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Ion-exchange membranes in chemical synthesis – a review

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Abstract: The applicability of ion-exchange membranes (IEMs) in chemical synthesis was discussed based on the existing literature. At first, a brief description of properties and structures of commercially available ion-exchange membranes was provided. Then, the IEM-based synthesis methods reported in the literature were summarized, and areas of their application were discussed. The methods in question, namely: membrane electrolysis, electro-electrodialysis, electrodialysis metathesis, ion-substitution electrodialysis and electrodialysis with bipolar membrane, were found to be applicable for a number of organic and inorganic syntheses and acid/base production or recovery processes, which can be conducted in aqueous and non-aqueous solvents. The number and the quality of the scientific reports found indicate a great potential for IEMs in chemical synthesis.

Keywords: ion-exchange membrane, chemical synthesis, membrane electrolysis, electrodialysis

List of abbreviations:

ED – electrodialysis

ME – Membrane electrolysis – AEM or CEM in 2-chamber stack (electrode reaction matters)

EED – Electro-electrodialysis – both AEM and CEM in 3-chamber stack (electrode reaction matters)

ED-M – Electrodialysis metathesis – 4-chamber repetitive unit

ISED – Ion substitution electrodialysis – modification of ED-M with two adjacent CEM or two AEM membranes

BMED – electrodialysis with bipolar membrane

EDI – electrodeionization

IEM – ion exchange membrane,

AEM – anion exchange membrane,

CEM – cation exchange membrane,

BPM – bipolar membrane

CE – current efficiency

SPE – solid phase electrolyte

1 Introduction

Ion exchange membranes are the most commonly used for electro-dialytic desalination of brackish and seawaters and for NaCl recovery [1]. In ordinary electrodialysis (ED), ion exchange membranes (IEMs) are organized alternatively to form a stack in which, under applied electric current, a transport of ions toward electrodes occurs with restriction by semi-permeable membranes in the adjacent compartments. As a result, the diluate (an ion-depleted solution, e.g. drinking water) and the concentrate are formed. However, ion-exchange membranes constitute a promising tool which, when used properly, can be applied in the synthesis of ionic compounds used in chemical and other industries. An interest in application of electrodialysis for chemical synthesis has grown, recently, which has resulted in an increasing number of scientific papers. The intention of this review is to provide a summary on the applicability of ion-exchange membranes and the prospects of electrodialysis-based processes in chemical synthesis.

2 Ion-exchange membranes

The most widely used IEMs consist of polymeric resins with attached, charged, functional groups [2,3]. Based on their selectivity, membranes are referred to as anion-exchange (AEM) and cation-exchange (CEM) membranes. AEMs contain positively charged functional groups, and thus by Donnan exclusion [1,2], retain cations and

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allow for the passage of anions, only. CEMs, in contrast, have negatively charged functional groups; thus, they reject anions and allow for the passage of cations only. IEMs can be either homogeneous or heterogeneous. Heterogeneous membranes, made from powdered ion-exchange resins and a binder, are thicker and more robust than homogeneous, but with the cost of higher specific resistance and lower permselectivity [2]. Homogeneous membranes, made mostly via in-situ polymerization or grafting, are currently the most widely used. Typical polymeric resins for traditional IEMs are styrene and divinylbenzene. Insufficient thermal and chemical stability of hydrocarbon membranes, especially in the presence of strong oxidizers, gave rise to perfluorinated CEM membranes, consisting of fluoropolymer with multiple strong carbon–fluorine bonds for the chlor-alkali industry [4,5]. No such high-performance AEMs were developed, however. AEMs have generally lower permselectivity than CEMs which, when combined with the restrictions posed by the nature of their ionic groups (mostly quaternary ammonium), limits the applicability of IEMs in many membrane synthesis processes, especially when acids are involved. Maximum concentration of acid is limited by a so-called proton leakage; the rate of which increases rapidly with an increase in acid (proton) concentration on the anode side of either AEM or bipolar membrane [2,6]. Currently, commercial AEMs with reduced proton leakage are produced, but for more concentrated strong acids, the efficiency of proton exclusion is still insufficient and severe leakage is reported [2,3,7].

Also, inorganic ion-exchange membranes or hybrid inorganic-organic monopolar membranes were prepared and are under investigation [3]. However, these membranes are not commercially available to date and, thus, are of less significance for chemical synthesis, despite possible advantages: the possibility of process-tailoring and high mechanical strength and chemical resistance.

Bipolar membrane (BPM) has the unique property of generation of hydroxyl ions and protons, particularly useful in the synthesis of acids and/or bases. BPM is a composite membrane consisting of a cation-exchange layer and an anion-exchange layer with a thin intermediate layer between them [2]. Dissociation of water in the intermediate layer is accelerated (even up to 7 orders of magnitude compared to the rate of water dissociation in aqueous solutions [8]) both by electric field and transport of ions from the intermediate layer through IEM layers towards the corresponding electrodes. Also, a weak acid or base catalyst can be used in the intermediate layer to further enhance the water splitting effect. Ideal BPM should be non-permeable for salt ions. However, for all commercial

BPMs, the salt ion fluxes result in the contamination of the products in compartments adjacent to BPM, especially at high concentrations [9–11].

The above-presented IEMs can be applied in chemical syntheses for either separation of the ionic product from the reaction mixture, ion introduction (or replacement) due to the formation of a desired product (in the case of monopolar membranes) or to generate hydrogen (H^+) or hydroxyl (OH^-) ions (BPM) for the synthesis of acids or bases as discussed in the following chapter.

3 Ion-exchange membrane based processes

Membrane techniques are distinguished by stack configurations and sometimes by the type of the membrane used. Since in literature there is some confusion on nomenclature of variants of electrodialysis, in this work, we provide a short description of each ED process/configuration together with a schematic representation of the stack. All the relevant details on applications of these processes are given in Section 4.

3.1 Membrane electrolysis

The simplest electro-membrane process, membrane electrolysis (ME), evolved directly from electrolysis in which a diaphragm was replaced by IEM. There, in a two-compartment stack, ME combines the permselective ion transport through an IEM and electrochemical reactions at electrodes (Fig. 1). Either AEMs or CEMs can be used (Fig. 1a or 1b respectively). Water electrolysis or other redox reactions at the electrodes, allows for electron exchange and provides ions to be selectively transported in the generation of products.

