



Review article

Membrane electrolysis—History, current status and perspective

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ABSTRACT

This review is devoted to membrane electrolysis, in particular utilizing ion-selective membranes, as an important part of both existing and emerging industrial electrochemical processes. It aims to provide fundamental information on the history and development, current status and future perspectives of membrane electrolysis. An overview of the history of electromembrane processes is given with the focus on brine electrolysis since it is the predominant electrochemical industrial technology utilizing ion-selective membranes. This is followed by a summary of the wide range of hydrogen-based energy conversion processes with different degrees of maturity, i.e. water electrolysis and fuel cells, which promise to become the next generation of major electromembrane processes. The overview of the state-of-the-art is rounded off by a number of smaller-scale processes utilizing ionically conducting solid electrolytes and ion-selective membranes that are already commercially available. The article concludes by considering potential future developments in this exciting field of electrochemistry.

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1. Introduction

Currently a broad range of electrochemical processes is used in industry. They comprise inorganic as well as organic compound production. Electromembrane processes are an important segment of electrochemical technologies. Chlorine and caustic production is by far the largest-scale electrochemical technology. It should be stressed that industrial chlorine and caustic electrolysis units installed during the past two decades are almost exclusively based on membrane electrolysis. This is due to numerous advantages over competing technologies, brought about by modifications to this process and consisting mainly of lower energy demands and minimal impact on the environment, while maintaining high product purity. The availability of new types of ionically conductive, selective and stable membrane materials has opened up this very promising field with high potential for future growth and for the solution of numerous serious problems facing industrially developed countries. The term “membrane” is specified more closely here, as it is often misinterpreted. In general, a membrane is defined as a barrier separating two fluid streams and facilitating selective mass transport between these two streams. The chemical (or electrochemical) potential gradient acts as a driving force. Whereas most of the membranes act on the principle of pore dimension or selective non-electrostatic interaction of transport species with the membrane material, ion-selective membranes are based on interaction between charge carrying species. They can be based either on incorporating an ionogenic functional group into the membrane structure (typical of polymeric materials) or on introducing vacancies into crystalline structure of a solid material. Membranes other than ion-selective membranes are not typically applied in electrochemical processes, as they would represent too large an ohmic barrier to the charge transport. In some cases porous separators, known as diaphragms, are used in electrochemical cells. These separators do not provide selective transport and thus cannot be denoted as membranes, even though this is often the case.

One of the problems that had to be solved on the way from the conception and development of many electrolysis processes to their industrial use was the separation of the anolyte and the catholyte. This was mainly motivated by the need to increase selectivity and to exclude the participation of precursors or intermediate electrolysis products in undesired reactions at the electrode with opposite or even the same polarity. Furthermore, the purity of the products, and thus the current efficiency of the process, was enhanced. Later, in the 1950s, the first systems were developed, enabling the classical liquid electrolyte to be replaced by a solid one and thereby fulfilling the role both of an electrolyte and a membrane/separator. At present, different types of porous separators (diaphragms) and semi-permeable (ion-exchange or ion-selective) membranes are used for this purpose. Membrane

selectivity has become one of the key factors of electrolysis processes with a high production capacity.

One of the main factors of the economic feasibility of an electrochemical process is the electrical energy requirements given in kWh/ton of product. This is directly connected to the operating voltage, the electrical charge connected with the required chemical change of the reactant and with the current efficiency of the process. The operating voltage consists of the thermodynamic cell potential, overpotential of the cathodic and anodic reaction, and potential loss caused by resistance of the electrolyte and the separator. Details of cell voltage and an evaluation of energy requirements are described, for example, in Refs. [1,2].

As follows from the above, the electrical resistivity of the membranes represent an important aspect of keeping ohmic potential losses of the cell to a minimum, the reason being that the ohmic resistivity of a solid electrolyte could be one order of magnitude higher, or even more, than that of free liquid electrolytes [3]. Theoretically, the introduction of a membrane to the cell may thus cause an increase in cell resistance. This is, however, only partially true. The presence of a membrane, on the other hand, enables the interelectrode gap to be reduced to a minimum (practically to the thickness of the membrane—the so-called zero gap system). Besides reducing the ohmic drop on the electrolyte phase, such an arrangement allows the gas phase, if formed as an electrode reaction product, to be eliminated from the interelectrode phase and thus to reduce the impact of this void phase on the cell behavior, as will be discussed later (see Section 3.2.2). At the same time membranes prevent mixing or undesired degradation of reaction products. A suitably designed membrane also permits operation in dramatically different environments in the individual electrode compartments. In selected cases this makes the direct production of a desired product possible. These aspects clearly prevail over the lower ionic conductivity of the membrane compared to the bulk liquid electrolyte solution.

Other aspects to be considered are the intensity of production described by the current density used. Lower current density implies lower energy costs of the process due to the reduction of potential losses related to electrode overpotential, to ohmic loss of the cell and longer life time of the membrane as a result of less harsh conditions. At the same time, however, it implies an increase in the investment costs due to the need to increase the electrode and the membrane area to achieve the desired production. Appropriate cell design is thus just one of the results of careful optimization.

This review focuses mainly on a discussion of membrane electrolysis processes related to the treatment of inorganic compounds together with the properties of the related membrane materials. Low (less than 100 °C), intermediate (100 to 300 °C) and high-temperature (600 to 1000 °C) processes are considered.

2. Historical aspects of membrane electrolysis

From a historical point of view electromembrane separation processes and diaphragm electrolysis can be regarded as forerunners of membrane electrolysis. The topic of electromembrane separation processes is a suitable starting point.

Probably the first application of a non-selective separator in an electrochemical process was an electrodialysis process proposed for sugar syrup demineralization in 1889 by Maigrot and Sabates [4]. The term “electrodialysis” (ED) was not used until about 10 years later [5]. It should be stressed that only after 1930 did ion-exchange materials on a polymer basis start to be produced, initially in the form of granules and then in the form of membranes. Therefore, ion-selective membranes were not used in this process until 1939 when Manegold and Kalauch [6] applied perm-selective anion and cation-selective membranes in a 3-compartment ED apparatus. With the development of stable, highly selective membranes with low electric resistance by Juda and McRae of Ionics Inc. in 1950 [7], Winger et al. at Rohm in 1953 [8] and Wyllie and Patnode of Gulf Research in 1950 [9], ED based on this material rapidly became an industrial process for demineralizing and concentrating electrolyte solutions [10]. The principle of ED is shown in Fig. 1A. As is visible in this scheme, ED is not connected with changes in the chemical nature of the individual streams, i.e. no chemical (electrochemical) reactions occur. It only results in desalinated and concentrated streams of the treated media. The low concentrations of the solutions treated limit the operating current density to below 1000 A m^{-2} . A modification of the ED process is electrodeionization (EDI), designed for ultra-pure water production or for desalination of media characterized by low conductivity. EDI is based on the application of an ion-exchange resin bed in a diluate (also, in selected cases, in a concentrate)

chamber of an ED unit, providing it with (i) sufficient conductivity and (ii) a three-dimensional phase interface between the treated stream and the ion-selective resin. It allows significantly more intensive mass exchange between the solid and the liquid phase compared with the two-dimensional ion-selective membrane interface in the ED process. An electric field thus ensures the continual removal of ions from the ion-selective phase to the concentrate stream. From this point of view, EDI represents a combination of ED with the conventional ion-exchange technology proposed in the 1970s [11,12]. Its main advantage consists in allowing continuous operation without the use of regenerating agents, thus reducing environmental pollution and saving the water required for treatment of the saturated ion-exchanger. EDI has now become a commercially successful technology [13].

Hence, strictly speaking, it cannot be designated as membrane electrolysis, but as an electromembrane separation process. In this respect there has recently been an interesting development in the field of ED, focusing on the employment of bipolar membranes, i.e. membranes containing separate anion-selective and cation-selective layers [14]. When correctly implemented in an ED unit, see Fig. 1B, this represents a transition state between a purely electromembrane separation process and membrane electrolysis. It provides not only a change in the concentration of the individual streams, but also a change in their chemical composition, i.e. in the chemical nature of the compounds present in the streams. Salt entering the cell is not only concentrated, but is at the same time converted into different species, namely acids and bases [15,16]. On the other hand, no redox change, which is a basic characteristic of any electrolytic process, is connected with this process, except the electrode reactions proceeding on the terminal electrodes used to apply the electric field to the membrane stack. In industrially operated units the number of membrane pairs installed inside the ED stack is significantly higher than shown in the scheme and typically amounts to several hundreds. This corresponds to the need for process intensification and lower investment costs per unit of production capacity.

In parallel to ED technology, membrane electrolysis processes were also developed. In contrast to ED, industrial membrane electrolysis processes require a significantly higher operating current density (typically above 2000 A m^{-2}). One of the current representatives of membrane electrolysis processes is water electrolysis. Water electrolysis in an undivided cell was first observed by the British researchers Nicholson and Carlisle in 1801 [17]. A month later, the German researcher Ritter reproduced the electrolysis experiment and succeeded in collecting the oxygen and hydrogen produced separately [18]. According to Trasatti [19], Volta had performed similar experiments earlier. By 1902 more than 400 water electrolysis units were already in operation. At this time a diaphragm served as a separator [20]. In 1927 a Norwegian company, Norsk Hydro Electrolyzers, implemented the first large industrial alkaline water electrolyzer installation for ammonium production. Later on, two additional plants with 300 electrolyzers (with hydrogen production greater than $60\,000 \text{ m}^3/\text{h}$) were built in Norway [21]. In 1948, the first pressurized industrial electrolyzer was manufactured by Zdansky/Lonza [20]. Porous inorganic (cement, asbestos) diaphragms were used in all alkaline water electrolyzers (using up to 40% solution of KOH or NaOH as an electrolyte) as separators. This resulted in a relatively high risk of explosive H_2/O_2 mixtures forming. At the same time, in the case of asbestos, handling the separator material represented a serious health hazard. Great efforts were invested in replacing this type of separator with more efficient diaphragms based on porous inorganic (oxides) and/or polymer materials [22–25]. Some of the proposed alternatives appeared to be quite successful, one noteworthy example being diaphragms based on polyantimonic acid, which gave a huge impetus to improving alkaline water

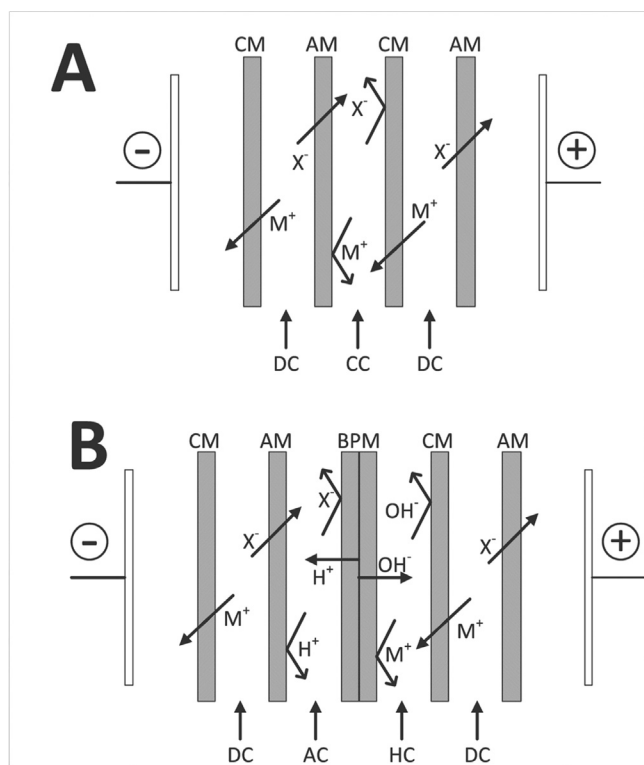


Fig. 1. Schematic sketch of the functioning of (A) traditional electrodialysis and (B) electrodialysis with bipolar membranes, M^+ —cation, X^- —anion, H^+ —proton, OH^- —hydroxyl, CM—cation-selective membrane, AM—anion-selective membrane, BPM—bipolar membrane, DC—diluate chamber, CC—concentrate chamber, AC—acid concentrate chamber, HC—hydroxide concentrate chamber. [10].

technology [26]. At present, non-asbestos diaphragms are used by all the main electrolyzer manufacturers (Norsk Hydro, Hydrogenics, De Nora, etc.), a development primarily determined by the end-users who sought a robust and reliable technology with minimum maintenance requirements. This was predetermined by the fact that water electrolysis was only used as a source of hydrogen in regions with a local excess of cheap electric energy or in technologies with high value-added. This resulted in these factors being regarded as more important than process efficiency. Recently, the problem of energy storage and recovery has changed this situation. The know-how accumulated during the long development and industrial use of water electrolysis technology represents a firm foundation for its further development to meet new challenges. This development is based predominantly on the use of a suitable solid electrolyte, either polymer-based or ceramic-based, as discussed later in this review.

