REVIEWS OF APPLIED ELECTROCHEMISTRY 5

Membrane cells for chlor-alkali electrolysis

D. BERGNER

Hoechst Aktiengesellschaft, Postfach 80 03 20, D-6230 Frankfurt/Main 80, Federal Republic of Germany

A description of the membrane process for the electrolytic production of chlorine, caustic soda and hydrogen from sodium chloride solutions is followed by a discussion of the present state of the art. This includes the development of cation exchange membranes and electrolysis cells. Finally, economic questions and trends for the future are discussed.

1. Introduction

In recent years the membrane process for the electrolytic production of chlorine, caustic soda and hydrogen has achieved a recognized position alongside the well established mercury and diaphragm processes. This development has been primarily due to the appearance on the market of perfluorinated cation exchange membranes.

The manufacture and properties of homogeneous ion exchange membranes with a high exchange capacity and high electrical conductivity were first described by Juda and McRae [1] and by Kressman [2] in 1950. The application of such ion-permselective membranes for the production of chlorine and caustic soda by the electrolysis of brine was first proposed by Ionics Inc. in 1951 [3] and 1953 [4]. At that time it was already clearly recognized that this process exhibited important advantages over the diaphragm and mercury processes [4]. Because the ion exchange membranes were made of hydrocarbon polymers with sulphonic or carboxylic acid groups, however, they were unstable in the presence of chlorine and the membrane process was therefore not suitable for chlor-alkali electrolysis. An attempt was made to protect the ion-exchange membrane from chlorine by combining it with a microporous diaphragm in a three-compartment cell [5] or by means of a perfluorocarbon membrane grafted with sulphonated styrene divinylbenzene [6].

Chemically stable ion-exchange membranes did not become available, however, until 1969. They were homogenous membranes consisting of fluorocarbon polymers with pendant sulphonic acid groups and were first used as solid electrolytes in fuel cells [7]. At the same time it was known that these ion-exchange membranes were stable to chlorine and caustic soda at temperatures up to 125° C [7], but the first report on the use of these membranes for the production of chlorine and caustic soda was only published in 1971 by Michalek and Leitz [8, 9].

In contrast to diaphragm cells, membrane cells lead to a caustic soda solution with a very low sodium chloride content, comparable to that from mercury cells. The inert perfluoropolymer membrane is used to separate the products in membrane cells; thus the use of asbestos, as in diaphragm cells, and mercury, as in mercury cells is avoided. The energy consumption and capital costs are also lower for the new process. In Table 1 it can be seen that membrane technology was introduced into commercial production in 1975. The number of membrane cells in commercial operation has increased steadily and now since the world production of chlorine is about 30 million tonnes, the share of the total now accounted for by the membrane process is about 1%. This relatively small share is mainly due to the depressed state of the chlorine market. Virtually no new capacities are being built and many plants are working well below capacity, but when existing electrolysis plants are replaced, it is by membrane plants. A further obstacle to the rapid introduction of membrane cells is the continuing rapid

Table 1. Membrane cell plants and their installed/planned capacity

Year	Total number	Total capacity NaOH $(t\,y^{-1})$
1975	2	60 000
1976	3	120 000
1977	5	170 000
1978	8	230 000
1979	9	240 000
1980	13	282 000
1981	20	351 000
1982	27	713 000
1983	30	880 000
1984	31	933 000
1985	32	960 000
not known	34	977 000

development of the technology, including ion exchange membranes and electrolysis cells. The extent of progress in the last few years becomes apparent if the summary presented here is compared with a review published in 1977 [10].

As a result potential users of membrane electrolysis await further refinement. However one should remember that the diaphragm process and the mercury process were first used for the commercial production of chlorine and caustic soda in the last decade of the 19th century. The technology of both processes has developed steadily up to the present. It is thus no wonder that the membrane process is also undergoing constant improvement.

2. Description of the membrane process

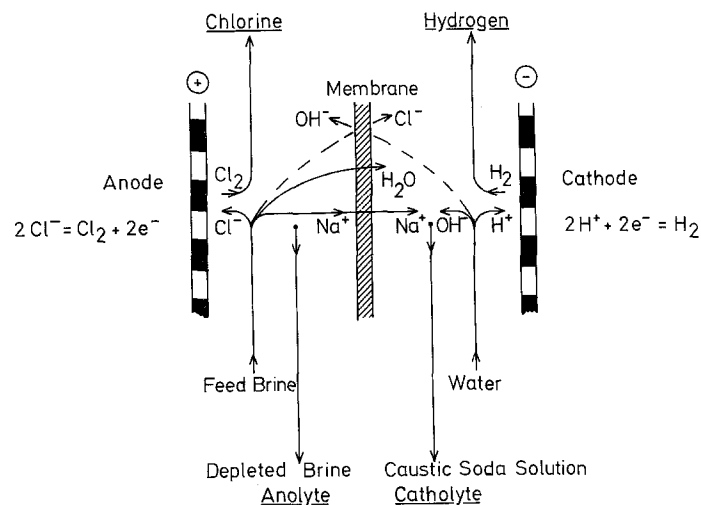Figure 1 shows schematically the basic reactions in a membrane cell. Brine enters the anode chamber and chlorine is generated at the anode; the brine depleted of sodium chloride leaves the cell along with chlorine gas. The cation exchange membrane, which divides the cell into an anode and a cathode chamber, is hydrodynamically impermeable but permits the passage of hydrated sodium ions. Water, from which hydrogen and hydroxyl ions are formed at the cathode, must be fed into the cathode chamber. Hydrogen and the caustic soda solution, concentration between 10% and 40% are drawn off from the cathode chamber.

