Electromembrane Processes in Environment Protection

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Abstract

The separation membrane techniques in which an external electric field is applied as a driving force (such as electrodialysis, electro-electrodialysis, and membrane electrolysis) are shortly described and their application in environment protection is presented. Attention was focused on recovery of valuable chemicals from effluents and waste gases. Examples of new production methods that eliminate environment polluting intermediate or by-products are presented. The possibility of the use of bipolar membrane is emphasized. The application of ion-exchange membranes in "green" power sources is also discussed.

Keywords: ion-exchange membranes, bipolar membranes, electrodialysis, electro-electrodialysis, membrane electrolysis, treatment of waste gases, water

Introduction

Membrane processes that use ion-exchange membranes and electric potential difference as the driving force for ionic species are called electromembrane processes. The following electromembrane processes can be distinguished:
- electrodialysis
- electro-electrodialysis
- membrane electrolysis.

In other techniques where ion-exchange membranes are used (such as diffusion or Donnan dialysis) the driving force is not external electric potential difference but a concentration difference.

Electromembrane processes are based on the selectivity of ion-exchange membranes. These membranes contain electrically charged groups fixed to the polymer matrix and allow permeation of ions of opposite sign through the membrane under the influence of an electric field. There are cation- and anion-exchange membranes depending on the sign of the permeating ions. Progress in electromembrane processes was closely connected with developing modern ion-exchange membranes in the early 1950s. The membranes fulfilled more and more the basic requirements important in electromembrane processes: today they are highly permselective, physically strong and have low electrical resistance [1, 2].

Electromembrane processes have found numerous practical applications and many of these are directly related to environment protection. The following area of application can be listed as the most important in that field:
- removal of harmful chemicals from effluents or waste gases,
- recovery and reuse of valuable compounds from wastes;
- closing the loops in technology;
- developing new production methods, that require lower energy consumption. Lower energy consumption causes a reduction in environmental pollution by mines, power stations etc.

In the forthcoming parts of this article electromembrane techniques will be characterized and examples of application will be presented.

Electrodialysis and Electro-Electrodialysis

Electrodialysis (ED) is usually defined as an electrochemical separation process in which electrically charged membranes and an electrical potential difference are used to separate ionic species from an aqueous solution and other uncharged components [2, 3, 4, 5, 6]. Electrodialysis as a method combining electrolysis and dialysis was proposed for the first time in 1890 by Maigrot and Sabates [7]. In the late 1930s Meyer and Strauss introduced a multicompartment ED apparatus consisting of two electrodes and a stack of ion-exchange membranes between them [1].
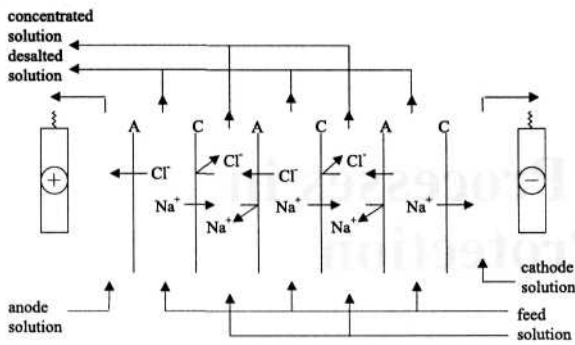
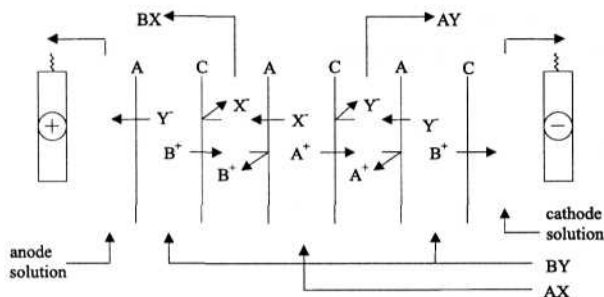Fig. 1. Classical ED; C, A - cation-, anion-exchange membranes.

Fig. 2. Double decomposition ED: AX+BY-»AY + BX; C, A - cation-, anion-exchange membranes.

Three types of electrodialysis can be distinguished:
- classical ED (Fig. 1)
- double decomposition ED (Fig. 2)
- electrodialysis with bipolar membranes EDBP (Fig. 4, described in the further section).

Classical ED is a process in which concentration and desalination of an electrolyte take place, as explained in. Apart from the separate loops of electrode solutions there are two loops - of concentrated and of diluted solutions.

In the double decomposition ED the double exchange reaction takes place:
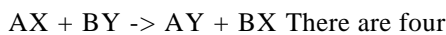
$$AX + BY \rightarrow AY + BX \text{ There are four}$$

loops - AX, BY, AY, and BX (Fig. 2).

Electro-electrodialysis (EED) is a technique that combines features of electrodialysis and electrolysis (Fig. 3). The products of EED are formed in anode and cathode compartments as a result of electrode reactions and a selective transport through ion-exchange membranes. The desalted solution is produced in the middle compartment.

