

# Bipolar Membranes and Their Applications

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**Abstract** : Bipolar membranes have gained increasing interest as a tool for an efficient production of acids and bases from the corresponding salts. A large number of potential applications have been identified in the chemical and biochemical industry have been identified and evaluated on a laboratory scale. In spite of extensive research efforts and laboratory and pilot plant test, there are hardly any large-scale commercial plants. In this paper the basic concept of the electrolysytic water dissociation with bipolar membranes are briefly reviewed. The limitations of today's bipolar membranes are indicated. Selected examples of successful applications of the bipolar membrane technology are discussed.

## 1. Introduction

Bipolar membranes are gaining increasing attention as an efficient tool for the production of acids and bases from the corresponding salts by electrolysytic water dissociation. The process is economically very attractive and has a multitude of interesting potential applications. The large-scale utilization of bipolar membranes, however, is still limited today by unsatisfactory membrane properties and by a lack of application know-how. A bipolar membrane should have adequate water dissociation capability, low electrical resistance, high permselectivity and a long useful life under operating conditions, which means that it must be stable in highly concentrated acid or alkaline solutions. The monopolar anion- and cation-exchange membranes which are also needed in the process should have good proton and hydroxide ion blocking capability in addition to stability in strong bases and acids. Although today's membranes do not meet all of these required properties they are used successfully in a number of relevant applications.

## 2. The Principle of Electrolysytic Water Dissociation

The process of electrolysytic water dissociation is illustrated in Figure 1, which shows the schematic diagram of a bipolar membrane consisting of a cation- and an anion-exchange layer arranged in parallel between two electrodes. If an electrical potential difference is established between the electrodes, charged species are removed from the interphase between the two ion-exchange layers. When all salt ions are removed from the interphase region further transport of electrical charges can be accomplished only by protons and hydroxide ions, which are available in a concentration of ca.  $1 \times 10^{-7} \text{ mol L}^{-1}$ . Bipolar membranes resemble a laminate of a cation- and an anion exchange layer with a very thin, i.e. 4-5 nm transition region in which the water dissociation occurs according to the water dissociation equilibrium given by:



The reversible energy required for the production of acids and bases in a bipolar membrane at constant temperature and pressure can be calculated by the

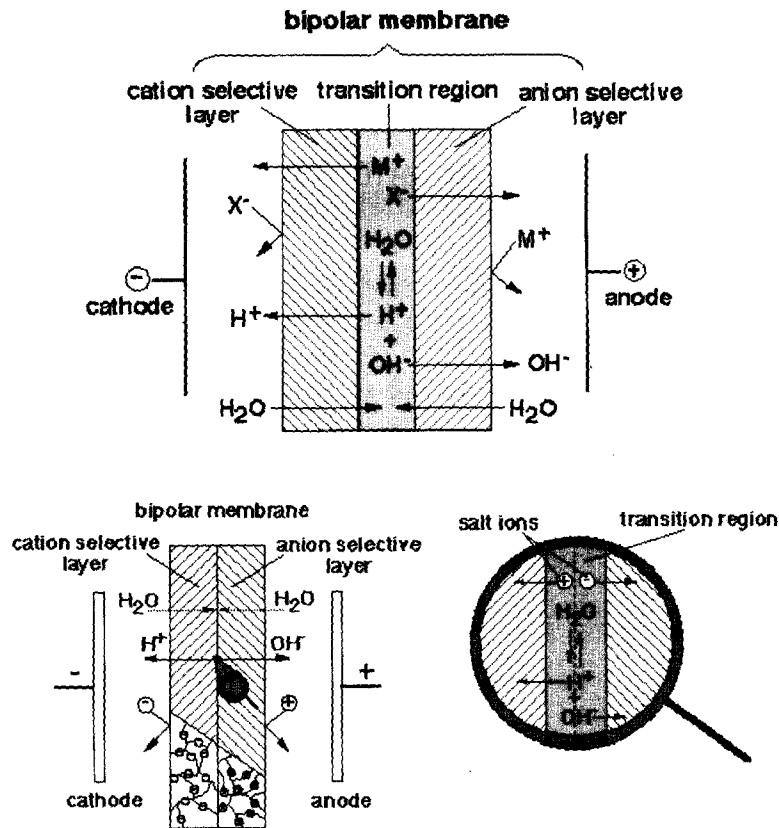


Fig. 1. Schematic diagram illustrating the principle of electrodialytic water dissociation in bipolar membranes.

Nernst Equation for a concentration change of solutions with different  $H^+$ -ion activities, i.e. pH-values:

$$\Delta G = F\Delta U = 2.3RT\Delta pH \quad (2)$$

Here is  $\Delta G$  the reversible Gibb's free energy,  $\Delta U$  the electrical potential difference between the two solutions,  $R$  is the gas constant,  $T$  is the absolute temperature,  $F$  is the Faraday constant, and  $\Delta pH$  is the difference between the pH-values of the two solutions separated by the bipolar membrane. For ln acid and base solutions in the two phases separated by the membrane  $\Delta U$  is 0.828 Volt and  $\Delta G$  is 0.022 kWh mol<sup>-1</sup> at 25°C.

