BIPOLAR MEMBRANES AND THEIR PRACTICAL APPLICATION

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Bipolar membranes are gaining increasing attention as an efficient tool for the production of acids and bases from the corresponding salts by electrodialytic 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.

The principle of electrodialytic water dissociation

The process of electrodialytic 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.
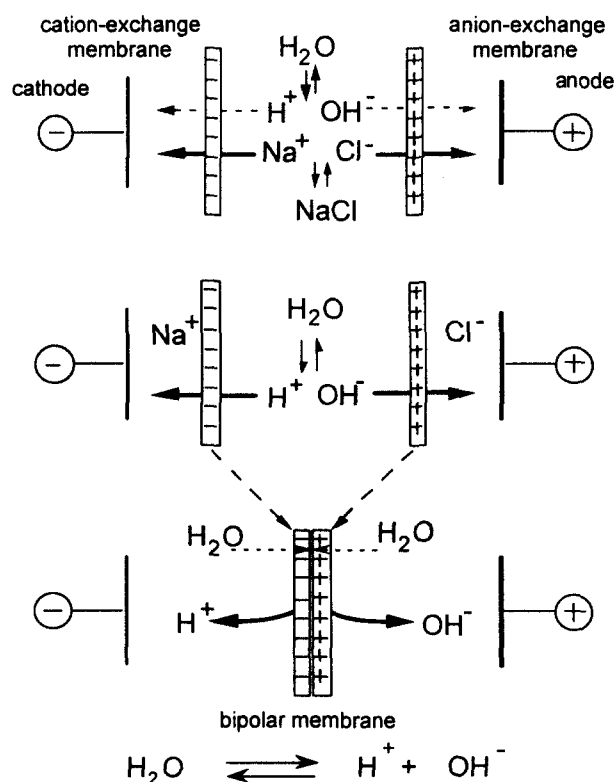

Fig. 1   Schematic diagram illustrating the principle of electrodiayltic water dissociation in   bipolar membranes

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. 1×10^{-7} mol L^{-1}. Bipolar membranes resemble a laminate of a cation- and an anion-exchange layer with an very thin, i.e. 4-5 nm transition region in which the water dissociation occurs according to the water dissociation equilibrium given by:

$$2\,H_2O \leftrightarrows H_3O^+ + OH^- \tag{1}$$

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

$$\Delta G = F\,\Delta U = 2.3\,RT\,\Delta pH \tag{2}$$

Here is ΔG the reversible Gibb's free energy, ΔU the electrical potential difference between the two solutions, R is the gas constant, T is the absolute temperature, F is the Faraday constant, and ΔpH is the difference between the pH-values of the two solutions separated by the bipolar membrane. For 1n acid and base solutions in the two phases separated by the membrane ΔU is 0.828 Volt and ΔG is 0.0222 kWh at 25°C.

To utilize bipolar membranes for the production of acids an bases from the corresponding salt solution they must be combined with monopolar ion-exchange membranes as illustrated in Figure 2.
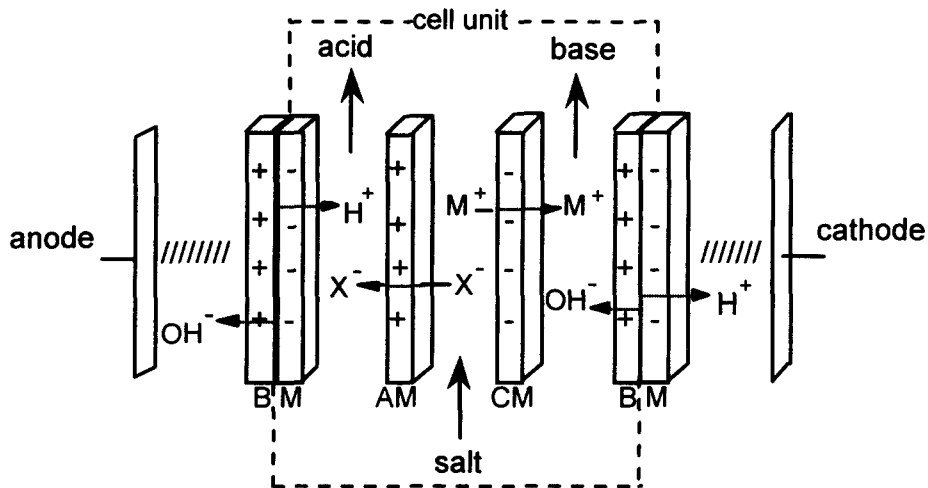