It is not enough place to discuss the current efficiency *(CE)* of each technique in detail. Below only *CE* of classical ED is presented to show how the nonideality of membrane influences this parameter. According to the formula (1) [8]:

$$CE = 1 - \bar{t}^A_+ - \bar{t}^C_- - M_0 \bar{m} (\bar{t}^A_0 + \bar{t}^C_0) - (P^A_s + P^C_s +$$
$$+ M_0 \bar{m} (P^A_0 + P^C_0)) \frac{F \Delta c_s}{I} \qquad (1)$$

CE is decreased by flows resulting from the nonideal selectivity of membranes - the electrical migration of cations through an anion-exchange membrane and anions through a cation-exchange membrane (expressed by the transport number of ions t^A_+, t^C_-), back diffusion of electrolyte (permeability coefficients of electrolyte P^C_s, P^A_s), osmotic flow of water (permeability coefficients of water P^C_0, P^A_0), and electroosmotic flow of water forced by the migration of counterions (electroosmotic transport number of water t^C_0, t^A_0). The last flow is inevitable because of hydration shells of transported ions. Other symbols denote: / is the current density, *F* - Faraday constant, ACj- the concentration difference between the concentrate and diluate compartments, *m* - the mean molality of solutions, and M_0 - molecular mass of water.

According to eq. (1) the current efficiency of ED increases with current density, because the negative effect of diffusion and osmosis is reduced. However, the upper
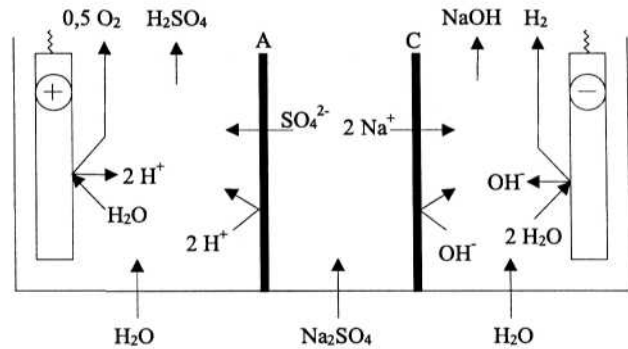

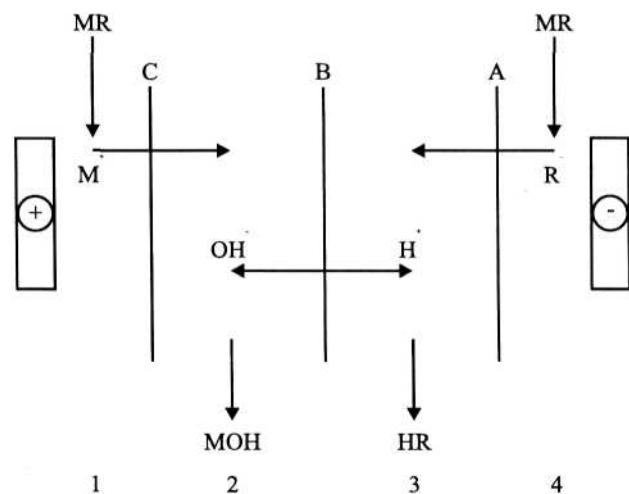Fig. 3. Three-compartment electro-electrodialysis - production of H_2SO_4 and NaOH from Na_2SO_4.

Fig. 4. Principle of salt splitting in the electrodialysis with bipolar membrane: B - bipolar membrane, C - cation-exchange membrane, A - anion-exchange membrane.

value of current density is limited by the polarization phenomena. The application of a higher current than the limiting current leads to water splitting, fouling, and scaling, and consequently to the decreased effectiveness of the process. The polarization depends on the concentration of dilute solution, temperature, ion mobility and on the hydrodynamic conditions governed by the flow rate and spacers, which can be optimised for a given process. To increase the current efficiency and reduce energy consumption different factors have been investigated, among them ion-exchange spacers [9, 10] and pulsating flow [11]. Both of them can increase limiting current density significantly.

One of the main steps in the development of ED was the introduction of reversal polarity operating mode. This mode, called electrodialysis reversal (EDR), is an ED process in which the direction of current is reversed at 15÷30 minute intervals for ca. 1 minute [12]. Although simple, it effectively removes foulants and scales from membrane surfaces. In this way ED can now successfully deal with highly contaminated waters like brine blown down from RO plants, cooling tower blowdowns, secondary effluents from sewage treatment plants, effluents from refineries, or "zerodischarge" power plants [13, 14].

In summary, the advantages of ED are: it can operate as a continuous process, regeneration steps are strongly reduced, and the rate of process is easily regulated.

Applications

Water Production

The most important large-scale application of ED is the production of potable water from brackish water. Other competitive techniques in this field are RO and multistage flash evaporation. Generally, for water of relatively low salinity (< 5000 ppm) ED is the most economic process. The advantage of ED is that salt solutions can be concentrated effectively to high values (18-20%) [2].

The advantage of ED over conventional methods of water pretreatment (coagulation and lime decarbonization) in removing humic acid from water was shown in [15]. To obtain water of good quality usually requires a combination of different techniques. A 3-step electrochemical water recovery system is presented in [16], and consists of electrolysis, ED, and posttreatment catalytic oxidation. In the electrolysis organic contaminants are oxidized forming the ions (organic acids) which (along with other dissolved salts) are separated by ED. The remaining trace organics are removed in the third step.

The commercial production of ultrapure water is performed by means of ED using mixed bed ion-exchange resin in the diluate compartments [2]. This version of ED, with resin beads filling the diluate compartments, is called electrodeionization (EDI) [17]. It was applied for the first time in [18] to clean radioactive wastes.