The potential drop across the bipolar membrane measured in a water dissociation experiment is always higher than the calculated theoretical value because of irreversible effects due to the electrical resistance of the membrane and the solutions.

To utilize bipolar membranes for the production of acids and bases from the corresponding salt solution they must be combined with monopolar ion-exchange membranes as illustrated in Figure 2. The schematic drawing shows bipolar and cation- and anion-exchange membranes arranged in parallel between two electrodes to form individual compartments.

If a salt solution is introduced in the middle compartment and an electrical potential difference between the electrodes is established, the cations in the salt solution will migrate towards the cathode. They will permeate the cation-exchange membrane and form a base with the hydroxide ions generated in the bipolar membrane. On the other side of the bipolar membrane the protons, which are generated simultaneously with the hydroxide ions, form an acid with the anions migrating from the salt solution through the anion-exchange membrane towards the anode. The net result of the entire

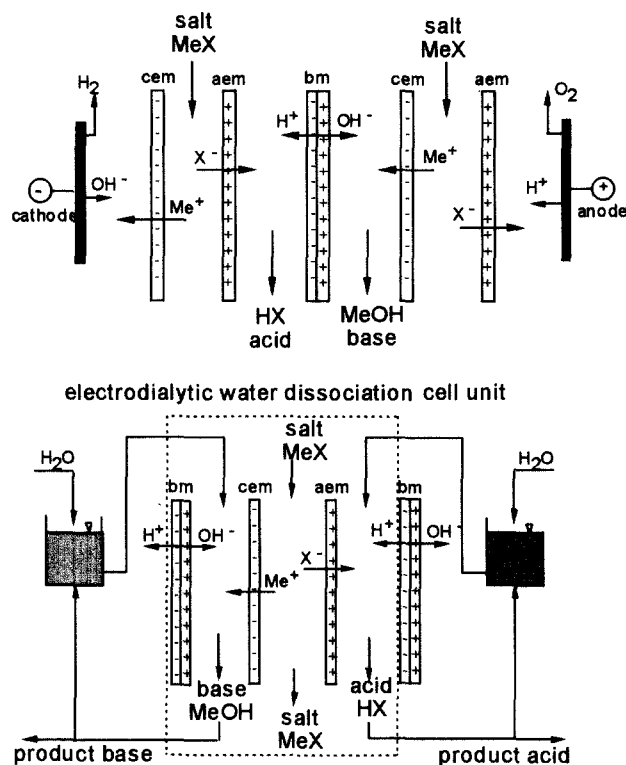


Fig. 2. Schematic drawing illustrating the principle of electrodiolytic production of acids and bases from the corresponding salts with bipolar membranes.

process is the production of an acid and a base from the corresponding salt solution in an electrodiolysis cell arrangement consisting of 3 individual compartments and three membranes, i.e. the bipolar and the cation- and anion-exchange membrane. As in conventional electrodiolysis a large number of the 3 compartment units can be stacked between electrodes.

### 3. The Mechanism of Water Dissociation in Bipolar Membranes

The water dissociation rate in the bipolar membrane determines to a large extent the overall efficiency of the process. It can easily be shown, however, that the dissociation rate constant of pure water is much too low to explain the experimentally determined high acid and base generation rate in bipolar membranes.

As indicated earlier a bipolar membrane consists

of a laminate of a cation- and an anion-exchange layer. The specific resistance  $\rho$  of a strong acid or base ion-exchange layer is in the order of 50 to 100  $\Omega\text{cm}$ . Assuming a thickness of 100  $\mu\text{m}$  for the cation- and anion-exchange layer, respectively, the total area resistance  $r$  of the ion-exchange layers of the bipolar membrane is in the order of 1-2  $\Omega\text{cm}^2$ .

The electrical resistance of the interphase layer of a bipolar membrane which is assumed to consist of deionized water can be calculated by:

$$r_m = \frac{\lambda}{\kappa} \quad (3)$$

Here  $r_m$  is the area resistance,  $\lambda$  the thickness, and  $\kappa$  is the specific conductivity of the interphase layer. If the interphase layer contains only pure water its specific resistance is ca.  $18 \times 10^6 \Omega\text{cm}$ . Thus, is the area resistance of an 1 nm thick interphase ca. 1.8  $\Omega\text{cm}^2$ . The above consideration,

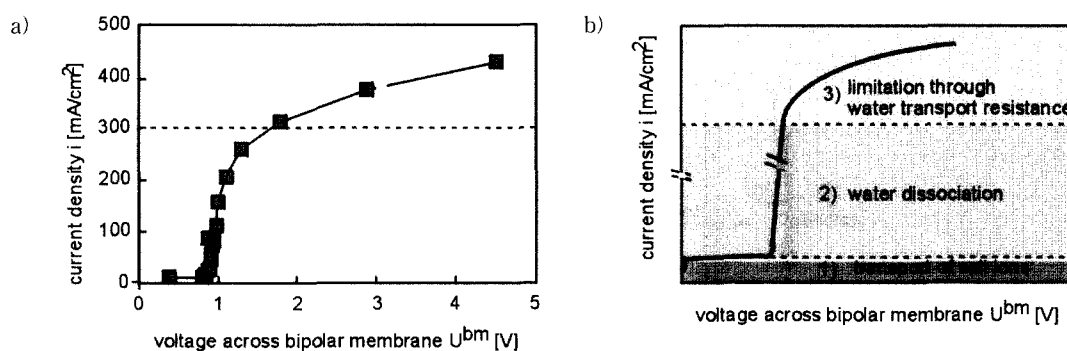


Fig. 3. Schematic diagram of the current density as a function of the applied voltage a) determined with a typical commercially available bipolar membrane and b) schematic diagram depicting three distinct areas of operation with bipolar membranes.