A few side reactions are also indicated in the diagram. The most important in terms of volume is the water transport (by electroosmosis) through the membrane which accompanies the Na^+ transport. Hydroxyl ion transport from the catholyte to the anolyte must be prevented by the membrane. Otherwise there is a reduction in current efficiency, both in the anolyte chamber through loss of caustic soda and in the anode chamber through chlorate formation and also oxygen discharge at the anode [11, 12]. Finally, we should mention chloride ion diffusion from the anolyte to the catholyte which, however, occurs only at an extremely low rate owing to the high selectivity of the newer membranes.

When the membrane process is compared with the other conventional electrolysis processes for the production of chlorine and caustic soda, we can note the following differences:

1. The caustic soda solution obtained from the membrane cell is less concentrated (12–35%) than the 50% solution produced in the mercury process, but it possesses the same degree of purity

Fig. 1. Schematic picture of a membrane cell showing electrode reactions and transport processes.

($\leqslant 0.01\%$ NaCl) and no mercury is required for its manufacture.

2. In the diaphragm process the cell liquor leaving the cathode compartment contains 12% NaOH and 16% NaCl and it must be concentrated to a 50% solution in order to remove the salt. The caustic soda solution thus obtained contains about 1% NaCl. In comparison the membrane cell caustic solution can be used without being concentrated by evaporation because of its low salt content. Furthermore, no asbestos for the diaphragm is required for its manufacture.

3. Membrane cells are not adversely effected by power supply interruptions or other sudden changes in current or voltage.

4. Membrane cells do, however, require very pure brine which requires additional purification steps because the membranes are vulnerable to even temporary lapses in brine quality.

Figure 2 presents a process diagram for a mem-

Fig. 2. Flow sheet of a caustic soda–chlorine plant using membrane cells.

brane cell plant. Following brine resaturation by salt dissolution, the diagram shows conventional primary purification of the brine (which may additionally include sulfate precipitation by means of barium carbonate) and secondary purification by means of ion exchange resins. The depleted brine is recycled but on each loop a fraction (here $\frac{1}{10}$th) is treated to remove chlorate by the reaction

$$NaClO_3 + 6HCl \rightarrow 3Cl_2 + NaCl + 3H_2O.$$
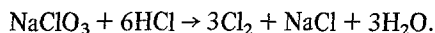
Additionally, Fig. 2 shows the caustic soda circuit. The catholyte leaving the cell is freed of hydrogen and collected in a receiver. From this receiver sodium hydroxide solution can be drawn off for direct use. More often, however, it is fed into an evaporator to yield more highly concentrated liquid caustic soda or solid caustic soda. Part of the catholyte is recycled to the cell (to act as electrolyte) after being replenished with the water required for electrolysis. The catholyte loop is used for two reasons. On the one hand this liquor circulation serves to remove the heat of reaction from the cell. The heat generated can be removed from the loop by cooling water in a heat exchanger or used for other purposes. A common purpose is the concentration of the caustic soda solution, for example in flash evaporators. The second reason for circulating the catholyte is that it simplifies the addition of water, which otherwise would have to be accomplished by the expensive process of metering small water streams into the individual electrolysis cells. Brine and catholyte circulation are completely separate from one another. One conceivable linkage, however, would be simply heating the feed brine before it enters the cell by means of heat exchangers in the caustic circuit.

3. Ion exchange membranes

3.1. *Membrane composition*

Membranes suitable for chlorine–caustic soda production are now being manufactured by a number of companies, some of which supply several types of cation exchange membranes for different applications. Examples include the Nafion® membranes of Du Pont [13], Flemion® membranes from Asahi Glass [14], Neosepta-F® from Tokuyama Soda [15] and Asahi Chemical membranes [16, 17]. In

1980 Du Pont opened a factory in Fayetteville, North Carolina, for the manufacture of Nafion resins and membranes. Du Pont supplies Nafion 901 for direct production of caustic concentrations of about 33% NaOH. With this membrane current efficiencies in the neighbourhood of 96% are obtained. For lower caustic concentrations the Nafion 100 series (without support cloth) and the 300 and 400 series (both with support cloth) are more suitable. The Flemion 230 supplied by Asahi Glass has properties comparable with those of Nafion 901. The Flemion 430 is suitable for lower caustic concentrations around 20% NaOH, and for KCl electrolysis Flemion 330 is the appropriate membrane. As the newest development Asahi Glass has announced the Flemion DX grades [18, 19]. Because of their hydrophilic surfaces these membranes can be operated with "zero gap", or more precisely, with minimum gap between them and the anode and cathode (cf. 3.2.). Interestingly, in 1981, Du Pont and Asahi Glass concluded an agreement covering the mutual exploitation of their patents on perfluorocarbon membranes. The prices for the membranes are governed by the type, order volume and other factors but are generally above \$400 m^{-2}. In Fig. 3 it can be seen that such cation exchange copolymers are made of tetrafluoroethylene (TFE) and sulphonated or carboxylated perfluorovinyl ethers. During polymerization, the ion exchange groups are protected as sulphonyl fluorides or esters and converted to the sulphonic acid or carboxylic acid form by hydrolysis before the membrane is used. Thus the
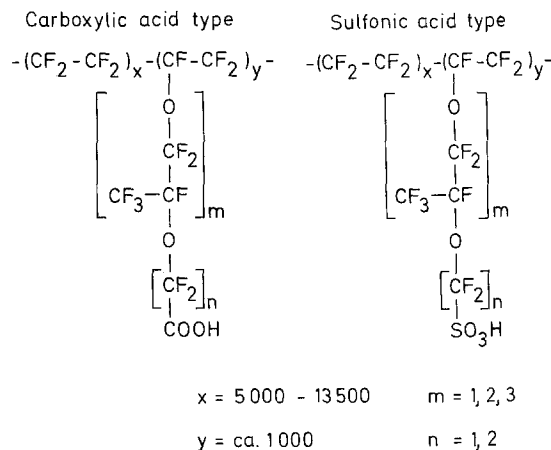
Carboxylic acid type   Sulfonic acid type