Fig. 2 Schematic drawing illustrating the principle of electrodialytic production of acids and   bases from the corresponding salts with bipolar membranes

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 process is the production of an acid and a base from the corresponding salt solution in an electrodialysis cell arrangement consisting of 3 individual compartments and three membranes, i.e. the bipolar and the

cation- and anion-exchange membrane. As in conventional electrodialysis a large number of the 3 compartment units can be stacked between electrodes.

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. Assuming an interphase layer thickness of 1 nm and a water dissociation rate constant k_d for pure water at 25° C of 2.5 x 10^{-5} s^{-1} the maximum current density through a bipolar membrane is ca. 1.4 x 10^{-8} 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 A cm^{-2} as demonstrated in Figure 3 a) which shows the current through a bipolar membrane as a function of the applied voltage.
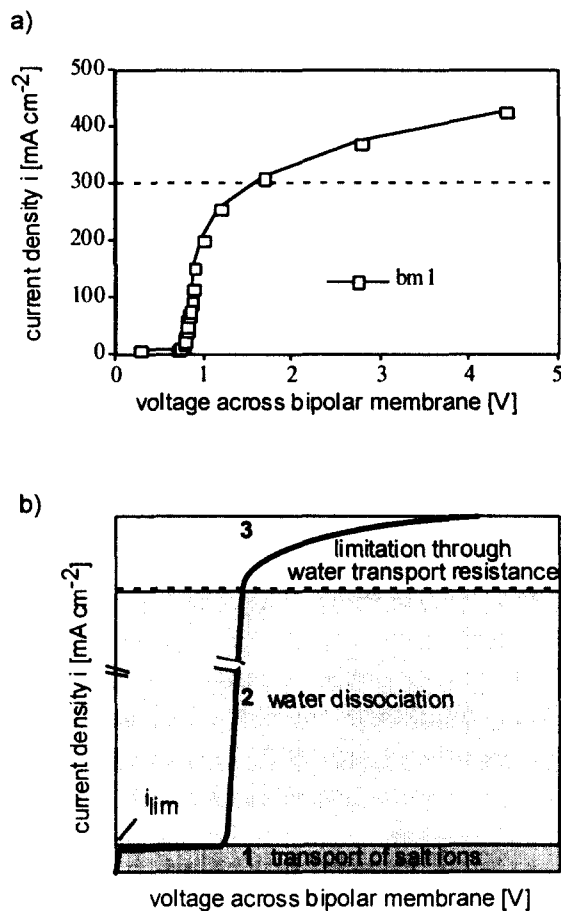
a)

b)

Fig.3 a) Current density as a function of the potential drop of a commercial bipolar membrane determined with a 1 mol L^{-1} Na_2 SO_4 solution and b) a schematic drawing indicating the limiting current density due to salt and water transport limitations

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 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 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.

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.

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.

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.

The performance of bipolar membranes and problems in practical applications

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 typical bipolar membrane is shown in Figure 3a). Here the current density is shown as a function of the potential drop across the membrane. The results indicate that the current density is low at potential differences of less than ca. 0.8 V. Then the current density increases up to 0.250 A cm^{-2} 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.