Probably the strongest motivation for the development of membrane electrolysis was the chlorine industry. In 1851, Watt obtained an English patent for producing chemicals, including chlorine, caustic soda and sodium hypochlorite, by electrolysis of brine [27]. In 1890, the German company Chemische Fabrik Griesheim-Elektron began to produce chlorine and potassium hydroxide in an electrolytic cell in which the anode and cathode were separated by a porous cement diaphragm [27]. The application of porous (including asbestos) materials as the separator or a mercury cathode in this process resulted in a significant improvement in this technology which thus remained unchanged for decades. In 1970 a new, safer and more efficient technology was sought [28]. Membrane technology represented a very good alternative. However, due to the strong oxidation capability of chlorine and its compounds, hydrocarbon polymers were not sufficiently stable to provide a membrane with sufficient lifetime. The development of chemically stable, homogeneous, perfluorinated sulfonated membranes with low ohmic resistance and high selectivity at the end of the 1960s [29–31] finally solved this problem and led to the development of a series of various membrane electrolysis processes described below. Due to the high price of the perfluorinated membrane many attempts were made to develop non-fluorinated (hydrocarbon) membranes. In the case of a highly aggressive environment, e.g. in chlorine production, however, the chemical stability of the non-fluorinated membranes developed is still not satisfactory [32]. Nevertheless, this endeavor led to the emergence of a wide spectrum of cation- and anion-selective membrane materials available nowadays from various producers (see Annex 1 in Supplementary material).

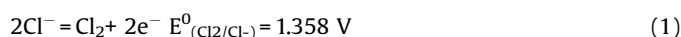
3. Present status of membrane electrolysis

The development of membrane materials that satisfied process demands opened the way to the rapid, widespread proliferation of electrochemical cells designed for the use of a solid membrane as an efficient separator of the electrode compartments and later as a solid electrolyte. As mentioned earlier, the greatest proliferation in terms of installed production capacities is the membrane cell used in brine electrolysis.

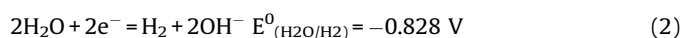
3.1. Brine electrolysis

The application of homogeneous ion-selective membranes in a brine electrolysis process was first proposed by Ionics Inc. in 1951–1953 [33]. However, industrial electrolysis of a solution of sodium chloride and water for chlorine and alkali production with perfluorinated membranes was first realized in 1975 by the Japanese Company Asahi Chemicals [34]. The most intensive development of this process continued to take place in Japan where, in 1986, all chlorine production using mercury cells was

changed to the membrane-type process. Subsequently, this process rapidly spread to other industrialized countries. Today, production capacity is roughly $76 \cdot 10^6$ t Cl_2 year⁻¹, with more than 50% of this amount being obtained by membrane electrolysis [35]. In chlor-alkali electrolysis units, bilayer perfluorinated membranes (see Section 5.1) with carboxylic and sulfo groups are used. This permits a decrease in membrane resistivity in the case of the sulfo-type membrane and a decrease in hydroxyl ion flow to the anode in the case of the carboxylic-type membrane. The distance between the cathode and the membrane is typically set at approx. 1 mm. These electrolysis units operate at atmospheric pressure and at a temperature of 80–95 °C [36]. The anode compartment of such an electrolyzer is fed with a saturated (26 wt% NaCl) brine solution [28] (the typical composition of the electrolyte in the anode compartment being about 180–240 g dm⁻³ NaCl, and pH of 1.0 to 4.5 [36]). At the anode, chloride ions are converted into gaseous chlorine:



The cathode compartment is fed with a water solution of sodium hydroxide, i.e. pH of 14. At the cathode, water is reduced to gaseous hydrogen and hydroxyl ions:



Whereas the chloride anion is oxidized on the anode to chlorine gas, sodium ions are transported through the cation-selective membrane from the anode to the cathode compartment. Here they recombine with hydroxyl ions to produce sodium hydroxide. The maximum achievable sodium hydroxide concentration of up to 35 wt.% is limited by water flux between the anode and the cathode compartments which is primarily connected with the solvation (hydration) shell of the Na^+ ion. In the case of brine electrolysis, this is close to 4 molecules H_2O per Na^+ ion, i.e. each Na^+ ion transported through the membrane carries 4 molecules of H_2O . Another aspect limiting the charge efficiency of the process is the finite separation efficiency of the membrane, leading to back diffusion of hydroxyl ions from the cathode to the anode compartment. Here they are neutralized by a reaction with protons. The charge loss corresponding to this process is approx. 5% [28]. The purity of the hydrogen and chlorine typically exceeds 99%. Moreover, the energy efficiency of the process is approx. 30% higher than that of electrolysis with a porous diaphragm. Safety improvement represents an additional important aspect [10,36,37]. The scheme of a cell based on the UhDeNora design is shown in Fig. 2. Besides the membrane, the electrodes and cell design are also undergoing intensive endeavors to improve process performance and save investment costs. The chlor-alkali membrane cells currently operated are equipped with titanium anodes coated with a $\text{RuO}_2/\text{TiO}_2$ layer and nickel-based cathodes with a surface modified by a catalytic layer based on high surface Ni compounds doped with platinum metals [35].

Chlor-alkali electrolyzer manufacturers are Asahi Kasei Chemicals Corporation, ThyssenKrupp Electrolysis (formerly UhDeNora), INEOS (formerly ICI) and Bluestar (Beijing) Chemical Machinery Co. The membranes are produced by DuPont (trade mark Nafion), Asahi Glass (trademark Flemion) and Asahi Kasei (trademark Aciplax) [28].

Membrane brine electrolysis typically operates at a current density of up to 7000 A m^{-2} [38] and a cell voltage of 3 to 4 V [37,39]. Under these conditions the current efficiency attains a level higher than 95% [40]. Whereas the voltage efficiency of the process (equilibrium cell voltage has a value of approx. 2.2 V) is mainly caused by activation overpotential of the anode reaction and ohmic drop on the membrane, current efficiency loss mainly accounts for the transport of hydroxyl ions from the cathode to the

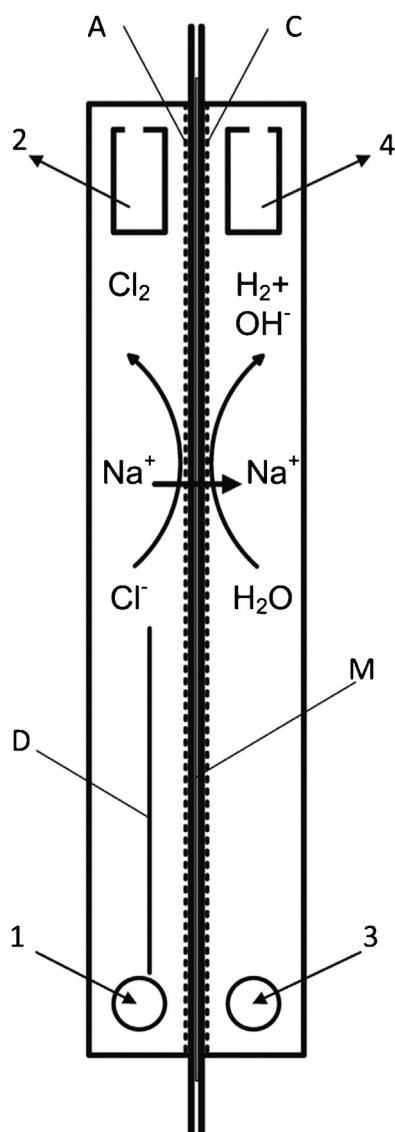


Fig. 2. Scheme of cell unit in the chlor-alkali process based on electrolysis design of ThyssenKrupp [38]. A—anode (perforated titanium activated by RuO_2), C—cathode (catalyst activated Ni mesh), M—perfluorinated membrane (pressed between anode and cathode), D—downcomer (ensuring brine circulation), 1—brine inlet, 2—depleted brine with chlorine collector (outlet), 3—diluted caustic soda inlet, 4—concentrated caustic soda with hydrogen collector (outlet).

anode compartment due to joint diffusion and migration. As the membranes are quite thin (about 100–200 μm), they are usually reinforced with polytetrafluoroethylene (PTFE) fibers to increase their mechanical strength. Another approach is to press electrodes on each side of the membrane to reduce ohmic potential loss in the electrolyte. This design is referred to as “zero gap”.

A significant reduction in electric energy consumption can be achieved by introducing oxygen-depolarized cathodes (ODC) [41,42]. Approximately 30% of the energy demand can be saved by changing the cathode reaction from hydrogen production to oxygen reduction [43]. By this means hydrogen generation is omitted and only hydroxyl ions are generated on the cathode. These cathodes are similar to gas diffusion electrodes (GDE), which are known from alkaline fuel cells, but large cells require special construction [41]. In the case of gaseous reactants, the transport of reacting molecules to the active electrode surface presents a problem if a sufficiently intensive electrode reaction is required. With traditional electrodes (net or expanded metal) the efficiency

of the process is low. This is solved by applying a porous, three-dimensional electrode with a high specific surface area, since only direct contact between the electrode and the electrolyte (under conditions of access of the reactant) allows the electrochemical reaction to occur. Such a location is typically called the three-phase contact region, a term derived from the fact that three phases (electron conductor, ionic conductor and gas phase) come into contact there, as shown in Fig. 3. These regions are fairly rare and, therefore, only a negligibly small part of the electrode surface is used for the desired reaction if it is not designed properly. To minimize the impact of this complication, the electrode construction must enable distributions of potential and, hence, current densities in percolated electronically and ionically conducting phases; pores also need to be connected. Such an electrode structure thus allows the electrode to be supplied by electric current and reactants. At the same time it permits removal of reaction products [41,42].

The technology using oxygen-depolarized cathodes was originally developed for hydrochloric acid electrolysis. Originating as a by-product of organic chlorination, HCl is an important source of chlorine. Several ways to treat it have been proposed. Besides the modified Deacon Process [28], electrolysis represents an economically interesting option. An electrolyzer equipped with a diaphragm was initially developed for this purpose. Today membrane processes are considered to be more effective. The DuPont Company developed a dry cell electrolysis process capable of operating at 13 kA m^{-2} and a cell voltage of 2 V [44,45]. This process uses a perfluorinated sulfonated membrane as the separator and gas diffusion electrodes developed by DeNora. Gaseous hydrogen chloride is thus oxidized to chlorine and proton without any contact with liquid water [46]. Currently, the most favorable perspective is the process developed by UhDeNora S.p.A in collaboration with Bayer AG using an ODC [46–48]. The main advantage is low electric energy consumption. The cell voltage has a value of 1.0 V at 0.4 kA m^{-2} [49], i.e. significantly lower than the diaphragm process of HCl electrolysis (0.5 kA m^{-2} at 2.2 V). On the other hand, no hydrogen is produced. This technology is now well-established on the market. The installed production capacity based on oxygen-depolarized cathodes exceeds $315,000 \text{ t Cl}_2 \text{ year}^{-1}$ worldwide [47]. This figure is valid for the HCl electrolysis process.