$-(CF_2-CF_2)_x-(CF-CF_2)_y-$ $-(CF_2-CF_2)_x-(CF-CF_2)_y-$

$$\begin{bmatrix} O \\ | \\ CF_2 \\ | \\ CF_3-CF \end{bmatrix}_m$$
$$O$$
$$\begin{bmatrix} CF_2 \end{bmatrix}_n$$
$$COOH$$

$$\begin{bmatrix} O \\ | \\ CF_2 \\ | \\ CF_3-CF \end{bmatrix}_m$$
$$O$$
$$\begin{bmatrix} CF_2 \end{bmatrix}_n$$
$$SO_3H$$

$x = 5\,000 - 13\,500$ $m = 1, 2, 3$

$y = ca.\ 1000$ $n = 1, 2$

Fig. 3. Chemical composition of perfluorinated polymers for cation-exchange membranes.

copolymers consist of a CF_2 backbone and side chains with pendant carboxyl and/or sulphonic groups. These functional groups form ionic clusters but the resin itself is not cross-linked. The most recent findings on cluster formation in ion exchange resin have been presented by Yeager and Steck [20] and by Gierke et al. [21].

The ion exchange resins are formed into films by conventional methods. These films can be used as single layer or multilayer membranes; in the latter, two films with the same ion exchange group but different ion exchange capacities are combined or a carboxyl and a sulphonyl film are laminated together. Another technique that has been used is the chemical formation of thin carboxyl layers on sulphonyl membranes or sulphonyl layers on carboxyl membranes in order to improve the selectivity or reduce the electrical resistance. The membranes are generally reinforced by being laminated on PTFE or PTFE/rayon cloth, but reinforcement with fluoropolymer fibrils has also been used. Reinforcement raises the tear-strength of the thin membranes, which have a thickness of 0.1–0.2 mm, and it helps increase the dimensional stability of the membranes. As a result of water sorption, the membrane can, on going from the dry state to various electrolyte solutions, contract or expand by a few per cent. It is important to keep these expansion and contraction processes under control because they can cause the membrane to form wrinkles in the electrolysis cell. Gaseous products of electrolysis can be trapped in these wrinkles and thus block part of the effective membrane surface, which in turn results in higher electrical resistance and higher cell voltage.

3.2. Chemical and physical properties, lifetimes of membranes

The aging of the membrane, which has long been known, is attributable to the deposition of only slightly soluble metal compounds, especially calcium salts, in the membrane [22]. These cause irreversible destruction of the membrane structure by the formation of micropores, which cause a decrease in the current efficiency due to increased migration of hydroxyl ions from the cathode chamber into the anode chamber. For this reason an especially pure brine is required for the operation of the membrane cell.

Conventional methods of brine purification, such as the use of soda ash and caustic soda, yield calcium concentrations of about 5 ppm in the brine. For the membrane process the brine must be subjected to a secondary purification stage, which usually employs ion exchange resins. The result is a reduction in calcium content by a factor of about 100 to final values of ≤ 50 ppb calcium in the brine. When brine with this level of purity is used, hydroxides can no longer be deposited on the anodic side of the membrane surface. Such hydroxide coatings lead to increased electrical resistance and hence to higher energy consumption.

Let us now consider the matter of membrane service life. One can never specify the service life without also stating such relevant factors as the cost of replacement membranes and the energy costs for electrolysis. The service life is chosen so as to optimize the net effect of these factors. Membrane costs are determined by the type of membrane and the sliding scale of membrane prices in relation to order volume. The energy costs depend on the price of electric power and the power consumption; the latter depends on cell voltage and current efficiency. The cell voltage is, in turn, a function of current density, the type of cell and electrodes used and the brine quality. To achieve high current efficiency it is especially important to have uniformly high brine quality. A membrane that is guaranteed for 2 years may not last this long if a disturbance in the brine supply should occur, but the lifetime can be extended beyond this period if the brine is of especially high quality.

An interesting phenomenon to be taken into account is the transport of water molecules through the membrane. It occurs because water of hydration is transported with the sodium ions. Depending on the type of membrane and the anolyte and catholyte concentrations, 3–9 moles H_2O per mole Na^+ are transported into the cathode chamber [12]. A large part and under certain conditions even the entire quantity of water required in the cathode chamber comes from the brine in this way. Consequently the amount of maximum-purity water required to be fed into the cathode chamber is less than that calculated for water decomposition and the dilution of caustic soda. That is to say the anolyte is concen-
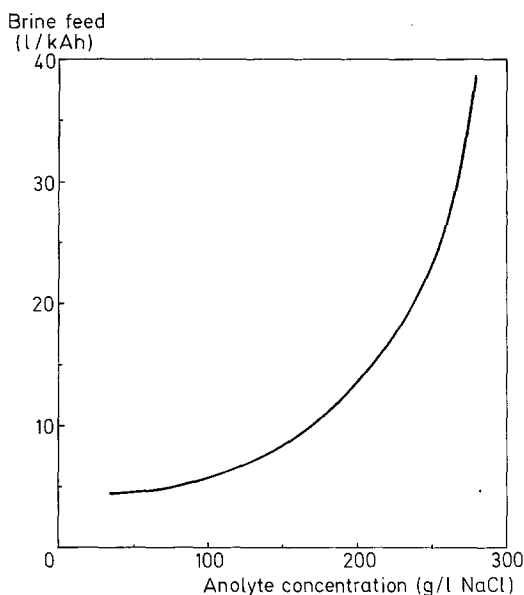
Fig. 4. Brine feed for membrane cells versus anolyte concentration.