In membrane electrolysis, each membrane stack can consist of only two compartments and two electrodes. Depending on the electrode material, this can add up to high capital cost of the process. Also, membranes placed near electrodes are exposed to harsh conditions (strong bases, strong acids, oxidizing atmosphere) and have to be chemically resistant. This poses certain limitations in the use of AEMs [12]; however, sufficiently chemically resistant, perfluorinated CEMs are already being applied. Concentration and purity of ME products is limited by permselectivity and chemical resistance of IEMs used and by water transport. Concentration of acid is limited by proton leakage through the AEM. ME is an efficient

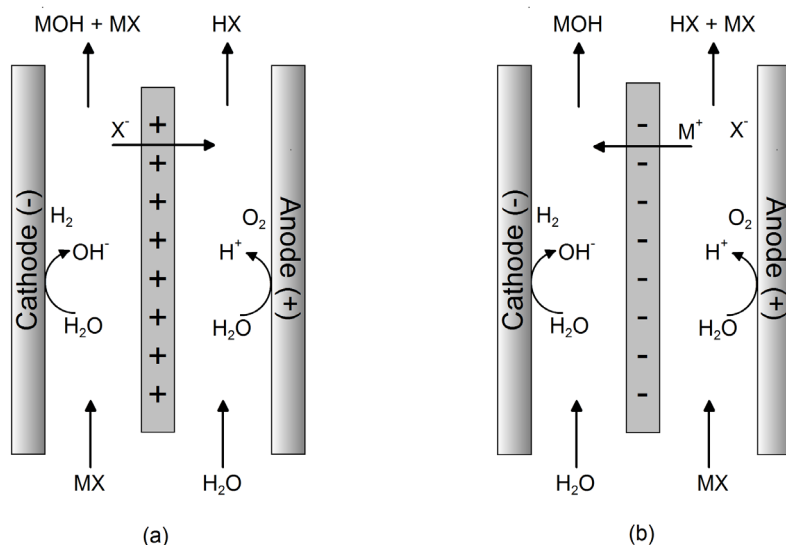


Figure 1: Schematic representation of membrane electrolysis with anion-exchange membrane (a) or cation-exchange membrane (b).

solution for base synthesis or when only acid or only base recovered from salt is necessary to be obtained with high purity.

3.2 Electro-electrodialysis

Electro-electrodialysis (EED) is a transitory process between ME and electrodialysis. In a three-compartment stack, salt solution is introduced to the compartment at the center, where cations are transported through the CEM towards the cathode and anions through AEM towards the anode resulting in depletion of the salt solution (Fig. 2a). In catholyte and anolyte, water electrolysis provides ions for formation of base and acid, respectively. In some variants, an additional CEM is placed to separate the anolyte compartment and reduce proton leakage (Fig. 2b).

An EED stack consists of one triplet of compartments, which increases capacity cost similar to ME. Depletion of salt solution increases the stack voltage and, thus, the operational cost. The concentration of products is limited by water transport, chemical resistance of IEMs and by proton leakage. Significant proton leakage results in acidification of the salt compartment, thus a decreased CE of the base – instead of metal, hydrogen ions are transported through CEMs and water is produced in catholyte [13,14]. Purity of the products can be very high as contaminating ions are removed from the process solutions by electro-migration (electrostatic field). All of the above, makes EED an efficient process designed for

the splitting of salt to recover/produce, simultaneously, its corresponding acid and base with high purity.

3.3 Bipolar membrane electrodialysis

Bipolar membrane electrodialysis (BMED) is a membrane technique distinguished by the application of BPM used in place of electrodes to generate hydroxyl ions and protons. In BMED, BPM is stacked together with monopolar IEMs into a membrane module, and the possible configurations depend on application. A three-compartment stack (Fig. 3a), with both AEMs and CEMs, is used for the treatment of relatively concentrated salt solutions which splits them into the corresponding acids and bases, analogously to EED. A two-compartment cell is used mostly for acid or base regeneration. This configuration can be used together with a CEM for acidification (Fig. 3b) or with an AEM for alkalization (Fig. 3c) of a salt stream. The configuration with two monopolar membranes allows for an increase in the ratio of acid (and base) to the product salt as the outlet of the compartment adjacent to BPM is recycled again into the compartment next to the BPM (Fig. 3d, 3e) [15-17]. It should be noted, however, that not all possible stack configurations are currently commercially available.

The selectivity of the BMED strongly depends on concentrations of salt, acid and base. This adds up to restraints inherent in the performance of monopolar membranes themselves (proton leakage, water transport). BPM restricts solution composition: multivalent metal ions should be removed from solutions prior to BMED,

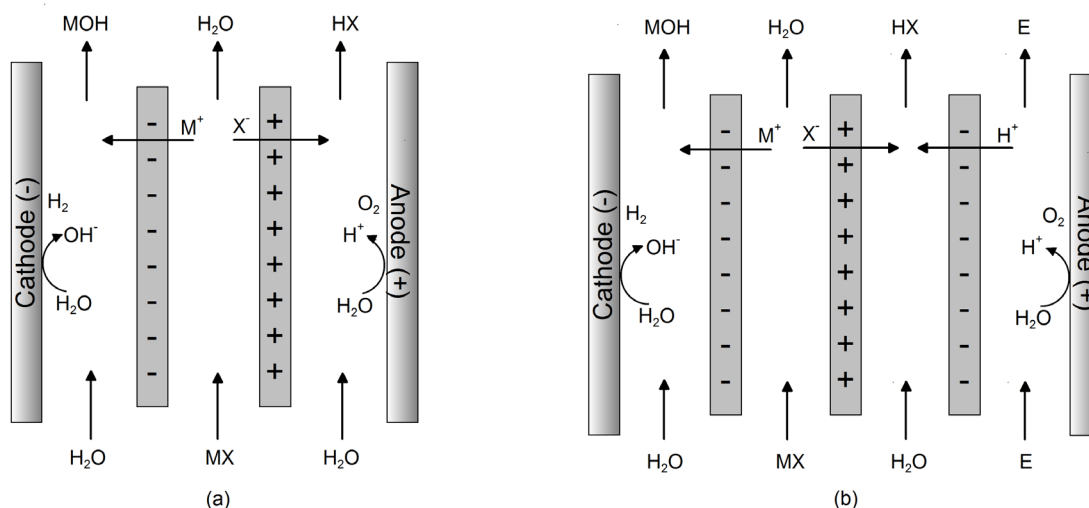


Figure 2: Schematic representation of electro-electrodialysis systems.

as their transport (leakage) through the anionic side of BPM results in hydroxide participation and damage of the membrane [2]. Concentration of products is limited, mostly, by permselectivity of monopolar membranes, leakage through BPM membrane and chemical stability of membranes (especially against bases) [2,16]. The major limitation for BMED production of strong acid/base lies in the possibility of obtaining concentrated solutions. When BMED is applied for production of strong acids, maximum concentration is about 1–2 M due to insufficient selectivity of the BPM and monopolar membranes. Whereas, for mostly organic, weak acids, the main process limitation lies in low conductivity of the process solutions, but quite concentrated (up to 6 M) product solutions are obtained [18]. Moreover, in a three-compartment configuration, the desalination degree cannot be too high – at low concentrations, the stack voltage increases due to electric resistance of the electrolyte solution.