however, is correct only if ion concentration in the interphase is constant and all ions which are removed by the electric current across the bipolar membrane are replenished by the water dissociation. This means that the ion fluxes from the bipolar membrane into the outer phases can not exceed the rate of their generation in the interphase. Thus the maximum flux of  $H^+$ - and  $OH^-$ -ions of the bipolar membrane is given by:

$$J_{H^+} + J_{OH^-} = k_d C_{H_2O} \lambda \quad (4)$$

Here  $J$  is the maximum ion flux from the bipolar membrane into the outer phases,  $k_d$  is the water dissociation rate constant,  $C$  is the concentration in the interphase, and  $\lambda$  is the thickness of the interphases. The subscripts  $H^+$ ,  $OH^-$  and  $H_2O$  refer to  $H^+$ -,  $OH^-$ -ions and water, respectively.

The water dissociation rate constant  $k_d$  for pure water at 25 °C is given in the literature as  $2.5 \times 10^{-5} \text{ s}^{-1}$ . According to Equation (4) the maximum fluxes  $J_{H^+}$  and  $J_{OH^-}$  from a bipolar membrane that has a 1 nm thick interphase of pure water would be  $1.4 \times 10^{-13} \text{ mol cm}^{-2} \text{ s}^{-1}$ .

The electrical current  $I$  through the bipolar membrane is proportional to the sum of all ion fluxes and given by:

$$I = F(J_{H^+} + J_{OH^-}) \quad (5)$$

Thus, the maximum current density through a

bipolar membrane is according to Equations (4) and (5) ca.  $1.4 \times 10^{-8} \text{ A cm}^{-2}$ . A current density exceeding this value would lead to a depletion of ions in the interphase and thus to a drastic increase in its electrical resistance. In practice, however, bipolar membranes can be operated at current densities in excess of  $0.1 \text{ A cm}^{-2}$  as demonstrated in Figure 3 a) which shows the current through a bipolar membrane as a function of the applied voltage.

When an increasing voltage difference across a bipolar membrane is established the current is hardly increasing until the voltage drop reaches a value of about 0.8 Volt which is corresponding to the concentration potential as calculated by Equation (2) for a pH-value difference between the two solutions outside the bipolar membrane of ca. 14. A further small increase in the voltage drop leads to a drastic increase in the current density to values in excess of  $0.2 \text{ A cm}^{-2}$ . Thus, in the current-voltage curves determined with bipolar membranes two plateau values are observed that indicated a limitation in the current with increasing voltage drop across the membrane as depicted in Figure 3b). The first plateau value indicates a limitation of the current density due to a limitation of ions in the interphase. At 0.8 Volt an accelerated water dissociation begins and the current is no longer limited by a lack of ions until the second plateau value is reached at ca.  $0.2 \text{ A cm}^{-2}$  and the water dissociation is limited by limitations in the water supply to the interphase. There are 3 distinct

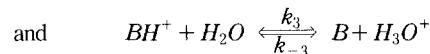
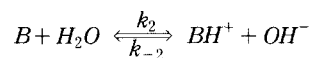
regions in the operation of a bipolar membrane. In the first region the current is very low and transported mainly by salt ions. In the second region high water dissociation rates are obtained and the current is transported by protons and hydroxide ions generated in the interphase. In the third region the production rate of protons and hydroxide ions is limited by the water transport rate into the interphase. Operation of bipolar membranes at current densities that exceed the second plateau value leads to a destruction of the membrane.

The experimentally determined current densities indicate that the simple model of a bipolar membrane as depicted in Figure 1 is incorrect. Either the water dissociation rate is faster by several orders of magnitude in the bipolar membrane than in free solution or the interphase is much thicker. That, however, would lead to a high area resistance of the interphase which is not the case. From scanning electron microscope photographs and calculations based on the Poisson and Boltzmann relation for the space charge at an interphase between differently charged ion-exchange membranes it can be concluded that the thickness of the interphase is less than 5 nm. This means that in bipolar membranes the water dissociation is at least  $10^6$  times faster than in free solution.

Various mechanisms have been suggested to explain the accelerated water dissociation in bipolar membranes. One possible explanation is suggested by Wien who observed that at high electric field densities the ion mobility as well as the degree of dissociation of weakly dissociated electrolytes increases with increasing field density. The increase in the dissociation constant of weak electrolytes by the electric field effect can be expressed by an increase in the water dissociation rate constant, assuming that the recombination rate of  $H^+$  and  $OH^-$  ions is unaffected.