Fig. 5. Cell voltage of a membrane cell at different distances between cathode and membranes of different hydrophilicity.

trated in the anode chamber. As a result, in membrane cells, which also permit the use of much lower sodium chloride concentrations ($\leqslant 200$ g dm^{-3} NaCl) than, for example, mercury cells ($\geqslant 265$ g dm^{-3} NaCl), brine consumption is comparatively low. This is shown in Fig. 4, where brine feed per unit charge consumed is plotted as a function of anolyte concentration [23]. Thus, in comparison with the mercury process, the flow rate of brine into membrane cells is very low, e.g., with a membrane cell with 200 g dm^{-3} NaCl in the anolyte, the flow rate may be only 0.2–0.25 that in a mercury cell. This reduces substantially the capital expenditure for setting up membrane electrolysis since less brine need be purified and pumps, pipes etc need not be as large.

A phenomenon which can cause problems particularly when the membrane cells are operated with minimum electrode gap, or so-called 'zero gap', is the adhesion of gas bubbles to the membrane. This was revealed in studies of the interaction between the electrodes and the membrane in water electrolysis. Interestingly this effect is more pronounced with hydrogen bubbles than with chlorine bubbles. Further, it occurs less with hydrophilic perfluorosulphonic acid membranes and more with the less hydrophilic but more ion-permselective perfluorocarboxylic acid
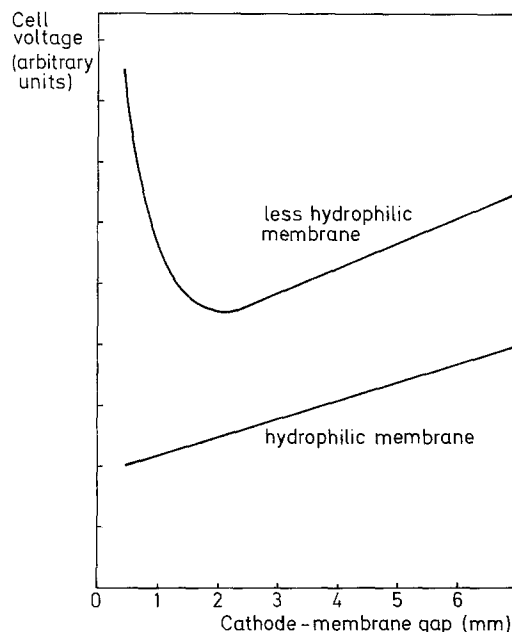
membranes. Gas blinding results in higher electrical resistance of the membrane and consequently, in increased cell voltage and energy consumption by the electrolysis. Hydrophilicity can be increased by various measures, such as the introduction of inert particles into the membrane surface [24] or mechanical roughening of the membrane [25], so that the gas bubbles no longer adhere. This effect can be demonstrated experimentally by measurement of the cell voltage of a membrane cell as one of the electrodes is moved closer to the membrane, as is shown in Fig. 5 [23]. As the cathode approaches the membrane the cell voltage falls, but contact of the hydrogen-covered cathode with the less hydrophilic membrane leads to a voltage increase. If the membrane has a hydrophilic surface this effect does not appear. With such membranes it becomes possible to operate the cell with zero or minimal gap, meaning that both the cathode and the anode are in contact with the membrane surface. This has the following advantages:

1. The voltage drop across both electrolytes, including the additional voltage drop resulting from the gas bubbles distributed throughout the electrolytes, is eliminated.

2. The voltage drop caused by the adhesion of the gas bubbles to the membrane, so-called gas blinding, is also eliminated.

3. The formation of wrinkles in the membrane is largely avoided owing to the pressure of the electrodes on both sides.

4. Because the membrane is supported on both sides by the electrodes, thinner membranes with lower electrical resistance can be used.

5. For the same reason the risk of damage to the membrane due to motion caused by pressure fluctuations or pressure surges is reduced.

The cell voltage of a membrane cell with minimal electrode gap is determined solely by the resistance of the membrane and the overvoltages on the electrodes. It can be predicted that such designs will replace the older designs with 2–4 mm electrode gaps because of their lower energy consumption and greater operational reliability.

3.3. Effects on product quality

In a discussion of product quality, interest centres on the caustic soda. The maximum caustic soda concentrations that can be achieved, even with the newer membranes, lie in the range 33–40% NaOH [18]; the optimal concentration in terms of efficient use of electrical energy probably lies between 33 and 36% NaOH. For most applications these concentrations are sufficiently high, so that only a fraction of the total output requires concentration to 50% NaOH. The melting points of 50% and 33% caustic soda solution are approximately equal ($+ 11°C$ and $+ 10°C$), so that the same temperature conditions apply for the transport of both grades of caustic soda. For lower caustic soda concentrations (10–25% NaOH) and caustic potash production other special membranes must be used [18]. The salt content of the caustic soda solution as it leaves the cell is around 10–50 ppm NaCl, which is even lower than that of the mercury cell caustic solution. The chlorate content of this solution has similarly low values.