In comparison to the previously described electrolysis-derived membrane processes, BMED is more efficient in terms of energy consumption. Energy requirement is theoretically about 40% of that of water electrolysis with gas evolution [14], and the stack can be built up from repeating units. The latter also decreases unit costs; however, operational costs are increased by the necessity for periodic replacement of costly BPM membrane. The efficiency of hydroxyl ion and proton generation is limited by BPM performance [19]. The amount of gaseous by-products (H_2 , O_2) is significantly reduced, as those are not formed in BPM. The salt leakage through BPM leads to contamination of acid/base with salt ions (estimated at 5% [20,21]). In conclusion, BMED is an effective process

designed for salt splitting and weak acid/base recovery. Economically, the most interesting applications of BMED are integrated processes with simultaneous acid/base production [16].

3.4 Metathesis-electrodialysis

The double exchange (metathesis) reactions can be conducted with proper configuration of monopolar membranes. In metathesis-electrodialysis (ED-M), AEMs and CEMs are alternatively placed between two electrodes which enables metathesis reactions in a four-compartment stack configuration (Fig. 4). With two different feeds (diluates), by migration of ions toward corresponding electrodes limited by IEMs, two different products (concentrates) are obtained.

Contrary to classic metathesis, ED-M is not an equilibrium process, and, thus, avoids the necessity for separation and removal of well-soluble contaminants from batch and formation of double salts at the salt crystallization stage. Also, the range of possible substrates for synthesis by double-exchange is broadened. The disadvantage is a relatively low concentration of product solutions, as salt crystallization in the module will lead to damage of IEMs. To obtain product in the solid form, subsequent evaporative crystallization is needed, thus, ED-M is more suitable for products that can be stored and transported in the form of a concentrated solution, e.g. for a further synthesis step. The rate of product formation can be controlled by applied current density which makes ED-M a safe route of synthesis. Concentration of products

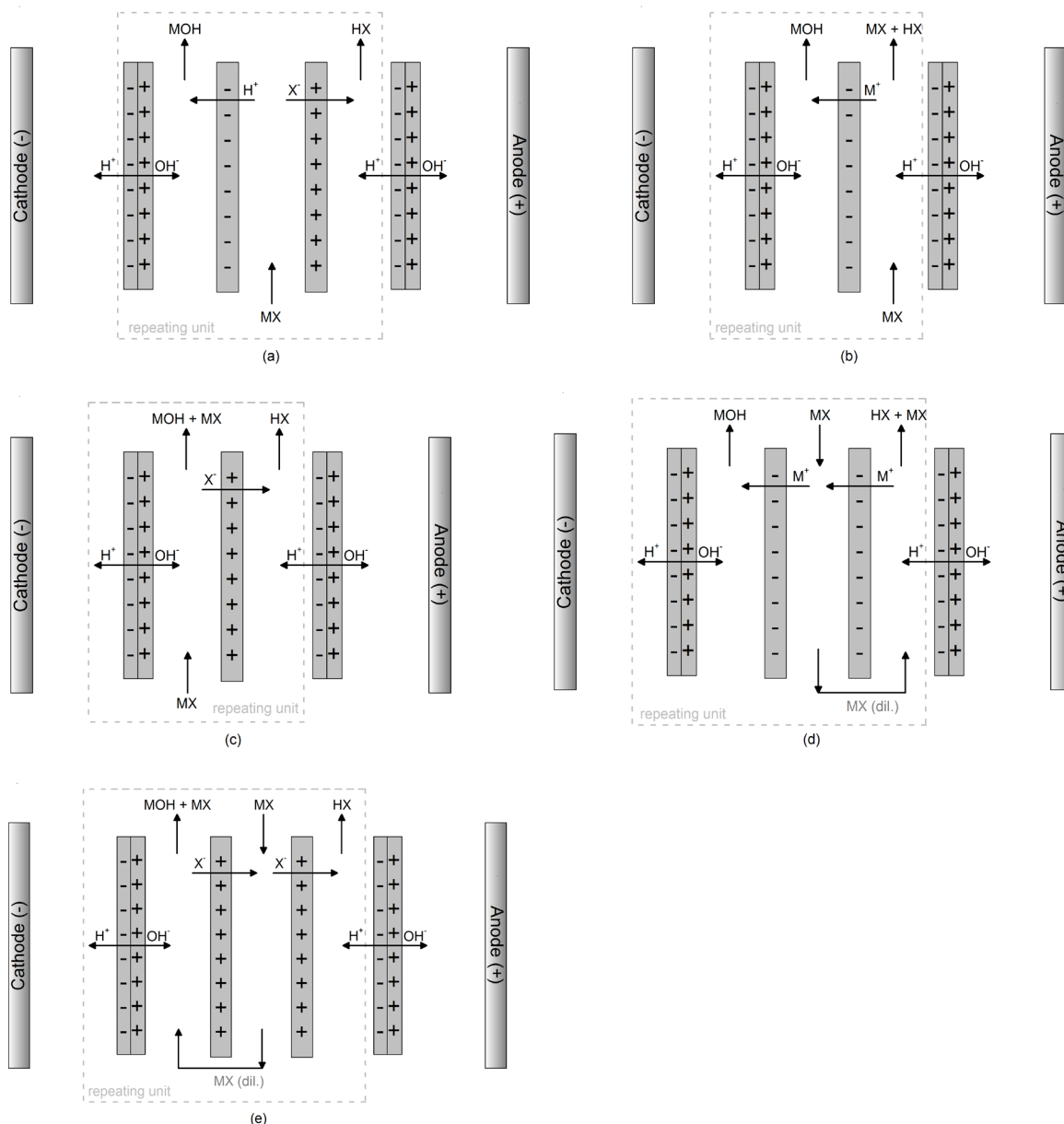


Figure 3: Schematic representation of bipolar membrane electro dialysis in a three-compartment (a), two-compartment (b, c) and high conversion (d, e) configuration.

is limited by the rate of water transport, and product purity is limited by permselectivity of membranes and back diffusion, analogously to ED [22,23]. ED-M has the potential to be an energy and cost-effective intermediate synthesis step and reevaluation tool for highly soluble ionic compounds.

3.5 Ion substitution electro dialysis

In ion substitution electro dialysis (ISED), the stack works as the ion exchanger. Instead of a strictly alternative

arrangement of IEMs, pairs of one type of monopolar membrane are used and separated by one IEM of opposite sign (Fig. 5a and 5b). Under an applied electric current, ions from donor solution (D) are transported to adjacent product; while ions from product are transported to an acceptor solution (A). Thus, ions in the product stream are substituted and donor solution salinity gets reduced during the course of the process. This arrangement is used mostly for wine deacidification in the food industry [24], which is not discussed in this work.