Other theoretical considerations and experimental evidence support a hypothesis that the accelerated water dissociation is caused by a reversible proton transfer reaction between charged groups and water. This means, that in the presence of certain ionic groups the water dissociation rate constant may be several orders of magnitude higher than in pure

water. In case of the bipolar membrane the anion-exchange groups of the membrane polymer adjacent to the interphase layer are assumed to react with the water molecules at the membrane surface as follows:



where B is a neutral base, i.e. a tertiary ammonium group.

Both models can explain the acceleration of the water dissociation in the interphases between the anion- and cation-exchange layer of the bipolar membrane and serve as theoretical basis for the development of bipolar membranes.

#### 4. Bipolar Membrane, Their Preparation and Performance

The properties required of bipolar membranes to be useful in practical applications are low electrical resistance at high current density, high water dissociation rates, low co-ion transport rate, high ion-selectivities, and good thermal and especially chemical stability since the cation-selective layer of the bipolar membrane is in direct contact with an acid and the anion-exchange layer with an alkaline solution.

Low electrical resistance of the cation- and anion-exchange layer of the bipolar membrane can be obtained by using a strong acid, such as sulfonic acid groups, and a strong base, such as quaternary ammonium groups as fixed charges in high concentrations in the polymer matrix. To minimize the resistance of the interphase between the cation- and the anion-selective layers the thickness of this interphase must be as thin as possible as indicated earlier. There are various ways to prepare bipolar membranes with satisfactory properties. Most of them are prepared as laminates with some kind of interphase which forms a transition

**Table 1.** Electrochemical properties of the cation- and anion-selective layers of a bipolar membrane prepared by the above described technique

	anion-exchange layer	cation-exchange layer
ion-exchange capacity (meq g <sup>-1</sup> )	1.2	1
membrane thickness(μm)	60	60
area resistance (Ωcm <sup>2</sup> )	1.05	1.31
permselectivity (%)	97.5	98.5
swelling (wt %)	8	12.5

region where the actual water dissociation takes place. In some membranes heavy metal hydroxides are deposited in the interphase to catalyse the water dissociation. However, tertiary ammonium groups as fixed charges at the surface of an anion-exchange membrane seem to have the same effect.

A bipolar membrane with satisfactory properties can be prepared, e.g. as a laminate of highly permselective anion- and cation-exchange layers which have good alkaline and acid stability. An anion-selective layer with the required properties can be obtained by reacting of chloromethylated polysulfone dissolved in *n*-methyl pyrrolidone with the mono-quaternary salt of 4,4'-diazabicyclo-[2.2.2]-octane. The cation-selective layer can be prepared by introducing sulfonic acid groups as fixed charges into a poly-ether-ether-ke-ton matrix using chlorosulfonic acid. The co-ion transport and the swelling behaviour can be controlled in both layers by partial cross-linking. The properties of the ion-exchange layers prepared the above described procedures are listed in Table I.

#### 4.1. The performance of bipolar membranes

Bipolar membranes are usually characterized in terms of their water dissociation capability, their resistance, and their long-term stability. The water dissociation rate and electrical resistance of a membrane prepared by the above described procedure is shown in Figure 3a). Here the current density is shown as a function of the potential drop across the membrane. The test solutions in both compartments adjacent to the bipolar membrane were 1 molar Na<sub>2</sub>SO<sub>4</sub> solutions. The results indicate that the current density is extremely low at potential