Whereas the hydrogen generated at the cathode is of high purity ($\geqslant 99.9\% \, H_2$), the chlorine content of the anode gas is only about 98–99%, depending on the caustic current efficiency and the anode material [11]. The remainder consists largely of oxygen (1–2%) and the hydrogen content is negligibly small. If the caustic soda current

efficiency falls it is because of OH^- transport through the membrane and this leads to oxygen evolution at the anode. This may be avoided by the addition of acid to the brine to neutralize hydroxyl ions that pass from the cathode chamber through the membrane into the anode chamber [11]. To achieve complete neutralization a volume, $V \, (dm^3 \, kA^{-1} \, h^{-1})$, of hydrochloric acid (37% HCl) is required:

$$V = 3.1 \, (1 - S_{NaOH}),$$

where S_{NaOH} is the caustic current efficiency expressed as a fraction of 1. If the acid addition to the brine exceeds this level so that the acidity of the discharged anolyte is greater than $pH = 2$, there is a danger that hydrogen ions will migrate through the membrane toward the cathode. This would lead to damage to the carboxyl membrane or, in the case of sulphonyl membranes, to a reduction in the caustic current efficiency.

4. Membrane cells

4.1. Electrical connection

A distinction is usually made between monopolar and bipolar cells. It is based not so much on a property of the cells as on the electrical interconnection of the individual cells in an electrolyser, which can consist of 15 to 150 cells. If the cells are connected in parallel, the electrolyser is monopolar; the electrolyser current is the sum of the individual cell currents and the voltage on the electrolyser is the same as that across a single cell. If the cells are connected in series, the electrolyser is bipolar; the electrolyser voltage is the sum of the cell voltages and the total current of the electrolyser is equal to that flowing through a single cell [26]. In a system containing many cells it is obvious that monopolar electrolysers require considerable currents (50–100 kA) and bipolar electrolysers high voltages (100–400 V).

Figure 6 illustrates the construction principles of both monopolar and bipolar cells.

4.2. Electrode materials

Normally the anodes are made of titanium and the cathodes of mild steel, stainless steel or nickel [27]. The passivity of titanium under anodic conditions
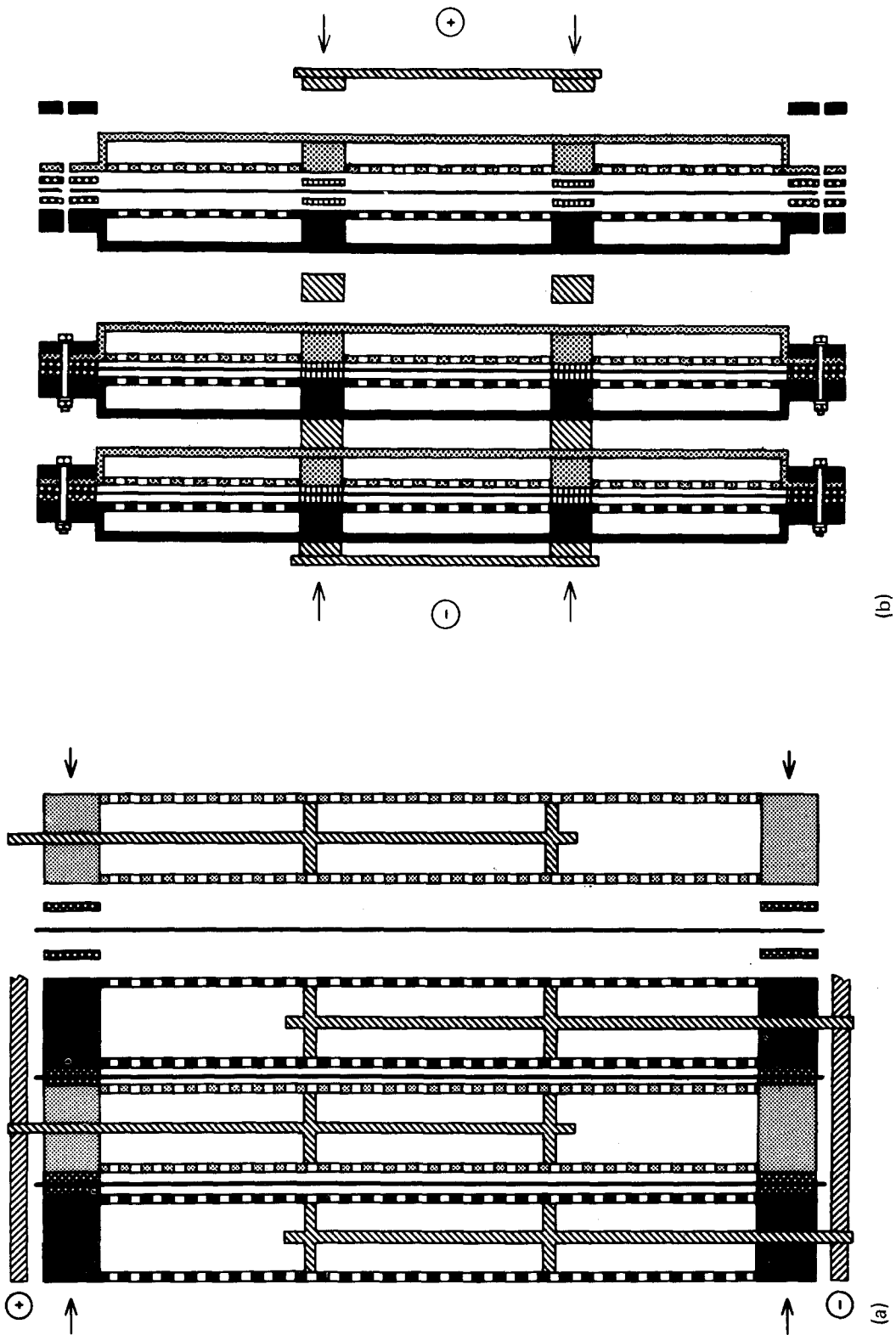
Fig. 6. Schematic drawing (horizontal section) of a monopolar (a) and bipolar (b) membrane cell. Materials are marked as follows: Steel (black), titanium (dotted), copper (hatched), gasket (crosshatched).

is overcome by oxide (e.g., RuO_2/TiO_2 [28], PdO [29]) or metallic (e.g. Pt/Ir [30]) coatings containing noble metals; thus the anode overpotential is very low. The 300–400 mV overvoltage for hydrogen evolution on the above cathode materials can be reduced by catalytic (noble-metal-containing) or high-surface-area (e.g. Raney nickel) coatings [31, 32]. In contrast with the anode materials, service-life problems are still being encountered with the cathode materials. It is not expected that the answer will be found in the cathode coatings containing noble metals [27].