Inorganic acids or bases are usually used as donor solutions [24]. In this case, initially high current

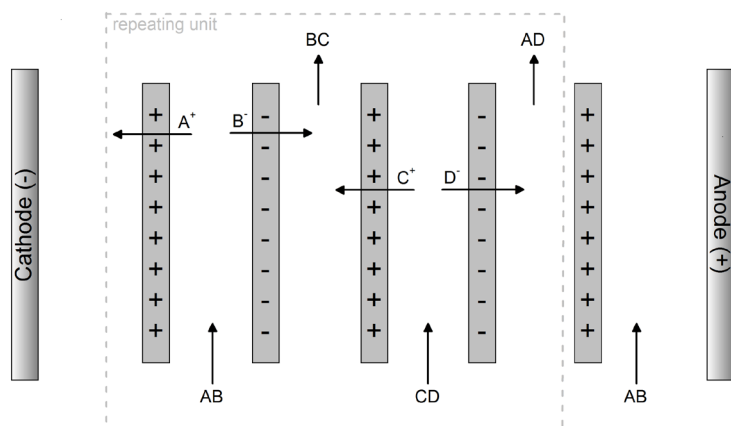


Figure 4: Schematic representation of metathesis-electrodialysis.

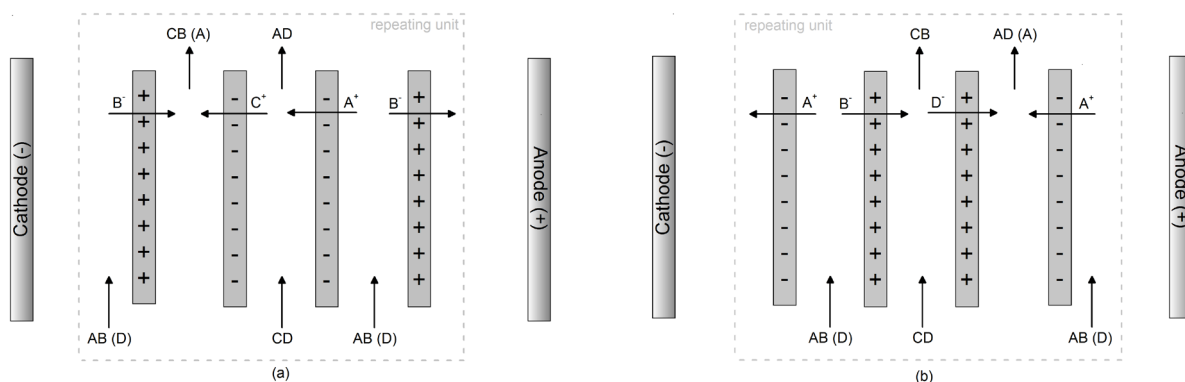


Figure 5: Schematic representation of two possible configurations of ion substitution electrodialysis. A-acceptor solution, D – donor solution.

efficiency, due to the high rate of diffusion, of products formed, decreases with increasing content of an acid in the product. Highly-mobile H^+ ions compete with metal cations transported to the acceptor solution; thus, the obtained product cannot be completely acid-free. This competition can be reduced in some cases by the use of monovalent-selective IEMs.

3.6 Donnan dialysis

Donnan dialysis (DD) is a no-electric current, diffusion-driven process, that can be also applied for continuous ion exchange when ionic radii of one of the ions is too large to be effectively transported through IEM. In this case, only comparably small anions are transported through AEM (Fig. 6a) or cations through CEM (Fig. 6b), leading to the substitution of ions. In this process energy consumption is low; it can lead to pure products (even > 99% [25]), However, it is time consuming, requires enormous membrane area

that increases unit costs and its application in chemical synthesis is very limited.

4 Applications of IEMs in chemical synthesis

4.1 Electromembrane synthesis by ME

IEMs in chlor-alkali industry

The oldest and most widespread application of membrane processes for synthesis lies in the chlor-alkali industry, where IEMs are used for simultaneous production of Cl_2 and alkali (NaOH or, to lesser extent, KOH) by electrolysis of aqueous, alkaline earth metal chloride solutions. The conventional process encountered two major obstacles: explosive reaction of chlorine with hydrogen and dissolution of chlorine in NaOH to form a hypochlorite solution. To overcome these issues, three technologies

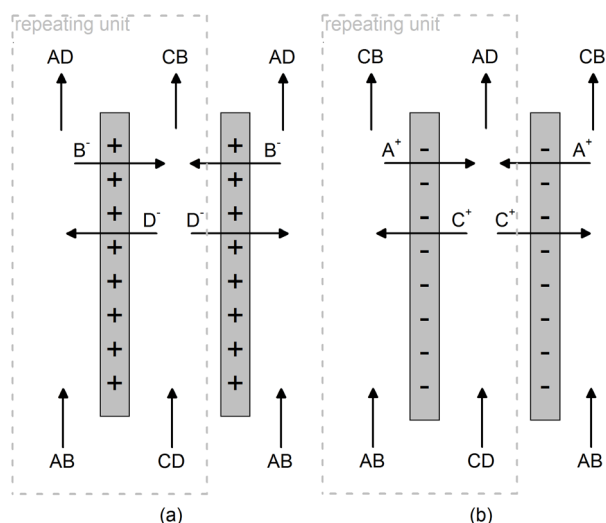


Figure 6: Schematic representation of Donnan dialysis.

were developed which differ in the method of keeping the chlorine produced at the anode separated from the caustic soda and hydrogen produced at the cathode: mercury, diaphragm and membrane cell electrolysis [26]. The latter, introduced in the 1970s, is considered to be the Best Available Technology due to ecological advantages and energy efficiency [27].

In membrane cell electrolysis, the anode and cathode are separated by a CEM. Brine is introduced to the anode compartment where chloride ions are oxidized to chlorine gas. Sodium ions migrate through the CEM toward the cathode compartment where water is electrolyzed, releasing hydrogen gas and hydroxide ions. Sodium and hydroxide ions combine to produce caustic soda solution which is concentrated by recirculation to 32–35% by mass. NaOH is continuously removed from the catholyte. CEM prevents the migration of chloride ions from brine to the cathode compartment, thus, ensuring high purity of the product (< 50 ppm NaCl). Depleted brine is discharged from the anode compartment. Further saturation of alkali to the commercial standard concentration of 50% is done by evaporation. Back-migration of hydroxide due to non-ideal permselectivity of CEM leads to an undesired formation of oxygen, hypochlorite and chlorate in the anode compartment, but the loss of CE does not typically exceed 3–7% with respect to caustic soda production [26].

The first CEMs suitable for membrane electrolysis were proposed by Ionics Inc. in the 1950s. Such a membrane should have high exchange capacity, high electrical conductivity, and stability in the presence of both chlorine and concentrated alkali at elevated temperatures. Suitable chemical stability was impossible to obtain with

hydrocarbon polymers, and it took almost twenty years until fluorocarbon membranes with sulphonic groups were developed by E.I. du Pont Co. (Nafion), followed by Asahi Glass (Flemion) [28]. Currently, perfluorinated CEMs used are composite membranes consisting of at least two layers of perfluorinated polymer. The carboxylate layer (adjacent to the cathodic side) with low water content ensures selective transport of sodium or potassium ions and largely prevents the transport of hydroxide, chloride, hypochlorite, and chlorate ions; while the sulphonate layer (adjacent to the anodic side) ensures good mechanical strength and a high ionic conductivity [4,16]. Reinforcement with PTFE fibers gave the membrane additional mechanical strength. A comprehensive literature review on Nafion structure and properties was done by Mauritz and Moore [5]. The lifetime of chlor-alkali membranes is most commonly reported as three years, but ranges between 2–5 years [27].