The electrodialytic 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 Figures 4 which illustrates the ion

transport in the bipolar membrane. Desired is a flux of H^+- and OH^- -ions from the interphase of the bipolar membrane as the result of the water dissociation. However, in additionally there is a flux of Na^+- and SO_4^{--} -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_4^{--} -ions and the acid by Na^+ -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
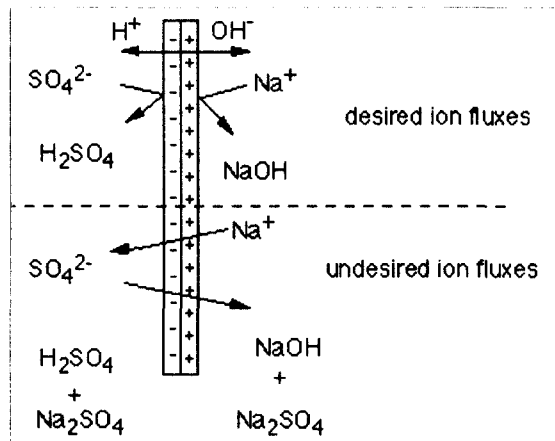

Fig. 4 Ion fluxes in a bipolar membrane during the production of acids and bases from a salt solution

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 5.
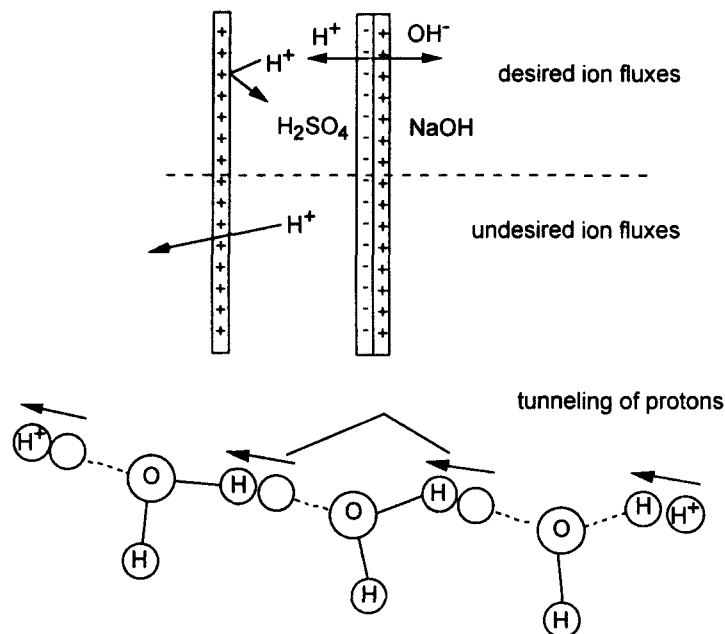
Fig. 5 Schematic drawing illustrating the desired and undesired ion transport through an anion-exchange membrane and the tunnelling transport mechanism of the protons in an aqueous medium

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 net result of the process is that protons and hydroxide ions generated in the bipolar membrane neutralize each other.

Applications of bipolar membranes

One interesting application of bipolar membranes is the production of caustic soda. The production of NaOH and H_2SO_4 from the corresponding salts has been investigated in great detail. 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 contamination by salt reaches values in excess of 0.03 mol L^{-1} at 4 molar base or acid concentrations. Thus, to improve the overall efficiency of the electrodialytic water dissociation with bipolar better proton blocking membranes have to be developed in addition to better bipolar membranes.

There are, however, a large number of other potential applications of the electrodialytic 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 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_2SO_4 and NaOH from Na_2SO_4 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_2, NO_x, etc. amines from waste air streams.

This list of potential applications of the electrodialytic 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 presentation three typical examples for the use of bipolar membranes w8ill be described in more detail. These are: 1) Recycling H_2SO_4 and dimethyl isopropyl amine from an acid scrubber, 2) Production of itaconic acid in a continuous fermentation process, 3)The electrodialytic production of sodium methylate by methanol dissociation.

Conclusions

Bipolar membranes can be prepared and operated efficiently at current densities in excess of 0.1 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 bipolar membrane properties others are caused by the lack of application know-how and practical experience.

Further reading

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