4.3. Cell design

The *monopolar cells* shown in Fig. 6 consist of square or rectangular frames, area about 1 m^2, which support on both sides expanded metal electrodes of the same type. In the anode chamber the frame and electrodes are made of titanium; the cathode material is mild or stainless steel. The current supply outside the cell is provided by copper rods or copper busbars, which penetrate the frame. In the cathode chamber they are clad with steel and in the anode chamber with titanium. As shown in Fig. 6, the frames are pressed together in an arrangement in which anode and cathode frames alternate. The division into anode and cathode chambers is provided by the ion exchange membrane, which together with gaskets is inserted between the frames. Not shown here or in the following figure are the feed pipes for brine and dilute caustic solution and the outlet pipes for chlorine/anolyte and hydrogen/catholyte. Thus each chamber, i.e., each frame, has one inlet pipe and one outlet pipe. Also not shown are the end plates which close the two open end frames of an electrolyser. An important feature of this design is that the anode and cathode chambers are separated from one another only by membranes and not by metal walls. A large number of such single frames are pressed together in a suitable device like the frames of a filter press. For this purpose one uses hydraulic presses (Asahi Glass) [33] or tie rods (Uhde) [34], or the different segments, e.g. the cathode elements, are bolted together individually (Diamond Shamrock) [35]. Metal *bipolar cells* of the filter press type are offered by Asahi Chemical [36] and Tokuyama Soda [37]. A bipolar cell of a different basic

design is shown in Fig. 6. The design shown here is not the filter press type, since each cell consists of half-cells or anode and cathode half-shells that are bolted together. The cathode half-shell consists of a steel frame that is closed on one side by a steel wall and on the other by the expanded metal cathode. The back wall and the cathode are connected by power-transmitting support elements of steel, which carry on the side adjacent to the membrane, spacers made of an insulating material.

The anode half-shell is similarly constructed except that this structure, consisting of a titanium back wall and a titanium anode, is provided with a steel support frame in order to save titanium. Again; in this case the anode and the back wall are connected by power-transmitting support elements of titanium and fitted with insulating spacers. After the membrane, together with gaskets, is inserted, each anode frame is bolted to a cathode frame along their periphery to form a cell. In principle a single cell of this type can be used alone for electrolysis after being hooked up to a suitable power supply. However, generally here too, a large number of single cells are mounted in a frame and pressed together by means of a single pressing device. The compressive force is transmitted through the above-mentioned insulating spacers within the cells and through copper contact pieces between the individual cells. This compression serves to facilitate current transmission from cell to cell and not the sealing of the individual cells, since this seal is provided by bolting the frames together. A system of this type has been developed by Hoechst [38].

Besides these two metal cells shown here as examples, there are also other membrane cells with plastic frames. They are constructed as bipolar filter press cells. The frame and partition wall are made of plastic; the anode and cathode of two adjacent frames are connected by power-transmitting connnectors. The current conductors through the partition wall must be gas and liquid tight. Furthermore, these plastic cells have a special feature that metal cells cannot be provided with, namely channels for feeding in the electrolytes and discharging the products. These channels are formed by openings in the frames similar to those in plate heat exchangers. From these channels the anode and cathode chambers can be supplied and tapped through small openings that

are also drilled in the frame. Cells of this type are offered by Hooker [27, 39], Ionics [40] and Krebskosmo [41, 42].

A type of cell that differs greatly from those described above is the monopolar FM 21 cell from ICI [43–46]. The distinguishing features are, first of all, the size of the membrane area, only $0.21 \, m^2$, and secondly, a special electrode design, which when compared with the expanded metal variety is very simple but extremely effective. The cell has electrolyte distribution and discharge channels and is thus very compact. The small size of the electrodes is advantageous in their manufacture and mounting, and in respect of the voltage drop in the electrode material. Because of their special structure the electrodes are suitable both for operation with normal electrode gap sizes (2–4 mm) and for operation with minimal or zero gap.

The newer cells with minimal electrode gap have not been described in detail. In 1980 the 'SPE' cell of the Oronzio de Nora company was introduced [47, 48]. It is a bipolar filter press cell with an electrode surface of about $1 \, m^2$. It is not known whether these cells are actually solid polymer electrolyte cells, similar to those developed by General Electric [49], where porous gas and liquid permeable metallic layers are bonded to the membrane surface as catalytic electrodes. In addition to SPE technology, De Nora also describes in the patent specifications [48] the possibility of employing zero gap electrodes without the special SPE electrode–membrane composite. It is possible that in the SPE process the membrane surfaces are hydrophilized by the bonding together of the electrodes and membrane, similar to the particle embedment technique or roughing of the membrane as described in section 3.2. If the current collectors pressed against either side of the membrane can function as electrodes when the electrode–membrane bond is damaged, SPE electrolysis should convert to zero-gap operation. Under these assumed conditions the zero gap process is certainly the less expensive alternative.