To avoid further evaporative concentration of caustic solutions, Fx-50 membrane was developed by Asahi Glass for direct production of 50% caustic soda, but due to the low conductivity of the modified membrane, the market demand for this product was too low for its successful commercial application [29,30].

To maintain the high performance and lifetime of the IEM, the feed brine must be purified from undesirable components (sulfates, calcium, magnesium and other multivalent metal ions, which hydroxides can precipitate inside the membrane) in an additional purification step, which increases operational cost [31].

Despite those two drawbacks: additional brine purification and following caustics concentration, membrane technology proves its usefulness in the chlor-alkali industry and is advantageous compared to the other two technologies. This can be proven by the fact that almost all chlor-alkali plants built after 1987 are based on membrane electrolysis [27].

IEMs in alkaline water electrolysis

Alkaline water electrolysis is currently the only industrial applied technology for water electrolysis. Alkaline solutions, KOH or NaOH, are circulated through catholyte and anolyte chambers where the decomposition of water and simultaneous production of very pure hydrogen and oxygen occurs [32]. A diaphragm is essential to separate gases produced in the electrode compartments to prevent an explosive reaction. Such a diaphragm can be replaced with IEM, either CEM or AEM. With the use of perfluorinated CEM, NaOH can be produced as a byproduct in the catholyte, similar to the chlor-alkali industry; however the energy efficiency of this process is low [33]. The use of

AEM could improve the process flexibility and efficiency. However, such membrane is subject to operate at elevated temperatures (about 80°C) and with concentrated alkali solutions, conditions that none of the commercially available products can handle [12,34].

Perfluorinated membranes are also used as solid polymer electrolytes in proton exchange membrane (PEM) water electrolysis (also named solid polymer electrolysis, SPE). The membrane there is responsible for the transport of protons to the cathode compartment, separation of electrode chambers and separation of gaseous products. This promising technology, despite high energy efficiency, struggles with a short lifetime and high unit costs due to the high membrane price [32].

IEMs as a replacement for diaphragms in various electro-membrane syntheses

In electro-synthesis of various compounds, replacement of diaphragms with IEMs increases the process efficiency. CEM was used for the production of potassium stannate in a process in which soluble tin anode dissolves in KOH electrolyte to form stannite which reacts rapidly with air to form stannate. CEM enables transport of K^+ ions from anolyte to catholyte where KOH is formed and later recirculated to anolyte, providing KOH for reaction [35,36]. The bleaching agent, sodium dithionite ($Na_2S_2O_4$), can be obtained by electro-membrane reduction of bisulfate ion [37]. Chlorine-free chlorine dioxide can be produced in a single step by ME of a diluted alkali metal chlorite solution [38]. In electro-oxidation of cerium(III) sulfate to cerium(IV) at the anode, AEM separates products and allows SO_4^{2-} transport from the cathode compartment to balance charges [39].

ME has also been successfully used to increase the concentration of hydroiodic acid by combining the redox reactions in the iodine-iodide system and directed proton permeation through perfluorinated CEMs [40-43]. As a result of ME concentration, HI content in the catholyte increased to over the quasi-azeotropic level (about 10 mol kg^{-1}), while its anolyte content decreased. This method of concentrating HI can be applied to increase the efficiency of the sulfur-iodine process.

A variety of organic electrochemical processes have been developed which require IEM for separation of electrode solutions. In electrohydrodimerization of acrylonitrile into adiponitrile (an important intermediate in the production of Nylon-66) by electrolysis, CEM prevents the oxidation of organic compounds present in the catholyte both by separating them from the oxygen released at the cathode and providing proton transport to the anolyte [44]. Sodium methanolate can be produced

either by ME of NaCl [45] or sodium acetate [46] in methanol solutions. In both cases, electroosmotic solvent flux limits product concentration. ME with CEM also enables synthesis of benzoquinone and hydroquinone [47], thus, obtaining trimethylhydroquinone from mesitylene [48] and p-anisidine by reduction of nitrobenzene in acidic methanol [49]. Replacement of porous separators with CEMs also prevented the migration of oxalate and glyoxalate anions to the anode and enabled a quantitative reduction of oxalic acid to glyoxalic acid [50]. The use of AEM in the above process prevented a migration of cations to contaminate the anolyte and allowed maintenance of the constant chloride concentration in the anodic compartment [51]. In anodic methoxylation of the methanol solution of olefins, yield strongly depended on the olefin structure [52]. Some attempts were also made at anodic dimethoxylation of furan [53], electroreduction of dibromo compounds [54], and methanol or p-xylene oxidation [55].

In most of the syntheses by ME, a membrane separates the product from an electrode at which undesired side reactions (oxidation/reduction) can possibly take place. In ME, applied electrical potential allows for control of the reaction rate, which is supported by the use of IEM. Also, the purity of product is often an advantage. The main limitation in the application of ME for organic syntheses in non-aqueous systems lies in a poor conductivity of the process solutions which implies the use of supporting electrolytes (i.e. KCl), which need to be removed in the subsequent steps.

IEMs as solid polymer electrolytes in electro-organic synthesis

In electrolytic oxidation or reduction of organic compounds by ME, the use of a supporting electrolyte is often essential to provide sufficient electrical conductivity in a module. This can be omitted with great improvement of the process by the use of a so-called solid phase electrolyte (SPE) where IEM directly contacts porous electrodes, replacing conductive fluid containing the supporting electrolyte. Thus, SPE allows elimination of the subsequent separation and recycling of a supporting electrolyte and the suppression of side reactions with such additives [56-58]. This is a significant improvement in organic synthesis while retaining its advantages of simplicity, low energy demand, moderate temperatures and pressures and ease of the process control. SPE synthesis products contain no contaminants and can be used as food or pharmaceutical grade reagents [57,58].

The electrochemical reactions take place at the interfaces between the IEM and electrocatalytically active

layers of porous electrodes. IEM itself plays the role of the ED compartment filled with electrolyte, thus providing the necessary ionic conductivity. Using the above strategy, a number of fuel cell technologies were developed on the base of oxidation of alcohol using SPE [59,60].

AEM is rarely used as SPE, as this type of IEM is still not robust enough, especially in the presence of oxidants [61]. In AEM, positively charged fixed ions, such as quaternary ammonium groups, act as charge carriers for OH^- ions formed at the cathode, which can be oxidized into oxygen at the anode. The most widely used SPEs are CEMs, which act like immobilized sulfuric acid due to the fixed sulfonate allowing migration of H^+ ions formed at the anode to the cathode compartment, where hydrogen ions are reduced to hydrogen.