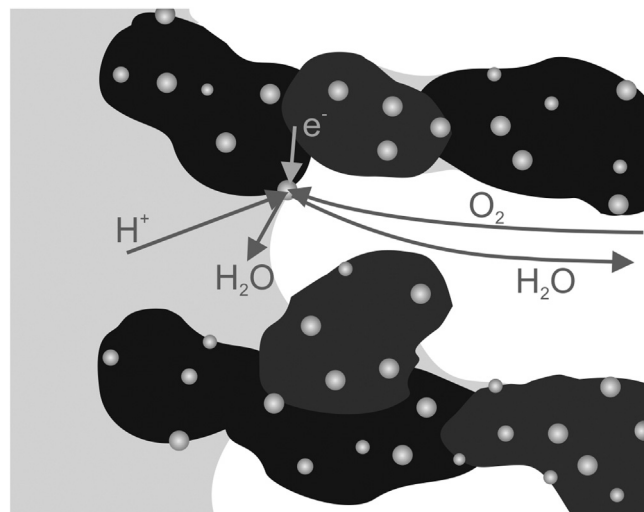


Fig. 3. Schematic sketch of the electrode reaction in a gas-diffusion electrode structure (three-phase-contact). Spheres indicate Pt catalyst particles, black areas stand for an electron conducting phase and grey area for ionically (proton) conducting phase.

3.2. Water electrolysis

Currently, membrane electrolyzers for the decomposition of water probably represent the most intensively developed electrochemical units employing a membrane. As already mentioned, this is connected with the need for a highly flexible and efficient technology for storage, and later recovery, of the transitory excess of electrical energy produced, which mainly originates from unstable and unpredictable renewable sources. Since fuel cells, being a recovery technology of energy stored in the form of hydrogen bond energy, are considered to be significantly more mature, the research community is increasingly focusing on electrolyzers. Three main routes are considered: (i) low-temperature ($<100^{\circ}\text{C}$), (ii) medium-temperature ($100\text{--}300^{\circ}\text{C}$) and (iii) high-temperature ($600\text{--}1000^{\circ}\text{C}$) routes. The low-temperature route is sub-divided into alkaline and acidic, whereby the acidic route is currently preferred, although the significance of the alkaline route has recently increased.

Zero-gap design has provoked a new approach to the design of the electrochemical cell. It has opened up a broad spectrum of alternatives regarding the construction of electrochemical cells and systems. The most important advantage involves the possibility of avoiding circulation of liquid electrolyte and operating electrochemical cells at temperatures up to 900°C . The zero-gap approach was first used in the design of high temperature fuel cells in 1937 [50,51]. For ion-selective membranes, however, zero-gap design is reported to have first been used in 1959 by General Electric [52] in the design of PEM-type fuel cells. Here, a polymeric membrane plays the role of a solid polymer electrolyte and gaseous reactants are used. Finally, zero-gap design has also been applied in systems using the reverse reaction to the fuel cell, i.e. PEM and high-temperature water electrolysis technology, in which deionized water in the form of liquid or steam can be used as a reactant, see Fig. 4. Excluding the liquid electrolyte from the system significantly simplifies the installation of auxiliaries because no corrosive, aggressive media have to be circulated.

Similar to the ODC electrode, an important issue is ionic contact between the electrode and the membrane. In the PEM system, typically polymer electrolyte is added to the active part of the GDE

electrode (usually a catalytic layer containing nanostructured catalyst particles). Such an addition results in the formation of a three-dimensional network inside the catalytic layer, providing ionically conductive pathways between the electrode and the polymer electrolyte. Where possible, material identical or chemically similar to membrane polymers is used. The content of the solid, ionically conducting phase in the catalytic layer usually varies in the range of 5 to 20 wt.% of catalyst [53–57]. A similar approach is used in the construction of the high-temperature water electrolysis cell [58]. An oxide-conducting electrolyte, typically yttria-stabilized zirconia (YSZ), mixed with nickel forms the cermet (a composite of ceramic and metal phase) cathode. Similarly YSZ mixed with perovskite-based electron-conductive material is used as the anode [59]. Possible membrane materials and construction issues are discussed in more detail in Section 3.2.4.

The operating temperature of the water electrolysis process is important for the theoretical electric energy consumption. The theoretical value corresponding to the enthalpy change of hydrogen production is 3.25 kWh m^{-3} for liquid water and 2.73 kWh m^{-3} for steam. The values are related to the so-called thermoneutral voltage, corresponding to isothermal conversion of water to hydrogen and oxygen. For liquid water, the thermoneutral voltage is 1.48 V at 25°C .

3.2.1. Low-temperature acidic water electrolysis

Acidic membrane water electrolysis has obvious advantages over traditional alkaline technology. It offers greater safety because of the membrane's relatively high mechanical strength and low gas permeability. At a current density of $20\text{--}30\text{ kA m}^{-2}$ the power consumption achieves approx. $4.0\text{--}4.2\text{ kWh m}^{-3}$ of hydrogen. A comparison of the energy demands with the theoretical values shown above documents the high efficiency of the process. Other positive aspects are high specific productivity (current density) and very high gas purity ($\text{H}_2 > 99.99\%$, $\text{O}_2 > 99.98\%$ in dry gas). The cell construction is based on a zero-gap design. Generally, there is a short inter-electrode distance (the membrane thickness is typically $100\text{--}300\text{ }\mu\text{m}$) and an absence of gas bubbles between the electrode and the membrane, thus minimizing ohmic voltage losses. Nanostructured, precious metal catalysts used in the electrode construction ensure low energy consumption and high specific productivity. Membrane properties also open up the possibility to carry out the electrolysis process at elevated pressure [60–64] or even in a type of electrochemical compressor [65] with a minimized risk of explosive gas mixtures forming. Producing hydrogen directly in compressed form offers interesting savings of the subsequent gas compression costs or energy expenses. At the same time, however, it leads to higher hydrogen 'cross-over' from the cathode to the anode compartment. In the case of electrochemical compression, i.e. lower pressure in the anode compartment than in the cathode compartment, the pressure gradient over the membrane represents the main driving force. In the case of a symmetrically pressurized electrolysis cell, the partial pressure gradient of hydrogen over the membrane increases as well. This effect is connected with the charge efficiency of the process and, in an extreme case, with the formation of an explosive mixture in the anode compartment. To minimize these negative aspects thicker membranes are required, especially for cells with asymmetric pressure, leading to increased ohmic losses of the cell. An operating pressure of up to 150 bars has already been achieved on a commercial basis [66]. Electrolyzers working at 300 bars are currently under development [67]. All these advantages have resulted in intensive development of PEM electrolyzer technology during the past decades. The development of this process started in the 1950s, with the first pilot electrolyzers being produced by General Electric for space projects 20 years later [20,68]. One of the

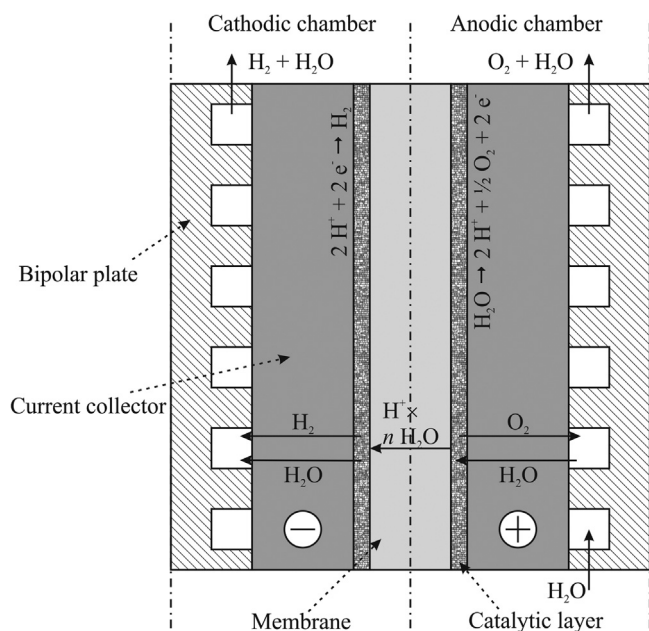


Fig. 4. Scheme of the principle of the PEM electrolysis cell.

first companies active in this field was ABB (formerly Brown, Boveri Ltd), Switzerland. From 1976 to 1989 [62] the technical feasibility of this technology was demonstrated on a 100-kW scale. Two units of this size were installed and operated at Stellram/ATEL (1987–1990 and 1991–present) and SWB, Solar-Wasserstoff-Bayern GmbH (1990–1996).

The first commercial-scale PEM electrolyzer installed at Stellram SA, a metallurgical specialty company, in Nyon, Switzerland, was designed to produce up to $20 \text{ Nm}^3/\text{h}$ of hydrogen at a pressure of 1–2 bars. A Nafion[®] 117 membrane was used as the polymer electrolyte. The plant was operated at 10 kA m^{-2} (80°C) and at a cell voltage of about 1.75 V. It was shut down in 1990 after approximately 15,000 hours of operation [69].

A few points have to be borne in mind. As perfluorinated sulfonated polymer electrolytes in a swollen state and in proton form represent the equivalent of approximately 0.5 to $1.0 \text{ M H}_2\text{SO}_4$ solution, the selection of materials for use as electrode reaction catalysts is confined to a relatively limited group. Platinum metal-based electrocatalysts represent the state-of-the-art in this field due to their long-term corrosion resistance. Whereas in the case of PEM fuel cells Pt is used on both electrodes, in the case of PEM water electrolysis Pt serves as a cathode catalyst and Ir, Ir/Ru or their oxides represent the materials of choice on the anode side [54,70–72].

Another aspect is the high price of the membrane which exceeded \$ 2000 per m^2 when the first commercial-size cell was constructed. Although the price of perfluorinated sulfonated membranes has meanwhile decreased, it still remains high by industrial standards, i.e. too expensive for most applications. A more detailed analysis can be found in Section 6. Additionally, the limited life-time of the cells impeded the development of PEM electrolyzers since their field of application was fairly restricted. Therefore, particular attention was paid to improving the membrane, the electrocatalyst and the electrocatalyst layer. Different methods were developed for the synthesis of the electrocatalyst (see, for example, [55,56,73–75]) and for its deposition on the membrane surface (catalyst layer formation). This layer typically consists of the catalyst (supported or unsupported) bonded by a suitable polymer. Its structure has to be such that it ensures not only sufficient percolation of the electronically and ionically conductive phase, but at the same time the supply of reactant and removal of the product. The formation of such a structure is one of the critical issues in PEM-type systems [76].