Special attention is now being directed towards the removal of nitrates. In heavily fertilized agriculturay regions the concentration of nitrates in ground water often exceeds 50 mg/dm^3 - the EC-standard for drinking water, which is going to be reduced to 25 mg/dm^3. The presence of nitrates in water is harmful to human health, it can cause methaemoglobinaemia or cancer risks due to nitrosamines or nitrosamides [19]. Although it is possible to remove nitrates using biological and chemo-physical technologies, ED shows many advantages which make this method favourable (high water recovery, no demand for chemicals, the possibility to work when needed, a reduction of water hardness). Tests of ED using a full-scale plant were conducted in 1996 in Austria [19]. The standard cation- and monovalent selective anion-exchange membranes were used. It was possible to concentrate nitrates from 120 mg NO$_3$/dm^3 to 889 mg/dm^3 and to decrease their content in the product water to 41 mg/dm^3. Regarding the disposal of the concentrate two possibilities were suggested: to use it in direct irrigation or discharge into the local sewage treatment plant. The applied anion-exchange membranes did not show any specific selectivity regarding nitrate and chloride ions. Therefore, both ions were removed from the water to the same extent. The exceptions were sulfate and bicarbonate ions.

Although it is possible to remove/concentrate nitrate using monovalent anion-exchange membranes the removal of chloride and other ions is not desired - such a demineralized water is not suitable for drinking for physiological reasons. The accumulation of chlorides in the concentrate is also not desired regarding irrigation. Moreover, the migration of chloride ions through a membrane decreases the current efficiency of ED with respect to nitrates. To solve these problems nitrate-selective membranes have to be developed, which is a serious problem due to the same charges of chloride and nitrate ions [20, 21, 22, 23, 24]. The results of Sata et al. have shown that the transport number of NO$_3^-$ relative to Cl$^-$ can be regulated by changing the hydrophobicity of anion-exchange membrane by different ways. Kesore et al. [25], applying cation-exchange spacers with granules of the nitrate-selective resin and a monovalent selective anion-exchange membrane, were able to separate nitrate from chloride ions very efficiently for current densities below 0.7 mA/cm^2. However, at current densities higher than 1.2 mA/cm^2 nitrate selectivity was practically lost.

Wastewater Treatment

A wide range of applications of ED and other membrane techniques can be found in many branches of industry such as hydrometallurgy, plating, paper, and photography [26]. The main objectives are: cleaning and recycling of wastewater, concentrating process solutions in order to reuse them, and recovery of valuable components from the effluents.

In the conventional methods of removing metals from effluents (chemical precipitation, absorption on charcoal, ion exchange, encapsulation/chelation) the large amounts of chemicals, resins, and supports which have to be regenerated are used [27]. In the ED or EED method this problem practically disappears. Today ED is applied for recovery of almost all heavy metals (Au, Pt, Ni, Cu, Ag, Pd, Cd, Zn, Sn, Pb) from plating baths [26]. The treatment of sludge samples containing Cu, Fe, and Zn by ED has been reported in [28]. To increase the effectiveness of separation of different metal ions the complexing

agents are used [31, 29, 30]. For example, with EDTA it is possible to separate silver from copper and zinc [29], or calcium from cadmium [30].

In general ED can concentrate the solution to a degree allowing for its reuse. For example, the recovery of chromic acid up to 280 g/dm^3 from the first rinsing bath during chromium plating, using EED, is reported in [31]. The recovery of nickel plating salts from galvanizing bath effluents is described in [26]. The concentrated nickel salts are recycled back to the plating bath. The regeneration of chemical cooper plating baths has been studied in a pilot plant stage [32]. The removal of inert electrolytes that build up in electroplating baths was investigated in [33]. Two plating solutions were studied - Zn-Sn bath (from which KOH has to be removed), and Ni-W bath (with excess Na_2SO_4). It was found that hydroxide can be effectively removed without significant loss of the heavy metals, whereas in the second case appreciable loss of W and Ni was observed during removal of the sulfate.

The application of electromembrane techniques in the plating industry has some limitations, e.g. it cannot be applied to acid effluents containing hydrochloric acid and zinc ions because of the formation of complexes between Zn^{2+} and Cl^- [34]. The problem of scaling in the recovery of cyanide electroplating rinse waters is discussed in [35]. It has been solved by monitoring and keeping the concentration of free cyanide high enough to keep the metal in soluble form.

The examples of application of ED in recovery of acid effluents can be found in [36, 37, 38]. In [36] the 3-compartment EED with perfluorinated sulfonic acid cation exchange membranes was used to separate dissolved metals from spent solutions from the acid pickling of stainless steel (see also EDBP process described further). The regenerated acids were returned to the pickling process. The recovery of sulfuric acid from effluents containing metallic salts (Mg, Zn, Mn), using Nafion cation exchange membrane modified *in situ* by electrodeposition of polyethyleneimine on one side of the membrane, is reported in [37]. The results are promising - the reduction of total metal leakage through the modified membrane to 0.5% at an insignificant increase in energy consumption. For such a purpose, an anion-exchange membrane has to posses low permeability to protons, whereas cation-exchange membranes should be characterized by a high permeability of protons and effectively reject the divalent metallic ions. References to the formation of such membranes can be found in [37].

ED can also solve some problems in the paper industry. It can be used to remove NaCl and KC1 from the chloridc/sulfate solution arisen in the production of kraft pulp [39]. A high concentration of chlorides causes corrosion and leads to more frequent mill shutdowns due to fouling of heat exchanger surfaces in the kraft recovery furnace. In [39] to separate chloride ions from sulphate ions the monovalent selective anion-exchange membrane and cation-exchange membrane were used. The desalted solution was recycled. These results encouraged pilot tests at a kraft pulp mill.