Ogumi and co-workers published a series of articles on the application of the SPE technique in organic electrosynthesis, eg. for hydrogenation of olefinic double bonds [62], Kolbe type reactions [63], oxidation of cyclohexanol to cyclohexanone [64], reduction of nitrobenzene [65,66] or oxidation of geraniol [67]. Jörisen investigated the application of SPE for electrooxidation of alcohols to acids, methoxylation of furane, alkoxylation of N-alkylamides [57], and methoxlation of p-methoxytoluene [68]. Pintauro et al. studied the hydrogenation of edible oils [69, 70]. It should be also mentioned that with SPEs the following syntheses were investigated: reduction of benzaldehyde [71], reduction of 2-cyclohexene-1-one [72], the electrosynthesis of p-methoxybenzaldehyde using a graphite SPE electrode [73], the oxidation of various alcohols [74], electrohydrogenation of ethylene [75].

4.2 Synthesis of ionic liquids

Ionic liquids are organic salts of great interest, recently, due to their unique properties as solvents, but the synthesis, especially of hydrophilic ionic liquids, encounters some problems. Application of ED-M allows avoiding the use of expensive silver salts used in conventional syntheses and is more environmentally friendly than the use of organic solvents [76]. Moreover, the modular construction, and its related ability to scale up the ED offers the potential to produce large amounts of ionic liquid in a relatively straightforward process [77]. Choline ionic liquids: thiocyanate, acetate and dicyanamide were successfully prepared by electrodialysis from the inexpensive precursor choline chloride with an overall CE of 65-80%, increasing with the decrease in ion size [76]. However, purity of the product was lower than in conventional methods, and the recovery ratio was low due to water transport. 1-butyl-3-

methylimidazolium tetrafluoroborate ([BMIM] BF_4) was synthesized by ED-M of [BMIM]Cl with NaBF_4 with a 92% yield ratio and purity over 95% [78].

BMED was also applied for synthesis of ionic liquids: to produce hydroxide precursors of the common cation 1-ethyl-3-methylimidazolium (EMIM) from [EMIM][EtOSO₃] [77]. A 5% solution of precursor obtained contained ultralow levels of residual anions.

Relatively small ions (like BF_4^- or choline) are effectively transported through the AEM in the electrical field, thus it is possible to produce these compounds effectively by ED-M. For large and hydrophobic organic ions, often constituting ionic liquids, the transport through IEMs is limited or even prevented. These ions can also cause fouling of IEMs [79]. In a synthesis route, when simple small inorganic ions are to be removed from the reaction mixture to obtain ionic liquids, the use of simple ED seems to be advantageous over other membrane processes since the rates of the transport of large organic ions through IEMs are going to be low due to the steric hindrance effects [80] or low diffusivity.

When one of the ions to be replaced to form ionic liquid is small, Donnan dialysis can be also applied. DD was successfully applied to purify ionic liquids from halides in the following mixtures: NaCl/NaAc, EMIM Cl/NaAc, EMIM Cl/NaOH, TBP Br/NaOH, TMSBr/NaOH and TMAcCl/NaOH [25]. Acetate and hydroxide ions were used as comparable in size; the latter was subsequently neutralized with glycine to prepare glycinate ionic liquid. A high degree of conversion and low content of cationic impurities in the product has proven the applicability of DD in the synthesis of ionic liquids.

4.3 Conversion of inorganic salts

Conversion of some inorganic salts to more useful products can be conducted by metathesis-electrodialysis (ED-M). Sodium sulfate was converted to sodium chloride by a double exchange reaction with either magnesium [81] or potassium [82] chlorides. In another work, potassium bicarbonate was prepared from sodium bicarbonate and potassium sulfate [83]. Production of KNO_3 from various substrates has recently gained some interest [84,85]. The aforementioned processes were characterized by high product current efficiency (close to 100%) and high purity. The concentration of products was, however, limited by inevitable water transport, caused mostly by electroosmosis [81,82]. Purity of product is crucial for the application of final product and depends mostly on selectivity of membranes and composition of raw materials

[22,23]. The main advantage of applying ED-M to synthesis or conversion of inorganic salts is its non-equilibrium character which allows for using substrates that will lead to the co-precipitation of undesired products or formation of double salts when components are simply mixed together, as in conventional metathesis. However, for reactions where all of the components are highly soluble, ED-M has to be followed by evaporation or crystallization to separate the final product.

4.4 Controlled synthesis of energetic compounds

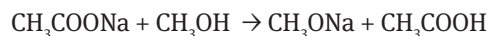
ED-M can also be considered as a safe method for the continuous synthesis of sensible (energetic, explosive) compounds, as it allows one to control the rate of synthesis via electric potential applied. Recently, synthesis of energetic compound: 2,2-dimethyltriazanium azide from sodium azide and 2,2-dimethyltriazanium sulfate by ED-M was first reported [86]. Such application is favorable when a reactive compound can remain in a solution, i.e. when used as a precursor or an intermediate for the subsequent synthesis steps.

4.5 Synthesis of quaternary ammonium hydroxides

Membrane techniques are applied to the synthesis of quaternary ammonium hydroxides, used as a phase transfer catalyst or template for nanoparticle preparation. Membrane electrolysis with CEMs is found to be more applicable for synthesis of lower molecular weight compounds [87] while AEMs allow for the formation of high molecular weight compounds [88,89]. Synthesis by BMED surpasses membrane electrolysis in terms of purity of the product [90,91,92], however, process performance decreases with an increase in the halide salt molecular weight [90]. Both membrane techniques provide lower energy consumption than traditional methods of quaternary ammonium hydroxide synthesis.

4.6 Synthesis in non-aqueous solvents

The BPM placed in alcohol solution can cause alcohol to split into alkoxide anions and a proton (H^+). This was initially reported by Sridhar [93]: sodium methoxide was synthesized from methanol solution of sodium acetate, according to the overall reaction:



BMED was also adopted to introduce alkoxy groups to the compounds. This process is particularly significant as it provides cheap chemicals for various syntheses, such as the Claisen condensation and the intramolecular Dieckmann condensation reactions [94]. In synthesis of acetoacetic ester, both steps of condensation and protonation can be carried out in a single ED step, with the alkoxide produced at the membrane immediately converted to the sodium enolate, and sodium ion recycled and conserved inside the system [94]. Methyl methoxyacetate, an important intermediate product, was produced by BMED in methanol, with $LiNO_3$ as a supporting electrolyte and methyl chloroacetate as a raw material [95]. Alkoxide was produced with a CE of around 60–70%; however, the following reaction steps showed rather low yields: 15% for methoxyacetate and 23% for ester.

It should be emphasized that in all the above-mentioned cases, conventional IEMs, designed for aqueous solutions, were used and optimal conditions for non-aqueous systems are still to be determined.