All these efforts have resulted in the development of membranes with catalyst layers on both surfaces in a single unit, known as a membrane electrode assembly (MEA). The techniques used to prepare a MEA include electro-less deposition, screen printing, electrocatalyst ink painting, electrocatalyst suspension spraying and electrocatalyst sputtering. Some of these techniques, such as chemical metallization [53,77], whereby the electrocatalyst is synthesized by chemical reduction of an appropriate precursor (e.g. H_2PtCl_6) using a suitable reducing agent (such as borohydride or formaldehyde) on the membrane surface, have proved very useful for laboratory research purposes [77]. However, they lack the necessary efficiency for industrial use. On the other hand, the application of a suspension of electrocatalyst in an ionomeric colloid solution (or ‘catalyst ink’) appears to be the most efficient technique for industrial purposes. The progress attained has permitted the electrocatalyst loading to be reduced from a value initially greater than 10 mg/cm^2 to that of $2\text{--}3 \text{ mg/cm}^2$ now [78]. It is worth mentioning that one of the best process efficiencies was obtained within the framework of the Japanese program WE-NET [79,80] in which an electrolytic unit was developed with an active area of $2,500 \text{ cm}^2$, operating at a cell voltage of 1.556 V, a temperature of 80°C and current density of 1 A cm^{-2} , i.e. with an

efficiency of energy transformation of 95.1% (related to thermo-neutral voltage, see Section 3.2). Equally, it must be stressed that these results were obtained using a very high platinum metal load (approx. 10 mg/cm^2).

PEM water electrolyzers are currently produced by several companies [81]: e.g. UTC Aerospace Systems (formerly Hamilton Sundstrand), Proton OnSite, Norsk Hydro Electrolyzers AS, Hydrogenics, Siemens and the Kurchatov Institute. The maximum productivity of one electrolyzer stack typically reached approx. 30 m^3 per hour. At the same time, very small electrolyzers (less than 1 dm^3 and up to several dm^3 per hour) are also manufactured for educational and demonstration purposes (for example by H-Tec company). Now, however, units with a capacity of up to 1.25 MW, i.e. 225 m^3 per hour, are already commercially available [82]. The drawbacks of precious metal catalysts and membrane costs have already been mentioned, but the construction materials for such electrolyzers are also a major problem. Due to the high sensitivity of the membrane to impurities, mainly to the cations present in the circulating water (especially multivalent cations, like Fe^{3+}), stainless steel cannot be used as a construction material for current collectors and bipolar plates. Carbon-based materials are only suitable for the cathode compartment. For the anode compartment, current collectors based on porous and bipolar plates on massive Ti are used. Ti also needs additional protection against oxidation, which increases precious metal loadings and thus the price of the electrolysis stack. Different technologies, including ion implantation and magnetron sputtering, have been developed to decrease precious metal loadings and at the same time corrosion of the construction materials [83]. Although the application of deionized water as a circulating medium increases product purity and reduces corrosion of the construction materials, it results in a critical limitation: electrolyzers cannot be used at temperatures lower than 0°C . Thus, the application of PEM electrolyzers in regions suffering from unsuitable climatic conditions, including low temperatures, implies additional energy demands to heat the active volume of the electrolyzer. This can significantly impact the overall system efficiency.

3.2.2. Low-temperature alkaline water electrolysis

The alkaline route has experienced a revival in the past 5 years as an alternative low-temperature water electrolysis technology [84,85]. Originally, this route was dismissed as irrelevant for several reasons, the most important ones being the lower intensity of the process compared to the acidic route and the absence of a suitable polymeric electrolyte comparable to perfluorinated sulfonated polymeric acids. However, due to the above-mentioned economic drawbacks of the acidic route, the alkaline route is becoming more and more attractive because a significantly broader spectrum of construction and catalyst materials based on non-precious metals can be used [86–88]. Electrodes are typically based on nickel (anode) and stainless steel (cathode) activated by suitable catalysts typically based on Ni, Co and Fe-based spinels and perovskites. Since the spectrum of sufficiently stable materials is significantly broader than in the case of PEM water electrolysis, rapid development is currently observable in this field but time is still needed to achieve a generally accepted solution. Moreover, a recent development in this field regarding alkaline anion-selective polymer electrolytes [86,87,89–92] is also promising, although progress still lags behind the acidic alternative. The reason for this is the insufficient stability of the currently available anion-selective polymer electrolytes under conditions of water electrolysis, especially at elevated temperatures which are preferable from the point of view of electrolyte conductivity and electrode reaction kinetics. Nowadays, in the case of utilizing an anion-selective membrane the operational temperature is limited to a range below 70°C due to the stability problem of the functional

groups [90]. This limit is not valid for cells based on traditional porous separators like, for example, asbestos.

Increased temperature enhances the ionic conductivity of the electrolyte. At the same time, however, it increases the partial pressure of water and thus increases the volume of the void phase in the interelectrode space. Together with the potential presence of spacers, this introduces additional ohmic loss of the cell, thus reducing its voltage efficiency. Since the gas phase is moved from the bottom to the top of the cell by buoyancy force, in contrast to stationary spacers, conductivity gradients are formed in the electrolyte. As a result, the local current density distribution in the cell cannot be considered to be homogeneous. In order to be able to assess the impact of the presence of a void phase in the electrolyte on its ionic conductivity, several empirical equations have been proposed, typical examples being Brugemann and Kirkpatrick, among others. More detailed information can be found, for example, in [93,94]. At the same time, the mobility of OH^- ions in the system is significantly lower than that of H^+ , which results in higher ohmic resistance of the system and lower process intensity compared to PEM water electrolysis. Another aspect is the limited stability of non-platinum electrocatalysts under switch-off conditions (cell repolarization). However, intensive research in this area is focusing on providing materials with the required properties [95].

3.2.3. Medium-temperature water electrolysis

This approach tends to utilize the advantages of both the low and high-temperature processes, i.e. rapid electrode reaction kinetics and less stringent demands on the stability of the construction material. In this temperature range there still remains the option of operating a cell using water in the liquid or gaseous state. The operation pressure used is the determining factor. For example, water remains liquid up to 235°C at a pressure of 30 bar. This means that the pressure needed to maintain the water in a liquid state, when required, does not present a difficulty from an industrial point of view. The main problem is the availability of sufficiently stable and at the same time conductive membrane materials. The traditional method, using a phosphoric acid-doped polybenzimidazole (PBI) membrane, has not proven to be viable due to the insufficient oxidative stability of this material under water electrolysis conditions [96,97]. An alternative, based on a porous separator containing immobilized $\text{KOH}/\text{H}_2\text{O}$ melt operating at 240°C , has recently been reported [98,99]. Water acts both as a reactant and as the medium that flows through the system, removes the gas produced and helps to provide corresponding heat management in the system. The zero gap arrangement with porous electrodes (Inconel foam cathode and silver plated nickel foam anode) pressed directly on the surface of the porous separator enable operation at a current density of 1 A cm^{-2} using a cell voltage of 1.48 V. Despite the similar design to PEM water electrolysis, the character of the separator used is closer to the diaphragm than to the membrane [99]. The electrolysis parameters reported illustrate the high potential of medium temperature alkaline water electrolysis for commercialization, although this stage has not yet been reached.

3.2.4. High-temperature water (steam) electrolysis

A high-temperature process operating at temperatures up to 900°C is now being intensively developed for water electrolysis [100,101]. Its development is based mainly on knowledge derived from solid oxide fuel cell (SOFC) technology [102]. The motivation to use such a high operational temperature is two-fold: (i) to obtain high process efficiency by means of electrocatalysts based on non-noble metals and (ii) to enable new reactions not, or hardly, achievable under low-temperature conditions like co-electrolysis of H_2O and CO_2 under syngas production [103,104]. Thus,

ultimately, this technology enables the production of synthetic fuel based on renewable energy sources. It is often referred to as power-to-gas technology, as the fuels produced are primarily of a gaseous nature.

An improvement in water electrolysis efficiency by increasing the operating temperature is connected with an enhancement of the electrode reaction kinetics and, thus, a reduction of the activation potential losses despite non-noble electrode materials. This is in agreement with Arrhenius's law. The second important aspect is the thermodynamics of this system. A schematic overview of its main parameters is given in Fig. 5. As follows from this diagram, the ΔH of the water decomposition reaction only slightly increases with increasing temperature. On the other hand, the ΔS of this reaction has a positive value. Thus $\Delta G = \Delta H - T\Delta S$ decreases significantly with increasing temperature. This indicates that, although the overall energy demands of the water decomposition reaction slightly increase with temperature, the equilibrium voltage of the corresponding electrolytic cell decreases from 1.23 V at 25°C to 0.97 V at 800°C . The difference can be covered by the heat energy consumed by the system. In the case of steam electrolysis at a temperature of 800°C , a sufficient production intensity of 0.25 A cm^{-2} has already been attained at a cell voltage of 1.0 V [105]. This corresponds to electric energy consumption of 2.22 kWh m^{-3} of hydrogen. At the same time the enthalpy of combustion of 1 m^3 of hydrogen corresponds to 2.80 kWh. Thus, during water decomposition 0.6 kWh have to be additionally provided in the form of heat energy. This process is, therefore, highly effective if high potential (high temperature) waste heat is available. Concentrated solar heat or generation IV nuclear reactors represent the options currently considered for this purpose.

It is possible to use such a high operational temperature due to the application of specific ceramic materials (for example ZrO_2 stabilized by Y or Sc oxides with O^{2-} conductivity) as the ion-conducting membrane material. The same material is used for the formation of ionically conductive pathways in porous electrodes operating exclusively with gaseous reactants under these conditions.

A high operating temperature determines not only the advantages, but also the disadvantages of this process. There are significant challenges to be overcome: besides the thermal stability of the materials and the sealing of the cell, tolerance of extreme differences in temperature leading to electrode delamination or mechanical damage of the cell due to differences in the thermal expansion coefficients of the individual phases (startup, shut down and steep variations in the current load being the main causes of such differences). A high operational temperature also allows mutual diffusion of the electrolyte-electrode components

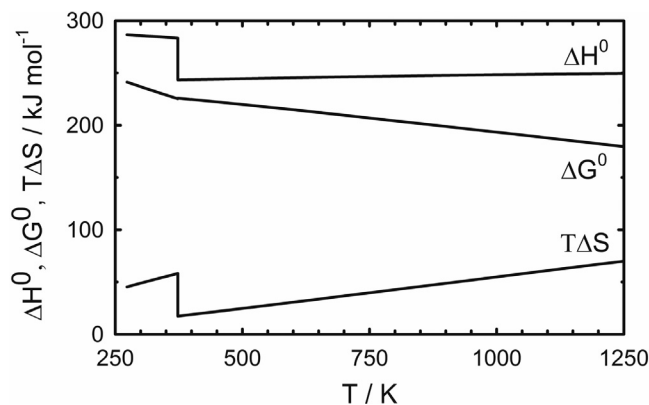


Fig. 5. Thermodynamic parameters of water electrolysis for 1 mol H_2O .

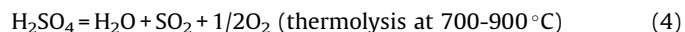
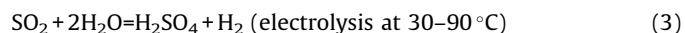
through the interface between these two parts of the cell. Such diffusion may result in the formation of a new phase of undesired conditions, e.g. of insulating properties. There is, therefore, still a long way to go before this technology will reach the commercialization stage.