The possibility of concentrating of sodium sulfate in a pickle liquor from the tanning process by ED is discussed in [40]. The authors concentrated the sulfate to level suitable for reuse in the tannery process. The diluate (total dissolved solids content < 1000 ppm) could be reused or safely discharged.

Research on the concentration/decontamination of radioactive aqueous wastes by means of ED started in the fifties [18] and still continues [41]. In [18] the 2-stage process was proposed. In the first step the desalination proceeded in the classical ED mode, in the second step the ED stack containing a mixed bed granular exchanger in the deionization compartment was used. In [41] the separation of the long-lived heat generating fission products Cs-137 and Sr-90 from acidic solutions was studied. Diffusion dialysis was taken as a pretreatment step to facilitate separation of the radionuclides from higher acidity.

A very serious problem in Poland is utilization of coal mine brines [42]. The comparison of ED with the Multi Stage Flash and RO was investigated by Turek et al. [42]. It was found that for mine waters of concentration less than 15 kg/m^3 and for product concentration ca. 165 kg/m^3 the ED method is competitive.

The industry produces not only wastewater or harmful gases. Many places can be found where the soil is contaminated by factories using old technologies or by military bases.

The usefulness of ED in decontamination of soil polluted with heavy metals was tested in [43, 44, 45, 46] on the laboratory scale. The contaminations originated from a wood preservation factory, a chlor-alkali plant (employing the amalgam method), and a copper rolling mill. It was found that copper is effectively removed from the soil (from 1360 to below 40 mg of Cu/kg of dry soil), whereas in the case of mercury, which reduces easily to metallic mercury, the oxidizing agents and chloride should be added to the soil to increase the rate of removal. It should be noted that the effectiveness of mercury removal is reduced by the poisoning of an anion-exchange membrane by mercury compounds [47]. The presence of other ions (which do not need to be removed like Ca^{2+}) also reduces the efficiency of the process [45].

It should be stressed that the cleaning of soil is much more difficult than of liquids which can be easily pumped through different membrane modules. It is only a hope that further investigation on the decontamination of soils will be unnecessary.

Food, Pharmaceutical and Chemical Industries

Generally, in food and pharmaceutical industries ED is used to desalinate and deacidify organic compounds (proteins, aminoacids, dextrines, sugar), separation of aminoacids, assistance of fermentation processes, etc. [48].

The most important application of ED in the food industry is the demineralization of cheese whey which contains many valuable components like lactose, protein, minerals, fat and lactic acid, but also salt. After salt removing the whey is used in the production of food, including babyfood. The partial demineralization of whey can be carried out quite efficiently by ED [4, 49]. According to data from 1992 [4] more than 150,000 tons/year of

desalted lactose is produced using > 35,000 m^2 of membrane area.

Although in that field the relation with environmental protection seems to be less clear, in many cases ED can simplify a technological process and reduce chemicals, energy consumption and wastewater production. Of particular interest is here the double decomposition ED (see Fig. 2). This method can eliminate many steps, like precipitation, ion-exchange, washing, etc. Recently it has been applied for the conversion of lactate to lactic acid [50,51], which is a substrate for producing biodegradable plastics. Another example is the integration of double decomposition ED with the fermentation production of l-malic from fumaric acid [52].

Electrodialysis with Bipolar Membrane

Bipolar membrane, a kind of ion-exchange membrane, was synthesized for the first time in the 1950's [53]. It consists of two adjacent layers with opposite charged polymer matrix groups. When the membrane in contact with aqueous electrolyte solutions is placed in the electric field, an enhanced water dissociation into hydrogen and hydroxyl ions occurs at the junction of anion- and cation-exchange layers (so-called interphase region). The mechanism of this phenomenon, also called water splitting, is not yet quite clear. The main explanations result from:
- a chemical reaction model that assumes chemical reactions involving water and ionic groups of the inter phase region, and
- a model based on the second Wien effect, that takes into account the influence of external electric field on the water dissociation rate constant [54, 55].

Electrodialysis with bipolar membranes is applied to production of acids (both mineral and carboxylic) and bases from the corresponding salts. This process called salt splitting is reversal of the neutralization reaction:

$$MR + H_2O \rightarrow HR + MOH$$
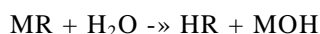
where MR represents a formula of salt.

The salt solution is introduced to compartments 1 and 4 (Fig. 4). Electrodialysis is carried out at the current density that ensures generation of hydroxyl and hydrogen ions. The ions migrate into solutions adjacent to the bipolar membrane (i.e. compartments 2 and 3, respectively). Under electric potential gradient the anions R$^-$ migrate through anion-exchange membrane into compartment 3, where they form acid (HR) with hydrogen cations. Analogously, the metal cations M$^+$ are transported through action-exchange membrane forming hydroxide MOH in compartment 2.

Generally, for practical applications it is important that due to the enhanced water dissociation bipolar membrane can be used as a source of hydrogen and hydroxyl ions. Electrodialysis with bipolar membranes is used for generating of acids and bases from salts, regeneration of acids and bases and an *in situ* acidification or alkalization. It is worth noticing that by electrodialysis with bipolar membrane the splitting of salts of all acids can be carried out. It is an important advantage compared to the

electro-electrodialysis or electrolysis where protons and hydroxyl ions result only from the electrode reactions. Application of bipolar membranes in processes carried out in non-aqueous media is also possible.