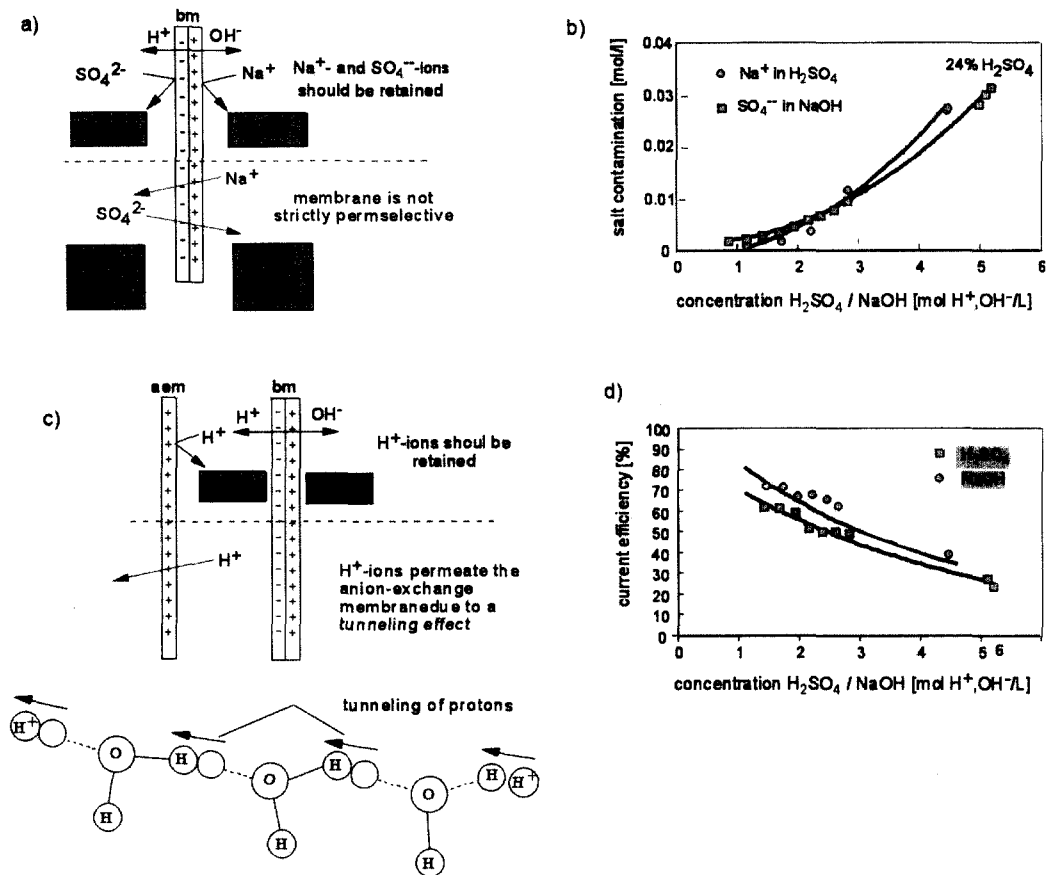
differences of less than ca. 0.8 V. Then the current density increases up to 0.250 A cm<sup>-2</sup> with very little increase in voltage drop. When this value is exceeded the resistance of the membrane increases drastically due to limitations in the water transport into the interphase region.

#### 4.2. Problems in practical applications of bipolar membranes

The electro-dialytic water dissociation with bipolar membranes is economically very attractive. There are, however, several severe problems in practical applications such as the contamination of the products by salts and low current efficiency at high acid and base concentrations.

The salt contamination of the products is related to the properties of the bipolar membrane and the poor current efficiency is the consequence of the proton and hydroxide-ion transport in monopolar membranes as indicated in Figure 4 which illustrates the conversion of Na<sub>2</sub>SO<sub>4</sub> into H<sub>2</sub>SO<sub>4</sub> and NaOH by electro-dialytic water dissociation.

Figure 4 a) shows the ion transport in the bipolar membrane. Desired is a flux of H<sup>+</sup> and OH<sup>-</sup> ions from the interphase of the bipolar membrane as the result of the water dissociation. However, in addition there is a flux of Na<sup>+</sup> and SO<sub>4</sub><sup>-</sup> ions through the bipolar membrane due to incomplete permselectivity of the anion- and cation-exchange layers. This leads to a contamination of the base by SO<sub>4</sub><sup>-</sup> ions and the acid by Na<sup>+</sup> ions. Since the permselectivity of the ion-exchange layers is decreasing with increasing acid and base concentration, the contamination is also increasing with increasing concentration as depicted in Figure 4b) which shows the salt concentration in sulphuric acid and



**Fig. 4.** Schematic diagram illustrating a) the contamination of an acid and a base by salt due to incomplete permselectivity of the cation- and anion-exchange layers of a bipolar membrane, b) experimentally determined salt contamination as a function of the acid and base concentrations, c) schematic drawing illustrating the decrease in current efficiency during the production of acids and bases due to poor acid blocking capability of the anion-exchange membrane, d) experimentally determined current efficiency as a function of the produced acid and base concentration.

sodium hydroxide produced by water dissociation in bipolar membranes from a 1 N Na<sub>2</sub>SO<sub>4</sub> solution as a function of the acid and base concentration.

The current efficiency in water dissociation with bipolar membranes is effected mainly by the properties of the anion-exchange membrane which has very poor retention of the protons as illustrated in Figure 4c). The transport mechanism of protons is based on a tunnelling mechanism with the consequence that protons can permeate the anion-exchange membrane rather freely. The same is true for the hydroxide ions which can permeate the cation-exchange membrane. The net result of the

process is that protons and hydroxide ions generated in the bipolar membrane neutralize each other. The proton and hydroxide fluxes and thus the current efficiency depend on the concentration as shown in Figure 4d). With increasing acid and base concentration the current efficiency is decreasing rapidly.

## 5. Applications of Bipolar Membranes

One interesting application of bipolar membranes is the production of caustic soda. The world wide demand for poly(vinyl chloride) and other chlorinated