3.2.5. Unitized regenerative fuel cells

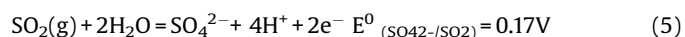
A further promising membrane electrolysis system, based on the same type of membranes as water electrolyzers, is the reversible fuel cell, known as the unitized regenerative fuel cell (URFC). In this system, electrochemical cells are used both as electrolyzers and fuel cells. The concept of the reversible PEMFC was put forward for the first time in the early 1960s, and in 1972 PEM-URFC technology was successfully tested by General Electric Co., leading to the development of a prototype for a space satellite [106]. However, the real breakthrough was achieved by Livermore National Laboratory [107,108]. In 2003, an 18.5 kW URFC (storage system energy density of approx. 450 Wh kg⁻¹) was installed in the Helios, a pilotless plane, and was tested on-board during test flights. In 1998 Proton Energy Systems [109] developed a commercial product (Unigen reversible module), consuming 15 kW in electrolysis mode and producing up to 5 kW of electric power in fuel-cell mode. Research and development of the URFC received attention from various US companies (Lynntech Inc., Glenn Research Center, Giner Inc.) and from the Canadian company Green Volt Power Corp [21], among others. URFCs have also been developed in Russia at the Kurchatov Center [110–112]. The main benefit of the URFC is the reduced weight and volume of the device and, of course, the costs, since only one unit is constructed instead of two separate technologies. However, differences between the requirements imposed on fuel cell and water electrolysis processes make its construction quite complex. At the present state of knowledge these problems are difficult to overcome. Currently, URFC technology is, therefore, almost exclusively confined to the domain of space and military applications. The rapid development of high-temperature solid oxide systems makes them increasingly interesting candidates for application in the energy storage sector as regenerative fuel cells. This is mainly due to the low kinetic limitations of the electrode reactions, allowing high energy storage cycle efficiency [113–115]. For this reason they have become the subject of increasing interest to the research and development community.

3.2.6. Thermochemical cycles as alternative water decomposition processes

An alternative to direct water electrolysis is the use of thermochemical cycles targeting the replacement of the electrical energy needed for decomposition by cheaper heat energy. However, one of the most developed thermochemical cycles, the “Mark-II cycle” (or “Westinghouse cycle”), also involves membrane electrolysis [21,116,117]. The main reactions of this cycle are as follows:



The hydrogen evolution reaction on the cathode is identical to the PEM water electrolysis process, but instead of the oxygen evolution reaction, the oxidation of SO₂ proceeds at the anode:



The standard equilibrium potential of this reaction 0.17 V makes this process attractive (compared to 1.23 V for oxygen evolution). A porous separator “membrane” was originally used [116,117]. In this

approach the electrolysis step can also be accomplished utilizing a PEM electrolyzer similar to that used for water electrolysis [118,119]. However, due to the limited SO₂ solubility in water (96 g SO₂ in 1 kg H₂O at 25 °C) current densities of 0.1–0.2 A cm⁻² are used at a cell voltage of approx. 0.8 V. Transfer limitations can be observed even at this low current density. Higher current densities up to 0.3 A cm⁻² could be achieved if gas diffusion electrodes with a Pt nanocatalyst on graphite are used. In this case SO₂ is fed to the anode in gaseous form. Due to the low anode potential, a graphite-based anode can be used. Perfluorinated sulfonated membranes have proven to be stable in this system, but other polymeric membranes have also been studied [120]. However, the PBI membrane has been identified as the best option from the point of view of a combination of performance and minimized SO₂ cross-over, with a 27% increase in current density. This contrasts with later work also using cross-linked PBI blended membranes for this process, but without revealing any advantages in comparison with Nafion membranes [121,122]. Similarly, anode depolarization by CO has also been studied, but hitherto without any significant success [123].

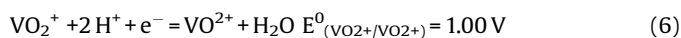
Additionally, PEM electrolysis of halogen acids (HBr or HI), which could be used in another type of thermoelectrochemical cycle, has been investigated, but has not yet found industrial application [118,124]. In this case thermal decomposition at high temperatures is preferred to accomplish their decomposition.

3.3. Selected membrane electrolysis processes applied on a commercial scale

Besides brine electrolysis, which represents the most important electrochemical industrial technology, there is a broad spectrum of electrochemical technologies of different scale and importance based on membrane electrolysis. However, it would go beyond the scope of this paper to list them all. The reason is not only their number, but more importantly the fact that the vast majority of these processes falls into the range of chemical specialties, information on which is not publicly available. Therefore, only larger-scale technologies are reported in this paper.

3.3.1. Redox flow batteries

The pressing need for energy storage technologies is accelerating the development of energy conversion related processes, such as the above-mentioned hydrogen technologies. The redox flow battery is one of the successful alternatives to hydrogen-based systems [125]. Its principle is very similar to that of the regenerative fuel cell mentioned earlier. However, the function of the redox flow battery is based on utilizing two redox couples serving as electrochemically active components in a divided electrochemical cell. The solutions of the two redox couples are stored in separated electrolyte tanks. During the charging period the redox couples are converted into a high-energy state by means of electrolysis. Conversely, in a discharge (“fuel cell”) mode they are converted back into the lower-energy state. In parallel, electrical energy is produced. Many redox couples suitable for this application have been reported in the literature, but the vanadium-based system represents the most well-developed one [126,127]. Reactions (6) and (7) document the above-described process.



Whereas the direction of the reactions from left to right corresponds to the discharge (“fuel cell”), the direction from right

to left corresponds to the electrolysis (charging) mode of operation.

The most important component of the redox flow battery cell is an effective barrier preventing the solutions of the two active components from mixing. The redox couple ions penetrating the separator cause self-discharging, thus significantly reducing the cell's performance and efficiency. Therefore, the quality of the separator is a vital parameter of the redox flow battery. Currently, perfluorinated sulfonated membranes represent the membrane of choice [125,127,128]. The membrane requirements are slightly different to those for applications in water electrolysis. An operating current density below 100 mA cm^{-2} [127] allows the use of less conductive membranes but of high selectivity preventing penetration of vanadium compounds between the individual compartments. To reduce the crossover of vanadium ions, typically membranes thicker than $100 \mu\text{m}$ are used [125]. On the other hand, low current density requires the use of a large membrane area in order to achieve the desired cell performance.

Thus, the high membrane costs and the high permeability of vanadium ions through the membrane represent two important issues hindering rapid development of large-scale vanadium redox flow batteries. These two aspects are accompanied by the unsatisfactory water balance in the system caused by electro-osmotic flow and water molecules dragged by the vanadium ions [128]. The main thrust of research work in this field today is to solve these problems. Encouraging results have been obtained, for example by using perfluorinated sulfonated membranes modified by suitable additives [129]. Several promising alternative cation-selective membrane materials are summarized in the review of Wu [128].

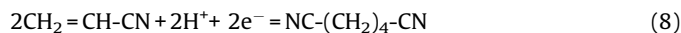
The application of an anion-selective membrane represents a different approach. Here, the main issue is the stability of the membrane in the presence of highly oxidative ions, e.g. VO_2^+ [127]. On the other hand, in this case the permeation of vanadium-based cations can, to a significant extent, be neglected. However, water transport during redox flow battery operation still remains a problem. Recently, the focus has been on porous separators, mainly due to their significantly lower price [130]. Standard porous separators modified by inorganic fillers provide an acceptable permeability ratio of H^+ to V^{n+} ions. Another approach is based on the separation capability of nanofiltration membranes [125,130]. The application of porous membranes is only possible due to the low current densities used in redox-flow battery technology. Despite the high potential of alternative materials, perfluorinated sulfonated membranes (Nafion) still represent the main separator used in commercial applications [127].

3.3.2. Electroorganic synthesis

Ion-selective membranes as selective separators are also a powerful tool in electro-organic synthesis. In contrast to inorganic industry (chlor-alkali process), electro-organic technologies are typically operated with significantly smaller production capacities because they represent a production route for fine chemicals with high value-added. Several processes are known to have been carried out in cells with an ion-selective membrane [131,132]. The application of ion-selective membranes for electro-organic synthesis is limited by the fact that membranes are usually permeable to electroneutral molecules, including water and non-polar organic solvents. The serious danger of the oxidation of undesired organic molecules on the anode or of the initiation of polymerization in the cell has to be considered. Therefore, the selection of a suitable electrode material should be a priority [133]. The largest electroorganic technology utilizing an ion-selective membrane on a production scale was the Monsanto process for the conversion of acrylonitrile to adiponitrile (an intermediate for nylon). The worldwide production capacity is $200\,000 \text{ t year}^{-1}$. Later on,

undivided cells were installed [134]. With the decreasing price of natural gas, the electrochemical synthesis of adiponitrile has declined over the last few years [135].

In this process, the main reaction is electroreduction coupled with dimerization on a cadmium cathode (Eq. (8)).



Oxygen evolution is the depolarization reaction on the counter-electrode. The main function of the cation-selective membrane is to prevent product oxidation on the anode and simultaneously enable proton transport from the anode to the cathode compartment.

Traditional electroorganic synthesis utilizes a supporting electrolyte to provide a reactant solution with sufficient ionic conductivity. The reason is that electroneutral molecules are typically used as reactants dissolved in a non-polar or weakly polar solvent and thus are non-conductive. Instead of a supporting electrolyte, a "zero gap" construction utilizing a solid polymer electrolyte is also possible. Progress in PEM fuel cell and electrolysis technology has inspired many researchers/industries to apply this set-up. The direct contact of the electrodes and the membrane allows the omission of a supporting electrolyte or the reduction of its content to a minimum. The absence of additional supporting electrolyte makes it possible to dispense with the next separation step, thus saving investment and operating costs. The huge potential of this arrangement is well documented by Ogumi [136–140]. Recently hydrogenation of furfural has been described by Green [141]. Electrooxidation processes do not need an external energy supply, therefore cogeneration of energy and electrochemical synthesis is an attractive option [142]. Sulfonated perfluorinated membranes dominate in electroorganic synthesis, but in the case of less aggressive media, other types may also be used in selected cases. One example is the process of electrochemical synthesis of glyoxylic acid in a cell with an anion-selective membrane based on polycarbonyl styrene [143].

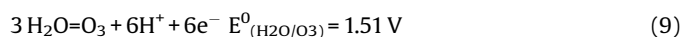
The electrodialysis of organic compounds in several variations, especially including bipolar membranes (e.g. succinic acid production), is a borderline case of membrane electrolysis technology and represents a rapidly developing field of applications [144].

4. Membrane electrolysis technologies under development

Besides well-established industrial technologies, a class of new membrane electrolysis processes, or their modifications, exists that are currently under development and have not yet reached the stage of industrial implementation. Selected cases will be discussed in the following section.

4.1. Ozone generation

A PEM electrolysis system with a different anode material is used for ozone generation [145–150]. Ozone represents an attractive alternative to chlorine as a powerful disinfectant. Its main advantage is that it does not form noxious residues in treated water. Perfluorinated membranes are used in PEM ozone generators [151,152]. Porous platinum typically serves as the cathode. Various anode materials have been used and currently boron-doped diamond electrodes (BDD) are being most intensively studied [152,153], but PbO_2 is the current state-of-the-art [154]. The standard electrode reaction potential of ozone formation (Eq. (6)) is 280 mV higher compared with the formation of oxygen.

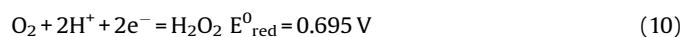


Thus, the energy consumption of this process is relatively high (cell voltage reaches $3\text{--}5 \text{ V}$) [133]. The composition of the output

gas of the PEM ozone generator varies in dependence on the anode material and electrolysis conditions. Currently it contains up to 30 mol.% of ozone [154]. Hydrogen gas is generated on the cathode. Similar to chlorine production technology, in this case oxygen depolarized cathodes are also proposed to reduce cell voltage [155]. Since the membrane is also exposed to the ozone generated, its chemical stability is crucial. Today sulfonated perfluorinated membranes almost exclusively manifest sufficient durability in this process [156].

4.2. Hydrogen peroxide production

Hydrogen peroxide is another important product that can be generated by PEM electrolysis. In the past, hydrogen peroxide was produced by electrochemical means. Former electrochemical production has now been replaced by organic autooxidation processes on a large industrial scale [157]. Nevertheless, new electrolytic cells have been successfully applied for on-site hydrogen peroxide generation [158]. A prospective future application is for water pollution abatement by the Fenton reaction. This reaction, based on the reaction of hydrogen peroxide with iron ions, is considered to produce OH^\cdot as a powerful oxidizing agent without harmful side-products. On-site peroxide generation is an attractive means to realize this continuous Fenton process [158]. Hydrogen peroxide can easily be produced in an electrolytic cell divided by a membrane. Oxygen is fed to the cathode where reaction (10) takes place.