The use of bipolar membranes in electrodialysis requires another arrangement of membranes in a stack in comparison with the classical electrodialysis. The basic repeating unit usually consists of three membranes: cation-, anion-exchange and bipolar - the so-called three compartment system (Fig. 4). Furthermore in contrast to the classical technique with only dilute and concentrate loops, in electrodialysis with bipolar membranes there are independent loops of electrolyte solutions (acid, base and salt).

Applications

Production of Acids and Bases from Salts, Recovery of Acids and Bases

Electrodialysis with bipolar membrane offers an elegant and simple method of the production of acids and bases from the corresponding salts. Because a considerable part of industrial waste water are salt solutions that are formed either directly during processing or due to neutralization of acid/base effluents, the recovery of valuable compounds in the form of acids or bases can help in environmental protection by decreasing the amount of salt allowed into rivers. For the production of pure acid and base the standard three compartment system described above is usually used. In the case of regeneration of acid or base a simplified two compartment system with bipolar and anion- or cation-exchange membrane can be applied (see examples below) [56, 57, 58, 59]. The salt splitting technology using bipolar membranes was first introduced by Aquatech Corp. (now Aqualytics).
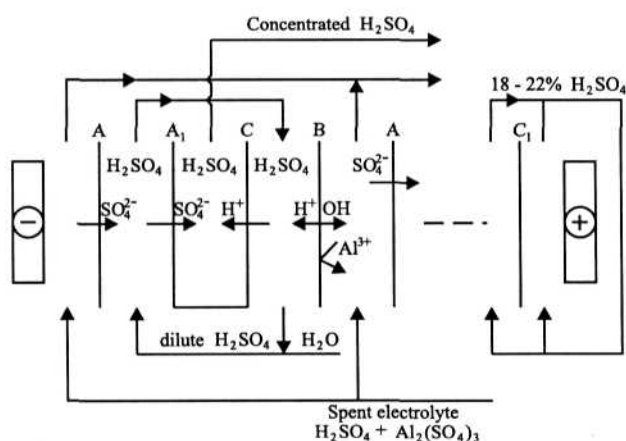
In literature the production of different mineral acids: sulfuric [57, 60, 61, 61, 62, 63], hydrochloric [64, 60] and nitric [65] by salt splitting with EDBP has been reported. Electrodialysis was typically carried out under the following conditions: current density of 50-150 niA/cm^2, temperature up to 323 K, a few ppm of Ca^{2+}, Mg^{2+} ions in the salt solution to be split. Concentration of the acid produced ranges 1-2 mol/dm^3. Concentration of the base was usually higher. Using Aquatech cell the overall process has a current efficiency of 80% or higher (at current density of 100 mA/cm^2). The energy consumption for production of 1 t sodium hydroxide ranges from 1400-2000 kWh [57] and is lower than in the case of other electromembrane techniques (see also section Membrane Electrolysis). For sodium sulfate splitting a detailed comparison of EDBP with the Ionic's electrolysis was given by Nagasubramanian et al. [60]. At the current efficiency 80-85% the energy consumption for producing 1 t NaOH by EDBP and electrolysis was 1650 kWh and 3440 kWh, respectively.

Mani et al. [57, 58] reported an example of EDBP that has been commercialized - a recovery of acid and base from spent stainless steel pickle liquor. During the production of stainless steel the surface is pickled using an acids mixture (2-5% HF, 8-15% HNO$_3$). The spent liquor from the pickling step is neutralized with potass-

ium hydroxide to precipitate metal hydroxides while soluble salts (i.e. potassium fluoride and nitrate) remain in solution. The KF/KNO_3 solution is directed to the three compartment cell, where potassium hydroxide and HF/HNO_3 mixtures are generated. Salt concentration decreases from 1.1-1.5 mol/dm^3 to 0.3-0.5 mol/dm^3 during the EDBP. This diluted salt solution is then desalted using conventional ED which produces the dilute containing 0.02-0.04 mol/dm^3 salt (used for washing the filter cake) and the concentrate which is returned to the salt loop of EDBP. The KOH solution (1.5 mol/dm^3) produced by EDBP is reused for neutralization of the spent pickle liquor, whereas the mixed acids (HF/HNO_3) are sent to the pickling step.

An interesting membrane arrangement for recovery of sulfuric acid from liquor from an anodic oxidation of aluminum (so-called Eloxal process) has been proposed by Greben et al. [66]. The liquor contains sulfuric acid contaminated with aluminum ions (- 15 g/dm^3). Regeneration of H_2SO_4 was carried out by electrodialysis with bipolar membrane in the system presented in Fig 5. At current densities 21-27 mA/cm^2 pure sulfuric acid of concentration - 140 g/dm^3 was obtained. Aluminum ion concentrations do not exceed 1.2 g/dm^3.

Fig. 5. EDBP system for recovery of sulfuric acid from the Eloxal process liquor: B - bipolar membrane, C - cation-exchange me-


mbrane, A — anion-exchange membrane.