hydrocarbons has led to the development of a large market for chlorine which is mainly produced by chlorine-alkaline electrolysis in which caustic soda is considered as a by-product that can be offered to the market at a very low price. Caustic soda on the other hand is a bulk chemical which is widely used in the chemical process industry as well as in many other relevant applications. Because of environmental problems caused by chlorinated hydrocarbons and the disposal of poly(vinyl chloride) wastes the demand for chlorine, however, is steadily decreasing and it can be expected that the demand for caustic soda will soon exceed that produced in the chlorine alkaline electrolysis and thus the interest in alternative process for obtaining caustic soda is increasing. Electrodialytic water dissociation with bipolar membranes is one of the more promising techniques for the future large scale economic production of caustic soda. It must, however, be realized that with today's available bipolar membranes it is difficult to obtain caustic soda without some salt contamination. The production of NaOH and H<sub>2</sub>SO<sub>4</sub> from the corresponding salts has been investigated in great detail. Test results obtained in laboratory studies were shown in Figure 4. These tests were carried out with a 1 M Na<sub>2</sub>SO<sub>4</sub> as feed at room temperature and an applied current density of 0.1 A cm<sup>-2</sup>. The test results indicate that acid and base concentrations up to 3 normal solutions can be achieved with a current utilization of 60 to 70%. The produced acid and base, however, are contaminated by salt and the salt concentration is increasing with increasing acid and base concentrations due to decreasing permselectivity of the bipolar membrane with increasing acid or base concentrations and reaches values in excess of 0.03 mol L<sup>-1</sup> at 4 molar base or acid concentrations. Thus, to improve the overall efficiency of the electrolytic water dissociation with bipolar membranes and to obtain less salt contamination when highly concentrated acids and bases should be produced better proton blocking membranes have to be developed in addition to higher permselective bipolar membranes.

There are, however, a large number of other potential applications of the electrolytic water dissociation where the purity of the product is not so critical and traces of salts can be tolerated. Typical applications of bipolar membranes with large industrial relevance are:

- Recovery of acids and bases such as sulfuric, hydrochloric, or hydrofluoric acid and sodium hydroxide from the salts generated in neutralization reactions.
- The recovery of organic acids such as formic, acetic, citric, lactic, and itaconic acid or certain amino acids from a fermentation broth.
- The adjustment of pH-values in fermentation or chemical production processes without increasing the ion potential.
- Regeneration of H<sub>2</sub>SO<sub>4</sub> and NaOH from Na<sub>2</sub>SO<sub>4</sub> obtained in industrial effluents, e.g. in the production of viscose or regenerated cellulose.
- Regeneration of acids and bases from scrubbers used to remove SO<sub>2</sub>, NO<sub>x</sub>, etc. amines from waste air streams.

This list of potential applications of the electrolytic water dissociation with bipolar membranes is by far not complete and with more efficient bipolar membranes becoming available in the future more interesting applications will certainly be identified. In this outline three typical examples for the use of bipolar membranes are described in more detail.

### 5.1. Recycling H<sub>2</sub>SO<sub>4</sub> and dimethyl isopropyl amine from an acid scrubber

Alkaline or acid scrubbers are often used to remove components that are harmful to the environment such as NO<sub>x</sub>, SO<sub>2</sub>, or certain amines from waste air streams. In these processes large amounts of acids or bases are consumed and salts are produced. In general, only dilute acids and bases are required in scrubbers. This makes the use of electrolytic water dissociation with bipolar membranes a very suited process to recover the acids or bases from the corresponding salts. The recovery of base from scrubbers used to remove



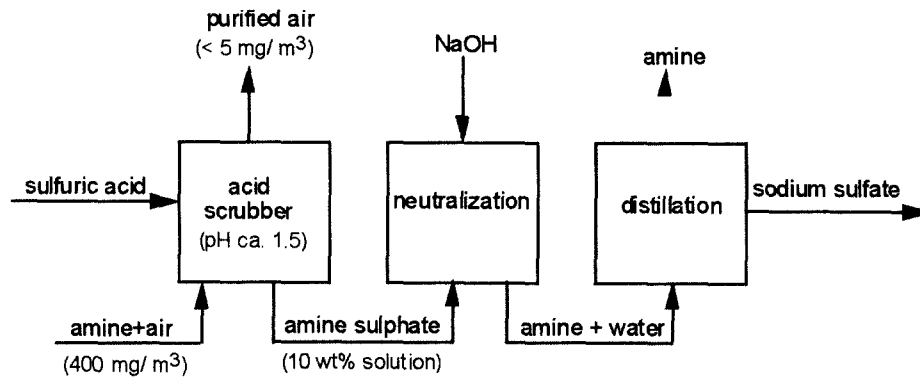


Fig. 5. Schematic diagram illustrating a conventional process for recovering an amine from a contaminated air stream using an acid scrubber.

SO<sub>2</sub> and NO<sub>x</sub> from coal burning power plants is described in detail in the literature.

Another interesting application of the electroalytic water dissociation is the recovery of dimethyl isopropyl amine removed from a waste air stream by a sulfuric acid scrubber. The waste air stream is generated when aluminium casting moulds are made from a sand/epoxy resin mixture by injecting dimethyl isopropyl amine in a mixture with air as catalyst to cure the resin instantaneously. The amine is not consumed in the process and emitted in a waste air stream containing ca. 0.5 g amine per m<sup>3</sup> waste air. It can, however, be recovered as amine sulfate in an acid scrubber as indicated in Figure 5 which shows the conventional process of using an acid scrubber to clean an amine contaminated air stream and recovering the amine for recycling. At a pH-value of less than 1.5 virtually all amine is precipitated as amine sulfate according to the equilibrium between the free amine and the amine sulphate. Thus, amine + H<sub>2</sub>SO<sub>4</sub> amine sulfate. Increasing the pH to a value ca.12 by addition of NaOH the free amine is formed again and can be recovered by distillation. Thus, amine sulfate + NaOH free amine + Na<sub>2</sub>SO<sub>4</sub>. The net result of the process, however, is the production of large amounts of sodium sulfate.