In principle, this represents a modification of PEM water electrolysis with an air (oxygen) depolarized cathode. The scheme of H_2O_2 and oxygen production is shown in Fig. 6. Neutral H_2O_2 solutions with concentrations of up to 8 wt% were obtained in a PEM system by this means [159]. The cathode is constructed as a porous, three-dimensional electrode or as a gas-diffusion electrode. Cathode materials based on pure carbon, such as RVC (reticulated vitreous carbon), carbon black, carbon nanotubes, activated carbon, vapor-grown carbon fibers, and a polytetrafluoroethylene or Nafion binder [160–162], have proven to be efficient for this type of process. As the membrane, perfluorinated cation-selective membranes are almost exclusively proposed because they are able to withstand the aggressive environment of hydrogen peroxide. The anode is typically based on IrO_2 or platinum-coated (activated) titanium. Oxygen evolution is the main reaction on the anode side. It can be captured and used for the cathode reaction. Another approach, based on a modification of the operating and construction parameters of the PEM fuel cell and designed to generate electrical energy and hydrogen peroxide simultaneously, has also been proposed [163]. However, so far the

electrolytic process represents a more suitable option for industrial application.

4.3. Hydrogen pump

The electrochemical membrane hydrogen pump (compressor) [164] for hydrogen purification and compression based on a Nafion-type membrane could also be attributed to membrane electrolysis. In this process, hydrogen molecules are oxidized on the anode, the hydrogen ions produced are transported through the membrane to the cathode where they are reduced, leading to hydrogen evolution. If the hydrogen pressure is equal on both sides of the membrane, the reversible cell voltage has a value of $E_r = 0.00 \text{ V}$. Nevertheless, the polarization of the electrodes and the ohmic losses result in a cell voltage of approx. 0.1–0.2 V with a practically acceptable current load of 0.2–0.6 A cm^{-2} . The purity of the hydrogen extracted from the gas mixtures attains 99.99% after dehumidification. Such a system represents an interesting possibility for hydrogen regeneration from fuel cell waste gases.

4.4. Oxygen separators

Similar to the hydrogen pump, oxygen separators based on oxide-conductive materials have also been developed [165]. The more common application of this device is, however, to control oxygen levels in a gas stream, e.g. in the automotive industry [166]. This concept involves the use of a high-temperature electrolyte (see Section 5.5). In contrast to high-temperature electrolysis, the oxygen electrode material is deposited on both sides of the membrane [167,168]. An operating temperature above 800 °C enables separation/concentration of oxygen even from low quality gas mixtures, e.g. CO_2 -rich mixtures [168]. Due to the fast electrode reaction kinetics, a high current density of 0.6 A cm^{-2} was reached at a cell voltage below 0.5 V in a commercial unit [167]. Furthermore, trials were conducted to separate oxygen in low-temperature PEM mode [169,170]. However, due to the slow reaction kinetics the cell voltage, reaching 1.4 V at 0.2 A cm^{-2} , is significantly higher.

4.5. CO_2 pollution abatement/Power-to-gas

Due to the increasing importance of global climate change the technologies related to CO_2 pollution abatement are under intensive development. Electrolytic processes offer technologies capable of converting CO_2 into energy-rich compounds (e.g. mixture of CO and H_2) [103]. Thus, the combination of renewable power sources and CO_2 electrolysis represents a highly interesting option [171]. The production of fuel from CO_2 is often referred to as power-to-gas or synthetic fuel production [172].

With respect to process efficiency, the performance of high-temperature co-electrolysis of CO_2 and steam is superior to that of the competing options. The process is based on high-temperature water electrolysis described in Section 3.2.4. If an appropriate amount of steam is added to the CO_2 stream, syngas, an important raw material for the chemical industry, can be produced. This type of process represents a significantly more viable option for CO_2 reduction than the low-temperature alternatives [104,173,174].

PEM electrolysis has also been tested for application in CO_2 pollution abatement. The target was to reduce CO_2 efficiently at the cathode under formation of an industrially interesting product [175]. However, the concept of a liquid electrolyte-free arrangement suffers from low current efficiency [176]. The introduction of pH buffer leads to an increase in selectivity and current efficiency [177,178], but low current density and efficiency in comparison to the high-temperature process prevent its commercial usage.

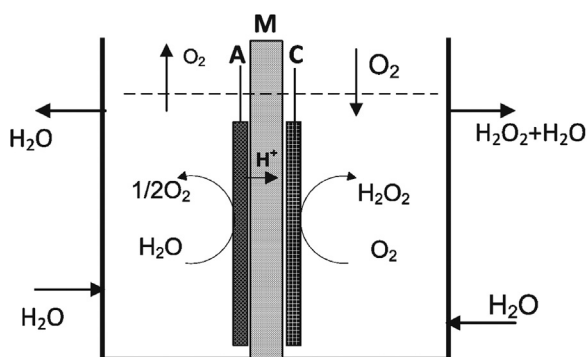


Fig. 6. Scheme of H_2O_2 production [162].

Nevertheless, one of the largest commercial projects, Audi e-gas, is based on alkaline water electrolysis with a total performance of 6 MW powered by wind energy with subsequent catalytic methanation [179]. It can thus be counted among the CO₂ pollution abatement technologies as well. In contrast to the above-mentioned low-temperature electrochemical technologies, however, it separates the steps of hydrogen production and CO₂ reduction.

It is important to point out that non electrolytic routes, such as thermochemical cycles, are also possible, but their practical realization faces serious material challenges [171].

4.6. Isotopic enrichment

In the majority of the PEM electrolysis processes described above, the membrane was used mainly as a reactant/product separator and/or as a solid electrolyte, making it possible to use gases or demineralized water efficiently as the reactants on the electrodes. Usually membrane selectivity is understood as the portion of the electrical charge carried through the membrane by the ions of one sign and sometimes of a different chemical nature. However, the difference in the mobility of individual isotopes of ions of the same chemical nature could also be of industrial interest. This effect can be used to separate and concentrate water containing deuterium ²H₂O in the molecule (so-called heavy water) [180–182].

Nevertheless, electrolysis was the first industrial process for heavy water production. It was first used in Norway before the Second World War (electrolyzers produced by Norsk Hydro). In the case of traditional alkaline water electrolysis, the separation factor originates from the different recombination rates of protium, deuterium and tritium atoms on the cathode surface during gas formation. Today, mainly water–hydrogen sulfide exchange or ammonia–water extraction processes are used for the production of hydrogen isotopes [183]. Due to their simplicity, electrolytic processes are currently incorporated into the subsequent stages for tritium separation [184]. In the case of a platinum electrode, the separation coefficient in water alkaline electrolysis (protium/deuterium) reaches 7.6, but for PEM electrolysis separation the coefficient was up to 9.5 (energy consumption about 4 kW h/m³ of gas mixture), which indicates the significant role of mass transport processes. For protium/tritium mixtures a separation coefficient of 19 was achieved using PEM electrolysis [180,181].

5. Ion-selective membranes, their types and fields of application

The application of membrane electrolysis processes is closely linked to the development of corresponding membrane materials and membranes. The main factor is typically the availability of membranes with properties suitable for the desired process. A common example is membrane brine electrolysis, whose realization was only possible after perfluorinated sulfonated membrane materials had been developed. From a historical point of view, polymer ion-selective membranes were the first to be developed and deployed on an industrial scale. Therefore, this type of materials will be addressed first.

Polymeric ion-selective membranes are divided into two basic types: cation-selective, containing negatively charged groups, such as $-\text{SO}_3^-$, $-\text{COO}^-$, $-\text{PO}_3^{2-}$, $-\text{C}_6\text{H}_4\text{O}^-$, etc., covalently bonded to the polymer backbone of the membrane. They thus preferably transport cations and, in an ideal case, reject anions. On the other hand, anion-selective membranes contain positively charged groups, such as $-\text{NH}_3^+$, $-\text{NRH}_2^+$, $-\text{NR}_2\text{H}^+$, $-\text{NR}_3^+$, $-\text{PR}_3^+$, $-\text{SR}_2^+$, etc., covalently bonded to the polymer backbone of the membrane. Consequently, they transport anions, but reject cations (see, for example, [185]).

Since this type of material is considered to be dense, i.e. non-porous, the transport of solvent and other species is limited and electrode compartments separated by this type of material are usually regarded as hydraulically separated, in contrast to the diaphragm. The development of a theoretical understanding of ion-selective membrane behavior can be traced back to 1890 to the work of Ostwald [10,186], who studied the properties of semi-permeable membranes. Ostwald discovered that a membrane can be impermeable to electrolyte if it is impermeable either to its cation or its anion. A so-called “membrane potential” at the boundary between a membrane and the surrounding solution was postulated.

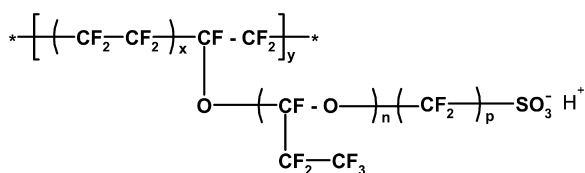
After polymeric ion-selective materials had been developed, rapid progress in the field of membrane development and production gave rise to new types of membranes with ion-selective properties [187]. The first heterogeneous membranes, i.e. membranes consisting of an ion-selective phase in the form of particles bonded to the compact membrane by means of a suitable inert polymer, attained an industrially applicable level of development in the 1950s [7,9,187]. Homogeneous polymer membranes, i.e. consisting of one polymer in their entire volume, were first synthesized in 1933 [187]. At that time, however, such materials did not possess suitable mechanical and chemical stability. They first became technically important with the commercial availability of perfluorinated ion-selective materials.

Surprisingly, ionically conductive inorganic oxide ceramics on the basis of zirconium oxide were first reported as far back as 1899 [188]. The reason was that ceramic materials had been developed centuries before, in contrast to polymeric materials which were still awaiting discovery at that time. Membranes based on zirconium oxide were already reported in 1937 [50,51]. Recently, the development of new types, namely inorganic membranes (mainly on the basis of ceramic materials) [189] and hybrid organic-inorganic membranes [10,190,191], have been introduced.

5.1. Homogeneous polymeric ion-selective membranes

Historically, homogeneous polymeric membranes represent the type first implemented in industrial practice and are probably the most widespread type of ion-selective membranes up to the present day. Around 1940, interest in industrial applications, especially in electrodialysis, led to the development of synthetic ion-selective membranes on the basis of phenol-formaldehyde polycondensation [192,193]. Homogeneous polymer membranes are still mainly obtained by copolymerization or polycondensation. They are based on aliphatic and aromatic (including heteroaromatic) hydrocarbons and fluorinated or perfluorinated polymers with functional groups. Homogeneous, non-perfluorinated membranes could be used in the same processes as heterogeneous membranes, but neither type is sufficiently stable under harsh conditions characteristic, for example, of chlorine production or water electrolysis. For a long time, the insufficient stability of ion-selective membranes based on hydrocarbon materials was the main obstacle to the proliferation of membrane electrolysis in important industrial areas.