Another field of application of EDBP is the production of organic acids. Organic acids in the calcium salt form are usually obtained by bacteria or mould fermentation. The conversion of calcium salts with sulfuric acid leads to pure acids and calcium sulfate - an environment-polluting byproduct. The use of bipolar membrane offers a new gypsum-free method of organic acid production by electrodialysis of sodium salts obtained both via fermentation and chemical synthesis. The application of EDBP in the production of the following acids: salicylic [67], itaconic [68, 69], lactic [70], propionic [71], acetic [71], citric [72] were reported.

Desulfurization of Flue Gases

The removal of harmful components from waste gases can be combined with EDBP; the Soxal process [73, 74] is an excellent example. Sulfur dioxide from stack gas is removed and recovered in two steeps. It is first absorbed in a scrubber using basic $NaOH/Na_2SO_3$ liquor. This solution is then converted by means of electrodialysis with bipolar membranes to concentrated SO_2 and regenerated alkaline solution. The spent scrubber liquor containing sodium bisulfite $NaHSO_3$ is divided into two streams and directed to a two-compartment electrodialysis stack with bipolar and cation-exchange membranes (Fig. 6). The typical composition of the spent scrubber liquor is 22.5% $NaHSO_3$, 2.2% Na_2SO_3 and 7.4% Na_2SO_4. Conversion of bisulfite and sulfite to sulfurous acid occurs in the acid compartments signed I in Fig. 6:

$$NaHSO_3 + H^+ - Na^+ -> H_2SO_3 \qquad (2)$$

$$Na_2SO_3 + 2H^+ - 2Na^+ -» H_2SO_3 \qquad (3)$$
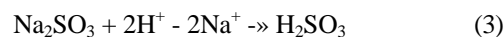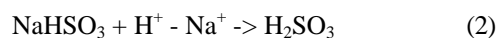
By heating the sulfurous acid solution sulfur dioxide is liberated and can be sent for further processing:

$$H_2SO_3 -» H_2O + SO_2$$

From equations 2 and 3 it follows that twice as much hydrogen ions are needed for conversion of sulfite as for conversion of bisulfite. In order to minimize the cost of SO_2 recovery it is thus important to achieve a high concentration of bisulfite in the scrubber spent liquor. In the base compartments (signed II in Fig. 7) sodium hydroxide and sulfite is formed:

$$Na^+ + OH^- -» NaOH$$

$$NaHSO_3 + OH^- + Na^+ -»Na_2SO_3 + H_2O$$

The $NaOH/Na_2SO_3$ solution obtained in the base compartments is reused for absorption of SO_2 in a scrubber. Desulfurization of flue gases also by means of techniques using ion-exchange membranes is still developed [75, 76]. Novalic et al. [76] proposed EDBP for the conversion of spent scrubber liquor containing sodium sulfate to NaOH and H_2SO_4. The conventional three compartment system with commercially available membranes (WSI - bipolar, Neosepta AMC and CMX - anion- and cation-exchange, respectively) was used.

Amines Removal

Another example of the use of EDBP in air purification is the removal of amine [68]. In the production of aluminum casting mold epoxy resins are cured with dimethyl isopropyl amine. The amine concentration in the exhaust air is 300 mg/m^3. It is absorbed in a scrubber sprinkled with sulfuric acid solution (pH = 1.5), the content of amine in the air purified decreases below 5 ppm. The scrubber effluent containing ~ 10% amine sulfate is converted free amine and sulfuric acid using a two-compartment electrodialyzer equipped with bipolar and ani-

on-exchange membranes (Fig. 7). Both recovered compounds are recycled: amine to curing resins, acid to absorption in scrubber.

Elimination of Dangerous Chemicals

EDBP offers a new alternative to the present production method and makes it possible to eliminate dangerous chemicals. For instance, acetoacetic ester, which is a starting substance for further synthesis, is produced on a technical scale by dehydration of acetic acid. The intermediate products are ketone and diketone - both toxic. Sridhar et al. [77] proposed a new method in which the intermediate product of condensation of methylacetate and sodium methoxide is protonated in electrodialysis stack equipped with bipolar and cation-exchange membranes. Protonation is carried out in methanolic medium. In the proposed method dangerous compounds are not employed. Furthermore, due to methanol splitting no waste salt is formed as in the case of the protonation with a mineral acid.

Electrodialysis with bipolar membranes looks very promising, particularly when environment-oriented laws will be introduced and technological changes will take place, e.g. closing of liquors loops, will be required. Nowadays, growth of bipolar membrane technology is limited by the high price of these membranes (8-9 times higher than that of monopolar membranes) and a small number of bipolar membrane manufacturers.

Membrane Electrolysis

Chlor-Alkali Electrolysis

Production of chlorine and caustic soda by membrane electrolysis is presently a process of significant importance. Membrane electrolysis was introduced into industrial practice in the mid 1970's as an alternative to the diaphragm and mercury-cathode methods. In 1990 about 20% of NaOH and Cl_2 were produced by the membrane electrolysis of brine [78]. The principle of the process is schematically drawn in Fig. 8. The electrolysis cell consists of two compartments separated by a cation-exchange membrane. The anode compartment is fed with brine. In the electric field the positively charged sodium ions are transported through the membrane into the cathode compartment, where gaseous hydrogen and hydroxyl ions are generated due to an electrode reaction. Migration of the negatively charged hydroxyl ions toward anode is prevented by the membrane. The third, besides NaOH and H_2, product of the electrolysis - gaseous chlorine is generated by oxidation of the chlorine ions on the anode. Nowadays the perfluorinated membranes, such as the Nafion membranes (DuPont), are widely used. These membranes guarantee good current utilization, quality product (typical contamination of NaOH less then 50 ppm of NaCl) and membrane lifetimes of several years under the operational conditions [2, 79].