4.7 Inorganic acid and base production and recovery

Production of inorganic acid and bases and/or their recovery from salts, can be done with ion-exchange membranes with various configurations and techniques. Recovered acid and base can be recycled or reused. For re-use in the same process, the purity of recovered acid and/or base does not have to be high, which remains an additional advantage.

Membrane electrolysis was used for recovery of acids from various sodium or potassium oxo-salts. Acid production efficiency increased in the following order: $HNO_3 > HCl > H_2SO_4$ [96,97]. ME was also used to recover NaOH from sodium sulfate [98] and to recover chromic acid from spent chromic/sulfuric acid etch baths [99,100]. In the latter case, however, presence of oxidative chromic acid solution significantly decreased AEM lifetime and EED was proposed as a better solution [101]. In EED, CrO_4^{2-} is transported through AEM to the anolyte, where chromic acid is recovered [99,102]. Diluted sulfuric acid may be introduced to the catholyte to prevent precipitation of metal hydroxides and CEM blockage [99,103]. EED was also successfully applied for the splitting of alkali sulfates into sulfuric acid and a hydroxide [13,14,104], NaCl into HCl and NaOH [105], conversion of ammonium nitrate from wastewaters into ammonia and nitric acid [106–

108], and regeneration of NaOH from spent caustics [130]. Ceramic membranes were proposed for salt splitting of radioactively contaminated sodium salt solutions [109]. To improve CE of the acid/base recovery process, deposition of a sodium-ion selective ceramic thin film on a polymeric cation-selective membrane was proposed [110].

Among membrane methods for inorganic acid recovery, BMED got the most attention. This process is favored for treatment of spent acidic solutions containing metal salts (such as metal pickling liquors) without any waste disposal needed as it produces both hydroxide for metal precipitation and regenerated acid to recirculate to the process [111-113]. BMED was also applied for the splitting of sodium sulfate [114,115-117], sodium chloride [9,118-121], sodium chlorate [122,123], sodium nitrate [124], sodium and potassium iodide salts [125], KF in the production of uranium fluoride [126] to treat nitrate wastewaters [127,128], spent caustics to regenerate NaOH [129,130] and to produce silica acid from sodium metasilicate [131]. However, despite lower energy requirements reported, BMED still possesses many of the disadvantages of EED/EM [132]. High purity acid and base at higher concentrations can be obtained rather by EED, although at the expense of higher cell voltage and energy consumption [10,20,130,133]. The concentration of strong acid obtained with IEMs is generally said to be limited to 2 M [105,127] due to proton leakage, however, with so-called “low proton leakage” membranes and careful stack configuration up to 6–8 M, nitric acid was produced by EED with good current efficiency [106]. BMED is more suitable for treatment of solutions with low salt concentration due to the relatively large ion leakage through BPMs resulting in the contamination of the acids or bases produced with salts [134]. To overcome the above limitations, a configuration with two adjacent monopolar membranes of the same type was proposed (Fig. 3d, 3e).

4.8 Organic acid and bases production and recovery

Organic acids have been widely used in foods, beverages, pharmaceuticals, plastics and other biochemical or chemical products [135]. In microbiological syntheses, final product is received in the form of organic salt and acids have to be subsequently recovered from fermentation broth. Purification stages can comprise up to 50% of production costs and generate large amounts of wastes (mostly gypsum); therefore, there is a great interest in the application of membrane processes to improve the process economy [136].

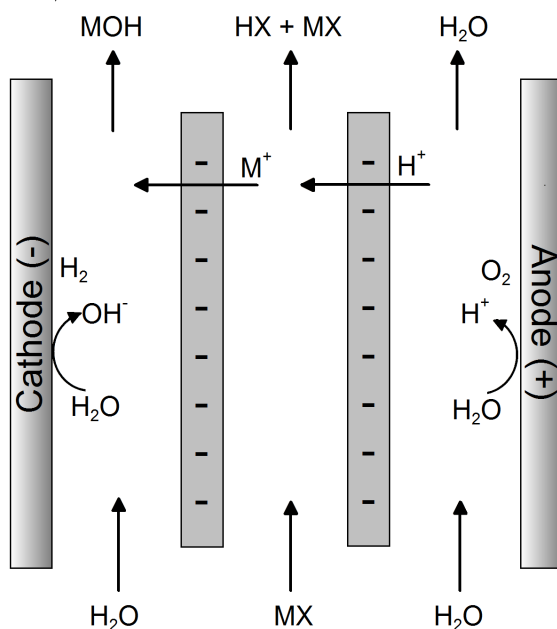


Figure 7: Schematic representation of EED combined with ISD.

Microbiological organic acid production can be done in one reactor with BMED, coupling the removal of product and pH control (by formation of side-product hydroxide) – the two crucial factors limiting commercial applications [137,138]. However, due to fouling of the membranes by bacteria [139,140], a more favorable solution is coupling conventional ED for salt concentration in the brine and removal of non-ionic species with an ED-based process to convert salt to acid and recovery of the base [135,141-146]. Such a solution improves synthesis efficiency, reduces the environmental impact by eliminating wastes and assures longer lifetime of membranes, especially of costly BPMs.

Different membrane techniques were used for production/recovery of organic acids or of aminoacids. ME was proposed as a simple method for recovery of lactic acid from its sodium salt, but AEM performance was insufficient [147]. ED-M allowed for the preparation of pyrazine 2,3-dicarboxylic acid from its potassium salt [148] or for the recovery of L-malic acid from a fermentation broth [149]. ISD allowed production of lactic acid from sodium lactate [150], L-lysine from its monohydrochloride [151] or to recover the malic acid from its salt [152]. EED was applied for recovery of organic acids from cyclohexanone wastes [153], and, in configuration with two CEMs (which is in fact closer to ISD as it doesn't allow pure product) (Fig. 7), was proposed for conversion of sodium glutamate into glutamic acid [138] and sodium salicylate into salicylic acid [154]. ED-M was shown to be effective in recovery of

lactic [155-157] and iminodiacetic [158] acids. However, BMED is the most widely used membrane technique for this purpose, and some pilot and commercial industrial plants are currently under operation worldwide, mostly to recover acids from fermentation broths [18,159]. BMED was also demonstrated to be effective in recovery of lactic acid [160-166], citric acid [167-172,191], fumaric acid [173] from fermentation broth, but also in salts conversion in the following acids: formic acid [174,175], acetic acid [176,177], gluconic acid [172,192], p-toluenesulfonic acid [178], salicylic acid [179], ascorbic acid [180, 181], lactobionic acid [182], aminoacids [183] and morpholine [184]. The above processes encounter typical obstacles characteristic of BMED: proton and hydroxyl leakage through monopolar IEMs, and ion leakage through BPM.