In the 1970s, a chemically stable, homogeneous cation-exchange membrane based on polytetrafluorethylene with sulfonated side chains (for the structural formula, see Fig. 7) was developed by DuPont de Nemours [29,30,194]. This type of material is obtained by copolymerization of tetrafluorethylene with a perfluorovinyl ether-containing sulfo group. It was introduced on the market under the commercial name Nafion[®]. Its chemical composition and structural formula are responsible for its extraordinary properties. The perfluorinated polymeric backbone provides a material with high chemical stability that is hydrophobic in character. On the other hand, the strongly acidic



The carboxylic functional group is less strongly acidic and its energy of hydration is, thus, lower. Therefore, this membrane is characterized by a higher concentration of fixed functional groups and at the same time by lower water content. These aspects

Modification of the membrane surface typically targets reducing the adhesion of gas bubbles. It is, therefore, mainly used in processes connected with gas evolution. A typical example is chlorine electrolysis where coating the membrane surface facing the cathode with a thin layer of a porous inorganic material

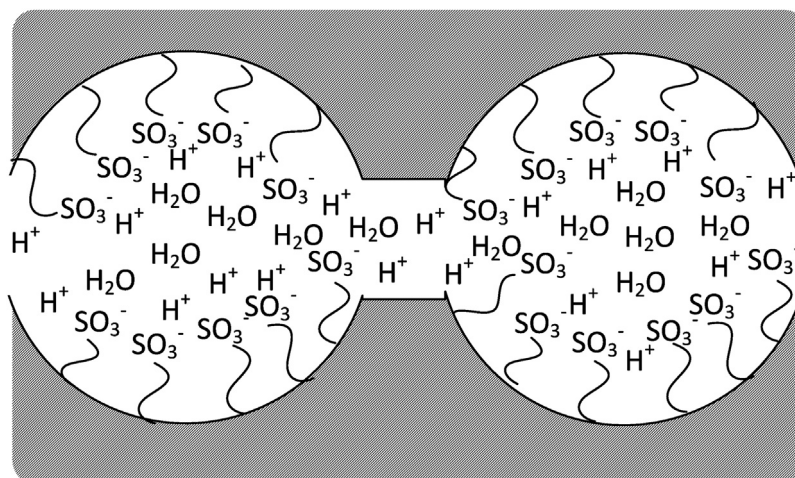


Fig. 8. Cluster structure of a Nafion-type membrane; SO_3^- represents negatively charged functional groups bonded to a polymeric chain compensated by protons, both including their solvation shell [196].

(zirconium dioxide, silicon carbide or titanium dioxide) improves the membrane's hydrophilicity [37,209].

Initially, the chemical stability of such membranes in PEM water electrolysis (and PEM fuel cells) was one of the key factors, since partial destruction of the membrane (side chains and polymer end groups with double bonds or oxide groups) took place due to the membrane's interaction with oxygen radicals and oxygen compounds (H_2O_2). The chemical stabilization of the membrane [210] did not totally succeed in excluding this problem, but it significantly reduced its importance. This especially concerned the water electrolysis process. At this stage, two further disadvantages of perfluorinated membranes should also be mentioned: (i) their relatively high hydrophobicity, resulting in a strong increase in membrane resistivity when operated in a gas phase (even at saturation water vapor pressure) [211,212] and (ii) their relatively low stability at elevated temperatures (up to 100–130 °C, depending on the operating conditions) [213–215].

5.2. Polymeric ion-conductive membranes for elevated temperatures

As indicated, an important challenge for homogeneous polymer electrolytes is an operational temperature above 100 °C. The motive for increasing the operational temperature is to enhance the electrode reaction kinetics. In the case of water electrolysis technology, if the increase in temperature is substantial, i.e. at least above 200 °C, part of the energy needed to complete the desired reaction can be provided in the form of heat instead of electrical energy, as discussed in Section 3.2.4. To overcome the operating limits of perfluorinated membranes, they were modified by impregnation with a suitable compound, e.g. zirconium phosphate [216], phosphoric acid [97,217–219], or ionic liquids [219–223]. Such a modification can be significant for membrane application in a fuel cell and in steam electrolysis [97,224–226]. Membranes modified in this way typically maintain their homogeneous character; they are mentioned at this juncture for the purpose of completing the overview of possible membrane modifications. The leaching of impregnation liquid and the low membrane conductivity are the main drawbacks of impregnated perfluorinated membranes. This is due to the fact that, under low humidity conditions, the ionic liquid used does not allow sufficient mobility of the proton. Proton, being a small cation, is typically not dissociated at temperatures used in the absence of a sufficient amount of solvating agent [221,223]. Therefore this particular approach does not seem very promising.

Since perfluorinated sulfonated membranes cannot withstand these conditions, there has been intensive research on alternative materials for this operational temperature range. One example of work in this direction is a project carried out at the Florida Solar Energy Center, testing several families of polymers as viable candidates: polyether ketones, polyether sulfones, polybenzimidazoles, and polyphenylquinoxalines. Polymers were converted into ionomers via sulfonation and membranes were prepared [227]. Although some promising results were obtained with sulfonated polyetheretherketone, the membranes did not have the necessary thermal and chemical stability for electrolysis processes at elevated temperatures. It was also shown that polyphenylene sulfides, polysulfones, polyketones and some polyimides were reasonably stable at 300 °C, but no candidates were found to be stable under steam/ O_2 at 400 °C [228]. No other attempts to develop cheaper, non-perfluorinated polymer electrolytes for a higher operational temperature have resulted in any results of practical importance. Nevertheless, these efforts are still on-going (see e.g. [229–231]). So far, only PBI (Fig. 9) membranes (and their derivatives) doped with phosphoric acid have become significantly widespread as to be regarded as a possible alternative to

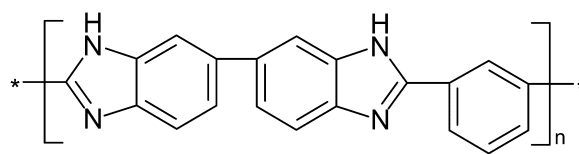


Fig. 9. General structural formula of poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (PBI) [218].

perfluorinated membranes for polymer membrane fuel cells with an operating temperature of up to 200 °C. PBI membranes employ a hopping mechanism in which immobilized anions, such as phosphates, can solvate protons and thus provide a path for rapid proton transport. The application of this type of membrane for steam electrolysis was tested. Mass transport limitations did not permit high specific productivity (current density) to be obtained [232–234]. Moreover, significant durability issues have recently been identified for this type of membrane in the water electrolysis process [96]. Besides for water electrolysis, the PBI membrane was found to be promising in thermochemical cycles for SO_2 electrolysis at 80 °C [120]. In this case the PBI membrane is doped with sulfuric acid. Due to the concentrated acid environment, the membrane is not endangered by acid leaching (drawback of phosphoric acid-doped membranes).

5.3. Heterogeneous polymeric ion-selective membranes

Heterogeneous membranes represent a class of ion-selective membranes with properties suitable for practical application [235]. The motivation for the development and use of heterogeneous membranes is two-fold: (i) need for greater robustness and (ii) the possibility to prepare ion-selective membranes from materials devoid of film-forming properties, or from materials that could not be dissolved or melted to produce a corresponding foil. Their production dates back to 1950 [9]. The main target was separation processes. Due to their non-uniform structure (see Fig. 10) [236], heterogeneous membranes are usually characterized by poorer electrochemical parameters compared with homogeneous materials, e.g. their conductivity is generally less than $0.01 \Omega^{-1} \text{cm}^{-1}$ (see Appendix in Supplementary material). This is clearly connected with the reduced electrochemically active cross-section of this material, as discussed in the Introduction section of this paper. Another aspect is the fact that, during transport through the membrane, electrically charged ions have to pass through the phase interface between the individual particles of the ion-selective phase many times. On the other hand, inert binder provides the membrane with stable mechanical support uninfluenced by the ion-exchange or conduction process. At the same time, it represents an additional protective barrier with respect to chemical attack on the ion-exchange phase through the “skin layer”. To further improve the mechanical stability of this material, often suitable reinforcement, typically in the form of cloth, is used. A broad spectrum of reinforcing materials is used, the most common being the polymers PES, PAD [237,238], PTFE, PVC [133], and also glass fibers [239], carbon or metal-based materials [240,241]. The incorporation of a support, however, results in further deterioration of the membrane's electrochemical properties caused by the shielding effect of the inert support and the limitation of the membrane swelling [242–245].

5.4. Hybrid ion-selective membranes

Another group of membrane materials, i.e. hybrid ones, are primarily related to the problem of the low conductivity of polymer ion-selective membranes, predominantly perfluorinated ones, under conditions of low relative humidity. Such conditions

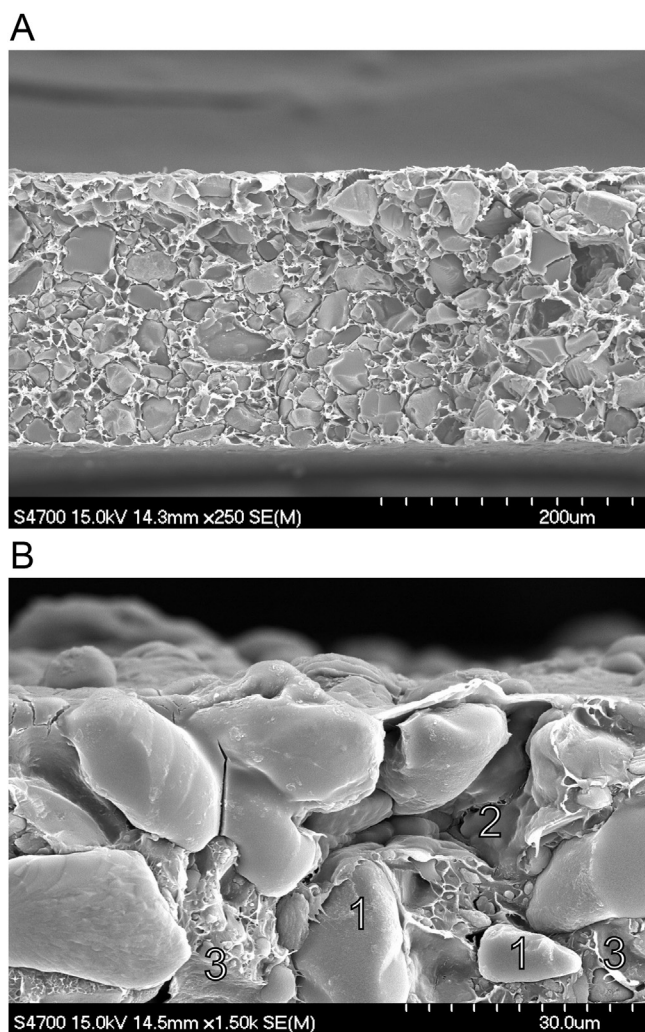


Fig. 10. SEM picture of a heterogeneous ion-exchange membrane. (A) Global view; (B) Detail of the structure of a heterogeneous ion-exchange material. 1—gel part with polymer chains with fixed ion-exchange groups; 2—internal part filled with neutral solution; 3—inert parts of polymer binder.

are fairly typical of fuel cells. A common approach consists of membrane modification by inorganic materials (Si and Ti oxides, zirconyl phosphate, etc.) mainly synthesized inside the membrane [32,218,246–250]. They are generally hygroscopic and maintain sufficient swelling of the membrane even under conditions of low relative humidity of the environment, or they are ionic conductors retaining their conductivity even under low relative humidity conditions. In one review [249] it is stressed that the impact of membrane modification by inorganic compounds could be quite different for homogeneous and heterogeneous membranes. For the latter type, not only an increase in conductivity, but also in selectivity could be achieved. An increase in the exchange capacity of a Nafion-type membrane modified by halloysite (aluminosilicate) nanotubes was reported in [251]. A significant increase in ionic conductivity of a Nafion-type membrane modified by inorganic compounds (i.e. hydrated silica) was attributed to an increase in the diameter of the channels between SO_3H -group clusters due to the formation of nanoparticles inside such channels. This was explained on the basis of the semi-elasticity of the pore wall model of the membrane [249,252]. Moreover, in the case of PEM water electrolysis, such membrane modification (inorganic solid phase) offers the possibility to decrease the gas crossover through the membrane [253].