Energy consumption in the membrane electrolysis of sodium chloride (2350 kWh/t NaOH) is lower than that in the diaphragm method (3230 kWh/t NaOH) and the
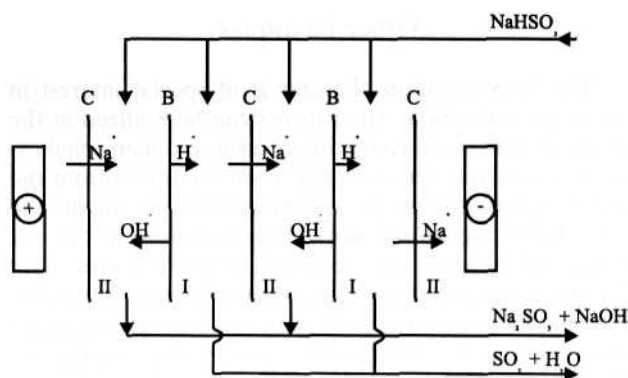
Fig. 6. Electrodialytic conversion of sodium bisulfite to sulfur dioxide and sodium sulfite in two-compartment system: B - bipolar membrane, C - cation-exchange membrane.

mercury-cathode method (2980 kWh/t NaOH) [78]. Furthermore, in membrane electrolysis mercury and asbestos pollution is avoided. These features of the membrane process are important advantages from both economical and ecological points of view.

A modification of the classical membrane electrolysis system makes it possible to save 20-30% of electrical energy. The modification proposed by Jorissen and Simmrock [80] consists of the use of an oxygen-consuming cathode made of silver-PTFE instead of a steel cathode. In the process there are only two products: caustic soda and chlorine. At current densities over 0.5 kA/m^2 it is possible to replace pure oxygen with air at high pressure (5 bar) without deterioration of process parameters.

The membrane electrolysis of sodium chloride has gained the position of a process widely used in industry. Electrolysis of other salts, such as potassium chloride [81, 82], sodium sulfate [80] or sodium borate [83], has also attracted interest. In the case of KCl electrolysis with the Nafion membranes current efficiency higher by 3-4% as compared with the NaCl electrolysis was found [81].
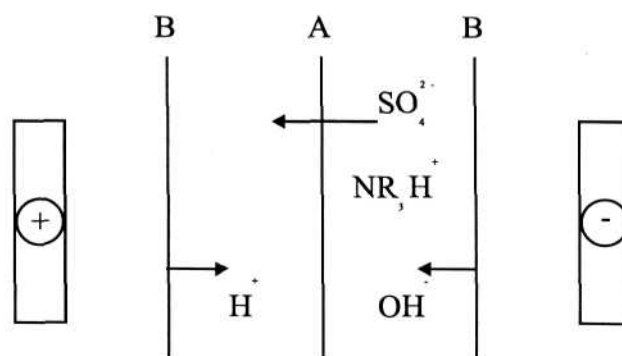
Fig. 7. Conversion of amine sulfate to amine and sulfuric acid: B - bipolar membrane, A - anion-exchange membrane.

Other Examples

The deoxygenation of water is of special interest in corrosion protection. The process can be realized in the electrochemical cell consisting of a three-dimensional cathode containing ion-exchange resin separated from the anode compartment by a cation-exchange membrane [84]. According to that work oxygen content at the cell inlet, 8000 µg/kg, was reduced to levels lower than 3 µg/kg at the outlet, the mean residence time being 10 s. Current efficiency was high (0.9) and energy consumption very low (0.06 kWh per cubic meter of oxygen-saturated water). This removal can be applied to several water systems, including potable and boiler waters.

Anhydrous hydrogen chloride is the by-product of many industrial manufacturing processes. A typical disposal method of hydrogen chloride (dilution in water, neutralization, and storage in deep wells) pollutes the environment. The possibility of recycling anhydrous HCl into a valuable product, chlorine, was investigated using a solid-polymer-electrolyte cell [85]. In the anode compartment, separated from the cathode by a cation-exchange membrane, the anhydrous HCl is oxidized to chlorine, the protons transfer through the membrane, and hydrogen gas is evolved at the cathode. The hydrogen can be used as a fuel for the hydrogen-oxygen fuel cells (see section below). The above method works if there is no overproduction of chlorine.

Ecological Power Sources

Nowadays there is a great demand for ecological power sources. With ion-exchange membranes it is possible to create two types of "green" energy sources - polymer electrolyte membrane fuel cells (or proton-exchange membrane fuel cells) and redox flow batteries which in the near future will be commercialized. A concentration battery should also be mentioned here - it is a classical ED stack in which the concentration difference is transformed into electrical energy (called reverse electrodialysis) [86]. That idea was suggested almost 50 years ago by Manecke and still has not been realized.
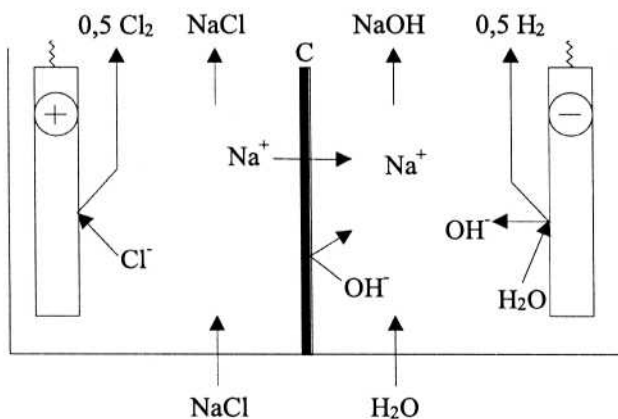

Fig. 8. Principle of electrolytic production of chlorine and caustic soda by the use of a cation-exchange membrane.