In the case of high molecular weight compounds, additional obstacles are poor solubility and often rather low conductivity of aquatic solutions which results in high energy consumption. To overcome this, processes are conducted at elevated temperatures [179], coupled with electrodeionization in which the presence of ion-exchange resin in the diluate compartment effectively decreases the stack electrical resistance [185], or process solutions are pre-concentrated by ED [135]. BMED conducted in mixed water-alcohol mixtures (so-called two-phase bipolar membrane electrodialysis, TPBMED) allowed for production of some acids: salicylic [186], sebacic [187], and long-chain linear acids of formula $C_nH_{2n+1}COOH$, with $n = 2 - 7$ [188] and $n = 7 - 15$ [189].

Apart from the membrane technique used, the stack configuration is often crucial for ion transport and for overall process performance: and many different configurations can be applied for production of the compound with different results [170,190-192], as it can minimize the possibility of leakage and contamination [191,193].

Organic base recovery is not as widely studied as that of organic acids; however, BMED was demonstrated to be successful in conversion of monoethanolamine chloride into monoethanolamine [195]. It was also reported that 2-amino-1-propanol can be recovered from its sulfate solution [194]. When recovering organic bases by BMED, a three-compartment stack configuration is usually applied (Fig. 3a). This has a significant impact on CE due to the proton leakage and subsequent transport of hydrogen ions through CEM leading to water formation [195].

BMED also constitutes a promising method for recovery of glyphosate from neutralization liquor in the pesticide industry; recovered HCl and NaOH can be used for hydrolysis of the intermediate products, making it a step towards a zero liquid discharge process [196].

4.9 Regeneration of spent sorbents in the flue gas treatment processes

Alkaline sorbents, such as sodium hydroxide or alkanolamines, are used for desulfurization of flue gas from power plants. BMED was found to be an attractive method for regeneration of spent solutions to recover alkali sorbent and sulfuric acid at relatively high efficiency (around 85%) and low cost as compared to metathesis and ion exchange [197]. BMED is also suitable for the regeneration of alkanolamine sulfates, formed in the course of desulfurization [198-200]. BMED, as an efficient and economically attractive method of regeneration of spent sorbent, was already commercialized as a part of Soxal flue gas desulphurization technology which integrates SO_2 absorption with BMED to convert sulfur dioxide from the flue gas into valuable sulfur compounds [1]. Recent reports on the use of EED to regenerate NaOH sorbent from flue-gas desulfurization and simultaneously produce H_2SO_4 as by-product show efficiency similar to the chlor-alkali industry (CE above 84%), which led the authors to the conclusion that EED can be considered as an economically feasible method [201,202]. It should be noted, however, that the investment costs were not assessed. The above reports indicate that some of the electromembrane processes can be effectively used to improve the efficiency and in some cases the economy of flue gas desulphurization units and generate valuable by-product.

Similar to desulfurization, alkaline sorbents such as alkanolamines, sodium hydroxide, potassium or sodium carbonate and ammonia are applied for CO_2 capture and sequestration. There, BMED can replace such a sorbent thermal decomposition (regeneration) step because acidification of spent solution, with the protons produced by BPM, leads to the release of gaseous CO_2 from the weak carbonic acid and thus allows for sorbent regeneration. This recovery process is attractive due to very low energy consumption – as low as $0.55 \text{ kWh kg}^{-1} CO_2$ for alkaline carbonates [203-205] and around $2-4 \text{ kWh kg}^{-1} CO_2$ for ammonia [206]. The main obstacle in BMED-based CO_2 desorption is CO_2 gas evolution inside the membrane module compartments, resulting in an increased stack resistance and high energy consumption at high current densities [207]. This was avoided by operating a BMED stack at elevated pressures, up to 6 atm and the controlled release of CO_2 dissolved outside of the module. This high-pressure operation of a BMED stack resulted in a 29% reduction in energy consumption, as compared to the stack operated at 1.5 atm, even at a high current density of around 1400 A m^{-2} .

In the newly-developed process for CO₂ capture, calcium or magnesium carbonates are generated for safe and permanent carbon storage [208,209]. This process consists of four steps: leaching of Ca/Mg from waste cement powder by acid, absorption of CO₂ from flue-gas in alkali (NaOH or KOH), precipitation of calcium (magnesium) carbonate by reacting two above-mentioned streams and BMED-splitting of the remaining salt solution to corresponding acid and base which are returned to an extraction and capture step, respectively. This process was found to be quite energy consumptive, however, energy demand decreased when weak acid, eg. acetic acid, was used for leaching.

The environmental impacts of BMED processing of sodium hydroxide-based CO₂ sorbents were evaluated in a pilot scale [210] with an important conclusion that a promising CO₂ capture efficiency (up to 530 g CO₂ per kg NaOH) can only be achieved if the electricity used for sorbent regeneration originates from the renewable sources. For conventional, carbon- based energy sources, the overall emission of CO₂ was found to exceed the amounts removed with sodium hydroxide. Such analysis and scale-up experiments may be crucial for evaluation of the applicability of electromembrane processes for CO₂ removal technologies.

5 Summary

As shown in the previous sections, IEMs can be effectively used in chemical syntheses either for separation of the ionic product from the reaction mixture, ion introduction (or replacement) due to the formation of the desired product (in the case of monopolar membranes) or to generate hydrogen (H⁺) or hydroxyl (OH⁻) ions (BPM) for synthesis of acids or bases. The list of the potential chemical synthesis processes that employ IEMs include: membrane electrolysis (ME), electro-electrodialysis (EED), electrodialysis metathesis (ED-M), ion-substitution electrodialysis (ISED) and electrodialysis with bipolar membrane (BMED). Some of these processes (ME) allow for electrosynthesis of inorganic and organic compounds by a redox (reduction or oxidation) reaction where the products are obtained at high current efficiency (CE) and with high yield and purity. The major role of IEM in ME is to separate reaction mixtures from the electrode at which any unintended reaction might take place. Other processes (EED, ED-M, ISED) allow for ion replacement reactions of inorganic and organic salts (including double-replacement – metathesis reactions) allowing the synthesis

of acids, bases and ionic liquids. The major role of IEMs in these processes lies in the membranes' selectivity towards either cations (CEMs) or anions (AEMs) which allows synthesis of compounds with very high purity. The main obstacle, however, iselectroosmotic solvent transport which limits the product concentration in the concentrate stream. Bipolar membrane based BMED allows for salt conversion, both in aqueous and non-aqueous solutions, due to the possibility of solvent (water, alcohol) splitting into a proton and a corresponding anion, inside the BPM. Thus, inorganic and organic salts can be effectively converted to acids and bases. The main limitation lies in the membrane stability towards concentrated acids or alkalis. All of the above processes can be applied for reuse or recovery of inorganic and organic acids or bases from the reaction mixtures; however, BMED seems to be the most promising method. It can be employed in such vital processes as regeneration of spent sorbents used for CO₂ removal from power plant flue gas.

The number and the quality of the scientific reports cited herein and in comprehensive patent review presented elsewhere [203] indicates a great interest in the application of IEM-based chemical syntheses. Given the large number of syntheses to which IEMs can be applied (redox, ion-substitution), we anticipate an incremental growth in successful applications of these processes in chemical and related industries.

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