A complete recycling of the amine, the sulfuric acid and water is achieved without the production of a salt by combining the electroalytic water dissociation with distillation. The process is

illustrated in Figure 6.

The waste air stream containing the amines is fed into an acid scrubber where the free amine is converted into amine sulfate. The effluent of the acid scrubber containing ca. 10% amine sulfate in a mixture with sulfuric acid is then fed into the electroalytic water dissociation apparatus containing bipolar membranes and anion- and cation-exchange membranes in alternating series between two electrodes. Here the amine sulfate is converted back into the free amine while the sulfate ions forms sulfuric acid which is recycled to the acid scrubber. The amine water mixture is distilled to recover the amine and the water is recycled to the electroalytic unit. Thus, the process allows a complete recovery of the amine from a waste air stream by combination of an acid scrubber and electroalytic water dissociation.

## 5.2. Production of itaconic acid in a continuous fermentation processe

One of the more promising applications of bipolar membranes is the adjustment of the pH-value of fermentation solutions and to recover the organic acids from the spent medium. As an example the production of itaconic acid will be discussed in this outline.

Conventionally itaconic acid is produced by a batch-type fermentation process. During fermentation the pH-value is shifting towards lower values due to the production of the acid. To avoid product

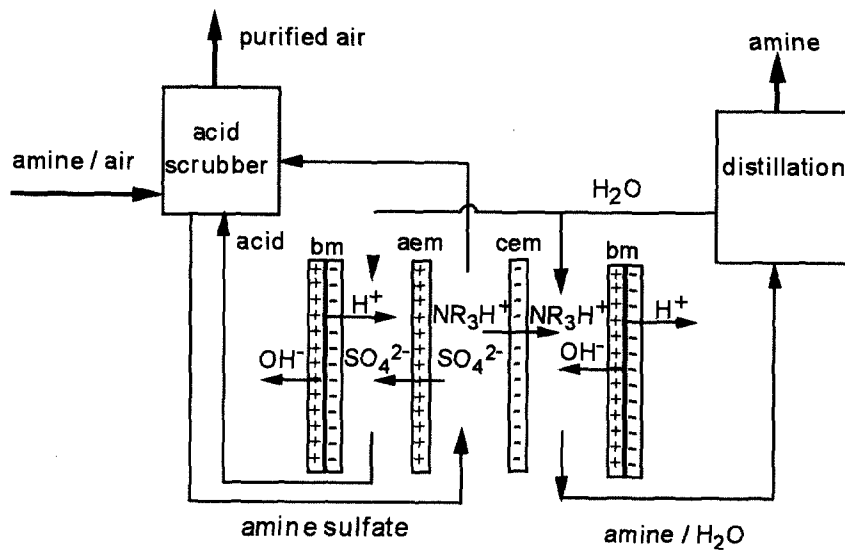


Fig. 6. Schematic diagram illustrating the recovery of dimethyl isopropyl amine from a waste air stream by combination of acid scrubber, diffusion dialysis electrodiolytic water dissociation using bipolar membranes and distillation.

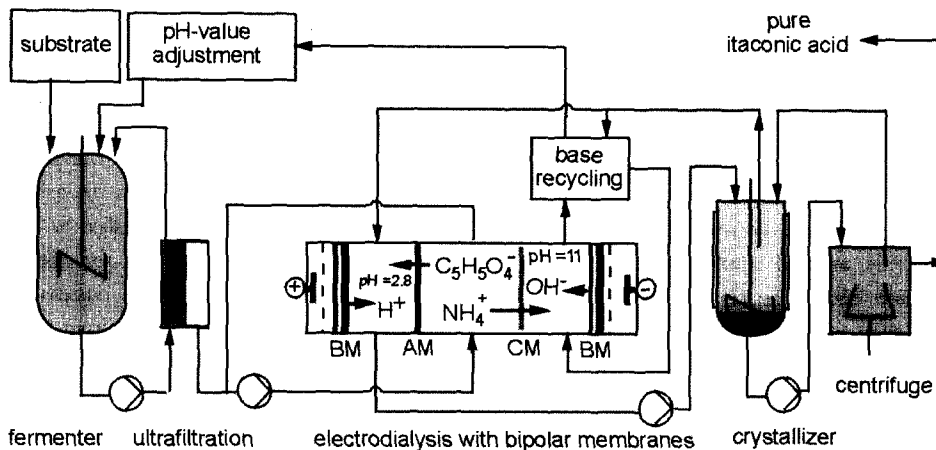


Fig. 7. Schematic diagram illustrating a continuous fermentation process for the production of itaconic acid without further addition of acids or bases using bipolar membranes.