5.5. Medium and high-temperature ionically conductive membranes

In conclusion, the last type of membranes, i.e. inorganic solid electrolytes, is addressed. Apart from polymeric ion-selective materials, an ion-selective membrane can also be prepared from an inorganic material, such as zeolites, bentonite or phosphate salts [191,254–257]. However, these membranes have not yet attained any practical importance due to their high cost and other disadvantages, such as unsatisfactory electrochemical properties and excessively large pores. On the other hand, they allow operation at significantly higher temperatures than polymeric membranes [258].

A traditional representative of this group of materials is, however, ZrO_2 ceramics stabilized with Y_2O_3 (YSZ), Sc_2O_3 (ScSZ) or other materials like CeO_2 doped with Gd_2O_3 (GDC). At sufficiently high temperatures (typically 800 to 900 °C) they exhibit O^{2-} conductivity through crystal lattice defects. In the field of membrane electrolysis, their typical application is in steam electrolysis [173,259–261] where they are used either in tubular or planar form. The electrolyte is not permeable to gases, hence extremely high purity (>99.999% in dry form) hydrogen and oxygen can be obtained. The conductivity of this class of materials is, however, even at high temperatures, lower, e.g. 1 S m^{-1} at 700 °C for YSZ (Fig. 11), than that of polymer and especially liquid electrolytes.

The ohmic resistance of the membrane thus becomes one of the key problems. Commercially available systems operate using membranes approx. 100 μm thick [262]. Currently, the main approach to solving this problem consists in reducing the thickness of the membrane, typically to 20 μm . This is done at the expense of limiting the mechanical stability of such a material [189]. None of the attempts to find oxides with a lower operating temperature [263] and/or with proton-type conductivity [264] have yielded industrially important results so far. This is mainly due to the low stability of such solid electrolytes under the desired operational conditions. A reduction of the operational temperature is, however, more a question of SOFC than of solid oxide electrolysis, which requires a high operational temperature to reduce the electric energy demand. A further class of new materials studied is based on ceria and doped lanthanum gallate [189,261], but their high price limits their use in practice.

6. Perspectives for membrane electrolysis

6.1. Electromembrane separation processes

Electrodialysis as a predecessor of membrane electrolysis is currently widely used for water purification with a relatively low

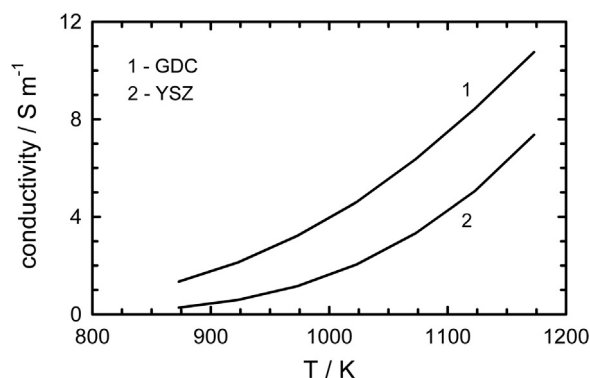


Fig. 11. An example of the dependence of solid oxide electrolyte conductivity on temperature. GDC stands for CeO_2 doped by Gd_2O_3 (10 mol.%) and YSZ for ZrO_2 doped by Y_2O_3 (8 mol.%).

concentration of mineral salts and for purification of selected technological streams. In this area, research is mainly focusing on increasing the desalination capacity of the electrodialysis stack and, thus, on reducing investment and operational costs per unit of treated water. It is anticipated that this trend will continue in the future. The second area concerns the development of tailored, typically small or medium-scale technologies for treatment of high value-added components, e.g. in the pharmaceutical industry, chemical industry (purification of organic substances, recycling of valuable components), food industry, etc. [265,266]. The growing, widespread use of electrodeionization as a modified form of electrodialysis is also expected. This is connected with an endeavor to optimize and reduce the costs of high purity water production, especially in the energy and heat industries. Combined processes, facilitating closed loop technologies to protect the environment, are a special topic [267,268]. One example is electrodialysis using bipolar membranes, which has recently reached the commercial application level [10,14,16]. This process allows the recycling, instead of disposal, of chemicals with reduced energy demands and/or production of valuable components in a simple, one-step process [269]. The focus in future will be mainly on the development of bipolar membranes, resulting in highly efficient processes with a satisfactorily long lifetime [16]. In this area there is still room for further improvements and optimization.

6.2. Chlor-alkali electrolysis

Membrane electrolysis systems for alkali and chlorine production are now widely used in the majority of industrially developed countries. The hydrogen gas produced at the cathode together with caustic solution (concentration ~35 wt%) from chlor-alkali cells is normally used for the production of hydrochloric acid or as a fuel to produce steam. Steam can subsequently be used as a heat-transferring medium or to produce electric energy. Another option, which has proven its feasibility on an industrial scale, is the utilization of hydrogen in PEM-type fuel cells. Electric energy produced by any of these two routes can be used to power partially the electrolysis process. Due to regulatory decisions and economic factors, the percentage of chlorine and caustics production covered by membrane electrolysis will further increase in the near future. In this connection, endeavors will continue to optimize this process and render it more efficient. This concerns both improvements in cell construction as well as in the further development of membrane material. Another target is to reduce back-migration of the hydroxide ions from the catholyte to the anolyte and thus to enhance the charge efficiency of electrolysis. Moreover, the purity of the potassium hydroxide solution produced with slightly higher contamination by chloride ions (in comparison to the mercury process) has reached levels that are unacceptable for specific end applications. This is the reason for two mercury plants operating in Japan for high-grade potassium hydroxide production [37].

6.3. PEM water electrolysis

At present, probably the most intensive research efforts of the scientific community in the field of membrane electrolysis are targeting the development of PEM water electrolyzers. This endeavor is motivated primarily by the search for an energy storage technology capable of stabilizing the electricity distribution grid, which is endangered by the integration of the increasing production capacity of highly unstable renewable energy sources. Another traditional application field is the space industry and remote or other “island” (off-grid) applications. The efficient conversion of excessive electrical energy into chemical energy stored in hydrogen facilitates energy storage and subsequent recovery. At the same time the hydrogen generated can be

regarded as sustainably generated valuable raw materials for the chemical and other industries.

The relatively slow penetration of PEM electrolyzers into industrial practice is mainly connected with the high costs of the membrane (today about 1600 \$ m⁻² for Nafion 117 [270]) and electrocatalysts based on platinum metal. The application of platinum metal is the prime impediment to the implementation of large-scale PEM electrolyzers. Therefore, the main activity in the development of PEM electrolysis is focused on optimizing construction materials and reducing the load of electrocatalysts on the basis of precious metals [63,78,271].

It is clear that further development of PEM water electrolysis is also closely connected with that of the membrane and membrane production. In the case of Nafion-type membranes, reduced thickness and more competitors on the market may push the price down to 450 \$ m⁻². Here, the application of the same type of membranes in PEM fuel cells would be helpful.

It is difficult, however, to envisage any radical improvements or the development of novel membranes in the near future. An increase in membrane conductivity due to an increase in the concentration of functional groups (increase of exchange capacity) does not seem viable since it would result in a decrease in the chemical and mechanical stability of the material on account of its excessive swelling. Hence, further development could be connected with membrane modification by inorganic compounds and optimization of its structure, although the contribution of these changes will remain limited or, at most, moderate. Therefore, the success of PEM electrolysis depends on the complex development of all the main components, including the stack design.

Another route to the overall enhancement of process efficiency (including hydrogen compression) centers on increasing the operational pressure (up to 130 bar and higher) [64,272,273]. Recently, attempts to develop electrolyzers for pressure up to 300 bars were undertaken at NRC “Kurchatov Institute”. However, it was found that gas permeation across the membrane results in a significant decrease in current efficiency (down to 90%) and in the formation of explosive gas mixtures. Special catalytic hydrogen burners could solve the safety problem, but not increase process efficiency, therefore pressure of about 200 bars may be the practical limit for the polymer electrolyte membranes currently used. This type of water electrolyzer is supposed to be sufficiently efficient for small, autonomous, renewable energy systems as they will permit hydrogen storage in relatively cheap standard hydrogen pressure vessels without additional compression. A further development of most other PEM systems (URFC), hydrogen compressors and concentrators, etc., is closely associated with the development and implementation of the hydrogen economy.

6.4. Alkaline water electrolysis

For large-scale applications, alkaline water electrolysis seems to be the more promising approach. It does not require platinum metals as electrocatalysts for the electrode construction. The main problem is the availability of the corresponding anion-selective polymer electrolyte membrane and catalytic layer binder. The chemical stability of the membranes currently available does not meet process requirements [90]. The availability of a stable anion-selective polymer with corresponding properties would open up an entirely new field of research for the development and optimization of the alkaline MEA and stack construction. An additional aspect is development in the field of cheap, stable and highly active electrocatalysts for both the anode and the cathode reaction. In an alkaline environment this spans a very broad spectrum of materials, ranging from the above-mentioned spinel and perovskite structure oxides to carbon materials, like graphene and graphene oxide.

6.5. Electroorganic synthesis

Additionally, organic electrosynthesis offers significant room for further exploitation of membrane electrolysis [136–140,274,275]. It is typically used for high value-added synthesis with small production capacities. The reason for this is that, due to the price of electrical energy and often also of electrode materials, large-scale electro-organic productions have to compete with alternative routes offering lower running costs. On a small scale this issue is often overcome, especially in the case of high value-added production, where the advantages of electrochemistry prevail (electron as a “clean reactant”, precisely controllable redox potential). Since the small production capacities of valuable components represent the more favorable direction of further development in highly industrialized and developed countries, intensive development in this field is to be expected. The development of novel membrane materials satisfying process requirements will open up new possibilities. The commercial availability of electrochemical cells of various scales suitable for application in this particular field will also support this strategy.

6.6. High-temperature steam electrolysis

An interesting challenge for the future development of membrane electrolysis is high-temperature steam electrolysis and its variants [189]. The chief problem is the materials. The development of novel inorganic membranes (solid electrolytes), among others, is mainly connected with endeavors to decrease operational temperature and increase conductivity, the latter aspect being related to the development of solid electrolytes with proton conductivity. Certainly the cell (stack) design is very important [173]. Among other things, it enables the membrane thickness to be reduced (to 20–50 micrometers) and thus to reduce both ohmic losses in the membrane and the operating temperature. A further prospect is an increase in operational pressure. The main issue here is the mechanical properties of sealing and the MEA. What is also important for the future is the development of the co-electrolysis process, mainly CO₂ with water steam leading to syngas. This process could be used to reduce CO₂ pollution, while allowing for carbon recycling in the form of useful compounds. Furthermore, CO₂ reduction to even lower oxidation states (down to CH₄), mainly for utilization in space applications, is envisaged.

7. Conclusion

The spectrum of membrane electrolysis technologies is very broad and offers a wide range of possibilities. A considerable obstacle to providing an exhaustive review is the fact that a significant part of the on-going activities in this field is carried out in industrial laboratories, thus their outcome is not publicly available. Therefore, the foremost aim of this study was to provide an overview of the state-of-the-art of the main existing and emerging processes closely related to the application of ionically conducting membranes. It is documented that membrane electrolysis represents a well-established industrial field with significant potential for further development. In this respect, intensive collaboration between material scientists with electrochemists and electrochemical engineers is highly desirable since only close collaboration can help to overcome the difficulties connected with progress in this multidisciplinary field.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2016.05.209>.

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