The Asahi Glass Zero Gap Electrolysis Cell (AZEC) [18, 19] is not an SPE cell in the sense used above, but a configuration in which both the anode and the cathode are an integral part of the cell structure and in contact with both sides of the membrane. This design requires specially prepared

hydrophilic membranes, such as the Flemion-DX type [18], as described in section 3.2.

The advantages and disadvantages of the different cell types, for example bipolar versus monopolar cells, are being constantly debated [15]. Here only two aspects will be chosen for discussion. A monopolar cell consists essentially of frame, gasket (or possibly a frame–gasket combination), electrodes and membranes. A bipolar cell has the same components, but additionally the partition wall between the anode and cathode chambers. The argument that this fact makes bipolar cells more complicated and expensive can be countered with the observation that small, isolated units operate more reliably. Nor is the argument that the leak currents in bipolar electrolysers lead to corrosion valid. There are many ways of suppressing these leak currents, which is proven by the fact that about 80% of installed membrane-cell capacity involves bipolar cells.

Currently the appearance of cells with a small electrode surface has provoked a discussion concerning their advantages and disadvantages. The advantages of small cells described above are counterbalanced by the disadvantage of the increased requirement for gasketing. Thus, for example, for a $100 \, t \, day^{-1}$ plant $(2 \, kA \, m^{-2})$; $3 \, m^2$ cells have 3.8 km of gasketing, $1 \, m^2$ cells have 6.6 km and $0.25 \, m^2$ cells 15.7 km of gasketing. Which argument carries more weight? Which system is better? Only many years of operation of both cell types can decide. The selection process will then lead to a few very similar cell types, a familiar occurrence in the history of technology.

5. Economics of the membrane process

5.1. *Capital costs*

A comparison of the capital costs for the three electrolysis processes is extremely difficult. Hence the following discussion will only provide a rough sketch of the capital costs situation. Whereas the capital costs for the power supply, the brine supply and chlorine treatment are about the same for all three electrolysis processes, there are larger differences in the costs for the cell room, which are lower for the membrane process than for the mercury process and lowest for the diaphragm process. The cost of the caustic soda extraction is

especially high for the diaphragm process, less than half as high for the membrane process and minimal for the mercury process. On the other hand with the mercury process additional capital costs are incurred for measures to prevent mercury emission. The overall picture that emerges is as follows: if the capital costs of the mercury process are taken as 100%, the costs of the diaphragm process run to 105% and for the membrane process 90% on the same scale. Similar results have been obtained by Nagamura et al. [33]. Overall then, if the estimation error is assumed to be ± 10% and all conditions are equal, the capital costs are the same for all three processes. Important advantages accrue for one process over the others when the conditions pertaining to the feedstock or product are changed. For example, the use of solution-mined rock salt favours the diaphragm process, and if pure 35% caustic soda can be used without concentration the advantage would shift toward the membrane process [50].

Table 2 shows the operating characteristics for the processes for sodium chloride electrolysis. The differences in current density are apparent, about $10 \, kA \, m^{-2}$ for the mercury cell and roughly $2 \, kA \, m^{-2}$ for the diaphragm and membrane cells. For the membrane cell higher current densities up to $3 \, kA \, m^{-2}$ are used, even current densities up to $4 \, kA \, m^{-2}$ have been achieved. However, depending on energy, capital and other costs the optimum current density lies between 2 and $3 \, kA \, m^{-2}$. Nagamura et al. [14] decided upon $2.1 \, kA \, m^{-2}$ as the optimum under their specific conditions. The cell voltages in Table 2 are valid for the present state of the art. The last line shows figures for expected technology in the membrane process, i.e., catalytic cathodes, thinner, hydrophilic membranes and minimal or zero electrode gap.

5.2. Energy costs

Of special interest are the energy consumption figures, shown in Table 2 as d.c. power consumption. The picture changes when the energy needed for caustic concentration are included. If 600 $kWh \, t^{-1} \, NaOH$ (1 t steam is equivalent to 285 kWh) are added to the energy consumption figures for concentrating the caustic soda to 50% NaOH in the diaphragm process and $200 \, kWh \, t^{-1} \, NaOH$ for the membrane process, then it will be seen that the mercury and diaphragm processes are the more energy-intensive processes (cf. also Nagamura et al. [33]). Also to the advantage of the membrane process are the low energy requirements for raising the concentration of the caustic soda solution by a relatively small amount from 35% to 50% NaOH and the fact that waste heat from the electrolysis can be used in flash evaporators. As mentioned in the discussion of capital costs, the picture becomes even more favourable for the membrane process if one can omit the caustic concentration stage. It can already be said that with decreasing cell voltage in the membrane process, more efficient use must be made of waste heat [51]. Otherwise it is not even possible to maintain the cell temperature at 80–90° C without an additional heat supply if the current density is not to be increased.