Fuel Cells

The operation principle of a hydrogen-oxygen fuel cell is shown in Fig. 9. The hydrogen is oxidized at the anode and the protons migrate through a cation-exchange membrane to the anode were they react with oxygen, forming water. The H_2/O_2 fuel cell was first applied in the Gemini program. After about forty years the development of fuel cells has reached a level enabling the introduction of fuel cells as a clean and efficient technology for automotive propulsion [87, 88]. They can be also considered as components of a long-term storage system in regenerative energy systems.
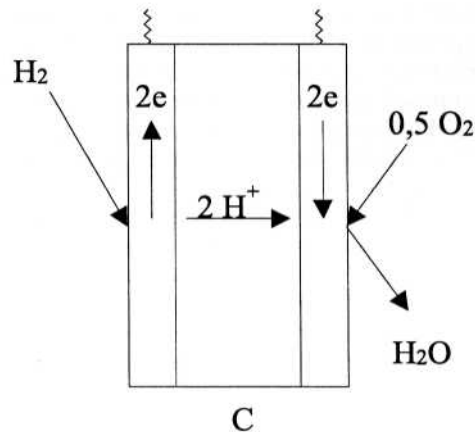

Fig. 9. H_2/O_2 fuel cell; C - cation-exchange membrane.

One of the basic problems which has hindered commercialization is the high cost of fuel cells. This is gradually being reduced by
- reductions in the electrode precious metal catalyst loadings [89],
- development of cheaper membranes, substitutes of expensive perfluorinated membranes [90, 91],
- development of a fuel cell design [92].

Beside H_2/O_2 (oxygen from the air), other redox couples such as H_2/CO [93], or CH_3OH/O_2 are being investigated. Compared to H_2/O_2, the CH_3OH/O_2 couple has the advantage of easy refuelling, which could be based on existing fuel supply systems. Unfortunately, the existing perfluorinated membranes, like Nafion, are not satisfactory for that kind of fuel. In these membranes methanol moves freely from the anode to the cathode causing a loss in fuel efficiency.

More about fuel cells can be found on the Internet (e.g. http://www.wplabs.com/technology/technology_research.html).

Redox Flow Battery

The redox flow battery can be used as a low-cost, high efficiency system for large-scale energy storage. The idea of this battery is shown in Fig. 10. where the redox couple Fe/Cr is presented. Two solutions, Cr^{3+}/Cr^{2+} and
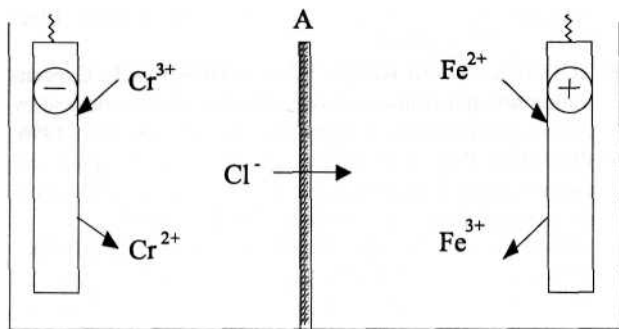
Fig. 10. Redox-flow Cr/Fe battery during a charging cycle; A - anion-exchange membrane.

Fe^{3+}/Fe^{2+}, are circulating through a cell divided by an anion-exchange membrane. During discharge Fe^{3+} is reduced to F^{2+} on the electrode, the electrons go to the electrode in the solution of chromium ions, where Cr^{2+} is oxidized to Cr^{3+}. To maintain electroneutrality the anions move through the membrane. There are many advantages of redox flow batteries, among them one should mention low cost for large storage capacities, high energy efficiency, and easy maintenance.

Among others the most promising seems to be the vanadium battery developed by Skyllas-Kazacos et al. [94, 95]. Several tests of vanadium batteries have been performed [96]. Small vanadium batteries have been tested in a demonstration solar house (ca. 5 kWh), in an electric golf cart, and as emergency back-up battery for submarine applications. In Japan a test of a 200 kW/800 kWh grid-connected vanadium battery started in 1997. The battery shows high energy efficiency of close to 80% at current densities of 80-100 mA/cm^2.

More papers on the vanadium redox battery can be found on the homepage of the University of New South Wales: http://www.ceic.unsw.edu.au/centers/vrb/.

Final Remarks

The presented examples of application have shown that electromembrane processes in environmental protection are very efficient, especially when combined with other techniques. Three main types of applications of ion-exchange membranes can be distinguished:
1) treatment of effluents, wastewater, and waste gases,
2) modification of technologies resulting in the substantial decrease of wastes or energy consumption,
3) separators in "green" energy sources.
   The field of applications, especially if the second point is considered, is limited by the separation abilities of membranes. The further applications of electromembrane processes depend on the development of better, more selective membranes [97].

For sustainable development clean technologies are more and more important [5, 98]. Electromembrane and other membrane techniques have already become an inseparable part of these technologies.

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