inhibition the pH-value has to be kept at a certain high level. This is done by addition of sodium or ammonium hydroxide which form soluble salts with the produced itaconic acid. The free acid is recovered from the spent medium by lowering the pH-value by addition of sulfuric acid. The adjustment of the pH-values in the fermenter as well as in the spent medium is not only costly, but also generates a significant amount of salts in a

mixture with the desired product and thus, further purification steps are required. By applying bipolar membrane technology the production of salts can be eliminated and the itaconic fermentation can be carried out more efficiently in a continuous process as illustrated in the production scheme depicted in Figure 7. The flow scheme shows a fermenter combined with an electrodiolysis unit with bipolar membranes. The fermenter is continuously fed with

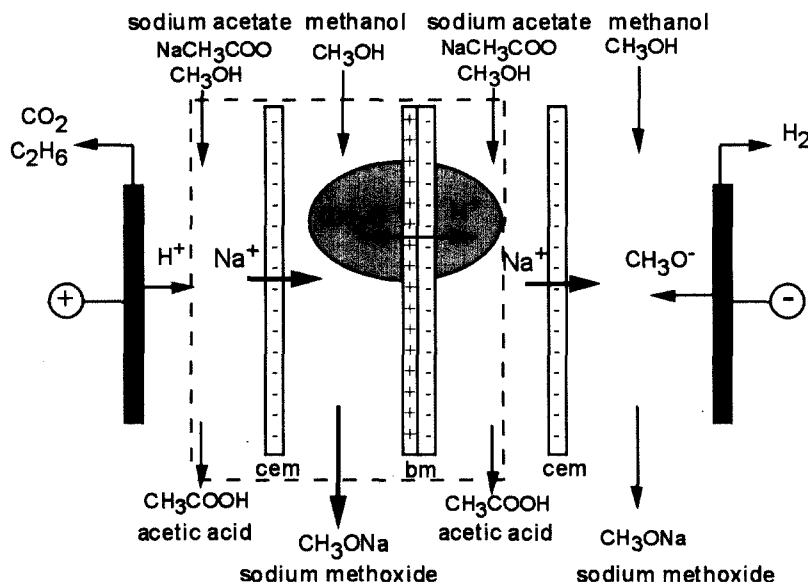


Fig. 8. Schematic diagram illustrating the electrochemical production of sodium methanolate from methanol and sodium acetate in bipolar membranes containing a two compartment cell unit.

substrate and its constituents passed through an ultrafiltration unit. The retained biomass is recycled into the reactor while the product containing filtrate is fed to the middle cell of a three compartment electrolysers repeating unit. In this cell the solution will be depleted of the ions. The cations, i.e. sodium or ammonium ions, permeate the cation-exchange membrane and form with the  $\text{OH}^-$  ions generated in the bipolar membrane  $\text{NaOH}$  which is concentrated and then fed back into the bioreactor to adjust the pH-value. The anions, i.e. the itaconate ions permeate the anion-exchange membrane and form with protons generated at the bipolar membrane the itaconic acid which is then concentrated and precipitated. Thus, the itaconic acid is produced in a continuous process without the addition of acids or bases, i.e. without the production of additional salts.

### 5.3. The electrochemical production of sodium methoxide by methanol dissociation

Bipolar membranes may not only be used for the electrochemical dissociation of water. They can also be applied for the dissociation of alcohol and thus

for the production alcohols as illustrated in the following example. Methanol, like water, is both a weak base and a weak acid. Its dissociation constant, however, is somewhat less than that of water. Thus, sodium methoxide can quite efficiently be produced from methanol and sodium acetate in non-aqueous media by the use of bipolar membranes according to the reaction scheme illustrated in Figure 8 which shows a bipolar membranes containing electrochemical stack consisting of two compartment cell systems in a repeating unit between electrodes.

Water free methanol and sodium acetate are fed into the cell formed by the bipolar and the cation-exchange membrane which is directed towards the cathode while water-free methanol is passed through the other cell. Under the driving force of an electrical potential gradient methanol is split in the bipolar membrane into protons and  $\text{CH}_3\text{O}^-$  ions which form  $\text{CH}_3\text{ONa}$  with sodium ion migrating from the sodium acetate containing cell towards the cathode. The acetate ions recombine on the other side of the bipolar membrane with the protons which were produced simultaneously with the  $\text{CH}_3\text{O}^-$  ions in the bipolar membrane to form acetic

acid. Thus, in the process sodium acetate and methanol are converted into sodium methanolate. The current efficiency is decreasing with increasing methylate concentration due to proton transfer from the acetic acid containing compartment through the bipolar membrane to the sodium methanolate containing cell. But all in all the process, however, seems to be technically feasible

## 6. Conclusions

The mechanism of the water dissociation in bipolar membranes can be rationalized by a hypothesis which postulates a catalytic reaction between a weak base and water. Based on this hypothesis chemical and thermal very stable bipolar membranes can be prepared and operated efficiently at current densities in excess of  $0.1 \text{ A cm}^2$ . The process has a many potential applications. There are, however, still a multitude of problems to be solved. Some are related to the poor selectivity of the bipolar membranes and poor acid blocking capability of the anion-

exchange membranes others are caused by the lack of application know-how and practical experience.

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