5.3. Present commercial processes

Table 1 reveals how far the construction of plants utilizing the membrane process has already progressed and what capacities will be built in the next few years. Table 3 contains, along with the cell data of various manufacturers, the electrolysis plants now in operation and those still to be built. All of them are comparatively small chlor-alkali

Table 2. Operating characteristics of mercury, diaphragm and membrane cells

Process	Current density (kA m^{-2})	Cell voltage (V)	Current efficiency (%)	Energy consumption (kWh t^{-1} NaOH)	Caustic soda	
					% NaOH	% NaCl
Mercury	10	4.15	96	2900	50	0.006
Diaphragm	2	3.3	95	2350	(12)	(14)
					50	1
Membrane	2	3.3	95	2350		
(present state of the art)	3	3.65	95	2600	33–35	0.004
Membrane	2	2.9	93	2100		
(future technology)	3	3.15	93	2250	33–35	0.004

Table 3. *Properties of different membrane electrolysers and their installed and planned capacity*

Company	Type	Anode area per membrane (m^2)	Current density (kA m^{-2})	Membranes per electrolyser	Production per electrolyser (t NaOH d^{-1})	Membrane type	Total capacity (kt NaOH y^{-1})	Total number of plants
Asahi Chemical	bipolar, metal	2.7	3.8	80	28	Asahi Chemical	520	7
Asahi Chemical	bipolar, metal	5.4	4.0	82	56			
Asahi Glass	monopolar, metal	2.0	2.0	64	8.8	Flemion®	54	4
Asahi Glass	monopolar, AZEC	3.0	3.0	—	—			
De Nora	SPE, metal	~1	3.3	—	—	Nafion®	—	—
Diamond Shamrock	bipolar, metal	1.02	3.1	32	3.3	Nafion®	42	3
Diamond Shamrock	monopolar, metal	1.44	3.1	12	1.7	Nafion®	117	6
Hoechst	bipolar, metal	1.15	3.0	30	3.5	Nafion® Flemion®	—	—
Hoechst	bipolar, metal	2.66	3.0	30	8.1			
Hooker	bipolar, plastic	1.6	3.0	50	8.2	Nafion®	42	3
ICI	monopolar, metal	0.21	3.0	120	2.4	Flemion®	125	2
Ionics	bipolar, plastic	~1	2.7	60	5.5	Nafion®	17	3
Krebskosmo	bipolar	0.5	3.0	30	1.5	Nafion®	—	—
Krebskosmo	bipolar	2.4	3.0	60	14.7	Nafion® Flemion®		
Olin	monopolar, metal	—	3.0	—	5	Nafion® Flemion®	—	—
Tokuyama Soda	bipolar, metal	1.25	3.1	50	7	Neo-septa-F®	37	2
Tokuyama Soda	bipolar, metal	2.70	3.1	90	25			
Uhde	monopolar, metal	1.68	3.0	50	8.6	Nafion® Flemion®	23	1

electrolysis plants. The most recently built mercury and diaphragm process plants have capacities in the range of 500–1000 t day^{-1}, equivalent to 180 000–360 000 t y^{-1}. In contrast, the membrane plants presented here have an average capacity of 18 000 t y^{-1} NaOH, with the smallest producing 4000 t y^{-1} NaOH. One can conclude therefore that small and very small plants can operate economically using the membrane process. This aspect makes the process interesting for users who require sodium hypochlorite solution, for example for pulp bleaching, the production of chemicals or sewage treatment.

The possibility of building plants with small capacities eliminates the necessity of transporting liquid chlorine and caustic soda solution by rail or water and also storage on the user's premises. An added advantage of the membrane cell is that its output can easily and quickly be adjusted to the requirements for electrolysis products or the availability of electric power or cheap peak power.

6. Outlook

With the appearance of improved membranes such as the Nafion 901 and Flemion 230, many processes designed to compensate for the deficient selectivity of older membrane types have become superfluous. They include the three-compartment cell [5] and the stepwise increase of caustic soda concentration by series catholyte-flow operation of membrane cells [12, 52, 53]. Also apparently belonging to this class are combinations of the membrane and the mercury processes [54, 55] and processes in which reactions (formation of carbonate [56] or phosphate [57] occur in the cathode chamber and consume the caustic soda as it forms.

Attempts have been made for years to replace hydrogen evolution in chlor-alkali cells by the introduction of oxygen or air consuming electrodes, which are familiar in fuel cell technology. This appears to be an especially promising approach for the membrane cell and many companies and research institutes in all parts of the world are engaged in the development of suitable electrodes and electrolysis cells. The aim is to replace the hydrogen-generating steel electrode

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

with an oxygen consuming catalytic cathode:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-.$$
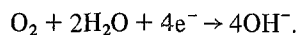
Although the change in the reaction at the cathode results in a 1.23 V reduction in the thermodynamic decomposition voltage, the practical decrease in the cell voltage amounts to about 0.8 V or roughly 20% because of the poor kinetics of oxygen reduction [58, 59]. Even so, many problems must be solved before this technology can be used in commercial cells. In principle, an alternative is to oxidize the hydrogen formed in a membrane cell in a separate fuel cell, but this would involve greater energy losses than the use of a membrane cell with an oxygen consuming cathode.

While membrane electrolysis normally operates at slightly above ambient pressure, at approximately 10 mbar, it is desirable and now also possible to achieve pressures in the range of 0.1 bar in order to save on blowers for the transport of the electrolysis gases. If electrolysis could be run at higher pressures around 10 bar, the apparatus for the treatment of the gaseous products could be smaller and electrolysis could operate at higher temperatures than presently, because due to the pressure there would be less water evaporation. One result should be a reduction in cell voltage. An added effect would be the possibility of liquefying the chlorine under pressure with cooling water after it is dried. This would mean savings in energy and capital costs for compressors and refrigeration equipment [60, 61].

The membrane cell of the future will probably be a design employing thinner hydrophilic membranes, with low over-voltage cathodes and minimal gap between anode and cathode. Operating at current densities of around 3 kA m^{-2}, such cells consume energy at a rate below 2250 kWh t^{-1} NaOH. They are currently being introduced to the market. Possibly these cells will also operate at higher pressures (0.1–1 bar). If it is assumed that the anode will retain its full effectiveness for five years, the membrane for at least two years and the catalytic cathode coating for as long as the membrane under technical conditions, then the membrane process is superior to the two older processes.
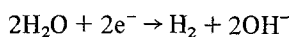
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