st	referring stack

Superscripts

b	constant
c	referring to concentration
d	referring to diluate
e	referring to electrode rinse solution
f	referring to feed

Greek letters

Δ	difference [-]
φ	electrical potential [V]
ξ	current utilization [-]

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